THE VIBRATIONS OF ICE I AND SOME CLATHRATE-HYDRATES BELOW 200°K

by

Arvid Holger Hardin
B.Sc.(Hons.), The University of British Columbia, 1963

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY in the Department of Chemistry

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

July, 1970
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study.

I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Chemistry

The University of British Columbia
Vancouver 8, Canada

Date Aug. 12, 1970
ABSTRACT

The vibrations of H$_2$O, HDO and D$_2$O molecules participating in the hydrogen bonding of vitreous and crystalline solids, and some alkyl halides and halogens encaged in these solids, were studied by infrared spectroscopy between 4.2 and 200°K over the 4000 to 160 cm$^{-1}$ frequency range. Four kinds of O-H····O hydrogen bonding lattices were investigated, vitreous and annealed (cubic) ice I and vitreous and annealed clathrate-hydrate mixtures.

In vitreous ice I the effects on the molecular and lattice vibrations were observed in detail for H$_2$O between 77 and 180°K during the phase transformation to cubic ice I, and the results of the transformation for HDO and D$_2$O were recorded. As well, the effects on the molecular and lattice vibrations of H$_2$O, D$_2$O, H$_2$O (5.94% HDO), and D$_2$O (4.00% HDO) cubic ices I were studied during warming from 4.2 to 200°K.

Similar studies were made for the vibrations of H$_2$O, HDO, D$_2$O and guest molecules, during the vitreous-crystalline phase transformation of seven clathrate-hydrate mixtures and during warming of the resulting annealed mixtures.

For ice I the method involved condensation of the vapour at 77°K, observation of the spectra during warming in stages to 185 ± 5°K, cooling to 4.2°K, and observation of the cubic sample spectra during warming to 200°K. The results were plotted as a function of temperature and were correlated to calculated O····O distances and RMS amplitudes of translation. As well four models for molecular libration were investigated.

Three approaches were taken to the clathrate-hydrate problem. In parallel to the ice I method gaseous stoichiometric mixtures were con-
densed, observed during transformation, cooled to 4.2°C and observed during warm-up. Other gaseous clathrate mixtures were condensed in an isolated sample chamber, to prevent sample fractionation, and treated as before. Finally, low temperature mulls of solid clathrate-hydrate mixtures were prepared and observed at 83 ± 3°C.

The results show that on warming the ice I phase transformation occurred between 120 ± 5 and 135 ± 5°C and required less than 18 minutes at 135 ± 3°C. Weak peaks due to oligomeric H₂O and D₂O units disappeared during annealing, while all hydrogen bonded H₂O molecular modes shifted to lower frequency and all lattice modes shifted to higher frequency. The half-height widths of the composite H₂O band (ν₂/2νₚ) appeared to increase upon annealing and to decrease upon warming while the (νᵣ, νᵣ + νₜ) and (ν₁, ν₃, ν₁ + νₚ) bands had the opposite behaviour. This was interpreted as indicating a weak 2νᵣ band underlying the stronger ν₂ absorption near 1600 cm⁻¹.

The frequency-temperature dependences of all cubic ice I bands were interpreted on a bilinear, high and low temperature basis (the lattice modes shifted to lower frequency and the molecular modes to higher frequency with increasing temperature). For HDO above 80°C Δν₉/ΔT was 0.200 ± 0.005 cm⁻¹/°K, Δν₁₀/ΔT was 0.123 ± 0.005 cm⁻¹/°K, the frequencies were "frozen-in" at 80 ± 5°C and 65 ± 5°C and had irregular behaviours between 50 and 70°C. The low temperature dependences were 0.047 ± 0.005 cm⁻¹/°K in both modes. An explanation is given for the apparent displacement of the HDO stretching frequencies from the H₂O and D₂O frequencies.

The HDO results also permitted the accurate determination of Δν₉/ΔR(O···O) as 1921 cm⁻¹/A and Δν₁₀/ΔR as 1281 cm⁻¹/A above 150°C and
as 8202 cm\(^{-1}\)/Å and 6629 cm\(^{-1}\)/Å below 100°K. As well, the HDO stretching frequencies gave an anharmonicity which increased from 4.2 to 80°K and then decreased between 80 and 200°K.

The clathrate-hydrate mixtures transformed on warming in the temperature range 125 ± 5 to 145 ± 5°K and required less than 18 minutes at 135°K as for ice I. Similarly, the weak oligomeric and guest absorptions disappeared upon annealing. From the comparison of the three sets of "clathrate" results and the behaviour of annealed sample peaks we concluded that cubic ice I and not clathrate-hydrate was probably formed.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>ii</td>
</tr>
<tr>
<td>Table of Contents</td>
<td>v</td>
</tr>
<tr>
<td>List of Tables</td>
<td>ix</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xi</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>xiv</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>Hydrogen Bonding</td>
<td>1</td>
</tr>
<tr>
<td>A. Theories of Hydrogen Bonding</td>
<td>2</td>
</tr>
<tr>
<td>B. Spectroscopic Manifestations of Hydrogen Bonding</td>
<td>6</td>
</tr>
<tr>
<td>Clathrate-Hydrates</td>
<td>12</td>
</tr>
<tr>
<td>A. The Clathrate-Hydrate Problem</td>
<td>12</td>
</tr>
<tr>
<td>B. The Structures of the Clathrate-Hydrates</td>
<td>12</td>
</tr>
<tr>
<td>C. Formation of Clathrate-Hydrates</td>
<td>17</td>
</tr>
<tr>
<td>D. Previous Investigations of the Clathrate-Hydrates</td>
<td>18</td>
</tr>
<tr>
<td>E. The Present Approach to the Clathrate-Hydrate Problem</td>
<td>19</td>
</tr>
<tr>
<td>Ice</td>
<td>20</td>
</tr>
<tr>
<td>A. The Ice Problem</td>
<td>20</td>
</tr>
<tr>
<td>B. Non-Spectroscopic Investigations of Ice</td>
<td>20</td>
</tr>
<tr>
<td>C. Spectroscopic Investigations of Ice</td>
<td>27</td>
</tr>
<tr>
<td>D. The Present Approach to the Ice Problem</td>
<td>37</td>
</tr>
<tr>
<td>CHAPTER ONE: APPARATUS</td>
<td>38</td>
</tr>
<tr>
<td>1.1 The Perkin-Elmer 112-G Spectrophotometer</td>
<td>38</td>
</tr>
<tr>
<td>1.2 The Perkin-Elmer 421 Spectrophotometer</td>
<td>40</td>
</tr>
<tr>
<td>1.3 The Perkin-Elmer 301 Spectrophotometer</td>
<td>42</td>
</tr>
<tr>
<td>1.4 The Hornig-Wagner Liquid Nitrogen Cell</td>
<td>42</td>
</tr>
<tr>
<td>1.5 The Duerig-Mador Liquid Helium Cell</td>
<td>45</td>
</tr>
<tr>
<td>1.6 The Metal Liquid Nitrogen Cell</td>
<td>45</td>
</tr>
</tbody>
</table>
CHAPTER TWO: METHODS AND MATERIALS

2.1 Water Samples and Clathration Materials

2.2 Infrared Windows and Sample Mounts

2.3 Preparation of Clathrate-hydrates
   A. Preparation of Solid Samples
   B. Preparation of Stoichiometric Gaseous Mixtures

2.4 Preparation of Infrared Specimens
   A. Low Temperature Mulling
   B. Isolated Chamber Condensation
   C. Open Chamber Condensation

2.5 Devitrification

2.6 Temperature Variation Methods

CHAPTER THREE: ICE I: EXPERIMENTAL AND RESULTS

3.1 The Vitreous-Cubic Ice Phase Transformation
   A. Experimental
   B. Results of Devitrification

3.2 Temperature Dependence of Cubic Ice I Absorptions
   A. Temperature Dependence of HDO Absorptions
   B. Temperature Dependence of H$_2$O and D$_2$O Absorptions

3.3 The H$_2$O, D$_2$O and HDO Ice I Absorptions at 83°K
   A. Experimental
   B. Results at 83°K

3.4 Summary of Ice I Results
   A. Vitreous-Cubic Ice I Transformation
   B. HDO in Cubic Ice I
   C. H$_2$O and D$_2$O in Cubic Ice I
CHAPTER FOUR: DISCUSSION OF ICE I

4.1 The Ice I Vitreous-Cubic Phase Transformation
   A. General Discussion
   B. Fundamental Lattice Mode Transformations
   C. Fundamental Molecular Mode Transformations
   D. Combination and Overtone Mode Transformatio
   E. Confidence in the Cubic Ice I Samples

4.2 Temperature Dependence of Cubic Ice I Absorptions
   A. Dependence of HDO Bands on Temperature
   B. Dependence of H2O and D2O Bands on Temperature

4.3 Assignments of the Cubic Ice I Absorption Bands
   A. The Fundamental Lattice Modes
   B. The Fundamental Molecular Modes
   C. The Overtone and Combination Modes

4.4 The Libration of HDO, H2O and D2O
   A. The Moments-of-Intertia Models
   B. The H2O3 Model of Ice
   C. A Summary of H2O, HDO and D2O Librations

CHAPTER FIVE: CLATHRATE-HYDRATE EXPERIMENTAL DETAILS AND RESULTS

5.1 The Vitreous-Crystalline Clathrate-Mixture Phase Transformation
   A. Experimental
   B. Results of Devitrification

5.2 Clathrate Mixture Guest Absorptions
   A. Condensation in an Open Chamber
   B. Condensation in an Isolated Chamber
   C. Low Temperature Muls

5.3 Temperature Dependence of the Crystalline Clathrate Mixture Absorptions
   A. Temperature Dependence of the HDO Absorptions
   B. Temperature Dependence of the H2O and D2O Absorptions
CHAPTER SIX: DISCUSSION OF THE CLATHRATE MIXTURES

6.1 The Clathrate Mixture Vitreous-Crystalline Phase Transformation
A. General Discussion
B. Annealing Cl\textsubscript{2}·7.67H\textsubscript{2}O on CsI
C. Oligomeric H\textsubscript{2}O Absorptions
D. Unannealed Sample Guest Absorptions

6.2 Guest Species Absorptions
A. Isolated Chamber Condensation
B. Low Temperature Mulls
C. Summary

6.3 The Temperature Dependences of Crystalline Clathrate Mixture Absorptions
A. HDO in Clathrate Mixtures
B. H\textsubscript{2}O and D\textsubscript{2}O in Clathrate Mixtures

CHAPTER SEVEN: SUMMARY

7.1 Suggestions for Further Work
A. Clathrate Mixtures
B. Ice Systems
C. Other Chemical Systems

7.2 Conclusions
A. Annealing Ice I\textsubscript{V}
B. HDO Studies
C. The H\textsubscript{2}O and D\textsubscript{2}O Studies
D. Clathrate Mixture Annealing

REFERENCES
## LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>Typical clathrate-hydrates and their properties.</td>
</tr>
<tr>
<td>0.2</td>
<td>Clathrate-hydrate unit cell dimensions, guest sizes and filled cavities.</td>
</tr>
<tr>
<td>0.3</td>
<td>Stable temperature ranges of vitreous, cubic and hexagonal ice I.</td>
</tr>
<tr>
<td>0.4</td>
<td>Some physical properties of the ices.</td>
</tr>
<tr>
<td>0.5</td>
<td>H₂O vapour, liquid and ice I frequencies and assignments.</td>
</tr>
<tr>
<td>III.I</td>
<td>Cubic and vitreous ice I frequencies at 82°K.</td>
</tr>
<tr>
<td>III.II</td>
<td>Vitreous ice I oligomeric absorptions.</td>
</tr>
<tr>
<td>III.III</td>
<td>H₂O composite band half-height widths.</td>
</tr>
<tr>
<td>III.IV</td>
<td>The behaviour of HDO stretching modes in cubic ice I.</td>
</tr>
<tr>
<td>III.V</td>
<td>The behaviour of HDO librational modes in cubic ice I.</td>
</tr>
<tr>
<td>III.VI</td>
<td>HDO stretching modes half-height widths.</td>
</tr>
<tr>
<td>III.VII</td>
<td>HDO stretching modes peak heights.</td>
</tr>
<tr>
<td>III.VIII</td>
<td>Ice I sample histories.</td>
</tr>
<tr>
<td>III.IX</td>
<td>Cubic ice I H₂O and D₂O absorptions.</td>
</tr>
<tr>
<td>III.X</td>
<td>Cubic ice I ν_T(H₂O) absorptions.</td>
</tr>
<tr>
<td>III.XI</td>
<td>(a) Present and previous H₂O assignments for cubic ice I.</td>
</tr>
<tr>
<td></td>
<td>(b) Present and previous frequencies for ν_T(H₂O).</td>
</tr>
<tr>
<td>III.XII</td>
<td>Present and previous HDO frequencies for cubic ice I.</td>
</tr>
<tr>
<td>III.XIII</td>
<td>Present and previous D₂O assignments for cubic ice I.</td>
</tr>
<tr>
<td>IV.I</td>
<td>Calculated and observed RMS amplitudes of translation for H₂O and D₂O.</td>
</tr>
<tr>
<td>IV.II</td>
<td>H₂O, HDO and D₂O moments-of-inertia.</td>
</tr>
<tr>
<td>IV.III</td>
<td>Symmetric G-matrix elements for H₂O₃.</td>
</tr>
<tr>
<td>TABLE</td>
<td>PAGE</td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>IV.IV</td>
<td>$H_2O_3$ and $D_2O_3$ force constants for ice I.</td>
</tr>
<tr>
<td>V.I</td>
<td>The clathrate-mixture sample histories</td>
</tr>
<tr>
<td>V.II</td>
<td>$H_2O$ frequencies in unannealed and annealed $CH_3Cl\cdot7.67H_2O$</td>
</tr>
<tr>
<td>V.III</td>
<td>Oligomeric frequencies at $83^\circ K$ in unannealed clathrate-mixtures</td>
</tr>
<tr>
<td>V.IV</td>
<td>Temperature dependences of oligomeric frequencies in unannealed clathrate mixtures</td>
</tr>
<tr>
<td>V.V</td>
<td>The stable temperature ranges of the oligomer peaks</td>
</tr>
<tr>
<td>V.VI</td>
<td>The alkyl halide guest absorptions in unannealed clathrate mixtures at $83^\circ K$</td>
</tr>
<tr>
<td>V.VII</td>
<td>The temperature dependence of the guest frequencies during annealing</td>
</tr>
<tr>
<td>V.VIII</td>
<td>The stable temperature ranges for the guest absorptions</td>
</tr>
<tr>
<td>V.IX</td>
<td>The behaviour of HDO stretching modes for annealed clathrate mixtures</td>
</tr>
<tr>
<td>V.X</td>
<td>HDO librations for three annealed clathrate mixtures</td>
</tr>
<tr>
<td>V.XI</td>
<td>Average $H_2O$ and $D_2O$ frequency-temperature data for annealed clathrate mixtures</td>
</tr>
<tr>
<td>V.XII</td>
<td>Data for $Cl_2\cdot7.67H_2O$ and $Br_2\cdot8.6H_2O$ on CsI and AgCl</td>
</tr>
<tr>
<td>VI.I</td>
<td>$H_2O$ frequencies for hydrated alkalai halide salts</td>
</tr>
<tr>
<td>VI.II</td>
<td>Oligomeric $H_2O$ and $D_2O$ peaks in clathrate mixtures and rare gas matrices</td>
</tr>
<tr>
<td>VI.III</td>
<td>Alkyl halide frequencies in pure solids and clathrate mixtures</td>
</tr>
<tr>
<td>FIGURE</td>
<td>PAGE</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>1.1 The stainless steel deposition tube.</td>
<td>44</td>
</tr>
<tr>
<td>1.2 The isolated sample chamber.</td>
<td>46</td>
</tr>
<tr>
<td>3.1 Representative spectra of vitreous and cubic ices.</td>
<td>60</td>
</tr>
<tr>
<td>3.2 Frequency shifts during phase transformation</td>
<td>61</td>
</tr>
<tr>
<td>3.3 Oligomeric H$_2$O and D$_2$O absorptions in vitreous ice I</td>
<td>64</td>
</tr>
<tr>
<td>3.4 Half-height width shifts for ($v_R$, $v_R + v_T$) and ($v_1$, $v_3$, $v_1 + v_T$).</td>
<td>66</td>
</tr>
<tr>
<td>3.5 Half-height width shifts for ($v_2$, 2$v_R$)</td>
<td>67</td>
</tr>
<tr>
<td>3.6 HDO stretching frequency shifts for cubic ice I</td>
<td>71</td>
</tr>
<tr>
<td>3.7 HDO librational frequency shifts for cubic ice I</td>
<td>73</td>
</tr>
<tr>
<td>3.8 HDO stretching mode half-height width shifts for cubic ice I.</td>
<td>75</td>
</tr>
<tr>
<td>3.9 HDO stretching mode peak height shifts for cubic ice I</td>
<td>78</td>
</tr>
<tr>
<td>3.10 The shifts of cubic ice I $v_3$</td>
<td>82</td>
</tr>
<tr>
<td>3.11 The shifts of cubic ice I $v_1$</td>
<td>85</td>
</tr>
<tr>
<td>3.12 The shifts of cubic ice I $v_2$</td>
<td>86</td>
</tr>
<tr>
<td>3.13 The shifts of cubic ice I $v_R$</td>
<td>88</td>
</tr>
<tr>
<td>3.14 The cubic ice I $v_T$(H$_2$O) band at 83°K</td>
<td>89</td>
</tr>
<tr>
<td>3.15 The shifts of cubic ice I $v_T$</td>
<td>90</td>
</tr>
<tr>
<td>3.16 The shifts of cubic ice I ($v_1 + v_T$).</td>
<td>92</td>
</tr>
<tr>
<td>3.17 The shifts of cubic ice I 3$v_R$.</td>
<td>93</td>
</tr>
<tr>
<td>3.18 The shifts of cubic ice I ($v_R + v_T$).</td>
<td>94</td>
</tr>
</tbody>
</table>
4.1 The calculated linear thermal expansion coefficient of cubic ice I ........................................ 128
4.2 The calculated cubic ice I lattice parameter as a function of temperature .......................... 129
4.3 The calculated 0⋯⋯0 distance for cubic ice I as a function of temperature ......................... 131
4.4 Cubic ice I HDO stretching frequencies as a function of R(0⋯⋯0) .................................. 132
4.5 Comparison of observed and predicted νOH(HDO) - R(0⋯⋯0) dependence .......................... 137
4.6 The calculated cubic ice I harmonic HDO frequency as a function of temperature ............ 143
4.7 The calculated HDO anharmonicity ................................................................. 144
4.8 A plot of HDO anharmonicity against R(0⋯⋯0) .................................................. 145
4.9 Calculated RMS amplitudes of translation <Δr^2> .................................................. 150
4.10 A plot of <Δr^2> against R(0⋯⋯0) ........................................................................ 151
4.11 A plot of νOH(HDO) and νOD(HDO) against <Δr^2> ................................................ 152
4.12 The cubic ice I v_3 dependences on R(0⋯⋯0) ........................................................ 165
4.13 The calculated hexagonal ice I v_3 dependence on R(0⋯⋯0) ........................................ 166
4.14 The calculated hexagonal ice I νOH(HDO) and νOD(HDO) dependences on R(0⋯⋯0) ...... 167
4.15 H_2O, HDO and D_2O vapour and cubic ice I phase frequencies .................................... 180
4.16 The effects of uncoupling on the HDO stretching frequencies ........................................ 184
4.17 The principal axes of H_2O, HDO and D_2O .......................................................... 189
4.18 The H_2O_3 model of H_2O in ice ........................................................................ 199
4.19 The internal coordinates of H_2O_3 ........................................................................ 202
4.20 The symmetry coordinates of H_2O_3 ........................................................................ 203
<table>
<thead>
<tr>
<th>FIGURE</th>
<th>Description</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>Clathrate-mixture frequency shifts during transformation</td>
<td>217</td>
</tr>
<tr>
<td>5.2</td>
<td>Typical annealing spectra for CH$_3$Cl, CH$_3$Br and CH$_3$I clathrate-mixtures</td>
<td>218</td>
</tr>
<tr>
<td>5.3</td>
<td>Typical annealing spectra for CHCl$_3$ and C$_2$H$_5$Br clathrate-mixtures</td>
<td>219</td>
</tr>
<tr>
<td>5.4</td>
<td>Typical annealing spectra for Br$_2$ and Cl$_2$ clathrate-mixtures</td>
<td>220</td>
</tr>
<tr>
<td>5.5</td>
<td>Consecutive spectra for annealing Cl$_2$·7.67H$_2$O on CsI</td>
<td>227</td>
</tr>
<tr>
<td>5.6</td>
<td>Frequency shifts for $\nu_{OH}$(HDO) of annealed CH$_3$Br·7.67D$_2$O (1.00% HDO)</td>
<td>235</td>
</tr>
<tr>
<td>5.7</td>
<td>Frequency shifts for $\nu_{OD}$(HDO) of annealed CH$_3$Br·7.67H$_2$O (5.94% HDO)</td>
<td>236</td>
</tr>
<tr>
<td>5.8</td>
<td>The half-height width shifts for $\nu_{OH}$ and $\nu_{OD}$ of several clathrate-mixtures</td>
<td>238</td>
</tr>
<tr>
<td>5.9</td>
<td>The shift of $\nu_R$(HDO) in annealed CH$_3$Br·7.67D$_2$O (4.00% HDO)</td>
<td>240</td>
</tr>
<tr>
<td>5.10</td>
<td>Shifts of $\nu_1$(D$_2$O) for annealed CH$_3$Br·7.67D$_2$O</td>
<td>242</td>
</tr>
<tr>
<td>5.11</td>
<td>Shifts of $\nu_3$(D$_2$O) for annealed CH$_3$Br·7.67D$_2$O</td>
<td>243</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

To Professor K.B. Harvey who has the assured faith in graduate students to allow them to choose and pursue a range of interests in vibrational spectroscopy, and who instills a beneficial but often frustrating independence of thought and action.

To Professors R.F. Snider and A. Bree who as members of my committee were also willing to discuss problems related to this work.

To the members of the mechanical, glass blowing and electronics workshops for their excellent craftsmanship and cheerful aid.

To Raymond Green and other students and faculty for the many opportunities to discuss diverse problems and for the ready mutual exchange of ideas.

And to my wife and family for their special help and the joy they provide.
DEDICATION:

To my parents

Karl Johan Frithiof Hardin

and

Beatrice Mary (Trojanski) Hardin
INTRODUCTION

The phenomenon of hydrogen bonding has played an increasingly important role in the theories of certain chemical and bio-chemical systems for more than three decades. Several models, depending on the physical property investigated, have been proposed to explain the experimental results. However, for crystals a unified hydrogen bond model has not yet developed which is consistent with all the chemical and physical properties of the solid state.

The present work is a spectroscopic investigation of solid state hydrogen bonding in vitreous and cubic ice I and in vitreous and crystalline clathrate-hydrate mixtures; the nature of the clathrate-hydrate solids formed by vapour condensation is uncertain. A detailed study of the large changes (relative to non-hydrogen-bonded solids) in the infrared (ir) absorptions as a function of temperature provides information on changes in hydrogen bonding as a function of the oxygen-oxygen nearest-neighbour distance (R(O····O)) both for individual molecules and for the collective solid arrays. These data help to describe precisely changes in one solid's molecular potential and should aid in the development of a unified hydrogen bond model.

Hydrogen Bonding

The main effects manifested by the hydrogen bond (A-X-H····Y-B) on the ir spectra are: 1) large frequency shifts, 2) alterations in intensity, 3) increased band width, and 4) the appearance of new bands associated with the deformation of the hydrogen bond. The general phenomenon of hydrogen bonding has been reviewed by Pimentel and McClellan (1), Sokolov and
Tschulanovski (2), and by Hadzi and Thompson (3). Recently Hamilton and Ibers (4) discussed the roles of hydrogen bonding in chemical structures. The specific effects of hydrogen bonds on the chemical and physical properties of ice are treated in books by Eizenberg and Kaufmann (5) and by Riehl, Bullemer and Engelhardt (6).

A. Theories of Hydrogen Bonding

Hydrogen bonding theories fall into two classes—classical and quantum mechanical; the latter includes three separate approaches—valence bond (VB), charge transfer (CT) and molecular orbital (MO) representations. The conclusions drawn from all the theories are that both electrostatic, charge migration and short range repulsion give concerted effects and both are concurrently important (7).

(i) Classical Theories

The classical electrostatic theories are based on Pauling's (8) description which assumed the H atom could form a single covalent bond only.

(a) Point charge models. In the early work (1933-1957) the charge distribution was approximated by a set of point charges (9-12). For the ice and clathrate-hydrate systems with O-H–O bonds, 4 electrons (2 in the O-H bond and 2 in the O lone pair) were considered and the remaining electrons and protons were assumed to form the molecular core. The charges were located so that the correct O-H and lone pair dipole moments were obtained. The interaction energy of the hydrogen bond, calculated by assuming a simple Coulomb potential, was then 6 kcal/mole. The theories have successfully explained the lengthening of the X-H bond \( r(X-H) \) and the X-H stretching frequency \( v_{XH} \) red shift.
Two conclusions have been drawn from the simple electrostatic model. First, electrostatic energy is important in hydrogen bonding as is indicated by the decreasing bond strength with decreasing electronegativity of the proton acceptor and proton donor. Secondly, electrostatic energy causes at least part of $\Delta R(X\cdots Y)$ and $\Delta \nu_{XH}$.

(b) Continuous charge distribution model. This model was presented in 1964 by Bader (13) for the O-H\cdots O system typical of ice and clathrate-hydrates. He considered all the electrons, by methods developed for hydrides and binary hydrides (14,15), in spherical charge distributions and calculated the electrostatic force by classical electrostatic methods. The conclusions and interpretation of Bader's model are the same as for the point charge model.

(c) Summary of the classical theories. The electrostatic theories ignore four important facts about hydrogen bonding. For example, hydrogen bonds may not be completely ionic since there is no correlation between dipole moments and hydrogen bond strengths in the hydroxides. As well, both the point and continuous charge distribution models assume the electronic charge distributions are undistorted by the formation of a hydrogen bond. Another point to consider is that the $X\cdots Y$ distances are much less than the covalent van der Waal's radii suggesting that forces other than repulsion are important. Finally, the electrostatic theories cannot explain the increase of intensity of the $X-H$ stretching mode.

(ii) Quantum Mechanical Theories

The first quantum mechanical theory of the hydrogen bond was published in 1952 by Sokolov (16), although such methods have become practical only recently. Since the results of this thesis are not interpreted in detail by the quantum theories, they will only be outlined and their results will be stated.
(a) Valence bond theories. The VB calculations (16,17) did not give exact physical solutions since the method has a largely empirical origin. As in the elementary electrostatic models only four electrons were considered. Later Tsubomura (18) showed that four effects contribute to the hydrogen bond and that the agreement of the electrostatic model with experiment may be fortuitous since the three non-electrostatic effects may cancel each other.

The four energies contributing to the hydrogen bond energy are: 1) the electrostatic energy, 2) the short-range repulsion energy, 3) the dispersion energy, and 4) the delocalization energy due to CT. Tsubomura characterized effects 2, 3 and 4 explicitly. He assumed there were 5 contributing resonant structures:

\[
\begin{align*}
\psi_1 & \quad X\text{-}H & Y & \text{covalent } X\text{-}H \\
\psi_2 & \quad X^- & H^+ & Y & \text{pure ionic} \\
\psi_3 & \quad X^+ & H^- & Y & \text{pure ionic} \\
\psi_4 & \quad X^- & \text{---} & Y^+ & \text{covalent } H\text{-}Y \text{ CT} \\
\psi_5 & \quad X & H^- & \text{---} & Y^+ & \text{covalent } X\text{-}Y \text{ CT}
\end{align*}
\]

Tsubomura's calculation showed that the delocalization energy amounts to 8.1 kcal/mole—about 1.5 times larger than the electrostatic energy. The repulsion energy and dispersion energy are of opposite sign to the delocalization energy and appear to cancel it.

The VB method has received more recent treatments (19,20). Hasegawa, Daiyasu and Yomosa (20) reported a four electron VB calculation of the hydrogen bond potential energy. They used Tsubomura's (18) 5 resonant structures and constructed the contributing \( \psi \)-functions from trigonal or tetrahedral Slater atomic orbitals. The proton potential was calculated as a function of \( R(O\cdots O) \) and \( r(O\text{-}H) \). As well, the shifts in \( r(O\text{-}H) \) and \( \nu_{OH} \)
upon hydrogen bonding were studied.

The calculations of Hasegawa et al. ignored the contributions of the CT structures, \( \psi_4 \) and \( \psi_5 \), and resulted in an asymmetric, single minimum potential. They deduced that to account for \( \Delta r(O-H) \) and \( \Delta \nu_{OH} \) the polarization of the surroundings must be considered, i.e. \( \psi_4 \) and \( \psi_5 \) must be included. When that was done a double minimum potential resulted.

One can summarize the VB theories by stating the following conclusions: 1) in addition to electrostatic forces other forces are important—dispersion, exchange repulsion and delocalization, 2) CT from \( Y \) to \( X \) is not negligible for short bonds but may be for long bonds, 3) the amount of CT changes very rapidly as a function of \( r(X-H) \) and \( r(X-Y) \)(the contribution of \( \psi_4 \) rises much faster (10 times) than the contributions of \( \psi_2 \), \( \psi_3 \) and \( \psi_5 \)).

(b) Charge transfer theories. Since a well developed theory for CT exists, several workers applied these techniques to the hydrogen bond (21, 22, 23). Bratoz (22) applied the CT theory to \( 0-H-\cdots-0 \) with four electrons in three orbitals, the \( OH \) bonding and antibonding orbitals and the \( O \) lone pair orbital.

The conclusions Bratoz (7) reached from these CT theories are: 1) the VB picture of the hydrogen bond is valid, 2) since the \( H \) atom is small, the short range repulsive forces are small and the \( H \) atom has a special role for this kind of intermolecular interaction, 3) a fraction of an electron exists in the \( OH \) antibonding orbital, reducing the bond strength and allowing longer \( r(X-Y) \) and weaker \( X-H \) force constants, 4) CT theories predict an increased polarity in the \( O-H-\cdots-0 \) complex and therefore an increased infrared \( \nu_{OH} \) intensity.
(c) Molecular orbital theories. The FH\textsubscript{2}F anion has been examined in detail since it is relatively small with respect to physical size, bond length and number of electrons. Larger systems such as (H\textsubscript{2}O\textsubscript{2}), (HF\textsubscript{2}), and (H\textsubscript{2}S\textsubscript{2}) cannot be treated exactly since drastic approximations must be made.

For O-H\cdots O Weissmann and Cohen (24) found a very asymmetric single minimum potential, in contrast to the empirical double minimum result of Lippincott and Schroeder (25). Weissmann's results predicted an H\textsubscript{2}O dipole moment of 2.40 D in ice, in good agreement with the experimental value of Eisenberg (5), 2.40-2.87 D, however, the method was less successful in predicting the r(X-H) and r(X-Y) distances. More recently, Rein, Clarke and Harris (26) studied the hydrogen bond of water by MO methods. The important point of this work is that the atomic charges and overlap populations indicate a substantial CT across the hydrogen bond.

Molecular orbital theories so far indicate 2 properties of hydrogen bonds: 1) formation of a hydrogen bond induces electron charge migration from the molecular core to the external region and 2) the H 2p\textsubscript{\Pi} atomic orbital contribution to the ground state is not negligible—there is a small amount of \pi character in the hydrogen bond.

B. Spectroscopic Manifestations of Hydrogen Bonding

As early as 1933 Bernal and Fowler (9) recognized in H\textsubscript{2}O the large shift in \nu\textsubscript{OH} (\Delta \nu\textsubscript{OH} = \nu\textsubscript{OH}(vapour) - \nu\textsubscript{OH}(hydrogen bonded)) caused by hydrogen bonding. Infrared techniques still remain the most versatile tool to investigate the hydrogen bonds in vapours, liquids and solids. However, the relatively large electron migrations induced by hydrogen bonds give large
changes in nuclear shielding and shifts in the 

nuclear transitions. The present work is concerned only with the ir manifestations of hydrogen bonding in the O-H····O system ice I and in clathrate-hydrates.

(i) The General Effects of Hydrogen Bonding

The four main spectroscopic effects in hydrogen bonded solids are often large in contrast to the small effects found between the vapour and solid phases of molecules incapable of hydrogen bonding. The first correlation made from the experimental data was the relationship between $R(X\cdots\cdots Y)$ and the $v_{XH}$ shifts from the monomer frequency in the bonded complex. Generally it is found that the shift, breadth and intensity of $v_{XH}$ depends on the strength of the hydrogen bond.

Those properties are largest for the strong hydrogen bonding system $\text{FHF}^-$, but are much smaller in the weak $\text{NH} \cdots \cdots \text{N}$ systems since the $\text{N}$ van der Waal's radii are larger. The four effects will now be considered in detail.

(a) Frequency shifts. Not all of the molecular vibration frequencies are strongly affected by hydrogen bonding. The $X$-$H$ stretching frequency is shifted to lower frequency by 10-50% of the vapour phase frequency and the $R$-$X$-$H$ bending vibration experiences a relatively smaller shift to higher frequency. The novelty of the large stretching mode shifts can be grasped by comparing non-hydrogen bonding and hydrogen bonding molecules.

<table>
<thead>
<tr>
<th>(a) no hydrogen bonding</th>
<th>Vapour $v_{HF}$</th>
<th>Solid $v_{HF}$</th>
<th>$\Delta v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO}_2$</td>
<td>1285 cm$^{-1}$</td>
<td>1285 cm$^{-1}$</td>
<td>0 cm$^{-1}$</td>
</tr>
<tr>
<td>$\text{CH}_4$</td>
<td>2914 cm$^{-1}$</td>
<td>2906 cm$^{-1}$</td>
<td>8 cm$^{-1}$</td>
</tr>
<tr>
<td>(b) hydrogen bonding</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) FHF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_{HF}$</td>
<td>4140 cm$^{-1}$</td>
<td>3440 cm$^{-1}$</td>
<td>1450 cm$^{-1}$</td>
</tr>
<tr>
<td>$\Delta v$</td>
<td>-700 cm$^{-1}$</td>
<td>-2690 cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$R(F\cdots\cdots F)$</td>
<td>2.55 Å</td>
<td>2.26 Å</td>
<td></td>
</tr>
</tbody>
</table>

(a) Nakamoto et al., Ref. 27. (b) $\text{CO}_2$ bonding mode.
Tables and plots of $v_{XH}$ as a function of $R(X....Y)$ were compiled by Nakamoto, Margoshes and Rundle (27) for the FHF, OHO, NHF, OHN, NHO, NHN, OHCl and NHCl families of hydrogen bonding compounds. For small $R(X....Y)$ the $v$ vs. $R$ relationships are linear as Pimentel and Sederholm (28) proposed. For large $R(X....Y)$ the $v$ vs. $R$ relationship is non-linear: the behaviour over all $R(X....Y)$ suggested an asymptotic relationship.

(b) Band broadening. An increased half-height width ($\Delta v^2$) is found for $v_{XH}$ and its overtones in hydrogen bonded systems (29). In contrast the effect is much smaller on the width of the $R-X-H$ bending modes.

In the early work the explanation for broadening was thought to lie in the form of the intermolecular potential perturbation. Such an explanation is sufficient only for weak or moderate strength hydrogen bonds, but not for strong hydrogen bonds. Strong hydrogen bonds give broad bands in the vapour phase as well as in the liquid and solid phases. Hence the breadth is independent of the non-hydrogen bond intermolecular forces to the first order.

Bratoz and Hadzi (30) and Reid (31) suggested that the breadth arises from the anharmonicity perturbations and changes or differences in the anharmonicity over many molecules. Generalizing the discussions of ice they suggested that in all $X-H....Y$ systems the breadth of the $v_{XH}$ absorption arises from a group of closely spaced bands.

(c) Band intensity. The integrated intensity coefficients often increase many-fold upon hydrogen bond formation. Also the overtones of $v_{XH}$ decrease in intensity. The apparent relationships among $\Delta v$, $\Delta v^2$ and intensity (large shift, broad band, large intensity) do not necessarily hold for all types of hydrogen bonding complexes.
There is little reliable data on integrated intensities due to experimental difficulties, however, early work by Huggins and Pimentel (29) established that hydrogen bonded complexes which show no increase in the intensity of $v_{XH}$ appeared to have non-linear hydrogen bonds.

The increased intensity of $v_{XH}$ and the unaffected intensity of $v_R$ cannot be explained by electrostatic theories of the hydrogen bond: Electrostatics requires that both $v_{XH}$ and $v_R$ increase in intensity. However, CT theories predict that only $v_{XH}$ increases in intensity.

(d) New absorptions. For X-H······Y systems new bands appear in the spectra associated with the deformation of the hydrogen bond. In ice the hydrogen bond stretch and hydrogen bond bend correspond to molecular translation ($v_T$) and molecular libration ($v_R$) modes, the so-called lattice modes.

(ii) The O-H······O Hydrogen Bond Effects

The discussions here have so far been concerned with correlations among different hydrogen bonding families. However, there is a very big problem involved in such comparisons, the different X-H······Y systems have differences in molecular polarizability, van der Waal's radii, sizes of orbitals, dispersion forces, etc. Therefore one must expect different relationships among $\Delta n_{XH}$, $\Delta n_{YH}$, intensity and $R(X······Y)$. These parameters in cubic ice I and the clathrate-hydrates can best be compared to other O-H······O systems and preferably to other H$_2$O allotropes, i.e., the high pressure ices.

In order to study $v_{XH}$ as a function of $R(O······O)$, Nakamoto et al. (27) compiled $\Delta n_{OH}$ and $R(O······O)$ data for 26 compounds. As well, they correlated $R(O······O)$ to $r(O-H)$ from neutron diffraction data. The results indicate
that as $R(0\cdots0)$ decreases then $r(0-H)$ increases **linearly** for long hydrogen bonds and **exponentially** for strong (short) hydrogen bonds. They felt that inclusion of covalency in the hydrogen bond was important, as in Tsubomura's (18) work.

In order to understand the potential energy of the proton as a function of $R(0\cdots0)$, Lippincott and Schroeder (25) constructed a one dimensional model of the hydrogen bond. By applying the conditions of equilibrium, they obtained relations for $\Delta v_{OH}$, $r(O-H)$, hydrogen bond energy and force constants as a function of $R(0\cdots0)$. Their results agree well with experiment: for ice, where $R(0\cdots0) = 2.76 \pm 0.1 \text{Å}$, their relationship between $v_{OH}$ and $R(0\cdots0)$ is linear. Unfortunately their formulas are not good for predicting the $v_{OH}$ of ice over a small range of $R(0\cdots0)$ since there is some arbitrariness in defining the hydrogen bond dissociation energy.

Reid (31) constructed the potential surface for simultaneous H and O motion in $O-H\cdots0$ hydrogen bonds over a wide range of $R(0\cdots0)$ and $r(O-H)$. He modified the Lippincott-Schroeder potential by changing the hydrogen bond dissociation energy from molecule to molecule, i.e., with changing $R(0\cdots0)$. Reid used his potential functions to interpret the changes in ir results with changes in crystalline lattice dimensions.

He proposed that the breadth of $v_{OH}$ was due to its strong dependence on $R(0\cdots0)$. During any $v_T$ vibration many $R(0\cdots0)$ distances occur and many $v_{OH}$'s are observed.

Recently Bellamy and Pace (32) reviewed the relations among $\Delta v_{XH}$ and $R(X\cdotsY)$. They deduced that $X$ and $Y$ can approach only to the combined van der Waal's radii, further approach of $X$ and $Y$ is permitted only if
hydrogen bonding occurs. For example in the O-H\cdots O system the van der Waal's radii give an O\cdots O closest approach distance of 3.6 Å. The weakest hydrogen bond has an R(O\cdots O) of 3.36 Å, therefore R(O\cdots O) contracts upon formation of the hydrogen bond. Extrapolations of the X-Y plots of Nakamoto et al. indicated that the limiting R(X\cdots Y) is the sum of X and Y van der Waal's radii but not including H:

\begin{align*}
\text{FHF}^- \text{ intercept } & 2.7 \text{ Å (calc. 2.7 Å)} \\
\text{OH}\cdots\text{O intercept } & 2.84 \text{ Å (calc. 2.8 Å)}
\end{align*}

This suggested that in hydrogen bonds the H orbital disappears or is completely overlapped and that there is no repulsion due to it.

Bellamy and Owen (33) extended this idea and proposed that the rate of increase of repulsion is proportional to the rate of increase in lone pair - lone pair repulsions. They adopted the 6-12 potential to describe the repulsive terms from lone pairs in X and Y and finally obtained an expression relating $\Delta v_{XH}$ and R(X\cdots Y). For O-H\cdots O this has the form

$$
\Delta v_{OH} = 50 \left[ \left( \frac{3.35}{R} \right)^{12} - \left( \frac{3.35}{R} \right)^{6} \right].
$$

This relationship gives good agreement with the work of Nakamoto et al.

However by inspection of Nakamoto's work one sees that no unique $v_{OH} - R(O\cdots O)$ relation exists for the O-H\cdots O family. There are too many variables. It seems more reasonable to study one molecular system like H$_2$O in a variety of crystal habits and to attempt to vary only R(O\cdots O) in some way. For example, a study of H$_2$O in all 9 ice phases and in clathrate-hydrates as a function of temperature may provide useful results.
Clathrate-Hydrates

A. The Clathrate-Hydrate Problem

Quantized rotation or libration of trapped (guest) molecules in the (host) lattice cavities has been suggested by previous ir (34,35) and nmr (36,37) studies. Now detailed ir assignments of the guest rotations and their behaviour in the host cavity are required to determine the form of the potential well surrounding the guest molecules. In order to determine the changes in the interactions of the guest molecules with the host lattice and the height of the barrier to guest rotations, it is necessary to know precisely how the guest molecule absorptions and host lattice absorptions vary as a function of temperature.

B. The Structures of the Clathrate-Hydrates

Clathrates are a type of inclusion compound in which one stable molecule forms a union with 2 or more other stable molecules, atoms or molecular elements without the existence of chemical bonds between the components. (The enclosing lattice which contains the cavities is called the host and the enclosed molecule is called the guest.) A common property of some important clathrate compounds is hydrogen bonding. Some examples of clathrates are:

1) $\beta$-quinol clathrates, $0.74$ Kr $\cdot 3$ C$_6$H$_4$(OH)$_2$
2) gas hydrates, Ar $\cdot 7.67$ H$_2$O
3) tetraalkylammonium clathrates, salt hydrates
   $[(n - \text{C}_4\text{H}_9)_4\text{N}] \text{C}_6\text{H}_5\text{CO}_2 \cdot 39.5 \text{H}_2\text{O}$
4) Ni(CN)$_2$NH$_3\cdot$C$_6$H$_6$.
A clathrate-hydrate is a clathrate compound formed with an H$_2$O host lattice in which a variety of small atoms and covalent molecules are trapped. The clathrate-hydrates can be separated into two classes: The gas hydrates are clathrates formed between H$_2$O (host) and small, covalent gases (guests, G) and liquid hydrates are clathrates formed between H$_2$O (host) and molecules of volatile liquids (guests, G).

Three crystal structures have been found for the clathrate-hydrates. The so-called gas hydrate clathrates, Type I, are cubic and have maximum ideal stoichiometries of $8G\cdot46H_2O$ or $6G\cdot46H_2O$. The so-called liquid clathrate-hydrates, Type II, are also cubic and have maximum ideal stoichiometries of $8G\cdot136H_2O$ or $16G'\cdot8G\cdot136H_2O$. Bromine liquid clathrate-hydrate, Type III, is tetragonal and has a maximum ideal stoichiometry of $20G\cdot172H_2O$.

(i) Type I Clathrate-Hydrates

These compounds form a cubic crystal of Pm3n symmetry (38,39) with a 12 Å unit cell edge and 46 H$_2$O molecules in a unit cell. Two pentagonal dodecahedrons are formed by 20 H$_2$O molecules each. Those two cavities are linked by the remaining 6 H$_2$O molecules to form 6 tetrakaidecahedra, giving a total of 8 cavities per unit cell.

In Type I clathrate-hydrates the nearly spherical pentagonal dodecahedra have free diameters of 3.95 Å and the spheroidal tetrakaidecahedra have free diameters of 5.8 Å (for a 12.0 Å unit cell). Molecules and atoms whose maximum dimensions are less than 5.1 Å can fill all 8 cavities and would have an ideal clathrate stoichiometry of $8G\cdot46H_2O$ (i.e. G = Ar, CH$_4$, H$_2$S). Molecules and atoms whose maximum dimensions are less than 5.8 Å but are larger than 5.1 Å will fill only the 6 tetrakaidecahedra and would have
Table 0.1 Some typical clathrates and their properties.

$P_{\text{diss}}$ gives the clathrate decomposition pressure at 0°C,
$T_{\text{max}}$ gives the maximum stable temperature of the clathrate and
$T_b$ gives boiling temperature of pure guest.*

<table>
<thead>
<tr>
<th>Type</th>
<th>Clathrate</th>
<th>$a_c$</th>
<th>$P_{\text{diss}}$ at 0°C</th>
<th>$T_{\text{max}}$</th>
<th>$T_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$^\circ$A</td>
<td></td>
<td>$^\circ$C</td>
<td>$^\circ$K</td>
</tr>
<tr>
<td>8$G \cdot 46H_2O$</td>
<td>Ar</td>
<td>--</td>
<td>95.5 atm</td>
<td>--</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>Kr</td>
<td>--</td>
<td>14.5</td>
<td>--</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>Xe</td>
<td>11.97</td>
<td>1.15</td>
<td>--</td>
<td>166</td>
</tr>
<tr>
<td>I</td>
<td>$H_2S$</td>
<td>12.00</td>
<td>698 Torr</td>
<td>29.5</td>
<td>213</td>
</tr>
<tr>
<td>(cubic) 6$G \cdot 46H_2O$</td>
<td>$Cl_2$</td>
<td>12.03</td>
<td>252</td>
<td>28.7</td>
<td>239</td>
</tr>
<tr>
<td></td>
<td>$CH_3Cl$</td>
<td>12.00</td>
<td>311</td>
<td>2.1</td>
<td>249</td>
</tr>
<tr>
<td></td>
<td>$CH_3Br$</td>
<td>12.09</td>
<td>187</td>
<td>14.5</td>
<td>277</td>
</tr>
<tr>
<td></td>
<td>$SO_2$</td>
<td>11.94</td>
<td>297</td>
<td>12.1</td>
<td>263</td>
</tr>
<tr>
<td>8$G \cdot 136H_2O$</td>
<td>$CH_3I$</td>
<td>17.14</td>
<td>74</td>
<td>4.3</td>
<td>316</td>
</tr>
<tr>
<td></td>
<td>$CHCl_3$</td>
<td>17.30</td>
<td>50</td>
<td>1.6</td>
<td>334</td>
</tr>
<tr>
<td>II</td>
<td>$C_2H_5Br$</td>
<td>17.26</td>
<td>155</td>
<td>--</td>
<td>311</td>
</tr>
<tr>
<td>(cubic) $CH_2Cl_2$</td>
<td>$C_2H_5$</td>
<td>17.31</td>
<td>116</td>
<td>1.7</td>
<td>315</td>
</tr>
<tr>
<td></td>
<td>$C_2H_8$</td>
<td>17.40</td>
<td>(1.74 atm)</td>
<td>5.69</td>
<td>228</td>
</tr>
<tr>
<td></td>
<td>$C_2H_5Cl$</td>
<td>17.30</td>
<td>201</td>
<td>4.8</td>
<td>286</td>
</tr>
<tr>
<td>20$G \cdot 172H_2O$</td>
<td>$Br_2$</td>
<td>$a_c$</td>
<td>23.8</td>
<td>43.90</td>
<td>332</td>
</tr>
<tr>
<td>III</td>
<td>$Br_2$</td>
<td>$c_o$</td>
<td>12.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(tetrag)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Reference 40
6G·46H₂O stoichiometry (Cl₂, SO₂, C₂H₆). Some properties of the clathrates formed in these two ratios are given in Table 0.1. One may also form a mixed hydrate of the form 2G·6G'·46H₂O, i.e. 2H₂S·6C₂H₆·46H₂O.

In the practical situation the unit cell dimension varies according to the size of the guest species, Table 0.2.

(ii) **Type II Clathrate-Hydrates**

These compounds form a cubic crystal of Fd3m (38) symmetry with a 17 Å unit cell edge and 136 H₂O molecules in a unit cell (i.e. G = CH₃I, CHCl₃, C₂H₅Br). There are 16 pentagonal dodecahedral cavities and 8 hexakaidecahedral cavities in one unit cell. The free diameters are 5.0 and 6.7 Å respectively (for a 17.4 Å unit cell).

Molecules which have a maximum dimension greater than 5.8 Å and less than 6.7 Å cannot form Type I clathrates, but do form Type II clathrates. That implies they occupy only the hexakaidecahedra with an ideal stoichiometry of 8G·136H₂O. Some Type II clathrates, the guest sizes, and the unit cell dimensions are given in Tables 0.1 and 0.2.

(iii) **Type III Clathrate-Hydrates**

The clathrate-hydrate of Br₂ was originally thought to be of Type II. However, work by Allen and Jeffrey (41) has shown that it forms a tetragonal crystal of symmetry 4/mmm with a = 23.8 and c = 12.2 Å unit cell edges and 172 H₂O molecules in a unit cell. They reported 20 polyhedral cavities large enough to accommodate Br₂ molecules, 10 small pentagonal dodecahedra, 16 tetrakaidecahedral and 4 pentakaidecahedral. The ideal stoichiometry is then 20Br₂·172H₂O. Some data are given in Tables 0.1 and 0.2.
Table 0.2 The types of cavities, the maximum allowed occupancy, guest sizes and unit cell dimensions of typical clathrate-hydrates.

<table>
<thead>
<tr>
<th>Type</th>
<th>Clathrate</th>
<th>$a_0$</th>
<th>$\alpha_0$</th>
<th>Guest size</th>
<th>$V_{12}$</th>
<th>$V_{14}$</th>
<th>$V_{15}$</th>
<th>$V_{16}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>8G·46H₂O</td>
<td>$A$</td>
<td>$A$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ar</td>
<td>--</td>
<td>3.76</td>
<td>2(2)*</td>
<td>6(6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kr</td>
<td>--</td>
<td>4.04</td>
<td>2</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Xe</td>
<td>$a_0$</td>
<td>11.97</td>
<td>2</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H₂S</td>
<td>12.00</td>
<td>4.40</td>
<td>2</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(cubic)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cl₂</td>
<td>12.03</td>
<td>5.17</td>
<td>0(2)</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₃Cl</td>
<td>12.00</td>
<td>5.06</td>
<td>0</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₃Br</td>
<td>12.09</td>
<td>5.33</td>
<td>0</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SO₂</td>
<td>11.94</td>
<td>5.00</td>
<td>0</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>8G·136H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₃I</td>
<td>17.14</td>
<td>5.70</td>
<td>0(16)</td>
<td></td>
<td></td>
<td>8(8)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CHCl₃</td>
<td>17.30</td>
<td>6.44</td>
<td>0</td>
<td></td>
<td></td>
<td>8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₂H₅Br</td>
<td>17.26</td>
<td>6.47</td>
<td>0</td>
<td></td>
<td></td>
<td>8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(cubic)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₂Cl₂</td>
<td>17.31</td>
<td>6.08</td>
<td>0</td>
<td></td>
<td></td>
<td>8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₃H₈</td>
<td>17.40</td>
<td>6.28</td>
<td>0</td>
<td></td>
<td></td>
<td>8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₂H₅Cl</td>
<td>17.30</td>
<td>6.20</td>
<td>0</td>
<td></td>
<td></td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>20G·172H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Br₂</td>
<td>$a_0$</td>
<td>23.8</td>
<td>0(10)</td>
<td>16(16)</td>
<td>4(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(tetrag)</td>
<td>$\alpha_0$</td>
<td>12.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$V_{12}$ - pentagonal dodecahedron, $V_{14,15,16}$ - tetrakai, pentakai, hexakaidodecahedrons.
* - numbers in brackets show maximum number of cavities per unit cell.
Since the present experiments attempt to accurately correlate $\nu_{OH}$ and $R(O\cdots O)$ for seven Type I, II, and III clathrate-hydrates, the $R(O\cdots O)$ distances are required. However, the structures were determined by assuming constant $R(O\cdots O)$ throughout the unit cell, e.g. 2.81 Å for a Type I clathrate (12.0 Å unit cell) and 2.78 Å for a Type II clathrate (17.3 Å unit cell). In order to accommodate the pentagonal dodecahedra and other polyhedra in the unit cell, the O-O-O angles were distorted from tetrahedral. Von Stackelberg (38) reported angles from 100.0° to 124.6°. It seems likely that in reality the O-O-O distances are also irregular and a range of $R(O\cdots O)$ exist for each clathrate-hydrate. That will unfortunately broaden the IR results even more than in ice I.

Indeed for Type I clathrate-hydrates (cubic, Pm3n) the H₂O oxygen atoms lie on 3 unit cell sites (k, i, and c). Consequently, there are 4 types of hydrogen bonds; k-k, k-i, k-c, i-i. It seems reasonable that these may not be identical in the real crystal.

C. Formation of Clathrate-Hydrates

A general phase diagram was proposed by Roozeboom and is shown in von Stackelberg's work (38). At constant temperature there are 2 boundary conditions to permit formation of clathrate-hydrates, raising the pressure of $G$ to form either guest $G$(gas) or $G$(liquid) plus hydrate. If the partial pressure of guest applied to the sample is less than the equilibrium dissociation partial pressure then the clathrate dissociates.

In a recent review Byk and Fomina (42) discussed the conditions for formation and the thermodynamics of formation. As well, Barrer and Ruzicka (43) studied the kinetics of rare gas clathrate formation at low temperatures.
Specifically, they investigated the formation of clathrate-hydrate from ice and Ar, Kr and Xe gases at 90°K and 195°K.

Their technique involved depositing a thin layer of H₂O in a glass bulb at 77°K. The sample was warmed to 195°K and either Ar, Kr or Xe (190 Torr) was admitted. The gas uptake as a function of time was measured. They found that Kr and Xe, but not Ar, reacted with ice at 195°K. Ar was found to react slowly at 90°K at 190 Torr. Their results suggested the ready formation of clathrate-hydrates at low temperatures with a critical formation pressure of less than 190 Torr.

D. Previous Investigations of the Clathrate-Hydrates

Contemporary interest in clathrates has been centered on the motion of the guest molecules in the host lattices. Thus the methods of dielectric relaxation (44-46), x-ray diffraction (38,47), nmr (48-51), thermodynamics (38), and ir spectroscopy (52-57, 34) have been applied to quinol clathrates and clathrate-hydrates to discover whether guest rotations are free or restricted, how fast they rotate, and what are the barriers to free rotation. Similarly, deductions with respect to hindered translations (rattling) of the guest have been made (48-51).

The first work on clathrate-hydrates in the ir was reported by McCourt (56). He studied the three Type I clathrate-hydrates of Ar, Kr, and SO₂. The main points of his thesis were: 1) there was an H₂O host band at 2425 cm⁻¹ in addition to the well known ice absorptions, 2) the νᵢ band was shifted -50 cm⁻¹ from ice I, 3) the 1600 cm⁻¹ and 2210 cm⁻¹ absorptions of the host were ν₂ (HOH bending) and ν₂ + νᵢ respectively, 4) SO₂ absorbed at 2455 cm⁻¹ and 3570 cm⁻¹ (a weak shoulder on ν₁ and ν₃, the symmetric and
assymmetric stretches, of $H_2O$) in the clathrate-hydrate.

Shurvell (57) followed up the above work by observing $SO_2$, $H_2S$, and Kr Type I clathrate hydrates ($SO_2 \cdot 46H_2O$). For $SO_2 \cdot 7.67H_2O$ Shurvell reported:
1) that $v_R (H_2O)$ was $40 \text{ cm}^{-1}$ less than that of ice, 2) that the $1600 \text{ cm}^{-1}$ band of ice was at $1640 \text{ cm}^{-1}$ in the clathrate and was therefore $v_2$ rather than $2v_R$, 3) that the $2230 \text{ cm}^{-1}$ was $v_2 + v_R$, and 4) that $H_2O$ in clathrates had a new feature at $2410 \text{ cm}^{-1}$ in addition to the ice bands. As well, he found that the $v_3(SO_2)$ had a central peak and 2 wings, 1336, 1342 and 1348 cm$^{-1}$. There was no splitting of $v_3(SO_2)$ as in the pure $SO_2$ solid and the clathrated $SO_2$ bands were broadened by "rattling" and rotational fine structure. The wings were thought to be due to combinations with librations (hindered rotations) and translations.

Both McCourt (56) and Shurvell (57) formed the clathrate-hydrates by condensation of stoichiometric gas mixtures on CsI windows at 77°K. Shurvell reported his samples were annealed to devitrify the condensed phase. The results of these preliminary investigations on Type I clathrate-hydrates were summarized by Harvey, McCourt and Shurvell (34).

E. The Present Approach to the Clathrate-Hydrate Problem

Three facets of the clathrate-hydrate ir absorptions were studied in this work. First, in order to analyze previous work (56,57), the forms of the clathrate-hydrate absorptions were determined from low temperature mulls of solid clathrate samples. Secondly, the vitreous-crystalline phase transformation was observed by ir spectroscopy as a function of temperature for clathrate-hydrates (types I, II and III) condensed from gaseous stoichiometric
mixtures. Thirdly, the temperature dependences were determined for the ir absorption of devitrified "clathrate" samples.

Ice

A. The Ice Problem

Many theories have been proposed to explain the origins of the frequency shifts, the large band widths and the large intensities in ice. Now data are required which will either support an existing theory or which will suggest some modifications to the theory. Specifically, the correlations of absorption band frequencies, widths and heights to $\Delta R(0\cdots 0)$ are required for ice I.

B. Non-Spectroscopic Investigations of Ice

(i) Structural Studies

Ice exists in at least twelve structural allotropes above 77°K and at pressures of up to 25,000 atmospheres. The ice phases stable at 1 atmosphere are all called ice I. In fact, there are three allotropes of ice I, the vitreous or amorphous, the cubic and the hexagonal phases (Iv, Ic and Ih). The ice I structural results up to 1958 were summarized by Lonsdale (58) and Owston (59). Recently, Brille and Tippe (60) measured by x-ray diffraction the ice Ih lattice parameters between 15° and 200°K. As well, Arnold, Finch, Rabideau and Wenzel (61) reported a neutron diffraction study of ice Ic.

(a) Hexagonal ice I. The ordinary phase of ice at S.T.P. is hexagonal ice I (Ih) in which the oxygen atoms form a P6$_3$/mmc unit cell with 4 molecules. * Assuming solid polywater is a unique solid of H$_2$O.
The unit cell dimensions are (62);

\[
\begin{array}{ccc}
\text{H}_2\text{O (163°K)} & a_0 & c_0 \\
4.493 \text{ Å} & 7.337 \text{ Å} \\
\text{D}_2\text{O (143°K)} & 4.495 & 7.335
\end{array}
\]

The oxygen-oxygen nearest-neighbour distances \((R(0\cdots0))\) in \(\text{H}_2\text{O}\) are 2.76 Å at 163°K. The molecules are hydrogen bonded to 4 nearest-neighbours in layers of hexagonal, puckered rings. The open structure has channels parallel and perpendicular to the \(c_0\) axis.

There is still some uncertainty about the unit cell dimensions of ice \(\text{Ih}\). The disagreement between Lonsdale's (58) expansion coefficients and the direct dilatometric measurements seems to arise from differences in crystallinity among the worker's samples. The x-ray diffraction work of La Placa and Post (63) agrees well with Dantl's (64) direct thermal expansion measurements: La Placa and Post's (63) work was confirmed by Brille and Tippe (60). The latter found that the \(c/a\) ratio is temperature independent, not reaching 1.633 even at 15°K; they found \(c/a = 1.6280 \pm 0.0002\).

(b) Amorphous ice \(\text{I}\). This phase is formed by the slow condensation of vapour onto a cold surface. Beaumont, Chihara and Morrison (65) found that amorphous ice \(\text{I}\) was formed when the deposition rate at 135°K was less than 0.04 g/cm\(^2\)/hour. The x-ray and electron diffraction patterns are diffuse and the samples are clear, transparent films. The samples have consequently been variously described as vitreous, amorphous or microcrystalline. Virtually nothing is known about the structure of amorphous ice \(\text{I}\).

(c) Cubic ice \(\text{I}\). Ice \(\text{Ic}\) can be formed by the irreversible transformation of amorphous ice \(\text{I}\) or from the high pressure ices. The vitreous-cubic ice \(\text{I}\) transformation has been reported to start as low as 110°K and as high
as 153°K by various authors, Table 0.3. The high pressure ice-cubic ice transformations have been studied by Bertie, Calvert and Whalley (66) at 77°K by release of pressure. Cubic ice I can also be formed by vapour condensation between 133° and 153°K. When warmed above 210°K cubic ice I transforms irreversibly to hexagonal ice I with a small enthalpy change, i.e. <1.5 cal/gm (65).

The crystal structure of the oxygen atoms in cubic ice I is the "diamond" structure, Fd3m with 8 molecules per unit cell. The oxygens are arranged in a similar fashion to that of hexagonal ice in layers of puckered hexagonal rings. However, the six O atoms adjoining 2 nearest-neighbours are eclipsed in cubic ice I and staggered in hexagonal ice I. The lattice parameters (62) at 143°K are a₀(H₂O) = 6.350 Å and a₀(D₂O) = 6.351 Å.

(d) Disorder in Ice I. The neutron diffraction work of Peterson and Levy (quoted in Lonsdale (58)) showed that each oxygen was surrounded by four 1/2 hydrogens at 1.01 Å. They asserted that the DOD angle = 000 angle and, therefore, that the hydrogen bonds are linear. Their results were the same at 123° and 223°K, indicating no ordering of the lattice down to 123°K. Pauling predicted a residual entropy at 0°K of Rln 3/2 or 0.805 e.u. However, Onsager and Dupuis (67) showed that Pauling's result is only the lower bound to the true calculated value. Nagle (68) found by lattice statistics that the theoretical value is 0.8145 ± 0.0002 e.u., compared to an experimental value of 0.82 ± 0.15 e.u. Disorder in cubic ice I was confirmed by electron diffraction (69).

Pitzer and Polissar (70) discussed the order-disorder problem in ice I and concluded that the ordered structure is more stable at low temperatures. However, they estimated that the transformation time may exceed a day. They
Table 0.3  
Temperature ranges of stability at 1 atmosphere of vitreous, cubic and hexagonal ice I by several experimental methods.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Low Temperature Phase and Range °K</th>
<th>Cubic Phase Range °K</th>
<th>Hexagonal Phase Range °K</th>
<th>Workers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>crystalline</td>
<td>144</td>
<td>273</td>
</tr>
<tr>
<td>heat capacity</td>
<td>77 - 144</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>amorphous</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>elect.diffrac.</td>
<td>77 - 107</td>
<td>107 - 190</td>
<td>190 - 273</td>
<td>Honjo et al. (b)</td>
</tr>
<tr>
<td>calorimetry</td>
<td>77 -(150 ± 10)</td>
<td>crystalline</td>
<td>150</td>
<td>273</td>
</tr>
<tr>
<td></td>
<td>amorphous</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>elect.diffrac.</td>
<td>77 - 151</td>
<td>151 - 173</td>
<td>173 - 273</td>
<td>Blackman et al. (d)</td>
</tr>
<tr>
<td>x-ray diffrac.</td>
<td>77 - 110</td>
<td>113 - 143</td>
<td>143 - 273</td>
<td>Dowell et al. (e)</td>
</tr>
<tr>
<td>diff.therm. anal.</td>
<td>77 - 149</td>
<td>149 - 186</td>
<td>186 - 273</td>
<td>McMillan et al. (f)</td>
</tr>
<tr>
<td>glass</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x-ray diffrac.</td>
<td>77 -(148 ± 8)</td>
<td>(148 ± 8) - (220±20)</td>
<td>220±20 - 273</td>
<td>Beaumont et al. (g)</td>
</tr>
<tr>
<td></td>
<td>amorphous</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>thermal analysis</td>
<td>77 - 154</td>
<td>154 - 208</td>
<td>208 - 273</td>
<td>Ghormley           (h)</td>
</tr>
<tr>
<td></td>
<td>amorphous</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>calorimetry</td>
<td>77 - 135</td>
<td>135 - 160</td>
<td>160 - 273</td>
<td>Sugisaki et al. (i)</td>
</tr>
<tr>
<td></td>
<td>amorphous</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Ref. 71, (b) Ref. 69, (c) Ref. 72, (d) Ref. 73, (e) Ref. 74, (f) Ref. 75, (g) Ref. 65, (h) Ref. 76, (i) page 329, Ref. 6.
also estimated the Curie point to be near 60°K.

(e) High pressure ices. The allotropes of ices II through IX may not constitute all possibilities. More allotropes may exist below 77°K and at higher pressures. Some of the crystallographic properties and structural parameters of the ice allotropes are given in Table 0.4. Phases II, VIII and IX are ordered and all others are disordered with respect to proton position. The higher densities of the high pressure ices derive not from shorter \( R(0,\ldots) \) but from distorted hydrogen bonds. The distortions result in much closer (3.2 Å) next-nearest-neighbours compared to ice Ih (4.5 Å). There is considerable distortion of the HOH angles: Ice II has 18 HOH angles between 80° and 128°.

(ii) Electrical Properties of Ice

Recently dielectric constant work was reported by Wilson et al. (77) and by Whalley and Heath (78). In general, they found that ice I has a large reciprocal dielectric relaxation constant (about \( 10^5 \) reorientations per second), and that the disordered high pressure ices have even larger \( \tau_d^{-1} \)'s. The \( \tau_d^{-1} \)'s of ordered ices, however, are small (no reorientations). The \( \tau_d^{-1} \) of ice I increases very rapidly with decreasing temperature due to the increasing electric field of the approaching neighbouring molecules: \( \tau_d^{-1} \) is 2000 times larger at 208°K than at 273°K. An accepted mechanism of re-orientation invokes the migration of Bjerrum (79) D- and L- defects.

(iii) Thermodynamic Properties of Ice

There is support for some ordering in ice Ih from heat capacity (Cp) and electricity measurements. Helmreich and Riehl (80) deduced from electricity measurements that the proton disorder is partially removed as
Table 0.4  Physical properties of the ices.*

<table>
<thead>
<tr>
<th>ICE</th>
<th>Ih</th>
<th>Ic</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>VIII</th>
<th>IX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space Group</td>
<td>P63/mmc</td>
<td>Fd3m</td>
<td>R3</td>
<td>P4₁2₁2</td>
<td>A2/a</td>
<td>A2/a</td>
<td>P4₂/mmc</td>
<td>Im3m</td>
<td>Im3m</td>
<td>P4₁₂₂</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>8</td>
<td>12</td>
<td>12</td>
<td>28</td>
<td>28</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>Density g/cm³</td>
<td>0.94</td>
<td>--</td>
<td>1.17</td>
<td>1.14</td>
<td>1.23</td>
<td>1.31</td>
<td>--</td>
<td>1.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>No.n-neighbours</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>8</td>
<td>8</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>R n-neighbours Å</td>
<td>2.74</td>
<td>2.75</td>
<td>2.75</td>
<td>2.76</td>
<td>2.76</td>
<td>2.81</td>
<td>2.86</td>
<td>2.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R n.n-neighbours Å</td>
<td>4.49</td>
<td>4.50</td>
<td>3.24</td>
<td>3.47</td>
<td>3.28</td>
<td>3.51</td>
<td>2.86</td>
<td>2.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O····O angle deg</td>
<td>109.5</td>
<td>109.5</td>
<td>80</td>
<td>87</td>
<td>84</td>
<td>76</td>
<td>100.5</td>
<td>109.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Table from ref. (5).
temperature decreases. The effects found were small and they therefore deduced a small fraction of the sample was ordered: A finite number of ordered domains in a disordered continuum. Pick (81) also suggested that regions of short-range ordering are formed as the temperature of ice I is lowered. However, he pointed out that the D- and L- defects responsible for reorientation (ordering) decrease in number exponentially with decreasing temperature. Hence the time for establishing an ordered crystal increases exponentially as temperature decreases.

The heat capacity of ice Ih above 15°K was first investigated by Giauque and Stout (82). They found that the samples attained thermodynamic equilibrium in the range 85° to 115°K only slowly. The reason is not understood.

Recently Flubacher et al. (83) studied the ice Ih Cp below 15°K. They found Cp extrapolates to zero at 0°K and is consistent with a continuous decrease. As well they pointed out that the translational, librational and internal energies are separable and that the librational contribution to Cp is explained well by an average frequency for H₂O of 620 cm⁻¹.

Leadbetter (84), in a comprehensive interpretation of the ice I thermodynamics, explained Cp in terms of the excitation of translational (νₜ) and librational (νᵣ) vibrations. Below 80°K, Cp was derived entirely from excitations of νₜ, while above 150°K νᵣ gave a significant contribution. He also predicted that between 0° and 273°K the νₜ frequency shifts by 8 ± 2% and that νᵣ shifts by 6 ± 2% for H₂O (for D₂O 10 ± 2% and 8 ± 2% respectively).

Blue's (85) elementary treatment of Cp gave a surprisingly good value for the librational average frequency, 660 cm⁻¹. He also gave a convenient formula for deducing the set of ir librational frequencies:
\begin{equation}
\nu_{R_n} = \frac{1}{2\pi c I_n} \left[ \frac{1}{2} \sum_i k_{in} r_{in}^2 \right]^{\frac{1}{2}} \tag{[1]}
\end{equation}

where \( I_n \) is the moment of inertia about axis \( n \) in gm/cm\(^2\),
\( k_{in} \) is the force constant restraining atom \( i \) from rotation about axis \( n \) in dynes/cm,
\( r_{in} \) is the normal distance of atom \( i \) to axis \( n \) in cm,
\( c \) is the velocity of light cm/sec.

**C. Spectroscopic Investigations of Ice**

The effects of hydrogen bonding have been observed in 3 fields of spectroscopy: electronic, nmr and vibrational. For example, both red and blue shifts (from the non-hydrogen bonded frequency) are observed depending on whether the hydrogen bond is stronger in the ground electronic state or in the excited state. In nmr spectra the proton signals of (H atoms in) hydrogen bonded molecules are shifted to a lower field than for the non-hydrogen bonded molecule. In ice, nmr has been used to find proton separations and to determine charge redistributions.

Vibrational studies of ice have been made by neutron inelastic scattering, Raman, and infrared spectroscopy. The previous work will be considered in two sections, modes occurring below and above 1000 cm\(^{-1}\) (the fundamental lattice and molecular mode regions). The results of previous works are tabulated in Chapter 3 for comparison to the results of the present work.

The \( \text{H}_2\text{O} \) molecule has 3 molecular vibrations; a symmetric and an asymmetric stretch and a symmetric HOH bend \( (\nu_1(a_1), \nu_3(b_1) \text{ and } \nu_2(a_1) \text{ respectively}) \). In cubic ice I (Fd\( \bar{3} \)m) with 2 molecules per primitive unit cell \((Z = 2)\) there are \((3n)Z\) (where \( n \) is the number of atoms/molecule) cm\(^{-1}\)
18 crystal vibrations. Of those, \((3n-6)Z\) or 6 of these are molecular vibrations, \(3Z\) or 6 are rotatory in nature, \(3(Z-1)\) or 3 are translatory vibrations and 3 are simple translations of the complete unit cell. Hence in a mole \((N)\) of unit cells there are \(6N\) molecular vibrations, \(6N\) rotatory vibrations, \(3N\) optical translations and \(3N\) acoustical translations.

Ice spectra are characterized by 5 very broad bands. Two bands occur below 1000 cm\(^{-1}\) in the \(\text{H}_2\text{O}\) ices. A band with at least 6 features and centred near 230 cm\(^{-1}\) is attributed to hydrogen bond stretching modes, the lattice translational modes \(\nu_T\). A band with from 3 to 16 features and centered near 830 cm\(^{-1}\) is attributed to hydrogen bond bending modes, the lattice hindered rotational modes, \(\nu_R\).

Between 1000 and 4000 cm\(^{-1}\) 3 bands are observed. The band near 1630 cm\(^{-1}\) has been attributed to \(2\nu_R\), \(\nu_2\) or to overlapping \(2\nu_R/\nu_2\). The band near 2200 cm\(^{-1}\) has been assigned to \(\nu_2 + \nu_R\) or \(3\nu_R\). The features of the 3200 cm\(^{-1}\) band have been assigned by various authors to: 1) \(2\nu_2\), \(\nu_3\), \(\nu_1\) (105), 2) \(\nu_1\), \(\nu_3\), \(\nu_3 + \nu_T\) (108), and 3) all as \(\nu_{\text{OH}}(\text{H}_2\text{O})\) (95). The vapour, liquid and ice I frequencies, with the various assignments are given in Table 0.5.

The analysis of the vibrations of crystalline materials usually begins with a factor group analysis based on the known diffraction symmetry, i.e. based on oxygen atoms and \(\frac{1}{2}\)H atoms. Now the disordered H positions are averaged in the time of a diffraction experiment, while in vibration spectroscopy the instantaneous symmetry of the unit cell is important.

(i) The Lattice Modes

(a) Translations. For ices Ih and Ic the factor group analysis, based on symmetric \(\frac{1}{2}\)H positions and the above diffraction symmetries, pre-
Table 0.5  \( \text{H}_2\text{O} \) vapour, liquid and ice Ih infrared absorption frequencies, half-height widths and intensities and the divergent assignments made to the bands of ice.

<table>
<thead>
<tr>
<th>(a) Vapour</th>
<th>(b) Liquid</th>
<th>(c) Ice I</th>
<th>(d) Ice Ice</th>
<th>(e) Ockman 1957</th>
<th>(f) Hornig 1958</th>
<th>(g) Pimentel 1959</th>
<th>(h) Whalley 1964</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>( \text{D}_2\text{O} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{cm}^{-1} )</td>
<td>( \text{cm}^{-1} )</td>
<td>( \text{cm}^{-1} )</td>
<td>( \text{cm}^{-1} )</td>
<td>( \nu_T )</td>
<td>( \nu_R )</td>
<td>( \nu_R )</td>
<td>( \nu_R )</td>
</tr>
<tr>
<td>160</td>
<td>232</td>
<td>weak</td>
<td>( \nu_R )</td>
<td>( \nu_R )</td>
<td>( \nu_R )</td>
<td>( \nu_R )</td>
<td></td>
</tr>
<tr>
<td>(170)</td>
<td>(218)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>650</td>
<td>800</td>
<td>200</td>
<td>strong</td>
<td>( \nu_2 )</td>
<td>( \nu_2 )</td>
<td>( \nu_2 )</td>
<td>( \nu_2 ), ( 2\nu_R )</td>
</tr>
<tr>
<td>(500)</td>
<td>(590)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>595</td>
<td>645</td>
<td>250</td>
<td>med.</td>
<td>( \nu_2 + \nu_R )</td>
<td>( 3\nu_R )</td>
<td>( 3\nu_R )</td>
<td>( 3\nu_R, 2\nu_R )</td>
</tr>
<tr>
<td>(1178)</td>
<td>(1178)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3657</td>
<td>3219</td>
<td>3142</td>
<td>very</td>
<td>( \nu_1 )</td>
<td>( 2\nu_2 )</td>
<td>( \nu_{OH}(\text{H}_2\text{O}) )</td>
<td></td>
</tr>
<tr>
<td>(2671)</td>
<td>(2347)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3756</td>
<td>3445</td>
<td>3252</td>
<td>strong</td>
<td>( \nu_3 )</td>
<td>( \nu_3 )</td>
<td>( \nu_{OH}(\text{H}_2\text{O}) )</td>
<td></td>
</tr>
<tr>
<td>(2788)</td>
<td>(2500)</td>
<td>(2440)</td>
<td>(250)</td>
<td>( \nu_3 + \nu_T )</td>
<td>( \nu_1 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3352</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HDO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{cm}^{-1} )</td>
<td>( \text{cm}^{-1} )</td>
<td>( \text{cm}^{-1} )</td>
<td>( \text{cm}^{-1} )</td>
<td>( \nu_R )</td>
<td>( \nu_R )</td>
<td>( \nu_R )</td>
<td>( \nu_R )</td>
</tr>
<tr>
<td>3707</td>
<td>3405</td>
<td>3275</td>
<td>80</td>
<td>very</td>
<td>( \nu_{OH} )</td>
<td>( \nu_{OH} )</td>
<td></td>
</tr>
<tr>
<td>(2727)</td>
<td>(2520)</td>
<td>(2416)</td>
<td>(2)</td>
<td>strong</td>
<td>( \nu_{OD} )</td>
<td>( \nu_{OD} )</td>
<td></td>
</tr>
</tbody>
</table>

(a) Ref. 116, (b) Ref. 98, (c) Ref. 108, (d) Ref. 106, (e) Ref. 105, (f) Ref. 97, (g) Ref. 95.
dicts 9 optical modes for Ih ($A_{1g}$, $B_{1g}$, $B_{2u}$, $E_{1g}$, $E_{2g}$, and $E_{2u}$) and 3 optical modes for Ic ($F_{1g}$). The normal $k = 0$ selection rules predict that all these modes are ir inactive and that all $g$ modes are Raman active. However, ir translational absorption ($\nu_T$) is observed (86) for both Ih and Ic ices. In fact the absorptions are nearly identical. The factor group analysis fails for $\nu_T$ of hexagonal and cubic ices, as well as for the other disordered ices, V and VI (86).

In contrast, the factor group analysis works well for $\nu_T$ of ices II and VIII, the ordered H atom ices (86).

The H atoms in ice Ic are not symmetrically placed along R(O---O) in the unit cell. Even if the H atoms were perfectly ordered, with 2 near and 2 away from each O atom, the crystal symmetry of ice Ic could not be Fd3m since the $T_d$ symmetry would be destroyed. One might expect ice Ic to order itself in a sub-group of Fd3m or similar to one of the structures in ices II, VIII or IX (R3, Im3n or $P_{4}2_12_1$). Then the $\nu_T$ modes may not be all inactive in the ir. If short range ordering is present (as suggested before) then the effective crystal symmetry may be a subgroup of $S_6$, $O_h$ or $D_4$, since the nearest molecules determine the effective potential at the central molecule.

(b) Disorder theory. Whalley and Bertie (87) proposed a theory to explain the activity of lattice modes in orientationally disordered crystals. They considered ice Ic to have (near) positional symmetry (order) of the O atoms but orientational disorder of the H atoms. They suggested that the result is a small effect on the mechanical form of the translational vibrations, therefore the translational modes are mechanically regular. However, since in the course of a vibration $\Delta u$ varies according to the local molecular orientations, then the crystal translational vibrations are electrically irregular.
Whalley and Bertie (87) assumed that the dipole derivative could be split into a symmetric part, \( M' \), (corresponding to diffraction symmetry part) and an asymmetric, irregular part, \( M'' \), due to the H atom disorder. Then they showed that the molecular intensity of absorption has a part for zero wave vector (\( k = 0 \)) transitions, which are the normal symmetry allowed transitions, and a finite intensity for all \( k \neq 0 \) transitions due to \( M'' \). Therefore they deduced that all translational vibrations are IR active.

In a subsequent paper Bertie and Whalley (88) used the above theory to describe the density of states in \( \nu_T \) of ices Ih and Ic. They assigned the 229.2 cm\(^{-1}\) peak to degenerate longitudinal and transverse optical modes at the zone center, the 160 cm\(^{-1}\) peak to the longitudinal acoustical mode of a zone boundary, and the 190 cm\(^{-1}\) shoulder to the longitudinal optical mode at the same zone boundary. They showed a density of states curve for ices Ih and Ic.

As well, Bertie and Whalley (88) found that \( \nu_T(H_2O) \) shifted by 7 cm\(^{-1}\) to lower frequency upon raising the temperature from 100° to 168°K. They attributed the red shift to excitation of hot bands.

The results of \( \nu_T(H_2O) \) for vitreous ice I are conflicting (88,89). Giguere and Arraudeau (89) indicated considerable band structure.

(c) Raman spectra. Scattering from \( \nu_T(H_2O) \) was reported by Val'kov and Maslenkova (90) with a medium intensity peak at 230 cm\(^{-1}\) and weak features at 291 and 310 cm\(^{-1}\). As well, Taylor and Whalley (91) reported the Raman spectra of ices Ih, Ic, II, III and II. They reported a peak at 225 cm\(^{-1}\) in ices Ic and Ih and at 151 cm\(^{-1}\) in ice II.

(d) Neutron inelastic scattering. Spectra were reported by Prask and Boutin (92) for ice Ih and Trevino (93) and Renker and Blanckenhagen
(94) calculated the $\nu_R$ spectra of ice I. The frequency distributions calculated and observed in neutron work agree quite well with Bertie and Whalley's (88) predictions from the ir.

(e) Libration. Hydrogen bonding also gives rise to hindered rotational transitions in the ices. For H$_2$O this absorption is seen from 1000 - 400 cm$^{-1}$ and for D$_2$O from 750 cm$^{-1}$ to 350 cm$^{-1}$. The ratio of $\nu_R$ for H$_2$O and D$_2$O would ideally be 1.41 for purely rotational motion and 1.05 for purely translational motion: The observed values lie closer to 1.35.

Blue's (85) treatment of H$_2$O libration was based on the assumption of three $\nu_R$ uncoupled, degenerate librators. The hydrogen bond bending force constant was assumed to be symmetric about the O-H···O axis and only nearest-neighbour interactions were considered. In such an approximation the libration about the $C_2v$ axis is ir inactive.

Bertie and Whalley (95), in contrast, pointed out that the very existence of the $\nu_R$ bands is due to the strong coupling of the 3N librations of N molecules in a mole of unit cells. The crystal field and hydrogen-bond coupling yield a broad band of crystal frequencies. Since ice Ic is disordered and has only symmetry E, all the crystal frequencies are ir active. However, the distribution of ir intensities across the band of crystal frequencies is unknown, and the shape of the ir absorption band is not necessarily the shape of the crystalline vibration band.

Bertie and Whalley (95) reported that the $\nu_R$ absorptions of ices Ic and Ih are identical. For H$_2$O they observed 5 features on $\nu_R$ between 900 and 555 cm$^{-1}$; for D$_2$O they observed 3 features between 675 and 425 cm$^{-1}$. (However, the mulling agent used obscured the results in some areas.) Similar bands were observed in the high pressure ices (96).
The ordered ice II appears to obey the factor group splitting predictions with respect to $v_R$. Bertie (86) suggested 12 $v_R$ ir active modes. In fact, 16(9) features were observed between 475 and 1066 cm$^{-1}$ with a band center at 800 (593) cm$^{-1}$. As well, Bertie and Whalley (96) suggested that a mode $v_R + v_T$ may be active in ice II.

The librational absorptions of vitreous, hexagonal and cubic ice I were reported also by Giguere and Arraudeau (89). For vitreous ice they reported features at 800(600), 840(635) and 900 (675) cm$^{-1}$. In cubic and hexagonal ice I they observed only two features, 835(625) and 890(673) cm$^{-1}$. The two crystalline modes were assigned to $v_R$ and $v_R + v_T$. For vitreous ice they suggested the $C_{2v}$ libration was active due to the asymmetric electric field. The observed frequency of 800(600) cm$^{-1}$ is in good agreement with the predictions of Blue's equation, 802(604) cm$^{-1}$.

Zimmermann and Pimentel (97) studied the temperature dependence of $v_R$ and $v_T$ between 93° and 273°K. From a normal coordinate analysis based on an $H_2O$ model they deduced that the hydrogen bond bending force constant varies from 0.095 to 0.085 x 10$^5$ dynes/cm between 93° and 273°K. This agrees with the concept of a weakening hydrogen bond as R(0•••0) increases.

(ii) Modes Above 1200 cm$^{-1}$

(a) Temperature dependences of the modes. Temperature dependences of the ice absorptions have been observed previously by at least 5 groups. Giguere and Harvey (98) reported frequencies for $v_R$, $v_2$ and $v_3$ at 103°, 217° and 268°K for $H_2O$ and $D_2O$. They observed solids formed by condensing the liquid or vapour phase.

Ice Ih ($H_2O$ and $D_2O$) single crystal Raman spectra were reported by Val'kov and Maslenkova (99) for several temperatures above 77°K. On the
basis of intense $a_1$ Raman scattering and the similarity to vapour phase
scattering, they assigned individual $v_1$ and $v_3$ ice frequencies. That is in
direct contrast to more recent work (95) which strongly coupled $v_1$ and $v_3$
into two separate but equally mixed bands. Val'kov and Maslenkova suggested
that the ratio $v_3/v_1$ for H$_2$O in the solid should be the same as for the
vapour, as well as for D$_2$O. They also observed other lines in the stretching
region which may have arisen from combinations with lattice modes.

Zimmermann and Pimentel (97) also reported the temperature dependences
of $v_2$ and $3v_R$ above 93°K. As the temperature was increased from 93° to
273°K they found that $v_R$ and $3v_R$ decreased and $v_2$ increased in frequency.
Thus the 1600 cm$^{-1}$ ice band could not be $2v_R$. As well, they found that at
93°K $v_2$(solid) < $v_2$(vapour).

The most accurate study of temperature dependences in ice was recently
reported by Ford and Falk (100) for the $v_{OH}$(HDO) and $v_{OD}$(HDO) modes. By pre-
paring a dilute concentration of HDO in H$_2$O or D$_2$O one maintains a constant
crystal field, but removes the dynamical intermolecular coupling of one HDO
mode to the surrounding lattice (101, 102). Consequently, Ford and Falk
observed relatively sharp HDO bands, the half-height width ($\Delta v^\frac{1}{2}$) was about
18 cm$^{-1}$ for $v_{OH}$(HDO) at 97°K. That is still much wider than for ice II,
$\Delta v^\frac{1}{2} = 5$ cm$^{-1}$, where the H atoms are ordered.

The widths of HDO bands in ice II are due to hot bands, overtones, and
sum and difference bands. (Hot and difference bands should be removed near
10°K.) The widths of the HDO bands in ice Ih are due to the above effects
plus H atom disorder (irregular Hydrogen bond potentials).

The problem of forming hydrated salt windows and not ice I was dis-
covered by Mutter, Mecke and Lutke (103) and was clarified by Schiffer (104).
Hydrated salt window absorptions are readily distinguished from those of ice.
(b) Infrared absorption spectra. The spectra of H$_2$O, HDO and D$_2$O were studied in detail by Hornig, White and Reding (105), Table 0.5. The fundamentals $\nu_1$ and $\nu_3$ were assumed to have reversed order in energy from the vapour phase order because of the stretch-stretch interaction constant. They also estimated that the barrier to proton jumping was 27 kcal/mole.

Unfortunately, it now appears their samples were of amorphous and not crystalline ice. (Many of their conclusions are still valid however.) Zimmermann and Pimentel (97) pointed out the need to anneal solid samples formed by vapour condensation. They demonstrated the IR effects of annealing amorphous ice, but did not study the phase transformation in detail.

Ice Ih spectra of H$_2$O, D$_2$O and HDO were obtained by Haas and Hornig (106) at 83°K. They observed $2\nu_{OH}$(HDO) and suggested that the barrier to proton transfer exceeded 23 kcal/mole. However, they suggested that proton tunneling may occur, leading to broad HDO bands. On the other hand, they used very high concentrations (8-10%) of HDO in H$_2$O and D$_2$O. The resulting HDO-HDO coupling (neighbours) gave wider bands as well as a pair of shoulders one on either side of the main HDO stretching band.

Their results showed that the width of hydrogen bonded O-H stretching bands was not a characteristic of the O-H···O bond but arose from extensive molecule-molecule coupling of O-H motions.

The work of Bertie and Whalley (95) is the most comprehensive study of cubic and hexagonal (H$_2$O, HDO and D$_2$O) ice I. Their results were obtained at 110°K by the low temperature mulling techniques developed by them (107). The cubic or hexagonal crystallinities of their samples were confirmed by x-ray diffraction.
Bertie and Whalley reported that the IR spectra of ice Ih and Ic were identical. As well, they obtained much sharper spectra than the previous workers (97, 105, 106, 108) due to the absence of amorphous ice. They rejected the interpretation of the bands in terms of \( \nu_1, \nu_2, \nu_3 \) and \( \nu_R \) on the basis of strong intermolecular coupling. For example, in ice crystals the neighbouring \( \nu_1 \) vibrations were assumed to couple with each other to form one broad, symmetric \( \nu_1 \) band. Similarly a broad symmetric \( \nu_3 \) band formed. Finally they suggested the \( \nu_1 \) coupled-band could interact with the physically and energetically adjacent \( \nu_3 \) coupled-band to give two broad bands which were equal admixtures of \( \nu_1 \) and \( \nu_3 \); two hybrid \( \nu_1-\nu_3 \) bands. Bertie and Whalley suggested that different portions of these coupled, broad bands were IR and Raman active, accounting for the differences between the IR and Raman results.

With respect to the widths of the ice I absorptions, they suggested that H atom disorder leads to local variations in O atom positions and variations in the local potential, as earlier suggested by Reid (31). Three other causes of the broad bands were also reviewed (96). These were:
1) the occurrence of sum, difference and hot bands with lattice modes,
2) the occurrence of proton tunnelling and the resulting increase in the width of the energy level by a decreased lifetime, and
3) Fermi resonance between the fundamental modes and overtones or combinations.

Bertie and Whalley (95) discussed the 1650 cm\(^{-1}\) absorption as arising from combined \( 2\nu_R \) and \( \nu_2 \) vibrations, but they pointed out that discussion in terms of a unimolecular \( \nu_2 \) mode is not meaningful. One must consider the \( N\nu_2 \) modes/mole of crystal.
D. The Present Approach to the Ice Problem

Three facets of the ice problem were studied in this work. First, to help clarify the discrepancies among ir and Raman results for ice I samples condensed from the vapour or crystallized from the liquid, the temperature dependences of vitreous ice absorptions were observed and the vitreous-cubic phase transformation was characterized. Secondly, the temperature dependences of cubic ice I absorptions were observed in order to make specific correlations of $v_{\text{STR}}$ to $R(0\cdots 0)$ and to discover the contributions of hot bands to the band widths. Thirdly, data from the two above methods were used to confirm previous ice I band assignments.
CHAPTER ONE

APPARATUS

1.1 The Perkin-Elmer 112-G Spectrophotometer

The Perkin-Elmer 112-G instrument is a high resolution single beam spectrophotometer based on a double pass (model 99) grating monochromator. The monochromator employs a 75 lines/mm replica echelette grating which is blazed to reflect maximum intensity at 12μ in the first diffraction order and has a grating-ghost between 1000 and 1070 cm⁻¹. Unwanted orders are eliminated by a fore-prism monochromator situated between a glober source and the grating monochromator. The fore-prism filter monochromator consists of a 60° KBr prism mounted in Littrow configuration. This monochromator arrangement gives an instrument resolving power of 0.5 cm⁻¹ or better. Spectral slit widths [calculated by Siegler's method (109)], are indicated on the appropriate spectra.

Thermal radiation is detected by a thermocouple or PbS sensor. However, only 2nd pass radiation is chopped at 13 cps and amplified in a standard model 107 amplifier. The 13 cps electrical signal is mechanically rectified synchronously with the optical chopper. This d.c. signal is applied to a conventional 10 mv Speedomax-G recorder.

In the experiments to be described, the P.E. 112-G was used from 5000 to 550 cm⁻¹ with thermocouple detection in all regions. The instrument was calibrated at each use with atmospheric H₂O and CO₂ or with NH₃(g).
Low temperature experiments on ice are hampered in the P.E. 112-G by the small sampling area and severe atmospheric absorption. The spectrophotometer was modified considerably to eliminate or reduce these and other difficulties. At the PbS detector mount a simple ellipsoidal-plane mirror system is placed which produces a monochromatic source image in free space 50.5 cm from the exit slits. A second detection unit (thermocouple, focussing optics and pre-amplifier) is mounted in series with the added optical system. These modifications offer several advantages over standard P.E. 112-G sampling facilities. For example, beam vignetting losses may be reduced and smaller samples may be used by placing the sample at the source image in the new sample area. Also, concurrent calibration and sample observation is possible when a calibration gas is placed at the standard sample mount and the sample is placed at the new sampling area. In addition, there is 15 cm of optical path length and ample surrounding free space for mounting bulky accessories, i.e. low temperature cells. A more important advantage is the decreased range of thermal radiation striking samples mounted in the monochromator exit beam. Tests indicate a 5% energy loss between the standard and modified detector configurations.

The complete instrument, excluding the new thermocouple detector unit, is placed in a metal-plexiglass drybox to reduce background atmospheric attenuation from H₂O and CO₂. The new detector unit has its own chamber, and sampling accessories are used to couple the two chambers. Spectrophotometer controls are easily operated outside the drybox by simple mechanical extensions. However, the grating drive and transmission are now located at the front of the instrument outside the drybox. A standard drybox air lock and rubber gloves permit the introduction and manipulation of conventional ir accessories in the primary sample mount. The N₂(g) drybox
atmosphere is circulated through one of two parallel molecular sieve columns (Linde 13X 1/16 in. pellets) to remove residual H$_2$O and CO$_2$. When the circulating system is in use one column is on-line while the other is regenerated by combined evacuation and heating. This system eliminates absorption from atmospheric H$_2$O but is less effective in reducing atmospheric CO$_2$ absorption.

To achieve maximum performance for fore-prism/grating monochromator assemblies of the P.E. 112-G type the two monochromators must transmit the identical frequencies. Normally, the fore-prism monochromator slits are set at the maximum widths which just separate the various grating orders. This allows the grating monochromator to be scanned with reasonable performance over varying, limited frequency ranges which depend on the region of the spectrum. A mechanical servo system was designed to link the two monochromators permitting them to be scanned in near resonance. Lengths of certain scans (at acceptable energy levels) can be doubled by this arrangement. The design uses a variable ratio, ball and disc gearbox, reduction gears, and linking driveshafts. A more powerful motor replaces the standard grating drive motor to compensate for the added load. Despite the difficulty in maintaining exact fore-prism/grating monochromator resonance, because of non-linear prism dispersion, the modification improves the scanning characteristics.

1.2 The Perkin-Elmer 421 Spectrophotometer

The Perkin-Elmer 421 instrument is a moderate resolution (1 cm$^{-1}$), double beam, null recording grating spectrophotometer of conventional design. A Nernst glower source and thermocouple detector are used in conjunction with interference filters (which eliminate unwanted orders) and a
single pass grating monochromator. Two removable, self-contained mono-
chromators are readily interchanged, permitting rapid conversion of the
scanned frequency range. Each interchange comprises the appropriate inter-
ference filters and a pair of gratings mounted back-to-back on a cosecant
drive: One interchange is used from 4000 - 530 cm$^{-1}$ and the other from
2000 - 220 cm$^{-1}$. Grating and filter operations are automated by pre-programmed
mechanical and electrical servo systems. Spectral slit widths [calculated
by the method of Roche (110)] are indicated on the appropriate spectra.

Some minor up-dating modifications have been made, i.e. installation
of a larger (0.8 amp) Nernst glower and alteration of the grating switching
 mechanism to prevent arcing. A local modification is the provision of inlet
and exhaust ports, in the monochromator and source housings respectively,
permitting the use of a circulating dryer (manufactured by P.E. Bodenseewerk
for the P.E. 225 spectrophotometer). This drying unit is remarkably effec-
tive in reducing atmospheric H$_2$O absorptions but is less effective with
respect to CO$_2$.

The P.E. 421 was operated under the normal, recommended conditions.
Specific conditions of operation are listed with the results. General con-
ditions of operation are listed below.

The automatic slit program was set at 2 x 10.00 which gave spectral
slit widths of 3.86 and 2.22 cm$^{-1}$ at 3300 and 800 cm$^{-1}$ respectively. Spectra
were recorded on U.B.C. Chemistry Department charts, which were printed on
Rolland Colonial Bond rag content paper. The charts have an inaccurate
frequency scale but frequency markers were applied with the absorbance
scale expansion switch to coincide with the frequency readout drum. The
drum was read to ± 0.05 cm$^{-1}$ and the marker was applied to within ± 0.1 cm$^{-1}$
but could be read from the charts to ± 1.0 cm$^{-1}$ for 100 cm$^{-1}$/in. recording.
1.3 The Perkin-Elmer 301 Spectrophotometer

The Perkin-Elmer 301 grating instrument is a far-infrared, double beam, recording spectrophotometer of the Halford-Savitsky type. Two complementary, readily exchangeable sources (a globar and a high pressure mercury lamp) are used to cover the instrument range from 650 cm\(^{-1}\) to 14 cm\(^{-1}\). Combinations of interference filters, scatter plates and crystal choppers (CsI or BaF\(_2\)) are used to reduce scattered radiation and to eliminate the energy of unwanted diffraction orders. A standard, single pass model 210 grating monochromator is used with 3 pairs of complementary, readily exchangeable gratings which are mounted back-to-back on kinematic mounts. The P.E. 301 optical design produces a large image at the detector and necessitates a detector with a large target. A golay sensor is suitable and is used over the full instrument range. Signal to noise ratios may be doubled if the instrument is operated in the single beam mode by replacing a split aperture (1/2 image) I-Io mirror with a full aperture I or Io mirror. An advantage of the P.E. 301 is the chopping of source radiation before it enters the sample chamber. Therefore radiation originating at the sample is not amplified.

The P.E. 301 was modified by installing inlet and exhaust ports for the P.E. Bodenseewerk dryer. Severe background atmospheric water problems can be almost completely eliminated by using this dryer.

1.4 The Hornig-Wagner Liquid Nitrogen Cell

The low temperature cell which proved most useful for obtaining spectra above 80\(^\circ\)K was constructed from a design originally given by Wagner and Hornig (111). Our cell, which has been described previously
(112, 57) has a glass body and reservoir, a brass sample block, and CsI or AgCl windows. Thermal contact between the sample window and sample block was improved with layers of silver conductive paint on contact surfaces. Temperature was measured with a fused Cu-constantan thermocouple soldered to the brass sample holder base. Thermocouple wires and cell windows were sealed to the cell with Cenco soft-seal Tackiwax. This wax is slightly plastic at room temperature, flows well and is ideal for vacuum sealing when extremely low pressure is not required.

Although liquid nitrogen coolant comes into direct contact with the brass sample block, the spectrophotometer source beam radiation raised the block temperature to 83 ± 3°K. Because of non-ideal thermal contact and low sample window thermal conductivity, sample temperature was considerably above that of the block. From melting point observations the sample window temperature was estimated to be 10°K higher than that of the sample block. Unless otherwise stated, all temperatures quoted in this work are not corrected for source heating.

Two sample deposition tubes were used with this cell, one of all-glass and the other of metal construction. Both were mounted with their tips 7mm from the sample window surface. At such a distance there are large heat losses (from the sample tube tip to the window and cooling block) permitting sample condensation at the cold tips. Dangers of selective H₂O condensation or fractionation of clathrate mixtures at the tube tips were avoided by using external heating on the stainless steel tube, Fig. 1.1.
Fig. 1.1 The stainless steel sample deposition tube: A - pyrotenax heater, B - Cu-Constantan thermocouple, C - deposition tube tip, D - B-19a conical glass joint, a Kovar metal glass joint, and a brass cap, E - needle valve and "swage-lok" fittings.
1.5 The Duerig-Mador Liquid Helium Cell

Spectra of samples below 83°K were observed through a liquid helium cell which is described elsewhere (112, 57) and is similar in design to that of Duerig and Mador (113). A principal modification incorporated in our cell is the use of a vacuum seal/bearing which permits the helium container and sample holder to be rotated through 90° for sample deposition. Thermal contact between sample windows (CsI or polyethylene) and the Cu sample block was improved by painting the contact surfaces with silver conductive paint. Sample block temperature was measured with a Au-Co/Ag-Au thermocouple. The thermocouple was calibrated at 4.2°K and with 9 boiling liquids or slushes from 77° to 273°K. Actual sample window temperature was estimated to be 10°K higher than the temperature indicated with the thermocouple.

1.6 The Metal Liquid Nitrogen Cell

To prepare clathrate-hydrates by deposition from the gas phase one must first ensure that the guest and host components condense in the proper stoichiometries. In an attempt to achieve the ideal clathrate condensation a liquid nitrogen cell was constructed containing an evacuable sample chamber, Fig. 1.2.

To help prevent fractionation in the sample chamber, one window is embedded in the cold block and the other is thermally insulated from the first by a stainless steel spacer ring (which provided the chamber body) and two teflon gaskets. Only one window is cooled to refrigerant temperature during the cell operation. The sample chamber body and sample tube were heated by a Pyrotenax wire heater. Sample block temperatures were monitored with a fused Cu-Constantan thermocouple soldered to the sample block.
Fig. 1.2 The isolated sample chamber: A - Cu cooling block and "cold" window, B - Cu-Constantan thermocouple, C - pyrotenax heater, D - coolant reservoir, E - deposition and evacuation tube, F - pyrotenax heater, G - pressure plate and stainless steel screws, H - sample window and holder, I - sample chamber, sample port and teflon gaskets.
2.1 Water Samples and Clathration Materials

Clathrate-hydrate guest molecules were either Matheson compressed gases, Fisher certified reagents, or British Drug House analar reagents. Bromomethane (99.5% pure), trichlorofluoromethane (99%), dichlorodifluoromethane (99.0%), chlorotrifluoromethane (99.0%) and chlorine (99.9%) were used directly from their lecture bottles. Chloromethane (99.5%) was supplied in a No. 4 cylinder and was used without purification. Trichloromethane (Certified Reagent, 99.9% purity), iodomethane (C.R. 99.9%), and bromoethane (C.R. 99.9%) were partially repurified before each use by freezing and pumping off non-condensible impurities. Bromine liquid (Analar Reagent, 99.0%) was also partially purified by freezing and pumping. Guest compound purity was checked by ir vapour phase absorption spectra.

Clathrate-hydrate host and ice I compounds used were H_2O, D_2O, H_2O (5.9% HDO), and D_2O (4.0% HDO). Before use the H_2O water was distilled, de-ionized and finally degassed by several cycles of freezing and pumping. D_2O was supplied by Merck, Sharpe and Dohme in 100g lots and had a stated purity of 99.7%; D_2O was degassed in the usual way. Mixtures of D_2O or H_2O with HDO were made by mixing 49.0 ml D_2O with 1.0 ml H_2O and 49.0 ml H_2O with 1.5 ml D_2O. In both cases the isotopic impurity was almost all present as HDO at equilibrium. Residual H_2O (or D_2O) was spectroscopically undetected. No quantitative analyses of the isotopic mixtures were undertaken.
2.2 Infrared Windows and Sample Mounts

Choice of window material is tempered by the necessary application of thermal stress and essential non-reactivity with applied samples. The latter property is important in studies of water containing compounds since, as Mecke (103) found and Schiffer (104) proved, thin hydrated layers may form on alkali halide crystals. CsI is suitable for all cryostats used here since it is relatively soft and ductile and accepts the considerable thermal shock. Only \( \text{Cl}_2 \cdot 7.67\text{H}_2\text{O} \) samples reacted detectably with CsI windows. That experiment was repeated using an AgCl sample mount. Silver chloride does not transmit as widely as cesium iodide over our range of interest, however AgCl is soft and easily withstands thermal shocks. Also, it is apparently non-reactive to chlorine and bromine.

Cell windows and a sample support used in the P.E. 301 experiment were cut directly from commercial high density polyethylene (A powdered polyethylene was also available). The windows were only used from 650 cm\(^{-1}\) to 160 cm\(^{-1}\) and through the temperature range 5\(^{\circ}\)K to 200\(^{\circ}\)K. The polyethylene was apparently non-reactive to the clathrate-hydrate mixtures investigated.

Polyethylene is not an entirely satisfactory sample support since its thermal conductivity is low and source heating may be high. To counteract source heating, sample supports were pressed from powdered polyethylene embedded with a brass or copper grid. The method consisted of placing a wire grid between two lightly pressed (7000 psi, unheated) 0.20 g discs, heating to the polyethylene flow temperature (130 \( \pm \) 5\(^{\circ}\)K) under light pressure (1000 psi) and pressing to 15,000 psi while cooling to less than 35\(^{\circ}\)C. The result was a low scattering pellet with 58% transmission at 361 cm\(^{-1}\).
and 171 cm\(^{-1}\). Energy transmission could be improved by reducing the effective reflecting surface area of the metal with finer gauge wire.

2.3 Preparation of Clathrate-hydrates

A. Preparation of Solid Samples

Clathrate-hydrates with stoichiometries 1M·17 H\(_2\)O, and whose guest molecules formed liquids at room temperature, were prepared by repeated cycles of cooling and warming stoichiometric liquid mixtures between 77°K and 265°K. To 3g H\(_2\)O (0.17 moles) in a 10 cm by 1.2 cm test tube was added 0.01 moles of liquid guest compound. The mixture was agitated and successively immersed for about 30 sec in an ice-water-sodium chloride bath (265°K) and 30 sec in a liquid nitrogen bath. The sample was then warmed to a viscous state. The procedure was repeated until a uniform, white solid formed—about 5 repetitions for each sample. Samples were stored over dry ice for a short time before use.

Clathrate-hydrate samples were prepared by two other methods, but such samples were not investigated spectroscopically. For clathrates whose guest molecules are ordinarily gases, the method of Allen (114) was used with some modification: a preparation cell similar to Allen's was constructed. For clathrates whose guest molecules are ordinarily liquids, the basic method of Allen (114) was used but with major modifications. A preparation cell of similar dimensions to the one above, but with provision for mechanical stirring and liquid guest addition, was constructed. Samples prepared by these two methods were also stored over dry ice and were analyzed with a gas burette.
B. Preparation of Stoichiometric Gaseous Mixtures

There are a number of criteria which must be satisfied in forming a stable, suitable sample. For example, the clathrate-hydrate or ice phase must form a stable thermodynamic system in the region $4.2^\circ$ to $200^\circ$K. Also, the method must maintain the clathrate stoichiometry, avoiding guest molecule loss by diffusion and dissociation—the equilibrium dissociation pressure of guest molecules must remain negligible. As well, since ice has very large $0$-$H$ extinction coefficients (~140) the samples must be thin—3 microns or less.

Deposition of water vapour or a gaseous stoichiometric clathrate mixture on a cold sample mount gives samples which satisfy some of these criteria (43).

The quantity of a stoichiometric gas mixture which can be prepared in a vacuum system is clearly limited by the saturation vapour pressure of H$_2$O at the given temperature and the mixing bulb volume. The calibrated mixing bulb (including a side bulb) had a volume of 3.853 l and contained 2.76 millimoles of H$_2$O at 293°K and 17.53 Torr H$_2$O. If uniformly deposited on a typical window with a surface area of 7 cm$^2$, 2.76 m moles of H$_2$O would form a layer approximately 70$\mu$ thick. A 3.853 l mixing bulb obviously supplies enough sample for several deposits.

The molar ratios for the 12 A cubic structure are 1 guest: 5.75 H$_2$O and 1 guest: 7.67 H$_2$O, while the corresponding ratios for the tetragonal and 17 A cubic structures are 1 guest: 8.6 H$_2$O and 1 guest: 17 H$_2$O. Clearly the numbers of guest mmoles required to combine with 2.76 m moles of H$_2$O are very small. Measurement of at best one-fifth of 2.76 (0.48) mmoles of gas in 3.853 l at 20°C is impractical due to the large error in measuring
small pressure differences. Gaseous guest aliquots were first isolated in a 0.1039 liter bulb and then expanded into the 3.853 liter mixing bulb. The numbers of guest mmoles and their pressures in the 2 bulbs are shown below for four clathrate structures.

<table>
<thead>
<tr>
<th>Clathrate</th>
<th>m mole X</th>
<th>Partial Pressure of Guest X</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.76 mm H₂O</td>
<td>0.1039 l bulb</td>
<td>3.853 l bulb</td>
</tr>
<tr>
<td>1 X ⋅ 5.75 H₂O</td>
<td>0.48</td>
<td>3.05 Torr</td>
</tr>
<tr>
<td>1 X ⋅ 7.67 H₂O</td>
<td>0.36</td>
<td>2.28</td>
</tr>
<tr>
<td>1 X ⋅ 8.60 H₂O</td>
<td>0.32</td>
<td>2.04</td>
</tr>
<tr>
<td>1 X ⋅ 17.0 H₂O</td>
<td>0.16</td>
<td>1.03</td>
</tr>
</tbody>
</table>

After the guest sample was expanded into the mixing bulb at 20°C, the chamber was saturated with H₂O vapour from liquid previously isolated and degassed in a side bulb. The system was equilibrated in that state for ten minutes before the liquid H₂O was again isolated from the mixing chamber. Since the densities of the gases in the bulb varied over the range from 17.3 x 10⁻⁶ g/cm³ for H₂O to 13.3 x 10⁻⁶ g/cm³ for Br₂ and 6.30 x 10⁻⁶ g/cm³ for CH₃Cl, the mixing was forced by heating the lower hemisphere of the chamber with an electric heating tape. Such convection mixing was maintained for a minimum of 30 minutes before sample deposition. Suitably mixed gases were used either directly from the mixing chamber, for deposition in the isolated chamber of the metal liquid nitrogen cryostat, or were transferred to a portable 3.0 liter bulb and attached to a Duerig-Mador or Hornig-Wagner cryostat.
2.4 Preparation of Infrared Specimens

A. Low Temperature Mulling

Clathrate-hydrates decompose if mounted at 293°K by the usual spectroscopic means, but they are metastable at 77°K. Low temperature mulls of the clathrate-hydrates were prepared by an adaptation of the method Bertie and Whalley (107) used for the high pressure ices.

Preparation of a suitable spectroscopic sample required approximately 0.5h. A few grams of solid clathrate were placed in liquid nitrogen in a mortar at 77°K and ground manually for 10 minutes. A small portion of the sample was placed in the center of a mounted window and enough condensed liquid mulling agent was dropped on the sample to prepare a uniform suspension. A second window was placed over the sample and secured in place by a retaining ring. The window assembly was placed in the sample block of a standard Wagner-Hornig nitrogen cryostat. The assembled cryostat was immediately evacuated.

Contamination of the sample by condensed atmospheric CO₂ and H₂O is most likely to occur during cryostat assembly. Blank runs, and runs with mulling agent only, made it clear that little impurity absorption was found even for the most intense H₂O stretching band [see also Whalley (107)].

Recalling that the transmission spectrum of a mulled sample can be distorted from the idealized absorption spectrum, one can have confidence in the low temperature mull spectra only if distortion is minimized by attention to the particle size of the sample and the refractive index of the mulling agent. Whalley (107) found that even for the most intense H₂O stretching frequencies, where reflectivity is greatest, the spectra of mulls were in good agreement with those of thin films.
B. Isolated Chamber Condensation

The sample chamber designed for approximate comparison of absorption intensities of clathrate-hydrates was described in detail in section 1.6 (page 45). A typical run with this isolated sample chamber involved degassing the metal surfaces, depositing the sample, annealing, and observing the absorption. Those metal surfaces exposed to the sample were degassed by heating to $393^\circ K$ while evacuating to $2.0 \times 10^{-5}$ Torr for two hours. Sample block temperatures from $300^\circ K$ to a maximum of $393^\circ K$ could be maintained with the coolant reservoir empty. Several blank spectroscopic runs were made to ensure that no impurities were being deposited. The sample tube heater was left on but the sample cooling block heater was shut off, while liquid nitrogen coolant was added to the reservoir. Twenty minutes after the collector plate window had recooled to $83^\circ K$, the background spectra were recorded from $550 \text{ cm}^{-1}$ to $4000 \text{ cm}^{-1}$. No impurity absorptions were observed.

For deposition the gaseous sample was expended in short bursts down the heated sample tube into the sample chamber which was held at $83^\circ K$ after the method of Barrer and Ruzicka (43). With the sample tube at $343^\circ K$ and the sample tube heaters on, some heating of the stainless steel spacer occurred which aided the thermal insulation of the second, "hot" window. The CsI sample mounts are poor thermal conductors and too rapid a sample condensation may produce sufficient localized heating to permit self-devitrification—diffusion of the guest molecules into clusters or diffusion out of the lattice completely.

Subsequently, samples were annealed to temperatures between $160 - 180^\circ K$ for 5 to 10 minutes. The sample chamber was not subject to pumping
and the sample tube was warmed to 343°K prior to annealing. The sample block heater was used only in the initial stages of annealing, i.e. up to 100°K. The warming was completed by passing a stream of dry, room temperature N₂ gas through the coolant reservoir. The rates of warming and recooling are described in section 2.5. After recooling the sample block to 83°K, the sample tube heaters were shut off and the spectra were observed in the desired range. The specific instrument conditions are listed with the results.

C. Open Chamber Condensation

Deposition of gaseous samples on a cold substrate, which was exposed to the cryostat cell body, was used for both the Wagner-Hornig cryostat and the Duerig-Mador cryostat for observation on either the P.E. 421 or P.E. 301 spectrophotometers. Gases used were either vapours evaporated directly from liquid H₂O, D₂O or H₂O/D₂O mixtures or were water/guest mixtures prepared as described in section 2.3. Cryostats were degassed by evacuation for a minimum of 10 hours before cooling with liquid nitrogen to 83°K. To ensure a minimum collector plate temperature, the source beam was blocked and the cryostat was allowed to equilibrate for 15 to 20 minutes.

Typically, samples were deposited as follows. Ten ml of sample (at a pressure at 8.7 Torr), were isolated in the sample deposition tube. Several of these aliquots were passed in bursts onto the collector plate at 83°K. The cryostat vacuum jacket was isolated from the pumping station during sample deposition to minimize distortion of the sample gas stream. The H₂O νOH stretching region was monitored briefly after each burst.
determine the intensity of absorption. We estimated that the sample thicknesses ranged from 0.6 µ for very thin samples to several microns for thick samples. The rates of deposition were estimated as 0.04 g/cm²-h. Such deposits were subsequently annealed by the standard procedure.

2.5 Devitrification

As was discussed in the introduction, deposition of water vapour on alkali halide substrates held near 80⁰K has led to doubts of sample crystallinity and confusion in the interpretation of the various IR results. The situation was clarified by Beaumont, Chihara and Morrison (65) through correlated heat capacity/x-ray diffraction studies. Their work accentuated the differences in sample crystallinity among the IR ice spectra of various authors (105, 106, 95, 97) and clearly demonstrated the processes of devitrification and transition linking the ice I allotropes.

In order to make comparative IR studies of ice I and clathrate-hydrates as a function of temperature in this work, one had to reproducibly form the ice I allotropes. However, no attempt was made to restrict self-annealing by limiting deposition rates to that recommended by Beaumont et al. -- 0.04 g/h-cm². That the samples did not undergo a high degree of self-annealing was demonstrated by the broad, featureless IR absorption bands observed immediately after deposition.

Attention was initially directed to annealing condensed, vitreous samples to the common ice phase, hexagonal ice I, whose transition temperature from cubic ice I lies between 200 and 250⁰K. The vitreous sample was warmed to the hexagonal transition at 5.0 to 12.5 deg/min from 83⁰K to 205 ± 5⁰K (with the sample source beam off and no pumping in the sample chamber). It was recooled to 83⁰K at 50 deg/min after being held for
2 to 3 min at the maximum annealing temperature. Unfortunately, the samples were unstable above 195°K with respect to this procedure.

In view of the great difficulty with sample stability and the low rate of transition from cubic to hexagonal ice, further attempts to devitrify at 205 ± 5°K were abandoned.

Further extensive tests showed that thin films of H₂O could be annealed under vacuum to 185 ± 5°K from 83 ± 5°K (at between 5 and 12.5 deg/min with no pumping and the source beam off), and maintained stable at 185°K for up to 5 minutes. The samples were successfully recooled at 50°K/min with little loss of sample as detected by slightly diminished absorption.

According to the data of Beaumont et al. (65) this should give a well developed polycrystalline cubic ice sample, since the transition temperature was well exceeded and the rate of transition is fast, i.e. a few minutes. Samples observed spent a minimum of 9 minutes at (or above) the transition temperature, 150°K. Before spectroscopic investigations began, the thin films were thermally equilibrated for 20 minutes with the sample source beam on.

Discussion of the nature of samples formed by condensing and annealing stoichiometric gaseous mixtures is left until Chapter 6.

2.6 Temperature Variation Methods

The purposes of this work are to study the variations of ice and clathrate spectra as a function of temperature and to show that gas condensation and devitrification gives legitimate crystalline samples. The same sample heating and IR observation techniques were used for both vitreous and crystalline sample studies.
All the samples studied as a function of temperature were formed in either the glass liquid nitrogen cell or the liquid helium cell by the methods of section 2.4(c). The nitrogen cell was mounted only in the P.E. 421 and was used for preliminary observations between 83° and 200°K. The helium cell was mounted either in the P.E. 301 or in the P.E. 421 spectrophotometer, and was used for the detailed studies between 4.2° and 200°K.

Two methods of warming these cryostats were used: 1) natural, unforced warming due to radiative and conductive heating, and 2) warming with a stream of N₂(g). The helium cell was allowed to warm from 4° to 83°K by the natural heat influx after evaporation of the liquid helium. Above 83°K the helium cell was warmed with N₂(g) (293°K) passing slowly through the reservoir. The nitrogen cell was held at 4 to 8 constant temperatures (± 3°K) for devitrification studies (at 83°K N₂(liq) was used and at higher temperatures 1-2 ml of N₂(l) were added to the empty reservoir at appropriate intervals).

Sets of spectra were obtained by continuously recycling the spectrometers over the spectral range desired as the cell warmed continuously, or spectra were recorded at certain successively higher constant (± 3°K) temperatures. Some sets of spectra were also recorded at successively cooler constant temperatures (± 3°K) from 190 ± 10°K to 83°K after devitrification as a check on the reversibility of absorption maxima shifts.
CHAPTER THREE

ICE I: EXPERIMENTAL AND RESULTS

This chapter is comprised of four main sections. The first section contains the results from temperature variation studies of vitreous ice I—observations of the vitreous-cubic phase transformation. The second section contains the results from temperature variation studies of cubic ice I—observations of $\Delta v/\Delta R$ for crystalline ice. The third section uses the results of sections one and two as an aid in assigning the ice absorptions. The fourth section is a brief summary of the results.

3.1 The Vitreous-Cubic Ice Phase Transformation

The spectra recorded during vitreous-cubic phase transformations exhibited diminishing oligomeric peak heights (I) and irreversible peak frequency and half-height width shifts.

A. Experimental

Two vitreous ice I ($H_2O$) samples were prepared (by the method of section 2.4(c)) and observed in the glass liquid nitrogen cell (section 1.4). Sample A was deposited on CsI at $82 \pm 3^0K$, warmed from $82^0$ to $169^0K$ in five stages over $105$ min and was annealed to a maximum temperature of $185 \pm 3^0K$. Sample B was deposited on CsI at $81 \pm 3^0K$, warmed from $81^0$ to $161^0K$ in four stages over $120$ min and was annealed to a maximum temperature of $182 \pm 3^0K$. Seven spectra were recorded for each of samples A and B during devitrification.
The basic spectrophotometer conditions were described previously (section 1.2). For these samples (A and B) P.E. 421 spectra were recorded at 100 cm\(^{-1}\)/in. No reference cell compensation was used, but the instrument was purged with dry N\(_2\)(g). The liquid nitrogen cell and the spectrophotometer sample compartment were masked so that the sample compartment was also purged.

**B. Results of Devitrification**

Infrared absorption spectra representative of samples A and B are shown in Fig. 3.1 (top). Frequency and half-height width (\(\Delta v^h\)) data were derived independently, but by the same methods, for the two sets of spectra. Peak absorptions were determined (to within \(\pm 10\) cm\(^{-1}\)) at the intersection of lines along the band sides, while shoulders were determined (to within \(\pm 14\) cm\(^{-1}\)) at the point of minimum slope. Band heights were measured on the absorbance scale (I) from the baseline and \(\Delta v^b\) was measured at (I/2).

(i) **The Effect of Devitrification on the Peak Maxima**

The vitreous H\(_2\)O ice I absorption maxima are plotted in Fig. 3.2 as a function of increasing temperatures. Important parameters derived from these graphs are given in Table III.I. Although devitrifications of D\(_2\)O ice and HDO bearing ice were not observed in detail, data from such samples, immediately before and after devitrification, are included in Table III.I for comparison to H\(_2\)O data. In Fig. 3.2, the transformation temperature ranges are indicated for \(v_1\), \(v_3\) and \(v_1 + v_T\). Transformation was assumed to have begun at the onset of peak shift and was assumed to have finished upon reversal of peak shift direction.
Fig. 3.1 Representative spectra of vitreous and cubic ices at various temperatures.

Top: A - cryostat background at 83°K (compensated), B - H$_2$O ice I$_v$ at 83°, C - sample B annealed to 185°K and recooled to 83°K (cubic ice), D - sample C at 7°K, and E - cubic ice (H$_2$O(5.94% HDO)) at 83°K.

Bottom: A - cryostat background, B - D$_2$O(4.0% HDO) vitreous ice at 83°K, C - sample B annealed to 185°K, cubic ice at 83°K.
Fig. 3.2  Shifts of H\textsubscript{2}O frequencies during the vitreous-cubic ice phase transformation and subsequent behaviour of cubic ice. The full circles and triangles are from spectra recorded during warm-up from 83°K to 185°K. The open circles and triangles give the behaviour after annealing.
Table III.I  The frequencies of cubic and vitreous ice I at 82°K, their differences, the transformation range and the cubic ice absorptions temperature dependences.

<table>
<thead>
<tr>
<th></th>
<th>Ice $I_v$ 82°K</th>
<th>Ice $I_c$ 82°K</th>
<th>$\Delta v$ $I_c-I_v$ 82°K</th>
<th>Transformation Temperature Range</th>
<th>Ice $I_c$ $\Delta v/\Delta T$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>± 5°K</td>
<td>cm$^{-1}$/°K</td>
</tr>
<tr>
<td>$v_{1+1T}$</td>
<td>3367 ± 7</td>
<td>3340 ± 7</td>
<td>-27</td>
<td>130 - 145</td>
<td>0.26 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>(2499)</td>
<td>(2465)</td>
<td>(-34)</td>
<td></td>
<td>(0.16)</td>
</tr>
<tr>
<td>$v_3$</td>
<td>3253 ± 5</td>
<td>3217 ± 5</td>
<td>-36</td>
<td>125 - 145</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>(2436)</td>
<td>(2413)</td>
<td>(-23)</td>
<td></td>
<td>(0.13)</td>
</tr>
<tr>
<td>$v_1$</td>
<td>3191 ± 7</td>
<td>3149 ± 7</td>
<td>-42</td>
<td>120 - 145</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>(2372)</td>
<td>(2321)</td>
<td>(-51)</td>
<td></td>
<td>(0.18)</td>
</tr>
<tr>
<td>$3v_R$</td>
<td>2220 ± 5</td>
<td>2235 ± 5</td>
<td>+15</td>
<td>115 - 130</td>
<td>-0.11</td>
</tr>
<tr>
<td></td>
<td>(1617)</td>
<td>(1635)</td>
<td>(+18)</td>
<td></td>
<td>(-0.11)</td>
</tr>
<tr>
<td>$v_2$</td>
<td>1570</td>
<td>1570</td>
<td>(-18)</td>
<td>115 - 130</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>(1212)</td>
<td>(1194)</td>
<td></td>
<td></td>
<td>(0.14)</td>
</tr>
<tr>
<td>$v'_R$</td>
<td>846 ± 7</td>
<td>881 ± 7</td>
<td>+35</td>
<td>115 - 130</td>
<td>-0.19</td>
</tr>
<tr>
<td></td>
<td>(661)</td>
<td>(661)</td>
<td>(+51)</td>
<td></td>
<td>(-0.16)</td>
</tr>
<tr>
<td>$v_R$</td>
<td>802 ± 5</td>
<td>833 ± 5</td>
<td>+31</td>
<td>115 - 130</td>
<td>-0.18</td>
</tr>
<tr>
<td></td>
<td>(600)</td>
<td>(627)</td>
<td>(+27)</td>
<td></td>
<td>(-0.12)</td>
</tr>
<tr>
<td></td>
<td>--</td>
<td>780 ± 7</td>
<td></td>
<td>115 - 130</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>675 ± 7</td>
<td>690 ± 7</td>
<td>+15</td>
<td></td>
<td>(-0.12)</td>
</tr>
<tr>
<td></td>
<td>535 ± 7</td>
<td>570 ± 7</td>
<td>+35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_T$</td>
<td>212.8 ± 1</td>
<td>227.8 ± 5</td>
<td>+15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

HDO

<table>
<thead>
<tr>
<th></th>
<th>$v_{OH}$ 2437</th>
<th>$v_{OH}$ 2442</th>
<th>$v_{OH}$ 2416</th>
<th>$v_{OH}$ 2392</th>
<th>$\Delta v/\Delta T$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$/°K</td>
</tr>
<tr>
<td>$v_{OH}$</td>
<td>3304 ± 1</td>
<td>3266 ± 1</td>
<td>-38</td>
<td>0.20 ± 0.005</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(2437)</td>
<td>(2442)</td>
<td>(-21)</td>
<td>(0.123 ± 0.005)</td>
<td></td>
</tr>
<tr>
<td>$v'_R$</td>
<td>--</td>
<td>854 ± 1.5</td>
<td>--</td>
<td>-0.154 ± 0.022</td>
<td></td>
</tr>
<tr>
<td>$v_R$</td>
<td>792 ± 1</td>
<td>819 ± 0.5</td>
<td>+27</td>
<td>-0.147 ± 0.012</td>
<td></td>
</tr>
</tbody>
</table>
There are five important effects to notice: 1) between 115° and 145°K the molecular modes shift towards lower frequencies while the lattice modes shift towards higher frequencies, 2) the reversal of peak shift direction, 3) the irreversibility of the devitrification transitions, 4) the large frequency displacements between the same bands in cubic and vitreous ice I at 82°K, and 5) the reversibility of peak shifts in cubic ice I.

These effects can be seen in Fig. 3.2 for the $v_3(H_2O)$ data. The frequency was constant up to 125 ± 5°K, and shifted irreversibly by 36 ± 2 cm$^{-1}$ to lower frequency between 125 ± 5 and 142 ± 5°K. The frequency attained a positive, reversible temperature dependence of +0.23 cm$^{-1}$/°K above 142°K. Subsequent warming and cooling cycles revealed a sample with an approximately linear frequency-temperature dependence between 82°K and 180°K. The remaining absorptions of ice I behaved similarly during devitrification. However, all internal modes exhibited positive, and all librational modes exhibited negative temperature dependences after devitrification.

(ii) Oligomeric H$_2$O Absorptions

In addition to all the expected vitreous ice I absorptions, weak absorptions were observed near the frequencies previously reported (115) for oligomeric H$_2$O and D$_2$O. Weak peaks (0.01 abs units) were found near 3690 cm$^{-1}$ in H$_2$O and 2720 cm$^{-1}$ in D$_2$O and H$_2$O shoulders near 3647 cm$^{-1}$ (Fig. 3.3). They persisted only up to 125 ± 5°K and did not reappear upon recooling the sample. Half-height widths were between 15 and 20 cm$^{-1}$. No detailed study was made for oligomers, but data from several samples are compiled in Table III.II.
Fig. 3.3 Oligomeric H$_2$O and D$_2$O absorptions in vitreous ice I at 83°K: 1) vitreous H$_2$O ice, 2) cubic H$_2$O ice, 3) vitreous D$_2$O ice, 4) cubic D$_2$O ice. The features were more or less accentuated depending on the deposition rate.
Table III.II  Oligomeric $H_2O(D_2O)$ $v_1$ and $v_3$ ir absorptions seen for vitreous ice I samples before and during warm-up. The $v_3(H_2O)$ absorptions were weak peaks and the $v_1(H_2O)$ and $v_3(D_2O)$ absorptions were weak shoulders. One $v_3(D_2O)$ absorption is given in brackets.

<table>
<thead>
<tr>
<th>$H_2O$ (D$_2$O)</th>
<th>Temperature of Observation, °K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>82</td>
</tr>
<tr>
<td>$v_3$</td>
<td>3692</td>
</tr>
<tr>
<td></td>
<td>3677</td>
</tr>
<tr>
<td>$v_1$</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>--</td>
</tr>
</tbody>
</table>

(iii) The Effect of Devitrification on H$_2$O Half-height Widths

A comparison of H$_2$O spectra B and C in Fig. 3.1 (top) shows that the composite bands $(v_1, v_3, v_1 + v_T), (v_2, 2v_R)$ and $(v_R, v_R + v_T)$ are sharper in cubic ice I than in vitreous ice I. Half-height widths for these composite bands from the sets of H$_2$O spectra (samples A and B) were measured as a function of temperature, Figs. 3.4 and 3.5. [The large scatter in the data arises from several sources: 1) the choice of baseline ($\pm 2$ cm$^{-1}$), 2) the error in assessing $I$ and $\frac{1}{2} I$ for intense peaks ($\pm 5$ cm$^{-1}$), and 3) atmospheric attenuation or distortion of the $v_2$ band.] The parameters are compiled in Table III.III.
Fig. 3.4 The shifts of H₂O half-height widths for the composite H₂O bands (ν₉, νᵣ+ν₉) and (ν₁, ν₃, ν₁+ν₉) during the vitreous-cubic ice transformation and subsequent to annealing. Solid circles and triangles are for the unannealed sample warm-up. Open circles and triangles are for the annealed sample warm-up.
The shifts of half-height width for the composite $\text{H}_2\text{O}$ ($v_2, 2v_R$) band during the vitreous-cubic phase transformation and subsequently for cubic ice I. Solid points were obtained during vitreous sample warm-up from 83° to 185°K. Open points were obtained from annealed samples.
Table III.III  The half-height widths of the vitreous and cubic H$_2$O ice composite bands at 82°K and their temperature dependences for cubic ice I.

<table>
<thead>
<tr>
<th>Composite Band</th>
<th>Vitreous $\Delta v_{1/2}$</th>
<th>Cubic $\Delta v_{1/2}$</th>
<th>Difference $\Delta v_{1/2}$</th>
<th>Transition Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>°K</td>
</tr>
<tr>
<td>$(v_1, v_3, v_1 + v_T)$</td>
<td>322 ± 7</td>
<td>287 ± 5</td>
<td>-35</td>
<td>115 ± 5 - 130 ± 5</td>
</tr>
<tr>
<td>$(v_2, 2v_R)$</td>
<td>350 ± 10</td>
<td>365 ± 10</td>
<td>+15</td>
<td>115 ± 5 - 140 ± 5</td>
</tr>
<tr>
<td>$(v_R', v_R + v_T)$</td>
<td>220 ± 5</td>
<td>195 ± 3</td>
<td>-25</td>
<td>115 ± 5 - 150 ± 5</td>
</tr>
</tbody>
</table>

During warming from 82°K the half-height widths of vitreous ice spectra shifted irreversibly over the transformation temperature range. Subsequent warming-cooling cycles showed that the cubic ice spectra half-widths shifted reversibly and that the vitreous and cubic data agreed above 150°K.

There are specific differences among the three sets of composite bands (see Figs. 3.4 and 3.5). These are as follows: 1) the stretching band $\Delta v^i$ increased, 2) the bending band $\Delta v^b$ decreased and 3) the librational band $\Delta v^b$ appeared to increase with increasing temperature. Also, the $v_2$ half-height width initially increased during devitrification, although it was expected to decrease.

Annealing effects on $v_T$(H$_2$O) were not observed in detail, but the differences between vitreous and cubic ice at 83°K were measured. The data are 62.8 cm$^{-1}$ and 23.2 cm$^{-1}$ for vitreous and cubic ice.
absorbance of $v_p$(cubic), $I = 1.285$, was almost exactly double that of $v_p$(vit.). The vitreous $v_T(H_2O)$ absorption features were: a peak at $212.8 \pm 0.5 \text{ cm}^{-1}$ and faint shoulders centered at $301 \pm 3$ and $271 \pm 3 \text{ cm}^{-1}$.

3.2 Temperature Dependence of Cubic Ice I Absorptions

A. Temperature Dependence of HDO Absorptions

The four observed HDO absorptions provided the best measurements of band parameters as a function of increasing temperature in cubic ice I.

(i) Experimental

Three samples of $D_2O(4.00\%$ HDO) and two samples of $H_2O (5.94\%$ HDO) were prepared (section 2.4(c)) and observed in the liquid helium cell (section 1.5). Samples C(1,2,3) were deposited at $85 \pm 3\text{K}$ on CsI, warmed from $85^\circ \text{K}$ to $187^\circ \text{K}$ in 9 minutes, annealed at $187 \pm 3^\circ \text{K}$ for 2 minutes and were recooled to $84^\circ \text{K}$ in 4 minutes. The resulting cubic C samples were then cooled to $4.2^\circ \text{K}$ and observed for 3 hours before warming began: Warming from $4.2^\circ \text{K}$ to $200^\circ \text{K}$ required 6-8 hours. Samples D(1,2) ($5.94\%$ HDO in $H_2O$) were deposited at $83 \pm 3^\circ \text{K}$ on CsI, warmed to $188 \pm 3^\circ \text{K}$ in 8 minutes, annealed at $188 \pm 3^\circ \text{K}$ for 4 minutes and rapidly recooled to $83^\circ \text{K}$. Samples D1 and D2 were then treated as in C above.

During warming sets of P.E. 421 spectra were recorded for each sample under identical spectrophotometer conditions. The basic spectrometer conditions were the same as those for samples A and B (section 3.1 a) with small variations. For example, HDO peaks were recorded at $20 \text{ cm}^{-1}$/in or $2 \text{ cm}^{-1}$/div, and a 10 cm path gas cell (in the reference beam) was used with the Bodenseewerk unit for effective instrument purging. Among the three
sets of C sample spectra, frequencies were reproduced to within $\pm 2 \text{ cm}^{-1}$ at $170^\circ K$ and $\pm 1 \text{ cm}^{-1}$ at $h^\circ K$, while among the two sets of D sample spectra frequency reproducibility was only $\pm 3 \text{ cm}^{-1}$ at $160^\circ$ or $h^\circ K$. Typical HDO spectra were shown in Fig. 3.1.

(ii) Results of Warming Cubic Ice Containing HDO

Frequencies, half-height widths and absorbances were obtained as in section 3.1(b). However, to inhibit personal systematic bias the spectra were analyzed randomly with respect to temperature and during analysis no reference to temperature was permitted. Because of $2 \text{ cm}^{-1}$/div recording, HDO peak frequencies were read to $\pm 0.5 \text{ cm}^{-1}$. No attempt was made to subtract the $3\nu_R(H_2O)$ weak absorption from $\nu_{OD}(HDO)$ absorption and consequently $\nu_{OD}(HDO)$ frequencies are slightly low. Baselines for absorbances and half-height widths were drawn from 3394 to 3140 cm$^{-1}$ for $\nu_{OH}(HDO)$ and from 2480 cm$^{-1}$ to 2340 cm$^{-1}$ for $\nu_{OD}(HDO)$.

(a) HDO frequencies. The behaviour of $\nu_{OH}(HDO)$ frequency with increasing temperature is shown in Fig. 3.6. The data were derived from one set of spectra during a single warming period. Errors in instrumentation and in the methods of data evaluation limited the precision to $\pm 1 \text{ cm}^{-1}$.

Pertinent parameters from Fig. 3.6 are compiled in Table III.IV. The low temperature limiting frequency was obtained by extrapolating the data to $0^\circ K$. Although the data are non-linear, they can be approximated by two straight lines—a low and a high temperature line. The low and high temperature frequency dependences were evaluated from these lines and the "freeze-in" temperature was chosen as their point of intersection. There is a slight indication of irregular behaviour between $45^\circ$ and $70^\circ K$ (Fig.3.6). Sample sublimation above $180^\circ K$ did not appear to affect the frequency data.
Fig. 3.6 The shifts of HDO stretching frequencies for cubic ice I. The temperatures are not corrected for source beam heating, +10°K should be added. Open points represent $\nu_{\text{OH}}$(HDO) and solid points represent $\nu_{\text{OD}}$(HDO). Data of Ford and Falk (100) is included for comparison.
Table III.IV  The low temperature behaviour of the HDO stretching modes in the \(H_2O \) and \(D_2O\) environments of cubic ice I.

<table>
<thead>
<tr>
<th></th>
<th>(v_{OH}(HDO))</th>
<th>(v_{OD}(HDO))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Temperature Limit</td>
<td>(3263.5 \pm 1)</td>
<td>(2412.0 \pm 1)</td>
</tr>
<tr>
<td>Ratio (v_{OH}/v_{OD})</td>
<td>(1.354 \pm 0.001)</td>
<td>(0.047 \pm 0.005)</td>
</tr>
<tr>
<td>Linear Low Temperature Dependence</td>
<td>(0.047 \pm 0.005)</td>
<td>(0.123 \pm 0.005)</td>
</tr>
<tr>
<td>Linear High Temperature Dependence</td>
<td>(0.200 \pm 0.005)</td>
<td>(0.047 \pm 0.005)</td>
</tr>
<tr>
<td>&quot;Freeze-in&quot; Temperature</td>
<td>(80 \pm 5)</td>
<td>(68 \pm 5)</td>
</tr>
<tr>
<td>Irregularities</td>
<td>(45 - 70)</td>
<td>(\sim 60)</td>
</tr>
</tbody>
</table>

Behaviour of \(v_{OD}(HDO)\) is shown in Fig. 3.6 and some parameters are compiled in Table III.IV. The comments made above concerning \(v_{OH}(HDO)\) apply equally well to \(v_{OD}(HDO)\).

The peak and shoulder near 800 cm\(^{-1}\) in the samples of \(D_2O\) (4.0\% HDO) [tracing C, bottom of Fig. 3.1] were assigned to HDO librations, \(v_R(HDO)\) and \(v_R(HDO) + v_T(D_2O)\) respectively. (For ease of notation \(v_R + v_T\) is designated \(v'_R\).) Temperature variations of \(v_R(HDO)\) and \(v_R'(HDO)\) are shown in Fig. 3.7 and some parameters are compiled in Table III.V. As shoulder positions are
Fig. 3.7 The shifts of $\nu_R$(HDO), $\nu_R'$(HDO) and $\nu_T$(H2O) for cubic ice I during warm-up. The librational shoulder $\nu_R'$(HDO) is assigned as $\nu_R$(HDO) + $\nu_T$(D2O). Temperatures are uncorrected for source heating.
Table III.V  The low temperature behaviour of the HDO librational modes in cubic ice I for dilute solutions of HDO in H₂O and D₂O.

<table>
<thead>
<tr>
<th></th>
<th>( v_R(\text{HDO}) )</th>
<th>( v_R(\text{HDO}) + v_T(\text{D}_2\text{O}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Temperature Limit</td>
<td>cm(^{-1})</td>
<td>823.3 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>cm(^{-1}/°K)</td>
<td>856.2 ± 1.5</td>
</tr>
<tr>
<td>Linear Low Temperature Dependence</td>
<td>cm(^{-1}/°K)</td>
<td>&lt; -0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt; -0.04</td>
</tr>
<tr>
<td>Linear High Temperature Dependence</td>
<td>cm(^{-1}/°K)</td>
<td>-0.147 ± 0.012</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-0.154 ± 0.022</td>
</tr>
<tr>
<td>&quot;Freeze-in&quot; Temperature</td>
<td>°K</td>
<td>55 ± 5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>65 ± 5</td>
</tr>
<tr>
<td>Irregularities</td>
<td>°K</td>
<td>105 - 120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>--</td>
</tr>
</tbody>
</table>

difficult to determine accurately, \( v_R \) data have a higher error than \( v_R --in this case ± 1.5 \text{ cm}^{-1} \). Spectra and data were obtained as in section 3.1.

(b) HDO half-height widths. The \( v_{OH}(\text{HDO}) \) and \( v_{OD}(\text{HDO}) \) half-height widths, Fig. 3.8, were obtained from the same sets of spectra as were the frequencies in the preceding section. Details of the plots are compiled in Table III.VI.

Errors in \( \Delta v_{OH}(\text{HDO}) \) (± 0.75 cm\(^{-1}\)) resulted from 1) inaccuracies in assigning baselines (± 0.005 absorbance), 2) errors in estimating 1/2 I for I = 1.0 absorbance (± 0.01 absorbance), and 3) errors in estimating widths
Fig. 3.8. The shifts of HDO stretching modes half-height widths during warm-up of cubic ice I. These data were obtained from the same spectra as were the frequencies of Fig. 3.6. Temperatures are uncorrected.
Table III.VI  The low temperature behaviour of the HDO stretching modes half-height widths for HDO in H$_2$O and D$_2$O cubic ice I.

<table>
<thead>
<tr>
<th></th>
<th>$v_{\text{OH}}$(HDO)</th>
<th>$v_{\text{OD}}$(HDO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Temperature Limit</td>
<td>cm$^{-1}$</td>
<td>35.5 ± 0.75</td>
</tr>
<tr>
<td>Ratio $\Delta v_{\text{OH}}/\Delta v_{\text{OD}}$</td>
<td></td>
<td>1.51</td>
</tr>
<tr>
<td>Linear Low Temperature Dependence</td>
<td>cm$^{-1}$/°K</td>
<td>&lt; 0.02</td>
</tr>
<tr>
<td>Linear High Temperature Dependence</td>
<td>cm$^{-1}$/°K</td>
<td>0.066 ± 0.005</td>
</tr>
<tr>
<td>&quot;Freeze-in&quot; Temperature</td>
<td>°K</td>
<td>87 ± 5</td>
</tr>
</tbody>
</table>

(± 0.5 cm$^{-1}$). Because of sample sublimation, data for $\Delta v_{\text{OH}}$(HDO) obtained above 190°K do not extrapolate into those obtained at lower temperatures.

Errors in $\Delta v_{\text{OD}}$(HDO) (estimated to be ± 1.0 cm$^{-1}$) resulted from:
1) inaccuracies in assigning baselines due to an underlying 3$v_{\text{R}}$(H$_2$O) absorption (± 0.01 absorbance), 2) errors in estimating 1/2 I for I = 0.70 absorbance (± 0.005 absorbance), and 3) errors in estimating widths (± 0.5 cm$^{-1}$).

In both cases above the HDO half-height widths were quoted and plotted only to the nearest 0.5 cm$^{-1}$.
(c) HDO absorbances. Peak heights (I) of $v_{OH}(\text{HDO})$ and $v_{OD}(\text{HDO})$ were measured (with errors of $\pm 0.01$ and $\pm 0.005$ abs. units respectively) from consistent baselines on the same sets of spectra as were frequency and half-height width. Absorbance data (I) are plotted in Fig. 3.9 and the details are listed in Table III.VII. Normalization of the two sets of intensities was not attempted.

Peak heights underwent a relatively smooth, continuous decrease from 28° to 190°K. Data obtained with the sample above 190°K indicate a sharp decrease in I as the sample sublimed. No estimate was made of cumulative sample loss due to sublimation during the whole experiment.

A slight, concave discontinuity centered at 125°K appears in an otherwise convex curve for these data. The data appear constant below 35°K indicating $I(v_{OD}(\text{HDO}))$ varied by less than $-0.24 \times 10^{-3}$ absorbance/°K.

Table III.VII The low temperature behaviour of the HDO stretching modes peak heights for cubic ice I.

<table>
<thead>
<tr>
<th></th>
<th>$I(v_{OH}(\text{HDO}))$</th>
<th>$I(v_{OD}(\text{HDO}))$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Temperature Limit absorbance</td>
<td>0.945</td>
<td>0.540</td>
</tr>
<tr>
<td>Linear Low Temperature Dependence absorbance/°K</td>
<td>$-0.69 \times 10^{-3}$</td>
<td>$-0.24 \times 10^{-3}$</td>
</tr>
<tr>
<td>Linear High Temperature Dependence absorbance/°K</td>
<td>$-2.26 \times 10^{-3}$</td>
<td>$-1.07 \times 10^{-3}$</td>
</tr>
<tr>
<td>&quot;Freeze-in&quot; Temperature °K</td>
<td>79 ± 5</td>
<td>76 ± 5</td>
</tr>
<tr>
<td>Irregularities °K</td>
<td>130(?)</td>
<td>125</td>
</tr>
</tbody>
</table>
Fig. 3.9 The shifts of the HDO stretching mode peak heights or absorbances (I) during warm-up of a cubic ice I sample. The I data were obtained from the same spectra as were the frequencies and Δν of Figs. 3.6 and 3.8.
B. Temperature Dependence of H$_2$O and D$_2$O Absorptions

Eight H$_2$O and D$_2$O absorptions provided less accurate measures of the primary spectral parameters than the three HDO absorptions, but they did yield information on cubic ice I.

(i) Experimental

Five sets of spectra from five specimens were recorded on the P.E. 421 or P.E. 301 spectrophotometers in the liquid helium dewar. Details of sample composition and preparation are given in Table III.VIII. General H$_2$O absorptions were observed in samples E and F and their results were combined with those of cubic samples A and B. General D$_2$O absorptions were observed in samples H and I and their results were combined with those of sample C. Samples E, F, H and I were observed on CsI in the P.E. 421. The $\nu_T$(H$_2$O) absorptions were observed in a separate sample (G) with polyethylene windows on the P.E. 301.

P.E. 421 function settings were again identical within one set of spectra and as consistent as possible between samples. Specific conditions were given in section 3.1. Only small alterations in instrument purging, reference beam attenuation and optical wedge settings were made.

The P.E. 301 was used in the $I/I_0$ mode between 666 cm$^{-1}$ and 160 cm$^{-1}$ with Bodenseewerk purging and no evacuated reference cell. Spectra were scanned at 40 cm$^{-1}$/min. and recorded at 4.4 cm$^{-1}$/div. Spectral slit widths varied but were usually less than 4 cm$^{-1}$. 
Table III.VIII  Details of depositing and annealing of H$_2$O, D$_2$O and HDO bearing ice I samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>E H$_2$O</th>
<th>F H$_2$O(D$_2$O)</th>
<th>G H$_2$O</th>
<th>H D$_2$O</th>
<th>I D$_2$O(H$_2$O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition Temperature (°K)</td>
<td>85</td>
<td>85</td>
<td>85</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>Time to warm from 85°K to 185°K (min.)</td>
<td>12</td>
<td>15</td>
<td>17</td>
<td>17</td>
<td>15</td>
</tr>
<tr>
<td>Maximum annealing Temperature (°K)</td>
<td>186</td>
<td>183</td>
<td>187</td>
<td>185</td>
<td>180</td>
</tr>
<tr>
<td>Time maintained at maximum annealing temperature (min.)</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Time to cool from 185°K to 85 °K (min.)</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Time to cool from 85°K to 8°K (min.)</td>
<td>30</td>
<td>24</td>
<td>18</td>
<td>21</td>
<td>18</td>
</tr>
<tr>
<td>Length of warmup run (min.)</td>
<td>245</td>
<td>170</td>
<td>269</td>
<td>210</td>
<td>123</td>
</tr>
<tr>
<td>Time maintained at 8°K (min.)</td>
<td>245</td>
<td>170</td>
<td>269</td>
<td>210</td>
<td>123</td>
</tr>
<tr>
<td>Length of warmup run (min.)</td>
<td>243</td>
<td>166</td>
<td>433</td>
<td>920</td>
<td>348</td>
</tr>
</tbody>
</table>
(ii) Results of Warming H$_2$O and D$_2$O Cubic Ice I

Frequency data were obtained as in section 3.1B. The sets of spectra were analyzed randomly with respect to temperature as in section 3.2A(ii). Each complete set of spectra was analyzed one band at a time. Because of the breadth of H$_2$O and D$_2$O bands, frequency data were accurate only to ±2.5 cm$^{-1}$.

(a) Fundamental H$_2$O and D$_2$O frequencies. The $v_3$ frequencies are plotted as a function of temperature in Fig. 3.10 and some plot parameters are compiled in Table III.IX. From Fig. 3.10 and Table III.IX it is apparent that liquid nitrogen and liquid helium cell data (samples A - B and E - F) do not concur.

For $v_3$(D$_2$O) no data were obtained between 51° and 83°K since a sudden slight rise in cryostat pressure (from traces of condensed residual O$_2$ and N$_2$) caused heat losses between the nitrogen shield and the helium dewar. Although the pressure rose only from $6.8 \times 10^{-6}$ Torr to $15 \times 10^{-6}$ Torr and dropped to $8.2 \times 10^{-6}$ in 2 - 3 minutes, the pressure rise was sufficient to rapidly warm the helium dewar and sample block.

The $v_1$ frequency variations during sample warming are plotted in Fig. 3.11 and some details of the behaviour are given in Table III.IX. For $v_1$(D$_2$O) the helium and nitrogen cell data agree reasonably well. For $v_1$(D$_2$O) a high scatter of points did not permit evaluation of low temperature dependence. No data was obtained between 51° and 83°K for the same reasons as with $v_3$, a rapid pressure rise.

Helium and nitrogen cell $v_2$ data do not agree (Fig. 3.12). Details of the plots are given in Table III.IX. Data for three helium cell samples and two nitrogen cell samples are plotted (including unannealed sample data at
Fig. 3.10 The shifts of cubic ice I $\nu_3$ during warm-up. For $H_2O$ the open circles represent data from experiments between 83° and 180°K on a Hornig-Wagner all-glass cell. Temperatures are uncorrected for source beam heating.
Table III.IX  The temperature dependences of cubic ice I $H_2O$ and $D_2O$ vibrational absorptions.

<table>
<thead>
<tr>
<th></th>
<th>Low temperature limit</th>
<th>Low temperature dependences</th>
<th>High temperature dependences</th>
<th>Freeze-in temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$/°K</td>
<td>cm$^{-1}$/°K</td>
<td>°K</td>
</tr>
<tr>
<td>$\nu_1 + \nu_T$</td>
<td>3334 ± 4</td>
<td>0.08 ± 0.05</td>
<td>+ 0.20 ± 0.08</td>
<td>80 ± 10</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>3204 ± 2</td>
<td>0.03 ± 0.03</td>
<td>+ 0.17 ± 0.05</td>
<td>70 ± 10</td>
</tr>
<tr>
<td></td>
<td>(3215 ± 5)</td>
<td>--</td>
<td>(+ 0.19 ± 0.04)</td>
<td></td>
</tr>
<tr>
<td>$\nu_1$</td>
<td>3133 ± 3</td>
<td></td>
<td>+ 0.34 ± 0.03</td>
<td>65 ± 5</td>
</tr>
<tr>
<td>$3\nu_R$</td>
<td>2239 ± 3</td>
<td>&lt; -0.09</td>
<td>- 0.12 ± 0.03</td>
<td>70 ± 10</td>
</tr>
<tr>
<td>$\nu_2/2\nu_R$</td>
<td>1562 ± 4</td>
<td>&lt; 0.14</td>
<td></td>
<td>70 ± 10</td>
</tr>
<tr>
<td></td>
<td>(1605 ± 10)</td>
<td></td>
<td></td>
<td>0.36 ± 0.10</td>
</tr>
<tr>
<td>$\nu_R'$</td>
<td>881 ± 7</td>
<td></td>
<td></td>
<td>80 ± 20</td>
</tr>
<tr>
<td>$\nu_R$</td>
<td>832 ± 5</td>
<td></td>
<td>- 0.19 ± 0.08</td>
<td>75 ± 10</td>
</tr>
<tr>
<td>$\nu_T$</td>
<td>229.2 ± 0.75</td>
<td></td>
<td>- 0.102 ± 0.012</td>
<td>95 ± 5</td>
</tr>
<tr>
<td></td>
<td>Low temperature limit</td>
<td>Low temperature dependences</td>
<td>High temperature dependences</td>
<td>Freeze-in temperature</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>$D_2^0$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_1 + v_T$</td>
<td>$2464 \pm 3$</td>
<td>--</td>
<td>$0.17 \pm 0.05$</td>
<td>$80 \pm 30$</td>
</tr>
<tr>
<td>$v_3$</td>
<td>$2413 \pm 4$</td>
<td>$&lt;0.06$</td>
<td>$0.13 \pm 0.04$</td>
<td>$100 \pm 20$</td>
</tr>
<tr>
<td>$v_1$</td>
<td>$2320 \pm 5$</td>
<td>--</td>
<td>$0.19 \pm 0.03$</td>
<td>$70 \pm 10$</td>
</tr>
<tr>
<td>$3v_R$</td>
<td>$1637 \pm 3$</td>
<td>$&lt;-0.07$</td>
<td>$-0.11 \pm 0.03$</td>
<td>$60 \pm 5$</td>
</tr>
<tr>
<td>$v_2/2v_R$</td>
<td>$1189 \pm 2$</td>
<td>$0.13 \pm 0.03$</td>
<td>$0.08 \pm 0.05$</td>
<td>$50 \pm 10$</td>
</tr>
<tr>
<td>$v_R'$</td>
<td>$663 \pm 6$</td>
<td>--</td>
<td>$-0.10 \pm 0.05$</td>
<td>$100 \pm 10$</td>
</tr>
<tr>
<td>$v_R$</td>
<td>$630 \pm 4$</td>
<td>--</td>
<td>$-0.11 \pm 0.04$</td>
<td>$65 \pm 15$</td>
</tr>
</tbody>
</table>
Fig. 3.11  The shifts of cubic ice I $\nu_1$ during warm-up. For $H_2O$ typical annealing run data are included for pre- and post-annealing behaviour (open circles and squares).
Fig. 3.12 The shifts of $v_2$ in cubic ice I during warm-up. For comparison to the helium cell data, nitrogen cell data for pre and post-annealing behaviour are included. Pimentel and Zimmerman's (97) data are also included for hexagonal ice I. Temperatures are uncorrected.
83°K for the helium runs). The \( \nu_2(D_2O) \) data were not obtained from the same set of spectra as the more intense \( \nu_3 \) and \( \nu_1 \) absorption data.

Data relating the \( \nu_R \) frequency temperature dependence are plotted in Fig. 3.13 and important parameters obtained from the figure are listed in Table III.IX. For \( \nu_R(H_2O) \), helium and nitrogen cell data are in good agreement. Because the \( \nu_R \) band is broad the maximum was difficult to determine accurately. Consequently, the low temperature data are poor and a low-temperature/frequency dependence could not be approximated.

The nature of translational \( H_2O \) absorptions is shown in Fig. 3.14. The peak frequency temperature dependence is given in Fig. 3.15. An irregular shift of 1.5 cm\(^{-1}\) occurs between 55 and 60°K and the frequency is invariant from 155° to 200°K. The details of the graph are listed in Table III.IX.

Several features of \( \nu_T(H_2O) \) were observed. The intersection of two lines along peak sides was read to \( \pm 0.50 \) cm\(^{-1}\) while shoulder positions were estimated to within \( \pm 3 \) cm\(^{-1}\). The peak near 165 cm\(^{-1}\) is distorted because of the rapid energy drop at the end of a grating range. Frequencies of peaks, minima, shoulder edges and baseline at 25°K are listed in Table III.X.

(b) Overtone and combination frequencies. The \( (\nu_1 + \nu_T) \) data are plotted in Fig. 3.16 and summarized in Table III.IX: One can see that the helium and nitrogen cell data agree. However, the data are too poor to permit an approximation of a linear low temperature dependence.

Both the \( H_2O \) and \( D_2O \) \( 3\nu_R \) frequencies (Fig. 3.17) decrease with increasing temperature at rates indicated in Table III.IX. Again the helium and nitrogen cell data agree near 80°K.
Fig. 3.13 The shifts of $\nu_R$ for cubic ice I during warm-up. For $\text{H}_2\text{O}$ Pimentel and Zimmerman's (97) data and liquid nitrogen cell data are included for comparison.
Fig. 3.14 The cubic ice I $\nu_T(\text{H}_2\text{O})$ band at 83$^\circ$K and the background spectrum through the blank cell at 83$^\circ$K. The feature near 218 cm$^{-1}$ arises from a filter change.
Fig. 3.15 The shifts of $\nu_m(\text{H}_2\text{O})$ for cubic ice I during warm-up. The sample was mounted on a polyethylene window 0.25 cm thick. The cell temperature did not reach helium temperature with the source on or off after 3 hours of cooling. Temperatures are uncorrected for source heating.
Table III.X  The interpretation of the $v_T(\text{H}_2\text{O})$ features for comparison to previous results.

<table>
<thead>
<tr>
<th>$v_T(\text{H}_2\text{O})$ Feature</th>
<th>Description</th>
<th>Frequency cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>peak</td>
<td>&lt;161</td>
</tr>
<tr>
<td>B</td>
<td>minimum</td>
<td>176.5 ± 1</td>
</tr>
<tr>
<td>C</td>
<td>shoulder edge</td>
<td>193 ± 3</td>
</tr>
<tr>
<td>D</td>
<td>shoulder edge</td>
<td>214 ± 3</td>
</tr>
<tr>
<td>E</td>
<td>peak</td>
<td>229.6 ± 0.5</td>
</tr>
<tr>
<td>F</td>
<td>shoulder edge</td>
<td>246 ± 3</td>
</tr>
<tr>
<td>G</td>
<td>shoulder edge</td>
<td>272 ± 3</td>
</tr>
<tr>
<td>H</td>
<td>shoulder edge</td>
<td>286 ± 3</td>
</tr>
<tr>
<td>I</td>
<td>shoulder edge</td>
<td>295 ± 3</td>
</tr>
<tr>
<td>J</td>
<td>baseline</td>
<td>334 ± 3</td>
</tr>
</tbody>
</table>

The $(v_R + v_T)$ data are plotted in Fig. 3.18 and summarized in Table III.IX. This band is a poorly defined shoulder on the intense $v_R$ band and thus could only be estimated to within ± 7 cm$^{-1}$. Helium and nitrogen cell data are not in good agreement. Low temperature dependences could not be defined.

(c) $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ half-height widths. Data for cubic ice I ($\text{H}_2\text{O}$) were plotted in Figs. 3.4 and 3.5 of section 3.1. The half-height widths of the composite stretching band and the composite librational band increased with increasing temperature. However, the composite $(v_2, 2v_R)$ band half-height width decreased with increasing $T$. 

Fig. 3.16 The shifts of \((\nu_1 + \nu_T)(H_2O)\) for cubic ice I during warm-up. For \(H_2O\) the nitrogen cell data are included. Temperatures are uncorrected.
Fig 3.17 The shifts of $3\nu_R$ for cubic ice I during warm-up. For H$_2$O annealing data and data of Pimentel and Zimmerman (97) are included. Temperatures are uncorrected.
Fig. 3.18 The shifts of \((v_R + v_T)\) for cubic ice I during warm-up. Nitrogen and helium cell data are included for \(H_2O\).
3.3 The H$_2$O, D$_2$O and HDO Ice I Absorptions at 83°K

In this section are listed the details of the H$_2$O, D$_2$O and HDO vitreous and cubic ice I absorptions at 83°K for comparison in Chapter 4 to the literature values.

A. Experimental

Typical spectra of vitreous and cubic ice were shown in Fig. 3.1: $v_T$(H$_2$O) was shown in Fig. 3.1h. The samples, spectra and methods of treatment were described in sections 3.1 and 3.2.

B. Results at 83°K

Vitreous and cubic ice I have the same skeletal absorption spectra (Fig. 3.1) but are easily distinguished in details of band structure, frequency and width. Frequencies observed for the H$_2$O, HDO and D$_2$O systems at 83°K are compiled in Tables III.XI, III.XII and III.XIII respectively. Results of previous workers are included for comparison.

(i) H$_2$O Absorptions at 83°K

Spectra of vitreous and cubic ice I obtained in this work are in sharp contrast and exhibit features not previously observed.

The stretching band of cubic ice I is composed of one peak and two well defined shoulders—3340 (2442)(sh)cm$^{-1}$, 3210(2416) cm$^{-1}$ and 3149 (2392)(sh)cm$^{-1}$. (D$_2$O data are given in brackets.) In contrast, vitreous ice I has very weak absorptions at 3686(2720) cm$^{-1}$ and 3640 cm$^{-1}$ in addition to a peak at 3253(2436) cm$^{-1}$ and two poorly defined shoulders at
Table III.XI(a)  The frequencies and assignments for cubic and hexagonal ice I of the present and previous workers.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>This Work</th>
<th>Whalley and Bertie(a)</th>
<th>Hornig and Haas(b)</th>
<th>Giguere and Harvey(c)</th>
<th>Val'kov and Maslenkova(d)</th>
<th>Ockman(e)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vitreous 93°K</td>
<td>Cubic 93°K</td>
<td>100°K</td>
<td>83°K</td>
<td>100°K</td>
<td>77°K</td>
</tr>
<tr>
<td>n&lt;sub&gt;3&lt;/sub&gt; olig</td>
<td>3686 vw</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>n&lt;sub&gt;1&lt;/sub&gt; olig</td>
<td>3640 vw</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>n&lt;sub&gt;1&lt;/sub&gt; + n&lt;sub&gt;T&lt;/sub&gt;</td>
<td>3367 ±5 sh</td>
<td>3340 ssh</td>
<td>3350 shs</td>
<td>(n&lt;sub&gt;1&lt;/sub&gt;) 3360 Msh</td>
<td>3321 (2)</td>
<td>3340</td>
</tr>
<tr>
<td>n&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3253 vs</td>
<td>3210±5 vs</td>
<td>3220±5 s</td>
<td>(n&lt;sub&gt;3&lt;/sub&gt;) 3210 vs</td>
<td>3260</td>
<td>3210 (4)</td>
</tr>
<tr>
<td>n&lt;sub&gt;1&lt;/sub&gt;</td>
<td>3191 ±5 sh</td>
<td>3149 ssh</td>
<td>3140 shs</td>
<td>(2n&lt;sub&gt;2&lt;/sub&gt;) 3125 Msh</td>
<td>3088 (10)</td>
<td>3140</td>
</tr>
<tr>
<td>3n&lt;sub&gt;R&lt;/sub&gt;</td>
<td>2220 w</td>
<td>2235 w</td>
<td>2266±20 vbw</td>
<td>.2225 s</td>
<td>2250</td>
<td>2235</td>
</tr>
<tr>
<td>n&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1660 m</td>
<td>1570±10 m</td>
<td>1650±30 vbw</td>
<td>1585 s</td>
<td>--</td>
<td>1580</td>
</tr>
<tr>
<td>1570 sh</td>
<td>--</td>
<td>--</td>
<td>(1130 msh)**</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n&lt;sub&gt;R&lt;/sub&gt; + n&lt;sub&gt;T&lt;/sub&gt;</td>
<td>846 ssh</td>
<td>881 ssh</td>
<td>900 sh</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>n&lt;sub&gt;R&lt;/sub&gt;</td>
<td>802 s</td>
<td>833 s</td>
<td>840 s</td>
<td>850</td>
<td>850</td>
<td>850</td>
</tr>
<tr>
<td>--</td>
<td>~780 sh</td>
<td>770 sh</td>
<td>--</td>
<td>--</td>
<td></td>
<td></td>
</tr>
<tr>
<td>~675 sh</td>
<td>~690 sh</td>
<td>660 sh</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>n&lt;sub&gt;R&lt;/sub&gt; - n&lt;sub&gt;T&lt;/sub&gt;</td>
<td>535 msh</td>
<td>570 msh</td>
<td>555 sh</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

* data from sample A section 3.1; ** observed only in samples annealed above 200°K.

(a) Ref. 95  (b) Ref. 106  (c) Ref. 98  (d) Ref. 99  (e) Ref. 108.
Table III.XI(b) The translational lattice mode features of vitreous, cubic and hexagonal ice I.

<table>
<thead>
<tr>
<th>$\nu_T$(H$_2$O)</th>
<th>This Work</th>
<th>93°K</th>
<th>93°K</th>
<th>Giguere and Arraudeau(a)</th>
<th>113°K</th>
<th>173°K</th>
<th>Whalley(b)</th>
<th>100°K</th>
<th>Hexag.&amp; Cub.</th>
<th>Pimentel(c)</th>
<th>93°K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>high frequency limit</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>shoulder</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>326 ± 3</td>
<td>334 ± 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>shoulder</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>271</td>
<td>296</td>
<td></td>
<td></td>
<td></td>
<td>295</td>
<td>293</td>
<td>300-310</td>
<td>(305)</td>
<td>(275)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>change of slope</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>peak</td>
<td>212.8±0.5</td>
<td>227.8±0.5</td>
<td>225 (ms)</td>
<td>223 m</td>
<td>229.2</td>
<td>229</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>change of slope</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>change of slope</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>shoulder</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>197</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>minimum</td>
<td>173</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>peak</td>
<td>162</td>
<td>154 (m)</td>
<td>152</td>
<td>164</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* taken from Fig. 3 of Ref. (97).

(a) Ref: 89  (b) Ref. 95  (c) Ref. 97.
Table III.XII  Comparison of the present and previous HDO vibration frequencies near 90°K.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>This work 93°K</th>
<th>Whalley and Bertie (a) 100°K</th>
<th>Hornig and Haas (b) 83°K</th>
<th>Ford and Falk (c) 93°K</th>
<th>Hornig et al. (d) 83°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>V&lt;sub&gt;OH&lt;/sub&gt;</td>
<td>3304 m 3266 s</td>
<td>3277 ± 4 s</td>
<td>3275 vs</td>
<td>3270 ± 5</td>
<td>3300</td>
</tr>
<tr>
<td>HDO in D&lt;sub&gt;2&lt;/sub&gt;O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V&lt;sub&gt;OD&lt;/sub&gt;</td>
<td>2437 m 2416 s</td>
<td>2421 ± 4 s</td>
<td>2416 vs</td>
<td>2418 ± 3</td>
<td>2440</td>
</tr>
<tr>
<td>HDO in H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V&lt;sub&gt;2&lt;/sub&gt;(HDO)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1490 s</td>
</tr>
<tr>
<td>HDO in D&lt;sub&gt;2&lt;/sub&gt;O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1470</td>
</tr>
<tr>
<td>V&lt;sub&gt;R&lt;/sub&gt; + V&lt;sub&gt;T&lt;/sub&gt;</td>
<td>792 w 819 mw</td>
<td>822 ± 6 m</td>
<td></td>
<td></td>
<td>800</td>
</tr>
<tr>
<td>HDO in D&lt;sub&gt;2&lt;/sub&gt;O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>620</td>
</tr>
<tr>
<td>HDO in H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>515 ± 10 m</td>
</tr>
</tbody>
</table>

(a) Ref. 95  (b) Ref. 106  (c) Ref. 100  (d) Ref. 105.
Table III.XIII  The frequencies and assignments of D$_2$O ice I (vitreous, cubic, hexagonal) near 90°K for the present and previous workers.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>This work 93°K</th>
<th>Whalley and Bertie (a) 100°K hex.and cub.</th>
<th>Hornig and Haas (b) 83°K cubic</th>
<th>Giguere and Harvey (c) 100°K hexagonal</th>
<th>Val'kov and Maslenkova (d) 100°K hexagonal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_3$ olig</td>
<td>2720</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_1$ olig</td>
<td>--</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_1 + \nu_T$</td>
<td>2499 ssh 2465</td>
<td>2485 ± 10 msh (2\nu_1, 2\nu_2) + 2495 msh</td>
<td></td>
<td></td>
<td>2542 (0.5)</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>2436 s 2413</td>
<td>2425 ± 5 s (\nu_3) 2432 vs 2450</td>
<td></td>
<td></td>
<td>2424 (3)</td>
</tr>
<tr>
<td>$\nu_1$</td>
<td>2372 ssh 2321</td>
<td>2332 ± 5 s (\nu_1, 2\nu_2) - 2336 s</td>
<td></td>
<td></td>
<td>2291 (10)</td>
</tr>
<tr>
<td>$3\nu_R$</td>
<td>1617 w 1635</td>
<td>1650 ± 30 s 1635 s 1630</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>1212 m 1194</td>
<td>1210 ± 10 s 1210 s 1210 ~1240</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_R + \nu_T$</td>
<td>ssh 661</td>
<td>675 sh</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_R$</td>
<td>600 s 627</td>
<td>640 s</td>
<td></td>
<td></td>
<td>630</td>
</tr>
<tr>
<td>$\nu_R - \nu_T$</td>
<td></td>
<td>425 sh</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Ref. 95  (b) Ref. 106  (c) Ref. 98  (d) Ref. 99.
3367(2499) cm$^{-1}$ and 3191(2372) cm$^{-1}$. For H$_2$O cubic ice I, the liquid helium and liquid nitrogen experimental $v_3$ data do not agree at 83°K (Fig. 3.10).

Two distinct values of $v_2$(H$_2$O) are indicated among liquid helium experiments and some liquid nitrogen experiments. All helium runs and some nitrogen runs gave $v_2$(83°K) at 1570 cm$^{-1}$. A few nitrogen runs with thin samples gave $v_2$(83°K) at 1604 cm$^{-1}$. Atmospheric H$_2$O absorptions may have attenuated the weak $v_2$(H$_2$O) absorptions of thin samples.

Ice samples annealed with care above 200°K showed two distinctions from those annealed below 200°K. The former gave spectra with a distinct shoulder at 1130 cm$^{-1}$ (on the side of $v_2$). As well, a deep minimum appeared between the 1130 cm$^{-1}$ shoulder and the $v_R$ band. Pimentel's (97) spectra showed the same features although he offered no explanations for them.

Inspection of the cubic ice I H$_2$O $v_T$ band (Fig. 3.14) shows two peaks and three shoulders. However, Whalley's (87) theory showed that additional $v_T$ features yield important information on the densities of phonon states. Accordingly, ten features of $v_T$(H$_2$O) at 93°K were reported in Table III.X. In contrast, the vitreous ice I $v_T$ band had no low frequency shoulder or peak. As well the 267 cm$^{-1}$ shoulder was poorly defined.

(ii) D$_2$O Absorptions at 83°K

D$_2$O ice I has the same sets of spectral features as H$_2$O ice I. Vitreous D$_2$O ice spectra have a weak oligomeric absorption at 2720 cm$^{-1}$ which has not been reported previously for ice. Oligomeric absorptions are absent in cubic D$_2$O sample spectra. As in H$_2$O ice I, the stretching band shoulders are better defined in cubic than in vitreous ice. The
problems caused by atmospheric H$_2$O attenuations encountered in H$_2$O ice I were eliminated by more efficient purging.

(iii) HDO Absorptions at 83°K

Only three HDO absorptions were observed, the OH and OD stretches and an HDO libration. In vitreous samples the three absorptions were broad, relatively weak and without shoulders. In cubic samples the $v_{\text{OH}}$ band had no shoulders, the $v_{\text{OD}}$ band had two shoulders and the $v_{\text{R}}$ band had one shoulder. No $v_{\text{R}}$(HDO) absorption was observed near 600 cm$^{-1}$ for HDO in H$_2$O.

3.4 Summary of Ice I Results

A. Vitreous-Cubic Ice I Transformation

1. All H$_2$O absorptions shift irreversibly in the temperature range 115 - 145°K; internal modes shift to lower frequencies while lattice modes shift to higher frequencies.

2. Above 150°K, vitreous and cubic frequency data concur and shift reversibly with respect to temperature.

3. Oligomeric H$_2$O absorptions are absent above 125°K.

4. Upon sample devitrification the absorptions are shifted, sharpened and better defined.

5. D$_2$O and HDO absorptions appear to have the same behaviour as those of H$_2$O.

6. Composite-band half-height widths exhibited unusual behaviour in the case of ($v_2$, 2$v_{\text{R}}$).
B. HDO in Cubic Ice I

1. Dilute concentrations of HDO in H$_2$O and D$_2$O gave accurate measures of frequency, half-height widths and absorbances as a function of temperature.

2. Plots of the HDO data provided low temperature limits, linear low and high temperature dependences and indications of irregular behaviour.

3. A new absorption was observed as a shoulder on $v_R$(HDO) and is designated $v_R$(HDO) + $v_T$(D$_2$O) or $v_R'$(HDO).

4. Internal mode cubic ice I HDO absorptions shift reversibly to higher frequency and lattice mode HDO frequencies shift reversibly to lower frequencies as a function of increasing temperature.

5. HDO stretching mode half-height widths increased as a function of increasing temperature.

6. HDO stretching mode absorbances decreased as a function of increasing temperature.

C. H$_2$O and D$_2$O in Cubic Ice I

These results provided measures of eight H$_2$O and seven D$_2$O absorptions that were less accurate, but of the same nature, as those from HDO.
CHAPTER FOUR

DISCUSSION OF ICE I

The data from cubic and vitreous ice I ir spectra contribute to detailed understandings of: 1) the origins of the absorptions, 2) the process of the vitreous-cubic phase transformation, and 3) the effects of increasing temperature, increasing R(0⋯⋯0) and decreasing hydrogen bond strength on the H₂O, D₂O, and HDO vibrations and potential well.

4.1 The Ice I Vitreous-Cubic Phase Transformation

The x-ray and electron diffraction experiments (58) indicated that the structure of the solid formed by condensing H₂O vapour at low temperatures depended on the rate of deposition and the substrate temperature: Amorphous, cubic and hexagonal ices were observed. The thermodynamic studies of the irreversible phase transformations indicated varying transformation temperature ranges and degrees of crystallinity. The confusion with respect to vitreous, cubic and hexagonal sample formation is reflected in the variations among the ir spectra of various authors (95, 97, 98, 105). Bertie and Whalley (88,95) obtained spectra of mulled, crystalline samples (checked by x-ray diffraction) and they criticized the use of a "recipe" such as that of Beaumont et al. (65).

With ir observations Zimmerman and Pimentel (97) pointed out the need to devitrify solids condensed from the vapour. While they were the first to detect the irreversible shift in the ir spectra between vitreous and cubic ice, they did not study the transformation in detail.
The transformation process was observed in this work in every H$_2$O ir absorption except $\nu_{T}(H_2O)$, but the results of the transformation for all H$_2$O, HDO and D$_2$O bands were recorded. The spectra gave four concurrent measures of the transformations: 1) the degree of increased hydrogen bonding, 2) the transformation temperature range, 3) the change in vibrational energy, and 4) the phase transformation rate. The studies showed that cubic samples formed by transformation of the vitreous phase gave as good spectra as mulled, crystalline samples (95).

A. General Discussion

Some general comments apply to all the H$_2$O band maxima in their behaviour before, during and after the vitreous-cubic phase transformation. Between $83 \pm 3^\circ$K and $120 \pm 10^\circ$K all H$_2$O band maxima had constant frequencies (Fig. 3.2). The absence of frequency shifts is indicative of no changes in the degree of hydrogen bonding. Below $120 \pm 10^\circ$K the thermal kinetic energy was insufficient to allow molecular reorientation, softening of the glass, and hydrogen bond formation.

The H$_2$O band maxima all shifted irreversibly during the vitreous-cubic transformation. However, the data (page 62) indicated different transformation temperature ranges for different bands: Ranges from $115 \pm 5^\circ$K to $130 \pm 5^\circ$K and $130 \pm 5^\circ$K to $145 \pm 5^\circ$K were found for $\nu_{R}$ and $\nu_{1} + \nu_{T}$. The differences appear to be caused by the increasing period the sample was held at one temperature while the spectra were recorded.

For example, frequencies plotted in Fig. 3.2 show that $\nu_{R}$ was constant up to $100^\circ$K and was completely shifted to the cubic $\nu_{R}$ frequency at $125^\circ$K.
That indicates, on first inspection, that the transformation for $v_R(H_2O)$ started at $115 \pm 5^\circ K$, about $10^\circ K$ lower than for other bands. Such a conclusion is incorrect.

Specifically consider the positions of the data indicated by solid triangles ($\blacktriangle$) at $125^\circ K$ in Fig. 3.2 for all six bands. The data were obtained from one sample during one run at constant temperature. At $125^\circ K$ the $v_1 + v_T$ band was unshifted from the vitreous frequency, the $v_3$ and $v_1$ bands were only slightly shifted, the $3v_R$ band was shifted approximately one-half the total shift towards $3v_R$ cubic, the $v_2$ band was shifted three-quarters the total shift and $v_R$ was completely shifted. The amount of shift is proportional to the time the sample was held at $125^\circ K$. In this work, spectra were scanned from 4000 to 530 cm$^{-1}$ in 20 minutes. Thus for $v_1 + v_T$, $v_3$, $v_1$, $3v_R$, $v_2$ and $v_R$ the vitreous sample had been progressively annealed at $125^\circ K$ for 3.7, 4.4, 4.7, 10.2, 13.4 and 18.3 minutes respectively. By the time $v_R$ was recorded the sample had completely transformed. If the transformation rate is assumed to be linear, then a plot of $(v_y - v_c)_t/(v_y - v_c)_t = \infty$ (where $t$ is the time at $125^\circ K$ and $t = \infty$ is maximum annealing shift) against time in minutes gives the transformation rate at $125^\circ K$ as $5.5 \times 10^{-2}$ min$^{-1}$.

One concludes that the transformation temperature ranges listed in Table III.I for $v_1 + v_T$, $v_3$, $v_1$, $3v_R$ and $v_2$ were artificially elevated by the recording technique. The transformation temperature range for all bands must be consistent, $120 - 135 \pm 5^\circ K$ (corrected for sample window heating).

During the transformation the lattice modes $v_R$ and $3v_R$ shifted irreversibly to higher frequency while the molecular modes shifted irreversibly to lower frequency due to large alterations to the intramolecular and intermolecular potentials which occurred. The shifts of molecular modes are
consistent with the formation of more and/or stronger hydrogen bonds. During the transformation the molecules attained sufficient thermal kinetic energy to permit molecular reorientation, the low polymers were then free to form long chains with complete hydrogen bonding, four per molecule. The complete sets of strong hydrogen bonds hindered libration and translation and increased the frequencies of those bands.

After the irreversible shift had occurred, i.e. above 150°C, and during all subsequent warming-cooling cycles the spectra had a reversible temperature dependence: the lattice modes decreased in frequency and the molecular modes increased in frequency as temperature increased. The sample devitrification was completed by warming to 185 ± 5°C for 2 - 5 minutes, followed by recooling to 83°C.

At 83°C the effects of reorientation and hydrogen bond formation (lengthening r(O-H) and orbital rehybridization) were measured for H_2O, D_2O and HDO. If the frequency shifts between cubic and vitreous ice did rise from hydrogen bond formation, then the relative effects on H_2O, D_2O and HDO frequencies should have been the same provided all the vitreous samples had comparable degrees of microcrystallinity. The frequency shifts would ideally be in the ratio Δν_1(H_2O) / Δν_1(D_2O) near 1.4, where Δν_1 = ν_i(cubic) - ν_i(vitreous) for the i-th vibrational mode. Only the peaks ν_3 and ν_R give reasonable agreement with the ideal ratio, i.e. 1.6 ± 0.3 and 1.1 ± 0.30 respectively. All the other bands were poorly defined and the ratios range from 0.79 ± 0.5 to 3.1 ± 0.5 for ν_1 + ν_T and ν_2 respectively. A modified product rule Δν_1Δν_2(H_2O) / Δν_1Δν_2(D_2O) does not improve the ratio.

For 4.00 % HDO in D_2O Δν_R(HDO) = Δν_R(D_2O) = +27 cm⁻¹, Δν_3(H_2O) / Δν_3(D_2O) = 0.94 and Δν_3(D_2O) / Δν_OH(HDO) = 1.1: None of these are in agreement with the ideal ratio. The ratio for Δν_OH(HDO) / Δν_OD(HDO) = 1.8 is much
higher than 1.4. The observed ratios of the cubic ice I fundamental frequencies are near 1.35 and one deduces that $\Delta \nu_{\text{OH}}(\text{HDO})$ is too large, $\Delta \nu_{\text{OD}}(\text{HDO})$ is too small (compared to pure $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$) or both. However, since samples were not identically deposited, they would have had different degrees of self-annealing, and different frequency displacements from the cubic ice values.

Each band will now be considered in turn.

B. Fundamental Lattice Mode Transformations

(i) The $\nu_T(\text{H}_2\text{O})$ Transformation

The $\nu_T$ band had remarkable differences between the vitreous and cubic samples at 83$^\circ$K: The vitreous band was broad and featureless while the cubic band was narrow and had nine features. That is understandable from the very different nature of the two solids. For example, since the positions of the atoms in a vitreous solid are ideally completely irregular, then forces acting on the atoms are irregular and the normal vibrations of the solid are also irregular (87). The resulting range of translational energy levels, and range of transitions among the levels, is very broad. Combined with the collapse of normal phonon selection rules (87), a very broad ir $\nu_T$ (vitreous) band is expected and observed. In contrast, cubic ice I has regular, long range ordering of oxygen atoms, but irregular, short range ordering of the protons (orientational disorder). Whalley (87) has shown that the orientational disorder does not have a significant irregular effect on the mechanical vibrations of cubic ice, but that it does affect the local electric oscillations. Consequently, one obtains a structured $\nu_T$ (cubic) band whose features are indicative of the crystalline state. It is suf-
icient here to compare our vitreous and cubic $v_T$ data (83°K) to those of Whalley (88) and Giguere (89).

Consider the $v_T$ data given on pages 89, 90, and 91 of Chapter 3. That $v_T$ (cubic), 227.8 cm$^{-1}$, was 7% higher than $v_T$ (vitreous) is understandable simply on the basis of the increased number of hydrogen bonds, the deepened hydrogen bond potential and increased force constants, and the increased hinderance to translation. These effects resulted from extension of hydrogen bonding closer to the limit (4 bonds/molecule), reduction of the mean O--O distance, and a change in the density in cubic crystals. However, in reality the explanation for the frequency shift may not be so simple. Formation of a well defined Brillouin zone in cubic samples may entail complex changes in the densities of states and selection rules from those of the vitreous sample.

The half-height width of $v_T$ (vitreous) was 62.8 cm$^{-1}$, in sharp contrast to that of $v_T$ (cubic) which was very nearly one-third of that value, 23.2 cm$^{-1}$. Increases in the densities of states at the Brillouin zone boundaries probably accounts for this dramatic change.

That the peak height of $v_T$ (cubic), 1.285 absorbance, was almost exactly double that of $v_T$ (vitreous) is probably due to two effects. The first effect is again the increased density of states in cubic ice I for $k \neq 0$ transitions. The second effect arises from the increase in oscillating dipole moments in completely hydrogen bonded lattices as compared to weaker dipoles in partially hydrogen bonded glasses.

The $v_T$ (vit.) band of this work compares very well with Whalley's (88) $v_T$ (vit.) but not with Giguere's (89) $v_T$ (vit.). The $v_T$ (vit.) band had no 162 cm$^{-1}$ peak or 173 cm$^{-1}$ minimum, as Whalley (88) also reported.
However, Whalley's \( \nu_T \) (vitreous) peak was 9 cm\(^{-1} \) higher than observed here, 212.8 cm\(^{-1} \). He did not list the positions of other vitreous band features and it is hard to determine if the difference is only due to calibration errors. [On the basis of the two sets of \( \nu_T \) (cubic) features, the latter seems unlikely.] In contrast Giguere's (89) \( \nu_T \) (vit.) band showed too much structure and suggested a largely crystalline sample. The present work supports Whalley's observations of \( \nu_T \) (vit.).

For \( \nu_T \) (cubic) the results of this work agree in general features with both Whalley (88) and Giguere (89). However the two peaks in the present work are nearly 2 cm\(^{-1} \) lower than Whalley reported, probably due to a calibration error. Whalley found that all cubic samples, either condensed from the vapour or formed under pressure and mulled, gave the same \( \nu_T \) absorptions. Since \( \nu_T \) observed in this work agrees with his results, one can conclude that the sample deposition and devitrification techniques used here gave legitimate cubic ice I samples with respect to \( \nu_T \).

(ii) The \( \nu_R \) Transformation

At 83\(^{\circ}\)K vitreous ice \( \nu_R(H_2O) \) had two distinct and two faint features: a distinct peak (802 cm\(^{-1} \)) and a distinct shoulder (535 cm\(^{-1} \)), and two faint shoulders (846 cm\(^{-1} \) and 675 cm\(^{-1} \)). However, vitreous ice \( \nu_R(HDO) \) and \( \nu_R(D_2O) \) each had only a single feature. In contrast, cubic ice \( \nu_R(H_2O) \) had five features (one peak and four shoulders) while \( \nu_R(HDO) \) and \( \nu_R(D_2O) \) had two features each (a peak and a high frequency shoulder). The HDO high frequency shoulder, \( \nu_R(HDO) + \nu_T(D_2O) \), has not been previously reported. Changes in frequency and half-height width between the \( \nu_R \) bands of vitreous and cubic \( H_2O \) ice samples were shown in Figs. 3.2 and 3.4 (pages 61 and 66) and the results of devitrification for \( \nu_R(H_2O, D_2O, HDO) \) were given in
Table III.I (page 62).

After the vitreous sample was annealed at 185 ± 5°C for 2 - 3 minutes and recooled to 83°C, one found all the νR features had shifted to higher frequency and that three new features appeared. Precisely, νR(H2O) shifted by +31 cm⁻¹, νR(HDO) by +27 cm⁻¹ and νR(D2O) by +27 cm⁻¹. As for ν̃T, the νR shift to higher frequency may be simply understood on the basis of hydrogen bonding. Cubic ice has more and stronger hydrogen bonds than vitreous ice. The results are a deeper hydrogen bond potential, larger hydrogen bond force constants, increased hinderance to libration and increased absorption frequency. However, as for ν̃T, complex changes in the crystal entail complex changes in the solid librations, densities of states and selection rules. The final explanation of νR behaviour must combine the changes in hydrogen bond potential with the lattice vibration theory.

The plot of half-height widths (ΔνR) of the composite band (νR, νR + ν̃T) was shown in Fig. 3.4 (page 66). It also indicated a "depressed" νR transformation temperature range (115 - 130 ± 5°C). However, the low range may be explained as in section 4.1A (page 105) for ν̃T(freq.). One also sees that the behaviour of ΔνR above 130°C did not conform to the reversible behaviour of fully annealed cubic samples, i.e. the half-height width continued to decrease. Finally, on completing the annealing and recooling of the sample to 83°C, one found that the disorder broadening due to irregular O positions was removed but that there remained the orientational disorder broadening. The half-height widths at 83°C decreased in the following way:
The differences may be due simply to errors in determining baselines, intensities and widths, or may arise from differences in microcrystallinity among the three vitreous samples formed.

C. Fundamental Molecular Mode Transformations

(i) The $v_2/2v_R$ Transformation

Absorptions between 1000 and 1800 cm$^{-1}$ in H$_2$O ice have been variously assigned to $2v_R$ or $v_2$. All previous workers (95, 97, 105, 106, 108) reported only a single feature in this range for both H$_2$O and D$_2$O ices (vitreous or cubic). However, Zimmermann and Pimentel's (97) Fig. 1 for cubic ice has shoulders at 1100 and 1530 cm$^{-1}$ and a peak at 1615 cm$^{-1}$: They treated the 1615 cm$^{-1}$ peak and 1530 cm$^{-1}$ shoulder as one band centered at 1580 cm$^{-1}$ (83$^\circ$K) in cubic H$_2$O ice.

Most thick vitreous H$_2$O ice spectra recorded in this work had two features, a peak at 1660 ± 10 cm$^{-1}$ and a shoulder at 1570 ± 20 cm$^{-1}$. In contrast, cubic samples annealed below 190$^\circ$K only had a peak at 1570 ± 10 cm$^{-1}$. Cubic samples annealed to 205$^\circ$K had a peak at 1570 ± 10 cm$^{-1}$ a shoulder at 1130 cm$^{-1}$, and a deep minimum at 1050 cm$^{-1}$, much like Zimmermann and Pimentel's (97) spectra. While the final assignments of the bands are left
until section 4.3 (page 175), it seems logical to consider the vitreous
1570 cm\(^{-1}\) shoulder and the 1660 cm\(^{-1}\) peak as being either \(v_2\) or \(2v_R\). Corresponding features were not observed in vitreous \(D_2O\) ice I.

The reasons for shifts to lower frequencies, \(\Delta v_2(H_2O) = -56\) cm\(^{-1}\) and \(\Delta v_2(D_2O) = -18\) cm\(^{-1}\), have been explained by Zimmermann and Pimentel (97) on the basis of a weakened molecular potential and decreased force constants. However, the large differences between \(v_2\) shifts for \(H_2O\) and \(D_2O\), observed here, is not understood. In Fig. 3.5 (page 67) one saw that the vitreous \(\Delta v_2\) was constant at 350 cm\(^{-1}\) up to 115 ± 5\(^\circ\)K and broadened to 390 cm\(^{-1}\) at 125 ± 5\(^\circ\)K. Above 125\(^\circ\)K \(\Delta v_2\) had a negative, reversible temperature dependence, -1.64 cm\(^{-1}\)/\(^\circ\)K. All other vitreous \(H_2O\), HDO and \(D_2O\) bands were narrower after the transformation and subsequently broadened with increasing temperature in the cubic phase.

The anomalous behaviour of \(\Delta v_2(H_2O)\) may be explained if the vitreous ice band is composed of a medium \(v_2\) absorption slightly below 1570 cm\(^{-1}\) and a \(2v_R\) absorption slightly above 1660 cm\(^{-1}\). Although \(v_2\) and \(2v_R\) both must narrow upon devitrification, their frequencies both shift away from 1570 cm\(^{-1}\) yielding a net broader \(v_2/2v_R\) band. For this explanation it is also necessary that the peak absorbance of \(2v_R\) decrease in the cubic phase. The negative temperature dependence of the \(v_2\) band results from the shift of a weak underlying \(2v_R\) to lower frequency (towards 1600 cm\(^{-1}\)) and the shift of \(v_2\) to higher frequency (towards 1600 cm\(^{-1}\)) with increasing temperature. As the two absorptions further coalesce, the composite band becomes narrower. However, the frequency dependence of the cubic band is determined by the more intense \(v_2\) absorption.

The \(v_2\) frequencies obtained for crystalline ice formed from the vapour
(this work, 97, 105, 106) do not agree with Whalley's (95) work. For all phases of ice Whalley found ν₂ to be higher than 1650 cm⁻¹. The ν₂ results of this work support Ockman's (108) observations for samples formed from the liquid. Ockman's (108) reflection spectra indicated a weak maximum at 1600 cm⁻¹. It is possible that Whalley's (95) mulling technique gave a different reflection spectrum than occurs for thin films and enhanced the high frequency portion of his ν₂. His results showed the mulling agent decreased reflection and scattering compared to powder spectra. On the other hand, reflection and scattering may be severe for thin films.

Finally, the weak shoulder and deep minimum (1130 cm⁻¹ and 1050 cm⁻¹) may have arisen from a strong Christiansen filter effect on the high frequency side of νᵣ.

(ii) The νSTR Transformations

In the region from 3000 to 4000 cm⁻¹ one observes the symmetric and asymmetric O-H stretching frequencies from H₂O molecules in various degrees of polymerization and the combinational absorption of ν₁ with the lattice modes. The corresponding O-D stretches are found between 2000-2800 cm⁻¹. Data for ν₁ and ν₃ of H₂O, HDO and D₂O in the vitreous and cubic phases were shown in Figs. 3.2 and 3.4 (pages 61 and 66) and were compiled in Table III.I (page 62).

(a) The ν₁ shoulder. The low frequency shoulder (ν₁) was very poorly defined (at 83°K) in vitreous ice (3191 ± 15 cm⁻¹) but was better defined in cubic ice (3149 ± 10 cm⁻¹). In contrast, for D₂O ice the ν₁ shoulder was well defined for both vitreous and cubic ice I (2372 ± 10 cm⁻¹ and 2321 cm⁻¹).
Like other molecular modes, $v_3$ shifted to lower energy because of weaker molecular bonds, a shallower potential well and weaker force constants.

(b) The $v_3$ peak. The vitreous ice stretching band frequency at 83°C was 3253 cm$^{-1}$ while for cubic ice $v_3$ was 3217 cm$^{-1}$, a shift of -36 cm$^{-1}$ ($\Delta v_3(D_2O) = -23$ cm$^{-1}$). The explanation for a negative shift follows from $v_1$ above.

(c) The HDO modes. The vitreous ice HDO absorptions were listed in Table III.I, $v_{OD} = 2437$ cm$^{-1}$ and $v_{OH} = 3304$ cm$^{-1}$. The cubic ice HDO frequencies were shifted -21 and -38 cm$^{-1}$ respectively from their vitreous values. Reference to Table III.I shows that these shifts correspond very well to the $v_3$ shifts of D$_2$O and H$_2$O respectively. The vitreous-cubic transformation had the same effect on $v_{OD}$ (asymm.) or $v_{OH}$ (asymm.) of H$_2$O, HDO and D$_2$O molecules whether they were in an H$_2$O or D$_2$O lattice. There appear to be no differences among the couplings of HDO, H$_2$O and D$_2$O molecules for either vitreous or cubic ice I. Finally, the explanation for the direction of shift follows from previous discussion.

The HDO stretch half-height widths sharpened from 77 to 23.5 cm$^{-1}$ and 115 to 35.5 cm$^{-1}$ between the vitreous and cubic phases (at 83°C). In vitreous ice both the O positional disorder and proton orientational disorder contributed to the widths. In cubic ice the O positions were ordered, but the proton disorder broadening remained. Even in the cubic phase the uncoupled HDO molecules had $\Delta v^I$ values about twice as large as expected for ordered solids. For example, Whalley (96) found $\Delta v^I$(HDO) data of 8 - 13 cm$^{-1}$ for an ordered high pressure ice.

The HDO peaks were uninhibited by band overlap and provided an excellent probe for making accurate transformation rate studies of vitreous
ice. The dilute H / D isotopic substitution should be employable in rate studies of other disordered systems.

(d) The oligomeric modes. All vitreous H$_2$O and D$_2$O ice samples observed in this work had very weak absorptions between 3600 and 3700 cm$^{-1}$ in H$_2$O (near 2620 cm$^{-1}$ in D$_2$O). Typical H$_2$O peaks were shown in Fig. 3.3 (page 64) and the frequencies were listed in Table III.II (page 65). These absorptions occurred quite close to the vapour phase monomeric frequencies. Shurvell (115) and Van Thiel et al. (117) studied the absorptions from dilute concentrations of H$_2$O and D$_2$O in various matrices. Van Thiel et al. assigned the (v$_3$, v$_1$) monomeric, dimeric and trimeric H$_2$O (in an N$_2$ matrix at 20°K) absorptions to (3725 and 3625 cm$^{-1}$), (3691 and 3546 cm$^{-1}$), and (3510 and 3355 cm$^{-1}$) respectively. For D$_2$O Shurvell reported (v$_3$, v$_1$) monomer and dimer absorptions for an N$_2$ matrix at (2765 and 2655 cm$^{-1}$) and (2725 and 2650 cm$^{-1}$) respectively. Our frequencies appear to rise from dimeric systems. We observed half-height widths of 15 - 20 cm$^{-1}$ which were slightly smaller than in matrix isolation, 20 - 30 cm$^{-1}$. Their oligomeric peaks were stable up to the softening temperatures of the matrix used, generally less than 30°K. Oligomeric absorptions observed in this work were stable up to the softening temperature of the H$_2$O glassy matrix, 125°K. That corresponds to the temperature of onset of peak shift in other bands, i.e. the temperature of molecular reorientation. The high softening temperature is consistent with the increased van der Waals forces in molecular solids compared to rare gas solids. For example, Shurvell (115) observed that H$_2$O oligomers were stable up to 80°K in a CCl$_4$ matrix.
For this work, one understands that the softening permits short-range molecular diffusion and reorientation resulting in progressively higher polymerization. The monomeric, oligomeric and medium polymers disappear as well as their absorptives. The high frequency side of the $v_{\text{STR}}$ band was greatly sharpened.

One can estimate the fraction of the sample which was in the form of dimers. In this work the ratio of $v_3$ absorbances for dimeric and fully polymerized H$_2$O is 1 to 70. Work by Ikawa and Maeda (118) on the crystalline solid (complete polymer) and by Ferriso and Ludwig (119) on the vapour phase (monomeric H$_2$O) showed that the extinction coefficients of monomeric and fully polymeric H$_2$O are in the ratio 1 to 30. Thus one finds 1 part of monomeric-dimeric H$_2$O to 2.3 parts of completely polymerized H$_2$O. There remains an unknown portion of the sample in intermediate stages of polymerization. However, while this estimate seems to be very high, the point is that a considerable amount of oligomeric H$_2$O and D$_2$O sample was formed by our condensation technique.

(e) The $\Delta v^3$ of the band ($v_1, v_3, v_1 + v_T$). The half-height width ($\Delta v^3$) of the composite band ($v_1, v_3, (v_1 + v_T)$) sharpened from $325 \pm 10$ cm$^{-1}$ to $285 \pm 10$ cm$^{-1}$ (83$^\circ$K) between vitreous and cubic ice. The band sharpened irreversibly between 115 $\pm$ 5$^\circ$K and 125 $\pm$ 5$^\circ$K by the specific loss of approximately 20% of the high frequency absorption. Such absorption arises from medium length H$_2$O and D$_2$O polymers with incomplete hydrogen bonding. In addition, the band sharpened by the increase of 0 positional ordering and the smaller range of molecular potential energies.
D. Combination and Overtone Mode Transformations

(i) The $3\nu_R$ Transformation

Absorption near 2200 cm$^{-1}$ in H$_2$O ice and near 1600 cm$^{-1}$ in D$_2$O ice has been variously assigned to $3\nu_R$ and $\nu_2 + \nu_R$. Specifically, the H$_2$O absorption had a single feature, a peak at 2220 or 2235 cm$^{-1}$ in vitreous or cubic ice. The shift upon annealing was to higher frequency, and was also found for $\nu_R$ and $\nu_T$. The nature of the shift was given in Fig. 3.2 (page 61) while data was given in Table III.I (page 62).

Cubic ice absorptions, 2235 and 1635 cm$^{-1}$ for H$_2$O and D$_2$O (at 83°K), agreed very well with the single crystal observations of Ockman (108), Table III.XI. As well, Haas and Hornig's (106) and Giguere and Harvey's (98) results were comparable. However, Whalley's (95,96) results were consistently higher. As for $\nu_2$, the differences in Whalley's results may have arisen from changes in the reflection spectrum caused by the mulling agents.

The shift by +15 cm$^{-1}$ (for H$_2$O) to higher frequency upon devitrification may provide a clue to the origin of this band. If the band is $\nu_2 + \nu_R$ then one would expect the shift $\Delta(\nu_2 + \nu_R)$ to be proportional to $\Delta\nu_2 + \Delta\nu_R = (-56 + 31) = -25$ cm$^{-1}$ for H$_2$O. If the band is $3\nu_R$ then one would expect $\Delta(3\nu_R)$ to be proportional to $3(\Delta\nu_R) = +93$ cm$^{-1}$. The observed shift to higher frequency by +15 cm$^{-1}$ in H$_2$O and +18 cm$^{-1}$ in D$_2$O supports the $3\nu_R$ assignment.

Finally, the $3\nu_R$ results suggest that our cubic sample formation technique is adequate since the results are consistent with results from crystalline samples prepared from the liquid, i.e. the results of Ockman (108) and Giguere (98).
(ii) The \((v_1 + v_T)\) Transformation

The high frequency shoulder \((v_1 + v_T)\) was very poorly defined in vitreous ice, but was well defined in cubic ice. As for other molecular modes, \((v_1 + v_T)\) shifted irreversibly towards lower frequency (-27 cm\(^{-1}\) for H\(_2\)O and -34 cm\(^{-1}\) for D\(_2\)O) between 130 and 145 K. Comments made above with respect to the origin of the molecular mode shifts and the temperatures of transformation also apply to \((v_1 + v_T)\).

E. Confidence in the Cubic Ice I Samples

Does devitrification provide a good cubic sample of iceI? Beaumont et al. (65) found that the vitreous-cubic transformation took only a few minutes to finish even at 150°K. As well they found that vitreous ice transformed cleanly to cubic ice. On the other hand, Dowell and Rinfret (74) estimated only a 30 per cent conversion to cubic ice and an average cubic crystallite size (embedded in the remaining 60% vitreous ice) of 400 Å. The results of Dowell and Rinfret (74) necessitate a heat of cubic-hexagonal phase transformation of 24 cal/gm. Such an evolution of heat was unobserved at higher temperatures by Beaumont et al. In fact they estimated the heat of cubic-hexagonal transformation to be less than 1.5 cal/gm.

If the samples in the present work were only 30% cubic ice with 60% vitreous ice remaining, then the spectra of annealed samples should have been characteristic of vitreous ice and might have exhibited separate maxima from cubic and vitreous ice. Only one stretching peak was observed and the bands matched very closely the spectra of hexagonal ice I (95). These facts support Beaumont's interpretation of the vitreous-cubic transformation.
The evidence suggests samples prepared in this work were transformed fully to cubic ice I. The presence of significant amounts of residual vitreous ice would have broadened the stretching bands asymmetrically, giving a tail on the high frequency side. The half-height widths and band shapes of spectra in Fig. 3.1 compared very favourably with spectra of hexagonal ice I formed from the liquid.

Deposition rates in these experiments lie near the maximum set by Beaumont et al. (65) — 0.04 gm/cm²/hour. Assuming a $\nu_3(H_2O)$ extinction coefficient of 140 for hexagonal ice I (119) the sample thickness was 0.5 - 1.0 microns. The volume of ice I sample was at least $1.4 \times 10^{-4}$ cm³. At a density of 0.924 gm/cm³ one had a minimum sample of $1.3 \times 10^{-4}$ gms. Such samples were applied in two bursts, of two seconds duration each, onto a window initially at 83°C. By assuming a 1.0 cm² image, the rate of deposition was at least 0.04 gm/cm²/hour.

During the deposition, $1.3 \times 10^{-4}$ gms of H₂O vapour release 0.09 cal (assuming the heats of sublimation of amorphous and hexagonal ice I are the same). There was sufficient heat of condensation to induce localized heating and to permit diffusion of individual molecules. The extent of heating and diffusion, or the amount of self-annealing, depended on the rate of dissipation of heat at the window-sample surface.

Several attempts, under various conditions, were made to form hexagonal ice. However, all attempts to anneal samples above 210°C led to almost instantaneous sublimation since the samples were uncovered. Such sublimation has also been the experience of other workers (120).

The extensive sharpening and alteration of the bands between vitreous and cubic ice I was due to two effects. The first was the diffusion and
reorientation of individual molecules into lattice sites in the cubic unit cell. The cubic unit cells put all molecules in the same electrical environment, but where the mechanical vibrations were broadened by asymmetries in proton orientation at equivalent unit cell sites.

The second effect was the extension of low, medium, and high polymer H$_2$O clusters of the vitreous phase into fully hydrogen bonded networks of the cubic phase. During the process of crystallization the clusters amalgamated into larger units where the deformed or absent hydrogen bonds at the contact surfaces between clusters (or crystallites) represented only a small fraction of the total number of hydrogen bonds.

4.2 Temperature Dependence of Cubic Ice I Absorptions

Accurate measurements of shifts in frequencies and half-height widths in H$_2$O, D$_2$O and HDO spectra between 4°K and 200°K permit accurate correlations of the shifts to changes in $R(0\cdots0)$ and changes in hydrogen bond strength. In this section values of $R(0\cdots0)$ for cubic ice I are calculated over the range 10° - 200°K and plotted against $v_{OH}(HDO)$ and $v_{OD}(HDO)$. That plot is compared to the predictions of an empirical equation which relates $v_{OH}(HDO)$ to $R(0\cdots0)$. In addition, values of $\omega_{OH}(HDO)$ and $X_{OH}(HDO)$ are calculated from $v_{OD}(HDO)$ and $v_{OH}(HDO)$ as a function of temperature.
A. Dependence of HDO Bands on Temperature

A few general remarks can be made concerning the low temperature limits and temperature dependences of all the absorption bands. The low temperature limiting frequencies were obtained by extrapolation to 0°K simply as a matter of convenience. The individual frequencies had virtually the same values when extrapolated to 5° or 0°K. There is the danger that the properties of ice are irregular below 5°K. However, Flubacher et al. (83) proved that the thermodynamics of ice I are well behaved down to 2°K.

The low temperature limiting frequencies, half-height widths and peak heights are for H₂O molecules at the distance of minimum approach. The O···H potential is deepest and the O-H potential is shallowest. The conditions at minimum approach permit the largest orbital overlap and degree of hydrogen bond covalency, the largest electrostatic effects, and the largest contribution of CT. As well, the low temperature limiting frequency gives the 0 → 1 energy level spacing for minimum root-mean-squared (RMS) amplitudes of H₂O translation and O-H vibration. Finally, the contours of the bands are least distorted by hot bands and vibrational perturbations of the potential.

As the temperature was raised the ice I sample expanded, giving increasing R(O···O) and resulted in the weakening of the O···H bonds and a strengthening of the O-H bonds. Hence the lattice mode and molecular mode force constants could be understood to decrease and increase respectively, i.e. the frequencies respectively decreased and increased. While the crystals expanded continuously and non-linearly during warm-up, the frequency-temperature dependence was approximated by two straight lines. The lines
corresponded to regions of slow and fast crystal expansions. Below 50°K the
effects of $\Delta R(0\cdots 0)$, changes in RMS amplitude of translation and hot bands
($v = 1 + 2$) were small.

Finally, some irregularities or discontinuities in the temperature
dependences indicate possible changes in the solid phase or changes in
energy level populations.

(ii) Dependence of HDO Frequencies on Temperature

(a) $v_R$(HDO) and $v'_R$(HDO). A full discussion of the origin and nature
of the librational modes is given in section 4.4. As expected, the tempera­
ture dependences were negative for both bands, $-0.02 \text{ cm}^{-1}/\text{K}$ below 55°K and
$-0.147 \text{ cm}^{-1}/\text{K}$ above 55°K. Below 55°K the effects of $v_R$ and $v_T$ hot bands
should have been negligible. Above 55°K, however, $v_R$ and $v_T$ hot bands may
have contributed significantly to the changes in band frequency, width and
height.

For $v_R$(HDO) (Fig. 3.7) one saw an apparent discontinuity between 105°
and 120°K. The change in slope may have arisen from significant population
of molecular mode hot bands. The "hot" molecules would be decoupled from
the remaining lattice molecules, and would have weaker hydrogen bonds.
Consequently, smaller librational frequencies would be seen.

(b) $v_{OH}$(HDO) from 4.00% HDO in $D_2O$. The shallow molecular potential
is demonstrated by the low temperature limiting $v_{OH}$(HDO) frequency, i.e.
3263.5 cm$^{-1}$ at 0°K compared to 3268 cm$^{-1}$ and 3288 cm$^{-1}$ at 80° and 180°K
respectively.

The HDO frequency-temperature plot (Fig. 3.6) showed unambiguously
that the frequency shift was continuous and non-linear in the high and
low temperature approximations. Since there is little point in doing a least-mean-squares fit to some arbitrary function, the data were approximated on a bilinear basis. Up to $45 \pm 5^\circ K$ $v_{OH}(\text{HDO})$ was constant within the random point scatter, $\pm 0.75 \text{ cm}^{-1}$. Within the sensitivity of the experimental technique and the spectrophotometer, changes in $v_{OH}(\text{HDO})$ due to changes in $R(0\cdots0)$ and the effects of $v_{OH}$ combination bands with translational hot bands are insignificant below $45^\circ K$.

Linear low temperature dependence was assumed for $v_{OH}(\text{HDO})$ below $80^\circ K$ $(+0.047 \pm 0.005) \text{ cm}^{-1}/^\circ K$. Above $45^\circ K$ one saw a definite effect due to increasing $R(0\cdots0)$, the shift of frequency exceeds the point scatter. Thus the thermal expansion data of Brille and Tippe (60) suggest that when $\Delta R(0\cdots0) > \pm 0.0001 \AA/^\circ K$ significant changes in $v_{OH}(\text{HDO})$ occur.

Linear high temperature dependence was assumed for $v_{OH}(\text{HDO})$ between $80^\circ$ and $190^\circ K$, i.e. $+0.200 \pm 0.005 \text{ cm}^{-1}/^\circ K$. Data of this work are in good agreement with the data of Ford and Falk (100). Their data were shown in Fig. 3.6 and were obtained from the best straight line through their Fig. 2. One sees that the steadily increasing $R(0\cdots0)$ in a cubic ice lattice yields a steadily increasing $v_{OH}(\text{HDO})$ frequency. The specific dependence of $v_{OH}$ on $R(0\cdots0)$ is given in the following section (page 137).

There was a slightly irregular shift of $v_{OH}(\text{HDO})$ between $45^\circ K$ and $70^\circ K$ in Fig. 3.6. The irregularity may have been due to a partial order-disorder phase transformation predicted to be near $60^\circ K$ by Pitzer and Polissar (70). However, they pointed out that the period of transition was probably greater than 24 hours. That period is far in excess of our very rapid cooling time of 15 - 20 minutes. An order-disorder phase transformation is also unsupported by any comparable shift in half-height width.
Alternately, the irregularity may have arisen from a transformation from an
as yet uncharacterized low temperature ice phase, or from one of the disordered
high pressure ices. A low temperature phase transformation in ice Ih was not
indicated by heat capacity experiments (82), although $C_p$ had a slight irre-
gularity near 80°C. The IR irregularity represents only 1 - 2% of the
total frequency and is probably undetectable in $C_p$ experiments since molecular
modes contribute little to $C_p$.

(c) $v_{OD}$(HDO) from 5.94% HDO in H₂O. The general comments made above
with respect to $v_{OH}$(HDO) apply as well to $v_{OD}$(HDO): However, there are
differences in details. Specific differences can be seen in Fig. 3.6 and
Table III.IV (pages 71 and 72). The low temperature limiting $v_{OD}$(HDO) fre-
quency was 2412.0 ± 1 cm⁻¹. The ratio of HDO frequencies, $v_{OH}/v_{OD}$, is
1.354 ± 0.001. That ratio is the same as reported by Whalley (96) for
ices I, II and III and is very close to the vapour phase ratio of 1.360.
From the ratios one can show that the HDO anharmonicity, as discussed by
Whalley (96), was the same at 0°C as he found at 100°C, i.e. about 100 cm⁻¹.
At both temperatures it is 25% larger than in the vapour phase. This does
not mean the anharmonicity is independent of temperature as is shown in the
next section.

The temperature dependence of $v_{OD}$(HDO) was different from that of
$v_{OH}$(HDO) in several ways. The $v_{OD}$(HDO) data were constant within the point
scatter up to 30 ± 5°C in contrast to 45 ± 5°C for $v_{OH}$(HDO). The low
temperature dependences of $v_{OH}$ and $v_{OD}$ were the same. However, the high
temperature dependence of $v_{OD}$ was (+0.123 ± 0.005) cm⁻¹/°C ($\Delta v_{OH}/\Delta T$ was
1.626 times higher), 0.200 cm⁻¹/°C). The differences in the high temperature
dependences probably arose from differences in the physical properties of
the two mediums. The $v_{OH}$ data are from HDO in D$_2$O while the $v_{OD}$ data are from HDO in H$_2$O.

Consider the percentage shift from the low temperature limiting frequencies for the asymmetric stretches in HDO, D$_2$O and H$_2$O,

$$\text{percentage shift} = \frac{v_{STR}^T - v_{STR}^O}{v_{STR}^O} \times 100$$

where $v_{STR}^T$ is the stretching frequency at temperature $T$, and $v_{STR}^O$ is the low temperature limiting frequency. One might have expected $v_3$ in H$_2$O and D$_2$O to shift by the same percentage of the low temperature frequencies. However, between 10° and 160°K the $v_3$ shifts of H$_2$O and D$_2$O increased from 0.6 x $10^{-2}$% to 82 x $10^{-2}$% and 0.0% to 36 x $10^{-2}$% respectively. The $v_3$ stretching frequencies do not shift proportionally. The shifts of $v_{OH}$(HDO) and $v_{OD}$(HDO) are not proportionally the same, nor do they compare to the percentage shifts of $v_3$ in H$_2$O and D$_2$O.

The $v_{OD}$(HDO) shift was faster than for $v_3$(D$_2$O) at all temperatures, while the $v_{OH}$(HDO) shifted proportionally faster than $v_3$(H$_2$O) only below 100°K.

The percentage shift from the low temperature limiting frequencies were:

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>$v_{OH}$(HDO)</th>
<th>Percentage Shift x $10^2$</th>
<th>$v_{OD}$(HDO)</th>
<th>$v_3$(H$_2$O)</th>
<th>$v_3$(D$_2$O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.9</td>
<td>0.4</td>
<td>0.6</td>
<td>0</td>
<td>--</td>
</tr>
<tr>
<td>40</td>
<td>2.5</td>
<td>3.7</td>
<td>1.8</td>
<td>1.2</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>7.0</td>
<td>9.1</td>
<td>4.0</td>
<td>3.7</td>
<td>7.0</td>
</tr>
<tr>
<td>80</td>
<td>14.4</td>
<td>17.4</td>
<td>9.3</td>
<td>7.0</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>23.6</td>
<td>26.1</td>
<td>21.2</td>
<td>11.6</td>
<td>17.0</td>
</tr>
<tr>
<td>120</td>
<td>35.2</td>
<td>36.1</td>
<td>37.4</td>
<td>25.2</td>
<td>36.0</td>
</tr>
<tr>
<td>140</td>
<td>46.9</td>
<td>46.0</td>
<td>60.5</td>
<td></td>
<td>55.9</td>
</tr>
<tr>
<td>160</td>
<td>59.4</td>
<td>57.6</td>
<td>81.7</td>
<td></td>
<td>--</td>
</tr>
<tr>
<td>180</td>
<td>73.2</td>
<td>70.1</td>
<td>--</td>
<td></td>
<td>--</td>
</tr>
<tr>
<td>200</td>
<td>89.2</td>
<td>84.2</td>
<td>--</td>
<td></td>
<td>--</td>
</tr>
</tbody>
</table>
Dantl (64) found the thermal expansion coefficients for H$_2$O and D$_2$O lattices were the same above 120°K. Hence, differences in ΔR/ΔT seem to be an unlikely source of the dispersion. The difference in temperature dependences may arise from differences in HDO coupling to H$_2$O and D$_2$O lattices. If HDO coupling to D$_2$O decreases faster than to H$_2$O then the OH(HDO) hydrogen bond to D$_2$O must weaken faster and the $v_{OH}$(HDO) frequency must shift faster than $v_{OD}$(HDO).

The $v_{OD}$(HDO) data are not in as good agreement with the data of Ford and Falk (100) as for $v_{OH}$(HDO). Again their data are from the best straight line through their Fig. 2. The $v_{OD}$ slopes agree but their data are displaced 2 cm$^{-1}$ to lower frequency. This is probably due to differences in instrument calibration.

(ii) Dependence of HDO Frequencies on R(0⋯⋯0)

The relationship between $v_{OH}$ and R(0⋯⋯0) for a large family of molecules was studied by various authors (27-30) and several empirical relationships were proposed (28,29,32) by neglecting specific differences in molecular properties. The empirical relationships give only an average $v_{OH}$/R(0⋯⋯0) behaviour. The HDO frequencies observed in this work permit the $v_{OH}$/R(0⋯⋯0) dependence for one molecular system to be accurately evaluated.

(a) Observed HDO frequency dependence on calculated R(0⋯⋯0). The observed HDO frequencies are known as a function of temperature (page 71) but not directly as a function of R(0⋯⋯0). One requires the variation of R(0⋯⋯0) in cubic ice I as a function of temperature.

A detailed study of the temperature dependence of the lattice parameters of cubic ice I has not been reported in the literature. However, the
cubic ice I lattice parameter was given by Wyckoff (62) for 143°K, $a_o(OH_2) = 6.350 \pm 0.008 \text{ Å}$ and $a_o(DO) = 6.351 \pm 0.008 \text{ Å}$. For hexagonal ice I, Brille and Tippe (60) made a detailed study of the lattice parameters between 13° and 193°K: $a_o$, $c_o$ and the linear thermal expansion coefficients were evaluated every 20° from 13° to 193°K. In addition, x-ray diffraction (58) and ir (95) studies indicated that the nature of the hydrogen bonding and the nearest-neighbour configurations are the same in hexagonal and cubic ice I. On that basis we assumed the linear thermal expansion coefficient of cubic ice I ($a_o^{\text{cub}}$) to be the average of the expansion coefficients of hexagonal ice I ($a_o^{\text{hex}}(T)$ + $a_o^{\text{hex}}(T)$), i.e.

$$a_o^{\text{cub}}(T) = \frac{1}{2}(a_o^{\text{hex}}(T) + a_o^{\text{hex}}(T)) \text{ at temperature } T.$$ 

Values of $a_o^{\text{cub}}(T)$ were determined every 10°K in the interval 10° to 200°K by the following method. Brille and Tippe's (60) ten $a_o$ and $c_o$ parameters were plotted as a function of temperature. Twenty values of $a_o^{\text{hex}}(T)$ and $a_o^{\text{hex}}(T)$ were determined at ten temperatures between 20° and 200°K, two values at each temperature. The pairs of coefficients at each temperature were obtained from intervals of 2° above and below that temperature, i.e.

$$a_o^{\text{hex}}(150°K) = \frac{1}{2}[a_o^{\text{hex}}(148°-150°) + a_o^{\text{hex}}(150°-152°)]$$

In the same way $a_o^{\text{hex}}(T)$ was evaluated. From the ten values of $a_o^{\text{hex}}(T)$ and $a_o^{\text{hex}}(T)$, ten values of $a_o^{\text{cub}}$ were obtained, Fig. 4.1.

Using Wyckoff's (62) $a_o^{\text{cub}}(OH_2)$ at 143°K (6.350 °) and the linear thermal expansion coefficients in Fig. 4.1, the cubic ice I lattice parameter $a_o^{\text{cub}}(T)$ was calculated every 2°K down from 143° to 10°K and every 2°K up from 143° to 200°K, $a_o^{\text{cub}}(T)$ is shown in Fig. 4.2. (Since the $a_o^{\text{cub}}(OH_2)$ and $a_o^{\text{cub}}(DO)$ lattice parameters were the same within experimental error,
Fig. 4.1 - The linear thermal expansion coefficient of cubic ice I as a function of temperature calculated from the hexagonal ice I data of Brille and Tippe (60).
Fig. 4.2 The cubic ice I lattice parameter as a function of temperature. The values were calculated from the experimental $a_o$ at $143^\circ K$ and the calculated thermal expansion coefficients.
only the $a_\text{cub}^0(H_2O)$ parameter was evaluated.] For the cubic ice I unit cell
the distance $R(0\cdots0) = (\sqrt{3} / 4)a_\text{cub}^0(T)$. The resulting cubic ice I $0\cdots0$
distances are plotted in Fig. 4.3 as a function of temperature.

HDO stretching frequencies from section 3.2A are plotted as a function
of $R(0\cdots0)$ in Fig. 4.4. Frequency and $R(0\cdots0)$ were correlated as a
function of common temperature. The frequencies were plotted as a function
of the experimentally measured temperature, uncorrected for source beam
heating (+10°K at 83°K) since the error may not be a linear function of tem­
peratures.

Both the $\nu_{OH}(\text{HDO})$ and $\nu_{OD}(\text{HDO})$ plots were linear from 150° to 200°K:

$$\frac{\Delta \nu_{OH}(\text{HDO})}{\Delta R(0\cdots0)} = 1.921 \times 10^3 \text{ cm}^{-1} \text{ Å}^{-1}$$

and

$$\frac{\Delta \nu_{OD}(\text{HDO})}{\Delta R(0\cdots0)} = 1.281 \times 10^3 \text{ cm}^{-1} \text{ Å}^{-1}$$

However, the $\nu_{OH}(\text{HDO})$ frequency should be plotted as a function of $R(0\cdots0)$
for D$_2$O ice I, since the $\nu_{OH}$ data were obtained from a sample of 4.0% HDO
in D$_2$O. There is no experimental evidence to suggest that the linear thermal
expansion coefficients of the H$_2$O and D$_2$O ices are different. However, it
may be incorrect to assume the same behaviour since the amplitudes of trans­
lation, libration and vibration are different.

From Fig. 4.4 one sees that the frequency--$R(0\cdots0)$ dependence is
also linear between 30° and 100°K:
Fig. 4.3  The calculated O⋯O distance in cubic ice I as a function of temperature compared to hexagonal ice I O⋯O distances from experimental data.
Fig. 4.4 The HDO stretching frequencies in cubic ice I as a function of $\text{R}(\text{O} \cdots \text{O})$. Frequency and $\text{R}(\text{O} \cdots \text{O})$ were correlated at common temperature.
\[
\frac{\Delta \nu_{\text{OH}}(\text{HDO})}{\Delta R(0\cdots0)} = 8.202 \times 10^3 \text{ cm}^{-1}/\text{Å}
\]

\[
\frac{\Delta \nu_{\text{OD}}(\text{HDO})}{\Delta R(0\cdots0)} = 6.629 \times 10^3 \text{ cm}^{-1}/\text{Å}
\]

Below 30°K the frequency shift was negligible. Between 100° and 150°K the frequency—R(0\cdots0) dependences were non-linear. The points of intersection of the low and high temperature linear dependences were at 125°K (2.748 Å) for both \(\nu_{\text{OH}}(\text{HDO})\) and \(\nu_{\text{OD}}(\text{HDO})\).

For 100°K Whalley (95) assumed a \(\Delta \nu/\Delta R\) dependence of 3000 cm\(^{-1}\)/Å to support his argument that the deviation of O\cdots'O distances arising from orientational disorder was only a few hundredths of an angstrom. The tangent to \(\nu_{\text{OH}}(\text{HDO})\) vs. R(0\cdots0) at 100°K in Fig. 4.4 has \(\Delta \nu/\Delta R\) equal to 6.750 \(\times 10^3\) cm\(^{-1}\)/Å, showing that Whalley's estimate was low by a factor of about two.

As well, Whalley (96) found that the most intense \(\nu_{\text{OH}}(\text{HDO})\) bands for ices II, III and V were 3323, 3318 and 3350 cm\(^{-1}\) respectively. Using \(\Delta \nu/\Delta R\) above, then the displacements of 51, 46 and 78 cm\(^{-1}\) from ice I \(\nu_{\text{OH}}(\text{HDO})\) (3272 cm\(^{-1}\)) were caused by larger O\cdots'O distances. Specifically, the most intense \(\nu_{\text{OH}}(\text{HDO})\) absorptions in ices II, III and V had R(0\cdots'O)'s larger than cubic ice I (100°K) by 0.008, 0.007 and 0.012 Å. Ice II also had two other \(\nu_{\text{OH}}(\text{HDO})\) absorptions (3357 and 3373 cm\(^{-1}\)) which suggest two other sets of O\cdots'O distances. They are longer than R(0\cdots'O) cubic (2.748 Å) by 0.013 and 0.015 Å respectively. Thus ice II appears to have three distinct O\cdots'O bond lengths, 2.756, 2.761 and 2.763 Å.
Ice III had one additional peak at 100°K, 3326 cm\(^{-1}\). That could be due to a second distinct O\(\cdots\)O distance, which is longer than R(O\(\cdots\)O) cubic by 0.008 Å. Thus ice III has two sets of O\(\cdots\)O distances, 2.755 and 2.756 Å.

Ice V has only a single O\(\cdots\)O distance, 2.760 Å.

How well the \(\Delta v/\Delta R\) relationships of ice I apply to other ices is not certain. The estimates of R(O\(\cdots\)O) above are only approximate.

At 0°K the half-height width for \(\nu_{\text{OH}}^\text{HDO}\) in D\(_2\)O cubic ice I was found to be 35.5 cm\(^{-1}\). That indicates that the O\(\cdots\)O distances vary by less than \(\pm 0.004\) Å from the average value in cubic ice I at 0°K. The \(\Delta \nu_{\text{OH}}^\text{HDO}\) rose to 42.5 cm\(^{-1}\) at 180°K. Thus the R(O\(\cdots\)O) deviation must have been less than 0.022 Å. Since the observed \(\Delta v\) data were twice the expected width for an ordered phase (96), then the deviations in R(O\(\cdots\)O) arising from orientational disorder were less than 1/2 the above values, \(\pm 0.002\) and \(\pm 0.011\) Å for 0° and 180°K respectively. Similarly by using \(\Delta \nu_{\text{OD}}^\text{HDO}\) and \(\Delta \nu_{\text{OD}}/\Delta R\) one finds dispersions in R(O\(\cdots\)O) of \(\pm 0.002\) and \(\pm 0.010\) Å at 0° and 180°K.

As one would expect the dispersions of R(O\(\cdots\)O) in H\(_2\)O and D\(_2\)O are equal but the changes in force constants are related by approximately \(1\sqrt{2}\).

Clearly one does not expect the HDO frequencies to be a linear function of R(O\(\cdots\)O) over all values of R(O\(\cdots\)O). If the hydrogen bond is truly partially electrostatic and partially covalent in nature then the strength of the hydrogen bond should increase as \((1/R(O\cdots O))^2\) as temperature is increased. Correspondingly the covalent nature of the bond will
change non-linearly. The effects of such changes in hydrogen bond strength are seen in the observed non-linear behaviour and in the four-fold increase in $\Delta v/\Delta R$.

(b) Comparison of observed and empirical $\Delta v/\Delta R$ relations. The detailed study of $v_{\text{OH}}(\text{HDO})$ absorption as a function of temperature and its correlation to $R(0\cdots 0)$ permitted detailed checks of empirical relations between stretching frequencies and hydrogen bond lengths in ice I. Many workers (27,28,33) have made correlations from data of large numbers of compounds in different hydrogen bonding families. The linear relationship of Pimentel and Sederholm (28),

$$
\Delta v = 4.43 \times 10^3 \times (2.84-R) \text{ cm}^{-1},
$$
satisfies neither the behaviour of $\Delta v/\Delta R$ in a family of $O-H\cdots O$ compounds as Nakamoto et al. (27) found, nor the behaviour of ice I as was shown in Fig. 4.4.

Recently Bellamy and Owen (33) gave a formula relating the frequency shift (from the monomeric frequency) to a maximum effective hydrogen bond length and the measured $O\cdots O$ distance:

$$
\Delta v_{\text{str}} = C \left[ \left( \frac{d}{R} \right)^{12} - \left( \frac{d}{R} \right)^6 \right]
$$

where $\Delta v_{\text{str}}$ = shift of the stretching frequency from the gas phase value,

$d$ = the sum of the collision radii of two oxygen atoms in Angstroms \( (d = 3.35 \text{ Å}), \)

$R$ = the $O\cdots O$ distance in Angstroms,

and $C$ = the constant of proportionality between the potential and the frequency shift.
For a family of O-H···O hydrogen bonding compounds, Bellamy and Owen (33) suggested a constant value of \( C = 50 \text{ cm}^{-1} \). Their predicted \( \Delta v_{\text{str}} \) agreed very well with the observed values, particularly at long O···O lengths, for a family of O-H···O systems.

By using the \( R(O···O) \) values determined in section (a) above for 10°K and 130°K, two values of the constant \( C \) were determined for ice I:

\[
C(10°K) = 58.890 \text{ cm}^{-1},
\]
\[
C(130°K) = 57.767 \text{ cm}^{-1}.
\]

The constants were determined by substituting the \( \Delta v_{\text{str}} \) values between \( v_{\text{OH}}(\text{HDO}) \) of the vapour phase (3757.5 cm\(^{-1}\)) and the cubic ice I values (10°K 3263.8 cm\(^{-1}\) and 130°K 3276.8 cm\(^{-1}\)). The constants were then used to calculate \( \Delta v_{\text{str}}(R) \). Since the thermal expansion of cubic ice I is only small between 10°K and 200°K, Bellamy and Owen's formula could only be checked over a small range of O···O distances. The predictions of Bellamy and Owen's formula and the observed \( \Delta v/\Delta R \) relation are shown in Fig. 4.5.

For the constant determined at 130°K the predicted behaviour was good above 130°K but did not follow the observed trend below 130°K. Over the O···O range 2.7470 Å to 2.7570 Å Bellamy and Owen's formula predicted \( \Delta v/\Delta R = 2.263 \text{ cm}^{-1}/\text{Å} \). Experimentally \( \Delta v/\Delta R = 7.360 \text{ cm}^{-1}/\text{Å} \) from 2.7470 Å to 2.7480 Å (10° to 110°K) and \( \Delta v/\Delta R = 2.144 \text{ cm}^{-1}/\text{Å} \) from 2.7485 Å to 2.7570 Å (130° to 200°K). Thus above 130°K Bellamy and Owen's formula reproduces the ice I experimental behaviour well. Below 130°K (R(O···O) less than 2.7485 Å) their formula fails.

Bellamy and Owen (33) started from the Lippincott-Schroeder potential and made certain assumptions about the intermolecular interaction. The Lippincott-Schroeder potential (25) consists of four terms, one term being
due to van der Waals repulsive forces. Bellamy and Owen investigated the van der Waals repulsion on the basis of a Lennard-Jones 6-12 potential by assuming the interaction of non-bonding filled orbitals was similar to that of non-polar spherical atoms. Bellamy and Pace (32) suggested that if the van der Waals's repulsion originates largely in the lone-pair/lone-pair repulsions of the two oxygen atoms then the 6-12 provides a good distance/energy relation. The relation between the potential energy and the frequency
shift was assumed to be linear.

From our results the assumptions of Bellamy and Pace (32) and Bellamy and Owen (33) are not contradicted between 130° and 200°K, but are contradicted below 130°K. That suggests that the van der Waals repulsion does not originate only in the lone-pair/lone-pair repulsions below 130°K, or that some complex change occurred in the system. The depopulation of \( \Delta v_{\text{str}} \) hot bands below 130°K is an unlikely source of the discrepancy since that would have resulted in a shift to higher frequency as temperature was lowered, in opposition to the observed increase in shift to lower frequency.

It is possible that the O-H stretching amplitude affects the strength of an individual hydrogen bond (and hence the frequency shift) by increased modulation of the potential energy as temperature increases reaching a limiting value at 130°K. However, the experimental amplitudes (5) continued to increase above 130°K and did not reach a limiting value, i.e., between 73° and 173°K the RMS amplitude of O-H stretch increased by 0.042 Å and between 173° and 273°K it increased by 0.028 Å. On the other hand, that does not mean that the modulation of the potential energy did not approach a limiting value.

The Bellamy and Owen (33) formula reproduced the \( \Delta v/\Delta R \) results for a large number of molecules observed near 300°K, while our results were obtained below 200°K. One is tempted to look for a property common to all samples above 130°K. Such properties may be the population of translational
hot bands and large amplitudes of translation. Molecular translation would modulate the $O\cdots O$ distance and hence the hydrogen bond energy. Larger amplitudes of translation would result in increased modulation of the potential, weaker hydrogen bonds and smaller shifts. If the translational amplitude modulation increases from $0\,^\circ K$ to a limiting value at $130\,^\circ K$ and above then the discrepancy can be understood. At room temperature the modulation of the hydrogen bond would be approximately the same in all molecules.

(c) The HDO anharmonicity ($X_{OH}$) and the HDO harmonic frequency ($\omega_{OH}$) and their dependences on temperature and $R(O\cdots O)$. According to Nibler and Pimentel (121) the anharmonicity $X_{OH}$ of HDO in the vapour phase is $91.2\, \text{cm}^{-1}$. For cubic ice I Haas and Hornig (106) predicted $X_{OH}$ (from overtone data) to be $125\, \text{cm}^{-1}$ while Bertie and Whalley (96) estimated it to be $100\, \text{cm}^{-1}$ (by a modified product rule). While Bertie and Whalley's (96) estimate was very approximate, the point is that the anharmonicity increases only a little from the vapour phase.

Since we did not observe the first overtone of $\nu_{OH}$(HDO) (near $6200\, \text{cm}^{-1}$) the HDO anharmonicity must be estimated by the method of Bertie and Whalley (96).

Application of free molecule theory to solids, particularly hydrogen bonded solids, is suspect but the method yields useful qualitative information. For a free, bent $XY_2$ molecule one finds that

\begin{align*}
\nu_1 &= \omega_1 - 2X_{11} - X_{12} - X_{13} \\
\nu_2 &= \omega_2 - 2X_{22} - X_{21} - X_{23} \\
\nu_3 &= \omega_3 - 2X_{33} - X_{31} - X_{32}.
\end{align*}
If $X_{ij}$ ($i \neq j$) are assumed to be small and are neglected then

\[ v_1 = \omega_1 - 2X_{11}, \]
\[ v_2 = \omega_2 - 2X_{22}, \]
\[ v_3 = \omega_3 - 2X_{33}. \]

For isotopic substitution one can employ the Teller-Redlich product rule

\[ \rho = \frac{i}{\omega_a \omega_b \ldots \omega_e} \quad \text{over } l \text{ symmetry representation} \]
\[ \omega_a \omega_b \ldots \omega_e \]

and by analogy to the diatomic case one also knows that

\[ \frac{X_{11}}{X_{jj}} = \frac{i}{\omega_4 \omega_1}. \]

For $v_3$ of $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ the application is straightforward since $v_1$ and $v_2$ are of $a_1$ symmetry while $v_3$ is of $b_1$ symmetry (assuming the $C_{2v}$ point group). Then

\[ \rho = \frac{\omega_3}{\omega_3} \quad \text{and} \quad \frac{X_{33}}{X_{33}} = \left( \frac{i}{\omega_3} \right)^2 = \rho^2. \]

Hence, one can write for $\text{H}_2\text{O}$

\[ v_3 = \omega_3 - 2X_{33}, \]

and for $\text{D}_2\text{O}$

\[ v_3 = \omega_3 - 2X_{33} = \rho \omega_3 - 2\rho^2 X_{33}. \]

By assuming that $\rho$ of the vapour phase (say from Nibl's and Pimentel's harmonic data) applies also to the solid and by using the observed $v_3$ $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ frequencies, then the two equations can be solved for $\omega_3$ and $X_{33}$ of ice I.
For HDO the problem is more complex. The strict product rule would be

\[
\rho = \frac{\omega_{\text{OH}} \omega_{\text{OD}} \omega_{\text{HOD}} \omega_{\text{T}}^x \omega_{\text{y}}^z}{\omega_{\text{T}}^1 \omega_{\text{T}}^2} \frac{\text{HDO}}{\text{H}_2\text{O}}
\]

Even by assuming that the librational and translational force constants approach zero and the frequencies approach zero (which they obviously do not), the product rule is still complex

\[
\rho = \frac{\omega_{\text{OH}} \omega_{\text{OD}} \omega_{\text{HOD}}}{\omega_{\text{T}}^1 \omega_{\text{T}}^2}
\]

As an approximation we can treat the problem as a diatomic molecule \( \text{H}-(\text{OD}) \) with the isotopic analogue \( \text{D}-(\text{OH}) \). Then the product rule is

\[
\rho = \frac{\omega_{\text{OD}}}{\omega_{\text{OH}}}
\]

The expected value of \( \rho \) is given by

\[
\frac{\omega_{\text{OH}}}{\omega_{\text{OH}}} = \frac{|G|^2}{|G|} = \frac{m_{\text{D}}^{-1} + (m_0 + m_{\text{H}})^{-1}}{m_{\text{H}}^{-1} + (m_0 + m_{\text{D}})^{-1}} = 0.7278
\]

From the vapour data of Nibler and Pimentel (121) one finds \( \rho = 0.7261 \).

Briefly the method of Bertie and Whalley (96) involved assuming such a modified product rule for HDO, where

\[
\frac{\rho}{\omega_{\text{OH}}(\text{ice})} = \frac{\omega_{\text{OD}}(\text{vapour})}{\omega_{\text{OH}}(\text{vapour})}
\]

and

\[
\frac{\lambda_{\text{OD}}}{\lambda_{\text{OH}}} = \rho^2
\]
Then \[ v_{\text{OH}} = \omega_{\text{OH}} - 2X_{\text{OH}} \] and \[ v_{\text{OD}} = \rho \omega_{\text{OH}} - 2\rho^2 X_{\text{OH}} \]

where \( \rho = 0.72608 \) of the vapour phase. The anharmonicity of the HDO stretching vibrations in ice I was then given by

\[ X_{\text{OH}}(T) = \frac{v_{\text{OD}}(T) - \rho v_{\text{OH}}(T)}{2\rho (1 - \rho)} \]

Hence the anharmonicity can be determined as a function of temperature between 10° and 200°K. The harmonic HDO frequency and the HDO anharmonicities calculated in this way are shown in Figs. 4.6 and 4.7 respectively. While the magnitude of the calculated anharmonicity is not accurate, the trend in \( X_{\text{OH}}(T) \) indicates some fundamental changes in the hydrogen bonded system. Between 10° and 80°K \( X_{\text{OH}} \) underwent a regular increase of 4% and from 80° to 200°K \( X_{\text{OH}} \) underwent a regular decrease of 4%. The low temperature limiting anharmonicity was 105.6 cm\(^{-1}\), the low temperature dependence was \( 3.25 \times 10^{-2} \) cm\(^{-1}\)/°K, and the high temperature dependence was \( -3.75 \times 10^{-2} \) cm\(^{-1}\)/°K. The anharmonicity reached a maximum at 80°K. The temperature dependence of \( \omega_{\text{OH}} \) was 0.138 cm\(^{-1}\)/°K if it was assumed to be linear. The maximum in the anharmonicity is also seen in the harmonic frequency. The anharmonicity was also plotted as a function of \( R(0\cdots0) \), Fig. 4.8. That plot looks surprisingly like a Lennard-Jones 6-12 potential energy curve.

The harmonic HDO frequency and the anharmonicity of HDO stretches as a function of temperature were estimated from observed \( v_{\text{OH}}(\text{HDO}) \) and \( v_{\text{OD}}(\text{HDO}) \) frequencies. Hence, the variations of \( \omega_{\text{OH}} \) and \( X_{\text{OH}} \) as a function of temperature arise from all sources present in the cubic ice I crystals.

There appear to be two major sources of changes in the anharmonicity as a function of temperature. As the crystal is cooled from 200°K to 5°K it contracts and \( R(0\cdots0) \) decreases. The hydrogen bond energy increases,
The harmonic HDO stretching frequency for cubic ice I as a function of temperature. The $\omega_{\text{OH}}^{\text{HDO}}$ was estimated from observed HDO cubic ice I frequencies.
Fig. 4.7 The HDO cubic ice I anharmonicity as a function of temperature. The $X_{OH}$ values were estimated from observed HDO stretching frequencies and the $\rho$ value of the vapour phase.
Hence one would expect a steady increase in the contribution of increasing hydrogen bond energy to the total anharmonicity down to about 80°K (the observed HDO stretching frequencies and the predicted harmonic frequency decrease, and the anharmonicity increases as long as $R(0\cdots 0)$ is decreasing).

**Fig. 4.8** The dependence of the anharmonicity $X_{OH}$ on the $R(O\cdots 0)$ distance between $10^9K$ and $200^9K$. 
R(0···0) freeze-in temperature. Changes in R(0···0) and the hydrogen bond energy are very small below 80°K.

The other source of anharmonicity is probably due to changes in the amplitudes of O-H stretch and HDO translation. The O-H stretching amplitude must be discussed in terms of the total population distribution among all the energy levels. Below 200°K virtually all of the molecules must be in the ground vibrational state. As was indicated previously, the O-H amplitudes have been measured experimentally (ref. 5, page 78) and increased from 0.150 Å at 1°K to 0.221 Å at 200°K in H₂O ice Ih. Corresponding O-D amplitudes for D₂O were 0.129 Å at 1°K and 0.217 Å at 223°K. Thus the anharmonicity experienced by the molecules can be expected to decrease below 200°K.

As well, the RMS amplitude of translation decreases from 200°K to 1°K. Since \( v_{OH} \), \( x_{OH} \), and \( \omega_{OH} \) are all strongly coupled to the instantaneous R(0···0), then decreases in the range of R(0···0) through decreased amplitudes of translation will give a smaller range of \( x_{OH} \) and a net smaller \( x_{OH} \)

We suggest that: 1) below 80°K \( \Delta x_{OH} \) from changes in amplitudes is greater than \( \Delta x_{OH} \) due to changes in hydrogen bond energy, 2) at 80°K the two kinds of \( \Delta x_{OH} \) are equal, and 3) that above 80°K \( \Delta x_{OH} \) (hydrogen bond energy) is greater than \( \Delta x_{OH} \) (amplitude).

(d) Correlation of the HDO stretching frequencies to the RMS amplitudes of translation. Since the HDO stretching frequencies are a function of R(0···0) and since the rate of increase of R(0···0) depends on the RMS amplitude of molecular translation, then it is interesting to consider the relationship between \( v_{str} \) and \( \langle \Delta r^2 \rangle^{1/2} \) as a function of temperature.
Decius (122) gave the mean-square displacement from the equilibrium distance between two atoms resulting from all modes of vibration as:

\[ \langle \Delta r_t^2 \rangle = \sum_k L_{tk}^2 \langle \alpha_k^2 \rangle \]  

[1]  

where \( \alpha \Delta r_t \) = the displacement distance of internal coordinate \( t \) due to all normal coordinates, \( k \),  
\( L_{tk} \) = the element of the matrix transforming normal coordinate \( k \) into internal coordinate \( t \),  
and \( \alpha_k \) = the \( k \)-th normal coordinate.

The mean-square amplitude of the \( k \)-th normal coordinate \( \langle \alpha_k^2 \rangle \) was given by Morino et al. (123) as:

\[ \langle \alpha_k^2 \rangle = \frac{\hbar}{\hbar \nu_k^2 \coth \frac{\hbar c \nu_k}{2kT}} \]  

[2]  

where \( \nu_k \) = the vibrational frequency of the \( k \)-th normal mode in cm\(^{-1}\),  
\( k \) = Boltzmann's constant,  
\( T \) = the temperature in degrees Kelvin,  
\( c \) = the velocity of light, and  
\( \hbar \) = Planck's constant.

The formulas [1] and [2] were derived for the isolated, free molecule case. In a rigorous treatment of ice it would be necessary to consider all internal and lattice modes in the sum over \( k \).

Cubic ice I has two \( \text{H}_2\text{O} \) molecules per primitive unit cell and there are three non-zero translational, six librational and six internal vibrational modes. If the pair of \( \text{H}_2\text{O} \) molecules is considered as a weakly bonded diatomic molecule, \( (\text{H}_2\text{O}) \cdots (\text{H}_2\text{O}) \), then there is one normal mode of vibration, the
R(0⋯0) stretch. The mean-square amplitude of translation between two
H₂O molecules can then be estimated. Equations [1] and [2] give

$$\langle \Delta r^2 \rangle = \frac{h}{8\pi^2 c \nu T} \coth \frac{hc \nu T}{2kT}$$

and for the (H₂O)₂ "diatom" LL' = G, which is easily evaluated for H₂O or
D₂O. The RMS amplitude of displacement is then given by

$$\langle \Delta r^2 \rangle^\frac{1}{2} = \left[ \frac{h}{m_1 \nu H^2 c \nu T} \coth \frac{hc \nu T}{2kT} \right]^\frac{1}{2}$$

where m₁ is the mass of H₂O or D₂O, and the variation of $$\langle \Delta r^2 \rangle^\frac{1}{2}$$ as a function
of temperature can be calculated by using the observed νₜ(H₂O) frequencies.

Two sets of $$\langle \Delta r^2 \rangle^\frac{1}{2}$$ were calculated between 10° and 200°K. In both
cases the νₜ(H₂O) frequencies used were from the best smooth curve through
the experimental points (Fig. 3.15). Since the νₜ(H₂O) frequency varied by
less than 5% between 10°K and 200°K, one set of $$\langle \Delta r^2 \rangle^\frac{1}{2}$$ was calculated at
constant νₜ, i.e. νₜ = 227.0 cm⁻¹ at 80°K. That is reasonable since 1/T
dominates the function. A corresponding set of $$\langle \Delta r^2 \rangle^\frac{1}{2}$$ for D₂O were calcu-
lated using the H₂O frequencies and D₂O masses. These data are compiled in
Table IV.I and are plotted in Fig. 4.9. For comparison, a set of H₂O

$$\langle \Delta r^2 \rangle^\frac{1}{2}$$ were calculated using the full range of observed frequencies. Those
data are also compiled in Table IV.I. The only significant change was a
slight decrease in the low temperature values and a slight increase in the
high temperature values.

Plots of R(0⋯0) against $$\langle \Delta r^2 \rangle^\frac{1}{2}$$ at equal temperatures and of
νₒH(HDO) and νₒD(HDO) against $$\langle \Delta r^2 \rangle^\frac{1}{2}$$ are given in Figs. 4.10 and 4.11 re-
psectively.
TABLE IV. The RMS amplitudes of translation calculated from H$_2$O $v_T$ and compared to results of thermodynamic calculations.

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$\langle \Delta r^2 \rangle_{H_2O}^{1/2}$</th>
<th>$\langle \Delta r^2 \rangle_{H_2O(T)}^{1/2}$</th>
<th>$\langle \Delta r^2 \rangle_{D_2O}^{1/2}$</th>
<th>$\langle \Delta r^2 \rangle_{H_2O}^{1/2}$ (Å)</th>
<th>$\langle \Delta r^2 \rangle_{D_2O}^{1/2}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.08</td>
<td>9.04</td>
<td>9.01</td>
<td>9.0</td>
<td>9.0</td>
</tr>
<tr>
<td>10</td>
<td>9.08</td>
<td>9.04</td>
<td>8.61</td>
<td>10.5</td>
<td>11.1</td>
</tr>
<tr>
<td>20</td>
<td>9.08</td>
<td>9.04</td>
<td>8.61</td>
<td>14.5</td>
<td>14.5</td>
</tr>
<tr>
<td>30</td>
<td>9.08</td>
<td>9.04</td>
<td>8.61</td>
<td>10.0</td>
<td>10.4</td>
</tr>
<tr>
<td>40</td>
<td>9.08</td>
<td>9.06</td>
<td>8.62</td>
<td>10.0</td>
<td>10.4</td>
</tr>
<tr>
<td>50</td>
<td>9.10</td>
<td>9.06</td>
<td>8.63</td>
<td>9.8</td>
<td>10.0</td>
</tr>
<tr>
<td>60</td>
<td>9.12</td>
<td>9.06</td>
<td>8.65</td>
<td>9.8</td>
<td>10.0</td>
</tr>
<tr>
<td>70</td>
<td>9.17</td>
<td>9.14</td>
<td>8.70</td>
<td>9.8</td>
<td>10.0</td>
</tr>
<tr>
<td>80</td>
<td>9.25</td>
<td>8.77</td>
<td>8.77</td>
<td>9.9</td>
<td>10.1</td>
</tr>
<tr>
<td>90</td>
<td>9.33</td>
<td>9.32</td>
<td>8.85</td>
<td>9.9</td>
<td>10.1</td>
</tr>
<tr>
<td>100</td>
<td>9.44</td>
<td>8.95</td>
<td>13.2</td>
<td>9.9</td>
<td>10.6</td>
</tr>
<tr>
<td>1</td>
<td>9.57</td>
<td>9.59</td>
<td>9.07</td>
<td>9.9</td>
<td>10.6</td>
</tr>
<tr>
<td>10</td>
<td>9.70</td>
<td>9.20</td>
<td>14.5</td>
<td>10.0</td>
<td>11.0</td>
</tr>
<tr>
<td>20</td>
<td>9.84</td>
<td>9.96</td>
<td>9.34</td>
<td>10.0</td>
<td>11.0</td>
</tr>
<tr>
<td>30</td>
<td>10.0</td>
<td>9.49</td>
<td>9.99</td>
<td>10.0</td>
<td>11.0</td>
</tr>
<tr>
<td>40</td>
<td>10.2</td>
<td>10.4</td>
<td>9.65</td>
<td>10.0</td>
<td>11.0</td>
</tr>
<tr>
<td>50</td>
<td>10.5</td>
<td>10.7</td>
<td>9.65</td>
<td>10.0</td>
<td>11.0</td>
</tr>
<tr>
<td>60</td>
<td>10.7</td>
<td>10.1</td>
<td>9.65</td>
<td>10.0</td>
<td>11.0</td>
</tr>
<tr>
<td>70</td>
<td>10.9</td>
<td>11.2</td>
<td>10.3</td>
<td>10.0</td>
<td>11.0</td>
</tr>
<tr>
<td>80</td>
<td>11.1</td>
<td>10.5</td>
<td>18.5</td>
<td>10.0</td>
<td>11.0</td>
</tr>
<tr>
<td>90</td>
<td>11.1</td>
<td>10.5</td>
<td>18.5</td>
<td>10.0</td>
<td>11.0</td>
</tr>
<tr>
<td>200</td>
<td>11.1</td>
<td>10.5</td>
<td>18.5</td>
<td>10.0</td>
<td>11.0</td>
</tr>
<tr>
<td>223</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>273</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Ref. 84.
The RMS amplitudes of $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ translation calculated with a constant $v_T(\text{H}_2\text{O})$ assuming an $(\text{H}_2\text{O})_2$ diatomic unit cell model.
Fig. 4.10 The correlation of RMS amplitude of translation to the calculated O⋯⋯O distance in cubic ice I. $R(0⋯⋯0)$ and $\langle \Delta r^2 \rangle^{1/2}$ were correlated as a function of common temperature.
Fig. 4.11 The dependence of the observed HDO stretching frequencies on the RMS amplitudes of translation of H\textsubscript{2}O and D\textsubscript{2}O. The frequencies continued to decrease although the \( \langle \Delta r^2 \rangle \) became constant at low temperatures.
From Table IV.1 one sees that the RMS amplitudes of translation for H$_2$O and D$_2$O agree at low temperatures, i.e., below 10°K, quite well with those calculated by Leadbetter (84) from thermodynamic data. His data appears to be linear in temperature over the whole range, 1° to 273°K. However, the temperature dependences of our calculated $\langle \Delta r^2 \rangle^\frac{1}{2}$ are non-linear and are much smaller than his. Between 100° and 200°K his RMS amplitude increased by $5.3 \times 10^{-4}$ Å/cm$^{-1}$ while ours increased by $1.6 \times 10^{-4}$ Å/cm$^{-1}$. For H$_2$O ice I at 200°K we calculated RMS amplitudes of 0.111 Å while he calculated 0.185 Å. There are probably several reasons for our low estimate, among which are neglect of translational hot bands above 50°K, neglect of two other translational modes, and the inadequacy of the free molecule theory. The contributions of the larger amplitudes of molecules in excited translational states must certainly increase drastically as the temperature approaches 200°K, with as much as 15% of the sample in excited states. The contribution of the lattice fundamental at 160 cm$^{-1}$ to the individual molecular amplitude must be even larger than for the 229 cm$^{-1}$ fundamental chosen above, although the apparent density of states is less.

The plot of $\langle \Delta r^2 \rangle^\frac{1}{2}$ against R(0⋯⋯0) in Fig. 4.10 showed that below 50°K our calculated RMS amplitude was constant although our calculated 0⋯⋯0 distance was still decreasing. As well, below 50°K the frequencies continued to decrease. These results also support the conclusion that below 100°K factors other than R(0⋯⋯0) affected the HDO stretching frequencies.
(iii) HDO Stretch Half-Height Widths

As can be seen from Fig. 3.8, the low temperature, limiting half-height widths for \( \nu_{OD}(\text{HDO}) \) and \( \nu_{OH}(\text{HDO}) \) were 23.5 cm\(^{-1}\) and 35.5 cm\(^{-1}\) respectively. At 100°K \( \Delta \nu_{OD}(\text{HDO}) \) was 23.5 cm\(^{-1}\) and \( \Delta \nu_{OH}(\text{HDO}) \) was 35.5 cm\(^{-1}\) which compared very well with the data of Ford and Falk (100) \( (23.5 \text{ cm}\(^{-1}\) and 33 cm\(^{-1}\) respectively) at similar temperatures. Ford and Falk (100), took great care to ensure they had very low and well known concentrations of HDO in D\(_2\)O and H\(_2\)O. For the dilute samples of HDO in H\(_2\)O and D\(_2\)O used in this work, care was taken to prevent accumulative exchange between atmospheric H\(_2\)O and D\(_2\)O liquid during handling. In our HDO in D\(_2\)O samples, exchange of D\(_2\)O with unwanted H\(_2\)O absorbed on preparative surfaces or H\(_2\)O vapour in the atmosphere enriched the concentration of HOD. The fact that our \( \Delta \nu_{OH}(\text{HDO}) \) was somewhat larger than Ford and Falk's (100) indicated our HDO/D\(_2\)O concentration was more than the 4.00% intended. Our \( \Delta \nu_{OH}(\text{HDO}) \) was probably broader than Falk's, due to increased coupling. Our widths were still much narrower than those observed by Whalley (96), i.e. \( \Delta \nu_{OH}(\text{HDO}) = 50 \text{ cm}\(^{-1}\) and \( \Delta \nu_{OD}(\text{HDO}) = 30 \text{ cm}\(^{-1}\).

It is important to recognize that the coupling-broadening does not necessarily originate from HDO-HDO pairs. Since at least one HDO stretching frequency is always coupled to the host, even at low concentration, and since the \( \nu_3 \) (H\(_2\)O or D\(_2\)O) bands are both very broad distributions of frequencies, then HDO may have a quite broad range of interaction energies with H\(_2\)O and D\(_2\)O neighbouring molecules. The consequent range of perturbations inflicted on the isolated HDO frequency also may be broad. Hence, as the concentration of HDO molecules increases, the group of HDO molecules will be exposed to
a wider range of perturbations giving increased $\Delta v$ even in the absence of HDO-HDO pairs. Clearly, the number of HDO molecules coupled to the fewer lattice molecules with stretching frequencies far down the sides of the $\nu_3$ band (fewer than the number oscillating at the central frequency) increases as the concentration of HDO increases. The absorption by such molecules increases in importance in the total HDO absorption. Our data for $\nu_{OD}(\text{HDO})$ from 5.94% D$_2$O in H$_2$O showed good agreement since exchange with atmospheric H$_2$O was only very slow and tended to deplete HDO rather than increase it.

Half-height widths of stretching modes in the high pressure ices were indicated by Whalley (96) to be: $\Delta v_{OD} = 5 \text{ cm}^{-1}$ and $\Delta v_{OH} = 18 \text{ cm}^{-1}$ for ices II and III. There was obviously a dramatic change in the ice crystal in transforming between ice I and ices II or III. Whalley (96) and others (100, 105, 106) suggested a number of reasons for the observed ice band widths. The postulates can be condensed into four main mechanisms. The first mechanism was first mentioned by Hornig (106), but Bertie and Whalley (96) have described it in more detail. The mechanism suggested the band width arose from closely spaced transitions between a range of closely spaced ground state energies and corresponding closely spaced first excited states found over a mole of crystal. It was understood that any individual molecule had only one narrow ground state and first excited state, but that over the whole crystal the sets of equivalent molecules sat in sites of varying O-H····O energies. The variation of O-H····O energies arose from the variation in O····O distances prescribed at equivalent oxygen sites by disorder allowed in the proton orientations. A result of the proton orientational disorder at equivalent oxygen positions in the set of unit cells
was the loss of site symmetry. Consequently, all vibrations became \( a \) or \( a' \) and the selection rules collapsed to one general selection rule allowing transitions between all forms of combination and overtone levels. The second mechanism of stretching region broadening was through Fermi resonance of any fundamental (or the fundamental sum and difference bands with low frequency lattice modes) with other overtone and combination bands such as \( 2v_2, 4v_R, \) and \( v_2 + 2v_R \). Notice that because of the lack of site symmetry through proton orientational disorder, Fermi resonance between any two near-degenerate levels was possible, not just between \( 2v_2 \) and \( v_1 \) as was expected from crystal site symmetry. The third mechanism invoked Heisenberg's uncertainty principle. Specifically, the energy level uncertainty, \( \Delta E \), was increased by a shortened half-life, \( \Delta t \), of the upper state by either proton tunnelling to an ionized state or by resonance interaction between the excited fundamental vibration and overtones of lattice modes giving the ground state, fundamental internal mode and excited lattice vibrations. Both proton tunnelling and ejection from the excited vibration to nearby upper lattice modes constituted radiationless transitions. The fourth mechanism of broadening was through the occurrence about the fundamental of sum and difference bands of the fundamental with low frequency translational lattice modes and the occurrence of nearby hot lattice modes.

The fact that neither \( \Delta v_{OD}^{1/2} (\text{HDO}) \) nor \( \Delta v_{OH}^{1/2} (\text{HDO}) \) underwent a smooth, continuous decrease at temperatures below \( 100^\circ \text{K} \) shows that the mechanisms of hot bands and difference bands as sources of broadening are not significant. If the observed stretching modes were broadened by difference and hot bands involving lattice modes, then the stretching modes should have undergone significant sharpening once the higher lattice energy levels were
depopulated at low temperatures: The stretching modes were not significantly sharpened as far down as 10\(^0\)K. A simple calculation of the ratios of numbers of molecules in the ground, 1st, 2nd and 3rd excited states for \(\nu_T ( \sim 229 \text{ cm}^{-1} )\) and \(\nu_R ( \sim 832 \text{ cm}^{-1} )\) showed that at 10\(^0\)K all upper levels were effectively depopulated. These observations removed mechanism four from consideration as a source of broadening.

The observed "freeze-in" of half-height width supported mechanism one, the proton orientational disorder mechanism. For that mechanism, as the sample was cooled and the lattice contracted, the mean deviation from the ideal symmetry site of the oxygen atoms decreased. Since the mean deviation of O\(\cdots\)O distances was also a measure of the range of hydrogen bond energies and the range of stretching frequencies, then as \(R(0\cdots0)\) decreased and \(\langle \Delta r^2 \rangle^{1/2}\) decreased so should the stretching band width. Once the O\(\cdots\)O distances were invariant, so was the half-height width.

A further modification to the stretching mode of dilute HDO molecules in a parent lattice was in lattice coupling. Ideally one wanted to compare the uncoupled OH stretch to the coupled OH stretch in identical crystal fields or lattice environments. At best one compared uncoupled, but perturbed OH stretch to coupled OH stretch in identical electron distributions. However, the periodic modulation of the electrons by lattice modes was different for the two cases. The conclusion is that if the stretching modes were broadened by lattice modes then the effect of broadening of OH(HDO) stretch by the \(^2\)H\(_2\)O lattice was different than the broadening of OH(H\(_2\)O) stretch by the H\(_2\)O lattice since H\(_2\)O and D\(_2\)O have different lattice fundamental frequencies and amplitudes.
The half-height widths had a near-linear temperature dependence of 
$13.5 \times 10^{-2} \text{ cm}^{-1}/\text{°K}$ for $\nu_{\text{OH}}$(HDO) and $7.0 \times 10^{-2} \text{ cm}^{-1}/\text{°K}$ for $\nu_{\text{OD}}$(HDO) in the high temperature range from 100° to 190°K. Those data compare well with our interpretation of the data of Ford and Falk (100) in the temperature range 100° to 200°K, $\Delta \nu_{\text{OH}}$(HDO) changed by $4.5 \times 10^{-2} \text{ cm}^{-1}/\text{°K}$. In the temperature range from 100° to 273°K we deduced from Falk's data that the slope of $\Delta \nu_{\text{OH}}$(HDO) = $16.2 \times 10^{-2} \text{ cm}^{-1}/\text{°K}$ and of $\Delta \nu_{\text{OD}}$(HDO) = 10.7 $(10^{-2}) \text{ cm}^{-1}/\text{°K}$. Our experimental data lie within their results, and our scatter of data is significantly lower than theirs.

(iv) Dependence of HDO Peak Heights on Temperature

The HDO stretching mode peak heights (I) and half-height widths were used to approximate the area of $\nu_{\text{OH}}$(HDO) as a function of temperature. Simple triangles were constructed which had heights equal to the peak height on a linear absorbance scale and a base at 1/2 of $\nu_{\text{OH}}$(HDO). The area of two such triangles, extended to the baseline, was assumed to represent the integrated intensity (A) approximately. Typical results are given below:

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$\Delta \nu^{1/2}$ (cm$^{-1}$)</th>
<th>I (absorbance)</th>
<th>A (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>35.5</td>
<td>0.94</td>
<td>133.5</td>
</tr>
<tr>
<td>50</td>
<td>35.5</td>
<td>0.92</td>
<td>130.6</td>
</tr>
<tr>
<td>100</td>
<td>36.5</td>
<td>0.85</td>
<td>124.1</td>
</tr>
<tr>
<td>150</td>
<td>39.7</td>
<td>0.72</td>
<td>114.5</td>
</tr>
<tr>
<td>180</td>
<td>42.5</td>
<td>0.60</td>
<td>103.2</td>
</tr>
</tbody>
</table>
The slow, smooth decrease in $\nu_{\text{OH}}(\text{HDO})$ peak height seems to predominate in the decreased band area and is consistent with the concept of a weakening hydrogen bond and a decrease in molecular dipole with increasing $R(\text{O} \ldots \text{O})$ as temperature increases.

Above 190°K the samples sublimed rapidly and presumably a small amount of the original decrease was due to cumulative sample loss by sublimation. A slightly concave portion of the $I(\nu_{\text{OD}}(\text{HDO}))$ between 110° and 140°K indicated first a more rapid and then a less rapid decrease in hydrogen bond energy. Some unusual heat capacity effects were noticed near 110°K (82), but it is not certain that the effects are related.
B. Dependence of $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ Bands on Temperature

(i) **Fundamental Lattice Mode Temperature Dependences**

(a) The $\text{H}_2\text{O}$ translational mode. Cubic ice I (Fd3m) has two molecules per unit cell which provide six translational modes, of which three are zero frequency translations of the whole finite crystal. Whalley and Bertie (87, 88) developed a theory for hexagonal and cubic ice I which incorporates proton orientational disorder in the description of $v_T$. They deduced from an approximate density of states relation that points of inflection, minima and shoulders, as well as peaks, are associated with specific branches of the optical and acoustical modes. The lattice modes of hexagonal ice I were also observed by neutron inelastic scattering (92, 93). Our observed $v_T(\text{H}_2\text{O})$ structural absorption features were given in Table III.IXb along with some previous results (88, 92, 93). The poor definition of the absorption features (other than the 229 cm$^{-1}$ peak maximum) made it impossible to follow their temperature dependences. The features recorded here at 83$^\circ$K agreed with the mull results of Bertie and Whalley (88) and the condensation results of Giguere and Arraudeau (89). The lowest temperature indicated by the (Au-Co) / (Ag-Au) thermocouple for this experiment was 25$^\circ$K, probably due to some solidified $\text{N}_2$ used to precool the helium dewar.

The low temperature (25$^\circ$K) limiting values of the $v_T$ features exhibited no special behaviour. From 25$^\circ$ to 70$^\circ$K the $v_T$ maximum underwent a stage of invariant frequency up to 55 ± 5$^\circ$K, and an apparent shift by 2 cm$^{-1}$ to lower frequency between 55 ± 5$^\circ$ and 70 ± 5$^\circ$K. From 70$^\circ$ to 90$^\circ$K $v_T$ was relatively constant in frequency, while above 90$^\circ$K $v_T$ had a con-
tinuous, near linear shift towards lower frequency of $-0.093 \text{ cm}^{-1}/\text{oK}$.

Above $160^\circ\text{K}$ $v_T$ (max.) remained constant at $221 \pm 0.5 \text{ cm}^{-1}$. In comparison, Zimmermann and Pimentel's (97) data indicated a slope of $-0.081 \text{ cm}^{-1}/\text{oK}$ from $90^\circ\text{K}$ to $250^\circ\text{K}$. The dependence (rate of change) of $v_T$ on the hydrogen bond energy was less than for the molecular modes, i.e. a given change in hydrogen bond energy had 0.5 to 0.3 times the effect on $v_T$ as it did on $v_R$ or the molecular modes. The sensitivity (minimum detectable change) of $v_T$ to hydrogen bond energy changes was the same as for $v_R$, $v_1$, $v_2$ and $v_3$, i.e. sensitive to changes of $\pm 0.0001 \text{ A/oK}$ in $R(0\cdots 0)$.

The origin of the sharp shift near $55^\circ\text{K}$ is unknown, but it may have arisen from a change in the crystal structure (and hence the unit cell and Brillouin zone), or a change in proton ordering. A similar effect was observed for HDO stretching modes and it was correlated to the predicted (70) ordering near $70^\circ\text{K}$.

(b) The $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ librations. The low temperature limiting $v_R(\text{H}_2\text{O})$ frequency (832 cm$^{-1}$) and $v_R(\text{D}_2\text{O})$ frequency (630 cm$^{-1}$) exhibited no special behaviour attributable to excited state depopulation, ordering of protons, or decreased anharmonicity. From $42^\circ\text{K}$ to $70 \pm 10^\circ\text{K}$ the frequency scatter of data points was large, $\pm 5 \text{ cm}^{-1}$ for $v_R(\text{H}_2\text{O})$ and $\pm 3 \text{ cm}^{-1}$ for $v_R(\text{D}_2\text{O})$ (Fig. 3.13). Within these frequency limits the absorption maximum was constant. The freeze-in temperature for $v_R(\text{H}_2\text{O})$ and $v_R(\text{D}_2\text{O})$ was $70 \pm 10^\circ\text{K}$ and agreed with other $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ bands but did not conform to our more precise measurements on HDO peaks. The sensitivity of $v_R(\text{H}_2\text{O}$ and $\text{D}_2\text{O}$) to changed hydrogen bond energy through AR(0\cdots 0) was larger than HDO, i.e.
> 0.0001 Å/°K. Between 70°K and 180°K \( \nu_R(H_2O\text{ and } D_2O) \) exhibited linear temperature dependences of \(-0.18 \text{ cm}^{-1}/°K\) and \(-0.11 \text{ cm}^{-1}/°K\) respectively. Again the frequency scatter of points was large and a curvilinear dependence may be true, as was indicated for \( \nu_R(HDO) \) (Fig. 3.7). Liquid nitrogen and liquid helium cell data agreed in their overlap region for \( \nu_R(H_2O) \). Zimmermann and Pimentel's (97) data for \( \nu_R(H_2O) \) indicated a slightly curvilinear temperature dependence of about \(-0.22 \text{ cm}^{-1}/°K\). Their points were approximately 10 cm\(^{-1}\) higher in frequency than ours: They chose the band center and ignored any \( \nu_R \) band structure (indicated in their spectra). Details of the origins, possible theoretical treatments, and the nature of the \( \nu_R \) modes will be given in section 4.4.

(ii) **Fundamental Molecular Mode Temperature Dependences**

(a) The \( \nu_1 \) and \( \nu_3 \) stretching modes. The low temperature limiting frequencies for \( \nu_1 \) and \( \nu_3 \) of \( H_2O \) and \( D_2O \) were 3133 (2320) cm\(^{-1}\) and 3204 (2413) cm\(^{-1}\) respectively. As for HDO that extrapolation to 0°K may not have been valid, but the thermodynamic data was regular down to 2°K (83). The effects of proton ordering should not be seen since the time for such a process is very long below 60°K (70). As well, translational, librational and vibrational excited levels are all depopulated at 5°K: Further effects from depopulation should have been negligible. Also, nuclear spin and electron spin perturbations (i.e. as in ortho-para hydrogen) were expected to be very small. No changes in hydrogen bonding were expected since the lattice was no longer contracting.

From 4.2°K to 60°K, \( \nu_1 \) and \( \nu_3 \) (\( H_2O \) and \( D_2O \)) absorptions were invariant within the errors of measurement. Over that temperature range the crystal
expanded very slowly, less than 0.0001 Å/°K. Accompanying changes in
$R(0\cdots0)$ and $v_1$ or $v_3$ were too small to be detected by this ir absorption
technique. The large frequency scatter in points was pre-determined by
the uncertainty in peak and shoulder positions. The $v_3(H_2O)$ data from
liquid helium and nitrogen cells did not completely agree (Fig. 3.10).
Liquid nitrogen cell data indicated a "freeze-in" frequency near 3215 cm$^{-1}$.
Liquid helium cell data indicated a "freeze-in" frequency near 3204 cm$^{-1}$.
The data were collected during warm-up from 77°K and 4.2°K respectively.
The discrepancy may be explained if the $v_3$ absorption peak underwent a
type of "hysteresis" during cooling from 77°K to 4.2°K, frequency shift
lagged behind temperature decrease. Since the samples were always held at
4.2°K for three hours, sufficient time may have been given for completion
of the hysteresis loop before warm-up observations began: Observations of
$v_3$ frequency shift during a cooling cycle are required to test the possibility.
Data from the same two cells for $v_1(H_2O)$ (Fig. 3.11) also suggested
hysteresis although the separation of points was not as well defined. Only
the results from the liquid helium cell were obtained for $v_1$ and $v_3$ of D$_2$O.

Above 60°K the $v_1$ and $v_3$ modes underwent regular shifts to the
progressively higher frequencies associated with progressively decreased
hydrogen bond strengths. The explanation follows that of $v_{OH}^{0}$ (HDO).

The ir high temperature dependences of $v_1$ and $v_3$ for cubic ice I
agree with the Raman observations of Val'kov and Maslenkova (90). The
Raman and ir $v_3$ (H$_2$O and D$_2$O) observations concurred directly. However,
the $v_1(H_2O$ and D$_2$O) Raman observations were all shifted (by 55 and 32 cm$^{-1}$
respectively) to lower frequency than the ir observations. By adding a
constant value of 55 cm$^{-1}$ to the $v_1(H_2O)$ and of 32 cm$^{-1}$ to the $v_1(D_2O)$
Raman data at all temperatures, then the Raman and ir data agreed. The following temperature dependences were observed by Val'kov and Maslenkova (90):

\[
\begin{array}{ccc}
\text{Raman} & \text{IR} \\
\text{cm}^{-1}/\text{oK} & \text{cm}^{-1}/\text{oK} \\
\hline
\Delta v_1 \over \Delta T & 0.254 & 0.26 \\
\Delta v_3 \over \Delta T & 0.246 & 0.24 \\
\Delta (v_1 + v_T) \over \Delta T & 0.222 & 0.20 \\
\hline
\end{array}
\]

\[
D_2O \quad \frac{\Delta v_3}{\Delta T} = 0.198 \\ \\
\frac{\Delta v_1}{\Delta T} = 0.143 \\ \\
\Delta T = 203 - 77^0K = 126^0K.
\]

The equivalence of Raman and IR temperature dependences for \( v_1 \) and \( v_3 \) shows that the hydrogen bond coupling of neighbours was independent of the applied electromagnetic radiation.

There is a potentially interesting extension of these cubic ice I temperature dependences to hexagonal ice I. It is known that the linear thermal expansion coefficients of hexagonal ice I are not equal (60) and that the \( 0\cdots0 \) distances parallel and non-parallel to the \( c \)-axis are not equal, Fig. 4.3. Hence, the temperature dependences of \( R(0\cdots0)_c \), i.e. parallel to the \( c \)-axis, and \( R(0\cdots0)_a \) are not equal and the single crystal spectra of the \( ac \) face of hexagonal ice I, polarized parallel and perpen-
dicular to the c-axis, should be distinguishable. For example, consider the six possible arrangements of the four protons about any one oxygen atom in hexagonal ice,

![Diagram of six possible arrangements of four protons around an oxygen atom](image)

Then the three arrangements 4, 5 and 6 have both protons along the shorter 0····0 distances and will give one band of frequencies. The 1, 2 and 3 arrangements, however, have asymmetric O-H bond lengths leading to a distorted potential and frequencies distinct from cases 4, 5 and 6. The frequencies observed parallel to the c-axis should be intermediate between those observed perpendicular to c and those expected if both protons had the R(0····0) along c.
One can predict the values and temperature dependences for $v_3(H_2O$ and $D_2O)$ of O-H stretches parallel and non-parallel to the hexagonal c-axis. From the temperature dependences of $v_3(H_2O)$ and $v_3(D_2O)$ (Fig. 3.10) and the temperature dependence of $R(0''''0)$ in cubic ice I(Fig. 4.3), one can determine the $R(0''''0) - v_3$ correlations for $H_2O$ and $D_2O$, Fig. 4.12. Then knowing the hexagonal $R(0''''0)_c$ and $R(0''''0)_a$ parameters as a function of temperature one can obtain a set of $v_3(H_2O)$ and $v_3(D_2O)$ frequencies parallel and non-parallel to the c-axis, Fig. 4.13.

For $v_3(H_2O)$ of hexagonal ice one sees that at 150°K the asymmetric stretching frequencies would be 3214 and 3229 cm$^{-1}$ parallel and non-parallel to the c-axis, while at 100°K the values would be 3202 and 3225 cm$^{-1}$. Similarly for $v_3(D_2O)$ the 150°K values are 2417 and 2429 cm$^{-1}$, and the 100°K values are 2411 and 2425 cm$^{-1}$. Ockman (108) was not able to detect the differences at 139°K probably because of the breadth of the bands, i.e. because $\Delta v_3$ is probably greater than 100 cm$^{-1}$, and because of the relatively small split between the bands.

In contrast the bands due to dilute concentrations of HDO in H$_2O$ or D$_2O$ are narrower and absorptions parallel and non-parallel to the hexagonal c-axis should be separable. Sets or predicted $v_{OH}(HDO)$ and $v_{OD}(HDO)$ frequencies in the two directions were determined as above (i.e. from Figs. 3.6 and 4.3) and are plotted in Fig. 4.14. Thus at 150°K $v_{OH}(HDO)$ along a and a should be separated by 16 cm$^{-1}$ and at 100°K by 26 cm$^{-1}$, while $v_{OD}(HDO)$ along c and a would be separated by 11 cm$^{-1}$ and 18 cm$^{-1}$ respectively. Accurate measurement of the differences in the a and c temperature dependences
Fig. 4.12 The correlations of $\nu_3$ of $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ to the $\text{O}\cdots\text{O}$ distances as a function of common temperature. The frequency data were uncorrected for source beam heating.
Fig. 4.13 The calculated $\nu_3$ frequencies of $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ in hexagonal ice I along the c and a axis as a function of temperature.
Fig. 4.14 The calculated $\nu_{OH}$(HDO) and $\nu_{OD}$(HDO) frequencies for HDO in hexagonal ice I and along the c and a axis as a function of temperature.
should yield valuable information on the anisotropic deformation of the hydrogen bond in hexagonal ice I.

(b) The $v_2$ bending mode. Absorptions near $1600 \text{ cm}^{-1}$ and $1200 \text{ cm}^{-1}$ in cubic ice I ($\text{H}_2\text{O}$ and $\text{D}_2\text{O}$) were very near the corresponding vapour phase $v_2$ fundamental absorptions of $1595 \text{ cm}^{-1}$ and $1179 \text{ cm}^{-1}$ respectively. Doubts arose in the previous literature assignments (Tables III.XI and III.XIII) of these ice frequencies to either $v_2$ or $2v_R$, which should nearly coincide. In fact, these absorptions in ice appear to be composite overlapping $v_2$ and $2v_R$ peaks as was previously described (page 112). The inconsistency between the liquid helium and liquid nitrogen cell $v_2$ data (Fig. 3.12) may have arisen from a temperature hysteresis, i.e. the lagging of frequency shift behind the temperature drop during cooling. Zimmermann and Pimentel's (97) results (Fig. 3.12) tend to discount that possibility for $v_2(\text{H}_2\text{O})$. Their results from liquid nitrogen experiments agree with the present results from liquid helium experiments. Much of the disparity in the present results probably arose from reference beam uncompensation for the liquid nitrogen cell data. The strong atmospheric water vapour absorption below $1595 \text{ cm}^{-1}$ and above $1615 \text{ cm}^{-1}$ may have distorted the $v_2(\text{H}_2\text{O})$ ice band severely, while a gap in the vapour spectrum between $1595$ and $1615 \text{ cm}^{-1}$ may have presented an artificial $v_2(\text{H}_2\text{O})$ ice maximum. However, such a maximum would be independent of the ice sample temperature.

For $v_2(\text{H}_2\text{O})$ the liquid nitrogen cell data indicated a low temperature limiting frequency of $1605 \text{ cm}^{-1}$, while the liquid helium cell data indicated a low temperature limiting $v_2$ frequency of $1560 \text{ cm}^{-1}$. Zimmermann and Pimentel's data were extrapolated to near $1570 \text{ cm}^{-1}$. Whalley (96) found the $v_2$ maxima in high pressure $\text{H}_2\text{O}$ ices were above $1680 \text{ cm}^{-1}$ and
argued that $\nu_2(\text{ice}) > \nu_2(\text{vapour})$. However, $2\nu_R$ may be more intense than $\nu_2$ in these cases. Whalley's (96) $\nu_2$ frequency for cubic and hexagonal ice I at 110°K in an isopentane mull was more than 25 cm$^{-1}$ higher than observed here, or by Ockman (108) ($\nu_2 = 1580$ cm$^{-1}$) and Hornig (106) ($\nu_2 = 1585$ cm$^{-1}$). The reflectivities of Whalley's (95,96) mulled samples may have been significantly different than for our condensed samples leading to his higher apparent maxima. However, Ockman found only a small (0.5%) increase in the one percent general reflectivity of crystalline ice over the range 1500 cm$^{-1}$ to 1700 cm$^{-1}$, the maximum reflectivity was at 1575 cm$^{-1}$ at 110°K. It is also possible that sample formation by vapour condensation accentuated the reflectivity, creating an artificial low frequency maximum in our results.

For D$_2$O the liquid helium cell data indicated a low temperature limiting $\nu_2$ frequency of 1189 cm$^{-1}$, however the D$_2$O liquid nitrogen cell experiments were not attempted. The region near 1200 cm$^{-1}$ was free from atmospheric H$_2$O vapour attenuations and the recorded D$_2$O spectrum was free of atmospheric absorption distortions. The D$_2$O observation of 1189 cm$^{-1}$ is greater than the D$_2$O vapour frequency, 1179 cm$^{-1}$. In contrast, Hornig (106) and Ockman (108) observed $\nu_2$(D$_2$O) to be even higher, i.e. near 1210 cm$^{-1}$ at 100 ± 10°K. These D$_2$O results were contrary to our $\nu_2$(H$_2$O) helium data as well as the nitrogen data of others, as noted above. Possibly in D$_2$O the relative positions of $2\nu_R$ and $\nu_2$ are altered from that of H$_2$O, giving a different peak maximum relative to the vapour.

Maximum $\nu_2/2\nu_R$(H$_2$O) absorption was constant over the temperature range 5°K to 70 ± 10°K, while maximum $\nu_2/2\nu_R$(D$_2$O) absorption was constant.
over the temperature range 5°K to 50 + 10°K. The low D$_2$O "freeze-in" temperature of 50°K was probably due to insufficient data. The cubic ice I v$_2$/2v$_R$ band exhibited the same dependence as the stretching modes in this low temperature range, constancy within ± 8 cm$^{-1}$. As a check on hysteresis in this temperature range, detailed observations should be made during fast and slow cooling, i.e. cooling in 10 - 20 min. and 150 - 200 min. respectively. The v$_2$/2v$_R$ absorption also exhibited the same sensitivity to changes in hydrogen bond length (energy) as did the stretching modes, i.e. it was sensitive to changes in R(O----O) greater than 0.0001 Å/°K.

The question of whether v$_2$(ice) is less than or greater than v$_2$ (vapour) is still unanswered. If the v$_2$/2v$_R$(D$_2$O) absorption maximum was due to more intense v$_2$ transitions then v$_2$ ice > v$_2$ vapour. If 2v$_R$(D$_2$O) was the more intense transition then 2v$_R$(D$_2$O) ice > v$_2$(D$_2$O) vapour and v$_2$(D$_2$O) ice may be less than v$_2$ vapour. Positive high temperature dependence indicated the peak maximum was v$_2$ and not 2v$_R$, since v$_R$ (and presumably 2v$_R$) had a negative frequency temperature dependence. The temperature dependence of the v$_2$/2v$_R$ H$_2$O absorption was also positive for either liquid helium or liquid nitrogen data. The maximum of absorption must then be v$_2$(H$_2$O) and 2v$_R$ must be masked. Whether v$_2$(H$_2$O) ice was greater than or less than v$_2$(H$_2$O) vapour could not be unambiguously determined.

Maximum v$_2$/2v$_R$(H$_2$O and D$_2$O) absorptions had approximately linear, positive temperature dependences of 0.37 cm$^{-1}$/°K and 0.15 cm$^{-1}$/°K respectively over the temperature range from 60° to 180°K. In contrast the H$_2$O data of Zimmermann and Pimentel (97) indicated a slope of 0.281 cm$^{-1}$/°K.
in the range from 90°K to 253°K. The relatively small temperature dependence of $v_2/2v_R(D_2O)$ may have resulted from the closer coincidence of $v_2(D_2O)$ and $2v_R(D_2O)$ than in $H_2O$. If the $H_2O$ and $D_2O$ bands had the same structure then their temperature dependences should have been simply related since their changes in $R(O\cdots O)$ were nearly the same.

(iii) The Combination and Overtone Mode Temperature Dependences

(a) The $3v_R$ or $(v_2 + v_R)$ mode. Broad weak absorptions near 2235 cm$^{-1}$ and 1635 cm$^{-1}$ in $H_2O$ and $D_2O$ cubic ice I exhibited temperature dependences of $-0.14$ cm$^{-1}$/°K and $-0.15$ cm$^{-1}$/°K respectively over the temperature range from 30° to 180°K. Both the $H_2O$ and $D_2O$ bands were less than one-half as intense as their corresponding $v_2/2v_R$ bands. First consider the $H_2O$ ice absorption at 2238 cm$^{-1}$. If the absorption arose from a $v_2 + v_R$ transition then the temperature dependence should have been positive, i.e.,

\[
\Delta v_R/\Delta T = -0.17 \text{ cm}^{-1}/\text{°K} \quad \text{and} \quad \Delta v_2/\Delta T = +0.36 \text{ cm}^{-1}/\text{°K},
\]

therefore $(\Delta v_2 + \Delta v_R)/ T = +0.19$ cm$^{-1}$/°K. However, the temperature dependence was observed to be negative. If the absorption arose from a $3v_R$ transition then the temperature dependence should have been negative, i.e., $\Delta (3v_R)/\Delta T = -0.51$ cm$^{-1}$/°K.

As was seen in Fig. 3.17, Pimentel's data (97) agrees well with ours, his slope was $-0.12$ cm$^{-1}$/°K compared to our measured value of $-0.15$ cm$^{-1}$/°K.

The measured $\Delta (3v_R)/ T = -0.15$ cm$^{-1}$/°K was nearly the same as $\Delta v_R/\Delta T = -0.17$ cm$^{-1}$/°K and one-third the predicted rate of $-0.51$ cm$^{-1}$/°K. Anharmonicity increases from the larger amplitudes at increased temperature could not be the source of this result.

Either the 2235 cm$^{-1}$ $H_2O$ absorption was a $v_R$ fundamental, or the $3v_R$ anharmonicity was decreasing with increased temperature, or energy level population redistribution was affecting the results. Such a high
frequency fundamental lattice mode seems unlikely, as do such large effects from populational redistribution. Alternately decreased anharmonicity of \(3v_R\) and \(v_R\) from decreased hydrogen bond energy may be larger than the increased anharmonicity arising from increased amplitude of libration at higher temperatures.

Consider the \(\text{D}_2\text{O}\) absorption at 1637 cm\(^{-1}\) where the same considerations apply as for \(\text{H}_2\text{O}\). Absorption arising from \(\text{D}_2\text{O}(v_2 + v_R)\) transitions would exhibit zero temperature dependence; \(\Delta(v_2 + v_R)/\Delta T = (\Delta v_2/\Delta T) + (\Delta v_R/\Delta T) = +0.15\ \text{cm}^{-1}/^\circ\text{K} - 0.15\ \text{cm}^{-1}/^\circ\text{K} = 0\). The temperature dependence was observed to be distinctly negative, -0.15 cm\(^{-1}/^\circ\text{K}\). In fact \(v_R(\text{D}_2\text{O})\) and the 1637 cm\(^{-1}\) \(\text{D}_2\text{O}\) band had the same observed temperature dependences.

Low temperature limiting \(3v_R\) absorption was 2235 cm\(^{-1}\) for \(\text{H}_2\text{O}\) and 1635 cm\(^{-1}\) for \(\text{D}_2\text{O}\). That implied an approximate \(\text{H}_2\text{O}\) low temperature limiting anharmonicity for \(3v_R(\text{H}_2\text{O})\) (from \(v_R = 833\ \text{cm}^{-1}\)) of -258 cm\(^{-1}\) and for \(3v_R(\text{D}_2\text{O})\) (from \(v_R = 627\ \text{cm}^{-1}\)) of -253 cm\(^{-1}\). The apparent \(\text{H}_2\text{O}\) and \(\text{D}_2\text{O}\) \(3v_R\) anharmonicities were nearly equal. Now the parent transitions underwent considerable isotopic shift: \(v_R(\text{H}_2\text{O}) = 833\ \text{cm}^{-1}\) and \(v_R(\text{D}_2\text{O}) = 627\ \text{cm}^{-1}\). The apparent \(\text{H}_2\text{O}\) anharmonicity of -258 cm\(^{-1}\) represented 11.5 percent of the observed absorption band frequency, 2235 cm\(^{-1}\). The increased \(\text{D}_2\text{O}\) percent anharmonicity was unexpected for the mass substitution made. For example, in the vapour phase the anharmonicity of \(\text{H}_2\text{O}\) \(x_{11} = -43.8\ \text{cm}^{-1}, x_{22} = -19.5\ \text{cm}^{-1}, x_{33} = -46.4\ \text{cm}^{-1}\) is almost halved in \(\text{D}_2\text{O}\) \(x_{11} = -22.8\ \text{cm}^{-1}, x_{22} = -10.44\ \text{cm}^{-1}, x_{33} = -24.9\ \text{cm}^{-1}\) for \(v_1, v_2,\) and \(v_3 (124)\), since the amplitudes of \(\text{D}_2\text{O}\) motion are smaller. Similar behaviour was expected for the solid, but the observed \(3v_R(\text{D}_2\text{O})\) anharmonicity was not one-half that of \(3v_R(\text{H}_2\text{O})\).

Thus the large shifts of \(3v_R\) below the expected frequencies cannot be simply
explained as anharmonicities.

The large shifts of $3\nu_R$($\text{H}_2\text{O}$, $\text{D}_2\text{O}$) below the expected frequencies ($3\nu_R$ observed = 2235 cm$^{-1}$, $3\nu_R = 3(833) = 2499$ cm$^{-1}$) may arise from different maximum transition moments for the band of ground state librational energies for the $\nu_R$ and $3\nu_R$ transitions. The extreme case is: molecules occupying the higher energies of the band have maximum transition moments for $(0 \rightarrow 1)$ transitions and minimum transition moments for $(0 \rightarrow 3)$ transitions, while molecules occupying the lower energies of the band have minimum transition moments for $(0 \rightarrow 1)$ transitions and maximum transition moments for $(0 \rightarrow 3)$ transitions. The maximum of the $(0 \rightarrow 1)\nu_R$ transition would occur above the center of the energy band and the maximum of the $(0 \rightarrow 3)\nu_R$ transition would occur below the center of the energy band. In support of this recall that the $\nu_R$ absorption had a $\Delta\nu_R$ of about 125 cm$^{-1}$, indicating a very large librational energy range.

Data on $3\nu_R$ from spectra recorded during warm-up from 5°K to 60°K showed that the $3\nu_R$ energy level had the same sensitivity to hydrogen-bond changes as the internal modes, i.e. it was insensitive to changes in hydrogen-bond energy from changes in $R(0 \cdots 0)$ that were less than 0.0001 Å/°K. Data from the liquid nitrogen and liquid helium cells agreed satisfactorily. The $3\nu_R$ freeze-in temperatures for $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$, $70 \pm 10$°K, concurred with previous data.

(b) The $(\nu_1 + \nu_2)$ band. The high frequency shoulder on the cubic ice I stretching band had low temperature limits of 3334 and 2464 cm$^{-1}$ for $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ respectively (Table III.IX). Those frequencies are 201 and 144 cm$^{-1}$ higher than the low temperature limiting low frequency shoulders at 3133 and 2320 cm$^{-1}$ respectively. The high temperature dependences of the high frequency shoulders were 0.20 and 0.17 cm$^{-1}$/°K, compared
to 0.34 and 0.19 cm$^{-1}/°K$ for the low frequency shoulders (Table III.IX). If the high frequency shoulders are in fact due to ($v_1 + v_T$) transitions then the $v_1$ to ($v_1 + v_T$) displacement should have been 229 cm$^{-1}$ (observed 201 cm$^{-1}$) for H$_2$O and the temperature dependence of ($v_1 + v_T$) of H$_2$O should have been approximately $(\Delta v_1/\Delta T) + (\Delta(v_1 + v_T)/\Delta T)$ or $(0.34 - 0.10)$ cm$^{-1}/°K$. That value of 0.24 cm$^{-1}/°K$ agrees well with the observed $v_1 + v_T$ value of 0.20 cm$^{-1}/°K$. For D$_2$O the high frequency shoulder appears to be composed of $v_1$(D$_2$O) and the LA translational mode near 160 cm$^{-1}$. The temperature dependence of $v_T$(D$_2$O) is not known however.

(iv) The Half-Height Widths Temperature Dependences

The temperature dependence of the composite stretching region band half-height width was positive (page 66), as expected. There appear to be two sources of the increasing width. One obvious effect common to all the modes was the increase in the amplitudes of vibration. A second source of broadening arose from increasing $R(0\cdots0)$: The increasing range of $0\cdots0$ distances gave a larger range of hydrogen bond energies and a broader range of possible transitions. Above 160°K (Fig. 3.4) the $\Delta(v_1, v_3, v_1 + v_T)$ data are not reliable since sample sublimation had a pronounced effect.

The observed temperature dependence of $\Delta(v_R, v_R + v_T)$ (Fig. 3.4) may have been anomalous. The scatter of data points was nearly as large as the range of points between 100°K and 200°K: The high temperature data was just outside the error limits of the low temperature data. As well, the temperature dependence of $\Delta(v_R, v_R + v_T)$ seems to be too small. It would be interesting to study the origin of $v_R$ in the solid, liquid and
vapour phases about the triple point as well as the origin of \( \nu_R \) as the critical point is approached from the vapour phase.

The temperature of \( \Delta(\nu_2, 2\nu_R)^{\frac{1}{2}} \) (Fig. 3.5) was opposite to that of \( \Delta(\nu_R, \nu_R + \nu_T)^{\frac{1}{2}} \) and \( \Delta(\nu_1, \nu_3, \nu_1 + \nu_T)^{\frac{1}{2}} \) in the amorphous and cubic ice I phases. An explanation was given in section 4.1C(i) (page 111).

4.3 Assignments of the Cubic Ice I Absorption Bands

A. The Fundamental Lattice Modes

(i) The Translational Modes

Two peaks (162 and 227.8 cm\(^{-1}\)) and three shoulders (191, 267 and 296 cm\(^{-1}\)) were observed at 93\(^\circ\)K for \( H_2O \) cubic ice I. The features of the band differed only slightly from those of Bertie and Whalley (88). In this work no calculations were made which disagreed with the assignments of Bertie and Whalley.

(ii) The librational Modes

The low temperature limiting frequencies of the observed librations are in the ratio, \( \nu_R/(\nu_R + \nu_T) = 0.963 \). That compares to the same ratios in \( H_2O \) and \( D_2O \) of 0.9444 and 0.953 respectively. The peak to shoulder separations at 10\(^\circ\)K were:

\[
\begin{align*}
[(\nu_R + \nu_T) - \nu_R]_{H_2O} & = 50 \pm 5 \text{ cm}^{-1} \\
[(\nu_R + \nu_T) - \nu_R]_{HDO} & = 33 \pm 1.5 \text{ cm}^{-1} \\
[(\nu_R + \nu_T) - \nu_R]_{D_2O} & = 31 \pm 5 \text{ cm}^{-1}
\end{align*}
\]
If the shoulder did arise by a combination transition of $\nu_R$ (HDO) and $\nu_T$ (host), then the value of $\nu_T$ to apply to HDO is that of the host D$_2$O since at a concentration of 4.0\% HDO in D$_2$O the lattice dynamics must surely be dominated by the D$_2$O molecules for any reasonable model. The fact that the D$_2$O peak to shoulder separation is 31 cm$^{-1}$ supports this conclusion. As well, the peak to shoulder separations of pure D$_2$O and of HDO in D$_2$O agree well. Presumably HDO in H$_2$O should have a $\nu_R$ peak to ($\nu_R + \nu_T$) shoulder separation of about 50 cm$^{-1}$. However, that has not been observed yet by any workers.

Recent work by Trevino (93) quoted experimental data of neutron inelastic scattering from hexagonal ice I and compared that data to the results of a theoretical model based on cubic ice I. His hypothesis noted that the Raman and ir observations from 50 to 3500 cm$^{-1}$ are the same for cubic and hexagonal ice I, and assumed that the basic dynamical lattice unit of cubic ice (one O atom surrounded tetrahedrally by 4 others) was a suitable model for hexagonal ice. That is supported by the fact that the nearest-neighbour configurations are the same. Trevino's (93) theory also assumed that the protons are in ordered positions, which they are not. However, the basic translational unit in ice is the O atom and the orientation of protons is relatively insignificant in this case.

For hexagonal ice I at 150°K the neutron inelastic scattering experiments (93) demonstrated lattice maxima at 63 cm$^{-1}$ (TA) depending on the assignment of peaks. Other workers (92) found (for H$_2$O hexagonal ice I at 261°K) lattice modes at 60 and 70 cm$^{-1}$. Clearly there exists a high density of H$_2$O translational states near 50 ± 10 cm$^{-1}$ at 150°K for hexagonal H$_2$O ice I. The corresponding modes for D$_2$O cubic ice I at 10°K may be lower than 50 cm$^{-1}$ since the mass difference would shift the frequency
to $0.9484 \times 50 \text{ cm}^{-1} = 47.5 \text{ cm}^{-1}$.

The observed neutron band width in $\text{H}_2\text{O}$ was $50 \text{ cm}^{-1}$. Of the broad band of real translational frequencies, the maximum transition moments do not have to occur over the same sections of the band for IR absorption and neutron inelastic scattering. The IR transition moment maximum may lie at lower frequencies than the neutron scattering transition moment maximum. Further, the overlap in the IR of $v_R$ and $(v_R + v_T)$ brings the instrumentally traced, summed absorptions closer together, i.e. if $v_R$ and $(v_R + v_T)$ could be resolved completely their peak positions would be separated by more than 50, 33 and 31 cm$^{-1}$ for $\text{H}_2\text{O}$, $\text{HDO}$ and $\text{D}_2\text{O}$ respectively. One may conclude that a single librational mode and a combination librational-translational mode were observed for $\text{HDO}$. Since $v_{Rx}$ and $v_{Ry}$ are expected to be about equally intense, and since only one band was observed, then $v_{Rx}$ and $v_{Ry}$ must be exactly or nearly degenerate. The same conclusions seem appropriate for $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$.

B. The Fundamental Molecular Modes

(i) The Stretching Modes

There are many conflicting assignments of the three main IR absorption features near 3200 cm$^{-1}$ for $\text{H}_2\text{O}$ and 2400 cm$^{-1}$ for $\text{D}_2\text{O}$. Ockman (108) assigned the low frequency shoulder to $v_1$, the main peak to $v_3$, and the high frequency shoulder to $(v_3 + v_T)$, while Hornig et al. (105) assigned the three bands as $2v_2$, $v_3$, and $v_1$. In contrast, Bertie and Whalley (95) assigned the low frequency shoulder and the main peak as a pair of bands composed of coupled $v_1 - v_3$ vibrations, and they eliminated the distinction
between \( v_1 \) and \( v_3 \) absorption bands of H\(_2\)O and D\(_2\)O. We propose that the low frequency shoulder is \( v_1 \), the main peak is \( v_3 \) and the high frequency shoulder is \((v_1 + v_T)\) in agreement with the Raman results of Val'kov and Maslenkova (99) and as Ockman (108) interpreted them.

The stretching frequencies of HDO do not lie at the positions expected on the basis of H\(_2\)O and D\(_2\)O shifts in cubic ice I. This result will be discussed in terms of a theory proposed by Pimentel and Hrostowski (101) and Hornig and Hiebert (102) in the early 1950's: They suggested that the two major effects on molecular vibrations in solids, crystal-field perturbations and inter-molecular coupling, were separable by dilute isotopic substitution.

(a) The H\(_2\)O and D\(_2\)O stretching modes. For the Raman spectra of hexagonal ice I Val'kov and Maslenkova (99) found peaks at 3088, 3210 and 3321 cm\(^{-1}\) of relative intensities 10:4:2. The 3088 cm\(^{-1}\) peak had a polarization ratio of less than 0.75, while the 3210 cm\(^{-1}\) peak was depolarized. The 3088 cm\(^{-1}\) Raman peak was unambiguously of \( a_1 \) symmetry, i.e. the \( v_1 \) symmetric stretch mode.

The suggestion of Bertie and Walsley (95,96) that \( v_1 \) and \( v_3 \) are coupled and indistinguishable cannot be entirely correct. If the \( v_1 \) and \( v_3 \) bands of coupled vibrators were largely mixed into two bands equally of \( v_1 \) and \( v_3 \) character, then the same set of energy levels would have been present for both the Raman and ir transitions, however the selection rules would change. For the mixed energy levels one would expect equally intense peaks at 3088 and 3210 cm\(^{-1}\), contrary to the 10 to 4 observed intensity ratio. Hence the \( v_1 \) and \( v_3 \) energy levels appear to be separated (lack of
non-resonant coupling) while \( \nu_1 - \nu_1 \) and \( \nu_3 - \nu_3 \) resonance coupling of neighbours may still be effective.

There remains the problem of the disparity between the \( \nu_1 \) ir and Raman frequencies, at 100 \( \pm \) 10\(^\circ\)K, i.e. \( \nu_1 \) (ir) = 3149 cm\(^{-1}\) and \( \nu_1 \) (Raman) = 3088 cm\(^{-1}\) at 100 \( \pm \) 10\(^\circ\)K. Similarly in D\(_2\)O ice I the \( \nu_1 \) results were 2321 and 2291 cm\(^{-1}\) respectively. Recall that both the symmetric and asymmetric stretching modes appear to be very broad bands due to \( \nu_1 - \nu_1 \) and \( \nu_3 - \nu_3 \) resonance coupling. Of the complete set of \( \nu_1 \) energy levels, the same portions of the band need not be both Raman and ir active nor with the same intensity factor. Thus for the Raman scattering only a narrow band in the lower one-half of the \( \nu_1 \) band was active while for the ir a large range of frequencies was observed and the maximum intensity occurred at a higher frequency. For the asymmetric \( \nu_3 \) mode the same portions of the band of frequencies was ir and Raman active. This may indicate a fundamental difference in \( \nu_1 - \nu_1 \) and \( \nu_3 - \nu_3 \) resonance coupling.

Thus the Raman scattering from hexagonal ice I indicated that in the ir absorption spectra the low frequency shoulder was \( \nu_1 \) and the main peak was \( \nu_3 \), i.e. \( \nu_3 \) (H\(_2\)O) = 3210 cm\(^{-1}\) and \( \nu_3 \) (D\(_2\)O) = 2413 cm\(^{-1}\). By assuming that the two \( \nu_3 \) assignments are correct, then the ratio of \( \nu_3 \) (ice)/\( \nu_3 \) (vapour) is 0.8546 for H\(_2\)O and 0.8655 for D\(_2\)O. If the effects of hydrogen bonding are the same on all O-H bonds, then \( \nu_1 \) and \( \nu_3 \) are expected to be in the same order as in the vapour phase and should have the same relative displacements from the vapour phase frequencies, Fig. 4.15. The \( \nu_3 \) (H\(_2\)O) cubic ice I absorption (3210 cm\(^{-1}\)) is 0.8546 times the \( \nu_3 \) (H\(_2\)O) vapour frequency (3756 cm\(^{-1}\)). In order to preserve the displacement due to hydrogen bonding
Fig. 4.15 The observed vapour phase and cubic ice I phase. H$_2$O, HDO and D$_2$O frequencies are shown as solid horizontal lines. The ratios of $\nu_3$(ice)/$\nu_3$(vapour) are shown on the diagonal solid lines. The H$_2$O, HDO and D$_2$O ice frequencies predicted with those ratios are shown as dotted horizontal lines.
then the $v_1^p(H_2O)$ ice (where p stands for predicted) frequency would have to be $0.8546 \times 3657 \text{ cm}^{-1} = 3125 \text{ cm}^{-1}$, compared to the observed $v_1(H_2O)$ frequency of $3149 \text{ cm}^{-1}$. By similar arguments $v_1^p(D_2O) = 0.8655 \times 2671 \text{ cm}^{-1} = 2313 \text{ cm}^{-1}$, compared to the observed value of $2321 \text{ cm}^{-1}$. The predicted $v_1$ frequencies, which preserved the relative effects of hydrogen bonding on $v_3$ and $v_1$, agree very well with the observed ir results. The agreement is probably better than indicated since the observed ir $v_1$ band was shifted to higher frequency by overlap with the adjacent $v_3$ band.

The alternate assignment of observed ice peaks which also retains the $v_1 - v_3$ order is $v_1 = 3210 \text{ cm}^{-1}$ and $v_3 = 3340 \text{ cm}^{-1}$. The ratio of $v_3(\text{ice})/v_3(\text{vapour})$ is then $0.8858$ and the predicted $v_1^p$ frequency is $3253 \text{ cm}^{-1}$, compared to the ir result, $v_1 = 3210 \text{ cm}^{-1}$. Neither the $v_1^p(H_2O)$ nor the $v_1^p(D_2O)$ frequency was a good approximation to an observed ir band. The second assignments of $v_1$ and $v_3$ were rejected.

The reasonable assumption of equal effects on $v_1$ and $v_3$ due to hydrogen bonding gives predicted frequencies in good agreement with observed features. The accepted assignments were $v_1 = 3149 \text{ cm}^{-1}$ and $v_3 = 3210 \text{ cm}^{-1}$, while the $3340 \text{ cm}^{-1}$ shoulder was probably $(v_1 + v_T)$.

(b) The HDO stretching modes. Use of dilute isotopic substitution to separate the crystal field and resonance coupling perturbations (101,102) was originally suggested for studying the molecular vibrations of DC1 under the influence of an HCl crystal field, but in the absence of intermolecular resonance coupling. The extensions of that concept to polyatomic molecules, which have more than one normal coordinate and where rapid isotopic exchange may occur, has led to some misinterpretations of experimental results, i.e. as in H$_2$O in D$_2$O (106,95). Because of the rapid isotopic exchange it
is impossible to isolate D$_2$O in H$_2$O or H$_2$O in D$_2$O at low concentrations. One obtains a dilute solution of HDO and very, very dilute residues of H$_2$O or D$_2$O. Now HDO has C$_5$ molecular symmetry and three internal coordinates, an OH stretch, an O-D stretch and an HOD bend. It is unreasonable to expect both of the HDO stretching modes to be completely uncoupled from the stretching modes of the H$_2$O or D$_2$O lattice. Just such an assumption by Hornig et al. (106) and by Bertie and Whalley (95) has resulted in misinterpretation of the ice I HDO ir results.

As a first approximation to ice I, consider the ir observations for HDO, H$_2$O and D$_2$O in the vapour phase, Fig. 4.15. One HDO stretching mode lies almost exactly midway between $v_3$ and $v_1$ of H$_2$O, while the other HDO stretch is observed nearly midway between $v_3$ and $v_1$ of D$_2$O. That is entirely understandable since the symmetric and asymmetric H$_2$O modes may be considered as constructed from a basis of two isolated O-H (HDO) stretches which interact weakly. Hornig et al. (105,106) claimed that such a picture of the H$_2$O and D$_2$O potentials should extend to the solid as well, i.e. in ice I they expected the HDO modes to lie between the $v_1/v_3$ modes of H$_2$O and D$_2$O. For ice I (Fig. 4.15) $v_{OH}$(HDO) was observed between two ir H$_2$O features, while $v_{OD}$(HDO) was almost coincident with a central ir D$_2$O feature. Ignoring the weight of Raman data to the contrary, Hornig et al. assigned $v_3$(H$_2$O) to 3210 cm$^{-1}$ and $v_1$(H$_2$O) to 3360 cm$^{-1}$ with $v_{OH}$(HDO) between them at 3275 cm$^{-1}$. Their central aim appears to have been the preservation of the $v_{OH}$(HDO) observed position between $v_3$ and $v_1$ of H$_2$O.

Bertie and Whalley's (95) discussion of the relationships between HDO, H$_2$O and D$_2$O stretches was confusing. They also assumed the nature of the H-OD (in D$_2$O) stretch was the same as the H-OH(in H$_2$O) stretch.
The above ratios of $v_3(\text{ice})/v_3(\text{vapour})$ for H$_2$O and D$_2$O (Fig. 4.15) yield interesting results when applied to HDO (vapour) frequencies. The observed vapour phase frequencies of HDO stretching are 3707 and 2727 cm$^{-1}$. The predicted HDO frequencies using the H$_2$O and D$_2$O $v_3$ ratios (0.8546 and 0.8655) are $v_{OH}^{P}(\text{HDO}) = 3168$ cm$^{-1}$ and $v_{OD}^{P}(\text{HDO}) = 2360$ cm$^{-1}$ compared to the observed HDO frequencies of 3263 cm$^{-1}$ and 2413 cm$^{-1}$ respectively. Thus the predicted frequencies lie close to the $v_1 - v_3$ mid-points, in agreement with the concept of Hornig et al. (105,106), but do not agree with the observed HDO frequencies.

On the basis of our assignments the observed $v_{OH}^{\text{HDO}}$ stretch (Fig. 4.16) was outside and above the $v_1 - v_3$ interval of pure H$_2$O. Correspondingly, the $v_{OD}^{\text{HDO}}$ stretch was just above $v_3(\text{D}_2\text{O})$, Fig. 4.16. A clear explanation of the mispositioning of the HDO stretches can be found by considering the coupling of HDO to H$_2$O and D$_2$O lattices.

Consider the case of 4.0% HDO in a D$_2$O cubic ice I lattice. Of the two HDO stretches only $v_{OD}^{\text{HDO}}$ can undergo reasonably strong near-resonance coupling to $v_3(\text{D}_2\text{O})$: $v_{OH}^{\text{HDO}}$ is "uncoupled" from the lattice vibrations. One then compares the observed $v_{OH}^{\text{HDO}}$ to $v_1$ and $v_3$ of H$_2$O on the assumption of equal hydrogen bond effects, Fig. 4.16. However, $v_{OH}^{\text{HDO}}$ lies 86 cm$^{-1}$ above the $v_1 - v_3(\text{H}_2\text{O})$ midpoint. A possible explanation is a lengthened DO-H···OH$_2$ distance due to the very process of uncoupling. For example the covalent character of the hydrogen bond is dependent upon an equal sharing of $e^-$ among the overlapped orbitals. If the orbital following of $e^-$ about vibrating nuclei is not at the same rate then the hydrogen bond may be weakened.
The relative positions of the observed H$_2$O, HDO and D$_2$O stretching vibrations are shown as horizontal solid lines. The expected positions of the HDO absorptions before and after the effects of uncoupling, are shown as dotted horizontal lines.
From section 4.2A(ii) we found that $\Delta \nu_{\text{OH}}/\Delta R(0\cdots0) = 1.921 \text{ cm}^{-1}/\text{Å}$. Hence, a $\Delta \nu_{\text{OH}}$ of 86 cm$^{-1}$ implies the D0H-D$_2$O $R(0\cdots0)$ distance was longer than "expected" by 0.045 Å. Correspondingly the HOD-D$_2$O $R(0\cdots0)$ distance should have been shorter than expected by 0.045 Å and $\nu_{\text{OD}}$ (HDO in D$_2$O) would have been 58 cm$^{-1}$ lower than expected (but it was unobservable lying under $\nu_1(D_2O)$), at 2311 cm$^{-1}$. (The $\nu_1 - \nu_3$ midpoints are 3180 and 2367 cm$^{-1}$ for H$_2$O and D$_2$O respectively.)

For 5.94% HDO in H$_2$O $\nu_{\text{OD}}$(HDO) was found at 2416 cm$^{-1}$, 49 cm$^{-1}$ above the center of $\nu_1 - \nu_3(D_2O)$ for cubic ice I, Fig. 4.16. That implies the uncoupling had lengthened $R(0\cdots0)$ for HO-D····H$_2$O by 0.038 Å. Similarly $R(0\cdots0)$ for DO-H····H$_2$O must have been shorter by 0.038 Å and $\nu_{\text{OH}}$ (HDO) would have been lower than normal by 73 cm$^{-1}$, at 3107 near $\nu_1(H_2O)$.

For HDO in H$_2$O and D$_2$O the point is that one HDO mode was coupled to the lattice and the other was uncoupled: The act of uncoupling weakened the hydrogen bond, lengthened one $R(0\cdots0)$ and shortened the other three $R(0\cdots0)$ of HDO. Consequently the uncoupled frequency was shifted to higher frequency and the other was shifted to lower frequency.

Our explanation of the observed positions of HDO frequencies in relation to the H$_2$O and D$_2$O frequencies cannot be readily confirmed by any meaningful calculation or conceived experiment. However it serves to point out an important fact in dilute isotopic substitution studies in solids: The molecules of mixed analogues are not all uncoupled from the lattice. The method is not generally useful nor applicable to molecules with mixed isotopes unless one recognizes that unusual effects can occur.
(ii) The Bending Mode

The position of the 1570 (1604) cm$^{-1}$ H$_2$O cubic ice I absorption (Table III.XI) indicates it could be either $v_2$ or $2v_R$ and possibly overlapping $v_2/2v_R$ absorptions. The vapour phase $v_2$(H$_2$O) frequency is 1595 cm$^{-1}$. The frequency shift upon annealing was to lower frequency (Fig. 3.2) a characteristic of molecular modes and thus favours the $v_2$ assignment. As well, the cubic ice I frequency shift was to higher frequency and similarly favoured $v_2$. However the half-height width increased upon annealing and for cubic ice I it decreased with increasing temperature (Figs. 3.12 and 3.15 and page 67). That data favours a combined $v_2/2v_R$ absorption. The $v_2$ absorption was more intense than the underlying $2v_R$ and was probably centered below 1595 cm$^{-1}$, i.e. near 1570 cm$^{-1}$. Similarly for D$_2$O the $v_2/2v_R$ band was found at 1194 cm$^{-1}$.

C. The Overtone and Combination Modes

(i) The 3$v_R$ Modes

The 2235 cm$^{-1}$ H$_2$O and 1635 cm$^{-1}$ D$_2$O absorptions have been interpreted as both 3$v_R$ and $v_2 + v_R$ (Table 0.5). The bands shifted to higher frequency upon annealing and as cubic ice I the frequencies shifted down (Figs. 3.2 and 3.17): Both of those facts indicate a lattice mode and we assign the absorption to 3$v_R$. However, there is at least one disconcerting factor, the relative intensities of $v_R$, $2v_R$ and 3$v_R$ that were observed. One expects the overtone intensities to fall very rapidly and thus the intensity of 3$v_R$ should be much less than 2$v_R$. However the 3$v_R$ absorption is only about 1/4 less intense than the combined $v_2/2v_R$ absorption, and
that indicates that $2\nu_R$ is less intense than $3\nu_R$. However, the interpretation in terms of individual molecular librations is weak and a complete solid state treatment is necessary.

(ii) The $(\nu_1 + \nu_T)$ Mode

The shoulder at 3340 cm$^{-1}$ in H$_2$O and 2465 cm$^{-1}$ in D$_2$O cubic ice I has been variously assigned as $\nu_1$, $\nu_3 + \nu_T$ and $\nu_1 + \nu_T$ (Table 0.5). Our previous discussion on the stretching modes of H$_2$O, D$_2$O and HDO (page 181) eliminated the $\nu_1$ assignment. The peak to high-shoulder separation ($\nu_3$ to "$\nu_3 + \nu_T"$) is 130 cm$^{-1}$ while the low to high frequency shoulder separation ($\nu_1$ to "$\nu_1 + \nu_T"$) is 191 cm$^{-1}$. The latter separation lies closer to our observed $\nu_T$(H$_2$O) band maximum and favours the $\nu_1 + \nu_T$ assignment. In addition, the Raman data (99) favours a $\nu_1 + \nu_T$ assignment on the basis of frequency separation and relative intensities, i.e. the relative $\nu_1$, $\nu_3$ to $\nu_1 + \nu_T$ intensities are 10:4:2.

4.4 The Librations of HDO, H$_2$O and D$_2$O

A. The Moments-of-Inertia Models

Past treatments of the librational lattice modes of the ices have dwelt upon the association of the librations to free rotation of oriented-gas or gas phase molecules (85,89). Implicit in such treatments have been comparisons of the moments-of-inertia (I) about the three principal axes of H$_2$O, HDO and D$_2$O. Blue (85) was the first to evaluate the librational frequencies through moments-of-inertia. We have extended the calculations
to include weighted lone-pair orbital contributions to the moments.

(i) The Non-Interacting Molecules Model

The molecular parameters and the positions of the principal axes are shown in Fig. 4.17. The moments-of-inertia are given in Table IV.II as well as the differences between the HDO, H\textsubscript{2}O and D\textsubscript{2}O moments. Under the molecular symmetries, librations about the H\textsubscript{2}O and D\textsubscript{2}O z-axes are ir inactive, while libration of HDO about z is ir active due to the loss of C\textsubscript{2v} symmetry and the orientation of the molecular dipole at 17°5 4' to the z-axis. However, \( \nu_{Rz}(\text{HDO}) \) is expected to be weak compared to \( \nu_{Ry} \) and \( \nu_{Rx} \) due to the small dipole reorientation. Notice that \( \nu_{Rx}(\text{HDO}) \) gives asymmetrically bent O-H\cdots O and O-D\cdots O hydrogen bonds. The D atom sweeps 0.004 Å/deg arc while the H atom sweeps 0.012 Å/deg arc in a classical approach.

The HDO moments are split between the H\textsubscript{2}O and D\textsubscript{2}O moments-of-inertia, Table IV.II. Hornig et al. (105) pointed out that on the basis of moments-of-inertia the observed HDO librations would be expected to split between the H\textsubscript{2}O and D\textsubscript{2}O librational frequencies. From the differences in the moments one sees that \( I_x(\text{HDO}) \) is nearer \( I_x(\text{H}_2\text{O}) \), \( I_z(\text{HDO}) \) is nearer \( I_z(\text{D}_2\text{O}) \), and \( I_y(\text{HDO}) \) is midway between \( I_y(\text{H}_2\text{O}) \) and \( I_y(\text{D}_2\text{O}) \). It does not necessarily follow that the HDO librational frequencies will be observed in a corresponding manner.

HDO librational absorption was observed here only for HDO in a D\textsubscript{2}O matrix: One peak and one shoulder were observed at 823 cm\textsuperscript{-1} and 856 cm\textsuperscript{-1} respectively (page 74). Assuming that the librational frequencies for HDO, H\textsubscript{2}O and D\textsubscript{2}O can be defined by a single function such as Blue's...
Fig. 4.17 The principal axes of H$_2$O, HDO and D$_2$O and their molecular parameters. The angles were assumed to be tetrahedral.

(page 27) then $v_{Rx}(HDO)$ should be relatively weakly coupled to any libration of the D$_2$O lattice since the HDO and D$_2$O librational frequencies observed were about 90% separated.

One of the absorptions at 856 and 823 cm$^{-1}$ must contain at least $v_{Rx}(HDO)$ since it has the lowest moment-of-inertia and is expected to be closest to the H$_2$O values. The other feature above cannot be due to $v_{Ry}(HDO)$ or $v_{Rz}(HDO)$ since the peak-shoulder separation was too small,
Table IV.II  The moments-of-inertia of H$_2$O, HDO and D$_2$O and a comparison of HDO to H$_2$O and D$_2$O. The parameters used to calculate the principal moments-of-inertia are given in the text.

<table>
<thead>
<tr>
<th></th>
<th>H$_2$O</th>
<th>D$_2$O</th>
<th>HDO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_x$</td>
<td>$0.89 \times 10^{-40}$</td>
<td>$1.61 \times 10^{-40}$</td>
<td>$1.08 \times 10^{-40}$</td>
</tr>
<tr>
<td>$I_y$</td>
<td>2.91</td>
<td>5.63</td>
<td>4.23</td>
</tr>
<tr>
<td>$I_z$</td>
<td>2.01</td>
<td>4.02</td>
<td>3.15</td>
</tr>
</tbody>
</table>

units gms-cm$^2$/molecule

Comparison of moments

$I_x$(HDO) - $I_x$(H$_2$O) = $0.19 \times 10^{-40}$  
$I_x$(D$_2$O) - $I_x$(HDO) = $0.53 \times 10^{-40}$

$I_y$(HDO) - $I_y$(H$_2$O) = 1.32  
$I_y$(D$_2$O) - $I_y$(HDO) = 1.40

$I_z$(HDO) - $I_z$(H$_2$O) = 1.14  
$I_z$(D$_2$O) - $I_z$(HDO) = 0.87

33 cm$^{-1}$. As mentioned earlier, the shoulder appears to be due to ($v_R + v_T$) absorption.

Alternately the peak and shoulder may have resulted from nearly degenerate $v_{Rx}$(HDO) and $v_{Ry}$(HDO) absorptions. Such an event implies that either $I_x$ and $I_y$ of HDO are degenerate through coupling, or that the librations cannot be treated on the basis of moments-of-inertia. Both of these possibilities will be treated in detail.
Assume that the librations of HDO, H₂O and D₂O can be simply related to the principal moments-of-inertia by Blue's (85) formula (page 27). Since the oxygen atoms lie close to each of the principal axes then the \( r_{0n}^2 \) are all small and since the restoring forces on the oxygen atoms are all small then Blue's equation reduces to:

\[
\nu_{Rn} (\text{cm}^{-1}) = \frac{1}{2\pi c_n} \left[ \frac{1}{2} (k_{H1n} r_{H1n}^2 + k_{H2n} r_{H2n}^2) \right]^{1/2}
\]

where: \( \nu_{Rn} \) is the librational frequency about axis \( n \)

\( k_{H1n} = k_{H2n} = k_H \) on the basis of symmetry

and \( r_{H1n}^2 \) is the distance of atom \( H_1 \) normal to axis \( n \).

Using the calculated moments-of-inertia from Table IV.II one obtains the librational frequencies in terms of the \( k_H \) force constants:

- \( \nu_{R_X} (H_2O) = 2.45 k_H \)
- \( \nu_{R_Y} (H_2O) = 2.77 k_H \)
- \( \nu_{R_Z} (H_2O) = 2.90 k_H \)
- \( \nu_{R_X} (HDO) = 2.60 k'_H \)
- \( \nu_{R_Y} (HDO) = 2.33 k'_H \)
- \( \nu_{R_Z} (HDO) = 2.23 k'_H \)
- \( \nu_{R_X} (D_2O) = 1.83 k_D \)
- \( \nu_{R_Y} (D_2O) = 1.99 k_D \)
- \( \nu_{R_Z} (D_2O) = 2.05 k_D \)

It is implicit in this treatment that the three librations of each molecule are non-degenerate. On the basis of the above equations the lowest observed frequencies of H₂O and D₂O must be associated with the \( \nu_{R_X} \)'s since they have the lowest force constant coefficients: Thus \( \nu_{R_X} (H_2O) = 833 \text{ cm}^{-1} \), and \( \nu_{R_X} (D_2O) = 627 \text{ cm}^{-1} \). Using those frequencies the force constants are

\[
k_H(H_2O) = (1.15 \pm 0.03) 10^5 \text{ dynes/cm}
\]

\[
k_D(D_2O) = (1.17 \pm 0.03) 10^5 \text{ dynes/cm}
\]

For HDO, \( \nu_{R_Y} (HDO) \) has the smallest force constant coefficient and we assign that (on a trial basis) to the 819 cm⁻¹ peak. Then the HDO force constant,
\( k_H \), is \((1.24 \pm 0.03) \times 10^5 \) dynes/cm, in reasonable agreement with the \( H_2O \) and D\(_2\)O force constants. By applying the above three force constants to the remaining functions one obtains the following set of frequencies:

<table>
<thead>
<tr>
<th></th>
<th>( H_2O )</th>
<th>HDO</th>
<th>D(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_{Rx} )</td>
<td>833 cm(^{-1})</td>
<td>916 cm(^{-1})</td>
<td>627 cm(^{-1})</td>
</tr>
<tr>
<td>( \nu_{Ry} )</td>
<td>940 _ _</td>
<td>819 _ _</td>
<td>682 _ _</td>
</tr>
<tr>
<td>( \nu_{Rz} )</td>
<td>984 _ _</td>
<td>785 _ _</td>
<td>702 _ _</td>
</tr>
</tbody>
</table>

where the observed frequencies which were used to define the force constants are underlined. Since libration about the \( y \) principal axis entails a greater distortion of one HDO hydrogen bond than for \( \nu_{Rx} \) of \( H_2O \) and D\(_2\)O then the slightly larger HDO force constant is understandable.

Of the nine frequencies listed above three were assigned from experimental observation. From the remaining six frequencies, two were expected to be ir inactive (i.e. \( \nu_{Rz}(H_2O) \) and \( \nu_{Rz}(D_2O) \)) while a third one (\( \nu_{Rz}(HDO) \)) is expected to be very weak. That leaves three predicted frequencies to compare with experiment: \( \nu_{Ry}(H_2O) \), \( \nu_{Rx}(HDO) \) and \( \nu_{Ry}(D_2O) \). Only the prediction of \( \nu_{Ry}(D_2O) \) at 682 cm\(^{-1}\) lies near an observed band, the D\(_2\)O cubic ice I band at 661 cm\(^{-1}\). However, even that prediction is out by more than 20 cm\(^{-1}\). As well, there were no observed absorptions near the 940 cm\(^{-1}\) or 916 cm\(^{-1}\) predicted frequencies. Therefore, \( \nu_{Ry}(H_2O) \), \( \nu_{Rx}(HDO) \) and \( \nu_{Ry}(D_2O) \) are either weak or inactive ir absorptions. Alternately those modes may be ir active and strong but degenerate with the other librational modes.
The conclusion must be that \( I_x \) and \( I_y \) are degenerate or Blue's formula is invalid. The moments-of-inertia can be made nearly degenerate by considering the masses of the detached (more distant) two protons as being attached to the lone-pair orbitals. As well, Blue's formula (85) oversimplifies the problem since it ignores the motion of the four adjacent molecules through the hydrogen bonds.

(ii) The Weighted Lone-Pairs Model

Consider one \( \text{H}_2\text{O} \) molecule as being suspended with neutral density in a cubic ice I lattice. The supporting lattice can be considered as having two principal effects. First, the principal moments of the two protons attached to the central molecule (\( \text{O-H} \cdots \text{O} \)) are decreased through reduction of their real masses to an effective mass by the "buoyancy" of the surrounding lattice through the hydrogen bonds. The mass "lost" by the two central protons is gained in the lone-pair orbitals of two neighboring molecules. Similarly, the two lone-pair orbitals of the central molecule gain an effective mass from the two detached protons (\( \text{O} \cdots \text{H-O} \)) associated with the central molecule hydrogen bonds. Hence the lone-pair effective masses restore the moments-of-inertia to near their initial values.

The second effect on the moments-of-inertia which arises from hydrogen bonding is the movement of the two attached protons away from, and the two detached protons closer to the central oxygen atom. Notice that cooling the sample decreases \( R(\text{O} \cdots \text{O}) \) and tends to centralize the four protons further. If the four protons were centered between \( \text{O} \cdots \text{O} \) and had masses equally shared by the pairs of oxygen atoms, then the molecules would be restrained spherical tops, \( I_x = I_y = I_z \).
A pseudo-symmetric top is approximated by smaller masses working at longer distances, i.e. weighted lone-pairs acting at the detached proton distance of 1.79 Å and a reduced protonic mass acting at the O-H distance of 0.95 Å. The point is that if the moments-of-inertia $I_x$ and $I_y$ are equal for $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ then by Blue's (85) formula $\nu_{Rx}$ and $\nu_{Ry}$ should be degenerate.

Consider the effect of reduced protonic masses and effective lone-pair masses where the molecular parameters will be assumed to be:

\[
\begin{align*}
  r_{\text{OH}} &= r_{\text{OD}} = 0.950 \text{ Å} \\
  R(\text{0} \cdots \text{H}) &= R(\text{0} \cdots \text{D}) = 1.790 \text{ Å} \\
  \text{mass of oxygen} &= 15.999 \text{ gms/mole} \\
  \text{the attached protons are H}_1 \text{ and H}_2 \\
  \text{the detached protons are H}_3 \text{ and H}_4 \\
  \text{the masses of H}_1 \text{ and H}_2 &= 0.75(1.008) \text{ gms/mole} \\
  &= 0.756 \text{ gms/mole} \\
  \text{the masses of H}_3 \text{ and H}_4 &= 0.25(1.008) \text{ gms/mole} \\
  &= 0.252 \text{ gms/mole}
\end{align*}
\]

(This is called the (3/4, 1/4) effective mass option.) The moments-of-inertia of $\text{H}_2\text{O} \cdots \text{H}_2$ are:

\[
\begin{align*}
  I_x &= 3.43 \times 10^{-40} \text{ gm-cm}^2/\text{molecule} \\
  I_y &= 3.15 \times 10^{-40} \\
  I_z &= 3.30 \times 10^{-40}
\end{align*}
\]

Substituting those values of the moments into Blue's (85) formula, [4], where the contributions of the oxygen force constants are still small, then:
\[ \nu_{R_x}(H_2O, 3/4, 1/4) = 2.87(0.282 \, k_H + 3.20 \, k'_H) \, \text{sec} \, \text{gm-cm} \]

\[ \nu_{R_y}(H_2O, 3/4, 1/4) = 2.99(0.602 \, k_H + 2.14 \, k'_H) \]

\[ \nu_{R_z}(H_2O, 3/4, 1/4) = 2.92(0.902 \, k_H + 1.10 \, k'_H) \]

where \( k_H \) is the 0-H\cdots0 bending force constant
and \( k'_H \) is the 0\cdotsH-0 bending force constant.

Our model supposes that \( \nu_{R_x} \) and \( \nu_{R_y} \) of H_2O are degenerate at 833 cm\(^{-1}\). By solving the first two expressions above one finds

\[ k_H = 0.60 \times 10^5 \, \text{dynes/cm} \]

and \[ k'_H = 0.21 \times 10^5 \, \text{dynes/cm} \].

Using those values of \( k_H \) and \( k'_H \) in the third expression above, then \( \nu_{R_z}^{\text{calc}}(H_2O, 3/4, 1/4) \) is 831 cm\(^{-1}\) which is degenerate with \( \nu_{R_x} \) and \( \nu_{R_y} \) within error.

How well do \( k_H(H_2O) \) and \( k'_H(H_2O) \) apply to D_2O\cdotsD_2? Using the above molecular parameters and deuterium effective masses of 0.75(2.014) gms/mole for the attached pair (D_1 and D_2) and masses of 0.25(2.014) gms/mole for the detached pair (D_3 and D_4) then the D_2O\cdotsD_2 moments-of-inertia are:

\[ I_x = 6.84(10^{-40}) \, \text{gm-cm}^2/\text{molecule} \]

\[ I_y = 6.28(10^{-40}) \]

and \[ I_z = 6.59(10^{-40}) \].

The corresponding set of expressions from Blue's formula are:
\[ \nu_{\text{calc}}(D_2O,3/4,1/4) = 2.03(0.268 \, k_H + 3.20 \, k_H') = 586 \, \text{cm}^{-1} \]
\[ \nu_{\text{calc}}(D_2O,3/4,1/4) = 2.12(0.902 \, k_H + 1.13 \, k_H') = 588 \, \text{cm}^{-1} \]
\[ \nu_{\text{calc}}(D_2O,3/4,1/4) = 2.07(0.602 \, k_H + 2.14 \, k_H') = 591 \, \text{cm}^{-1} \]

where \( k_H \) and \( k_H' \) of \( H_2O \) were used. The three \( D_2O \) librational frequencies are reasonably degenerate and lie 6% below the main observed band at 627 cm\(^{-1}\). This is as much accuracy as can be expected from so simple a model.

By invariance of the potential energy to symmetry operations \( k_H(0_1-H_1\cdots0_2) = k_H(0_1-H_2\cdots0_3) \) and \( k_H'(0_1-H_3\cdots0_4) = k_H'(0_1-H_4\cdots0_5) \). However, it does not follow that \( k_H(0-H_1,2\cdots0) = k_H'(0\cdots H_3,4\cdots0) \), since they are not interchangeable by site or point symmetry.

That \( k_H \) is 0.309 times \( k_H \) may be rationalized on the following basis. The potential for libration is the same in all directions normal to \( R(0\cdots0) \), i.e. the "potential" has a conical cross-section along the \( 0\cdots0 \) axis. While the shape of the potential is the same at protons \( H_1 \) and \( H_2 \) as well as being the same at \( H_3 \) and \( H_4 \), only the moments of the forces acting at the two protonic distances must be equal. Since the \( 0-H_1,2 \) and \( 0\cdots H_3,4 \) distances are 0.94 and 1.79 Å respectively, then the ratio \( (r_{\text{OH}}^2)/R(0\cdots H)^2 = 0.345 \). The moment of the force acting at \( H_1 \) and \( H_2 \) is \( k_{H,0}^2 = 0.53 \times 10^{-11} \) dyne-cm compared to the moment acting at \( H_3 \) and \( H_4 \), \( k_{H'}^2R(0\cdots H)^2 = 0.67 \times 10^{-11} \) dyne-cm.

There is at least one disconcerting fact about this model that is seen for the case of 4.0% HDO in \( D_2O \). The effective masses added to the HDO lone-pairs are 0.25 times the deuterium mass not the protonic mass. Thus HDO librational frequencies would be calculated nearer to the \( D_2O \) values than the \( H_2O \) values, contrary to our observations.
Another weighted lone-pairs option was investigated, the \((H_2O, 1, 1/4)\) option. In this model the two attached protons were assigned full protonic masses, while the two detached protons were assigned masses of 0.25 times the full mass. Such a model seems unreasonable since the mass sums are not conserved. By the same treatment as above one finds:

\[
\begin{align*}
    k_H(H_2O, 1, 1/4) &= 0.783 \times 10^5 \text{ dynes/cm} \\
    k'_H(H_2O, 1, 1/4) &= 0.213 \times 10^5 \text{ dynes/cm}.
\end{align*}
\]

The predicted \(v_{R_2}(H_2O)\) frequency is 829 \(\text{cm}^{-1}\) for this model and the predicted \(D_2O\) frequencies are 582, 592 and 586 \(\text{cm}^{-1}\), much as for the \((3/4, 1/4)\) model. Notice that the moments of the forces acting at \(H_{1,2}\) and \(H_{3,4}\) are now nearly equal, 0.69 \(\times 10^{-11}\) dyne-cm and 0.67 \(\times 10^{-11}\) dyne-cm respectively.

In summary let us consider the results of the two models considered. First, Blue's (85) formula for non-interacting molecules gave three non-degenerate, widely separated frequencies for the three librations. That is contrary to the observed spectra and must be rejected. Secondly, for degenerate \(v_{Rx}\) and \(v_{Ry}\) the moments-of-inertia must be equal. Using a weighted lone-pairs model it was necessary to consider two kinds of hydrogen bond bending force constants, which were not accurately transferable between \(H_2O\) and \(D_2O\) molecules. As well, the hydrogen bond bending force constants calculated were about as large as the molecular HOH bending force constant, i.e. Zimmermann and Pimentel (97) found the HOH bending force constant in ice to be 0.49 \(\times 10^5\) dynes/cm. The value of 0.60 \(\times 10^5\) dynes/cm seems to be an unsatisfactorily high \(O-H\ldots\cdot O\) bending force constant.
B. The $\text{H}_2\text{O}_3$ Model of Ice

An alternate approach to the librations of $\text{H}_2\text{O}$, HDO and $\text{D}_2\text{O}$ molecules in ice is the normal coordinate analysis of an extended molecule, $\text{H}_2\text{O}_3$. The structure and parameters of the $\text{H}_2\text{O}_3$ molecule are shown in Fig. 4.18. For a freely rotating and translating $\text{H}_2\text{O}_3$ molecule there are nine degrees of freedom and nine internal coordinates ($R$) are defined as:

\[
\begin{align*}
R_1 &= \Delta r_1 \\
R_2 &= \Delta r_2 \\
R_3 &= \Delta r_3 \\
R_4 &= \Delta r_4 \\
R_5 &= \Delta \phi \\
R_6 &= \Delta \theta_1 \\
R_7 &= \Delta \theta_2 \\
R_8 &= \Delta \theta_1' \\
R_9 &= \Delta \theta_2'
\end{align*}
\]

A similar model was studied by Zimmermann and Pimentel (97) in order to calculate the hydrogen bond bending and stretching force constants associated with molecular libration and translation.

With $C_{2v}$ point symmetry the $\text{H}_2\text{O}_3$ molecule has the reducible representation composed of $5a_1$, $2a_2$, $5b_1$ and $3b_2$ irreducible representations. The representations of vibration, translation and rotation of the $\text{H}_2\text{O}_3$ molecule, as well as the representations of the sets of symmetry coordinates, are shown below:
Fig. 4.18 The H$_2$O$_3$ model of H$_2$O in ice I. The OOO and HOH angles were assumed to be tetrahedral. The hydrogen bond bending coordinates $\theta_1$ and $\theta_2$ are in the HOH plane and $\theta_1'$ and $\theta_2'$ are perpendicular to them.

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$a_{xz}$</th>
<th>$a_{yz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$a_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$b_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$b_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\Gamma(H_2O_3) & \quad E \quad C_2 \quad a_{xz} \quad a_{yz} \\
& \quad 15 \quad -1 \quad 5 \quad 1 \\
\Gamma(\text{Rot.}) & \quad 3 \quad -1 \quad -1 \quad -1 \\
\Gamma(\text{Trans.}) & \quad 3 \quad -1 \quad 1 \quad 1 \\
\Gamma(\text{vib.}) & \quad 9 \quad 1 \quad 7 \quad -1 \\
\Gamma_1(R_1,R_2) & \quad 2 \quad 0 \quad 2 \quad 0 \\
\Gamma_2(R_3,R_4) & \quad 2 \quad 0 \quad 2 \quad 0 \\
\Gamma_3(R_5) & \quad 1 \quad 1 \quad 1 \quad 1 \\
\Gamma_4(R_6,R_7) & \quad 2 \quad 0 \quad 2 \quad 0 \\
\Gamma_5(R_8,R_9) & \quad 2 \quad 0 \quad -2 \quad 0 \\
\end{align*}
\]

$5a_1 + 2a_2 + 5b_1 + 3b_2$

$a_2 + b_1 + b_2$

$a_1 + b_1 + b_2$

$4a_1 + a_2 + 3b_1 + b_2$

$a_1 + b_1$

$a_1 + b_1$

$a_1$

$a_1 + b_1$

$a_2 + b_2$
The symmetry coordinates of H$_2$O$_3$ are:

\[
\begin{align*}
S_1 &= \frac{1}{\sqrt{2}} (R_1 + R_2) \\
S_2 &= \frac{1}{\sqrt{2}} (R_3 + R_4) \\
S_3 &= R_5 \\
S_4 &= \frac{1}{\sqrt{2}} (R_6 + R_7) \\
S_5 &= \frac{1}{\sqrt{2}} (R_1 - R_2) \\
S_6 &= \frac{1}{\sqrt{2}} (R_3 - R_4) \\
S_7 &= \frac{1}{\sqrt{2}} (R_5 - R_6) \\
S_8 &= \frac{1}{\sqrt{2}} (R_8 - R_9) \\
S_9 &= \frac{1}{\sqrt{2}} (R_8 + R_9)
\end{align*}
\]

In matrix notation the transformation from internal to symmetry coordinates is

\[
S = U R
\]

where S and R are column matrices of symmetry and internal coordinates, and U is an orthogonal matrix. The solution of the secular equation is simpler in symmetry coordinates and the F(R) and G(R) matrices must also be transformed from internal coordinates (F(R) and G(R)) to symmetry coordinates (F(S) and G(S)) by the transformations

\[
\begin{align*}
F(S) &= U F(R) U^T \\
G(S) &= U G(R) U^T
\end{align*}
\]

The F(S) and G(S) matrices each are diagonalized into block form containing a $(4 \times 4)a_1$, a $(3 \times 3)b_1$, a $(1 \times 1)a_2$ and a $(1 \times 1)b_2$ block. The form of G(S) in terms of G(R) elements and the numerical values of the G(S) blocks are given in Table IV.III. The form of the F(S) elements in terms of F(R) elements is the same as shown in Table IV.III for G(S).

Before proceeding further with the normal coordinate analysis, the normal modes of vibration, rotation and translation of H$_2$O in ice I must be assigned to the internal vibrations of the H$_2$O$_3$ molecule as represented
Table IV.III  The symmetric G matrix elements in terms of the internal coordinates and their numerical values for the H$_2$O$_3$ model in units of (gm$^{-1}$ Å$^2$ moles).

$$G(S) = \begin{bmatrix}
\varepsilon_{11}^+ & \varepsilon_{12} & \varepsilon_{13}^+ & \varepsilon_{14} & 2\varepsilon_{15} & \varepsilon_{16}^+ & \varepsilon_{17} \\
\varepsilon_{13}^+ & \varepsilon_{14} & \varepsilon_{33}^+ & \varepsilon_{34} & 2\varepsilon_{35} & \varepsilon_{36}^+ & \varepsilon_{37} \\
2\varepsilon_{15} & 2\varepsilon_{35} & \varepsilon_{55} & 2\varepsilon_{56} & 2\varepsilon_{56} & 2\varepsilon_{56} & 2\varepsilon_{56} \\
\varepsilon_{17}^+ & \varepsilon_{16} & \varepsilon_{36}^+ & \varepsilon_{37} & 2\varepsilon_{56} & \varepsilon_{66}^+ & \varepsilon_{76}
\end{bmatrix} = \begin{bmatrix}
1.034 & 0.992 & 0.088 & 0.062 \\
0.992 & 1.055 & 0 & 0 \\
0.088 & 0 & 2.393 & 2.511 \\
0.062 & 0 & 2.511 & 2.733
\end{bmatrix}$$

$$G(S) = \begin{bmatrix}
\varepsilon_{11}^- & \varepsilon_{12} & \varepsilon_{13} & \varepsilon_{16}^- & \varepsilon_{17} \\
\varepsilon_{13} & \varepsilon_{33}^- & \varepsilon_{34} & \varepsilon_{36} \\
\varepsilon_{16}^- & \varepsilon_{17} & \varepsilon_{36} & \varepsilon_{66}^- & \varepsilon_{76}
\end{bmatrix} = \begin{bmatrix}
1.076 & 0.992 & 0.062 \\
0.992 & 1.055 & 0 \\
0.062 & 0 & 2.595
\end{bmatrix}$$

$$\begin{array}{c}
s_2 \\
g(S) = [\varepsilon_{88} - \varepsilon_{89}] = 2.595
\end{array}$$

$$\begin{array}{c}
b_2 \\
g(S) = [\varepsilon_{88} + \varepsilon_{89}] = 2.733
\end{array}$$

by the symmetry coordinates above. The displacement vectors of each kind of internal H$_2$O$_3$ coordinate are shown in Fig. 4.19. The corresponding displacement vectors of the symmetry coordinates constructed from those internal coordinates are shown in Fig. 4.20. The H$_2$O ice I normal mode associated with each H$_2$O$_3$ internal vibration is listed in Fig. 4.20.

The symmetry coordinates $S_7$, $S_8$ and $S_9$, which correspond to $v_{R_x}$, $v_{R_z}$, and $v_{R_y}$ respectively, are of particular interest for this discussion.
Fig. 4.19 The internal coordinates of the H₂O₃ model shown as symmetrically equivalent pairs. The displacement vectors are not to scale and give only an approximate representation of the coordinates.
The symmetry coordinates of the H$_2$O$_3$ model were constructed as simple linear combinations of the internal coordinates. Each symmetry coordinate was assigned to an H$_2$O ice I normal mode simply on the basis of the diagrammatic representation.

Inspection of $G_{77}$, $G_{88}$ and $G_{99}$ in Table IV.III shows that the two librations ($\nu_{Rx}$ and $\nu_{Rz}$) are "kinetically" degenerate and that $\nu_{Ry}$ is very nearly degenerate with them.
If the forces restraining libration about x and y are equal (which they are for \( H_2O_3 \) by symmetry) then \( v_{Rx} \) is degenerate with \( v_{Ry} \).

The secular equation can be solved for the diagonal symmetry force constants by an iteration formula given by Green (125):

\[
k_{ii}^{n+1} = \lambda_i \left\{ G_{ii} + \sum_{j \neq i} \frac{(G_{ij})^2 k_{ij}^p}{\lambda_i - \lambda_j} \right\}^{-1}
\]

The \( b_2 \) block is trivial and gave the solution of \( k_{99} = 0.149 \times 10^5 \) dyne-cm when \( v_{Rx} \) was assigned to the peak at 833 cm\(^{-1}\). The \( a_2 \) block is also trivial and gave the solution \( k_{88} = 0.157 \times 10^5 \) dyne-cm, in good agreement with \( k_{99} \) (\( v_{Rx} \) and \( v_{Rz} \) were assumed to be degenerate at 833 cm\(^{-1}\)).

For the \((3 \times 3)b_1 \) block the \( S_5, S_6 \) and \( S_7 \) symmetry coordinates were associated with \( v_3(H_2O), v_{T_{x1}}(H_2O) \) and \( v_{R_y}(H_2O) \), respectively. Applying the iteration formula:

\[
k_{55}^i = \lambda_5 \left\{ G_{55} + \frac{(0.992)^2 k_{55}^i}{\lambda_5 - \lambda_6} + \frac{(0.062)^2 k_{77}^i}{\lambda_5 - \lambda_7} \right\}^{-1}
\]

\[
k_{66}^i = \lambda_6 \left\{ G_{66} + \frac{(0.992)^2 k_{55}^i}{\lambda_6 - \lambda_5} \right\}^{-1}
\]

\[
k_{77}^i = \lambda_7 \left\{ G_{77} + \frac{(0.062)^2 k_{55}^i}{\lambda_7 - \lambda_5} \right\}^{-1}
\]

where \( \lambda_i = \left( v_i / 1303.1 \right)^2 \). Initial force constants \( k_{ii}^0 = 1.000 \) were assumed and the formulas converged to \( \pm 0.001 \) in eleven iterations. The force constants determined were:
\[
\begin{align*}
    k_{55} &= 5.481 \times 10^5 \text{ dynes/cm} \\
    k_{66} &= 0.192 \times 10^5 \text{ dynes/cm} \\
    k_{77} &= 0.154 \times 10^5 \text{ dyne-cm}
\end{align*}
\]

Notice that the symmetry force constant associated with \( v_{R_y} \), \( k_{77} = 0.154 \times 10^5 \text{ dynes/cm} \), does not agree with those of \( v_{R_x} \) and \( v_{R_z} \).

Finally the \((4 \times 4)_{a_1}\) block was solved for the \( H_2O_3 \) symmetry force constants. The \( S_1, S_2, S_3 \) and \( S_4 \) symmetry coordinates were assigned to \( v_1(H_2O), T_2(H_2O), v_2(H_2O) \) and \( v_2'(H_2O) \) respectively. The symmetry coordinate was assumed to be a redundant, non-genuine \( H_2O \) bending mode, although it was a genuine mode of \( H_2O_3 \). As a redundant coordinate terms due to \( S_4 \) in \( E(S) \) and \( G(S) \) were set equal to zero. Then the symmetry block reduced to a \((3 \times 3)_{a_1}\) matrix.

Using the observed \( v_1, v_T \) and \( v_2 \) frequencies of \( H_2O \) (Table III.XI) and initial force constants of \( k_{11} = 1.000 \), then the three iteration formulas converged in fifteen steps to:

\[
\begin{align*}
    k_{11} &= 5.369 \times 10^5 \text{ dynes/cm} \\
    k_{22} &= 0.231 \times 10^5 \text{ dynes/cm} \\
    k_{33} &= 0.601 \times 10^5 \text{ dyne-cm}
\end{align*}
\]

With better choices of initial force constants, the formulas converged in four to five steps to \( \pm 0.001 \times 10^{-5} \text{ dynes/cm} \). To convert \( k_{33}, k_{77}, k_{88} \) and \( k_{99} \) units from dyne-cm to dynes/cm it is only necessary to divide by the lengths of the arms forming the bending coordinates. The set of \( H_2O \) internal mode force constants were estimated:
\[ k_{11}(v_1) = 5.369 \]
\[ k_{55}(v_3) = 5.482 \]
\[ k_{33}(v_2) = 0.666 \times 10^5 \text{ dynes/cm} \]

Of the three possible \( H_2O \) translations only two force constants were estimated:

\[ k_{22}(T_z) = 0.231 \]
\[ k_{66}(T_y) = 0.192 \times 10^5 \text{ dynes/cm}. \]

Finally, three force constants associated with the three possible librations were estimated:

\[ k_{99}(R_x) = 0.088 \]
\[ k_{77}(R_y) = 0.091 \]
\[ k_{88}(R_z) = 0.092 \times 10^5 \text{ dynes/cm}. \]

The above symmetry force constants were transformed back to internal coordinates force constants for comparison to those of other workers. For example, the symmetry force constants in terms of internal force constants are:

\[ k_{11}(v_1) = k(r_1r_1) + k(r_1r_2) \]
\[ k_{55}(v_3) = k(r_1r_1) - k(r_1r_2) \]
\[ k_{33}(v_3) = k(\phi\phi) \]
\[ k_{99}(R_x) = k(\phi\phi) + k(\phi_1\phi_1) \]
\[ k_{77}(R_y) = k(\phi_1\phi_1) - k(\phi_1\phi_2) \]
\[ k_{22}(T_z) = k(r_3r_3) + k(r_3r_4) \]
\[ k_{88}(R_z) = k(\phi_1\phi_1) - k(\phi_1\phi_2) \]
\[ k_{66}(T_y) = k(r_3r_3) - k(r_3r_4) \]
Thus one found that the internal coordinates force constants for H$_2$O are (in $10^5$ dynes/cm):

<table>
<thead>
<tr>
<th>Internal</th>
<th>Translational</th>
<th>Librational</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k(r_1r_1)$</td>
<td>$k(r_3r_3)$</td>
<td>$k(\theta_1\theta_1')$</td>
</tr>
<tr>
<td>5.425</td>
<td>0.212</td>
<td>0.090</td>
</tr>
<tr>
<td>$k(r_1r_2)$</td>
<td>$k(r_3r_4)$</td>
<td>$k(\theta_1\theta_2')$</td>
</tr>
<tr>
<td>-0.056</td>
<td>0.019</td>
<td>-0.002</td>
</tr>
<tr>
<td>$k(\phi\phi)$</td>
<td></td>
<td>*$k(\theta_1\theta_1)$</td>
</tr>
<tr>
<td>0.666</td>
<td></td>
<td>0.093</td>
</tr>
</tbody>
</table>

Since the other symmetry coordinate involving $\theta_1$ and $\theta_2$ was assumed redundant and eliminated, then $k(\theta_1\theta_2)$ could only be evaluated by assuming that $k(\theta_1\theta_2) = -0.002 \times 10^5$ dynes/cm.

A set of D$_2$O force constants was estimated in the same way (from D$_2$O) as for H$_2$O. The results of the H$_2$O and D$_2$O ice I force constant models are listed in Table IV along with the results of Zimmermann and Pimentel (97) and Trevino (93). Our $k(\theta_1\theta_1)$ is an in-plane hydrogen bond bend while $k(\theta_1\theta_2')$ is the out-of-plane bend. Our in-plane hydrogen bond bend is approximately 1.5 times Trevino's value: Part of the difference is probably due to differences in the models, Trevino's (93) was extended further and in a three-dimensional lattice while ours was planar.

The following comments can be made about the H$_2$O force constants estimated using the H$_2$O$_3$ model and equation [5]:

- the OH stretching force constant ($k(r_1r_1) = 5.425 \times 10^5$ dynes/cm) is less than the gas phase value and is in the region predicted from the ratio of frequencies for harmonic oscillators,
Table IV.IV The force constants of ice I from the H$_2$O$_3$ and D$_2$O$_3$ models as well as the results of Pimentel and Zimmerman and Trevino.

<table>
<thead>
<tr>
<th>Force Constant</th>
<th>Associated Motion</th>
<th>Pimentel (a)</th>
<th>This Work (f)</th>
<th>This Work (f)</th>
<th>Trevino (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>i.r.</td>
<td>i.r.</td>
<td>i.r.</td>
<td>neutron</td>
</tr>
<tr>
<td>$k(r_1r_1)$</td>
<td>O-H str.</td>
<td>(d)</td>
<td>(d)</td>
<td>(d)</td>
<td>(d)</td>
</tr>
<tr>
<td>$k(r_1r_2)$</td>
<td>O-H, O-H interaction</td>
<td>-0.049</td>
<td>-0.049</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k(r_3r_3)$</td>
<td>H···O str.</td>
<td>0.178</td>
<td>0.225</td>
<td>0.212</td>
<td>0.25</td>
</tr>
<tr>
<td>$k(r_3r_4)$</td>
<td>H···O, H···O interaction</td>
<td>0.023</td>
<td>0.019</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k(\theta_1\theta_1)$</td>
<td>O···H-O i.p.b.</td>
<td></td>
<td>0.093</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>$k(\theta_1\theta_2)$</td>
<td>O···H-O, O···H-O interaction</td>
<td>(-0.002)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k(\theta_1'\theta_1')$</td>
<td>O···H-O o.p.b.</td>
<td>0.095</td>
<td>0.099</td>
<td>0.090</td>
<td>0.08</td>
</tr>
<tr>
<td>$k(\theta_1'\theta_2')$</td>
<td>interaction</td>
<td>-0.002</td>
<td>-0.002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k(\phi\phi)$</td>
<td>HOO bending</td>
<td>0.49</td>
<td>0.730</td>
<td>0.666</td>
<td>0.62</td>
</tr>
</tbody>
</table>

(a) Pimentel and Zimmerman, Ref. 97  (b) i.p.b. = in-plane (linear) bend.
(c) o.p.b. = out-of-plane (linear) bend. (d) all force constants are $10^5$ dynes/cm. (e) Trevino, Ref. 93. (f) This work, Green's formula, H$_2$O$_3$ model.
the hydrogen-bond stretching force constant \(k(r_3r_3) = 0.212 \times 10^5 \text{ dynes/cm}\) is of the order of magnitude expected on the basis that the hydrogen bond strength (5-10 Kcal/mole) is about \(1/25\)th of the \(0-\text{H}\) bond strength,

- the \(\text{H-O-H}\) bending force constant \(k_{33} = k(\phi\phi) = 0.666 \times 10^5 \text{ dynes/cm}\) is slightly decreased from the gas phase value \((0.69 \times 10^5 \text{ dynes/cm})\) as expected from the shift in frequency, and

- the out-of-plane hydrogen bond bending \((0\cdots\cdot\cdot\text{H-0})\) force constant \(k(\theta_1\theta_1') = 0.090 \times 10^5 \text{ dynes/cm}\) is very small, this may be interpreted as indicating the hydrogen bond is relatively insensitive to bending through small angles.

It is interesting to notice that for every diagonal, internal coordinate force constant the \(\text{D}_2\text{O}\) values are larger than the \(\text{H}_2\text{O}\) values by 5 to 10%. The source of this effect is in the nature of the force constant model. Green's (125) formula [5] assumes a diagonal force field and a harmonic oscillator approach. Since \(\text{D}_2\text{O}\) energy levels are lower, and since \(\text{D}_2\text{O}\) internal coordinates displacements are smaller than \(\text{H}_2\text{O}\) displacements, then our \(\text{D}_2\text{O}\) "sees" a lower, more symmetric portion of the "true" potential curve. The simulated \(\text{D}_2\text{O}\) parabola is thus narrower and steeper than the simulated \(\text{H}_2\text{O}\) parabola and consequently the \(\text{D}_2\text{O}\) force constants are larger than the \(\text{H}_2\text{O}\) force constants. It is obvious that such diagonal \(\text{H}_2\text{O}_3\) and \(\text{D}_2\text{O}_3\) models assumed no anharmonicity in ice. Such a case seems highly unlikely in view of the strong neighbour-neighbour interaction through strong hydrogen bonds. In spite of this oversimplification, the force constants appear to give a faithful representation of the spectrum.
The test of any set of force constants, however, lies in its ability to reproduce the observed frequencies of isotopic analogues.

To check the force constants derived from \( \text{H}_2\text{O}_3 \) for the \( \text{H}_2\text{O} \) internal, translational and librational vibrations in ice, the frequencies of \( \text{D}_2\text{O} \) ice frequencies were calculated. Formula [5] was inverted and solved:

\[
\lambda_i = k_{ii} \left[ G_{ii} + \sum_{i \neq j} \frac{G^{2}_{ij} k_{jj}}{\lambda_i - \lambda_j} \right]
\]

where \( k_{ii}, k_{jj} \) are taken from \( \text{H}_2\text{O}(\text{H}_2\text{O}_3) \)

\( \lambda_j \) is taken to be the observed value, and

\( \lambda_i \) is to be calculated.

The \( a_2 \) and \( b_2 \) blocks are easily solved of course since they reduce to the form

\[
\lambda_i = k_{ii} G_{ii}
\]

in the absence of off-diagonal \( G(S) \) elements. The \( (3 \times 3) b_1 \) block and the \( (3 \times 3) a_1 \) (reduced from \( (4 \times 4) \) by elimination of the redundant \( S_4 \) coordinate) yield two quadratic and one cubic equation each. The frequencies of the normal modes of \( \text{D}_2\text{O} \) ice I were found and are compared to the observed values below:

<table>
<thead>
<tr>
<th>( \nu )</th>
<th>( \nu_{\text{calc.}} )</th>
<th>( \nu_{\text{obs.}} )</th>
<th>( \nu_{\text{calc.}} - \nu_{\text{obs.}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_3 )</td>
<td>2325</td>
<td>2413</td>
<td>-88</td>
</tr>
<tr>
<td>( \nu_1 )</td>
<td>2258</td>
<td>2321</td>
<td>-63</td>
</tr>
<tr>
<td>( \nu_2 )</td>
<td>1138</td>
<td>1194</td>
<td>-56</td>
</tr>
<tr>
<td>( \nu_{Rx} )</td>
<td>595</td>
<td>627(a)</td>
<td>-32</td>
</tr>
<tr>
<td>( \nu_{Ry} )</td>
<td>594</td>
<td>627(a)</td>
<td>-33</td>
</tr>
<tr>
<td>( \nu_{Rz} )</td>
<td>601</td>
<td>627(a)</td>
<td>-26</td>
</tr>
<tr>
<td>( \tau_X )</td>
<td>229</td>
<td>220(b)</td>
<td>+9</td>
</tr>
<tr>
<td>( \tau_Z )</td>
<td>232</td>
<td>220(b)</td>
<td>+12</td>
</tr>
</tbody>
</table>

(a) \( \nu_{Rx}, \nu_{Ry} \) and \( \nu_{Rz} \) are assumed to be degenerate

(b) Reference 96.
The $\text{D}_2\text{O}$ ice internal mode frequencies ($\nu_1, \nu_2, \nu_3$) calculated from formula [6] using $\text{H}_2\text{O}(\text{H}_2\text{O}_3)$ force constants were all too low (-63 cm$^{-1}$, -56 cm$^{-1}$, -88 cm$^{-1}$) by 3 to 5%. The $\text{D}_2\text{O}$ translational lattice frequencies calculated in the same way were too high by 5%. The modes of interest, for which the $\text{H}_2\text{O}_3$ model was constructed, are the librational lattice modes. Their calculated frequencies were also too low by 5 - 6%. It is interesting that the librational $\text{D}_2\text{O}$ frequencies from the $\text{H}_2\text{O}_3$ model are nearly the same as those predicted for $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ in the weighted-lone-pair, moment-of-inertia model previously discussed. There the frequencies calculated were 586 cm$^{-1}$, 588 cm$^{-1}$ and 591 cm$^{-1}$ for $\nu_{Rx}$, $\nu_{Ry}$ and $\nu_{Rz}$ respectively.

One can conclude that the $\text{H}_2\text{O}_3$ normal coordinate analysis, as a basis for $\text{H}_2\text{O}/\text{D}_2\text{O}$ ice librations offers no improvement over a weighted lone-pairs moment-of-inertia model. The $\text{H}_2\text{O}_3$ model does give reasonable internal and lattice mode frequencies and reasonable ice force constants.

C. A Summary of $\text{H}_2\text{O}$, HDO and $\text{D}_2\text{O}$ Librations

Three models of ice libration were presented: Blue's (85) harmonic, hindered oscillator model using moments-of-inertia, a weighted lone-pairs moments-of-inertia model, and a normal coordinate analysis of the $\text{H}_2\text{O}_3$ extended molecule. Blue's formula [4] gave widely dispersed $\nu_{Rx}$ and $\nu_{Ry}$ frequencies in $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$, i.e. separation of about 100 cm$^{-1}$. This did not conform to the observed IR absorption. The last two models were discussed on the assumptions that the librational modes were degenerate or nearly degenerate and that $\nu_{Rx}$ and $\nu_{Ry}$ are of equal intensity while $\nu_{Rz}$ was weak or inactive.
Transfering effective mass from a nearest-neighbour proton to the central molecule's lone-pair orbitals produced a nearly spherical top. The three principal moments-of-inertia differed by only ± 5 percent for the \((\text{H}_2\text{O}, 3/4, 1/4)\) option.

The force constants for molecular libration were \(k_H = 0.60 \times 10^5\) dynes/cm at the attached proton and \(k'_H = 0.21 \times 10^5\) dynes/cm at the detached proton. These two force constants were deduced from Blue's formula assuming \(\nu_{Rx} = \nu_{Ry} = 832\ \text{cm}^{-1}\). Application of \(k_H\) and \(k'_H\) to formula [4] in D\(_2\)O parameters predicted D\(_2\)O frequencies of:

\[
\nu_{Rx} = 586\ \text{cm}^{-1} \\
\nu_{Ry} = 588\ \text{cm}^{-1} \\
\nu_{Rz} = 591\ \text{cm}^{-1}
\]

The D\(_2\)O frequencies are reasonably degenerate, but lie six percent below the observed band maximum. Analogous results were obtained for an \((\text{H}_2\text{O}, 1, 1/4)\) effective mass option. Transferability of force constants among isotopic analogues was violated in the effective mass model, force constants estimated from H\(_2\)O and D\(_2\)O frequencies did not agree.

Normal coordinate analysis of the H\(_2\)O\(_3\) extended molecule produced very good valence force constants and hydrogen-bond force constants. However, the H\(_2\)O force constants did not duplicate the D\(_2\)O frequencies. The dispersion was explained by considering the difference in shape of harmonic potential simulated by formula [5]. Degeneracy of the librational modes was acceptable in this model with respect to force constant evaluation.
Further improvements in the analysis of ice may be found by treating it as an extended three dimensional polymer. Techniques of normal coordinate analysis of polymers are now expanding. Zerbi's review (126) outlines the approach, a modification of the traditional Wilson FG method, and lists some references.
CHAPTER FIVE

CLATHRATE-HYDRATE EXPERIMENTAL DETAILS AND RESULTS

5.1 The Vitreous-Crystalline Clathrate-Mixture Phase Transformation

A. Experimental

Warm-up studies of the ir absorptions of vitreous, condensed mixtures of H₂O and guest species were completed in the liquid nitrogen cell (page 42). Stoichiometric gaseous mixtures corresponding to the three classes of clathrate-hydrate were prepared and condensed in the same manner as the ice samples (page 58). Samples studied in the first clathrate class (page 13) 6G·4H₂O were G = CH₃Cl, CH₃Br and Cl₂, while for the second clathrate class (page 15) 8G·13H₂O the samples were for G = CH₃I, CHCl₃ and C₂H₅Br. Only one sample from the third class, 20G·17H₂O (page 15), was studied, i.e. G = Br₂. The conditions of sample formation and annealing are listed in Table V.1. In order to avoid separation of the clathrate mixture, all these samples were deposited through the heated metal deposition tube (page 44).

As with the H₂O, HDO and D₂O samples, the source beam was blocked when the clathrate mixture samples were warmed above 180°C, in order to prevent sublimation. As well, the cell chamber was not pumped when above 160°C. The temperatures quoted here are those which were measured by the copper-constantan thermocouple attached to the brass sample block: The sample temperatures were 10°C higher due to source beam heating. However, the maximum annealing temperatures do not need to be corrected in that way since the source beam was off then.
Table V.I. The clathrate mixture sample histories for the deposition and annealing procedures. The deposition temperature refers to the sample block temperature with the source off.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B2</th>
<th>Cl(C4)</th>
<th>D</th>
<th>E</th>
<th>F1(F6)</th>
<th>G3</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar gas ratio</td>
<td>1CH₂Cl:</td>
<td>1CH₃Br:</td>
<td>1CH₃I:</td>
<td>1CHCl₃:</td>
<td>1C₂H₅Br:</td>
<td>1Cl₂:</td>
<td>1Cl₂:</td>
<td>1Br₂:</td>
</tr>
<tr>
<td></td>
<td>7 H₂O</td>
<td>7 H₂O</td>
<td>17H₂O</td>
<td>17H₂O</td>
<td>17H₂O</td>
<td>7 H₂O</td>
<td>7 H₂O</td>
<td>8.6H₂O</td>
</tr>
<tr>
<td>Deposition Rate</td>
<td>10 sec</td>
<td>1.5 min</td>
<td>5 sec</td>
<td>2 sec</td>
<td>3 sec</td>
<td>3 sec</td>
<td>(2 min)</td>
<td>3 sec</td>
</tr>
<tr>
<td>Sample Substrate</td>
<td>CsI</td>
<td>CsI</td>
<td>CsI</td>
<td>CsI</td>
<td>CsI</td>
<td>CsI</td>
<td>AgCl</td>
<td>AgCl</td>
</tr>
<tr>
<td>Deposition</td>
<td>°K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>83</td>
<td>84</td>
<td>83</td>
<td>83</td>
<td>81</td>
<td>81</td>
<td>83</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>(83)</td>
<td>(83)</td>
<td>(105)</td>
<td>172</td>
<td>170</td>
<td>103</td>
<td>15</td>
<td>240</td>
</tr>
<tr>
<td>Annealing Time</td>
<td>Min</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>139</td>
<td>265</td>
<td>98</td>
<td>172</td>
<td>170</td>
<td>103</td>
<td>15</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>(189)</td>
<td>(189)</td>
<td>(189)</td>
<td>(189)</td>
<td>(189)</td>
<td>(189)</td>
<td>(190)</td>
<td>(190)</td>
</tr>
<tr>
<td>Maximum Annealing</td>
<td>°K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>200</td>
<td>199</td>
<td>188</td>
<td>189</td>
<td>189</td>
<td>189</td>
<td>190</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>(189)</td>
<td>(189)</td>
<td>(189)</td>
<td>(189)</td>
<td>(189)</td>
<td>(189)</td>
<td>(190)</td>
<td>(190)</td>
</tr>
<tr>
<td>Time at Maximum</td>
<td>Min</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>12</td>
<td>45</td>
<td>16</td>
<td>15</td>
<td>16</td>
<td>12</td>
<td>11</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>(18)</td>
<td>(15)</td>
<td>(18)</td>
<td>(15)</td>
<td>(15)</td>
<td>(15)</td>
<td>(15)</td>
<td>(15)</td>
</tr>
</tbody>
</table>
All annealing processes were observed on the P.E. 421 spectrophotometer during warm-up from 85 ± 50K to 180 ± 100K. Spectrophotometer controls were set for optimum response and were the same as for ice I (page 59) with small variations. The spectra were recorded at 85 ± 50K immediately after deposition and at several temperatures between 850° and 1800°K. Peaks and shoulders were assigned as for ice I (page 59).

B. Results of Devitrification

While the degree of crystallinity of the samples condensed from the vapour phase depended upon the sample history, the basic results for all the unannealed, vitreous samples were the same. Consequently, only one set of normal annealing results will be discussed in detail. Some irregularities were observed for 6Cl₂·46H₂O condensed and annealed on a CsI window. Those results will be discussed separately. Each of the H₂O skeletal bands (v₁ + v₉), v₃, v₁, 3v₂, v₂/2v₉ and v₉ was analyzed, as were those guest absorptions which were observed. No distinction between the classes of clathrates was noticed in this work.

(i) The Effect of Devitrification on the Lattice Peak Maxima

For the seven samples listed previously (page 215) only the results of the chloromethane clathrate mixture will be given. The six other samples (including Cl₂ on CsI) had the same behaviour within the limits of error. The frequency-temperature dependences of the main H₂O skeletal features are shown in Fig. 5.1. The absorption spectra of some unannealed and annealed samples (all at 83 ± 30K) are shown in Figs. 5.2, 5.3 and 5.4. Some details of the CH₃Cl·7.67H₂O clathrate mixture annealing (Fig. 5.1) are
Fig. 5.1 The shifts of the unannealed clathrate mixture (CH$_3$Cl·7.67H$_2$O) H$_2$O peaks during warming from 83 ± 3°K to 200 ± 5°K. The data are typical of all the clathrate mixtures and appear to be the same as for ice IV. The data are numbered in the order of observation.
Fig. 5.2 The infrared absorption spectra of some clathrate mixtures. In all cases spectra numbered "A" are backgrounds through the low temperature cell. (a) CH₃Cl·7.67H₂O unannealed at 83 ± 3°K (B), at 83 ± 3°K but annealed to 160 ± 3°K (C), and at 200°K (D). (b) CH₃Br·7.67H₂O unannealed at 83 ± 3°K (B), at 83 ± 3°K but annealed to 158 ± 3°K (C) and at 189 ± 3°K (D). (c) CH₃I·17H₂O unannealed at 83 ± 3°K (B), annealed to 190 ± 5°K but observed at 83 ± 3°K (C) and at 188 ± 3°K (D). The same frequency scale applies to all of the spectra, i.e. for each absorbance scale.
The effects of annealing clathrate mixtures of CHCl$_3$ and C$_2$H$_5$Br·17H$_2$O. (a) CHCl$_3$·17H$_2$O unannealed at 83 ± 3°K (B), at 129 ± 3°K (C), at 149 ± 3°K (D) and at 189 ± 5°K (E). (b) C$_2$H$_5$Br·17H$_2$O unannealed at 83 ± 3°K (B), at 129 ± 3°K (C), at 149 ± 3°K (D) and at 189 ± 3°K (E). The same frequency scale applies to each absorbance scale, i.e. a shorter span of frequencies is shown for D than for E.
Fig. 5.4 (a) Br₂·8.6 H₂O on AgCl unannealed at 83 ± 3°K (B,C), at 130 ± 3°K (D,E) and at 170 ± 3°K (F). Spectra B and C were recorded six hours apart while spectra D and E were recorded thirty minutes apart. (b) Cl₂·7.67H₂O on AgCl unannealed at 83 ± 3°K (B) and at 83 ± 3°K but annealed to 190 ± 5°K (C). (c) Cl₂·7.67 H₂O on CsI unannealed at 83 ± 3°K (B) and at 83 ± 3°K but annealed to 190 ± 5°K for 15 minutes (C).
in Table V.II. As for ice I, the frequency shifts of the vitreous sample peaks were irreversible. The points in Fig. 5.1 are numbered in the sequence in which they were obtained for each band. The sixth point was obtained by cooling the sample to 83 ± 3°K after annealing it at 160 ± 3°K for 20 minutes and before warming to higher temperatures.

Table V.II The H₂O frequencies of the CH₃Cl·7.67H₂O clathrate mixture before (vᵤ) and after (vₐ) annealing to 200 ± 5°K. The transformation temperature range and the temperature dependence after annealing are shown.

<table>
<thead>
<tr>
<th></th>
<th>82°K unannealed vᵤ</th>
<th>82°K annealed vₐ</th>
<th>Δv vₐ - vᵤ</th>
<th>Transformation Temperature Range</th>
<th>Δv/ΔT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm⁻¹</td>
<td>cm⁻¹</td>
<td>cm⁻¹</td>
<td>cm⁻¹/°K</td>
<td></td>
</tr>
<tr>
<td>v₁ + vₜ</td>
<td>3382±5</td>
<td>3364</td>
<td>-18</td>
<td>(140-170)±10</td>
<td>0.10</td>
</tr>
<tr>
<td>v₃</td>
<td>3258±3</td>
<td>3219</td>
<td>-39</td>
<td>(140-160)±10</td>
<td>0.12</td>
</tr>
<tr>
<td>v₁</td>
<td>3195±5</td>
<td>3146</td>
<td>-49</td>
<td>(130-155)±10</td>
<td>0.25</td>
</tr>
<tr>
<td>3vₚ</td>
<td>2209±5</td>
<td>2227</td>
<td>+18</td>
<td>(125-155)±10</td>
<td>-0.09</td>
</tr>
<tr>
<td>v₂</td>
<td>1654±3</td>
<td>1610</td>
<td>-44</td>
<td>(125-140)±10</td>
<td>0.18</td>
</tr>
<tr>
<td>vₚ</td>
<td>792±4</td>
<td>823</td>
<td>+31</td>
<td>(115-140)±10</td>
<td>-0.16</td>
</tr>
</tbody>
</table>
The five conclusions made with respect to the ice I devitrification (page 63) apply to H$_2$O in these clathrate mixtures also.

Typical visual observations of the annealing process are illustrated by those for CH$_3$Cl·7.67H$_2$O:

- at 83 ± 3°K (before annealing) a transparent film around a translucent, milky-white mass about 0.25 inches in diameter,
- at 168 ± 3°K an opaque white mass opposite the nozzle surrounded by a thin transparent film, and
- at 188 ± 3°K the sample appeared to be totally white and opaque.

In general, the source image was centered on the thinner portion of the sample. The Br$_2$·8.6H$_2$O mixtures were not white, but were orange and yellow-orange depending on the thickness.

(ii) The Effects of Devitrification on the Oligomeric H$_2$O Bands

Weak peaks and shoulders on the high frequency side of the skeletal unannealed H$_2$O stretching band had the same appearance as for vitreous ice I (Fig. 3.3) and can be seen in Figs. 5.2, 5.3 and 5.4. The positions of these oligomeric H$_2$O absorptions for various unannealed clathrate mixtures at 83 ± 3°K immediately after deposition are given in Table V.III: In some cases a number of specimens were observed. The positions of the peaks depend on the rate of sample deposition. For example, the three CH$_3$Br sets of results were obtained from mixtures deposited through a needle valve in 4.5, 1.5 and 11 minutes respectively. The temperature dependences of the H$_2$O oligomeric absorptions from a number of clathrate mixtures are given in Table V.IV. With a single exception the oligomeric H$_2$O absorptions began to diminish in peak height between 120 and 129°K and had disappeared below 170°K, Table V.V.
Table V.III  The frequencies at \(83 \pm 3^\circ K\) of the weak peaks and shoulders associated with oligomeric \(H_2O\) units in several unannealed clathrate mixtures.

<table>
<thead>
<tr>
<th>CH(_4)Cl</th>
<th>CH(_3)Br</th>
<th>CH(_3)I</th>
<th>CHCl(_3)</th>
<th>C(_2H_5)Br</th>
<th>Br(_2)</th>
<th>C(_6I)</th>
<th>AgCl</th>
<th>Cl(_2)</th>
<th>H(_2O)</th>
<th>ice I(_v)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(17.67H_2O)</td>
<td>(17H_2O)</td>
<td>(17H_2O)</td>
<td>(8.6H_2O)</td>
<td>(17H_2O)</td>
<td>(17H_2O)</td>
<td>(17H_2O)</td>
<td>(17H_2O)</td>
<td>(17H_2O)</td>
<td>(17H_2O)</td>
</tr>
<tr>
<td>(\pm5) cm(^{-1})</td>
<td>(\pm5) cm(^{-1})</td>
<td>(\pm5) cm(^{-1})</td>
<td>(\pm5) cm(^{-1})</td>
<td>(\pm5) cm(^{-1})</td>
<td>(\pm5) cm(^{-1})</td>
<td>(\pm5) cm(^{-1})</td>
<td>(\pm5) cm(^{-1})</td>
<td>(\pm5) cm(^{-1})</td>
<td>(\pm5) cm(^{-1})</td>
<td>(\pm5) cm(^{-1})</td>
</tr>
<tr>
<td>3645 (vw)</td>
<td>3580 (w)</td>
<td>3689 (vww)</td>
<td>3643 (vw)</td>
<td>3691 (vww)</td>
<td>3689 (vww)</td>
<td>3635 (vw)</td>
<td>3687</td>
<td>3654 (vww)</td>
<td>3605 (vw)</td>
<td>3639 (vww)</td>
</tr>
</tbody>
</table>
Table V.IV The temperature dependences of the oligomeric H$_2$O absorption frequencies of some clathrate mixtures and unannealed ice I.

<table>
<thead>
<tr>
<th>H$_2$O Ice I$_v$ cm$^{-1}$</th>
<th>85±3°K</th>
<th>94±3°K</th>
<th>110±3°K</th>
<th>125±3°K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3687</td>
<td>3689</td>
<td>3690</td>
<td>3690</td>
</tr>
<tr>
<td></td>
<td>3658</td>
<td>3674</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3637</td>
<td>3650</td>
<td>3647</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHCl$_3$·17 H$_2$O cm$^{-1}$</th>
<th>83±3°K</th>
<th>109±3°K</th>
<th>129±3°K</th>
<th>149±3°K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3689 (sh)</td>
<td>3687 (sh)</td>
<td>3673 (sh)</td>
<td>3672 (sh)</td>
</tr>
<tr>
<td></td>
<td>3639(0.11)</td>
<td>3640(0.10)</td>
<td>3640(0.06)</td>
<td>3634(0.04)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C$_2$H$_5$Br·17 H$_2$O cm$^{-1}$</th>
<th>83±3°K</th>
<th>110±3°K</th>
<th>129±3°K</th>
<th>150±3°K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3643 (wsh)</td>
<td>3669 (wsh)</td>
<td>3658 (wsh)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3565 (msh)</td>
<td>3569 (msh)</td>
<td>3563 (msh)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cl$_2$·7.67 H$_2$O cm$^{-1}$</th>
<th>81±3°K</th>
<th>109±3°K</th>
<th>129±3°K</th>
<th>149±3°K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3689 (vvw)</td>
<td>3688 (vvw)</td>
<td>3688 (vvw)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3635 (wsh)</td>
<td>3630 (wsh)</td>
<td>3636 (wsh)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Br$_2$·8.6 H$_2$O cm$^{-1}$</th>
<th>83±3°K</th>
<th>130±3°K</th>
<th>130±3°K</th>
<th>170±3°K</th>
<th>83±3°K+0.5 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3691(0.02)</td>
<td>3693(0.02)</td>
<td>3609(0.06)</td>
<td></td>
<td>3563 (sh) 3528 (sh)</td>
</tr>
<tr>
<td></td>
<td>3612(0.10)</td>
<td>3616(0.08)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table V.V  The temperatures at which the oligomeric peak heights began to decrease (T₁) and the maximum temperature at which they were observed (T₂)

<table>
<thead>
<tr>
<th>Guest</th>
<th>T₁</th>
<th>T₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃Cl</td>
<td>±5°C</td>
<td>120</td>
</tr>
<tr>
<td>CH₃Br</td>
<td>±5°C</td>
<td>120</td>
</tr>
<tr>
<td>CH₃I</td>
<td>±5°C</td>
<td>&lt; 138</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>&lt; 138</td>
<td>120</td>
</tr>
<tr>
<td>C₂H₅Br</td>
<td>&lt; 138</td>
<td>&lt; 149</td>
</tr>
<tr>
<td>Br₂</td>
<td>&lt; 138</td>
<td>&gt; 185</td>
</tr>
<tr>
<td>Cl₂(CsI)</td>
<td>&lt; 138</td>
<td>&lt; 149</td>
</tr>
<tr>
<td>H₂O ice</td>
<td>110</td>
<td>125</td>
</tr>
</tbody>
</table>

For the Br₂·8.6H₂O mixture the oligomeric absorptions were observed at 170 ± 3°C during annealing and even at 83 ± 3°C after annealing, Fig. 5.4. The visual appearance of the Br₂·8.6H₂O sample changed markedly during annealing above 185 ± 3°C (with the source beam off): The sample was annealed for 10 minutes at 185 ± 3°C, 10 minutes at 190 ± 3°C and for 3 minutes at 200 ± 3°C. After 1 minute at 200 ± 3°C the sample changed from orange-brown to a rusty-brown surface layer. After 3 minutes at 200 ± 3°C the rusty-brown layer had sublimed off.
The Effects of Devitrification on Cl$_2$·7.67H$_2$O Mixtures

Gaseous mixtures of Cl$_2$·7.67 H$_2$O condensed on CsI and annealed for long periods appeared to react with the CsI. Consequently the Cl$_2$·7.67 H$_2$O mixture was studied on two substrates, i.e. CsI and AgCl, samples F and G respectively. In all six samples were studied on CsI and three on AgCl.

(a) Cl$_2$·7.67H$_2$O on CsI (sample F). The ir absorption spectra of Cl$_2$·7.67H$_2$O at 83 ± 3°K before and after annealing to 189°K were shown in Fig. 5 (sample F), while the temperature-frequency dependences of the H$_2$O skeletal absorptions were the same as for CH$_3$Cl·7.67H$_2$O (Fig.5.1). The effect of annealing Cl$_2$·7.67H$_2$O to progressively higher temperatures is shown in Fig. 5.5 (sample F). The visual appearance of sample F before and during annealing was:

- (between 83 ± 3 and 110 ± 3°K) a cone of opaque white material which became gradually more transparent at the base of the cone,
- (at 169 ± 3°K) a generally opaque white sample 0.5 inches in diameter, and
- (at 83 ± 3°K after annealing) a uniformly white opaque sample.

The visual appearance of sample F before and during annealing was the same as for sample F. By visual observation no distinction could be drawn between the samples annealed to 170 ± 3, 180 ± 3 and 190 ± 3°K although their spectra differed.

In the spectrum of sample F the absorption between 3000 cm$^{-1}$ and 2400 cm$^{-1}$ increased as the sample was annealed to higher temperatures.

Also notice the dramatic effect on the stretching band due to annealing to
Fig. 5.5 Spectra of one sample of $\text{Cl}_2\cdot7.67\text{H}_2\text{O}$ on CsI at $83^\circ\text{K}$ with various successive annealing times:

(A) Unannealed, (B) annealed to $170^\circ\text{K}$ for 15 minutes, (C) annealed after (B) to $180^\circ\text{K}$ for 15 minutes, (D) then annealed to $190^\circ\text{K}$ for 15 minutes, (E) then annealed to $190^\circ\text{K}$ for 30 minutes, and (F), background through low temperature cell at $83^\circ\text{K}$.
190 \pm 2^\circ K, i.e. the intensity of the low frequency shoulder increased and a new high frequency shoulder appeared. Annealing to 170 \pm 2^\circ K or 180 \pm 2^\circ K gave only the characteristic sharpening into 1 peak and 2 shoulders. As well, the nature of the \nu_2 absorption changed.

(b) \text{Cl}_2\cdot7.67\text{H}_2\text{O} on \text{AgCl} (\text{sample G}). Detailed studies of the annealing process of amorphous solid \text{Cl}_2\cdot7 \text{H}_2\text{O} on an \text{AgCl} substrate were not made. Spectra were recorded at 83 \pm 3^\circ K before and after annealing to various temperatures. The visual appearances were as before, i.e. a clear and transparent sample except for one spot opposite the nozzle before annealing and a uniform opaque white sample after annealing. \text{Cl}_2 \text{guest} absorption as might be expected was not observed and the \text{H}_2\text{O} skeletal absorption was shown in Fig. 5.4.

None of our attempts to split the \text{Cl}_2\cdot7.67\text{H}_2\text{O} stretching band into 1 peak and 3 shoulders succeeded for samples on an \text{AgCl} window. Nor was the nature of the \nu_2 band changed. As well, no increased absorption between 3000 \text{cm}^{-1} and 2400 \text{cm}^{-1} was observed. The positions of the \text{Cl}_2\cdot7.67\text{H}_2\text{O} bands on \text{CsI} and \text{AgCl} will be discussed in section 5.3 (page 234).

5.2 Clathrate Mixture Guest Absorptions

The ir absorptions due to the guest molecules which were expected to be trapped in the cages of the \text{H}_2\text{O} host lattice were formed and observed by three techniques. In the first method (section 5.1) the stoichiometric gaseous mixtures were condensed rapidly onto a substrate held at 83 \pm 3^\circ K in an open chamber (section 2.4C). To ensure that the guest molecules were not diffusing out of the host lattice, a second and a third method
were investigated. The second method was condensation of the mixtures in an isolated chamber (section 2.4B), and the third method was the preparation and observation of low temperature mulls (section 2.4A) of solid clathrate mixtures (section 2.3A). Of the seven clathrate mixtures studied, Cl$_2$·7.67H$_2$O and Br$_2$·8.6H$_2$O should have no guest IR absorptions.

A. Condensation in an Open Chamber

During devitrification of these samples the temperature at which the guest absorption peak heights began to diminish and the temperature at which they were absent varied considerably from sample to sample. However, since the behaviours were generally the same only one or two cases will be described in detail.

For example, the CH$_3$Cl·7.67H$_2$O guest absorptions were observed at 2957 (m), 1443 (m), 1437 (sh), 1347 (w), 1338 (vw), 1021 (vw) and 700 (ms) cm$^{-1}$ (Fig. 5.2(a)) near the solid CH$_3$Cl absorptions. They were observed up to 100 ± 3°K with undiminished intensity and up to 160 ± 3°K with diminishing intensity. In contrast CH$_3$I·17H$_2$O guest absorptions were undiminished up to 138 ±2°K and nil at 168 ± 2°K for one specimen, while for a second specimen the CH$_3$Br absorptions were slightly diminished at 110 ± 3°K and slowly diminishing up to 189 ± 3°K (the 1235 cm$^{-1}$ peak was still present). The guest absorptions from a number of unannealed clathrate mixtures at 83 ± 3°K, immediately after deposition, are listed in Table V.VI. The variations of those guest absorptions as a function of temperature are given in Table V.VII and the temperatures of the onset of alteration in guest absorptions and the maximum temperature at which they were observed are given in Table V.VIII.
Table V.VI The alkyl halide guest absorptions at 83 ± 3°K in a number of alkyl halide clathrate mixtures before annealing began

<table>
<thead>
<tr>
<th></th>
<th>CH₃Cl</th>
<th>CH₃Br</th>
<th>CH₃I</th>
<th>CHCl₃ • 17H₂O</th>
<th>C₂H₅Br • 17H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm⁻¹</td>
<td>cm⁻¹</td>
<td>cm⁻¹</td>
<td>cm⁻¹</td>
<td>cm⁻¹</td>
<td>cm⁻¹</td>
</tr>
<tr>
<td>2957 (m)</td>
<td>3020 (sh)</td>
<td>2965 (sh)</td>
<td>2950 (w)</td>
<td>2936 (vw)</td>
<td>3020 (m)</td>
</tr>
<tr>
<td>1443 (m)</td>
<td>1347 (w)</td>
<td>1338 (vw)</td>
<td>1200 (sh)</td>
<td>1233 (sh)</td>
<td>1234 (w)</td>
</tr>
<tr>
<td>1021 (vw)</td>
<td>700 (ms)</td>
<td>750 (s)</td>
<td>1054 (vw)</td>
<td>665 (w)</td>
<td>665 (w)</td>
</tr>
</tbody>
</table>

Table V.VII  The temperature dependences of the guest absorptions during the annealing of clathrate mixtures. These data are typical of all samples.

<table>
<thead>
<tr>
<th></th>
<th>83±3°K</th>
<th>110±3°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃I·17H₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2950 (w)</td>
<td>2960 (sh)</td>
</tr>
<tr>
<td></td>
<td>1238 (w)</td>
<td>1247 (w)</td>
</tr>
<tr>
<td></td>
<td>1233 (sh)</td>
<td>1240 (vw)</td>
</tr>
<tr>
<td></td>
<td>83±3°K</td>
<td>139±3°K</td>
</tr>
<tr>
<td></td>
<td>2936 (vww)</td>
<td>2939 (vww)</td>
</tr>
<tr>
<td></td>
<td>2915 (vww)</td>
<td>2917 (vww)</td>
</tr>
<tr>
<td></td>
<td>1244 (sh)</td>
<td>1244 (sh)</td>
</tr>
<tr>
<td></td>
<td>1234 (w)</td>
<td>1236 (w)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>83±3°K</th>
<th>110±3°K</th>
<th>129±3°K</th>
<th>150±3°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>±2 cm⁻¹</td>
<td>±2 cm⁻¹</td>
<td>±2 cm⁻¹</td>
<td>±2 cm⁻¹</td>
<td></td>
</tr>
<tr>
<td>C₂H₅Br·17H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2985 (vw)</td>
<td>2983 (vw)</td>
<td>2981 (vw)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1254 (vww)</td>
<td>1255 (vw)</td>
<td>1252 (sh)</td>
<td>1258 (sh)</td>
</tr>
<tr>
<td></td>
<td>1242 (vw)</td>
<td>1245 (w)</td>
<td>1245 (vw)</td>
<td>1245 (vww)</td>
</tr>
<tr>
<td></td>
<td>955 (w)</td>
<td>956 (w)</td>
<td>952 (vw)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>760 (sh)</td>
<td>760 (sh)</td>
<td>763 (sh)</td>
<td></td>
</tr>
</tbody>
</table>
Table V.VIII  The temperature at which the guest absorptions peak heights began to decrease \((T_1)\), and the maximum temperature at which they were observed \((T_2)\).

<table>
<thead>
<tr>
<th>Guest</th>
<th>(T_1)</th>
<th>(T_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(G\cdot7.67\text{H}_2\text{O})</td>
<td>±3°K</td>
<td>±3°K</td>
</tr>
<tr>
<td>(\text{CH}_3\text{Cl})</td>
<td>100</td>
<td>160</td>
</tr>
<tr>
<td>(\text{CH}_3\text{Br})</td>
<td>138</td>
<td>&lt; 170</td>
</tr>
<tr>
<td>(\text{G}\cdot17\text{H}_2\text{O})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{CH}_3\text{I})</td>
<td>138</td>
<td>&lt; 168</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>&gt; 189</td>
</tr>
<tr>
<td>(\text{CHCl}_3)</td>
<td>129</td>
<td>&lt; 189</td>
</tr>
<tr>
<td></td>
<td>&gt; 169</td>
<td></td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_5\text{Br})</td>
<td>110</td>
<td>&lt; 170</td>
</tr>
</tbody>
</table>

The guest frequencies shifted very little, if at all, upon warming for devitrification, however the peaks did sharpen near 125 ± 5°K. For example, in annealing \(\text{CHCl}_3\cdot17\text{H}_2\text{O}\) (Fig.5.3(a)) the absorptions near 1200 cm\(^{-1}\) sharpened at 129 ± 3°K. In fact it split into two distinct peaks at 1223 and 1203 cm\(^{-1}\) and a shoulder at 1214 cm\(^{-1}\). As well the guest absorptions near 3000 cm\(^{-1}\) and 750 cm\(^{-1}\) sharpened at 129 ± 3°K. Although the two \(\text{CHCl}_3\) peaks at 1223 and 1203 cm\(^{-1}\) were observed as high as 149 ± 3°K, the point is that they were unobserved after annealing.
B. Condensation in an Isolated Chamber

The condensation apparatus and the technique were described in sections 1.6 and 2.4B respectively. Stoichiometric mixtures of \( \text{Cl}_2 \cdot 7.67\text{H}_2\text{O} \), \( \text{SO}_2 \cdot 7.67\text{H}_2\text{O} \), \( \text{CH}_3\text{Cl} \cdot 7.67\text{H}_2\text{O} \), \( \text{CH}_3\text{Cl} \cdot 7.67\text{H}_2\text{O} \), \( \text{CH}_3\text{Br} \cdot 7.67\text{H}_2\text{O} \), \( \text{CCl}_3\cdot 17\text{H}_2\text{O} \), and \( \text{CH}_3\cdot 17\text{H}_2\text{O} \) were condensed rapidly in a precooled chamber and annealed to \( 185 \pm 5^\circ\text{K} \) for 2 - 5 minutes. Spectra were subsequently recorded at \( 83 \pm 3^\circ\text{K} \) on the P.E. 112-G spectrophotometer.

The results of this method were the same as for condensation and devitrification in an open chamber. No guest absorptions were observed in the annealed samples, while the \( \text{H}_2\text{O} \) "host" absorptions were the same as for section 5.1 but with considerably more scattering. As well these samples had spectra much like \( \text{Cl}_2 \cdot 7.67\text{H}_2\text{O} \) (on CsI) between 3000 and 2200 cm\(^{-1}\) (Fig. 5.4(c)).

C. Low Temperature Mulls

The technique was described in section 2.4A and spectra were recorded on the P.E. 421 spectrophotometer. The present samples were mulled from ground solids prepared by freezing-warming cycles on stoichiometric liquid mixtures. At \( 83 \pm 3^\circ\text{K} \) \( \text{CH}_3\cdot 17\text{H}_2\text{O} \) and \( \text{CCl}_3\cdot 17\text{H}_2\text{O} \) had no guest absorptions and the \( \text{H}_2\text{O} \) skeletal absorptions were like those reported in section 5.1 for annealed samples. However, the scattering was greater than in methods 5.2A or 5.2B.

Some guest absorptions may have been masked by the \( \text{C}_3\text{H}_8 \) and \( \text{CClF}_3 \) mulling agent absorptions, but it seems unlikely that all the \( \text{CH}_3\text{I} \) peaks would be masked by both agents. Several thicknesses of samples and amounts of mulling agent were tried, all with the same results.
5.3 Temperature Dependence of the Crystalline Clathrate Mixture Absorptions

The results of warming annealed samples of clathrate mixtures from 4.2°K or 77°K to 200°K are in general the same as for cubic ice I, i.e. only the H₂O ir absorptions were observed. Thus only a few typical clathrate mixture results will be quoted and the remaining clathrate mixture results will be given in tabular form or as an average over all samples.

A. Temperature Dependence of the HDO Absorptions

(i) Experimental

The data reported here for ν OH(HDO) in CH₃Cl·7.67D₂O, CH₃Br·7.67D₂O and CH₃I·17D₂O, for ν OD(HDO) in CH₃Br·7.67H₂O, and for ν R(HDO) in CH₃Br·7.67D₂O were obtained from gaseous samples condensed in an open chamber followed by devitrification (section 5.1). The observations were made with the liquid helium dewar and the P.E. 421 spectrophotometer. Details of the sample histories were typical of those for ice I (page 69) as were details of spectrophotometer operating conditions. The HDO peak maxima were determined as before (page 69) and were estimated to within ± 0.5 cm⁻¹.

(ii) Results of Warming Clathrate Mixtures Containing HDO

(a) The HDO stretching bands. These bands appeared to be the same as in cubic ice I (Fig. 3.1) and typical spectra will not be reproduced. The temperature dependences of ν OH(HDO) and ν OD(HDO) for CH₃Br·7.67H₂O are shown in Figs. 5.6 and 5.7: They are typical of the other clathrate
Fig. 5.6 The temperature dependence of $\nu_{OH}$(HDO) for CH$_3$Br·TD$_2$O (4.00% HDO) after annealing. This was typical of all the annealed clathrate mixtures of the alkyl halides.
Fig. 5.7  The temperature dependence of $v_{OD}(\text{HDO})$ for CH$_3$Br·7.67H$_2$O (5.94% HDO) after annealing. This behaviour was typical of other alkyl halide clathrate mixtures.
mixtures and are very similar to cubic ice I. The details of the frequency-temperature dependences for all clathrate mixtures containing HDO are given in Table V.IX. The samples were prepared from the same H2O (5.94% HDO) and D2O (4.00% HDO) specimens as were the cubic ice I samples. The peak heights and half-height widths for HDO in these clathrate mixtures behaved in the same way as for HDO in cubic ice I. Some $\Delta v$ data are given in Fig. 5.8.

Table V.IX Some parameters derived from the plots of $v_{OH}(HDO)$ and $v_{OD}(HDO)$ against temperature for four annealed clathrate mixtures.

<table>
<thead>
<tr>
<th>Clathrate Guest G</th>
<th>CH3Cl</th>
<th>CH3Br</th>
<th>CH3I</th>
<th>CH3Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode Observed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low Temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Limit</td>
<td>cm$^{-1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$v$</td>
<td>3263.9</td>
<td>3264.0±1</td>
<td>3265.0±1.0</td>
</tr>
<tr>
<td></td>
<td>$\Delta v$</td>
<td>49.8</td>
<td>46.5±1</td>
<td>44.0±1.5</td>
</tr>
<tr>
<td></td>
<td>$\Delta v$</td>
<td>±2.3</td>
<td>±2.3</td>
<td>±2.3</td>
</tr>
<tr>
<td>Low Temperature</td>
<td>cm$^{-1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dependence</td>
<td>$\nu$</td>
<td>0.0375</td>
<td>0.0507</td>
<td>0.0368</td>
</tr>
<tr>
<td></td>
<td>$\Delta v$</td>
<td>±0.020</td>
<td>±0.027</td>
<td>±0.03</td>
</tr>
<tr>
<td>High Temperature</td>
<td>cm$^{-1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dependence</td>
<td>$\nu$</td>
<td>0.183</td>
<td>0.166</td>
<td>0.194</td>
</tr>
<tr>
<td></td>
<td>$\Delta v$</td>
<td>±0.012</td>
<td>±0.060</td>
<td>±0.09</td>
</tr>
<tr>
<td></td>
<td>$\Delta v$</td>
<td>±0.026</td>
<td>±0.026</td>
<td>±0.026</td>
</tr>
<tr>
<td>&quot;Freeze-in&quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature, °K</td>
<td>$\nu$</td>
<td>75±5</td>
<td>75±5</td>
<td>87±5</td>
</tr>
<tr>
<td></td>
<td>$\Delta v$</td>
<td>100±20</td>
<td>100±20</td>
<td>95±5</td>
</tr>
<tr>
<td>Irregularities in</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Frequency Shift, °K</td>
<td>$\nu$</td>
<td>42-48</td>
<td>42-65</td>
<td>63-75</td>
</tr>
</tbody>
</table>
Fig. 5.8 The half-height widths for $\nu_{OH}^{1/2}(HDO)$ and $\nu_{OD}^{1/2}(HDO)$ in several clathrate mixtures after annealing. These data were almost twice as large as for the cubic ice I data.
(b) HDO librations. Data for \( \nu_R(HDO) \) of CH\(_3\)Br·7.67D\(_2\)O (4.0% HDO) are given as a function of temperature in Fig. 5.9. This data is typical of other clathrate mixtures as well. The details of the temperature dependences are given in Table V.X.

B. Temperature Dependence of the H\(_2\)O and D\(_2\)O Absorptions

(i) Experimental

The H\(_2\)O and D\(_2\)O absorption features for the annealed clathrate mixtures were observed by the same methods as were cubic ice I samples (page 79). Seven H\(_2\)O absorptions were observed for each of the seven samples \( (\nu_1 + \nu_T, \nu_3, \nu_1, 3\nu_R, \nu_2/2\nu_R, \nu_R' \text{ and } \nu_R) \). However for D\(_2\)O clathrate mixtures the stretching band was studied in detail for CH\(_3\)I·17D\(_2\)O, CH\(_3\)Cl·7.67D\(_2\)O and CH\(_3\)Br·7.67D\(_2\)O, and the \( (\nu_R', \nu_R) \) band was studied only in CH\(_3\)Br·7.67D\(_2\)O. All mixtures except Cl\(_2\) and Br\(_2\) were studied between 4.2°K and 200°K, while Cl\(_2\) and Br\(_2\) were observed only above 77°K. Sample histories and spectrometer conditions were typical of the ice experiments.

(ii) Results of Warming Clathrate Mixtures Containing H\(_2\)O and D\(_2\)O

The temperature dependences of the H\(_2\)O and D\(_2\)O absorptions in the annealed clathrate mixtures were the same as for cubic ice I. Typical spectra for \( \nu_3 \) and \( \nu_1 \) of CH\(_3\)Br·7.67D\(_2\)O are given in Figs. 5.10 and 5.11. The details of these samples were averaged for CH\(_3\)Cl, CH\(_3\)Br, CH\(_3\)I, CHCl\(_3\) and C\(_2\)H\(_5\)Br mixtures and are compiled in Table V.XI. The details of several Cl\(_2·7.67H_2O\) and Br\(_2·8.6H_2O\) mixtures above 83 ± 3°K are given in Table V.XII. The spectra and plots were treated in the same manner as for
Fig. 5.9 The temperature dependence of $\nu_R^{(HDO)}$ for annealed CH$_3$Br·7.67D$_2$O (4.00% HDO) clathrate mixture. This data is typical of other alkyl halide clathrate mixtures.
Table V.X The parameters for the HDO librations of three annealed clathrate mixtures.

<table>
<thead>
<tr>
<th></th>
<th>CH$_3$Br·7.67D$_2$O (4.00% HDO)</th>
<th>CH$_3$Br·7.67D$_2$O (4.00% HDO)</th>
<th>CH$_3$I·17D$_2$O (4.00% HDO)</th>
<th>CH$_3$Br·7.67D$_2$O (4.00% HDO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>v$_R$ (HDO)</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
</tr>
<tr>
<td>Low Temperature Limit</td>
<td>814.0±2.0</td>
<td>817.8±1.0</td>
<td>816.3±1.3</td>
<td>853.3±2.8</td>
</tr>
<tr>
<td>Low Temperature Dependence</td>
<td>cm$^{-1}$ / °K</td>
<td>cm$^{-1}$ / °K</td>
<td>cm$^{-1}$ / °K</td>
<td>cm$^{-1}$ / °K</td>
</tr>
<tr>
<td>&lt; -0.03</td>
<td>&lt; -0.03</td>
<td>--</td>
<td>&lt; -0.09</td>
<td></td>
</tr>
<tr>
<td>High Temperature Dependence</td>
<td>cm$^{-1}$ / °K</td>
<td>cm$^{-1}$ / °K</td>
<td>cm$^{-1}$ / °K</td>
<td>cm$^{-1}$ / °K</td>
</tr>
<tr>
<td>-0.064±0.031</td>
<td>-0.135±0.055</td>
<td>-0.164±0.045</td>
<td>-0.125±0.028</td>
<td></td>
</tr>
<tr>
<td>&quot;Freeze-in&quot; Temperature</td>
<td>°K</td>
<td>°K</td>
<td>°K</td>
<td>°K</td>
</tr>
<tr>
<td>75±10</td>
<td>70±5</td>
<td>62±5</td>
<td>80±5</td>
<td></td>
</tr>
<tr>
<td>Irregularities in Frequency shifts</td>
<td>°K</td>
<td>°K</td>
<td>°K</td>
<td>°K</td>
</tr>
<tr>
<td>48-58</td>
<td>47-57</td>
<td>56-72</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 5.10 The temperature dependence of $\nu_3(D_2O)$ for annealed CH$_3$Br·7.6D$_2$O. Data from two specimens which had similar sample histories are given.

ice I to determine the details of the samples behaviours.

The liquid helium and liquid nitrogen cell frequency data did not always coincide within the errors of the two experiments. In general, the liquid helium cell data have been quoted in regions of doubt. However, the frequency-temperature dependences were equal for both sets of data.

For the $3\nu_R(H_2O)$ region considerable error was introduced by atmospheric CO$_2$ absorption and the resulting instrument imbalance near 2300 cm$^{-1}$. 
Fig. 5.11 The temperature dependence of $\nu_1(D_2O)$ for annealed CH$_3$Br·7.67D$_2$O. Data from the same two experiments as in Fig. 5.10 are shown.

The best study of $3\nu_R(H_2O)$ was made for a thick sample of Br$_2$·8.6H$_2$O. The frequency-temperature dependence was distinctly negative.

Samples of Cl$_2$·7.67H$_2$O on CsI support windows gave anomalous behaviour after annealing to 190 ± 5°K. The stretching band split into two peaks and three shoulders, Fig. 5.4(c). A sharp weak band and a very, very weak shoulder appeared on top of the general, broad $\nu_2$ absorption: A peak at 1628 cm$^{-1}$ and a shoulder near 1620 cm$^{-1}$. Samples of Cl$_2$·7.67H$_2$O on AgCl support windows did not exhibit such behaviour. The high frequency absorp-
Table V-XI  The temperature dependences of H$_2$O (D$_2$O in brackets) modes averaged over the five alkyl halide annealed clathrate mixtures.

<table>
<thead>
<tr>
<th></th>
<th>Low Temperature Limit</th>
<th>Low Temperature Dependence</th>
<th>High Temperature Dependence</th>
<th>Freeze-in Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$/°K</td>
<td>cm$^{-1}$/°K</td>
<td>°K</td>
</tr>
<tr>
<td>H$_2$O</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(D$_2$O)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_1 + v_T$</td>
<td>3331±5 (sh) (2440±5)</td>
<td>&lt;0.06 (0.06±0.03)</td>
<td>0.17±0.05 (0.14±0.06)</td>
<td>82±10 (93±15)</td>
</tr>
<tr>
<td>$v_3$</td>
<td>3208±3 (vs) (2416±2)</td>
<td>&lt;0.06 (0.05±0.03)</td>
<td>0.19±0.05 (0.12±0.04)</td>
<td>81±15 (88±10)</td>
</tr>
<tr>
<td>$v_1$</td>
<td>3127±5 (sh) (2316±2)</td>
<td>&lt;0.15 (&lt;0.08)</td>
<td>0.24±0.05 (0.24±0.05)</td>
<td>85±20 (86±10)</td>
</tr>
<tr>
<td>$v_2/2v_R$</td>
<td>1588±6 (m)</td>
<td>&lt;0.2</td>
<td>0.36±0.15</td>
<td>80±15</td>
</tr>
<tr>
<td>$v_R'$</td>
<td>896±5 (sh) (677±3)</td>
<td>-0.07±0.01 (&lt;0.03)</td>
<td>-0.18±0.05 (&lt;-0.15±0.07)</td>
<td>83±15 (80±10)</td>
</tr>
<tr>
<td>$v_R$</td>
<td>831±5 (s) (646±3)</td>
<td>-0.05 ±0.01 (&lt;-0.02)</td>
<td>-0.14±0.06 (&lt;-0.15±0.07)</td>
<td>85±17 (90±10)</td>
</tr>
</tbody>
</table>
Table V.XII: The frequencies at 80°K and the high temperature dependences of Cl$_2\cdot$7.67H$_2$O on AgCl and CsI and of Br$_2\cdot$8.6H$_2$O on CsI.

<table>
<thead>
<tr>
<th>Sample Support Window</th>
<th>Host Lattice</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$_2$</td>
<td>Cl$_2$</td>
<td>Cl$_2$</td>
</tr>
<tr>
<td>CsI</td>
<td>CsI</td>
<td>AgCl</td>
</tr>
<tr>
<td>Frequency</td>
<td>$v_1 + v_T$</td>
<td>3368</td>
</tr>
<tr>
<td>at 80°K from</td>
<td>$v_3$</td>
<td>3218</td>
</tr>
<tr>
<td>Extrapolated</td>
<td>$v_1$</td>
<td>3145</td>
</tr>
<tr>
<td></td>
<td>$v_R$</td>
<td>2220±10</td>
</tr>
<tr>
<td>Linear</td>
<td>$v_R'$</td>
<td>1628±2</td>
</tr>
<tr>
<td>Dependence cm$^{-1}$</td>
<td>$v_R$</td>
<td>894</td>
</tr>
<tr>
<td>Frequency</td>
<td>$v_1 + v_T$</td>
<td>-0.12</td>
</tr>
<tr>
<td>Dependence on $v_3$</td>
<td>0.13</td>
<td>0.12</td>
</tr>
<tr>
<td>Dependence on $v_1$</td>
<td>0.19</td>
<td>0.54</td>
</tr>
<tr>
<td>Temperature $cm^{-1}$</td>
<td>$v_R$</td>
<td>-0.06</td>
</tr>
<tr>
<td></td>
<td>$v_R'$</td>
<td>-0.09</td>
</tr>
<tr>
<td></td>
<td>$v_R$</td>
<td>-0.17</td>
</tr>
</tbody>
</table>
tion attributed to \((v_1 + v_1)\) was a peak near \(3365 \text{ cm}^{-1}\) for \(\text{Cl}_2\cdot7.67\text{H}_2\text{O}\) on CsI. That was about \(30 \text{ cm}^{-1}\) higher than the shoulder observed in other samples and for \(\text{Cl}_2\cdot7.67\text{H}_2\text{O}\) on AgCl. Also, the frequency-temperature dependence of \((v_1 + v_1) (\text{H}_2\text{O})\) from samples of \(\text{Cl}_2\cdot7.67\text{H}_2\text{O}\) on CsI was negative. In other samples \((v_1 + v_1) (\text{H}_2\text{O})\) had a positive temperature dependence. The \(\text{H}_2\text{O}\) features from \(\text{Cl}_2\cdot7.67\text{H}_2\text{O}\) on CsI and AgCl windows at 83°C were:

<table>
<thead>
<tr>
<th>CsI Window</th>
<th>AgCl Window</th>
</tr>
</thead>
<tbody>
<tr>
<td>3412 (sh) cm(^{-1})</td>
<td>--</td>
</tr>
<tr>
<td>3368 (s)</td>
<td>3338 (sh) cm(^{-1})</td>
</tr>
<tr>
<td>3285 (sh)</td>
<td>--</td>
</tr>
<tr>
<td>3218 (vs)</td>
<td>3221 (vs)</td>
</tr>
<tr>
<td>3145 (sh)</td>
<td>3147 (sh)</td>
</tr>
<tr>
<td>2220 (w)</td>
<td>2225 (w)</td>
</tr>
<tr>
<td>1883 (w)</td>
<td>--</td>
</tr>
<tr>
<td>1628 (sharp, weak)</td>
<td>--</td>
</tr>
<tr>
<td>c.a. 1600 (broad, m.)</td>
<td>1609 (broad, m.)</td>
</tr>
<tr>
<td>894 (sh)</td>
<td>886 (sh)</td>
</tr>
<tr>
<td>839 (m)</td>
<td>841 (m)</td>
</tr>
</tbody>
</table>

The sharp peak at 1628 cm\(^{-1}\) from the CsI window experiment exhibited no temperature dependence.
CHAPTER SIX

DISCUSSION OF THE CLATHRATE MIXTURES

6.1 The Clathrate Mixture Vitreous-Crystalline Phase Transformation

A. General Discussion

The nature of the samples formed by rapid condensation of clathrate mixtures was probably much the same as for vitreous ice I. Thus much of the discussion on annealing ice I applies here also, i.e. the onset of crystallization, the effects on the ir spectra and the processes involved in reorientation. As before the H$_2$O lattice modes shifted to higher frequency and the molecular modes shifted to lower frequency. The H$_2$O bands sharpened and had better defined features after annealing. The transformation temperature range began at 115 ± 5°C (uncorrected for source beam heating) and took about 18 minutes at 125°C. However, the range for the clathrate mixtures seemed to be extended to higher temperatures by about 10°C. The vitreous samples shifted irreversibly below 150°C and reversibly once warmed above 150°C. It was not clear that annealing vitreous clathrate mixtures produced the desired cubic 12 Å or 17 Å unit cell structures. We suspect that not a clathrate structure, but cubic ice I was probably formed. The longer transition temperature range suggested the vitreous clathrate mixtures were more stable than the vitreous H$_2$O or D$_2$O ice samples.

While the mechanism for H$_2$O or D$_2$O frequency shift was the same as in ice I (the formation of a fully hydrogen-bonded network of each oxygen to four nearest-neighbour oxygen atoms at about the same distance as in ice I) there should be a fundamental difference for the ir spectra of clathrate-hydrates. X-ray crystallography had shown that the alkyl halide
and halogen clathrates had varying cage sizes and varying O⋯O distances (Table 0.2). Peak positions of annealed clathrate samples should have varied regularly as a function of unit cell size. The annealing results did not support this concept, but results on H₂O and D₂O were subject to large errors. HDO results were better and are discussed in section 6.3A.

B. Annealing Cl₂·7.67H₂O on CsI

Samples of Cl₂·7.67H₂O which were deposited on CsI and annealed to 190 or 200°K for 10 to 15 minutes gave unique H₂O spectra (Figs. 5.4(c) and 5.5), while the same samples annealed to only 180 ± 3°K gave typical H₂O spectra (Fig. 5.5). As well, the spectra from samples of Cl₂·7.67H₂O annealed on AgCl windows to 190 or 200°K for long times were typical of ice, as were the spectra of CH₃Cl, CH₃Br, CHCl₃ and C₂H₅Br clathrate mixtures annealed on CsI at 195°K for more than 10 minutes.

The Cl₂·7.67H₂O on CsI samples had five stretching band features (three shoulders at 3412, 3285 and 3145 cm⁻¹ and two peaks at 3368 and 3218 cm⁻¹) compared to three features in ice I and other annealed clathrate mixtures (two shoulders at 3338 and 3147 cm⁻¹ and a peak at 3221 cm⁻¹ for Cl₂·7.67H₂O on AgCl). As well there appeared a weak, sharp peak and an adjacent shoulder (1628 and 1607 cm⁻¹) on top of the broad ν₂(H₂O) absorption. The weak peak and shoulder frequencies were independent of temperature. Other absorption features which arose were a peak at 1883 cm⁻¹, a distinct shoulder at 1100 cm⁻¹ and pronounced absorption between 2300 cm⁻¹ and 3000 cm⁻¹ (Fig. 5.4(c)). The last effect may have been due to increased scattering losses if the substrate surface became pitted by the sample, while
the shoulder at 1100 cm$^{-1}$ may have been due to a Christiansen filter effect.

Mecke et al. (103) observed four well defined bands in their "ice I$_h$" spectra on NaCl windows (Table VI.I). However, Schiffer (104) studied a number of dihydrated sodium halides and showed that Mecke's "ice" was NaCl·2H$_2$O. The data of Table VI.I suggest that the Cl$_2$·7.67H$_2$O condensed and annealed on CsI may have formed a hydrated cesium halide layer on the substrate, i.e. CsI·xH$_2$O, CsCl·xH$_2$O or CsICl$_2$·xH$_2$O.

The presence of hydrated cesium halide substrate was supported by the appearance of the sharp, weak peak at 1628 cm$^{-1}$ and a shoulder at 1607 cm$^{-1}$ in the spectra of Cl$_2$·7.67H$_2$O on CsI. These were similar to peaks observed by Mecke et al. (103) and Schiffer (104), Table VI.I.

That substrate hydration did not occur for Cl$_2$·7.67H$_2$O on AgCl nor for CH$_3$Cl, CH$_3$Br, CH$_3$I, CHCl$_3$ and C$_2$H$_5$Br clathrate mixtures is not surprising. For AgCl and Cl$_2$·7.67H$_2$O it is probable that the Cl$_2$ does not oxidize AgCl, whereas it may oxidize CsI. As well, AgCl is chemically more resistant to hydration.

It is possible that Cl$_2$ reacted with CsI to form CsCl and ICl or else CsICl$_2$. Intermediate steps may have allowed the formation of hydrated halide salts. Although hydrates of CsCl, CsI and CsICl$_2$ are not stable at 20°C, they may be stable at 200°C and lower.

We have already estimated that our samples were about 1μ (10,000 Å) thick. From the relative intensities of the ice I and hydrated salt absorptions one might expect 10% or more of the H$_2$O in the original sample to be attached as water of hydration. Thus the formation of several hundred monolayers of CsICl$_2$ is unlikely since ICl$_2^-$ is too long to fit
Table VI.I  The ir absorptions due to H$_2$O stretches in dihydrated salts, "Mecke's ice", and annealed Cl$_2$·7.67H$_2$O on CsI (all at 83 ± 3°K.

<table>
<thead>
<tr>
<th>Cl$_2$·7.67H$_2$O</th>
<th>Ice on CsI</th>
<th>NaCl·2H$_2$O (a)</th>
<th>NaBr·2H$_2$O (b)</th>
<th>NaI·2H$_2$O (b)</th>
<th>CaSO$_4$·2H$_2$O (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
</tr>
<tr>
<td>3412 (sh)</td>
<td>3555 (m)</td>
<td>3538 (s)</td>
<td>3539 (s)</td>
<td>3563 (sh)</td>
<td>3549 (vs)</td>
</tr>
<tr>
<td>3368 (ms)</td>
<td>3471 (s)</td>
<td>3468 (vs)</td>
<td>3469 (vs)</td>
<td>3506 (s)</td>
<td>3496 (s)</td>
</tr>
<tr>
<td>3285 (sh)</td>
<td>3407 (s)</td>
<td>3405 (vs)</td>
<td>3406 (vs)</td>
<td>3461 (s)</td>
<td>3404 (vs)</td>
</tr>
<tr>
<td>3218 (s)</td>
<td>3245 (w)</td>
<td>3310 (vww)</td>
<td>3360 (sh)</td>
<td>3437 (sh)</td>
<td>3242 (m)</td>
</tr>
<tr>
<td>3145 (sh)</td>
<td></td>
<td>3265 (mw)</td>
<td>3242 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1628 (vw)</td>
<td>1645 (m)</td>
<td>1643 (s)</td>
<td>1635 (s)</td>
<td>1626 (sh)</td>
<td></td>
</tr>
<tr>
<td>1607 (sh)</td>
<td>1616 (m)</td>
<td>1615 (s)</td>
<td>1614 (s)</td>
<td>1613 (s)</td>
<td></td>
</tr>
</tbody>
</table>

(a) Ref. 103     (b) Ref. 104     (c) Ref. 127

into an interior I$^-$ lattice site: It may however occupy an I$^-$ surface lattice site. As well it seems unlikely that a solid-solid reaction would lead to deep penetration of Cl$_2$ or Cl$^-$ into CsI since Harrison et al. (128) found some alkali halide single crystals were very resistive to exchange with Cl$_2$ even at room temperature.

The origin of the new absorption at 1883 cm$^{-1}$ is not known. It lies well above the calculated $v_2$(H$_2$O) position of Hornig et al. (105), 1780 cm$^{-1}$. It may be due to ($v_2 + v_T$) for the hydrated salt $v_2$(H$_2$O) and the H$_2$O lattice $v_T$. 


C. Oligomeric H$_2$O Absorptions

All the unannealed clathrate mixtures exhibited very weak peaks or shoulders in the region 3500-3700 cm$^{-1}$, Table VI.II. Similar absorptions were found for H$_2$O and D$_2$O ice I$_V$ and the clathrate mixture peaks were also assigned to oligomeric H$_2$O and D$_2$O units. As was shown for CH$_3$Br·7.67H$_2$O (Table V.III) in three different specimens the positions, intensity and number of oligomeric features were dependent on the rate of sample deposition. The 3690 cm$^{-1}$ peak was obtained from a CH$_3$Br·7.67H$_2$O sample deposited in 11 minutes, while the 3620 cm$^{-1}$ peak was obtained from a sample deposited in 1.5 minutes and the peaks at 3645 and 3605 cm$^{-1}$ were obtained from samples deposited in 4.5 minutes. Fast deposition produced more localized heating and H$_2$O polymerization than slow deposition. Van Thiel et al. (117) suggested monomeric, dimeric and trimeric H$_2$O absorbed at (3725 and 3625), (3691 and 3546), and (3510 and 3355) cm$^{-1}$ respectively. On that basis we appear to have formed residual dimeric H$_2$O in the unannealed clathrate mixtures.

The presence of oligomeric H$_2$O and D$_2$O suggests a low mobility of molecules during condensation. However, low mobility of guest molecules does not necessarily follow. Finally, it may be possible to follow the rate of crystallization in ice I and clathrate mixtures by following the peak heights of oligomeric H$_2$O.

D. Unannealed Sample Guest Absorptions

Guest absorptions in unannealed clathrate mixtures due to alkylhalides were observed for all specimens. During annealing the general experience was
Table VI.II  The weak peaks and shoulders attributed to oligomeric H$_2$O and D$_2$O $v_1$ and $v_3$ stretching modes in some clathrate mixtures and in some inert matrices.

<table>
<thead>
<tr>
<th>M</th>
<th>CH$_3$Cl</th>
<th>CH$_3$Br</th>
<th>CH$_3$I</th>
<th>CHCl$_3$</th>
<th>C$_2$H$_5$Br</th>
<th>Cl$_2$</th>
<th>Br$_2$</th>
<th>Ar(a)</th>
<th>Kr(a)</th>
<th>N$_2$(a)</th>
<th>CCl$_4$(a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles M</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>300</td>
<td>380</td>
<td>240</td>
<td>1000</td>
</tr>
<tr>
<td>Moles R</td>
<td>7.67</td>
<td>7.67</td>
<td>17</td>
<td>17</td>
<td>17</td>
<td>7.67</td>
<td>8.6</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>cm$^{-1}$</th>
<th>3690*</th>
<th>3687</th>
<th>3689</th>
<th>3690</th>
<th>3691</th>
<th>3708</th>
<th>3700</th>
</tr>
</thead>
<tbody>
<tr>
<td>R is H$_2$O</td>
<td>3668</td>
<td>3670</td>
<td>3699</td>
<td>3687</td>
<td>3686</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3654</td>
<td>3645</td>
<td>3648</td>
<td>3639</td>
<td>3643</td>
<td>3634</td>
<td>3634</td>
</tr>
<tr>
<td></td>
<td>3620X</td>
<td></td>
<td>3625</td>
<td>3617</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3605</td>
<td>3612</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R is D$_2$O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2648</td>
<td>2644</td>
<td>2647</td>
<td>2637</td>
<td>2635</td>
<td>2655</td>
<td>2643</td>
</tr>
<tr>
<td></td>
<td>2635</td>
<td>2632</td>
<td>2650</td>
<td>2662</td>
<td>2625</td>
<td>2639</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2615</td>
<td>2614</td>
<td>2617</td>
<td>2614</td>
<td>2610</td>
<td>2614</td>
<td></td>
</tr>
</tbody>
</table>

(a) Ref. 115

* Very slow deposit  X fast deposit
that guest absorptions were observed with undiminished peak heights up to 120 \( \pm 5 \)°K, but they were unobserved above 170 \( \pm 5 \)°K or after recooling the samples to 83 \( \pm 3 \)°K. The peak heights of bands in different clathrate types decreased at different rates, while the peak heights of several specimens of one clathrate mixture (i.e., \( \text{CH}_3\text{Br} \cdot 7.67\text{H}_2\text{O} \)) decreased at about the same rate. As one might expect the drop in guest peak heights began at the same temperature as the oligomeric \( \text{H}_2\text{O} \) disappeared (near 130 \( \pm 10 \)°K).

Frequencies of guest absorptions in the unannealed clathrate-hydrates and of pure, solid guest molecules (all at 83 \( \pm 3 \)°K) are listed in Table VI.III. For unannealed clathrate mixtures of \( \text{CH}_3\text{Cl}, \text{CHCl}_3 \) and \( \text{C}_2\text{H}_5\text{Br} \) all strong and medium intensity absorptions of the pure solid were observed. In contrast, for \( \text{CH}_3\text{Br} \) and \( \text{CH}_3\text{I} \) unannealed clathrate mixtures, only some of the pure solid absorptions were observed. Strong unannealed clathrate guest absorptions expected near 3050, 1420, 895 or 964, and 596 \( \text{cm}^{-1} \) were unobserved. Also in the \( \text{CH}_3\text{Br} \cdot 7.67\text{H}_2\text{O} \) sample, peaks were observed in the clathrate (1218, 1200, and 750 \( \text{cm}^{-1} \)) which were unobserved in the pure solid. The clathrate guest peaks were shifted only slightly from the pure solid peaks. However, where the pure solid had multiplets of peaks the clathrate peaks were singlets.

We can offer no explanation for the missing \( \text{CH}_3\text{I} \) and \( \text{CH}_3\text{Br} \) peaks nor for the extra \( \text{CH}_3\text{Br} \) peaks. The loss of guest band splitting between the pure solid and clathrate was not unexpected, the splitting of degeneracies in pure crystals being lost due to the range of absorption frequencies arising from the inhomogeneity among the guest sites in the vitreous mixtures.

There are at least three explanations of the loss of the clathrate guest absorptions in the annealed samples. First, there was too much guest in
Table VI.III  Alkyl halide ir absorptions in the pure solid state and in some unannealed clathrate mixtures at 83 ± 3°K.

<table>
<thead>
<tr>
<th>CH₃Cl</th>
<th>CH₃Br</th>
<th>CH₃I</th>
<th>CHCl₃</th>
<th>C₂H₅Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clath. solid(a)</td>
<td>Clath. Solid(a)</td>
<td>Clath. Solid(b)</td>
<td>Clath. Solid(c)</td>
<td>Clath. Solid(a)</td>
</tr>
<tr>
<td>cm⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2957 m</td>
<td>2950 w</td>
<td>3020 sh</td>
<td>3036 m</td>
<td>3035 m</td>
</tr>
<tr>
<td>2965 sh</td>
<td>2954 s</td>
<td>2936 vs</td>
<td>2935 s</td>
<td>2915 vvw</td>
</tr>
<tr>
<td>2846 m</td>
<td>2830 m</td>
<td>2803 m</td>
<td>2803 m</td>
<td>2803 m</td>
</tr>
<tr>
<td>1444 sh</td>
<td>1436 m</td>
<td>1426 ms</td>
<td>1426 ms</td>
<td>1426 ms</td>
</tr>
<tr>
<td>1443 s</td>
<td>1432 vs</td>
<td>1420 s</td>
<td>1401 ms</td>
<td>1401 ms</td>
</tr>
<tr>
<td>1437 sh</td>
<td>1436 m</td>
<td>1420 s</td>
<td>1401 ms</td>
<td>1401 ms</td>
</tr>
<tr>
<td>1347 w</td>
<td>1345 m</td>
<td>1293 sh</td>
<td>1244 sh</td>
<td>1241 vs</td>
</tr>
<tr>
<td>1338 vs</td>
<td>1336 m</td>
<td>1292 vvw</td>
<td>1291 vs</td>
<td>1234 w</td>
</tr>
<tr>
<td>1218 vvw</td>
<td>1200 sh</td>
<td>962 vw</td>
<td>895 vs</td>
<td>888 vs</td>
</tr>
<tr>
<td>1021 vw</td>
<td>1020 m</td>
<td>955 vs</td>
<td>888 vs</td>
<td>752 m</td>
</tr>
<tr>
<td>700 s</td>
<td>700 vs</td>
<td>750 s</td>
<td>589 sh</td>
<td>663</td>
</tr>
<tr>
<td>697 sh</td>
<td>585 vs</td>
<td>570 m</td>
<td>663</td>
<td>663</td>
</tr>
<tr>
<td>692 s</td>
<td>585 vs</td>
<td>570 m</td>
<td>663</td>
<td>663</td>
</tr>
</tbody>
</table>

(a) This work  (b) Ref. 129  (c) Ref. 130
the unannealed mixture formed on the window. The excess guest diffused out and sublimed off the window during annealing, while the remainder was too small to detect. Secondly, all of the guest molecules may have diffused out of the H₂O lattice and sublimed off the window. Thirdly, the guest molecules may have been present but ir inactive due to some cage effect. The third possibility is unlikely since cage perturbations are more likely to induce anharmonicities, peak shifts or even enhance the intensities. The first explanation also seems unlikely since H₂O condenses at a much higher temperature than most of the guests, if anything the samples may have been deficient in guest. The expulsion of all guest molecules from the H₂O lattice seems most probable.

Further work, to be described later, was done to check which of the above reasons was most probable. One further logical method to use (which we did not) is observing clathrate-hydrates in Raman spectroscopy. There the H₂O bands are sharp, while most alkyl halide bands are ir and Raman active and thus the bulk samples may be prepared and observed, in contrast to the thin films of our ir technique.

6.2 Guest Species Absorptions

It was suggested in section 6.1 that sample condensation and annealing in an open cell chamber leads to expulsion of the foreign guest molecules from the H₂O or D₂O lattice in the absence of the equilibrium dissociation pressure of the clathrate. Two further experiments tested the possibilities of sample fractionation between the sample deposition tube and the substrate surface, and simple sample dissociation.
A. Isolated Chamber Condensation

Gaseous clathrate mixtures condensed in an isolated chamber (Fig. 1.2) and unannealed exhibited guest absorptions with approximately the same intensities relative to H$_2$O bands as open chamber samples. Therefore we concluded that the open chamber samples did not fractionate during deposition. The design of the closed chamber cell ensured that all of the gaseous sample condensed on one window while for open chamber condensation the heated deposition tube ensured that no H$_2$O or guest molecules condensed on the deposition tube tip.

Clathrate mixtures condensed in a closed chamber, but annealed to 185 ± 5°K and recooled to 83°K, exhibited no guest absorptions: The same behaviour exhibited by open chamber samples. That was contrary to Shurvell's (57) results and probably arose from the differences in maximum annealing temperature: He annealed only to 145 ± 5°K. The annealing process was not followed in detail (spectroscopically) for closed chamber samples, but the annealed sample spectra for 83°K appeared the same as those in section 6.1 and in ice I.

The same spectroscopic results were obtained for unannealed or annealed samples whether they were observed in open or closed sample chambers. The guest molecules must have been expelled from the H$_2$O or D$_2$O lattice in the closed chamber, due to the absence of a positive clathrate stabilizing pressure of guest vapour at 185 ± 5°K.
B. Low Temperature Mulls

The obvious alternative was to form clathrate-hydrate samples in bulk and observe their spectra by low temperature mulling. It was difficult to grind the samples at 77°K to a very fine powder and considerable scattering was observed from the large particle size. Whalley (95) obtained much better spectra (of ice) apparently with finer powders. The indices of refraction of the mulling agents and ice agreed fairly well in the visible region, but the indices change very rapidly over absorption bands and this seems to induce considerable scattering between 1700 to 2000 cm\(^{-1}\) and 2300 to 3000 cm\(^{-1}\).

It was of course unnecessary to anneal mulled samples since the crystalline samples were initially cooled from 273°K to 83°K at 1 atmosphere of N\(_2\)(g). However, no guest absorptions were observed for either the mull of CH\(_3\)I·17H\(_2\)O or CCl\(_3\)F·17H\(_2\)O. Most of the CH\(_3\)I or CCl\(_3\)F guest absorptions should have been observed in either the C\(_3\)H\(_8\) or CCl\(_3\)F mulling agent.

Two explanations are possible. First, during transferal of sample from the preparation tube to the mortar and pestle the sample was warmed to 273°K momentarily and it may have dissociated. However, the CH\(_3\)I and CCl\(_3\)F clathrates were chosen specifically for their guests liquid states and low vapour pressures at 273°K and their clathrates low dissociation pressures. Secondly, the CH\(_3\)I and CCl\(_3\)F molecules may have been very soluble in liquid C\(_3\)H\(_8\) and liquid CCl\(_3\)F even at low temperature. However, the clathrate samples were not observed to dissolve in the mulling agents. If the guests did dissolve in the mulling agent then they should still have been observed in the spectra as a solid solution.
We could not establish with confidence that the clathrate samples had not decomposed during preparation of the mull. The samples may have dissociated either during transfer to the pestle or during evacuation of the cryostat (with the sample temperature between 100 and 150°K). No attempts were made to analyze the small quantities of vapour evolved after warm-up of the cell to room temperature.

The H$_2$O skeletal absorptions observed in mulls were much like previous cases: Scattering distorted the bands considerably. One difference did occur, however, the $\nu_2$ absorption was well defined at 1570 cm$^{-1}$ at 83°K. In most spectra the region from 1600 to 3000 cm$^{-1}$ was just one broad band which steadily increased in intensity.

C. Summary

Infrared observations by Hexter and Goldfarb (53) on HCl, H$_2$S, CO$_2$ and SO$_2$ clathrated in hydroquinone demonstrated that for weakly absorbing guests the guest absorption was unobserved in the clathrate, but strong absorbers like CO$_2$ and SO$_2$ were easily observed. They pointed out that in the amount of HCl-quinone clathrate used for the ir observations, only about 5% of the HCl needed for a reasonable HCl(g) spectrum was present. Davies and Child (55) also observed ir absorption by guests in quinone clathrates. They suggested that the shifts in guest frequencies were no larger than for solutions of guests in CCl$_4$. Their conclusion was that the cage had perturbing influences no larger than a non-polar solvent. We deduce that in our annealed clathrate-hydrate mixtures the guests all could not have been present and ir inactive.
We concluded that for unannealed clathrate mixtures, since there was no fine structure associated with the guest absorptions, guest rotation and translation was hindered. If the binding in the unannealed samples was not physical, but chemical, then we expected new guest functional group frequencies. The evidence indicates our methods were insufficient to form clathrate-hydrates.

6.3 The Temperature Dependences of Crystalline Clathrate Mixture Absorptions

A. HDO in Clathrate Mixtures

Discussion of the results from annealed clathrate-hydrate mixtures collapses to a discussion of cubic ice I: We assume the guest was all dispersed and a cubic ice I lattice formed at 185 ± 5°K. The clathrate studies became independent checks of the reproducibility of cubic ice I experiments.

Consider the $\nu_{OH}$(HDO) frequencies from CH$_3$Cl, CH$_3$Br and CH$_3$I mixtures with D$_2$O (4.00% HDO). Except for one set of CH$_3$Br results, the clathrate-mixture low temperature limits, low temperature dependences, high temperature dependences, "freeze-in" temperatures and irregularities in frequency-temperature shifts agreed, within error, with HDO cubic ice I data. Clathrate mixture $\nu_{OD}$(HDO) frequency limit, temperature dependences, "freeze-in" temperatures, etc., agreed, within error, with $\nu_{OD}$(HDO) of cubic ice I.

Half-height width data from clathrate-mixtures did not agree with cubic ice I HDO data. Both $\Delta\nu_{OH}^\frac{1}{2}$ and $\Delta\nu_{OD}^\frac{1}{2}$ from clathrates were at least 25 percent larger than in cubic ice I. Contrary to cubic ice I, $\Delta\nu_{OD}^\frac{1}{2}$ was
30 percent larger than $\Delta v^h_{\text{OH}}$. One can understand the increased $\Delta v^h_{\text{OH}}$ over cubic ice I on the basis of further H$_2$O exchange into the D$_2$O(H$_2$O) mixture as the sample aged, in spite of precautions. One cannot rationalize increased $\Delta v^h_{\text{OD}}$ in that way.

Notice that if a true clathrate had been formed from the CH$_3$Br mixture, for example, then the $v_{\text{OH}}$(HDO) frequency would have been expected at a much higher frequency than observed. Since CH$_3$Br forms a cubic type I clathrate (CH$_3$Br·7.67H$_2$O ideal stoichiometry) with a 12.09 Å cell parameter (Table 0.2) then the average 0···0 distance must be 2.809 Å at 273°C. For $R(0···0) = 2.755$ Å in cubic ice I we found $v_{\text{OH}}$(HDO) = 3290 cm$^{-1}$ (Fig. 5.12) and $\Delta v/\Delta R = 1921$ cm$^{-1}$/Å. Since the 0···0 distances differed by 0.054 Å we expected a $\Delta v$ of 104 cm$^{-1}$. Thus CH$_3$Br·7.67D$_2$O(H$_2$O) clathrate should have had $v_{\text{OH}}$(HDO) absorbing near 3394 cm$^{-1}$(273°C). Assuming the same frequency-temperature dependence as in ice then at 83°C $v_{\text{OH}}$(HDO) should have absorbed at 3394 cm$^{-1} - 190°C (0.200 \text{ cm}^{-1}/°\text{K}) = 3356 \text{ cm}^{-1}$. The absence of such absorption also supported the conclusion that clathrates did not form. The same principles could be applied to CH$_3$I·17D$_2$O(HDO) and CH$_3$Br·7.67H$_2$O(HDO) mixtures.

The distribution of 0···0 distances is much greater in clathrates than in ice I due to four unique distances, each of which must have an ice-like distribution. One would expect considerably broader HDO bands in clathrates.

Librations of HDO in clathrate mixtures and cubic ice I also agreed within error with respect to high temperature frequency dependence, "freeze-in" temperature and frequency shift irregularities. The low temperature limits did not agree within our stated errors. The disagreement was not
sufficient to suggest clathrate had formed, i.e. increased \( R(0\cdots0) \) in clathrates suggested a shift of \((15 - 20) \text{ cm}^{-1} \) from cubic ice I.

The irregularities observed in frequency shifts with increasing temperature were discontinuous shifts by \( 2 - 3 \text{ cm}^{-1} \), generally to higher frequency in the case of stretches and to lower frequency in the case of librations. Another break in the curves appeared near \( 80^\circ \text{K} \). These breaks may have been related to partial ordering, as was suggested before.

B. \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \) in Clathrate Mixtures

Discussion of \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \) absorptions in annealed clathrate-hydrate mixtures also reduces to a discussion of cubic ice I. The behaviour of \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \) clathrate mixture absorption frequencies, half-height widths and temperature dependences were the same as in cubic ice I.

If true clathrate hydrates had formed on annealing then low temperature limits and half-height widths should have been significantly different from ice: They were not. The low temperature limits of each individual \( \text{H}_2\text{O} \) or \( \text{D}_2\text{O} \) absorption agreed within error, Table V.XI, for the set of clathrate mixture data. The average for each band, over all clathrate mixtures, agreed with the observed \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \) ice I data. The only exceptions were for \( \nu_1 + \nu_T(D_2\text{O}) \), \( \nu_R'(D_2\text{O}) \) and \( \nu_R(D_2\text{O}) \). Those three sets of data were obtained from broad shoulders or ill-defined peaks, both of which were hard to define consistently. High temperature frequency dependences for each clathrate-mixture band agreed within error, Table V.XI, over
the set of clathrate mixtures. The "freeze-in" temperature data were also compatible.

There were two special points to consider, the negative temperature dependence of \( \nu_1 + \nu_T \) from \( \text{Cl}_2\cdot7.67\text{H}_2\text{O} \) on CsI and zero temperature dependence of the weak 1628 cm\(^{-1}\) (CsI\(\cdot2\text{H}_2\text{O}\) ?) band. Negative temperature dependence was characteristic of lattice modes. Since such an intense lattice overtone was unlikely, the 3368 cm\(^{-1}\) band may have been a combination of \( \nu_1 \) with an overtone of a low frequency lattice mode (say 2\( \nu_T \')). The shift of \( \nu_1 + \nu_T \) to higher frequency by 30 cm\(^{-1}\) was understood in terms of the smaller overlap with \( \nu_3 \) than in ice I. Insensitivity of the weak, sharp 1628 cm\(^{-1}\) absorption to temperature is characteristic of non-hydrogen-bonded-lattice \( \text{H}_2\text{O} \): That supports its assignment to \( \nu_2 \) of, say, CsI\(\cdot2\text{H}_2\text{O}\).

Results of section 5.3 on \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \) in annealed clathrate mixtures differed from those of McCourt (56) and Shurvell (57). We failed to detect their additional 3\( \nu_R \) absorption near 2400 cm\(^{-1}\). However, we experienced problems from instrument imbalance through atmospheric CO\(_2\) between 2280 and 2360 cm\(^{-1}\). As well, attempts to duplicate their (56,57) SO\(_2\) results failed. McCourt's samples do not appear to have been annealed, as suggested by the shape and positions of the \( \text{H}_2\text{O} \) absorptions. Inspection of McCourt's (56) and Shurvell's (57) original background spectra revealed slight, 0.02 abs. units, negative CO\(_2\) absorptions from 2280 to 2360 cm\(^{-1}\). For thick samples, requiring extensive reference beam attenuation and very small instrument source signals, the negative CO\(_2\) absorption would be proportionally greater and could give the appearance of 2 (3\( \nu_R \)) bands instead of one. The position of the minimum between their 2 (3\( \nu_R \)) peaks corresponds closely to the CO\(_2\) (gas) maximum. There was also evidence of oligomeric \( \text{H}_2\text{O} \) absorption in
their original spectra. We concluded their samples were unannealed and vitreous and that no extra $3\nu_R (H_2O)$ absorption appeared. Finally, the nearly identical spectra of the various ices suggests that similar spectra should be expected for the clathrates.
CHAPTER SEVEN

SUMMARY

7.1 Suggestions for Further Work

Extensions and new applications of this work are proposed under three headings: further work in the H₂O-HDO-D₂O ice systems, applications of isotopic substitution to other chemical systems, and further work on clathrate-hydrates.

A. Clathrate Mixtures

We recommend observation of bulk clathrate-hydrate samples in glass preparation tubes by laser Raman spectroscopy. Shifts of peak frequency, half-height width and intensity as a function of temperature should be easily followed. It is important to choose guest species which are strong Raman scatterers and whose frequencies are widely separated from the H₂O frequencies. In that case the guest frequencies would be perturbed the least by coupling to the H₂O lattice.

As an extension of the effect of the lattice, one could study clathrates whose guests frequencies are close to H₂O frequencies and would be expected to couple (to ν₃(H₂O) say, which is weak in the Raman effect). One could also study the perturbing effect of the lattice on the guest by observing the D₂O clathrate analogues.
Finally, careful technique should permit one to grow clathrate-hydrate single crystals in glass tubes, simultaneously allowing one to confirm the clathrate structure by x-ray crystallography and to observe polarized Raman spectra.

We also recommend further attempts to observe low temperature mulls of clathrate-hydrates whose structures are confirmed by x-ray powder diffraction. Use of clathrate-hydrates which are more stable under ambient conditions (i.e., tetrahydrofuran hydrate) should facilitate mull preparation, but may make the spectroscopy more complicated.

**B. Ice Systems**

Some extensions of this work which should be completed are listed below.

1. Use dilute HDO frequencies to follow the annealing or vitreous-cubic ice I transformation in detail.

2. Determine the rates of transformation at various constant temperatures by following the shifts in HDO frequencies as a function of time.

3. Study $v_2$ and $\Delta v_2$ in detail for liquid helium and liquid nitrogen experiments to resolve the $v_2 - 2v_R$ dilemma.

4. Check cubic ice I cooling and warming curves for hysteresis under slow and fast cooling (0.5 - 20 hours).

5. Investigate hydration of sample windows by Cl$_2$ and H$_2$O.

Some other projects related to this work are included below.
1. Carefully check the properties of cubic ice I in the temperature range 40 - 70°K by Raman scattering, infrared absorption and n.m.r. of HDO in D₂O considering the shift in stretching frequency in that range.

2. Investigate the behaviour of HDO frequencies below 10°K to check the extrapolation of our data.

3. Study HDO absorptions in the family of high pressure ices as a function of temperature over their stable ranges. This will permit the extension of hydrogen-bond force constants over a wider range of R(O⋯O) in similar electronic environments.

4. Obtain detailed linear expansion coefficients of cubic ice I down to 4°K.

5. Study the origin of νR as the H₂O triple point is approached from the three phases.

6. Use our HDO frequencies, ωOH and XOH to investigate various models of hydrogen-bonding as a function of R(O⋯O) and attempt to relate Δν to changes in the covalent and electrostatic nature of the hydrogen-bond.

7. Study the anisotropy of hexagonal ice I single-crystals by observing differences in HDO frequencies and Δν/ΔR (as a function of temperature) along the a and c axes.

8. Determine the proton jump energy by observing at what temperature during warm-up a thin layer of D₂O embedded between thick layers of vitreous H₂O leads to the formation of characteristic HDO peaks. Deposition rates would have to
be extremely slow at \(\frac{1}{2}^\circ\text{K}\). Heat of sublimation may be too large to permit isolation of a few mono-layers of \(\text{D}_2\text{O}\) on \(\text{H}_2\text{O}\).

**C. Other Chemical Systems**

Several possible applications of the dilute isotopic substitution and temperature variation technique are listed below.

1. Study single-crystals of organic acids, whose crystal structures and linear expansion coefficients are known, as a function of temperature and relate \(v_{\text{OD}}(\text{HDO})\) to \(R(0\cdots0)\) to better characterize the hydrogen-bond potential.

2. Study carbohydrates, hydrogen-bonding polymers and long chain molecules to determine the nature and variation of 0-H\(\cdots\cdots\)0 hydrogen bonding.

3. Use dilute isotopic substitution in biological systems generally since the \(\text{H}_2\text{O}\) medium masks spectroscopic observations of \(\text{H}_2\text{O}\).

4. Use dilute \(\text{HDO}\) and temperature variation to study the nature of hydrogen bonding in poly-water.
7.2 Conclusions

A. Annealing Ice I

Our infrared result for the transformation temperature range (120 - 135 ± 5°K corrected for source beam heating) does not agree completely with the ranges of some other workers (Table 0.3). Our range seems to agree best with that of Dowell and Rinfret (74) and perhaps that of Sugisaki et al. (6). However, these ir results do not support Dowell's (74) conclusion that only 30% of the vitreous ice I was transformed to cubic ice I. However, their results may indicate that only 30% of their original sample was vitreous. The irreversible transformation frequency shifts (at 145°K) were: $\Delta \nu_1 = -42$, $\Delta \nu_3 = -36$, $\Delta \nu_2 = -56$, $\Delta \nu_R = +31$ and $\Delta \nu_T = +12$ cm$^{-1}$. The transformation temperature range was independent of deposition rate, but transformation frequency shifts were not, faster depositions gave smaller shifts.

Oligomeric (probably dimeric and trimeric) H$_2$O and D$_2$O were present in considerable concentration in amorphous ice I: Slower depositions gave higher concentrations of oligomers. The oligomers were stable units up to 135 ± 5°K. As much as 30% of the amorphous sample may have been in the form of oligomers.

B. HDO Studies

The assumption that dilute concentrations of HDO in H$_2$O or D$_2$O gave completely uncoupled HDO vibrators is invalid. At least one HDO frequency is coupled to a parent H$_2$O or D$_2$O frequency.
The low temperature limits of $v_{OH}(\text{HDO})$ and $v_{OD}(\text{HDO})$ were 3263.5 cm$^{-1}$ and 2412.0 cm$^{-1}$ respectively. The low temperature dependences of $v_{OH}$ and $v_{OD}$ were both 0.047 cm$^{-1}$/°K between 10°K and 80°K. The high temperature dependences of $v_{OH}$ and $v_{OD}$ were 0.200 and 0.123 cm$^{-1}$/°K between 80°K and 200°K.

Insofar as $\omega_{OH}$ and $\chi_{OH}$ were a measure, the potential of HDO molecules in H$_2$O/D$_2$O lattices changed its shape irregularly with temperature, i.e. the changes in $\omega_{OH}$ were not linear as temperature increased.

Hot bands and difference bands did not contribute significantly to the breadth of $v_{OH}$ and $v_{OD}(\text{HDO})$ and, by extension, not to stretches in H$_2$O or D$_2$O. Half-height width data supported the orientationally disordered proton theory of Whalley (88).

The temperature dependences of $\Delta v_{OH}(\text{HDO})$ and $\Delta v_{OD}(\text{HDO})$ from 100° - 200°K were 0.135 and 0.070 cm$^{-1}$/°K. Within the limits of the infrared technique, $v_{OH}(\text{HDO})$ and $v_{OD}(\text{HDO})$ peak frequencies were sensitive to changes in $R(0'\cdots 0)$ greater than 0.0001 Å. HDO stretching absorptions were not linear functions of $R(0'\cdots 0)$ over the whole temperature range 10° - 200°K.

The low temperature dependences $\Delta v_{OH}/\Delta R$ and $\Delta v_{OD}/\Delta R$ were $8.202 \times 10^3$ cm$^{-1}$/Å and $6.629 \times 10^3$ cm$^{-1}$/Å from 10° - 100°K, while the high temperature dependences $\Delta v_{OH}/\Delta R$ and $\Delta v_{OD}/\Delta R$ were $1.921 \times 10^3$ cm$^{-1}$/Å and $1.283 \times 10^3$ cm$^{-1}$/Å from 150 - 200°K.

The calculated low temperature limit of $R(0'\cdots 0)$ for cubic ice I was 2.753 Å assuming $a_0 = 6.350$ Å exactly at 143°K. The calculated changes in $R(0'\cdots 0)$, with temperature were $\Delta R/\Delta T = 8.28 \times 10^{-6}$ Å/°K from 0° - 80°K and $10.52 \times 10^{-6}$ Å/°K from 130° - 200°K.
Bellamy and Owen's (33) formula gave a good approximation to the relation between \( R(0\cdots0) \) and \( \nu_{\text{OH}}(\text{HDO}) \) in the temperature range 130°K to 200°K with the constant set at 57.77 cm\(^{-1}\).

Anharmonicity correction, \( X_{\text{OH}} \), had a low temperature limit of 105.6 cm\(^{-1}\), a low temperature (0 - 60°K) dependence of +0.032 cm\(^{-1}\)/°K, a high temperature dependence (100° - 200°K) of -0.038 cm\(^{-1}\)/°K, and a maximum value of 108.7 cm\(^{-1}\) at 80°K.

The HDO harmonic stretching frequency had a low temperature limit at 347.37 cm\(^{-1}\), a temperature dependence (30°K - 200°K) of +0.138 cm\(^{-1}\)/°K and a maximum displacement of 4 cm\(^{-1}\) from linearity at 80°K.

\( \nu''_R(\text{HDO}) \) had a low temperature limit of 823 cm\(^{-1}\) and the shoulder (assigned to \( \nu''_R + \nu_T \)) had a low temperature limit of 856 cm\(^{-1}\). Various calculations indicated \( \nu_{Rz} \), \( \nu_{Ry} \) and \( \nu_{Rz} \) were degenerate for \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \) and non-degenerate for HDO. The negative temperature dependence of lattice modes was understood in terms of a shallower potential and increasing excited state populations as temperature increased.

C. The \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \) Studies

The order of \( \nu_1 \) and \( \nu_3 \) in the gas and cubic ice I phases was the same: Hydrogen bonding affected \( \nu_1 \) and \( \nu_3 \) of the gas phase equally, shifting them down proportionally. We conclude that the molecule-molecule coupling of \( \nu_1 \) to \( \nu_1 \) and \( \nu_3 \) to \( \nu_3 \) were similar in nature and that in cubic ice I, \( \nu_1 \) and \( \nu_3 \) were distinct transitions. The assignments of major \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \) absorptions at 0°K were \( \nu_1 + \nu_T = 3334 \), \( \nu_3 = 3204 \), \( \nu_1 = 3133 \), \( 3\nu_R = 2239 \), \( \nu_2 = 1562 \), \( \nu_R + \nu_T = 881 \), \( \nu_R = 832 \), and \( \nu_T = 229.2 \) cm\(^{-1}\) for
$\text{H}_2\text{O}$ and $\nu_1 + \nu_T = 2464$, $\nu_3 = 2413$, $\nu_1 = 2320$, $3\nu_R = 1637$, $\nu_2 = 1189$, $\nu_R + \nu_T = 663$, and $\nu_R = 630$ cm$^{-1}$ for $\text{D}_2\text{O}$, in basic agreement with previous authors. The absorption near 1600 cm$^{-1}$ in $\text{H}_2\text{O}$ definitely had a $2\nu_R$ underlying absorption.

Temperature dependence of $\nu_3$ and $\nu_1$ in absorptions for $\text{H}_2\text{O}$ (above 100°K) confirmed the Raman temperature dependence of Val'kov (99). The data of HDO applied to $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ as well.

Blue's (85) formula led to anomalous results when applied to simple $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ molecules in ice. Assuming effective masses for two attached and two detached protons and also assuming that the three librations were degenerate or near-degenerate, then reasonable hydrogen bond bending force constants were calculated by Blue's method. From the ($\text{H}_2\text{O}$, 3/4, 1/4) option we found $k(0-\text{H}\cdots0) = 0.60 \times 10^5$ dynes/cm and $k'_H(0\cdots\text{H}-0) = 0.21 \times 10^5$ dynes/cm. These force constants predicted nearly degenerate $\text{D}_2\text{O}$ librations (586, 588 and 591 cm$^{-1}$) about 6% below the observed value. The effective mass concept did not apply well to HDO.

An $\text{H}_2\text{O}_3$ model of ice gave a set of $\text{H}_2\text{O}$ internal and lattice force constants in good agreement with those deduced by Trevino (93) and poorer agreement with Pimentel's results (97). That $k_{\phi\phi}(\nu_2) (0.66 \times 10^5$ dynes/cm) was smaller than the gas phase value was consistent with the lower ice frequency. $\text{H}_2\text{O}_3$ force constants were used to predict $\text{D}_2\text{O}$ frequencies: Internal mode $\text{D}_2\text{O}$ frequencies were 2–3% too low and lattice mode $\text{D}_2\text{O}$ frequencies were 4–6% too high. The $\nu_R(\text{D}_2\text{O})$ calculated were about the same as from the effective mass model.
D. Clathrate Mixture Annealing

Condensation of a gaseous, stoichiometric mixture of H$_2$O or D$_2$O and guests, followed by annealing to 185 ± 5°K, did not form crystalline clathrate-hydrate compounds. Guest species absorptions in amorphous H$_2$O masses were not subject to such large crystal field splittings as pure guest solids were.
REFERENCES


48. Reference 37.


80. Reference 6, page 231.
81. Reference 6, page 344.
94. Reference 6, pp. 287-304.


120. M. Falk, private communication.


