THE FAR-INFRARED ABSORPTION SPECTRUM OF LOW TEMPERATURE HYDROGEN GAS

By

Edward Hyman Wishnow

B.A., Reed College, 1980

M.Sc., University of British Columbia, 1985

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE STUDIES

PHYSICS

We accept this thesis as conforming

to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

February 1993

© Edward Hyman Wishnow, 1993

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 or her representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.



Physics The University of British Columbia 2075 Wesbrook Place Vancouver, Canada V6T 1W5

Date:

3 may 1993

Abstract

The far-infrared absorption spectrum of normal hydrogen gas has been measured from 20– 320 cm⁻¹ (λ =500–31 μ m), over the temperature range 21–38 K, and the pressure range 0.6–3 atmospheres. The spectra cover the very weak and broad collision-induced translational absorption band of H₂ which at these low temperatures is observed well isolated from the H₂ rotational lines. Translational absorption occurs when two molecules collide and absorb a photon via a transient induced dipole moment. The molecules emerge from the collision with altered translational energies, and the rotational, vibrational, and electronic energy states remain unaffected. The present spectra are the lowest temperature, lowest pressure, and highest resolution studies of the H₂ translational spectrum.

In order to observe the weak translational absorption band, a long pathlength multireflection absorption cell ('White cell'), cooled by the continuous flow of helium vapour, has been designed and constructed. The cell has an f/10 optical beam that allows long wavelength radiation to be transmitted, with low diffraction losses, over an optical path of up to 60 m. The cell is coupled to a Fourier transform interferometer and H₂ spectra are obtained at a spectral resolution of 0.24 cm^{-1} , 10 times higher than previous experiments.

Low temperature absorption spectra are due to not only transitions between molecular translational energy states, but also rotational transitions between the bound states of the van der Waals complex formed by two hydrogen molecules. The integrated absorption of the measured H_2 translational spectrum is consistent with the binary absorption coefficient calculated using the Poll and Van Kranendonk theory of collision-induced absorption. The calculation is based on the quantum mechanical pair distribution function derived from the Lennard-Jones intermolecular potential, and it includes contributions from H_2 dimer bound states. Although dimer transitions contribute to the translational continuum, no sharp spectral features are observed that can be attributed to dimer transitions. These low temperature, low pressure spectra are the first experimental searches for dimer structure across the translational band.

The H₂ spectra show the sharp R(0) line of HD superposed on the translational band at 89.2 cm⁻¹, where the HD is present in the gas in natural abundance. The electric dipole moment of HD has been measured from the intensity of this line and it equals $(0.81 \pm 0.05) \times 10^{-3}$ debye.

The low temperature H_2 spectra provide an experimental test of the theory of collisioninduced absorption and the model of the H_2 intermolecular potential. Furthermore, since the present experimental conditions are close to those found in the atmospheres of the planets Uranus and Neptune, these spectra also have relevance to astronomical observations of H_2 . This work demonstrates, in particular, the feasibility of using measurements of the HD R(0) line and the underlying H_2 translational band to obtain planetary D/H ratios.

In addition to hydrogen, spectra of H₂-He mixtures, D₂, N₂, O₂; and mixtures of N₂, CH₄, and CO with Ar, have been obtained at 78 and 88 K over the spectral region 20–180 cm⁻¹. The N₂ and N₂-Ar spectra exhibit structure superposed on the collision-induced translational-rotational band; this structure has not been previously observed and it is probably due to dimer transitions.

Table of Contents

A	Abstract						
$\mathbf{L}_{\mathbf{i}}$	List of Tables						
Li	List of Figures						
A	cknov	wledge	ement	vii			
1	Intr	oduct	ion	1			
	1.1	Collisi	ion-Induced Absorption	2			
	1.2	Plane	tary Atmospheres	5			
	1.3	Hydro	ogen Dimers	8			
	1.4	Hydro	ogen Molecular Clouds	9			
	1.5	HD.		11			
	1.6	Synop	sis	12			
2	The	Theo	ry of Collision-Induced Absorption	14			
	2 .1	Introd	uction	14			
	2.2	The In	ntegrated Translational Absorption Coefficient	16			
		2.2 .1	Formalism of the Invariant Binary Absorption Coefficient	16			
		2.2.2	The Pair Induced Dipole Moment	19			
		2.2.3	Remarks on the Quadrupole Induced Dipole Moment	23			
		2.2.4	The Evaluation of the Binary Absorption Coefficient	25			

		2.2.5	The Pair Distribution Function and the Calculated Translational	
			Absorption Coefficient	29
	2.3	The S	pectral Density Formalism	37
	2.4	The T	heoretical Spectrum of Hydrogen	40
	2.5	The B	irnbaum-Cohen Lineshape	47
		2.5.1	The Synthetic B-C Spectra	49
3	Exp	erime	ntal Apparatus and Procedures	55
	3.1	Introd	uction	55
	3.2	The L	ow Temperature Far-infrared Absorption Cell	57
		3.2.1	The Cell Optical Design	58
		3.2.2	The Cell Mechanical Design	60
		3.2.3	The Cell Thermal Design	63
		3.2.4	Temperature and Density Measurements	66
	3.3	The Ir	nterferometer	69
		3.3. 1	The Optical System	69
		3.3.2	Interferometer Scanning and the Infrared Source	70
		3.3.3	Beamsplitters and Filters	71
	3.4	Transf	er Optics and Windows	73
	3.5	Electro	onics and Data Acquisition	74
	3.6	Gas Handling Equipment		
	3.7	Experimental Procedures		
	3.8	Liquid	Nitrogen and Argon Transfers	77
	3.9	Liquid	Helium Transfers	78
	3 .10	Tempe	erature Gradients and Turbulence	78
	3 .11	Interfe	rometer Scanning and Chopping Rates	80

	3.12	Optica	al Alignment and Turbulence	81
	3.13	Cell In	mprovements Recommended for the Future	81
		3 .1 3 .1	Mirror Adjustments	81
		3.13.2	Reduction of Turbulence	82
	3.14	Ortho	-Para Measurements	83
4	The	Trans	slational Absorption Band of Hydrogen	85
	4.1	Introd	uction	85
		4.1.1	On the Discrepancy Between the LF and HF Spectral Regions $\ . \ .$	86
	4.2	Genera	al Remarks on the Absorption Spectra	87
		4.2.1	The Spectral Band and Interferogram Averaging	87
		4.2.2	Temperature, Density, and Spectral Accuracy	88
		4.2.3	Typical Spectral Features	89
	4.3	The T	emperature Dependence of the H_2 Spectrum	89
		4.3.1	The Spectrum Fitting Procedure	91
		4.3.2	The Frequency of the Peak and the Bandwidth vs. Temperature .	9 1
		4.3.3	The Spectral Invariants vs. Temperature	94
		4.3.4	The B-C Parameters vs. Temperature	96
	4.4 Hydrogen Dimers		gen Dimers	96
		4.4.1	Introduction and Previous Work	96
		4.4.2	The Predicted Dimer Structure in the Translational Band	98
		4.4.3	Experimental Dimer Search	99
	4.5	The H	² Composite Average Spectra at 25.5 and 36 K \ldots	101
		4.5.1	The Removal of a Residual Baseline	101
		4.5.2	The Averaging Procedure	103
		4.5. 3	The Composite Average Spectra at 25.5 and 36 K	105

.

-

	4.6	6 The Low Temperature Spectra Compared to Previous Measurements .		
		4.6.1	The Spectral Invariants vs. Temperature	115
		4.6.2	The B-C Parameters vs. Temperature	118
5	HD			121
	5.1	Introd	luction	12 1
		5.1.1	The D/H Abundance Ratio	122
	5.2	The H	ID Spectra	123
		5.2.1	The Integrated Absorption Coefficient	125
		5.2.2	Line Fitting	126
	5.3	The H	ID Dipole Moment	128
		5.3 .1	The Density Dependence of the Dipole Moment	128
		5.3.2	The Measured HD Dipole Moment	129
		5.3.3	The Density Dependence of the HD Linewidth and Frequency	129
		5.3.4	A Determination of the HD Concentration in $D_2 \ldots \ldots \ldots$	1 3 1
	5.4	Future	e Investigations of HD Dimers	131
6	Exp	erime	ntal Errors	133
	6.1	Tempe	erature, Pressure, and Density Errors	133
	6.2	Optica	al Errors	1 3 4
		6.2.1	Spectrometer Calibration	134
		6.2.2	The Reproducibility of Background Spectra	134
		6.2.3	Sources of Repeatability Errors	136
		6.2.4	Additional Sample Spectra Errors	137
		6.2.5	Pathlength Errors	138
	6.3	Water	Ice	139
		6.3.1	Ice Absorption	139

		6.3.2	Phase Effects	. 140	
	6.4	Detect	tor Non-Linearities	. 144	
		6.4.1	Interferogram Contrast	. 145	
		6.4.2	A Computer Simulation of Detector Nonlinearity	. 146	
		6.4.3	Corrected Interferograms	. 147	
		6.4.4	Detector Nonlinearity Tests	. 148	
		6.4.5	Detector Nonlinearity Comments	. 149	
7	Oth	ier Spe	ectroscopic Studies	150	
	7.1	The D	euterium S(0) line	. 150	
	7.2	Hydro	gen-Rare Gas Mixtures	. 151	
	7.3	Nitrog	en-Argon Mixtures	. 154	
	7.4	Metha	ne-Argon Mixtures	. 156	
	7.5	Carbo	n Monoxide-Argon Mixtures	. 157	
	7.6	Oxyge	n	. 159	
8	Con	clusio	n	161	
Aj	Appendices				
A	The	Absor	rption Cell Optical Tests	164	
Bi	bliog	raphy		167	

List of Tables

2 .1	The Thermal de Broglie Wavelength of H_2 vs. Temperature	3 0
2.2	The Calculated Binary Absorption Coefficient at Various Temperatures .	33
2.3	The Binary Absorption Coefficient of the Translational Band of Normal H_2	35
3.1	The Pathlength Limits Due to Diffraction	59
3.2	The Beamsplitters and Low-pass Filters	71
A .1	The Spot Size as a Function of Pathlength due to Astigmatism	165
A.2	The Ratio of the Far-Infrared Signal Maximum/Minimum as a Function	
	of Pathlength	166

List of Figures

The Far-infrared Spectrum of Normal H_2 at 77 K $\dots \dots \dots \dots$	5
The Voyager Infrared Spectrum of Jupiter	7
The Voyager Infrared Spectrum of Uranus	7
H_2 Dimer Spectral Features Near the $S(0)$ and $S(1)$ Lines	9
The Submillimeter Spectrum of Normal H $_2$ at 36 K \ldots	13
The Lennard-Jones intermolecular potential of H_2	32
The pair distribution function of H_2 at 20 K \ldots \ldots \ldots \ldots	32
The Expansion Coefficients of the Dipole Moment	43
The S(0) rotational spectrum of H_2 at 77 and 20 K- measurements and	
calculations	44
The translational-rotational band of H_2 at 300 and 77 K-measurements	
and calculations	45
The B-C Synthetic Spectrum of H_2 at 297 K $\ldots \ldots \ldots \ldots \ldots$	52
The B-C Synthetic Spectrum of H_2 at 77 K	52
The B-C Synthetic Spectrum of H_2 at 25.5 K	53
A schematic diagram of the experimental apparatus	56
The Cell Mechanical Design	61
The Laser Spot Pattern on the Field Mirror	62
The Folding Mirror Mechanism	62
The Low Temperature Absorption Cell	64
The Outer Radiation Shield	64
	The Far-infrared Spectrum of Normal H2 at 77 KThe Voyager Infrared Spectrum of JupiterThe Voyager Infrared Spectrum of UranusH2 Dimer Spectral Features Near the S(0) and S(1) LinesThe Submillimeter Spectrum of Normal H2 at 36 KThe Lennard-Jones intermolecular potential of H2The pair distribution function of H2 at 20 KThe Expansion Coefficients of the Dipole MomentThe S(0) rotational spectrum of H2 at 77 and 20 K- measurements andcalculationsThe translational-rotational band of H2 at 300 and 77 K-measurementsand calculationsThe B-C Synthetic Spectrum of H2 at 277 KThe B-C Synthetic Spectrum of H2 at 25.5 KA schematic diagram of the experimental apparatusThe Cell Mechanical DesignThe Laser Spot Pattern on the Field MirrorThe Low Temperature Absorption CellThe Outer Radiation Shield

3.7	The Optical Path of the Michelson Interferometer	70
3.8	Examples of LF and HF Background Spectra	72
4.1	The LF absorption spectrum of H_2 at 34.4 K	9 0
4.2	The LF absorption spectrum of H_2 at 25.0 K $\ldots \ldots \ldots \ldots \ldots$	9 0
4.3	The peak of the translational band vs. the square root of the temperature	92
4.4	The width of the translational band vs. the square root of the temperature	92
4.5	The half-width of the translational band lineshape vs. the square root of	
	the temperature	93
4.6	α_{1tr} vs. temperature for the LF H ₂ spectra \ldots \ldots \ldots \ldots \ldots	95
4.7	$\gamma_{1 \mathrm{tr}}$ vs. temperature for the LF H ₂ spectra $\ldots \ldots \ldots \ldots \ldots \ldots \ldots$	95
4.8	$ au_1$ and $ au_2$ vs. temperature for the LF H ₂ spectra $\ldots \ldots \ldots \ldots \ldots$	97
4.9	The B-C parameter S vs. temperature for the LF H ₂ spectra	97
4.10	The predicted H_2 translational emission spectrum $\ldots \ldots \ldots \ldots$	100
4.11	The LF H ₂ translational absorption spectrum at 22.4 K \ldots	100
4.12	The composite average spectrum at 36 K, HF multiplier=1.00	106
4 .1 3	The composite average spectrum at 36 K, HF multiplier=1.05	107
4.14	The composite average spectrum at 36 K, HF multiplier=1.10	108
4.15	The composite average spectrum at 25.5 K, HF multiplier=1.00	109
4.16	The composite average spectrum at 25.5 K, HF multiplier=1.05	110
4.17	The composite average spectrum at 25.5 K, HF multiplier=1.10	111
4.18	The lineshape function $G(\sigma)$ at 36 and 25.5 K	114
4.19	α_{1tr} vs. temperature for the translational band of H ₂	116
4.20	$\gamma_{1 tr}$ vs. temperature for the translational band of H ₂	116
4.21	$ au_1$ and $ au_2$ vs. temperature for the translational band of $ ext{H}_2$	119
4.22	S vs. temperature for the translational band of H ₂	119

5.1	Absorption spectra of H_2 and D_2 at various densities and temperatures .	124
5.2	The fit to the $R(0)$ line	127
5.3	The density dependence of the HD dipole moment and the $R(0)$ linewidth	130
6.1	The repeatability of the LF backgrounds	135
6.2	The repeatability of the HF backgrounds	135
6.3	The effects of window distortions	138
6.4	The 'absorption spectrum' of HF backgrounds taken at the end, and the	
	beginning, of a low temperature run	141
6.5	The absorption spectrum of ice II	141
6.6	The absorption spectrum of ice I	142
6.7	The phase diagram of water ice	143
6.8	The spectrum of helium demonstrating the effect of ice	1 43
6.9	The interferogram contrast vs. the detector signal amplitude \ldots	145
7.1	The spectra of D_2 near $S(0)$	152
7.2	The spectrum of H_2 and a H_2 -He mixture	152
7.3	The absorption spectra of N ₂ and N ₂ -Ar mixtures \ldots	155
7.4	The absorption spectra of CH_4 and CH_4 -Ar mixtures $\ldots \ldots \ldots$	155
7.5	The sample spectrum of CO	158
7.6	The spectrum of a 23/73 CO-Ar mixture	158
7.7	The rotational spectrum of O_2	160

•

Acknowledgement

I would like to thank my mother and grandmother, and the rest of my family and friends, for their continued support. I have also enjoyed the hospitality of the people of Canada.

The expert assistance of Peter Haas and the Physics department machine shop, and Stan Knowtek and the Physics department electronics shop was crucial to the development of the experimental apparatus. I am indebted to Alex Leung for executing the detailed mechanical design of the low temperature multipass cell.

Scientific discussions with C. Bulmer, M. Legros, N. Poulin, B. Price, and I. Shinkoda, have been invaluable in the course of my thesis work. I have benefited greatly, throughout graduate school, from discussions and collaborations with Mark Halpern. Irving Ozier has contributed valuable suggestions to the direction of my experiments, to their analysis, and to the completion of this document.

Finally, it has been a great privilege to work with Herbert Gush. I thank him for his support, his scientific guidance, and for the memorable experiences of working on truly beautiful experiments.

Chapter 1

Introduction

Hydrogen is the most abundant element in the universe. Cold dark regions of the galaxy that are shielded from ultraviolet radiation are expected to contain vast quantities of hydrogen in its molecular form H₂. The atmospheres of massive planets are also an environment composed primarily of H₂. Observational evidence for molecular hydrogen is not, however, easily obtained since H₂ is transparent to both visible and radio frequency radiation. By contrast, the presence of atomic hydrogen in stars is indicated by the Balmer absorption lines and the emission of H_a radiation by solar flares. Interstellar space is also filled with a sparse gas of atomic hydrogen which is detected via the 1420 MHz hyperfine transition using radio telescopes. H₂ can be detected if it exists in moderately dense conditions, as collisions between H₂ molecules result in the weak absorption of infrared radiation. The present investigation of the submillimeter absorption spectrum of cold hydrogen gas is relevant to the longstanding astronomical problem of detecting H₂.

 H_2 is also the simplest diatomic molecule, and for this reason many of its properties can be calculated from first principles. Historically, the quantum mechanical nature of atoms and molecules has been elucidated through the study of hydrogen. The characterization of intermolecular forces, again via the study of hydrogen, is an important area of research in molecular physics. The present experiments are directly relevant to the study of intermolecular interactions, particularly the van der Waals binding of two H_2 molecules at low temperatures. This thesis reports laboratory measurements of the submillimeter spectrum of low temperature ~ 30 K, low pressure (1-3 atm.) hydrogen gas over the wavenumber range 20-320 cm⁻¹ (λ =0.5-0.031 mm). This spectral region covers the collision-induced translational absorption band of H₂. The phenomenon of translational absorption arises when two molecules collide, absorb a photon, and emerge from the collision with altered translational energies. Only transitions between translational energy states contribute to this absorption band, and the rotational, vibrational, and electronic energy states of the collision pair remain unaffected.

In order to study the low frequency translational band, a long pathlength (up to 60 m), cryogenic, multi-reflection absorption cell has been designed and built, and it has been coupled to a Fourier transform interferometer. Spectra of hydrogen have been obtained at a higher spectral resolution than previous measurements, over new temperature and pressure regimes. These low temperature and low pressure experiments approximate the conditions found in planetary atmospheres, and the results are relevant to the interpretation of planetary spectra. Translational absorption is very weak, and in the present experiments radiation passes through an amount of gas equivalent to 1.4 km of H₂ gas at STP (1 atm. pressure at 0° C). Using the same spectrometer-cell apparatus, less detailed studies have also been made of the far-infrared spectra of deuterium, oxygen, nitrogen, methane, carbon-monoxide, and mixtures of the latter gases with argon.

1.1 Collision-Induced Absorption

An isolated hydrogen molecule in the electronic ground state has a center of symmetry and therefore has no permanent electric dipole moment; the derivative of the dipole moment with respect to internuclear distance is also zero. As a result, H_2 does not exhibit a normal infrared rotational or vibrational spectrum. The H_2 molecule does possess an electric quadrupole moment which gives rise to weak transitions between vibrational and rotational energy states with the rotational selection rules $\Delta J = 0, \pm 2$, and vibrational selection rules $\Delta v = 0, \pm 1, \pm 2, \ldots$ A sample of dense hydrogen gas is observed, however, to absorb radiation over a continuum of frequencies near the vibrational and rotational frequencies of the H₂ molecule. This phenomenon is called collision-induced absorption, and it results from transient dipole moments induced in pairs (or clusters) of colliding molecules by intermolecular forces. Collision-induced absorption is still weak, but it is the dominant mechanism responsible for the far-infrared spectra of compressed gases composed of: homonuclear diatomic molecules such as H₂ and N₂; other symmetric molecules with no permanent dipole moments as CO₂ and CH₄, and rare gas mixtures such as He-Ar and Ne-Ar. Collision-induced spectroscopy was initiated by Welsh and co-workers [1], and contemporary work in this field appears in recent reviews [2], [3].

The collision-induced dipole moment arises via a long-range interaction where the quadrupolar electric field of one molecule polarizes the other and via a short-range overlap distortion of the colliding molecule's electronic distributions. The induced dipole moment is a function of the internuclear separations and relative orientations of the colliding molecules, and as a result, molecular vibrational and rotational transitions become infrared active. In the case of hydrogen, prominent fundamental vibrational lines $Q_1(0)$ and $S_1(0)$ occur near 4161 and 4498 cm⁻¹, respectively; prominent pure rotational lines S(0), S(1), and S(2) occur near 354, 587, and 814 cm⁻¹. The induced dipole moment is modulated by the translational motion of the colliding molecules and transitions between translational energy states become possible. Translational energy transitions are responsible for the broad linewidths of the collision-induced spectrum and they also give rise to a pure translational spectrum, a quasi-continuum extending from 0 to about 300 cm⁻¹.

The integrated intensity of a collision-induced spectral line is found to vary as the

square of the gas density (for moderate densities), where this demonstrates that only collisions between pairs of molecules are responsible for absorbing radiation. The theory of collision-induced absorption shows that the integrated intensity of the collision-induced spectrum (normalized to unit density and pathlength) depends on: the nature of the dipole moment induction process; the properties of the molecule such as its quadrupole moment, polarizability, and size; and the intermolecular potential. The theory of collision-induced absorption was developed by Van Kranendonk and co-workers [4], [5], [6], [7], and it is discussed in chapter 2.

Collision-induced lines and the translational band of H₂ are very broad and differ in this regard from sharp lines due to allowed dipole or quadrupole transitions. The breadth of these spectral lines can be interpreted in terms of the Heisenberg uncertainty principle $\Delta E \Delta t \geq \hbar$, where the duration of a room temperature collision is extremely short, $\sim 2 \times 10^{-14}$ sec. and the range of energy transitions is very large, ~ 300 cm⁻¹. In general, the translational band and the rotational lines of most diatomic molecules overlap, but the rotational constant of H₂ is large (~ 60 cm⁻¹), and the rotational lines are widely spaced. If spectral linewidths are reduced by performing measurements on a cold gas sample, the pure translational band band can be observed.

The measurements of the rotational spectrum of H₂ and H₂-rare gas mixtures by Kiss, Gush, and Welsh first indicated that the spectrum below ~400 cm⁻¹ includes contributions from translational absorption [9],[10]. Following these measurements, the high frequency wing of the pure translational absorption spectrum of rare-gas mixtures was observed by Kiss and Welsh [11]. Figure 1.1 is the spectrum of H₂ at 77 K measured by Bosomworth and Gush; it shows the first observation of the isolated translational spectrum of H₂ [8]. Notice that the absorption peak of the translational band is about 10 times weaker than the S(0) peak, and that the region of the translational peak has not



Figure 1.1: The far-infrared spectrum of normal H₂ at 77.3 K measured by Bosomworth and Gush [8]. The collision-induced translational band extends from 0-400 cm⁻¹ and it partially overlaps the S(0) rotational line which peaks near 371 cm⁻¹.

been measured with high precision. Subsequent measurements of the entire translationalrotational spectrum of H_2 have been conducted over a wide range of temperatures [12], [13], [14], but measurements of the translational band remain imprecise due to its extremely low absorption and the difficulties inherent in submillimeter spectroscopy. In the present work, efforts have been made to obtain precise spectra over the peak of the translational band. By using very low temperature H_2 , the peak absorption is enhanced, and the translational band is virtually isolated from the S(0) line (see Figure 1.5).

1.2 Planetary Atmospheres

Knowledge of the collision-induced translational-rotational spectrum of H_2 is essential to the study of the atmospheres of the giant gaseous planets. The translational band in particular is responsible for the thermal opacity of the cold planets Uranus and Neptune [15], [16]. Far-infrared spectra of the planets Jupiter, Saturn, Uranus, and Neptune have been obtained by the IRIS spectrometer onboard the Voyager spacecraft [17],[18],[19],[20],[21],[22]. Figures 1.2 and 1.3 show the spectra of Jupiter and Uranus.

Many properties of a planet's atmosphere may be deduced from the Voyager spectrum. Laboratory measurements of the H₂ absorption spectrum are used to estimate, at each frequency, the pressure at which the optical depth of the atmosphere equals unity. This is the atmospheric layer primarily responsible for the emission of radiation, and the brightness temperature plotted in Figures 1.2 and 1.3 corresponds to the emitting layer's temperature. As a result, the brightness temperature spectrum reveals the atmospheric temperature profile as a function of pressure (or height) [24],[25]. The chemical composition of the atmosphere is found by comparing radiative transfer calculations to the measured spectrum. The abundance of helium in particular is determined using the He enhancement of the H₂ collision-induced spectrum due to the H₂-He overlap interaction (see Figure 7.2). In practice the atmospheric temperature profile and composition are determined using infrared spectra in conjunction with radio occultation data; this is partially due to the limited accuracy of laboratory H₂ spectra. The Voyager spectra continue to be extremely valuable and a recent analysis of Jupiter's spectrum has determined the H₂ ortho/para ratio as a function of height [26].

Figure 1.2 shows the low frequency emission spectrum of Jupiter which is dominated by the S(0) and S(1) collision-induced lines, and the sharp low frequency lines due to ammonia. The brightness temperatures of the strongly absorbing S(0) and S(1) peaks are low because emission at these frequencies originates from high atmospheric regions with low pressures (0.2–0.3 bar) and temperatures. The weaker translational band is emitted from deeper atmospheric layers with pressures of 1–2 bars, and consequently warmer temperatures.



Figure 1.2: The Voyager spectrum of Jupiter [23]. The planetary emission spectrum has been converted to that of an equivalent blackbody per measured frequency interval. The sharp lines below 300 cm⁻¹ are due to ammonia. The boxes enclose the locations of H_2 dimer features near the centers of the collision-induced lines S(0) and S(1).



Figure 1.3: The Voyager infrared spectrum of Uranus [21]. Since the planet's temperature is ~ 60 K, emission occurs primarily over the translational band and this band is further enhanced by the presence of helium. The dotted curves are theoretical spectra calculated using the atmospheric temperature profile obtained from radio occultation measurements and they are scaled for different values of the helium mole fraction.

Figure 1.3, the emission spectrum of Uranus, is noisy above 350 cm⁻¹ because little power is radiated at these frequencies by a 59.4 K equivalent blackbody. This figure shows how the He enhancement of the H₂ translational band is used to determine planetary helium abundances, quantities which were unknown prior to the Voyager missions. The molar helium abundances of the other gaseous planets are: Jupiter, 0.12; Saturn, 0.04; and Neptune, 0.15 [22]. The emission spectra of Uranus and Neptune originate in atmospheric layers at pressures of 1-2 bar, and temperatures of ~ 60 K; note that this environment is quite close to the conditions employed in the present experiments.

1.3 Hydrogen Dimers

A pair of hydrogen molecules may become bound together as a van der Waals complex or dimer since the intermolecular potential is attractive over a range of intermolecular separations. The binding energy of H₂ dimers is very low, ~ 2.5cm⁻¹ (~ 3.6 K), and dimers form only if collisions involve low kinetic energies. Spectral structure due to dimers exists only if the dimers have relatively long lifetimes, and hence, only if collisions in the gas are infrequent. The H₂ dimer possesses a small permanent dipole moment, provided both molecules are not in the J = 0 state, and rotational transitions between dimer states are observed as sharp features superposed upon the broad vibrational and rotational collision-induced lines.

Dimer structure in the rotational band of H_2 was first observed as small ripples near the centers of the S(0) and S(1) features of the Voyager spectrum of Jupiter (see Figure 1.2). The low temperature, low pressure environment of planetary atmospheres, along with the extremely long optical path, provide good conditions for observing dimers. Subsequent laboratory measurements by McKellar have confirmed the identification of these ripples as dimer features [27], and this spectrum is presented in Figure 1.4.



Figure 1.4: The S(0) and S(1) lines of equilibrium H₂ at 77 K as measured by McKellar [27]. The ripples in the spectrum correspond to rotational transitions of the H₂ dimer. Note the similarity of this spectrum to Figure 1.2, the spectrum of Jupiter.

In Figure 1.4 the sharp features on either side of the S lines are due to dimer bound state transitions, and the broader ripples on the high frequency side are due to bound-free transitions. The H₂ dimer spectrum near S(0) has been observed at ~ 20 K using the spectrometer-cell apparatus described in chapter 3, and by McKellar [28]. On the basis of these observations, it is expected that dimer transitions should also appear in the low frequency region of the translational band. The search for dimer structure in this band has been one of the major efforts of the present work.

1.4 Hydrogen Molecular Clouds

Giant Molecular Clouds are cold (20-100 K) regions of the galaxy composed primarily of hydrogen molecules with a density of $\sim 1000 \text{ cm}^{-3}$, roughly 1000 times the density of interstellar space. Particularly dense regions within molecular clouds are believed to be the birthplace of stars. In the absence of strong H₂ infrared transitions, the distribution of molecular clouds in the galaxy is generally traced indirectly by observations of the CO $\Delta J = 0 \leftarrow 1$ emission line at 115 GHz; where the CO/H₂ abundance ratio is roughly 10^{-4} . In certain circumstances, however, molecular hydrogen is directly observable in emission or absorption. Interstellar H₂ absorbs radiation in the far-ultraviolet, via electronic transitions, but these observations require a UV background star and spaceborne instruments. Infrared vibrational-rotational transitions are observed in emission from photo-dissociation regions where H₂ molecules are excited by an ultraviolet radiation field, or by shock waves. Observation of these H₂ vibrational quadrupole lines is becoming an important astronomical technique for studying excited molecular gas. The S(2) pure rotational line of H₂ has been observed in the Orion nebula, and the detection of the S(1) line has been recently reported [29]. Despite these direct observations, H₂ within molecular clouds is largely undetected, and the distribution of interstellar molecular hydrogen remains an important unsolved problem in astrophysics [30], [31], [32].

The emission of low frequency radiation by H_2 molecules is predicted to occur within cold molecular clouds [33]. Hydrogen molecules are presumably formed when hydrogen atoms recombine on the surfaces of dust grains. Newly formed H_2 molecules are ejected from the grain, but molecules may recondense on the grain, provided the temperature is low. If the gas density in the neighbourhood of the grain is sufficiently high, H_2 molecules will interact and thereby radiate in the frequency range 0–60 cm⁻¹. The translational emission band is predicted to exhibit structure due to free-bound H_2 pair transitions and resonances between free-free transitions (see Figure 4.10). The low temperature, low pressure, low frequency H_2 spectra described in chapter 4 are the only measurements that can be compared to this predicted translational spectrum.

It was suggested that H_2 translational emission might explain the anomalous intensity observed at frequencies above 12 cm⁻¹ in Gush's 1978 spectrum measurement of the Cosmic Background Radiation [34], [35]. Subsequent measurements of the CBR spectrum using a rocket-borne, liquid helium cooled, differential Michelson interferometer, performed by Gush, Halpern, and Wishnow, show that the CBR has a Planckian spectrum characterized by a temperature of 2.736 ± 0.017 K, with no intensity excess at high frequencies [36]. This is the most precise measurement of the CBR temperature to date, and it is consistent with the CBR temperature of 2.735 ± 0.060 K, obtained by the FIRAS spectrometer onboard the COBE satellite [37].

The submillimeter spectrum of the galaxy has also been measured by the FIRAS spectrometer and it is modelled by emission from two populations of dust [38]. Radiation from 20.4 K dust is the dominant component of the galactic emission spectrum and there is a minor contribution from 4.77 K dust. No explanation is given for the origin of the low temperature dust, but it is conceivable that translational emission by molecular hydrogen contributes to the submillimeter spectrum of the galaxy.

1.5 HD

All of the low temperature hydrogen spectra obtained during the present experiments show a sharp absorption feature superposed upon the translational band at 89.2 cm⁻¹. This feature is identified as the R(0) line of hydrogen deuteride, where the HD is present in the hydrogen sample as a naturally occurring isotopic impurity. The isotopically substituted molecule HD possesses a small permanent electric dipole moment, and therefore rotational transitions with selection rules $\Delta J = \pm 1$ are infrared active. The intensity of the R(0) line is analyzed in chapter 5, and the dipole moment of HD is measured to be $(0.81 \pm 0.05) \times 10^{-3}$ debye. This work has been previously reported by Wishnow, Ozier, and Gush [39].

Even though the dipole moment of HD is quite small, and the HD/H_2 abundance is

about 1/3165, the peak intensity of the R(0) line is about 1/10 the peak absorption of the collision-induced translational band. It is possible that HD rotational line emission from cold molecular clouds is more intense than the H₂ rotational quadrupole emission spectrum. The R(0) and R(1) rotational lines of HD could potentially act as direct tracers of interstellar molecular hydrogen [40].

The D/H abundance ratio of planetary atmospheres is one of the important measurable quantities in cosmology. The D/H ratio, along with the other light element abundances, is a probe of the radiation and particle energy densities of the early nucleosynthesis phase of the universe [41]. The deuterium abundance of the pre-solar nebula is believed to be preserved in Jupiter's atmosphere, and the cosmological D/H ratio is deduced from this using a model of the evolution of the galaxy. The present H₂ spectra qualitatively resemble the predicted high resolution spectra of the planets Uranus and Neptune [42]. An important aspect of these experiments is the demonstration that D/H ratios of planetary atmospheres may be determined by measuring the intensities of the HD R(0) line, and the underlying H₂ collision-induced translational band.

1.6 Synopsis

Figure 1.5 is the submillimeter absorption spectrum of hydrogen gas at 36 K (see Figure 4.14). The broad collision-induced translational band extends from zero frequency to a peak near 50 cm⁻¹, and it starts to overlap the sharply rising S(0) line near 270 cm⁻¹. The peak intensity of the translational band is enhanced with respect to Figure 1.1, and the translational band is considerably better isolated from the S(0) line at 36 K than at 77 K. The sharp feature at 89.2 cm⁻¹ is the R(0) line of HD, and no other obvious spectral structures are observed.



Figure 1.5: The submillimeter absorption spectrum of normal H_2 at 36 K. Notice that the peak of the translational band is higher, and its overlap with the S(0) line less, than Figure 1.1. The sharp line at 89.2 cm⁻¹ is the R(0) line of HD. The gap in the spectrum is due to an absorption band of the crystal quartz detector filter. See Figure 4.14

The goal of the present work has been to measure the the collision-induced H_2 translational absorption band with improved spectral resolution, sensitivity, and accuracy. This work is the first investigation of the submillimeter H_2 spectrum at low temperatures and pressures, and these measurements are consistent with the Poll and Van Kranendonk theory of translational absorption [7]. At the present time, these H_2 spectra are the only measurements which may be compared to theoretical predictions of dimer structure in the translational band. In addition, these spectra are important to the understanding of astrophysical environments composed of cold molecular hydrogen gas.

Chapter 2

The Theory of Collision-Induced Absorption

2.1 Introduction

In order to introduce terminology used throughout this work, a review of the theory of collision-induced absorption is presented in this chapter. Aspects of this theory are not well known outside the community of specialists in the field, and the present review develops the concepts which underlie the analysis and interpretation of the experimental data. Since comparisons are made between the predictions of theoretical models and measured spectra, the results of previous important experiments in this field are also discussed.

The theory of collision-induced absorption was developed by Van Kranendonk [4],[5]. Following the first measurements of pure translational absorption, Poll and Van Kranendonk extended the theory to collision-induced translational absorption [43], [7]. This theory relates the integrated absorption coefficient of the translational spectrum to the physical properties of the colliding molecules. Among these properties are the molecular quadrupole moments and polarizabilities, and the intermolecular potential. The notable feature of this theory is that the integrated absorption of a collision-induced spectrum can be calculated without the complexity of finding explicit dipole moment matrix elements.

The integrated absorption coefficient depends upon both the model of the induction process and the pair distribution function. Poll and Van Kranendonk adopt the socalled exp-4 model to describe the collision-induced dipole moment. The dipole moment arises from two induction processes: (1) the long-range quadrupolar interaction which has a $1/R^4$ dependence, and (2) the short-range overlap distortion interaction which is proportional to $e^{-R/\rho}$, where R is the intermolecular distance and ρ is a range parameter. The pair distribution function is proportional to the probability that two molecules will be found at a certain distance apart, given a temperature and intermolecular potential. The pair distribution function may be calculated either classically or quantum mechanically, where at high temperatures the classical value is valid, but at temperatures below 80 K quantum mechanical effects must be taken into account.

The spectrum bandshape, as distinguished from the integrated absorption, is calculated by expressing the absorption coefficient at a given frequency in terms of a spectral density [44]. The spectral density is the Fourier transform of the autocorrelation function of the electric dipole moment, and it is proportional to the probability of absorption. Theoretical spectrum calculations are based on expressing a global spectral density as a superposition of spectral densities, each associated with a term of the expansion of the dipole moment operator in spherical harmonics. Recent calculations of collision-induced H_2 rotational lines utilize ab-initio models of the H_2 intermolecular potential (including anisotropic terms), and the induced dipole moment [45],[28]. The calculated spectrum involves transitions between bound and free states of a pair of H_2 molecules, and it is consistent with the measured spectrum, including the dimer structure. At the present time, no comparable calculations of the H_2 translational absorption spectrum have been reported.

In order to fit experimental data or model planetary atmospheres, it is useful to approximate the spectral density by a lineshape which has a simple analytic form. A lineshape proposed by Birnbaum and Cohen [46], is often used to fit experimental absorption spectra. This lineshape has only 3 free parameters and spectra calculated using this lineshape fit well the entire translational-rotational H_2 spectrum over the temperature range 77 to 300 K [14], [13].

2.2 The Integrated Translational Absorption Coefficient

2.2.1 Formalism of the Invariant Binary Absorption Coefficient

This section reviews the work of Poll and Van Kranendonk [43], [7]. The absorption coefficient per unit pathlength measured experimentally is

$$A(\sigma) = \frac{1}{l} \left(-\ln \frac{I_s(\sigma)}{I_b(\sigma)} \right)$$
(2.1)

The absorption coefficient is independent of the optical pathlength, but is a function of the density of the sample gas. σ is the frequency in cm⁻¹, l is the absorption pathlength, $I_b(\sigma)$ is the background spectrum, and $I_s(\sigma)$ is the sample spectrum. The measured integrated absorption coefficient is

$$\alpha' = \int A(\sigma)d\sigma = \frac{1}{c}\int A(\nu)d\nu \qquad (2.2)$$

The absorption coefficient associated with a given frequency ν in Hz (or cm⁻¹) is given by [47]

$$A(\nu) = \frac{4\pi^2}{3\hbar c V} \nu \sum_{i < f} (P_i - P_f) |\mu_{if}|^2 \delta(\nu - \nu_{if})$$
(2.3)

where V is the volume. P_i and P_f are the populations of the initial and final states, μ_{if} is the matrix element of the dipole moment of the system between the states *i* and *f*, and ν_{if} is the frequency of a molecular transition.

$$\nu_{if} = (E_f - E_i)/h \tag{2.4}$$

The integrated absorption coefficient is

$$\alpha = \frac{\kappa}{V} \sum_{i < f} (P_i - P_f) |\boldsymbol{\mu}_{if}|^2 h \nu_{if}$$
(2.5)

where $\kappa = 8\pi^3/3h^2c$ and the summation takes place over all states $E_i < E_f$. The transition moment is equal to the sum of the squares of the components of the dipole moment matrix element, that is,

$$|\boldsymbol{\mu}_{if}|^2 = |(\boldsymbol{\mu}_{if})_x|^2 + |(\boldsymbol{\mu}_{if})_y|^2 + |(\boldsymbol{\mu}_{if})_z|^2$$
(2.6)

The evaluation of the integrated absorption requires knowledge of the wavefunctions in order to calculate the matrix elements of the dipole moment. However, the integrated absorption coefficient can be written in the form of a trace which is invariant under unitary transformations, and it may thereby be evaluated in terms of an arbitrary complete set of functions. The summation in eqn. 2.5 may be unrestricted by noting that the equation is symmetric in *i* and *f* (that is, for $E_f < E_i$, ν_{if} is negative). If the factor $h\nu_{if}$ is written out in terms of energy,

$$\alpha = \frac{\kappa}{V} \sum_{if} P_i |\boldsymbol{\mu}_{if}|^2 (E_f - E_i)$$
(2.7)

and,

$$\alpha = \frac{\kappa}{V} \sum_{if} (P_i \mu_{if} E_f \mu_{fi} - P_i \mu_{if} \mu_{fi} E_i). \qquad (2.8)$$

Because μ is Hermitian and $H\psi = E\psi$, the above becomes

$$\alpha = \frac{\kappa}{V} \langle \mu[H, \mu] \rangle \qquad (2.9)$$

where the brackets denote an ensemble average over the system in thermal equilibrium. H is the Hamiltonian of the 2 molecule system, and in general, it includes the translational-rotational-vibrational motion of the molecules. $[H, \mu]$ is the commutator of H and μ . The invariant form is now

$$\alpha = \frac{\kappa}{V} \operatorname{Tr} \{ P \boldsymbol{\mu}[H, \boldsymbol{\mu}] \}$$
(2.10)

where P is the density operator defined by

$$P = \frac{e^{-\beta H}}{\operatorname{Tr} e^{-\beta H}}$$
(2.11)

and $\beta = 1/kT$.

The integrated intensity may be expanded in powers of the density,

$$\alpha = \alpha_1 \rho^2 + \alpha_2 \rho^3 + \dots \qquad (2.12)$$

where α_1 is the binary absorption coefficient, α_2 the ternary absorption coefficient, etc... Only the binary absorption coefficient needs to be considered for low density gases; it is

$$\alpha_1 = \frac{1}{2} \frac{\kappa}{V} \operatorname{Tr} \left\{ P_2(12) \mu(12) [K(1) + K(2), \mu(12)] \right\}$$
(2.13)

where $P_2(12)$ is the first term in the density expansion of the density operator, K(1)and K(2) are the kinetic energies of molecules 1 and 2, and $\mu(12)$ is the dipole moment induced by the interaction of the two molecules. Note that in eqn. 2.13 only the kinetic energy appears in the commutator; this occurs because the potential commutes with μ . Any interaction between rotational and translational terms in the Hamiltonian influences only the density operator.

The expression of the binary absorption coefficient may be reformulated in terms of the relative motion of the colliding molecules. In a coordinate system where R_c denotes the center of mass position, and R the intermolecular separation, integration of eqn. 2.13 over R_c yields

$$\alpha_1 = \frac{\kappa}{2} \frac{\lambda^3}{Z^2} \operatorname{Tr} \left\{ e^{-\beta H} \mu[K, \mu] \right\}$$
(2.14)

K is the kinetic energy and H the Hamilitonian of the relative rotational and translational motions of the molecules, where the Hamiltonian is assumed to be separable into translational and rotational parts. $\lambda = (\frac{\hbar^2}{2\pi m kT})^{1/2}$ is the thermal de Broglie wavelength, where m is the reduced mass of a pair of H₂ molecules, $m = m_1 m_2/(m_1 + m_2)$. λ is equal to $(V/Z_t)^{1/3}$, where Z_t is the translational partition function [43]. Z is the rotational partition function of a single molecule,

$$Z = \sum_{J} g_{J} (2J+1) e^{-\beta E(J)}$$
(2.15)

E(J) is the rotational energy level for a H₂ molecule given by,

$$E(J) = B_0 J(J+1) - D_0 (J(J+1))^2 + H_0 (J(J+1))^3$$
(2.16)

where, J is the rotational quantum number, and $B_0 = 59.3392$, $D_0 = 0.04599$, $H_0 = 5.2 \times 10^{-5}$ (in cm⁻¹) [14].

The rotational partition function for equilibrium H_2 involves values of the nuclear spin degeneracy, $g_J = 1, 3$, for even or odd J respectively. In the case of normal hydrogen, the partition function is treated as two separate partition functions, one for each species para and ortho, and the spin degeneracy is considered to be 1. The fractional population of a given rotational state is then weighted by the normal relative population of each species: para=0.2508, ortho=0.7492 (see eqn 2.40).

2.2.2 The Pair Induced Dipole Moment

The pair induced dipole moment μ is a function of the distance \vec{R} between the molecules and the orientations of their molecular axes $\vec{r_1}$ and $\vec{r_2}$. In a space fixed coordinate system, the orientations of $\vec{R}, \vec{r_1}$, and $\vec{r_2}$ are denoted by the angles

$$\Omega = (\theta, \phi), \ \Omega_1 = (\theta_1, \phi_1), \ \Omega_2 = (\theta_2, \phi_2)$$

The drawing below depicts molecules 1 and 2 and the angles θ and ϕ associated with \vec{R} . The other angles are not drawn, but are determined by a parallel translation of the XYZ coordinate system to the centers of mass of molecules 1 and 2. The angular



dependence of μ can be expanded in terms of the spherical harmonics of Ω , Ω_1 , and Ω_2 . This expansion uses as a basis the complete set of eigenfunctions of J_1^2 , J_{1Z} , J_2^2 , J_{2Z} , L^2 , L_Z . J_1 and J_2 are the angular momenta of molecules 1 and 2, and L is the relative angular momentum of the pair. Evaluation of the matrix elements requires a change of basis to the eigenfunctions of J_1^2 , J_2^2 , L^2 , J_i^2 , J^2 , J_Z , where $J_i = J_1 + J_2$ and $J = J_1 + J_2 + L$. The wavefunctions include the Clebsch-Gordan coefficients owing to this change of basis. The wavefunctions are denoted

$$\psi_{J_{\mathcal{V}}}^{J_1J_2LJ_i}(\Omega,\Omega_1,\Omega_2)$$

where ν indicates the spherical components $0,\pm 1$. The spherical components of μ relative to the Cartesian components are

$$\mu_o = \mu_z, \quad \mu_{\pm} = \pm \frac{1}{\sqrt{2}} (\mu_x \pm i \mu_y)$$
 (2.17)

Each component is written as an expansion over the complete set of functions ψ .

$$\mu_{\nu} = \left(\frac{64\pi^3}{3}\right)^{1/2} \sum_{\lambda_1 \lambda_2 \Lambda L} A(\lambda_1 \lambda_2 \Lambda L; R) \psi_{1\nu}^{\lambda_1 \lambda_2 L \Lambda}(\Omega, \Omega_1, \Omega_2)$$
(2.18)

The coefficients $A(\lambda_1\lambda_2\Lambda L)$ are independent of the chosen coordinate system and they classify the dipolar induction mechanisms in terms of the parameters $\lambda_1\lambda_2\Lambda L$. The exp-4 model describes two general catagories of dipole induction: short-range overlap distortions of the molecule's electronic distributions, and long-range interactions between the quadrupolar electric field of one molecule and the polarizability of the other. The magnitude of the overlap dipole is proportional to $e^{-R/\rho}$ and that of the quadrupolar induced dipole is proportional to R^{-4} .

The dominant cause of infrared absorption in the translational-rotational band of H_2 is the quadrupolar interaction, but the anisotropic overlap induced dipole moment and the 'interference' between the quadrupolar and overlap moments also contribute to

absorption. He-Ar mixtures demonstrate translational absorption which is entirely due to an angle independent overlap induced dipole moment; this mechanism does not cause absorption in pure hydrogen gas due to the symmetry of H_2 - H_2 collisions. The collisioninduced vibrational absorption spectrum of H_2 is due to the derivative of the induced dipole moment with respect to internuclear separations. In this case, S and O branches are due primarily to a quadrupolar induced dipole, and the Q branch is due to both a substantial isotropic overlap induced dipole and a quadrupolar induced dipole moment [5].

The most significant $A(\lambda_1\lambda_2\Lambda L)$ coefficients of the exp-4 model and its subsequent extensions are presented in the following list [48],[47]. Included in the list are brief descriptions of the dipole moment induction mechanisms and the selection rules for transitions $(J'' \leftarrow J')$. The selection rules are derived from forming matrix elements of the dipole moment operator. The wavefunctions are written as triple products of spherical harmonics (eqn 2.31), and the components of the dipole moment operator are also expressed as triple products of spherical harmonics (eqn. 2.18). The matrix elements involve integration over the angles Ω, Ω_1 , and Ω_2 , and the resulting nonzero terms satisfy the triangle conditions [49]

$$\Delta(J_1''\lambda_1J_1'), \ \Delta(J_2''\lambda_2J_2'), \ \Delta(L''LL').$$

Other limitations on the allowed transitions result from the symmetry of the H₂ molecule and the H₂ dimer [28]. The selection rules listed below apply to cases of large angular momenta, and when only low J states are occupied the triangle rules determine the allowed transitions. For instance, if $J_1=1$, $J_2=0$, and L=0, then the allowed transitions due to the A(2023) induced dipole component are: $\Delta J_1 = 0, +2; \Delta J_2 = 0;$ and $\Delta L = +3$.

- A(2021) = -A(0221) = ξ₁e^{-R/ρ}, anisotropic overlap L=1,
 ΔJ₁ = 0, ±2; ΔJ₂ = 0; ΔL = ±1; or ΔJ₁ = 0; ΔJ₂ = 0, ±2; ΔL = ±1.
 Allows a rotational transition in one molecule of a pair, pure translational transitions, and transitions between the dimer bound states L = 0, 1.
- 3. $A(2233) = \sqrt{8/15} \gamma Q/R^4$, quadrupole moment-anisotropic polarizability, $\Delta J_1 = 0, \pm 2; \ \Delta J_2 = 0, \pm 2; \ \Delta L = \pm 1, \pm 3.$

Allows simultaneous rotational transitions of both molecules, so called double transitions. A(2211) is similar, but $\Delta L = \pm 1$.

4. A(4045) = -A(0445) = √5 αφ/R⁶, hexadecapole moment-isotropic polarizability, ΔJ₁ = 0, ±2, ±4; ΔJ₂ = 0; ΔL = ±1, ±3, ±5; or ΔJ₁ = 0; ΔJ₂ = 0, ±2, ±4; ΔL = ±1, ±3, ±5.

Allows single molecule rotational transitions up to $\Delta J = 4$, has a minor influence on the high frequency wings of rotational lines.

5. $A(0001) = \xi e^{-R/\rho}$, isotropic overlap, $\Delta L = \pm 1$.

Applies to H₂-He or rare gas collisions, allows pure translational transitions only.

 α is the mean polarizability, γ is the anisotropy of the polarizability, Q is the quadrupole moment, ϕ is the hexadecapole moment, and ξ_i are strength parameters for the overlap induced dipole moment. The relative strengths of these induced dipole components as functions of intermolecular distance are plotted in Figure 2.3.
2.2.3 Remarks on the Quadrupole Induced Dipole Moment

The dipole moment induced in one molecule due to the quadrupolar electric field of the other is

$$\boldsymbol{\mu} = \boldsymbol{\alpha} : \mathbf{E} \tag{2.19}$$

This is a tensor product of α , the polarizability tensor, and E, the electric field. The electric field at a point in space is given by

$$\mathbf{E} = -\nabla \mathbf{V} \tag{2.20}$$

The potential V, at the center of mass of molecule 1, due to the charge distribution of molecule 2 may be written as a multipole expansion

$$V(1) = \sum_{n=0}^{\infty} \frac{1}{R^{n+1}} \int r^n P_n(\cos \theta) \rho \, d\tau$$
 (2.21)

The situation is described by the drawing below. The molecules 1 and 2 are separated



by a distance R, ρ is the charge density of molecule 2, r and θ are the coordinates of the volume element $d\tau$ with respect the center of mass of molecule 2, θ is the angle between r and R, and $P_n(\cos \theta)$ are the Legendre polynomials. The integral is over the volume of molecule 2.

Homonuclear diatomic molecules are neutral and symmetric, and the first non-zero term in the multipole expansion is the n=2 quadrupole term given below. If molecule 2

is in the J = 0 state, even this term is zero.

$$V(1) = \frac{1}{R^3} \int r^2 \left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right) \rho \, d\tau \tag{2.22}$$

For a set of discrete charges the quadrupole moment is defined by [47]

$$Q = \left\langle \sum_{i} e_{i} r_{i}^{2} P_{2}(\cos \theta_{i}) \right\rangle$$
(2.23)

where e_i, r_i, θ_i are the magnitude, and coordinates of the *i*th charge with respect to molecule fixed coordinates, and P_2 is the Legendre polynomial. The brackets denote the expectation value over the electronic ground state. The magnitude of the electric field of molecule 2 at the center of mass of molecule 1 is

$$\mathbf{E} \propto \frac{1}{R^4} Q$$

The equation for μ is simplified by choosing a coordinate system with the z axis oriented along molecule 1 (as drawn). In this coordinate system, the polarizability tensor for a linear molecule is diagonal and may be expressed as

$$\begin{bmatrix} \alpha_{xx} & & \\ & \alpha_{yy} & \\ & & \alpha_{zz} \end{bmatrix} = \alpha \begin{bmatrix} 1 & & \\ & 1 & \\ & & 1 \end{bmatrix} + \gamma \begin{bmatrix} -1 & & \\ & -1 & \\ & & 2 \end{bmatrix}$$
(2.24)

This is a sum of an isotropic part and an anisotropic part, where

$$\alpha_{xx} = \alpha_{yy} = \alpha_{\perp}, \quad \alpha_{zz} = \alpha_{\parallel} \tag{2.25}$$

and

$$\alpha = \frac{1}{3}(2\alpha_{\perp} + \alpha_{\parallel}), \quad \gamma = (\alpha_{\parallel} - \alpha_{\perp})$$
(2.26)

The components of μ , in a spherical basis, in a space fixed coordinate frame, are expressed by rotations of Euler angles applied to the diagonal polarizability tensor, and inverse rotations applied to the components of the electric field [50]. μ now has the form

$$\boldsymbol{\mu} = [\boldsymbol{\alpha}\mathbf{I} - \boldsymbol{\gamma}\mathbf{M}] : \mathbf{E}$$
 (2.27)

where I is the identity matrix and M is a product of rotations applied to the second term in eqn. 2.24. The components of μ are in this way written in terms of the spherical harmonics of two of the Euler angles.

Equation 2.27 demonstrates that the dipole moment induced in molecule 1, due to the quadrupole field of molecule 2, is a sum of two terms which are proportional to:

$$rac{lpha \; Q}{R^4} \quad ext{and} \quad rac{\gamma \; Q}{R^4}$$

Note that the quadrupole moment of molecule 1 also induces a dipole moment in molecule 2 and the net pair induced dipole moment is

$$\boldsymbol{\mu} = \boldsymbol{\mu}_1 + \boldsymbol{\mu}_2. \tag{2.28}$$

2.2.4 The Evaluation of the Binary Absorption Coefficient

The binary absorption coefficient, eqn. 2.14, is evaluated using the expression of the dipole moment in terms of the spherical harmonics, eqn. 2.18. The Hamiltonian for the relative motion of molecules 1 and 2 is

$$H = -\frac{\hbar^2}{2m} \nabla_R^2 + \frac{\hbar^2}{2I} \mathbf{J}_1^2 + \frac{\hbar^2}{2I} \mathbf{J}_2^2 + V(R)$$
 (2.29)

where I is the moment of inertia of the hydrogen molecule, and V(R) is the intermolecular potential. The first three terms constitute the kinetic energy operator which may be written as a sum of the following four terms

$$K = -\frac{\hbar^2}{2m}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} + \frac{\hbar^2}{2mR^2}\mathbf{L}^2 + \frac{\hbar^2}{2I}\mathbf{J}_1^2 + \frac{\hbar^2}{2I}\mathbf{J}_2^2$$
(2.30)

The eigenfunctions of the Hamiltonian have the form

$$\psi(R,\Omega,\Omega_1,\Omega_2) = \chi_{kL}(R)Y_{LM}(\Omega)Y_{J_1m_1}(\Omega_1)Y_{J_2m_2}(\Omega_2)$$
(2.31)

 $\chi_{kL}(R)$ denotes the radial part of the wavefunction, where k is the radial quantum number, and Y_{LM} , $Y_{J_1m_1}$, $Y_{J_2m_2}$ are the spherical harmonics. The trace in eqn. 2.14 is evaluated by taking the sum, over the complete set of eigenfunctions ψ , of the quantity $\langle \psi | P \mu[K, \mu] | \psi \rangle$. Details may be found in [7],[43], and [51].

The result below reflects the four terms of the kinetic energy operator and they are associated with modulation of the dipole moment by changes in R, Ω, Ω_1 , and Ω_2 .

$$\alpha_{1} = \frac{2\pi^{2}}{3c} \sum_{\lambda_{1}\lambda_{2}\Lambda L} \int_{0}^{\infty} \left[\frac{1}{m} |A(\lambda_{1}\lambda_{2}\Lambda L; R)'|^{2} + \left(\frac{L(L+1)}{mR^{2}} + \frac{\lambda_{1}(\lambda_{1}+1)}{I} + \frac{\lambda_{2}(\lambda_{2}+1)}{I} \right) |A(\lambda_{1}\lambda_{2}\Lambda L; R)|^{2} \right] \times g(R) R^{2} dR$$

$$(2.32)$$

The prime denotes differentiation with respect to R. g(R) is the pair distribution function and it is discussed in the following section. The above expression gives the complete integrated binary absorption coefficient for the far-infrared spectrum of a diatomic gas; it includes translational and rotational transitions.

In general, the rotational and translational bands of diatomic gases are blended together (i. e. for N₂ and O₂). The wavefunction of the colliding pair is separable into an angular and radial part only if the intermolecular potential is strictly isotropic. In the case of H₂, the energy difference between rotational states is so large that even if a small anisotropy of the potential mixes rotational energy levels, the effect on the rotational energies is insignificant; in the present context the Hamiltonian is considered separable. Phenomenologically, an isotropic potential dictates that H₂ molecules in a bound dimer act like free rotors, and the complex rotation is independent of the rotational state of the molecules. Treated in the greatest detail, this is not true, and some modern models utilize a potential with small anisotropic components. The integrated binary absorption coefficient for the translational band alone is

$$\alpha_{1\mathrm{tr}} = \frac{2\pi^2}{3mc} \sum_{\lambda_1\lambda_2\Lambda L} \sum_{\Delta J} L_{\lambda_1}(\Delta J) L_{\lambda_2}(\Delta J) \int_0^\infty \left[|A(\lambda_1\lambda_2\Lambda L; R)'|^2 + \frac{L(L+1)}{R^2} |A(\lambda_1\lambda_2\Lambda L; R)|^2 \right] g(R) R^2 dR \qquad (2.33)$$

where

$$L_{\lambda}(\Delta J) = \sum_{J} P(J)C(J,\lambda,J+\Delta J;00)^{2}$$
(2.34)

P(J) is the fractional population of the Jth state, and $C(J,\lambda, J+\Delta J; 00)$ are the Clebsch-Gordan coefficients. The translational band results from transitions where there is no change in the net rotational energy of the colliding pair; this includes a subcategory of double transitions where $(J_1, J_2) \rightarrow (J_2, J_1)$, and $J_1 \neq J_2$. The present experimental study involves temperatures below 77 K; only the J = 0 and 1 rotational states are populated, and double transitions are irrelevant to the translational band. Finally, the integrated absorption coefficient, including double transitions as the second term, is given by [43]

$$\alpha_{1tr} = \left[a_1^2 \mathcal{I}_1 + a_3^2 \mathcal{I}_3 + b^2 \mathcal{J} + ba_3 \mathcal{K}\right] L_2(0)\eta + \left[L_2(0)^2 + 2L_2(+2)L_2(-2)\right] d^2 \mathcal{J}\eta \quad (2.35)$$

where a_1 , a_3 , b, and d are dimensionless and are expressed in terms of the exp-4 induction model. η has the dimensions of an absorption coefficient.

$$a_{1} = (\xi_{1}/e\sigma)e^{-\sigma/\rho} = \sim 10^{-4}$$

$$a_{3} = (\xi_{3}/e\sigma)e^{-\sigma/\rho} = 0.6 \times 10^{-4}$$

$$b = (\alpha Q/e\sigma^{5}) = 5.0832 \times 10^{-4}$$

$$d = \sqrt{\frac{4}{45}}(\gamma Q/e\sigma^{5}) = 5.6703 \times 10^{-5}$$

$$\eta = (\pi e^{2}\sigma^{3}/3mc) = 1.2089 \times 10^{-28} \text{cm}^{5} \text{sec}^{-1}$$

$$(2.36)$$

 σ is the size parameter for a Lennard-Jones potential, here equal to 0.2928 nm=5.5331 a₀ (Bohr radii), ρ is a range parameter for the overlap interaction, and $\rho/\sigma = 0.126$.

Physical quantities used in the above constants are: $\alpha = 5.439a_0^3$ [52], $Q = 0.48468ea_0^2$ [53], $\gamma = 2.035a_0^3$ [52], $e = 4.8032 \times 10^{-10}$ esu. The integrals $\mathcal{I}_1, \mathcal{I}_3, \mathcal{J}, \mathcal{K}$ are written below, where $x = R/\sigma$.

$$\mathcal{I}_{L} = 4\pi \int_{0}^{\infty} e^{-\frac{2\sigma}{\rho}(x-1)} \left(\left(\frac{\sigma}{\rho}\right)^{2} + \frac{L(L+1)}{x^{2}} \right) g(x) x^{2} dx$$

$$\mathcal{J} = 336\pi \int_{0}^{\infty} x^{-8} g(x) dx$$

$$\mathcal{K} = 32\pi \sqrt{3} \int_{0}^{\infty} e^{-\frac{\sigma}{\rho}(x-1)} \left(\frac{\sigma}{\rho} + \frac{3}{x}\right) g(x) x^{-3} dx$$

(2.37)

The quantities $L_2(\Delta J)$ are given by eqn. 2.34, where the relevant Clebsch-Gordan coefficients squared for rotational transitions of $\Delta J = 0, \pm 2$ are:

$$C(J,2,J;00)^{2} = J(J+1)/(2J-1)(2J+3)$$

$$C(J,2,J+2;00)^{2} = (3/2)(J+1)(J+2)/(2J-1)(2J+3)$$

$$C(J,2,J-2;00)^{2} = (3/2)J(J+1)/(2J-1)(2J+1)$$
(2.38)

The term $L_2(+2)L_2(-2)$ denotes the contribution to the translational band from collisions in which both molecules undergo a rotational transition, but the net rotational energy of the pair is unchanged. The term $L_2(-2)$ therefore involves the population of the upper rotational state, and the value (J + 2) must be inserted for J in the coefficient $C(J,2,J-2;00)^2$ above. The fractional population of a state J for normal hydrogen is

$$P(J)_{even} = \frac{1}{Z_{even}} (2J+1) e^{-\beta E(J)} (0.2508)$$

$$P(J)_{odd} = \frac{1}{Z_{odd}} (2J+1) e^{-\beta E(J)} (0.7492)$$
(2.39)

The binary absorption may now be calculated, provided the pair distribution function is known.

2.2.5 The Pair Distribution Function and the Calculated Translational Absorption Coefficient

The pair distribution function is proportional to the probability that two molecules in thermal equilibrium are separated by a distance R. It is normalized such that $g(R) \rightarrow 1$ as $R \rightarrow \infty$. Classically, the pair distribution function is

$$q(R) = e^{-\beta V(R)} \tag{2.40}$$

where V(R) is the intermolecular potential. For hydrogen gas, the Lennard-Jones intermolecular potential

$$V(R) = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^{6} \right]$$
(2.41)

is adequate to represent the virial coefficients when $\epsilon/k = 37$ K and $\sigma=0.2928$ nm. ϵ is the depth of the potential well and σ is the radial distance at which the potential crosses zero.

The integrated absorption coefficient is calculated using the classical pair distribution function in the expressions for the integrals $\mathcal{I}_1, \mathcal{I}_3, \mathcal{J}, \mathcal{K}$. The integrals are calculated numerically and the integrated absorptions for various temperatures are presented in Table 2.2. The terms in eqn. 2.35 which dominate the integrated absorption are $b^2\mathcal{J}$ and $ba_3\mathcal{J}$, the quadrupole induced dipole moment, and the 'interference' between the quadrupole and anisotropic overlap dipole moment, respectively.

At low temperatures the de Broglie wavelength of an individual H₂ molecule becomes comparable in size to σ . The 'hard shell' model of repulsion between molecules is therefore invalid, and a classical treatment of the system is inappropriate. Poll and Miller calculate the quantum mechanical pair distribution function for a Lennard-Jones potential [54]; it is given by

$$g(r_1, r_2) = 2\lambda^6 \sum_{i} P_i \sum_{\nu} \chi_{\nu}^*(r_1, r_2) e^{-\beta H} \chi_{\nu}(r_1, r_2)$$
(2.42)

where r_1 and r_2 are the positions of two molecules, P_i is a normalized Boltzmann factor, H is the Hamiltonian of the translational motion, and $\chi(r_1, r_2)$ form a complete set of translational wavefunctions. $\lambda = (\frac{\hbar^2}{2\pi m kT})^{1/2}$ is the thermal de Broglie wavelength [54].

The thermal de Broglie wavelength is the cube root of the quantum volume V_Q which relates the chemical potential μ_c , to the number density n, of an ideal monoatomic gas [55]

$$e^{\mu_c/kT} = nV_Q . \qquad (2.43)$$

In the case of an ideal diatomic gas, the right hand side is divided by the rotational partition function. λ for the hydrogen molecule is tabulated below for a few representative temperatures.

Thermal de Broglie Wavelength of H ₂						
Temperature (K)	300	200	80	40	20	
Wavelength (Å)	0.7	0.9	1.4	1.9	2.8	

Table 2.1: The thermal de Broglie wavelength of H_2 as a function of temperature

The wavefunctions are obtained by solving the one dimensional Schrodinger equation,

$$\chi''(R) + \left[k^2 - \frac{l(l+1)}{R^2} - \frac{2m}{\hbar^2}V(R)\right]\chi(R) = 0$$
(2.44)

where $k^2 = 2mE/\hbar^2$, m is the reduced mass of the H₂ pair, E is the relative translational energy, and V(R) is the Lennard-Jones potential. The solutions of the Schrodinger equation have discrete and continuous energy eigenvalues. The discrete eigenvalues correspond to two weakly bound states characterized by l = 0 and l = 1. Figure 2.1 shows the location of the two bound states, the two quasi-bound states l = 2, 3, and the Lennard-Jones potential. The effective potential curves correspond to adding the rotational energy of the H₂ pair to the intermolecular potential energy, and expressed in cm⁻¹,

$$V(R)_{eff} = \left(\frac{2m}{\hbar^2}V(R) + \frac{l(l+1)}{R^2}\right)\frac{h}{8\pi^2 mc}$$
(2.45)

Poll and Miller have calculated the quantum mechanical pair distribution function of hydrogen at various temperatures and tabulated the results [54]. In these calculations the symmetry of the wavefunction with respect to the coordinate exchange of the two H₂ molecules does not contribute significantly to the pair distribution function unless the temperature is below 5 K. At these very low temperatures, H₂ bound states dominate the pair distribution function, but their effect is negligible at temperatures above ~ 150 K. Figure 2.2 shows the classical and the quantum mechanical pair distribution functions of H₂ using a Lennard-Jones potential at a temperature of 20 K.

The figure shows that at large separations the pair distribution curves are equivalent, but the area under the classical curve is much greater than the area under the quantum curve. The calculated absorption using the classical pair distribution function is therefore much larger than the absorption calculated quantum mechanically.

The integrals $\mathcal{I}_1, \mathcal{I}_3, \mathcal{J}, \mathcal{K}$ are evaluated numerically by interpolating the tabulated quantum mechanical pair distribution functions of Poll and Miller [54]. The binary absorption coefficient for the translational band is then calculated at T = 20, 40, and 80 K. Table 2.2 lists the contributions to the binary absorption coefficient from the various terms of eqn. 2.35. Although the terms are calculated to high accuracy, they rely on the Lennard-Jones intermolecular potential, and hence, the validity of these results is limited by this approximation.



Figure 2.1: The energy levels of the $(H_2)_2$ complex superimposed on the Lennard-Jones intermolecular potential (l = 0) and 'effective' potential curves for l = 1, 2, 3, from [56].



Figure 2.2: The pair distribution function of H_2 at 20 K from [54]. The relations for the classical and quantum functions are given in the text, WK denotes the Wigner-Kirkwood expansion.

CLASSICAL RESULTS							
Temperature	20.00	40.00	80.00	200.00	3 00.00		
\mathcal{I}_1 Integral	0.2379E+03	0.1425E + 03	0.1409E+03	0.2055E + 03	0.2623E + 03		
\mathcal{I}_3 Integral	0.2696E+03	0.1624E + 03	0.1619E + 03	0.2393E + 03	0.3075E + 03		
${\mathcal J}$ Integral	0.6196E + 03	0.3286E + 03	0.2719E + 03	0.2976E + 03	0.3324E + 03		
${\cal K}$ Integral	0.7338E + 03	0.4094E + 03	0.3703E + 03	0.4738E + 03	0.5706E + 03		
$L_{2}(0)$	0.2997E + 00	0.2997E + 00	0.3003E + 00	0.3166E + 00	0.3221E + 00		
$L_2(+2)L_2(-2)$	0.8981E-01	0.8981E-01	0.9080E-01	0.1277E + 00	0.1653E + 00		
The Five Terms of the Integrated Absorption Coefficient							
\mathcal{I}_1	0.8620E34	0.5161E-34	0.5116E-34	0.7866E-34	0.1021E-33		
\mathcal{I}_3	0.3517E-34	0.2118E 3 4	0.2116E-34	0.3298E-34	0.4309E-34		
\mathcal{J}	0.5800E-32	0.3076E-32	0.2551E-32	0.2944E-32	0.3343E-32		
κ	0.8108E33	0.4523E33	0.4100E-33	0.5531E33	$0.6775E{-}33$		
Double trans.	0.2163E-34	0.1147E-34	0.9596E- 3 5	0.1477E34	0.2135E-34		
	The	e Binary Absor	ption Coefficie	ent	······································		
	0.6753E-32	0.3613E-32	0.3043E-32	0.3623E-32	0.4188E-32		
				······································			
QUANTUM RESULTS							
Temperature	20.00	40.00	80.00				
\mathcal{I}_1 Integral	0.1420E + 03	0.1257E + 03	0.1395E + 03				
\mathcal{I}_3 Integral	0.1639E + 03	0.1454E + 03	0.1619E + 03				
\mathcal{J} Integral	0.2930E + 03	0.2441E + 03	0.2414E + 03				
${\cal K}$ Integral	0.3732E + 03	0.3230E + 03	0.3426E + 03				
$L_{2}(0)$	0.2997E + 00	0.2997E + 00	0.3003E + 00				
$L_2(+2)L_2(-2)$	0.8981E-01	0.8981E-01	0.9080E-01				
The Five Terms of the Integrated Absorption Coefficient							
\mathcal{I}_1	0.5143E-34	0.4553E-34	0.5065E-34				
\mathcal{I}_3	0.2138E-34	0.1896E-34	0.2116E-34				
\mathcal{J}	0.2742E-32	0.2285E-32	0.2265E-32				
κ	0.4124E-33	0.3569E-33	0.3793E-33				
Double trans.	0.1023E- 3 4	0.8522E-35	0.8520E-35				
The Binary Absorption Coefficient							
	0.3238E-32	0.2715E-32	0.2724E-32				

Table 2.2: The calculated binary absorption coefficient for the translational band of normal H_2 at various temperatures using the Poll and Van Kranendonk theory of collision-induced absorption. The table shows the values of the integrals and various terms of eqn. 2.35. The pair distributions functions are based on the Lennard-Jones intermolecular potential; the classical cases are are given by eqn. 2.40 and the quantum mechanical cases are obtained from interpolating the tables of Poll and Miller [54]. The binary absorption coefficient is in the units cm⁵ sec⁻¹.

Comments on the Binary Absorption Coefficient

Comparisons can be made at this point between the calculated binary absorption coefficient, α_{1tr} , and the measured experimental integrated absorption coefficient, α , by recalling that

$$\alpha_{1 \mathrm{tr}} \simeq \frac{\alpha}{n^2} = \frac{c}{n_0^2} \int \frac{A(\sigma)}{\rho^2} d\sigma$$
(2.46)

n is the gas density (in mol. cm⁻³), which is equal to ρn_0 , where ρ is the density in amagat units, and n_0 is Loschmidt's number (2.687 × 10¹⁹ cm⁻³). An amagat is the ratio of the sample gas density to that of an ideal gas at 0° C and 1 atm. pressure. The measured quantity $A(\sigma)/\rho^2$ has the units cm⁻¹ amagat⁻²; integrating it over the absorption band, and multiplying by c/n_0^2 , yields a result in the units cm⁵ sec⁻¹. Table 2.3 compares the calculated binary aborption coefficients using classical and quantum mechanical pair distribution functions to measurements at a number of temperatures.

The translational and rotational absorption bands overlap, especially at high temperatures, and the intensity of the translational band alone must be inferred from fitting the entire translational-rotational band. The absorption spectrum is fit by a superposition of the translational band and rotational line profiles, each with the appropriate population weighting and a common lineshape function. The lineshape used by Bosomworth and Gush [8], is a modified Lorentzian with an exponential tail, and that used by Bachet et al. [14] and Dore et al. [13] is the B-C lineshape, which is discussed later in this chapter. The integrated absorption between 37 and 22 K is obtained by fitting low frequency spectra (LF 'group' spectra), described in chapter four, with the B-C spectrum over the region 20-180 cm⁻¹, and extrapolating to 1000 cm⁻¹.

Table 2.3 shows that the integrated absorption measured at high temperatures, substantially exceeds the calculated absorption. This excess is probably not attributable to the inference of the translational band absorption from measurements of the entire band.

Temp. (K)		Theory	Experiment		
	Classical		Quantum	$(\times 10^{-33} \text{ cm}^5 \text{ sec}^{-1})$	
300	4.19			5.60ª	
				5.12^{b}	
				5.96 ^c	
200	3.62			4.95 ^c	
80	3.04		2.72	2.50^{a}	
				3.58^{b}	
				3.02^{c}	
40	3.61		2.72		
37.2				3.08	
35.0				3.04	
34.4				2.94	
25.5				3.05	
25.2				3.22	
25.0				3.23	
24.4				3.37	
22.4				3.38	
20	6.75		3.24		

Table 2.3: The binary absorption coefficient of the translational band of normal H_2 . The classical and quantum mechanical calculations are given in Table 2.2. The measurements are: a, [8]; b and c are inferred from [12] and [13]; the low temperature measurements are from the low frequency spectra (LF group spectra) reported in this thesis, see chapter four.

Bachet et al. compared measurements of the integrated absorption at 300 and 195 K to calculations of the absorption due to only the quadrupolar induced dipole moment using a variety of intermolecular potentials. The discrepancy between the measured and calculated absorptions was interpreted as the overlap contribution, where this contribution varied widely in response to the choice of the intermolecular potential [14]. The present low temperature calculations use a quantum mechanical pair distribution function based on the Lennard-Jones potential, and include the overlap and interference contributions to the integrated absorption. Table 2.3 shows that the calculated and measured low temperature integrated absorption coefficients are consistent.

The formalism of Poll and Van Kranendonk relates the integrated translational absorption to the molecular quadrupole moment and polarizabilities, and the intermolecular potential. Collision-induced absorption may be used to measure molecular quadrupole moments, provided that the polarizability and intermolecular potential are accurately known. Alternatively, the variation of the integrated absorption as a function of temperature is a probe of the intermolecular potential, since the molecular properties do not change with temperature. The discussion of the comparison between measured and calculated binary absorption coefficients is continued in chapter four.

Trafton extended the theory of collision-induced absorption by calculating the H₂ translational absorption bandshape [57]. This work stems from eqn. 2.3 where the absorption at a given frequency is calculated from the matrix elements of the dipole moment. The wavefunctions are separated into an angular part ϕ which is a product of spherical harmonics, and a radial part χ which is is obtained by numerical integration of the Schrodinger equation. The matrix elements of the dipole moment are then formed by integrating the product of the wavefunctions and the dipole moment operator over all

space.

$$\langle f | \boldsymbol{\mu} | i \rangle = \int \phi_f^* \left[\int_0^\infty \chi_f^*(R) \, \boldsymbol{\mu} \, \chi_i(R) \, dR \right] \, \phi_i \, d\Omega \tag{2.47}$$

Trafton's calculated H_2 translational bandshape is comparable to the Bosomworth and Gush 77 K spectrum, the only quasi-isolated H_2 translational band measurement at that time. Integrating over the calculated 300 K translational band yields an absorption coefficient within 1.2% of Poll and Van Kranendonk's result. This calculation does not include wavefunctions associated with H_2 bound states and therefore the bandshape is only accurate at high temperatures.

Trafton applied these bandshape calculations to modelling planetary atmospheres, and the collision-induced absorption of H_2 was shown to be largely responsible for the thermal opacity of Jupiter's atmosphere [15],[16]. Prior to this demonstration, a large internal heat source was required to explain Jupiter's infrared emission (a small internal heat source may still be required).

2.3 The Spectral Density Formalism

Modern theoretical treatments of collision-induced absorption utilize the spectral density formalism to calculate the spectral bandshape [58], [59], [46], and the following discussion is from [44]. The spectral bandshape is related to the Fourier transform of the dipole correlation function, and as a result, a connection is made between the microscopic motion of molecules and the absorption spectrum of a macroscopic system.

Equation 2.3 gives the absorption of radiation at a given frequency due to allowed electric dipole transitions. It is repeated below in terms of ω , the angular frequency $(=2\pi c\sigma)$.

$$A(\omega) = \frac{4\pi^2}{3\hbar cV} \omega \sum_{i < f} (P_i - P_f) |\overline{\mu_{if}}|^2 \delta(\omega_{if} - \omega)$$
(2.48)

The matrix element $\overline{\mu}$ refers to the net dipole moment of the entire system, and summation takes place over all states $E_f > E_i$, and $\omega_{if} = (E_f - E_i)/\hbar$. The expression for $A(\omega)$ is cast into a different form by: (1) assuming the system to be in thermal equilibrium, (2) replacing the delta function by its integral representation $\delta(\omega_{if} - \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(\omega_{if} - \omega)t} dt$, and (3) changing the description of the time dependent dipole matrix elements from the Schrodinger representation to the Heisenberg representation [60]. The absorption coefficient is now written

$$A(\omega) = \frac{2\pi}{3\hbar cV} (1 - e^{-\beta\hbar\omega}) \omega \int_{-\infty}^{\infty} e^{-i\omega t} \langle \overline{\mu(0)\mu(t)} \rangle dt \qquad (2.49)$$

where the brackets denote an ensemble average of the expectation value of $\overline{\mu(0)\mu(t)}$ over all states.

The dipole moment correlation function for collision-induced absorption at low densities is

$$\langle \overline{\mu(0)\mu(t)} \rangle = \frac{N^2}{2} \langle \mu(0)\mu(t) \rangle$$
 (2.50)

where the dipole moments on the right side refer to the pair induced dipole moment, and N is the number of molecules in the optical path.

The expression for absorption in terms of a spectral density function $g(\omega, T)$ is

$$A(\omega) = \frac{2\pi^2 n^2}{3\hbar c} \omega (1 - e^{-\beta\hbar\omega}) Vg(\omega, T)$$
(2.51)

where n = N/V is the molecular number density, T is the temperature, and $g(\omega, T)$ is the spectral density function.

$$g(\omega,T) = \sum_{if} P_i |\mu|^2 \delta(\omega_{if} - \omega)$$
(2.52)

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \langle \boldsymbol{\mu}(0) \boldsymbol{\mu}(t) \rangle dt \qquad (2.53)$$

The upper equation stems from eqn. 2.48 and the lower equation is from eqn. 2.49. $g(\omega, T)$ is a measure of the transition probability and it is the Fourier transform of the pair dipole moment correlation function as shown above. The general significance of the spectral density formalism is that spectral lineshapes can be directly related to processes which affect the dipole correlation function. For example, the Fourier transform of a sinusoidally oscillating dipole moment decaying exponentially in time yields the Lorentzian lineshape. Conversely, the microscopic behaviour of a system, such as the inhibitions of molecular rotations in a liquid, may be obtained by inverse Fourier transformation of a spectrum [49].

The spectral moments of $g(\omega)$ are defined by

$$M_n = V \int_{-\infty}^{\infty} \omega^n g(\omega) d\omega \qquad (2.54)$$

The spectral moments are related to the time derivatives of the dipole moment correlation function, and they also connect the theoretically derived and experimentally measured spectra. In the equations below, the experimental quantities on the left are called spectral invariants, and they are related to the spectral moments by [44]

$$\gamma_1 = \int \gamma_1'(\omega) \, d\omega = \frac{\beta \hbar}{2} \int \frac{A(\omega)/n^2}{\omega \tanh(\frac{\beta \hbar \omega}{2})} d\omega = \frac{\pi^2 \beta}{3c} M_0 \tag{2.55}$$

$$\alpha_1 = \int \frac{A(\omega)}{n^2} d\omega = \frac{2\pi^2}{3\hbar c} M_1 . \qquad (2.56)$$

The absorption coefficient per unit pathlength, $A(\omega)$, retains the definition used throughout this chapter, eqn. 2.1. The experimentally measured absorption coefficient, per unit density squared per unit pathlength, is defined by eqn. 4.1 and equals $A(\omega)/n^2$.

The spectral invariant α_1 , is the same as the integrated binary absorption coefficient multiplied by 2π . The lineshape function is defined by

$$G(\sigma) = \frac{A(\sigma)/n^2}{\sigma(1 - e^{-hc\sigma/kT})}$$
(2.57)

The lineshape function is the absorption coefficient divided by the frequency and the stimulated emission factors, and $G(\sigma)$ is proportional to the probability of absorption

[48]. The spectral invariant γ_1 is analogous to an integrated lineshape function; however, it stems from an absorption coefficient that involves a spectral density $g_+(\omega)$ which is the Fourier transform of a symmetrized pair dipole moment correlation function [44],[58]. In this formulation, the factor $\tanh(\frac{\beta\hbar\omega}{2})$ has the role of a stimulated emission term, but it is not exactly the same. The relation between $G(\sigma)$ and $\gamma'_1(\omega)$ is demonstrated by the ratio (neglecting constant factors)

$$\frac{\gamma_1'(\omega)}{G(\sigma)} \propto \frac{(\tanh(hc\sigma/2kT))^{-1}}{(1 - e^{-hc\sigma/kT})^{-1}} = (1 + e^{-hc\sigma/kT})$$
(2.58)

For $hc\sigma \gg kT$, the ratio is 1, but for low frequencies (below 10 cm⁻¹ at T = 30 K) the ratio approaches 2. In order to remain consistent with previous experimental and theoretical studies, the spectral invariants α_{1tr} and γ_{1tr} for the measured translational band are obtained in chapter four using the definitions above.

The spectral density function for collision-induced absorption includes contributions from the various $A(\lambda_1\lambda_2\Lambda L)$ components of the induced dipole moment, the superposition of which produces the measured spectrum. For a given component, the spectral invariants, and ratios of spectral invariants, depend on such properties as the polarizabilities, quadrupole moment, overlap range and strength parameters, and the intermolecular potential. Measured spectral invariants at various temperatures allow a test of these molecular parameters, or a test of the models used for the intermolecular potential and the induced dipole moment [48], [59].

2.4 The Theoretical Spectrum of Hydrogen

Schaefer [61], Schaefer and McKellar (SM) [45], [28]; and Meyer, Frommhold, and Birnbaum (MFB), [62], have produced the most sophisticated calculations of the absorption spectrum of molecular hydrogen. These calculations include contributions to the spectrum by free-free, free-bound, bound-free, and bound-bound H_2 pair transitions. Both groups use an ab-initio induced dipole moment in the calculations instead of the exp-4 model. SM utilize an anisotropic intermolecular potential and the discussion below generally follows this formulation.

The absorption at a given frequency is given by eqn. 2.51, where the spectral density is

$$g(\omega,T) = \sum_{rr'} P_r \sum_{tt'} P_t \left| \langle r't' | \boldsymbol{\mu}_{r,r'} | rt \rangle \right|^2 \delta(\omega_{rr'} + \omega_{tt'} - \omega)$$
(2.59)

 P_r is the fractional population of a rotational state, P_t is the normalized Boltzmann factor for translation

$$P_t = \frac{\lambda_0^3}{V} e^{-\beta E_t} \tag{2.60}$$

where λ_0 is the thermal deBroglie wavelength. Transitions take place between rotational states denoted r, r' and translational states t, t'.

The wavefunctions are obtained by solving the Schrodinger equation

$$\left(\frac{-\nabla_{\mathbf{r}}^2}{2m} + H_1 + H_2 + V(\vec{r_1}, \vec{r_2}, R)\right)\psi = 0.$$
(2.61)

 H_1 and H_2 are the rigid rotor Hamilitionians of the individual H_2 molecules; R is the intermolecular separation; and $\vec{r_1}$ and $\vec{r_2}$ point along the axes of the two molecules. The intermolecular potential is written as a triple product of spherical harmonics analogous to the expansion of the dipole moment operator. The expansion coefficients are obtained from ab-initio calculations, and are scaled to fit the experimental data of second virial coefficients and molecular beam magnetic resonance transitions [28], [63]. Band-shape calculations performed with this potential demonstrate more spectral detail and are computationally more complex than those which use an isotropic potential. MFB employ an isotropic potential; the wavefunctions are therefore separable, and only the radial Schrodinger equation needs to be solved [62].

The wavefunctions obtained from solving the Schrodinger equation are correct for a colliding pair composed of two H_2 molecules in different states. H_2 molecules are bosons

and if the H_2 dimer is treated as a quasi-diatomic molecule, the total wavefunction of a dimer of para H_2 is purely symmetric. The total wavefunction of an ortho dimer, with a nuclear spin of 0, 1, or 2, is a sum of symmetric and antisymmetric wavefunctions, with weights 2/3 and 1/3 respectively.

The wavefunctions are now applied to the induced dipole moment operator. The induced dipole moment operator has been calculated from first principles by treating the collision complex as a molecule and calculating the electronic distribution [63]. The expectation value of the complex dipole moment is dependent on the intermolecular separation and orientations of the two H₂ molecules, and the dipole moment operator is expanded as a triple product of spherical harmonics, as in eqn 2.18. Figure 2.3 shows the R dependence of the expansion coefficients $D(\lambda_1\lambda_2\Lambda L)$ which are associated with the same dipole induction mechanisms as the previous coefficients $A(\lambda_1\lambda_2\Lambda L)$. The ab-initio induced dipole moment is very similar to the exp-4 model and the dominant D(2023) component has an approximately $1/R^4$ dependence.

Finally, the spectral density is calculated by obtaining the matrix elements of the dipole moment for all dipole moment expansion coefficients. The spectral density includes transitions between all initial and final rotational and translational energy states, where the states are weighted by the relevant population statistics and Clebsch-Gordan coefficients. A theoretical spectrum is then calculated from the spectral density.

SM characterize the spectrum in terms of the contributions due to the free-free, freebound, bound-free, and bound-bound H₂ pair transitions. Each contribution is composed of a sum over all the dipole moment expansion coefficients $D(\lambda_1 \lambda_2 \Lambda L)$. Figure 2.4A shows Schaefer's synthetic spectrum of the entire translational-rotational band of equilibrium H₂ at 77 K. The upper curve is the total absorption spectrum, and the lower curve is the free-free contribution; the bound state contributions are reflected by the difference between them. Figures 2.4B and 2.4C show the calculated spectrum and McKellar's



Figure 2.3: The expansion coefficients of the ab-initio induced dipole moment [63]. The coefficients and primary interaction mechanisms are: 2023,0223, quadrupole moment-isotropic polarizability; 2021,0221, anisotropic overlap; 2233 and 2211, quadrupole moment-anisotropic polar.; and 4045,0445, hexadecapole moment-isotropic polar.

recent measurements of the S(0) rotational line for equilibrium H_2 at 77 K, and para H_2 at 20 K. The experimental measurements are the noisy solid curves, the total calculated spectra are the smooth solid curves, and the dotted curves are the free-free contributions. Note that the 20 K spectrum is more intense and the dimer features are sharper than the 77 K spectrum.

The SM calculations correspond closely to the measured spectra. The inclusion of the anisotropic intermolecular potential accurately reproduces the details of the dimer structure, although some deviations between the calculated and measured spectra occur at frequencies higher than the S(0) transition frequency. In general, these graphs demonstrate the validity of the theory of collision-induced absorption and the ab-initio H_2 intermolecular potential.

MFB classify the theoretical spectrum in terms of the dipole moment expansion coefficients, where each component involves a summation over all types of H_2 pair transitions.



Figure 2.4:

A: The calculated translational-rotational band of equilibrium H_2 at 77 K, [61] B: The S(0) line of equilibrium H_2 at 77 K, from Schaefer and McKellar [45] C: The S(0) line of para H_2 at 20 K, from McKellar and Schaefer [28] The various curves are explained in the text.



Figure 2.5:

A: The translational-rotational spectrum of H_2 at 297.5 K. The measurements are from Bachet et al. [14], and the calculations are from MFB [62]. The components of the spectrum are described in Figure 2.3.

B: The translational-rotational spectrum of equilibrium H_2 at 77 K. The measurements are from Birnbaum [12], and the calculations are from MFB [62].

Figure 2.5 shows the decomposition of the entire H₂ translational-rotational band in terms of the induced dipole components. The calculations are those of MFB [63], and the measurements at 295 and 77 K are by Bachet et al. [14] and Birnbaum [12], respectively. The spectra have been measured and calculated at low resolution (10 cm^{-1}) and therefore the dimer structure does not appear. The D(2023) component of the induced dipole moment clearly dominates the H₂ spectrum and only in the high frequency wings of the rotational lines is there a noticeable contribution from other mechanisms. In the 77 K spectrum, at the location of S(0), the minor dipole moment components contribute only 1 part in 100 to the total absorption. Minor dipole contributions to the translational band are further reduced as the temperature is lowered, because double transitions are eliminated since only the J=0 and 1 rotational states are populated. These graphs justify the assumption used in previous experiments and in the analysis of the present low temperature spectra, that the measurements can be reasonably fit using the B-C lineshape function which is attributed to the D(2023) component of the induced dipole.

A Comment on the Interference Between the Quadrupolar and Overlap Induced Dipole Moments

An apparent discrepancy exists between the results of the above bandshape calculations and those of Poll and Van Kranendonk. In the calculation of the integrated binary absorption coefficient, an 'interference' term between the quadrupolar and overlap induced dipole moments accounts for about 18% of the total absorption of the translational band at 300 K (see Table 2.3). In the pure rotational band the interference effect is negative and it results in an $\sim 8\%$ reduction of the integrated absorption [6]. The theoretical bandshape calculations of SM and MFB, however, make no reference to an interference effect between dipole induction mechanisms.

The two points of view may be reconciled by realizing that the interference term

results from expressing the integrated absorption in the form of the trace of $P\mu[K,\mu]$ over a complete set of states (eqn. 2.14). Evaluation of this inner product involves terms of the form μ'^2 and μ^2 [7], [51]. The A(2023) dipole moment expansion coefficient is expressed as the sum of two terms, the quadrupolar and overlap term. The square of the dipole moment operator will therefore yield cross products, or the 'interference' terms.

On the other hand, the transition moments which constitute part of the spectral density, eqn. 2.59, involve terms of the form $|\langle f|\mu|i\rangle|^2 = \langle i|\mu|f\rangle\langle f|\mu|i\rangle$. Matrix elements are calculated by numerical integration, where the wavefunctions and the dipole moment operator are expanded in products of spherical harmonics. The total matrix element is calculated, the result is then squared, and no cross products explicitly occur. The integrated absorption obtained from either formalism is the same, as both start from the same premise and merely do the calculation differently.

2.5 The Birnbaum-Cohen Lineshape

Detailed quantum mechanical calculations of collision-induced absorption are computationally complex, and yet it is obviously desirable to compare measurements to theory and to other measurements. In order to make comparisons of this kind, an empirical lineshape function has been devised, and a spectrum is synthesized by superposing lineshapes positioned at molecular transition frequencies, where the lines are weighted by the appropriate population statistics, frequency factors, and transition moments.

The B-C lineshape function, suggested by Birnbaum and Cohen, is well suited to modelling collision-induced spectra of homonuclear diatomic molecules [46]. They derive a spectral density function from the Fourier transform of a physically plausible pair dipole moment correlation function. This spectral density includes a lineshape that fits well the asymmetric collision-induced lines, and in addition, spectral features due primarily to the same induction mechanism can be represented by the same lineshape function.

The MFB quantum mechanical calculations of low resolution translational-rotational spectra of H₂ (Figure 2.5) can be reproduced accurately by associating a B-C lineshape function with each component of the induced dipole moment [64]. The dominant A(2023) induced dipole component is well described by the B-C lineshape. The anisotropic overlap component A(2021) is, however, better represented by another lineshape function. The A(0001) isotropic overlap component which is significant in H₂-rare gas collisions is also modelled more accurately by the alternate lineshape. An extended version of the B-C model combines both lineshape functions for each dipole component, and it is used to reproduce the quantum mechanical calculations of H₂ absorption over a wide range of frequency and temperature [64]. In addition, radiative transfer calculations of the atmosphere of Jupiter have used the B-C lineshape in modelling the Voyager infrared spectra.

Many experimental measurements of H_2 absorption have been analyzed by fitting the observations with a single B-C lineshape function [14],[13]. The measurements are represented in this way by an 'effective' A(2023) component, where it encompasses the other induced dipole components. This procedure is used to analyze the present spectra. The following discussion is primarily from Bachet et al. [14].

The B-C lineshape, for a particular transition $E_i \rightarrow E_f$ is given by

$$\Gamma_{if}(\omega_{-}) = \frac{\tau_{1}}{\pi} e^{(\tau_{1}/\tau_{2} + \tau_{0}\omega_{-})} \frac{zK_{1}(z)}{1 + (\omega_{-}\tau_{1})^{2}}$$
(2.62)

Terms within this equation are defined as

$$\begin{aligned}
\omega_{-} &= \omega - \omega_{if} \\
\tau_{0} &= \beta \hbar/2 \\
z &= \left(1 + (\omega_{-}\tau_{1})^{2}\right)^{1/2} (\tau_{2}^{2} + \tau_{0}^{2})^{1/2} / \tau_{1}
\end{aligned}$$
(2.63)

and $K_1(z)$ is the modified Bessel function of the second kind; it is approximated by

$$K_1(z) = \left(1 + \frac{\pi}{2} z \frac{z + 0.56232}{z + 0.46671}\right)^{1/2} \frac{e^{-z}}{z}$$
(2.64)

The parameters τ_1 and τ_2 are decay constants of the pair dipole moment correlation function. The duration of a collision is approximated by $(\tau_1\tau_2)^{1/2}$, and this is inversely proportional to the width of a spectral line. The B-C lineshape successfully accounts for the observed upward frequency shift of the rotational lines; for instance, the peak of the S(0) collision-induced line at 77 K, is at 371 cm⁻¹, as compared to the Raman scattering line at 354 cm⁻¹.

2.5.1 The Synthetic B-C Spectra

The translational absorption band, in general, overlaps the S(0) and S(1) H₂ rotational lines. At low temperatures these lines are well separated, but some overlap persists in the wings. In order to understand the absorption due to the translational band alone, the measured spectra are fitted by synthetic spectra obtained from the B-C lineshape. The integrated intensity α_{1tr} and spectral invariant γ_{1tr} are thereby obtained for the isolated translational band.

The synthetic B-C spectra have three adjustable parameters: τ_1 , τ_2 , and S, where τ_1 and τ_2 are the B-C decay constants, and S is a linestrength. The absorption at a given frequency is given by eqn. 2.48, and it is rewritten below with the assumption that the spectral density is composed of a superposition of B-C lineshapes (double transitions are not included) [14].

$$A(\omega) = \frac{2\pi^2 n^2}{3\hbar c} \omega (1 - e^{-\beta\hbar\omega}) \left(\sum_{JJ'} P(J) \sum_{L\lambda} C(J,\lambda,J';00)^2 S_{L\lambda} \Gamma_{L\lambda}(\omega - \omega_{JJ'}) \right)$$
(2.65)

where $\omega_{JJ'}$ denotes the frequency of a transition $J' \leftarrow J$.

The summation over L, λ denotes the inclusion of all the components of the induced dipole moment, where a linestrength S and a lineshape Γ are associated with each component. The H₂ spectrum is so clearly dominated by the A(2023) component (see Figure 2.5), that a reasonable synthetic spectrum is obtained using only this component. The quadrupole induced dipole, in turn, dominates the A(2023) component of the dipole moment, and the line strength for quadrupolar induction is given by

$$S = 24\pi \int_0^\infty \left(\frac{\alpha Q}{R^4}\right)^2 g(R) R^2 dR \qquad (2.66)$$

An S obtained by fitting measured spectra should exceed that which is calculated above using known values of α and Q, since the measured S encompasses the contributions to absorption from: the quadrupolar, overlap, and interference interactions associated with the A(2023) dipole component, and the other minor dipole components.

Synthetic absorption spectra based on eqn. 2.65 are generated by the superposition of a translational band and rotational lines according to

$$A(\omega) = A_T(\omega) + A_{S(0)}(\omega) + A_{S(1)}(\omega) + \dots$$
 (2.67)

where

$$A_{T}(\omega) = \frac{2\pi^{2}n^{2}}{3\hbar c}\omega(1 - e^{-\beta\hbar\omega})\sum_{J}P(J)C(J, 2, J; 00)^{2}S\Gamma(\omega)$$
(2.68)

and

$$A_{S(J)}(\omega) = \frac{2\pi^2 n^2}{3\hbar c} \omega (1 - e^{-\beta\hbar\omega}) P(J) C(J, 2, J+2; 00)^2 S \Gamma(\omega - \omega_{S(J)})$$
(2.69)

 Γ is the B-C lineshape, given by eqn. 2.62; P(J) is the fractional population of the Jth state, given by eqn. 2.40; and the Clebsch-Gordan coefficients are given by eqn. 2.39.

Figure 2.6 shows the synthetic spectrum of H₂ at 297 K using the values of τ_1 , τ_2 and S obtained by Bachet et al. from fitting the measured spectrum (not shown) with a B-C spectrum. The temperature, τ_1 , τ_2 (in units of 10⁻¹⁴ sec), and S (in units of K Å⁶) are written sequentially on Figures 2.6–2.8. Deviations between the measured spectrum at 297 K and its synthetic counterpart are less than 0.5% of the peak absorption. The deviations occur in the high frequency wing of the rotational lines and stem from the failure to include double transitions and the U(1) hexadecapole transition in the synthetic spectrum [14].

Figure 2.7 shows the reconstructed synthetic spectrum of normal H₂ at 77 K, where the B-C parameters are obtained from measurements by Dore et al. [13]. Figure 2.8 depicts a B-C synthetic spectrum of normal H₂ at 25.5 K, where the B-C parameters are obtained from fitting the translational spectrum shown in Figure 4.16. These figures demonstrate the dramatic increase in peak intensities and line resolution which are obtained by measuring the H₂ spectrum at low temperatures. The translational band peak at 25.5 K is stronger than at higher temperatures, but it is still lower than the intensity minimum between the S(0) and S(1) lines. This fact further illustrates the very weak absorption of the translational band.

The spectral invariants α_1 and γ_1 obtained from the translational-rotational synthetic spectra differ only slightly from the measured quantities. At 300K, α_1 and γ_1 obtained from Figure 2.6, differ from those measured by 0.5% and 1.0%, respectively. The difference between the synthetic and measured spectral invariants at 77 K is: α_1 , 1.3%; γ_1 , 0.4%. The correspondence between the measured spectral invariants and those obtained from fitted spectra demonstrates the usefulness of modelling the H₂ spectrum using the B-C lineshape.

Spectral invariants obtained from measuring the entire translational-rotational spectrum do not depend upon a lineshape function. This is not the case for the translational band alone, since this band must be extracted from the overall spectrum using some lineshape. The integrated absorption coefficients of the translational band listed in Table 2.3 are inferred from the B-C parameters of previously measured H₂ spectra between 300



Figure 2.6: The B-C synthetic spectrum of H₂ at 297 K using the values of τ_1, τ_2 (×10⁻¹⁴ sec), and S (K Å⁶) of Bachet et al. [14].



Figure 2.7: The B-C synthetic spectrum of H₂ at 77 K using the values of τ_1, τ_2 (×10⁻¹⁴ sec), and S (K Å⁶) of Birnbaum [13].



Figure 2.8: The B-C synthetic spectrum of H₂ at 25.5 K using the values of τ_1, τ_2 (×10⁻¹⁴ sec), and S (K Å⁶) from the present measurements (see chapter four).

and 77 H₂. In the present low temperature work, the spectral invariants α_{1tr} and γ_{1tr} are obtained from eqns. 2.56 and 2.55 using the B-C translational band which best fits the measurements.

The spectral invariants of a B-C synthetic spectrum are directly related to the B-C lineshape parameters. For instance the area under the B-C translational-rotational spectrum, the spectral invariant α_1 , may be written in terms of τ_1 , τ_2 and S [14]. The spectral invariants of the translational band alone in terms of the B-C parameters are (not including double transitions):

$$\alpha_{1tr} = \left(\frac{2\pi^2}{3\hbar c}\right) \left(\frac{\beta\hbar/2}{\tau_1\tau_2}\right) \sum_J P(J)C(J,2,J;00)^2 S$$

$$\gamma_{1tr} = \frac{\pi^2\beta}{3c} \sum_J P(J)C(J,2,J;00)^2 S$$
(2.70)

and the ratio of the two invariants is

$$\frac{\alpha_{1\mathrm{tr}}}{\gamma_{1\mathrm{tr}}} = \frac{1}{\tau_1 \tau_2} \tag{2.71}$$

The close correspondence between the measured low temperature H₂ spectra and the fitted B-C synthetic spectra is demonstrated in chapter four. The B-C lineshape is used in the analysis of the measured spectra, and the variation of the spectral invariants and the parameters τ_1, τ_2 , and S with temperature is examined.

Chapter 3

Experimental Apparatus and Procedures

3.1 Introduction

The precise measurement of the translational band of hydrogen is difficult for several reasons. Firstly, collision-induced absorption by hydrogen is very weak, and the intensity of a light beam is diminished significantly only by passing it through a large amount of gas. This is accomplished by using either high density gas samples, or long absorption paths. Secondly, the translational band and the S(0) rotational line are quite broad, owing to the short duration of molecular collisions, and the two features are resolved only if the gas temperature is quite low. The observation of the H₂ dimer spectrum requires both low temperatures and low densities, otherwise the weakly bound pairs are broken apart by energetic and frequent collisions. In these experiments, even though the pathlength is over 52 meters and the temperature is below 40 K, the H₂ absorption is still weak and the measurement requires high experimental sensitivity and stability.

The configuration of the experiment is depicted in Figure 3.1. Infrared radiation emitted by a mercury arc lamp is modulated by a chopper. This light enters a dualinput dual-output Michelson interferometer, and is split into two beams by a Kapton beamsplitter. The reflected and transmitted beams propagate to either side of a moving mirror carriage and return to the beamsplitter where they recombine. The IR radiation is then focussed on to the interferometer output aperture. A He-Ne laser enters the second interferometer input, and propagates through the interferometer to the second output



Figure 3.1: A schematic diagram of the experimental apparatus. Modulated radiation passes through the interferometer and the multipass cell to the bolometric detector. The rectified detector signal, the interferogram, is digitized according to triggers generated by the laser interference fringes, and recorded on magnetic tape. The cell is cooled by circulating helium vapour through the heat exchanger tubing. Absorption spectra are obtained from ratios of sample spectra with respect to empty cell or He background spectra. where interference fringes are detected. The transfer optics relay the infrared beam from the interferometer to the multipass absorption cell. The infrared beam is brought to a focus at the field mirror edge and then it fills the opposing folding mirror; this continues back and forth up to a 60 m path. The light leaving the cell is focussed by the transfer optics on to a bolometric detector.

The cell is cooled by the continuous flow of a cryogenic liquid or gas through the heat exchanger tubing attached to the cell outer wall. The cold cell is surrounded by radiation shields and the assembly sits within a vacuum tank. The optical cell is filled and evacuated via the gas handling plumbing. Four vacuum pumps (not shown) are necessary for the evacuation of the interferometer and transfer optics, vacuum tank and cell, gas handling system, and the detector.

The chopped signal from the bolometer is rectified using a lock-in amplifier. The resulting signal, the interferogram, is sampled by a 16 bit A-D converter which is triggered by the zero-crossings of the laser fringes, and then recorded on magnetic tape. The interferograms are averaged and Fourier analysed on the UBC mainframe computer.

3.2 The Low Temperature Far-infrared Absorption Cell

The objective of this study is to observe weak absorptions at low pressures, low temperatures, and long wavelengths. Previous work on collision-induced absorption has utilized low temperature multipass cells [65], [56], but these cells have not been optimized for long wavelength studies, where diffraction losses must be kept to a minimum. The cell built for the present work is unique, in that it allows absorption to be measured over pathlengths from 4 to 60 m, at temperatures as low as 20 K, over a wavelength range from 0.5 mm to the visible. The cell optical design and a computer model of the cryogenic system have been discussed previously [66]. In the following sections the cell optical, mechanical, and thermal designs are reviewed.

3.2.1 The Cell Optical Design

A multipass mirror cell or 'White cell' consists of three spherical mirrors, a field mirror and two folding mirrors, all of the same radius of curvature [67]. The distance between the mirrors is set to the radius of curvature and the pathlength is adjusted by changing the angle between the folding mirrors. The advantage of an optical cell of this type is that radiation from a divergent source propagates efficiently over long paths. In the present cell, the Pyrex mirrors, made by Interoptics Ltd. of Ottawa, Ont., have a 1 m radius of curvature and are coated with gold on chromium. The field mirror is 20 cm wide, and 8 cm high; the folding mirrors are 'D' shaped and 10 cm wide.

A light beam is focussed at the field mirror edge such that the beam fills the opposing folding mirror. The folding mirror then forms an image of the input spot on the field mirror. Radiation successively diverges to the folding mirrors, and is focussed again on the field mirror, until it reaches the opposite edge of the field mirror and exits the cell. The optical path length L is

$$L = (2n+2)l (3.1)$$

where l is the distance between the mirrors, and n is the number of spots on the field mirror. Figure 3.3 shows the alignment laser spot pattern across the field mirror for a 12 m pathlength.

The cell has an f/10 optical system, a much 'faster' beam than other low temperature White cells reported in the literature. The large diameter optics minimize the diffraction of long wavelength radiation and allow the cell optical system to be efficiently matched to the f/5 exit cone of the interferometer. An image of the interferometer exit aperture, magnified by only a factor of 2, forms the input to the cell, and in so doing, many small
spots can be stacked across the field mirror.

Long wavelength radiation is diffracted by the effective aperture of the folding mirrors. The diffraction pattern caused by a circular aperture, at the focus of a converging spherical wavefront, is an Airy pattern [68]. The Airy radius to the first dark ring is $r = (1.22\lambda/D)R$, where R is the distance from the aperture, D is the aperture diameter, and λ the wavelength. The longest optical path is determined by the size of the diffraction spot and the number of spots which can fit across the 16.8 cm distance between the entrance and exit field mirror slots. The table below gives the diffraction spot size as estimated from the Airy disk diameter for a point source input, and the maximum pathlength attainable for different frequencies.

σ	λ	spot size	pathlength
20 cm^{-1}	0.5 mm	1.22 cm	56 m
30 cm^{-1}	0.33 mm	$0.85~\mathrm{cm}$	80 m

Table 3.1: The pathlength limits due to the diffraction spot diameter

The ultimate cell pathlength is limited by the optical aberrations of diffraction and astigmatism, both of which cause the broadening of spots on the field mirror. Visible light tests of these aberrations and infrared spot overlap tests are described in Appendix 1. In practice the maximum pathlength which can be obtained with virtually no overlap between neighbouring spots at the cell exit is 52 m and the overlap is tolerable for pathlengths up to 60 m. Background spectra obtained with a 24μ m thick Kapton beamsplitter demonstrate that the spectrometer-cell system transmits radiation down to ~ 15 cm⁻¹ (Figure 3.8). However, this beamsplitter has low efficiency at long wavelengths and an accurate measurement of the cell transmission below 20 cm⁻¹ requires a wire grid polarizing interferometer.

3.2.2 The Cell Mechanical Design

Figure 3.2 shows the cell, vacuum tank, and transfer optics in cross-section. The position of the field mirror F is fixed with respect to the cell end-flange lid by invar bars S. In this way the contraction of the cell body C with temperature does not affect the mirror spacing. The folding mirrors D are mounted on a complex set of hinged plates such that one mirror may be tilted with respect to the other, and this tilt is preserved as the mirrors fold symmetrically for pathlength adjustment. Figure 3.4 shows the folding mirror mechanism. The pathlength can be changed and the mirrors aligned while the cell is cold using the adjustment rods A. The cell is evacuated and filled via the pumping line P which is baffled to prevent room temperature radiation from entering the cell. Pyrex windows W in the cell mechanical end-flange lid, inner radiation shield, and vacuum tank lid, allow inspection of the laser alignment spots on the field mirror. The infrared beam enters the cell through windows or field lenses L which are positioned near the edge of the field mirror on extension tubes attached to the optical end-flange lid.

The cell body C is a stainless steel tube of 8.66" O.D., 8.35" I.D., length 46", and 35 liters volume. The cell exterior has been electroplated with copper (~0.030" thick) to insure good thermal conductivity. This copper coating is porous and to supplement it six copper strips, 0.020" thick and 1.750" wide, were soldered along the length of the cell. The heat exchanger tubing H is 50 ft. of 1/2" copper tubing soldered on to the cell body. This tubing runs the length of the cell, turns, and runs back upon itself, in nine helical turns. The temperature of the cell is monitored by five platinum resistance thermometers fixed to the cell outer wall in the positions numbered 1,2,3,4,5 (no. 3 only works at room temperature). Eighteen 2.2 K Ω 3 Watt resistors are fixed to the cell in three rings of six and these can be used to heat the cell if necessary. The cell emissivity is reduced by wrapping it with aluminized Mylar superinsulation. Figure 3.5 is a photograph of the





F, field mirror; D, folding mirrors; S, invar spacing bars; C, cell body; A, mirror adjustments; P, pumping line; W, viewing window; L, IR entrance and exit windows; 1,2,4,5, platinum resistance thermometers; H, heat exchanger; I and J, inner and outer radiation shields; K, Kevlar suspension rings; V cell vacuum tank; T, transfer optics vacuum tank; O, transfer optics; B, bolometer dewar.



Figure 3.3: The laser spot pattern on the field mirror for an optical path of 12 m.



Figure 3.4: The folding mirror mechanism. The design permits one mirror to be tilted with respect to the other and this tilt is preserved as the mirrors fold symmetrically for pathlength adjustment.

absorption cell with the heat exchanger tubing and copper strips.

The cell is cooled by the continuous flow of cryogenic liquids; helium, nitrogen, and argon have been used. The cryogen flows through a siphon, through the cell heat exchanger H, and then around an inner radiation shield I and an outer shield J. Each shield is made of polished copper and has one helix of copper tubing running along its length. Figure 3.6 shows the outer radiation shield. The entire assembly is suspended within the stainless steel vacuum tank V by Kevlar rings K which have $\sim 1/10$ the thermal conductivity of stainless steel for an equivalent tensile strength. The cell and shields are mounted to the Kevar rings by stainless steel clips.

The transfer optics vacuum tank T is isolated from the cell vacuum tank by polypropylene windows. Radiation is focussed into, and out of, the cell by mirrors O which are mounted on a plate fixed to the end-flange lid of the cell vacuum tank. Light from the cell is focussed by the output transfer optics into a detector dewar B placed on top of the transfer optics case.

3.2.3 The Cell Thermal Design

The Predicted Helium Consumption

A detailed computer model of the predicted thermal performance of the cell is described by Wishnow [66]; it is derived from a similar calculation by Gush used to estimate the helium consumption of the cooled rocket-borne spectrometer [36], [69]. The calculation is based on balancing the conductive and radiative heat inputs to each cell component with the heat extracted by the helium vapour coolant. The set of equations is solved numerically for the unknowns of the helium mass flow rate, and the temperatures of the inner and outer radiation shields, given a desired cell operating temperature.

The predicted liquid helium consumption ranges from 3 to 23 liters/day to maintain



Figure 3.5: The low temperature absorption cell. The cell is electroplated with copper and then the longitudinal copper strips and the helical heat exchanger tubing are soldered on to it. The temperature is sensed by 4 platinum resistors mounted on the cell exterior.



Figure 3.6: The outer radiation shield. The shield is made of polished copper and the heat exchanger tubing wraps around it.

the cell at 20 K. The prediction depends primarily on the assumed values of the cell and shield emissivities since their surface areas are quite large. Values of emissivities corresponding to the low consumption rate are: 0.015 for superinsulation surrounding the cell, 0.02 for polished copper shields, and 0.03 for the stainless steel vacuum tank [70]. The emissivities corresponding to the high consumption rate are 10 times the values listed above, and are considered worst possible cases.

The Cell Thermal Performance

In practice, a liquid helium flow rate of about 1.5 liters/hour maintains the cell at ~ 25 K. Cooling the cell down from liquid nitrogen temperature requires a flow rate of 3 to 4 l/hr and consumes 25-30 liters. The net consumption of helium during an experiment is much higher than 1.5 l/hr because the sample gas is admitted to the cell at room temperature and must be cooled. This generally requires a flow rate of ~ 4 l/hr and a wait of about 1-2 hr; the net helium consumption is about 3 l/hr. Overall, an experimental run of about 30 hr duration involving cooling the cell, obtaining background spectra, filling with the cell with the sample gas and cooling, and then maintaining low temperatures during the collection of sample spectra and final backgrounds, will consume just over 100 liters. The temperature uniformity and stability of the cell are discussed in the section on experimental procedures.

The helium flow of 1.5 l/hr to maintain the cell at 25 K, vaguely corresponds to the maximum predicted flow rate. This correspondence suggests that the emissivities of the cell components are very much worse than those described in the literature; it is not clear why this is the case. A possibility is that the superinsulation is not thermally well connected to the cell, and thus the cold cell wall is not the shiny aluminized surface, but the porous copper electroplated surface.

The predicted helium consumption may not be accurate since the thermal model of

the cell does not include all the heat sources encountered in practice. Among these are the conduction of heat to the cell by the sample gas which fills the cell pumping line. The optical end-flange lid is exposed to room temperature radiation via holes in the radiation shields which allow the infrared beam in and out of the mirror cell. Infrared filters for these holes have been omitted in order to transmit as much radiation as possible, and the alignment laser. Finally, the thermal conductivity of the Kevlar rings may have been underestimated since their resin content is unknown.

3.2.4 Temperature and Density Measurements

The temperature of the sample gas is sensed by four platinum resistance thermometers attached to the cell outer wall as indicated in Figure 3.2. The resistors are type KGC-0108 from Omega Engineering, $\alpha = (R_{373}/R_{273} - 1)/100 = 0.003925$, and they have a nominal resistance of 100 Ω at 0° C. This type of resistor is low cost (~\$10) and has a larger α (and thus higher purity) than industrial platinum resistors, where $\alpha = 0.00385$. The higher purity allows resistance ratios measured with these resistors to be compared to tabulated ratios obtained from precision platinum resistors. Resistance is measured using a four-wire, low power, AC auto resistance bridge.

The thermometer calibration utilizes the consistency of the ratio of resistance differences with temperature, known as Cragoe's Z function. For a given element, the quantity

$$Z = \frac{R_T - R_{T_0}}{R_{T_1} - R_{T_0}},\tag{3.2}$$

is the same for all resistors, where R_T is the resistance at a temperature T, and R_{T_0} and R_{T_1} are the resistances at two calibration temperatures [70]. The assumption underlying the Z function is that all platinum resistors share the same dependence of resistance on temperature and differences between resistors are due to impurities which do not vary

with temperature. Calibration of these resistors requires measuring their resistances at 273.15 and 4.222 K. The temperature associated with a given resistance is then obtained by referring to a table of Z as a function of temperature for calibrated precision platinum resistors [71].

The absolute accuracy of the temperature reading using the platinum resistors and the Z function is better than 0.2 K over the entire temperature range 14 to 373 K; over the range 14 to 40 K the accuracy is better than 0.1 K. The accuracy of the resistance temperature readings was obtained by comparing them against 21 temperatures determined using the following thermometric standards: the triple point and vapour pressure of normal hydrogen (13.956-20 K), the vapour pressure of oxygen (58-90 K), the ice point (273.15 K), and boiling water (373.15 K).

The platinum resistors sense the temperature on the outside of the cell and not the actual temperature of the gas within. The determination of the gas temperature is made by a simple average of the four resistance temperatures, where two resistors are located on the cell body (no.'s 2 and 4) and one on each lid (no.'s 1 and 5). In practice, the average resistance is found and then the temperature is determined; any error related to averaging resistance rather than temperature is less than 0.1 K. The cell temperature is not exact since there is a temperature gradient across the cell and the temperature drifts in time during data collection.

The sample gas pressure is measured using an Ashcroft K-3 strain gauge pressure transducer. According to the manufacturer's specifications it has a accuracy of 0.2% of the full scale reading of 10 Volts at 60 psi. The sensitivity of the gauge is 310.3 Torr/Volt, and thus the accuracy in the pressure reading is 6.2 Torr, or $\sim 0.5\%$ at pressures used in these experiments. This gauge suffered from instabilities in both the zero offset and sensitivity, and it has been discontinued by the manufacturer. Once the instabilities were recognized, the gauge readings at vacuum and atmospheric pressure were checked

prior to each day of data collection. In general the gauge has an error roughly twice that specified, although a few cases of larger sensitivity changes may have occurred. The gauge is mounted at the room temperature end of the cell pumping line.

During data collection the cell temperature and gas pressure are recorded every 10– 15 minutes and these readings are converted to densities using the following procedure. The volume occupied by 1 mole of a pure sample gas (not a gas mixture) in thermal equilibrium is obtained from

$$\frac{P}{RT} = \frac{1}{V} + \frac{B(T)}{V^2} + \frac{C(T)}{V^3} + \dots$$
(3.3)

where P is the pressure reading in atm., R is the gas constant (82.056 cm³ atm./mole K), T is the temperature reading in K, V is the volume in cm³/mole, and B and C are the 2nd and 3rd virial coefficients. The density of the gas in amagat units is a ratio of the gas density to that of an ideal gas at NTP and is given by

$$\rho = \frac{V_0}{V} \tag{3.4}$$

where $V_0 = 22413.6 \text{ cm}^3/\text{mole}$. The hydrogen sample gas density is obtained using only the 2nd order virial coefficients obtained from tables [72]. The error in density from using 2nd rather than 3rd order coefficients at a density of 16.0 Am. at 25 K is 0.02 Am.; at 35 K it is 0.01 Am. If the ideal gas law is used to find the hydrogen density, the result is 1.3 Am. too low at 25 K, and 0.5 Am. too low at 35 K.

During an experiment the cell is filled with a hydrogen sample and sealed. The temperature, and consequently the pressure, is varied to obtain different conditions, but the gas density remains constant provided the gas is not liquified. The densities obtained from temperature and pressure measurements of a sealed H_2 sample over the range 23-38 K have a maximum variation of 2%, and a standard deviation of 1%.

3.3 The Interferometer

3.3.1 The Optical System

The principles of Fourier transform spectroscopy have been widely reported, and interferometer design and data analysis procedures are discussed in Bosomworth and Gush [73]. The optical design of the present interferometer has been reported by Buijs and Gush [74], and its application to absorption spectroscopy has also been described [75]. Figure 3.7 is a schematic diagram of the interferometer optical path. The interferometer is a high throughput $(A\Omega \sim 1.6 \times 10^{-3} \text{ cm}^2 \text{ str.})$, dual-input dual-output, Michelson interferometer with a folded optical path such that a mechanical motion of 25 cm produces a 1 m optical delay. Novel features of the optical system include: two dimensional corner reflectors on the moving mirror carriage, and a laser which is co-aligned with the infrared beam for accurate measurement of the interferometer path difference. The corner reflectors reduce optical alignment and delay errors due to mirror rotations as the carriage moves, and long pathlength differences can be achieved without dynamic alignment techniques. A Spectra Physics 116A single mode He-Ne laser propagates through the interferometer and the laser interference fringes, detected by a PIN photodiode, trigger the sampling of the interferogram.

The inset of Figure 3.7 shows the configuration of the beamsplitter assembly in which the glass laser beamsplitter is suspended by a three-legged spider mount over a hole cut in the center of the infrared pellicle beamsplitter. The two beamsplitters are made parallel by the use of an autocollimator. Alternatively, an alignment laser is reflected off the Kapton beamsplitter and the assembly is translated to reflect the laser off the glass beamsplitter. The glass beamsplitter is then adjusted so that the laser spot on a distant screen does not move when the assembly is translated.



Figure 3.7: The optical path of the Michelson interferometer [75]. S, source; B, beamsplitter; M, moving mirror carriage; D, detector. Alternate source and detector postions: \hat{S} and \hat{D} . The center of B is a glass beamsplitter for the laser which monitors the path difference. The inset shows the configuration of the beamsplitter assembly.

3.3.2 Interferometer Scanning and the Infrared Source

The moving mirror carriage is driven continuously by a Teflon nut riding on a precision threaded rod which is turned by a PMI DC motor. The performance of the driving system is not exactly the same for forward and reverse directions, and the interferograms analyzed are all forward direction scans. The interferometer is set up to obtain path length differences of -4 to +103 cm, but only symmetric interferograms of path difference ± 2.3 cm are acquired for the hydrogen spectra.

The interferometer scanning is controlled by issuing ASCII commands to a Z80 microprocessor system built by the physics department electronics shop. The experiments were conducted using a mirror scan speed which produced 570 Hz laser fringes or a mechanical carriage motion of 9.02×10^{-3} cm/sec. Further comments on the choice of scan speed are found in the procedures section. The far-infrared source for the absorption measurements is a Phillips HPK-125W high pressure mercury arc lamp operated at a constant DC current of about 0.85 A. The arc lamp has proven to be very stable, and over the range 20-100 cm⁻¹ it radiates 2-4 times more power than an approximately 1100 K (dull orange glow) blackbody oven source used in initial experiments. Over the range 120-180 cm⁻¹ the arc lamp intensity is about 1.25 times that of the blackbody source.

3.3.3 Beamsplitters and Filters

The spectrum of hydrogen has been measured over more than a decade in frequency using two spectral bands. The table below lists the frequency range, beamsplitter thickness, and the cold low-pass filters for the low frequency (LF) and high frequency (HF) spectral regions. In order to maximize the signal during the LF experiments the interferometer output aperture is a slit, $3 \ge 7$ mm. The HF experiments use a 3 mm diameter circular output aperture.

Region	$freq.(cm^{-1})$	beamsplitter	low-pass filter
	20 - 100	$24 \ \mu m \ Kapton$	2 mm thick wedged Teflon
LF			0.13 mm black polyethylene
	125 – 180	24 μ m Kapton	(same as above)
		(2nd order)	
			IR labs 1 mm crystal quartz wedged
HF	50 - 320	8 μ m Kapton	with 5/10 μ m diamond powder
			0.13 mm black polyethylene

Table 3.2: The beamsplitters and low-pass filters used for the LF and HF measurements.

Figure 3.8 displays empty cell background spectra obtained at 35 K which are representative of the two frequency regions. Features of note in the low frequency spectrum are: the peak of the beamsplitter efficiency at 55 cm⁻¹, the beamsplitter null at 110



Figure 3.8: Examples of LF and HF background spectra obtained at 35 K The heavy curve is a LF background and the light curve is a HF background. The null of the LF beamsplitter efficiency is at 110 cm⁻¹. Teflon absorption bands occur near 45 and 55 cm⁻¹ and the cutoff is at 190 cm⁻¹. In the HF spectra, crystal quartz absorption bands occur at 133 and 260-270 cm⁻¹ and the cutoff is at 350 cm⁻¹. 'Channel' spectra with a \sim 70 cm⁻¹ period are due to polypropylene windows.

cm⁻¹, the Teflon absorption lines near 45 and 55 cm⁻¹ and the cutoff at 190 cm⁻¹. The high frequency spectrum shows the peak of the beamsplitter efficiency at ~165 cm⁻¹, the absorption bands of crystal quartz at 133 and 260–270 cm⁻¹, and the quartz cutoff at 350 cm^{-1} . 'Channel spectra' are observed in both backgrounds with a ~70 cm⁻¹ period, where this is due to six polypropylene windows, each 0.002" thick, in the spectrometer-cell optical path.

Quartz has a lower cutoff frequency than sapphire ($\sim 370 \text{cm}^{-1}$) and it was used as the low-pass filter in order to restrict the spectra to the translational band only. During the course of the experiments, it was observed that the sensitivity of the absorption measurements was limited by the maximum absorption; therefore, eliminating the S(0) line improved the signal-to-noise of absorption over the much weaker translational spectrum.

3.4 Transfer Optics and Windows

The interferometer, including the source and chopper, is enclosed by a large vacuum tank which is evacuated to a pressure of 0.15 Torr by a Stokes mechanical pump. Although this is not a particularly low pressure, it is stable and water vapour lines cancel consistently. The interferometer tank twists slightly with respect to the optical cell when it is evacuated, but a motorized mirror mount within the tank can be adjusted to compensate for this motion.

The transfer optics couple the f/5 interferometer output beam to the f/10 mirror cell optics, and the mirror cell output to the f/5.5 detector input. The transfer optics, excluding elements in the interferometer tank, are mounted on a plate fixed to the cold cell vacuum tank lid which is contained within an independent vacuum chamber.

The vacuum chambers of the interferometer, transfer optics, cold cell, and detector dewar are all separated by polypropylene windows. The advantage of isolated vacuum systems is that the detector can be dismounted for helium transfer, and repairs or alterations of the interferometer can take place while the cell is cold. The disadvantage of this system is the strong channel spectra present in Figure 3.8.

Polypropylene is a good window material since it has a low index of refraction of 1.48, and a piece 0.002" thick is better than 90% transmissive over the frequency range $0-500 \text{ cm}^{-1}$. Polypropylene is less reflective and absorptive than an equivalent sheet of Mylar. The pressure at which a 1.75" diameter window 0.002" thick bursts has been measured to be ~100 psi, and the bursting pressure has been observed to be roughly inversely proportional to the window area. The largest window, 2.4" in diameter, safely supports atmospheric pressure, and the absorption cell windows 0.875" in diameter are estimated to burst at 400 psi. (this has *not* been measured). The strength of the material rises when cold, and the cell windows may support even larger pressures.

At room temperature, helium diffuses through polypropylene making leak detection difficult, but at liquid nitrogen temperatures the windows are virtually impermeable. Hydrogen does not diffuse rapidly enough through these windows to show a measureable decrease in the sample cell pressure.

3.5 Electronics and Data Acquisition

The detector is a germanium bolometer, serial number 777, made by Infrared Laboratories. The detector operates at roughly 1.6 K by pumping on the helium reservoir. The sensitivity of this detector is measured to be approximately 5×10^5 Volts/Watt, operating with a 4 Volt bias. The sensitivity is obtained from bench top measurements of the detector response to a Barnes blackbody source operating at 600° C. The detector preamplifier has a gain of 1000 leading to an overall sensitivity of 5×10^8 V/W. The noise of the detector-preamp system measured at 104 Hz by an HP audio spectrum analyzer is about 48 μ V/ $\sqrt{\text{Hz}}$, leading to an N.E.P. of 9.6 × 10⁻¹⁴ W/ $\sqrt{\text{Hz}}$, where IR labs quotes a value of 9.1 × 10⁻¹⁴ W/ $\sqrt{\text{Hz}}$. The system spectral noise density and sensitivity diminish with frequency due to the detector time constant, and at 162 Hz the noise is about 30–40 μ V/ $\sqrt{\text{Hz}}$. The detector linearity has been examined and is discussed in the chapter six.

During an experiment a typical detector signal is a 162 Hz rounded triangle wave of 2.5 to 5 V peak-to-peak amplitude. This signal passes through a voltage divider of gain 0.198 to an Ithaco 391A lock-in amplifier with a filter time constant set at 4 msec. The lock-in output is filtered by a Stanford Research Systems low-pass amplifier with an adjustable cutoff which was set at 13.5 Hz and 20 Hz, for the LF and HF experiments respectively. The amplifier is AC coupled and is set to a gain of 10 dB yielding an interferogram signal of 4 to 8 V when the interferometer path difference is zero (zpd), and 0 V far from zpd.

The interferogram signal is sampled by a 16 bit A-D converter-computer system with an input range of ± 10 Volts, and a data rate up to 1000 Hz. The A-D has a digitizing noise of 1.3 bits at a sampling rate of 285 Hz; this corresponds to a spectral noise density of about 23 μ V/ $\sqrt{\text{Hz}}$, or about 1/2 to 3/4 of the detector noise. This A-D converter is under the control of the PDP Micro-11 computer (the A-D converter in the Z80 interferometer controller has not been used since pickup from the Z80 clock causes even worse digitizing noise). The interferogram is sampled at constant pathlength difference via A-D triggers generated by the zero-crossings of the He-Ne laser fringes. In these experiments every two fringes produces a trigger pulse, and the 'folding' frequency is therefore $1/(2 \times 2 \times 632.9 \text{nm}) = 3950 \text{ cm}^{-1}$.

The digitized detector signal is read, and written to tape, via a high speed interrupt driven assembly language program running on the PDP Micro-11 computer. The program searches for the interferogram maximum and scans symmetrically forwards and backwards across it. Asymmetric interferograms consisting of forward scans starting at the scan reversing switch and extending some specified length may also be acquired.

The interferograms are read from the tape on to the UBC mainframe computer and they are averaged by aligning the maximum point of of each interferogram. Forward and reverse scans are averaged separately and the interferograms are not interpolated to find the true zpd. The failure to interpolate prior to interferogram averaging has no effect on the spectrum for frequencies below 200 cm⁻¹, and produces an error less than 1% for frequencies less than 300 cm⁻¹. Symmetric interferograms consisting of 32768 points acquired in the forward scanning direction are Fourier transformed and power spectra are obtained, where the value of the power spectrum at a frequency sigma is

$$P(\sigma) = (cosine \ coeff.(\sigma)^2 + sine \ coeff.(\sigma)^2)^{1/2}$$
(3.5)

The optical path length difference of the interferogram corresponds to a resolution limit of 0.241 cm⁻¹ and the interferograms are not apodized since the broad features of the hydrogen spectrum are well resolved.

3.6 Gas Handling Equipment

Sample gas cylinders are attached to a manifold and gases are flowed through a container of 300 gms. of Union Carbide molecular sieve 5A. The hydrogen sample gas and helium background gas are both UHP grade, 99.999% pure, supplied by Linde. The only significant impurity in the spectral regions studied is H_2O which is present in these gases at a concentration under 5 ppm. In the case of hydrogen, the sieve is placed in an ice bath so that ortho-para conversion does not take place, otherwise the sieve may be cooled in a liquid nitrogen bath. The gas is further dried by passing it through a coil of copper tubing immersed in liquid N_2 . In order to prevent pump oils from entering the cell, the gas passes through a final stainless steel cold trap which is located at the entrance of the cell pumping line.

Observation of water ice absorption at 230 cm⁻¹ demonstrates that the gas drying procedures are inadequate (see chapter six). In fact, the efficiency of molecular sieves depends on the H₂O vapour pressure and for these very pure gases the sieve is inactive. Completely pure hydrogen for future experiments can be obtained by passing the gas through a palladium diffusion filter, but this will not work for other gases. A better water vapour trap using phosphorus pentoxide or a large surface area liquid nitrogen trap is desirable. Despite the fact that gases pass through a number of cold traps, they warm to nearly room temperature before entering the cell. Modifying this system to precool gases to liquid N₂ temperature before they are admitted to the cell would save both time and liquid helium.

3.7 Experimental Procedures

The quality of the results obtained using the spectrometer-cell apparatus depends upon procedures adopted during the experiments. Methods of transfering cryogenic liquids have been developed which minimize audio noise in the interferograms due to vibrations and turbulence. In addition, the source chopping rate and mirror scanning speed have been chosen to move the audio frequencies in the interferogram away from audio noise sources. Another procedural issue is the realignment of the cell optical path between background and sample spectra.

3.8 Liquid Nitrogen and Argon Transfers

The cell is precooled (or operated at 78 K) using liquid N₂ siphoned from a 250 liter storage dewar. The transfer is controlled by pressurizing the dewar with an external

cylinder of helium or by adjusting the dewar relief valve overpressure. Liquid is initially transferred at about 2.5 psi. pressure, and once nitrogen temperature is reached the transfer pressure is reduced. The minimum transfer pressure for liquid N₂ is about 1.5–2.0 psi, and for liquid Ar it is 3.0-3.5 psi, since its density is much greater than liquid N₂. In the cases of liquid N₂ and Ar coolants, liquid circulates through the cell heat exchanger and boils in the tubing causing vibrations. These vibrations can cause audio frequency variations in the transmitted light intensity.

3.9 Liquid Helium Transfers

Helium circulates through the heat exchanger as a cold vapour and boiling is not a source of vibration. In general, background spectra at ~ 30 K are quieter than those at 78 or 88 K. However, maintaining a stable flow rate using liquid helium is somewhat difficult. An oscillation with a ~ 20 sec. period appeared in the interferogram and it was coincident with pressure fluctations at the heat exchanger outlet. Apparently, liquid helium from the storage dewar enters the heat exchanger and rapidly boils, since the cell is ~ 30 K. The boiling generates a local high pressure region which temporarily blocks the liquid transfer. The transfer resumes after the pressure blockage dissipates. These oscillations have been corrected by insuring that the highest flow impedance is in the liquid transfer line and not in the heat exchanger. A syringe needle has been put at the bottom of the transfer siphon, in the liquid helium, and this restricts the liquid flow rate.

3.10 Temperature Gradients and Turbulence

Once the periodic flow fluctations are eliminated, subtle effects of cell temperature nonuniformity appear. Despite the fact that the heat exchanger is a helix which turns back upon itself, and that the cell is electroplated with copper, the point where helium first contacts the cell is the coldest region. A steady helium flow, necessary to maintain low temperatures, produces a ~ 2 K temperature gradient across the cell. The temperature gradient causes an ambiguity in measuring the gas temperature, and drives convection within the sample gas. The gas convection causes slow optical signal variations, mostly below 0.5 Hz, where these variations are presumeably due to bulk gas motions. The dominant problem caused by the gas turbulence is the inability to align precisely the cell optics and maximize the detector signal.

Two schemes have been developed to reduce the cell temperature gradient. The first solution is to stop the helium flow during data collection (drift technique). The cold spot warms up, in fact it now becomes the warmest point, and the temperature gradient is greatly reduced. The turbulent noise in the signal is virtually eliminated; however, the overall cell temperature rises during the $\sim 1/2$ hour data collection period. The second solution is to vapourize the liquid helium before it enters the heat exchanger and thereby eliminate localized cooling due to evaporating the liquid. An insert to the transfer siphon has been built which contains a heated copper mesh to vapourize the liquid followed by a platinum resistor to sense the vapour temperature. The vapour flow rate is set by the helium dewar overpressure, and the heater power determines the vapour temperature. The device permits steady helium transfers and stable cell operating temperatures, but it does not eliminate turbulence.

Using the drift technique at about 25 K results in a maximum temperature gradient of 0.75 K across the cell, but the cell rises 2.3 K in 30 min; at 35 K the temperature rises 1 K in 30 min. The helium vapourizer technique results in a temperature gradient of about 1.8 K where the average temperature drift is kept below 0.5 K in 30 min. At temperatures below 25 K, the minimum temperature gradient obtained using the vapourizer is 1.3 K, where it is tuned so that the temperature rises about 0.8 K in 30 min. It is apparent that

the thermal conductivity of the cell is too low to allow a stable operating temperature without a thermal gradient.

3.11 Interferometer Scanning and Chopping Rates

The interferometer scanning speed and chopping rate are chosen to avoid including the audio frequencies of vibration and turbulence in the interferogram signal. The interferometer system employs a chopper and lock-in detection technique, rather than a rapid scan technique, in order to accurately define the infinite absorption level. An advantage of this system is that the frequency of detection may be raised well above low frequency vibrations. Room and pump vibrations occur below about 30 Hz, and resonances of the optical system and detector microphonics occur at higher frequencies. 162 Hz was chosen as the chopping frequency since this region is consistently free of electrical interference and transfer related noise.

Once the chopping frequency is established, the scan speed of of the interferometer is chosen to place the audio frequencies of interest in the interferogram away from audio noise sources. In general, higher scanning speeds are desirable since this allows the collection of many interferograms in a given measurement time, and turbulent noise can be reduced by averaging. The scan speed setting ('10.0 slow') corresponds to a He-Ne laser fringe rate of 570 Hz, where the optical path length difference varies at a speed of 570 Hz/15800 cm⁻¹=0.036 cm/sec. At this scan speed 20 cm⁻¹ occurs in the interferogram at 0.72 Hz, higher in frequency than most of the gas turbulence which occurs from 0.05 to 0.5 Hz; 350 cm⁻¹ corresponds to an audio frequency of 12.6 Hz, and this is free from electrical interference at 180 Hz. The time constant of the lock-in amplifier is set at 4 ms. and the low pass filter is set at 20 Hz so that the highest audio frequencies associated with 350 cm⁻¹ are not attenuated by the electronics.

3.12 Optical Alignment and Turbulence

Pressurizing the cell with the sample gas results in a small shift of the spots on the field mirror and optical realignment is required. If ignored, the shift is large enough to move from one exit spot to another when long paths are used. After the cell is filled, the correct path length must be found and the signal maximum obtained. The cell path length is reduced until 15 spots are counted visually across the field mirror, and then the folding mirrors are adjusted by finding successive signal maxima until the correct path is found. Long period turbulence in the gas makes finding the exact position of the signal maximum difficult, and this causes an error in the absorption measurement. In addition, the location of the spots on the field mirror for sample spectra may not be exactly that of the backgrounds, again causing an absorption error.

3.13 Cell Improvements Recommended for the Future

3.13.1 Mirror Adjustments

The screws which adjust one folding mirror with respect to the other are too coarse (1/4-20) and this contributes to optical alignment difficulties. This design error permits a slight movement in the folding mirror's relative positions as the folding angle is changed and these adjustments should be replaced by screws with fine threads.

If the folding movement was highly reproducible, a new measurement technique could be implemented. Short path measurements, with the absorption cell filled, could serve as backgrounds for long path measurements of the sample spectra, and the absorption coefficient can be obtained from the ratio of these spectra. The time between taking backgrounds, filling the cell, and taking sample spectra would be greatly reduced. This pathlength altering technique reduces errors due to experimental drifts with time, eliminates error associated with cell pressure changes such as window shape or water ice reflectivity, and allows data to be collected more efficiently during a measurement run. However, new systematic problems arise since it is now necessary to precisely measure the transmission of the cell as a function of pathlength (Note that the transmission will vary with temperature and depend on the amount of ice coating the mirrors).

3.13.2 Reduction of Turbulence

Turbulence within the gas cell can make obtaining precise absorption measurements difficult. The following proposals raise the cell thermal conductivity and thereby reduce the cell thermal gradient, the driving source of the gas turbulence.

The cell thermal conductivity would be improved by applying a thicker copper coating to the cell exterior, either by a plasma spray technique, or by more electroplating. The simplest proposal is to drive a copper sleeve of about 0.030" wall thickness into the cell interior. This sleeve will certainly improve the conductivity along the cell, but it will not help in cooling the end-flange lids. Alternatively, a thermally floating shield, a copper tube with end caps which encloses the optical path and the mirrors, could be suspended from the invar bars in the cell. This shield, with holes for light to enter and exit the mirror cavity and for the viewing port, would not be in contact with the cell walls, and would reach some average temperature of the sample gas. The temperature gradients within the shield would certainly be less than the temperature gradient of the cell outer walls. The sample gas temperature should be measured within the shield, as the present resistors mounted on the exterior of the cell may not indicate the correct temperature. Finally, the cell body could be remade out of a copper tube designed to fit the present end-flange lids. It is not certain, however, that the present indium vacuum seals would work, even though copper and stainless steel have similar thermal expansion coefficients.

3.14 Ortho-Para Measurements

A cold gas composed entirely of H_2 molecules in the J = 0 rotational state exhibits no translational absorption spectrum. A H_2 molecule in the J = 0 state is spherically symmetric, that is, the expectation value of any particular orientation of the molecular axis is zero [76]. Therefore, there is no external electric field due to the molecule, and no quadrupolar induced dipole moment during binary collisions (even though the J = 0matrix element of the quadrupole moment in the molecule fixed frame is non-zero). Likewise, the anisotropic overlap induced dipole is zero since it also depends on the colliding molecule's orientations. The present low temperature experiments have used 'normal' hydrogen, with an ortho-para ratio of 0.7492:0.2508, so that a relatively strong translational absorption spectrum is observed. Ortho-to-para conversion of the H₂ sample may take place via adsorption on the cold cell walls or by passing the gas through the cold traps. In order to understand if conversion has taken place, samples of H₂ gas are taken during the absorption measurements and their ortho-para ratio is tested.

A resistance bridge built by Dr. Walter Hardy compares the ortho-para ratio of a sample gas to that of normal hydrogen [77]. The apparatus consists of two glass bulb pirani vacuum gauges which form two arms of a DC resistance bridge and are immersed in liquid N₂. The method utilizes the difference in the specific heat at constant volume between para and ortho H₂ at 77 K ($\frac{C_V para}{C_V ortho} = \frac{0.52}{0.008}$ in units cal deg⁻¹ mole⁻¹), and hence, the higher thermal conductivity of para with respect to ortho H₂ [78]. A fixed current of 650 mA passes through both pirani gauges, and the bridge current is nulled when both the sample and reference bulbs contain normal H₂ at 40 Torr. The sample bulb is then evacuated and refilled to the same pressure with the H₂ sample to be tested. If the sample is pure para H₂, a bridge current offset results. This is because the para gas conducts heat from the pirani filament better than the normal gas, and as a result,

the filament is colder and its resistance is lower than the normal reference gauge. The bridge current offset is nearly linearly proportional to the sample para concentration and it is calibrated by the above comparisons of normal to normal, and para to normal, H_2 . Excluding cases of extreme errors due to leaks into the sample gas flasks, all samples taken from the absorption cell retained the normal ortho-para ratio to within the 1% precision of this apparatus.

The normal hydrogen reference sample is taken from the same gas cylinder as the H_2 used in the absorption spectra. The ortho-para apparatus also has a built-in UHP hydrogen reference cylinder, but measurements conducted using this gas produced a consistent current offset when compared to two other UHP hydrogen samples. In both cases the offset corresponds to an ortho-para ratio of 0.69:0.31, and the built-in reference cylinder is believed to be contaminated.

Chapter 4

The Translational Absorption Band of Hydrogen

4.1 Introduction

The collision-induced translational absorption band of hydrogen has been measured over the temperature range 21 to 38 K, and the pressure range 0.6 to 3 atmospheres, using an optical path of 52 and 60 meters. H₂ spectra are obtained over the wavenumber range 20 to 320 cm⁻¹ with considerably higher resolution (0.24 cm^{-1}) and sensitivity than previous studies. The new low temperature and low pressure experimental conditions allow the pure translational band to be observed virtually isolated from the H₂ rotational lines. Previous studies using 1–3 meter light pipes have been limited to temperatures above 77 K, resolutions greater than 2 cm⁻¹, and have required densities of over 100 amagat to observe any appreciable absorption in the translational band [8],[12],[13],[14]. The present low pressure, high resolution measurements permit details of the submillimeter spectrum of H₂ to be examined for the first time. In addition, the low pressure, low temperature experimental conditions employed in the present study are close to those found in planetary atmospheres.

The analysis of the measured hydrogen spectra is presented in this chapter. The general features of the spectra, and the variation of the best fit B-C lineshape parameters, are examined as a function of the temperature. The experimental conditions of a low temperature, low density gas allow the formation of H_2 bound pairs, and the search for dimer transitions in the translational band is presented. Average spectra which combine

data from the low and high frequency spectral regions are obtained at temperatures of 25.5 and 36 K, and the spectral invariants of these 'composite' spectra are compared to previous measurements and theoretical calculations.

4.1.1 On the Discrepancy Between the LF and HF Spectral Regions

The measurements of the hydrogen spectrum extend from 20 to 320 cm⁻¹, a factor of 16 in frequency. This frequency range is too great to be covered with a high signal-to-noise ratio by a single interferogram, because of the limited dynamic range of the bolometer detector. For this reason the spectrum was split into a low frequency (LF) region, 20–180 cm⁻¹, and a high frequency (HF) region, 50–320 cm⁻¹; the beamsplitters and filters for these spectral regions are given in Table 3.2. Since a special effort was made to find evidence for dimers, most observing time was spent on the low frequency region, and a total of 4 independent LF experimental runs were undertaken. As a result considerable data exists on which to form an estimate of the reproducibility of the spectra. The HF region was studied during only one experimental run, and the cell was kept cold continuously for 30 days as different gas densities and temperatures were investigated.

Upon subsequent analysis of the results, a discrepancy of $\sim 10\%$ between the intensities of the LF and HF absorption spectra has been observed in the region of overlap; this discrepancy is larger than the errors of internal consistency within the two sets of measurements. It has not yet been possible to explain definitively this discrepancy, and the HF experiments could not be repeated because of the substantial cost. In the region of overlap the shapes of the two spectra are nearly the same, and an intensity mismatch of this kind might result from errors such as: incorrectly counting the number of passes in the cell, or a departure from a 'normal' ortho-para ratio of the HF gas sample. These explanations, however, conflict with the written records made during the experiments.

In the following analyses, the greatest weight is given to the low frequency data

which is regarded as the most reliable. The effect of the higher frequency data on, for example, the fitted line shape parameters turns out to be small, and despite this troubling discrepancy, the derived physical data is valid.

4.2 General Remarks on the Absorption Spectra

4.2.1 The Spectral Band and Interferogram Averaging

The LF spectra cover the H₂ translational spectrum from the half-maximum on the low frequency side of the peak to the half-maximum on the high frequency wing of the band. The HF spectra cover the spectrum from roughly the peak of the translational band to the low frequency wing of the S(0) rotational line. Examples of LF and HF absorption spectra are shown in Figures 4.12-4.17; examples of LF and HF absorption spectra prior to dividing by $\rho^2 l$ are shown in Figures 5.1 and 7.2, respectively; and the LF and HF background spectra are shown in Figure 3.8.

The temperature dependence of the translational band of normal H_2 is examined using 28 LF spectra obtained over the temperature range 22-38 K, and the density range 7.65 to 23.28 amagat. These studies are depicted in Figures 4.3-4.9. Low temperature LF spectra are also examined for evidence of spectral structure due to H_2 dimers. The LF spectra were concentrated around 25 and 35 K, and HF spectra were subsequently obtained near these temperatures in order to obtain complete spectral coverage over the translational band. The composite average spectra, composed of both LF and HF spectra, are shown in Figures 4.12-4.17. The composite average spectra are used in the comparison of the present results to previous experiments and the calculated integrated absorption coefficient, Figures 4.19-4.21.

Power spectra are obtained from the Fourier transformation of averaged symmetric interferograms according to the procedures described in chapter three. In general, each 'individual' spectrum is derived from 4-6 sample interferograms and 6-8 background interferograms. The interferograms are acquired in the interferometer forward scanning direction. The duration of an interferogram is 2.5 minutes, and the time required to collect the set is about 20-30 minutes.

Absorption spectra per unit density squared, per unit pathlength are given by

$$A(\sigma) = \frac{1}{\rho^2 l} \left(-\ln\left(\frac{I_s(\sigma)}{I_b(\sigma)}\right) \right)$$
(4.1)

where ρ is the sample gas density in amagat, and l the pathlength. I_s is the sample spectrum, and I_b is the background spectrum, an average of empty cell spectra taken before and after the sample data.

4.2.2 Temperature, Density, and Spectral Accuracy

The measurement of the sample gas temperature and density is discussed in chapter three. In brief, the cell temperature measurements vary by less than ± 1 K due to either thermal gradients along the cell, or drifts in temperature during the data collection period. The average temperature reported for a given spectrum is estimated to be accurate within ± 0.25 K, and the relative temperatures of the various spectra are stated to a precision of 0.05 K. The gas pressure is measured to an accuracy of about 1%, and the absolute density is estimated to have an uncertainty of $\pm 1\%$.

The accuracy of the absorption spectra is limited primarily by long term experimental drifts and an intensity mismatch between the LF and HF spectral regions. Within each spectral region, the uncertainty of the H₂ translational absorption band measurements is estimated to be $\pm 2\%$ of the peak absorption from 40–90 cm⁻¹, $\pm 3\%$ across the LF region, and $\pm 5\%$ across the HF region. The H₂ spectra are free of water vapour lines, although water ice contamination is observed above 200 cm⁻¹. The issue of spectral accuracy is covered more fully in chapter six.

4.2.3 Typical Spectral Features

Typical LF absorption spectra are presented in Figures 4.1 and 4.2, where the broad collision-induced translational band is the dominant spectral feature, and contributions from the S(0) line are negligible. The solid curve is the measured spectrum and the dashed curve is the best fit B-C synthetic spectrum. The filename; density (in amagat), temperature; B-C lineshape parameters τ_1, τ_2 (×10⁻¹⁴ sec) and S (in K Å⁶); and spectral invariants α_{1tr} (cm⁵ sec⁻¹) and γ_{1tr} (cm⁵ sec) are given sequentially on the graph.

The LF absorption spectra often droop below a B-C spectrum over the frequency region 90-130 cm⁻¹. This aberrant shape occurs at frequencies near the LF beamsplitter null, and an anomalously low absorption is also seen in the HF spectra below 65 cm⁻¹. The aberrations occur in frequency regions where the background spectra have low intensity (see Figure 3.8), and they are partially caused by a residual baseline intensity which underlies the spectra. The subtraction of the residual baseline is discussed in the section on the composite average spectra.

Small distortions of the smooth bandshape near 45 and 55 cm^{-1} are related to the inexact cancellation of steep regions in the sample and background spectra due to the absorption bands of the teflon cold filter. The topic of spectral distortions is discussed further in the dimers section.

The sharp spike superposed on the translational band at 89.2 cm⁻¹ is the R(0) line of HD which is present in the hydrogen gas sample as a naturally occurring isotopic 'impurity'. The analysis of the HD line is discussed in the following chapter.

4.3 The Temperature Dependence of the H₂ Spectrum

The set of LF absorption spectra illustrates the detailed temperature dependence of the H_2 translational band for the first time. In previous higher temperature spectra, the



Figure 4.1: An example of a LF absorption spectrum of H₂ at 34.4 K. In this and the following figure, the solid curve is the measured spectrum and the dashed curve is the best fit B-C spectrum. The density and temperature; B-C parameters τ_1 , τ_2 , and S; and α_{1tr} and γ_{1tr} ; are given sequentially on the graph.



Figure 4.2: An example of a LF absorption spectrum of H_2 at 25.0 K. The format of the graph is the same as that above.

shape of the translational band has been obscured by the substantial overlap of the S(0) rotational line. The present H₂ spectra show clearly the translational band shape, and demonstrate the validity of fitting the spectrum with the B-C lineshape function.

4.3.1 The Spectrum Fitting Procedure

The measured spectrum is fitted by a synthetic spectrum characterized by the temperature and the B-C lineshape parameters τ_1 , τ_2 , and S, using a non-linear least squares fitting routine. The synthetic B-C spectra are discussed in chapter two. The fit is weighted by a frequency dependent function which is the product of the absorption spectrum (prior to dividing by $\rho^2 l$), and a generic LF background spectrum. This weighting procedure emphasizes fitting the peak of the absorption spectrum, between 45 and 60 cm⁻¹, and the region of maximum signal-to-noise of the spectrometer, between 60 and 80 cm⁻¹. The fit of the B-C synthetic spectra to individual spectra is illustrated in Figures 4.1 and 4.2, and the fitting procedure determines the B-C parameters to better than 1%. The best fit B-C synthetic spectra are then used in the following examination of the temperature dependence of the translational band.

4.3.2 The Frequency of the Peak and the Bandwidth vs. Temperature

The absorption spectrum depends on the population distribution of the molecular translational energy states. Figure 4.3 shows that the frequency of the translational band peak varies as $T^{1/2}$, where this variation reflects the temperature dependence of the peak of a Maxwellian velocity distribution. Figure 4.3 may be linearly extrapolated to a peak frequency of 90 cm⁻¹ at 77.4 K where Birnbaum has measured a peak at approximately 86 cm⁻¹ [12].

Figure 4.4 shows the dependence of the full width at half-maximum (FWHM) as a function of the square root of the temperature. The translational band has a broad peak



Figure 4.3: The frequency of the peak of the translational band vs. the square root of the temperature. In all figures of this section, + denotes a LF H₂ spectrum, and \Box denotes a composite average spectrum; the y intercept and the slope of the fitted line are given in the top left.



Figure 4.4: The width (FWHM) of the translational band vs. the square root of the temperature.



Figure 4.5: The half-width of the translational band lineshape function vs. the square root of the temperature. The lineshape function is given by eqn. 4.2.

which broadens further as the temperature increases. The data are somewhat noisy as the position of the high frequency half-maximum falls within the lower signal-to-noise region of the beamsplitter. The FWHM of the translational band is considerably broader than the FWHM of the rotational lines S(0) and S(1) since stimulated emission affects the spectrum more strongly at low frequencies. At 37 K, the FWHM of the translational band, the S(0), and S(1) lines are: 145, 83, and 81 cm⁻¹ (based on a B-C spectrum extrapolation of the translational band measurements).

The half-width of the lineshape function $G(\sigma)$ from zero frequency to the halfmaximum frequency, or from the S(0) or S(1) free-molecule transition frequency to the half-maximum on the high frequency side, does not depend on the transition. $G(\sigma)$ is given by

$$G(\sigma) = \frac{A(\sigma)}{\sigma(1 - e^{-hc\sigma/kT})}$$
(4.2)

where for the present purposes, $A(\sigma)$ is the best fit B-C spectrum to the experimental data. Figure 4.5 shows the half-width of $G(\sigma)$ as a function of $T^{1/2}$. This plot is less

noisy than Figure 4.4, because the half-maximum of the lineshape function occurs in a spectral region with higher signal-to-noise than the half-maximum of the absorption spectrum.

The data points in Figures 4.3-4.5 are the results of 28 independent experiments. The scatter of the points is on the order of $\pm 5\%$, where this is consistent with the reproducibility of the spectra (see chapter six).

4.3.3 The Spectral Invariants vs. Temperature

The variation of the spectral invariants α_{1tr} and γ_{1tr} with temperature is shown in Figures 4.6 and 4.7. α_{1tr} is the integrated binary absorption coefficient in terms of ω , eqn.2.56, and it is related to the physical properties of hydrogen by the Poll and Van Kranendonk theory of collision-induced absorption as described in chapter two. γ_{1tr} is given by eqn.2.55, and it is analogous to an integrated lineshape function (the relationship between $G(\sigma)$ and γ_{1tr} is discussed in chapter two). The present results are the first investigations of α_{1tr} and γ_{1tr} for the absorption spectrum of H₂ below 77 K. The variation of the spectral invariants with temperature is related to the pair distribution function and hence to the intermolecular potential. Figure 4.6 demonstrates that α_{1tr} increases as the temperature decreases, where this effect is due to an increase in the lifetime of molecular collisions, and to an increase in the contribution of H₂ bound pairs to the pair distribution function, as the temperature is lowered (see Table 2.2). A detailed evaluation of the implications of these new results for the theory of collision-induced absorption requires complex quantum mechanical calculations, outside the scope of this thesis. The results should, however, stimulate new work in the field.

The errors in the determinations of the spectral invariants are $\sim \pm 5\%$, as accessed by the variations of the data points in Figures 4.6 and 4.7. The larger deviations of α_{1tr} at low temperatures are related to the fact that lower sample gas densities must be used to


Figure 4.6: α_{1tr} vs. temperature for the LF H₂ spectra. The variation of the integrated binary absorption coefficient of the translational band with temperature. α_{1tr} is defined by eqn. 2.55.



Figure 4.7: γ_{1tr} vs. temperature for the LF H₂ spectra. The variation of the spectral invariant γ_{1tr} of the translational band with temperature. γ_{1tr} is defined by eqn. 2.54.

avoid liquification, and thus the absorption measurement has a lower signal-to-noise than at higher temperatures. Systematic errors due to turbulence and the formation of ice also become more influential at low temperatures. γ_{1tr} is less noisy at low temperatures than α_{1tr} because it emphasizes the low frequency portion of the spectrum; the spectral region over which the spectrometer is the most sensitive, the H₂ absorption is the greatest, and ice is not absorptive.

4.3.4 The B-C Parameters vs. Temperature

Figures 4.8 and 4.9 demonstrate the variation of the B-C lineshape parameters τ_1 , τ_2 , and S for the translational band as a function of temperature. Previous experiments have examined the variation of these parameters for the entire translational-rotational band over the temperature range 77 to 300 K, and the synthetic spectra which are fitted to these measurements are therefore dominated by the S(0) and S(1) lines [13],[14]. Figures 4.8 and 4.9 provide new information on the H₂ absorption spectrum since the present study concentrates on the translational band and extends the temperature range of previous experiments.

4.4 Hydrogen Dimers

4.4.1 Introduction and Previous Work

The formation of bound states for a pair of H₂ molecules is predicted by solving the Schrodinger equation for an intermolecular potential with an attractive part [43],[79], [80],[45]. The energy levels and intermolecular potential for the H₂ dimer are shown in Figure 2.1, and transitions between rotational states are allowed according to the selection rules $\Delta l = \pm 1, \pm 3$, where *l* describes the end-over-end rotation of the complex. Bound-bound and bound-free transitions of molecular hydrogen pairs were first observed



Figure 4.8: .

The B-C lineshape parameters τ_1 and τ_2 vs. temperature for the LF H₂ spectra. + denotes τ_1 , and × denotes τ_2 .



Figure 4.9: The B-C lineshape parameter S vs. temperature for the LF H₂ spectra.

in the fundamental vibrational band at 20 K by Watanabe and Welsh [56]. Radiation is absorbed at frequencies near those of the free H_2 molecule when an H_2 dimer transition occurs simultaneously with a vibrational and/or rotational transition of one of the dimer molecules. The matrix element of the electric dipole moment of these transitions is nonzero, and structure is observed superimposed upon the broad collision-induced vibrational and/or rotational lines.

Structure in the H₂ rotational band was first observed in the far-infrared spectrum of Jupiter obtained by the Voyager spacecraft, Figure 1.2, and this was subsequently interpreted as evidence of dimer absorption [81],[82]. Dimer transitions near S(0) and S(1) have been observed in the laboratory by McKellar at 77 K [27],[45], and in H₂ and D₂ at 20 K [28]; this work is shown in Figures 1.4 and 2.4. Dimer structure has also been observed superposed on the S(0) line of H₂ and D₂ using the present spectrometer-cell apparatus near 20 K, and a spectrum of the S(0) region of D₂ is shown in Figure 7.1.

Pure H₂ dimer bound state transitions are expected to appear at frequencies lower than 10 cm⁻¹, below the frequency range of the present spectrometer. A new polarizing interferometer, patterned after the rocket-borne instrument COBRA [36], [69], is under construction with the intention of observing H₂ dimer bound state transitions.

4.4.2 The Predicted Dimer Structure in the Translational Band

The existence of dimer structure in the translational band of low temperature H₂ has been predicted by Schaefer and Meyer [33], and the astronomical basis for this proposal is described in the introduction. Figure 4.10 shows the calculated low temperature H₂ emission spectrum [63]. The ripples superimposed upon the translational band are due to continuum-bound dimer transitions (below 30 cm⁻¹), and resonances between continuum-continuum H₂ pair transitions. The structure of a H₂ absorption spectrum would qualitatively resemble that of the emission spectrum, but the absorption spectrum would have a different frequency dependence and include stimulated emission. The search for dimer structure in the translational band of H_2 has been a major focus of the present low temperature spectroscopic studies.

4.4.3 Experimental Dimer Search

Figure 4.11 is the spectrum of hydrogen at 22.4 K, obtained using a gas density of 9.39 amagat and a pathlength 60 m. The sample spectrum is an average of 4 spectra, each consisting of 6 interferograms, and the total observation time is 60 min. The background spectrum is composed of an average of 2 empty cell and 3 helium spectra taken before, and 2 helium and 3 empty cell spectra taken after the H₂ spectra. All background spectra are acquired at the same temperature as the H₂ spectra, and the helium backgrounds are obtained at the same pressure as the H₂ spectra in order to cancel the effects of window distortions. No 'channel' spectra are observed in the helium spectra, and using both the empty cell and helium filled backgrounds reduces systematic errors due to experimental drifts. A substantial effort has been made to obtain high quality low temperature spectra, and in order to do this, transfer noise, temperature gradients, and window distortions have been kept to a minimum.

The sample density and temperature have been determined on the basis of previous observations of dimer lines near S(0), where dimer lines are observed to broaden significantly above ~ 10 amagat, and dimer structure is enhanced as the temperature is lowered, particularly for densities below ~ 4 amagat. The condition chosen for the present spectra is a compromise between temperature and density; the density must be high enough to cause measurable absorption, yet the sample should not liquefy. The peak absorption corresponding to data shown in Figure 4.11 is 23%, and the uncertainty in the absolute absorption of this spectrum is ~4% of the peak.

In the region of highest signal-to-noise, from 40-80 cm⁻¹, no obvious structure is



Figure 4.10: The predicted H_2 translational emission spectrum, from [30]. The structure below 30 cm⁻¹ is due to free-bound transitons and that at higher frequencies is due to resonances between free-free transitions.



Figure 4.11: The LF H₂ translational absorption spectrum at 22.4 K. The filename, temperature, and density in amagat are written on the graph, and the the pathlength is 60 m. Note the absence of obvious dimer features.

observed in the spectrum. Likewise, over the region 20-40 cm⁻¹, no structure is apparent, although the measured spectrum is noisier. The spectrum does not display any structure which might be associated with H₂ dimers at a level greater than 1% of the translational band peak. The evidence is that dimers make only a continuous contribution to the H₂ absorption spectrum under these experimental conditions, that is at T = 22.4 K and $\rho = 9.39$ amagat.

4.5 The H₂ Composite Average Spectra at 25.5 and 36 K

Complete translational band absorption spectra have been obtained by averaging the LF spectra, covering 20-180 cm⁻¹, and the HF spectra covering 50-320 cm⁻¹. The HF spectra have been collected using the same procedure as the LF spectra, but are concentrated near the temperatures of 25 and 35 K. A weighted average of the LF and HF spectra is obtained for the temperatures 25.5 and 36 K, and the results are presented in this section. A discrepancy of about 10% exists between the intensities of the LF and HF spectra, and an effort to eliminate this discrepancy by removal of a residual baseline in the raw spectra is discussed. The spectral invariants of the complete spectra are obtained and compared to previous experimental work and the calculations of chapter two.

4.5.1 The Removal of a Residual Baseline

We believe that the 10% intensity discrepancy between the LF and HF spectra, over the frequency range where they overlap, is caused by a detector non-linearity. The HF background spectra, with a larger bandwidth and thus higher interferogram signal, may have been reduced in intensity; this topic is examined further in chapter six. A residual baseline in the raw spectra may be a consequence of the detector non-linearity, and regardless of the cause, will perturb the absorption measurements.

The Residual Baseline Intensity of the Background Spectra

Figure 3.8 shows typical background spectra for the LF and HF cases, and a small residual intensity across the band, about 0.5% of the LF peak, is observed. The residual baseline has roughly the same amplitude for both LF and HF backgrounds, and is most evident in the following regions: $0-10 \text{ cm}^{-1}$; near the LF beamsplitter null; and at 135 cm⁻¹ and 263-273 cm⁻¹, the crystal quartz absorption bands. In all of the above regions, it is reasonable to expect a background spectrum with zero intensity. Although the baseline intensity is a small fraction of the spectrum peak, it is greater than 10% of the HF spectrum intensity below 60 cm⁻¹.

The Influence of a Baseline on the Absorption Spectrum

An absorption spectrum obtained from a sample and a background spectrum which both include a residual baseline is anomalously low. Suppose a background spectrum $I_b(\sigma)$ and a sample spectrum $I_s(\sigma)$ are both composed of a true part *I*, and a residual part *I'*. Suppose also that the sample transmits some fraction *f* of the background intensity, and that the residual part is independent of the transmitted intensity. The measured absorption is

$$A = -\ln\left(\frac{I_s + I'}{I_b + I'}\right) = -\ln\left(\frac{f \cdot I_b + I'}{I_b + I'}\right)$$
(4.3)

If the true background intensity is 1.0, the true transmission of the sample is 0.6, and the residual part is 0.1, the measured absorption is 0.45; whereas the true absorption is 0.51, a difference of 12%. In these experiments, the residual part is not the same for the sample and background spectra, and this illustration exaggerates the absorption error.

The Baseline Removal

The residual baseline is removed separately from all the LF and HF sample and background spectra. The procedure applied to each LF spectrum involves the following: fit the spectrum over the region $10-25 \text{ cm}^{-1}$, and find the minimum value of the fitted curve; fit the spectrum over the region $100-119 \text{ cm}^{-1}$, and find the minimum of the fit; find the average value between $263-273 \text{ cm}^{-1}$; find the average value between $325-335 \text{ cm}^{-1}$; and set the point at 520 cm^{-1} to zero. Fit a line to the above 5 points and subtract this line from the LF spectrum. The procedure applied to each HF spectrum is: fit the spectrum over the region $20-50 \text{ cm}^{-1}$, and find the minimum value of the fit; find the minimum value of the spectrum near 135 cm^{-1} ; average the spectrum over the regions 263-273, 410-420, $485-490 \text{ cm}^{-1}$; and set the point at 690 cm^{-1} to zero. Fit a line to the above 6 points and subtract this line from the HF spectrum.

After baseline removal both the LF and HF raw spectra are very close to zero over the relevant spectral regions, but the corrected LF and HF absorption spectra are still inconsistent. However, the baseline removed HF absorption spectra more closely resemble the LF spectra over the translational band peak, 55–70 cm⁻¹, and the droop of the LF spectra near 110 cm⁻¹ is reduced. In regions of high signal-to-noise, the baseline removed absorption spectra are nearly identical to the unprocessed spectra, as is expected.

4.5.2 The Averaging Procedure

The composite average translational band spectra are obtained by a two step procedure. First, individual absorption spectra obtained on the same day under nearly the same conditions are averaged as a 'group'. Second, the groups are averaged according to the weighting procedure given by eqn. 4.4 below.

The group average consists of 8 to 20 sample interferograms, and 14 to 24 background

interferograms. Helium backgrounds have been used rather than empty cell backgrounds when possible. In some cases, spectra obtained on a given day at moderate densities ρ_b serve as backgrounds for high density spectra ρ_s , and a new group spectrum is obtained at a density of $\rho' = \sqrt{\rho_s^2 - \rho_b^2}$.

The maximum temperature variation of the individual spectra which comprise the 25.5 K composite spectra is +2/-1 K for the LF case, and +4/-3 K for the HF case. The maximum temperature variation of the individual spectra which compose the 36 K composite spectra is +2/-1.5 K for the LF case, and +2.5/-3 K for the HF case. The 36 K composite spectrum is obtained from 3 LF and 8 HF group spectra, and the 25.5 K spectrum is obtained from 5 LF and 7 HF group spectra (except Figure 4.17 which is obtained from 4 LF and 3 HF group spectra).

The composite average spectrum at a frequency σ is

$$A_{avg}(\sigma) = \frac{1}{\sum_{i} wt_{i}(\sigma)} \sum_{i} wt_{i}(\sigma) A_{i}(\sigma)$$
(4.4)

where the weighting function is

$$wt_i(\sigma) = \left(\frac{A_i(\sigma)}{A_{max}}\right) \left(\frac{B_i(\sigma)}{B_{max}}\right) \left(\frac{Nint_i}{Nint_{max}}\right).$$
(4.5)

 $A_i(\sigma)$, $B_i(\sigma)$, and Nint_i are: the absorption intensity (prior to dividing by $\rho^2 l$), the background intensity, and the number of interferograms, of a group spectrum *i*. A_{max} , B_{max} , and Nint_{max} are: the maximum absorption, the maximum background intensity, and the maximum number of interferograms which compose a group spectrum, within the set of group spectra. The number of interferograms in a LF group is multiplied by m = (# HFgroup spectra/ # LF group spectra), in order to balance the contribution of the larger number of HF groups in the average.

Intermediate averages of LF average spectra and HF average spectra are also obtained, weighted by a similar procedure for each separate spectral region. The weighting function of eqn. 4.5 is averaged and normalized, and the result is then used to weight the fit of the B-C synthetic spectrum to the composite average spectrum.

4.5.3 The Composite Average Spectra at 25.5 and 36 K

The comparison of the LF average spectra to the HF average spectra illustrates the intensity mismatch between these regions. The upper graphs of Figures 4.12-4.17 show the LF and HF average spectra as a heavy and light line, respectively. This series of figures shows that the discrepancy between these spectral regions is reduced by simply multiplying the HF spectra by a constant factor prior to averaging. The filename of the LF average spectrum and the average temperature, and the filename of the HF average spectrum and the average temperature, are written on the graph.

The lower graphs of Figures 4.12-4.17 show the composite average spectrum as a solid line, the dotted lines show the contributions of the translational band and the S(0) line to the best fit B-C synthetic spectrum denoted by the broad dashed line. Written on these graphs are: the filename; the temperature; the B-C lineshape parameters τ_1, τ_2 (×10⁻¹⁴ sec), and S (in K Å⁶); the spectral invariants α_{1tr} (cm⁵ sec-1), and γ_{1tr} (cm⁵ sec); and the residuals from the fit.

In Figures 4.12 to 4.14, the 36 K average spectrum is obtained by multiplying the HF spectra by the factors 1.0, 1.05, and 1.10, respectively. The lowest residuals between the average spectrum and the best fit B-C spectrum are found by using an HF multiplier of 1.10, but this is only slightly better than a multiplier of 1.05. The composite spectrum reflects the intensity mismatch in the regions $100-120 \text{ cm}^{-1}$ and near 135 cm^{-1} , since the weights of the LF and HF spectra over these regions is zero, respectively.

Figures 4.15 and 4.16 show the 25.5 K LF and HF average spectra and the composite average spectra obtained by multiplying the HF spectra by the factors 1.0 and 1.05. The 25.5 K average spectrum, like the 36 K average spectrum, is better fit by a B-C spectrum



Figure 4.12: (A) The LF and HF average spectra at 36 K. The heavy line is the LF spectrum and the light line is the HF spectrum ($\times 1.00$). The LF & HF filenames and avg. temps. are on the graph.

(B) The composite average spectrum at 36 K, using a HF multiplier=1.00. The solid curve is the spectrum, the dotted curves are the B-C translational band and S(0) line, and the dashed curve is the net fitted spectrum. Written on the graph are: the filename; the temp; τ_1 , τ_2 , and S; α_{1tr} and γ_{1tr} ; and the residuals from the fit.



Figure 4.13: (A) The LF and HF average spectra at 36 K. The heavy line is the LF spectrum and the light line is the HF spectrum ($\times 1.05$). The LF & HF filenames and avg. temps. are on the graph.

(B) The composite average spectrum at 36 K, using a HF multiplier=1.05. The solid curve is the spectrum, the dotted curves are the B-C translational band and S(0) line, and the dashed curve is the net fitted spectrum. Written on the graph are: the temp; τ_1 , τ_2 , and S; α_{1tr} and γ_{1tr} ; and the residuals from the fit.



Figure 4.14: (A) The LF and HF average spectra at 36 K. The heavy line is the LF spectrum and the light line is the HF spectrum ($\times 1.10$). The LF & HF filenames and avg. temps. are on the graph.

(B) The composite average spectrum at 36 K, using a HF multiplier=1.10. The solid curve is the spectrum, the dotted curves are the B-C translational band and S(0) line, and the dashed curve is the net fitted spectrum. Written on the graph are: the temp; τ_1 , τ_2 , and S; α_{1tr} and γ_{1tr} ; and the residuals from the fit.



Figure 4.15: (A) The LF and HF average spectra at 25.5 K. The heavy line is the LF spectrum and the light line is the HF spectrum ($\times 1.00$). The LF & HF filenames and avg. temps. are on the graph.

(B) The composite average spectrum at 25.5 K, using a HF multiplier=1.00. The solid curve is the spectrum, the dotted curves are the B-C translational band and S(0) line, and the dashed curve is the net fitted spectrum. Written on the graph are: the temp; τ_1 , τ_2 , and S; α_{1tr} and γ_{1tr} ; and the residuals from the fit.



Figure 4.16: (A) The LF and HF average spectra at 25.5 K. The heavy line is the LF spectrum and the light line is the HF spectrum ($\times 1.05$). The LF & HF filenames and avg. temps. are on the graph.

(B) The composite average spectrum at 25.5 K, using a HF multiplier=1.05. The solid curve is the spectrum, the dotted curves are the B-C translational band and S(0) line, and the dashed curve is the net fitted spectrum. Written on the graph are: the temp; τ_1 , τ_2 , and S; α_{1tr} and γ_{1tr} ; and the residuals from the fit.



Figure 4.17: (A) The LF and HF average spectra at 25.5 K. The heavy line is the LF spectrum and the light line is the HF spectrum ($\times 1.10$). The LF & HF filenames and avg. temps. are on the graph.

(B) The composite average spectrum at 25.5 K, using a HF multiplier=1.10. HF spectra are taken either at the beginning of the run or use a low density H₂ background to avoid the ice band (180-300 cm⁻¹ in the previous 25 K figures). The solid curve is the spectrum, the dotted curves are the B-C translational band and S(0) line, and the dashed curve is the net fitted spectrum. Written on the graph are: the temp; τ_1 , τ_2 , and S; α_{1tr} and γ_{1tr} ; and the residuals from the fit.

if the HF spectra are multiplied by a factor of 1.05. The composite spectra show an excess absorption with respect to the B-C synthetic spectrum in the frequency region $180-300 \text{ cm}^{-1}$. Note that the weighting of the fit emphasizes the translational band peak, so the high frequency excess does not strongly affect the fitted B-C spectrum. The measured spectrum has been contaminated by absorption due to very small amounts of water ice. The dip at 230 cm⁻¹ corresponds closely to an ice phonon line at 229 cm⁻¹, and in general the band corresponds to absorption by the crystalline phases of ice, I and II, and vitreous ice. The distortion of the H₂ spectra due to ice is discussed further in chapter six.

Figure 4.17 shows the average 25.5 K spectrum obtained by multiplying a subset of the HF spectra by 1.10. The group spectra are selected from absorption spectra which are obtained using at least some helium filled backgrounds, or from hydrogen backgrounds at a lower pressure. This selection of group spectra partially avoids problems that are associated with changes in the ice absorption or reflection due to cell pressure changes.

The intensity variation of the LF group spectra which compose the 25.5 and 36 K average spectra is $\pm 4\%$ and $\pm 3\%$ of the peak absorption, respectively. The variation of the HF group spectra which compose the 25.5 and 36 K average spectra is similar to the LF case, provided the ice band is excluded. If the procedure of applying the simple HF multiplier is correct, a reasonable estimate of the uncertainty of the average spectra is $\pm 5\%$ of the absorption peak. However, the most conservative estimate of the uncertainty of the average spectra includes the value of the HF multiplier and is therefore +3/-10% of the peak intensity. The uncertainty of previous measurements of the translational-rotational band of H₂ can be interpreted as $\pm 5\%$ of the S(1) peak at 297 K [14]; therefore, the present measurements of the translational band of H₂ are about 10 times more precise than previous studies.



Figure 4.18:

(A) The lineshape function $G(\sigma)$ for the H₂ translational band at 36 K obtained from the spectrum of Figure 4.14 (HF multiplier=1.10). The filename and temperature are written on the graph.

(B) The lineshape function $G(\sigma)$ for the H₂ translational band at 25.5 K obtained from the spectrum of Figure 4.17 (HF multiplier=1.10). The filename and temperature are written on the graph.

Figure 4.18 shows the lineshape function $G(\sigma)$ for the translational band of hydrogen at 36 and 25.5 K. These graphs are derived from the composite average spectra which involve HF multipliers of 1.10, Figures 4.14 and 4.17. The lineshape function is proportional to the transition probability and the figure demonstrates the increase in the probability of low frequency translational energy transitions as the temperature is lowered. It is notable that the amplitude of the semi-empirical B-C lineshape function drops slightly at frequencies below $\sim 12 \text{ cm}^{-1}$. The experimental data near 20 cm⁻¹ is rather noisy, but it does not indicate that the lineshape function drops at low frequencies. In fact, the large increase in the curves at low frequencies differs distinctly from the B-C lineshape; this is another interesting issue for future low frequency measurements.

4.6 The Low Temperature Spectra Compared to Previous Measurements

The preceding figures present new measurements of the complete translation absorption band of normal H_2 at 25.5 and 36 K. The translational band of H_2 has been measured with high sensitivity, at a spectral resolution 10 times higher than previous work, over a new temperature range. The low temperature measurements demonstrate quantum mechanical aspects of the pair distribution function, and yield new information regarding the hydrogen intermolecular potential.

The spectral invariants α_{1tr} and γ_{1tr} , and the B-C parameters for the composite spectra have been obtained from the best fit B-C synthetic spectra in accordance with the procedure applied to the LF individual spectra. In Figures 4.19 through 4.22, the boxes denote the results of the composite average spectra (Figures 4.12-4.17), and the error of the spectral invariants and the B-C parameters is indicated by the spread of the boxes. It is apparent that although the accuracy of the spectra is at worst $\pm 10\%$, the variation of the integrated absorption coefficient is only about $\pm 4\%$. The uncertainty of the spectral invariants is not particularly sensitive to the discrepancy between the LF and HF spectra because the fit of the B-C synthetic spectra to the absorption measurements is weighted most heavily over the low frequency spectral region.

4.6.1 The Spectral Invariants vs. Temperature

The spectral invariants for the translational band of H_2 are compared to previous higher temperature measurements in Figures 4.19 and 4.20. The crosses denote the values of the translational band spectral invariants which are inferred from the B-C parameters of the entire translational-rotational band of normal H_2 measured by Dore et al. [13], Bachet et al. [14], and Birnbaum [12]. The diamonds are the measurements of Bosomworth and Gush, where the translational band has been extracted from the entire spectrum using a modified Lorentzian with an exponential tail [8]. The circles denote the integrated binary absorption coefficients calculated using the Poll and Van Krandendonk formalism and the Poll and Miller quantum mechanical pair distribution function at 20, 40, and 80 K; the points at 200 and 300 K are calculated using a classical pair distribution function. Both the quantum and classical pair distribution functions are derived from the Lennard-Jones intermolecular potential. Note that α_{1tr} differs from the integrated binary absorption coefficient of Tables 2.2 and 2.3 by a factor of 2π .

Discussion of the Integrated Absorption Coefficient

Figure 4.19 shows that at higher temperatures there is a discrepancy between the measured and calculated binary absorption coefficients. The low temperature results form the closest correspondence between measurements and theory, where this may be partially due to the advantage of measuring the translational band isolated from the rotational lines.



Figure 4.19: α_{1tr} vs. temperature for the translational band of H₂. \Box are the composite average spectra, + denotes data from Dore et al. [13], Bachet et al. [14], and Birnbaum [12], \Diamond are from Bosomworth and Gush [8], and \circ are calculations based on the theory of Poll and Van Kranendonk (the values plotted differ from Table 2.3 by a factor of 2π)



Figure 4.20: γ_{1tr} vs. temperature for the translational band of H₂. γ_{1tr} is defined by eqn. 2.55. \Box are the composite average spectra, and + denotes data from Dore et al. [13], Bachet et al. [14], and Birnbaum [12].

It is possible, but unlikely, that the high temperature discrepancy is due to the high sample densities (over 100 amagat) used in previous experiments. The measured excess absorption might then be due to tertiary collision-induced mechanisms. However, many previous experiments have verified that H₂ absorption is dependent on ρ^2 , [12],[14], and specifically, the ρ^2 dependence of the translational band has been reported [8]. It is also possible that previous high temperature experiments have been contaminated by impurity absorption, by water vapour for example. In the low temperature experiments, all impurities in the sample gas are frozen out, and the possibility of excess absorption is greatly reduced.

The inferred translational band measurements of α_{1tr} in Figure 4.19 exceed the calculations using the classical pair distribution function by ~ 33% at both 200 and 300 K. A similar discrepancy was found by Bachet et al., where α_{1tr} measured over the entire translational-rotational band exceeded that calculated using a Lennard-Jones potential by 13% at 195 K and 25% at 300 K, [14]. However, they calculated the absorption coefficient due to only the quadrupolar induced dipole moment and interpreted the discrepancy as the contribution of the overlap and 'interference' between the overlap and quadrupolar induced dipole moments. The present calculations of the translational band, however, already include the overlap and interference terms (see Table 2.2).

Unlike the high temperature results, the low temperature measurements of α_{1tr} are quite close to those calculated using a quantum pair distribution function based on the Lennard-Jones potential. The variation of the integrated absorption as a function of temperature is a probe of the intermolecular potential in the sense that low temperature, slowly moving, molecules interact over relatively long ranges, whereas high speed molecules can penetrate the potential to smaller distances. The comparison of measurements and Lennard-Jones calculations shown in Figure 4.19 leads to the conclusion that the long-range portion of the H_2 intermolecular potential is well described by a Lennard-Jones potential, but the short-range repulsive part of the intermolecular potential is not. The present measurements could serve as a valuable test of the H_2 ab-initio potential which was used to model the low temperature S(0) and S(1) rotational lines (see Figure 2.4).

Figure 4.20 shows the variation of the spectral invariant γ_{1tr} as a function of temperature. The low temperature data points at 25.5 and 36 K continue the roughly T^{-1} behaviour of γ_{1tr} from higher temperatures. The variation of the low temperature data points of Figure 4.20 is less than 4.19 because γ_{1tr} emphasizes the low frequency region of the translational spectrum (see the above discussion of Figures 4.6-4.7). The variation of the measured α_{1tr} and γ_{1tr} with temperature, displayed in Figures 4.19 and 4.20, generally resemble the variation of both the measured and calculated invariants of the entire translational-rotational band [62].

4.6.2 The B-C Parameters vs. Temperature

Figures 4.21 and 4.22 show the variation of the B-C parameters with temperature, where the parameters have been obtained from fitting the composite average spectra, and from previously reported fits of measurements of the entire translational-rotational band. The time constants τ_1 and τ_2 increase smoothly as the temperature is lowered, and the ratio τ_1/τ_2 is approximately 2 over the temperature range 25 to 300 K. The duration of a collision, $(\tau_1\tau_2)^{1/2}$, also increases as the temperature decreases. The parameter S is proportional to the integrated absorption [14], and Figure 4.22, the variation of S with temperature, resembles Figure 4.19.

Figures 4.21 and 4.22 provide sufficient information to predict the entire translationalrotational absorption spectrum of H₂, from 25 to 300 K. The parameters τ_1 , τ_2 , and S may be obtained by interpolating the graphs, and the B-C synthetic spectrum is then calculated according to the prescription of chapter two. The B-C synthetic spectrum reproduces the measured collision-induced absorption spectrum of hydrogen, and the predicted spectrum is valid over a wavelength range of two orders of magnitude. The accuracy of the predicted spectrum is limited primarily by the accuracy of the experimental spectra from which the B-C parameters are derived, and at low temperatures by the failure to include dimer transitions in the model.

Chapter 5

HD

5.1 Introduction

In the course of measuring the low temperature translational band of H₂, a weak absorption feature has been observed at a frequency of $89.23 \pm 0.01 \text{ cm}^{-1}$. This line is identified as the R(0) $J = 1 \leftarrow 0$ transition of hydrogen deutride which occurs naturally as an isotopic 'impurity' in ordinary hydrogen. The identification of this line is based on the correspondence of its frequency to previous measurements of $\sigma = 89.227950 \text{ cm}^{-1}$ [83], and the fact that any other candidate gas is frozen out at these low temperatures. In addition, a weak R(1) line at 178 cm⁻¹ has been observed in the 77 K H₂ spectra. The observation of these lines was surprising, as we did not anticipate that the low concentration of HD in H₂, combined with the small dipole moment of HD, would cause measurable absorption.

The HD molecule in the electronic ground state possesses a small permanent electric dipole moment and rotational transitions are allowed according to the selection rules $\Delta J = \pm 1$. The dipole moment originates from the fact that the molecular center of mass and center of charge do not coincide. The nuclei of the molecule undergo a zero-point vibrational motion, and if the electrons do not follow the nuclear motion exactly, an oscillating dipole moment occurs [84].

The rotational spectrum of HD was first observed by Trefler and Gush [85], and the absorption spectrum has subsequently been investigated in the pure gas and in gas mixtures over a temperature range of 77 to 300 K [86],[87]. The above precise frequency measurement of the R(0) line was obtained using the radiation produced by nonlinear mixing of CO₂ lasers [83]. Recent measurements of the intensities and frequencies of higher J lines have been reported using laser diode spectrometers [88], and Fourier transform spectrometers [89]. Theoretical aspects of the infrared spectrum of HD have been reviewed by Poll [90].

5.1.1 The D/H Abundance Ratio

The distribution of molecular hydrogen in cold regions of the galaxy can in principle be traced using astronomical observations of HD rotational line emission, as mentioned in the introduction. The observation of HD lines can also be used to understand the D/H abundance ratio, one of the few measurable quantities in cosmology. Deuterium is formed during the early nucleosynthesis phase of the universe and is subsequently consumed by stars. The D/H abundance ratio, along with the abundances of ⁴He,³He, and⁷Li, is determined by the energy and particle densities of the early universe. Big Bang nucleosynthesis calculations are consistent with measured elemental abundances only if the ratio of the number of baryons to photons is ~ 10⁻⁹. Therefore, the mass density of the universe in the form of baryons, $\Omega_B < 0.2$, is considerably less than the closure density, and this mass deficiency is presently seen as the strongest argument for the existence of non-baryonic 'dark matter' [41].

The measured D/H ratio varies, depending upon the astrophysical environment: on Earth, D/H=1.58 × 10⁻⁴ [91]; in Jupiter's atmosphere, ~ 3.5×10^{-5} [25]; and in the interstellar medium, $1-2\times10^{-5}$ [41]. Present day D/H ratios must be interpreted using a model of the chemical evolution of the galaxy to obtain the cosmological abundance ratio. The atmospheres of the giant gaseous planets are expected to preserve the abundance ratio of the pre-solar nebula, but D/H ratios measured spectroscopically using lines of deuterated methane (CH₃D) require further interpretation via models of atmospheric chemistry. Planetary D/H ratios are also measured using visible and near-infrared HD vibrational overtone transitions, but these observations involve modelling the scattering of short wavelength radiation by clouds and haze [42].

Bezard, Gautier, and Marten have proposed observing the R(0) and R(1) lines of the giant planets as a probe of the atmospheric deuterium abundance [42]. This measurement avoids the above problems, and the submillimeter HD lines are reasonably free of obscuration by other molecular lines. The present results demonstrate the feasibility of determining D/H ratios from planetary spectra using the intensities of the R(0) line and the underlying H₂ collision-induced translational band.

5.2 The HD Spectra

The HD line is observed in all the H₂ spectra, and the results presented in this section are obtained from LF H₂ spectra, over a temperature range of 23 to 38 K, a density range of 5.5 to 23.3 amagat, and pathlengths of 52 and 60 meters. These HD spectra are a subset of the LF spectra of the H₂ translational band studies. One set of LF D₂ spectra was acquired at temperatures near 28 K, at a density of 2.9 amagat, over a 52 meter path (see Figure 7.1). Sample spectra obtained on same day under the same conditions are averaged as a 'group' and each average consists of 8–20 interferograms, where the maximum optical path difference of an interferogram corresponds to a spectral resolution of 0.22 cm⁻¹. Background spectra are composed of empty cell spectra taken before and after the sample spectra. In order to estimate the uncertainty of the R(0) line intensity, the average sample spectra are also ratioed against background spectra composed of a different set of empty cell spectra (generally backgrounds taken before the sample spectra).

Some of the absorption spectra are shown in Figure 5.1, where the HD line at 89.2

Chapter 5. HD



Figure 5.1: Absorption spectra of H_2 and D_2 , the sharp line at 89.2 cm⁻¹ is the R(0) line of HD. The H_2 densities, temperatures, and pathlengths are: a, 16.00 am, 37.2 K, 52 m; b, 13.68 am, 25.2 K, 52 m; c, 10.24 am, 25.5 K, 52 m; d, 7.65 am, 23.7 K, 60 m. Curve e is D_2 at 2.93 am, 28.0 K, 52 m.

 cm^{-1} is observed on top of the H₂ translational continuum. The HD lines are unresolved, that is, the pressure broadened linewidth is less than the width of the interferometer lineshape function. In spite of the small amount of HD in the absorption cell, the high sensitivity of the spectrometer-cell apparatus yields a detection of the line at a signalto-noise of ~15. The present spectra allow the measurement of the HD dipole moment under very different temperature, pressure, and concentration conditions than previous measurements. In order to measure the dipole moment two assumptions are made: (1) the mixing ratio HD/H₂ of the gas sample is 1/3165, where this is based on the deuterium abundance of deep ocean water [91] and all deuterium is in the form of HD; and (2) the HD lineshape is Lorentzian.

5.2.1 The Integrated Absorption Coefficient

The dipole moment μ of a diatomic molecule is related to the integrated absorption coefficient α_0 (per unit density, per unit pathlength) of a rotational line by

$$\alpha_0 = \frac{8\pi^3}{3hcZ} n_o \sigma_0 (e^{-E(J)/kT} - e^{-E(J+1)/kT}) (J+1) \mu^2$$
(5.1)

where n_0 is Loschmidt's number, σ_0 is the frequency of the transition, and the equation includes Boltzmann factors for the lower and upper state. μ is the magnitude of the permanent electric dipole moment and it is related to the sum of the squares of the dipole moment matrix elements for transitions $\Delta J = \pm 1$ by

$$\mu^{2} \frac{(J+1)}{(2J+1)} = |\mu|^{2} = |\mu_{x}|^{2} + |\mu_{y}|^{2} + |\mu_{z}|^{2}$$
(5.2)

where the dipole moment operator and the wavefunctions are written in spherical polar coordinates [92]. Z is the rotational partition function (eqn. 2.40), and the rotational energy states are obtained from the HD rotational constants: $B_0 = 44.665379$; $D_0 =$ 0.0257502; $H_0 = 0.19039 \times 10^{-4}$, all in cm⁻¹ [89]. It should be noted that one of the reasons the R(0) line is observable in the present spectra is that virtually all the HD molecules are in the ground state at these low temperatures.

5.2.2 Line Fitting

Figure 5.2 shows an expanded section of the H₂ absorption spectra that are interpolated to a frequency step size 8 times smaller than Figure 5.1. The interpolated spectra are obtained by Fourier transforming interferograms lengthened by zero-filling. The area under the interpolated HD line is found by assuming that the measured lineshape is the convolution of a Lorentzian absorption line with an instrumental lineshape function of the form $\sin x/x$. From the convolution theorem, the interferogram component which is responsible for the HD line is a cosine at an angular frequency ω_0 with an exponentially decaying amplitude.

$$G(t) = e^{-a|t|} \cos \omega_0 t, \quad -T \le t \le T$$

= 0, $|t| > T$ (5.3)

where t is the time delay between the two arms of the interferometer, and T is the time delay associated with the maximum interferometer optical path difference. The Fourier transform of G(t) is the lineshape $g(\omega)$,

$$g(\omega) = \frac{2}{\Delta\omega^2 + a^2} \left[a - e^{-aT} (a \cos \Delta\omega T - \Delta\omega \sin \Delta\omega T) \right]$$
(5.4)

where $\Delta \omega = \omega - \omega_0$. The HD spectral feature is described by the lineshape $g(\omega)$, where the integrated area of $g(\omega)$ is 2π . $g(\omega)$ is fitted to the measured spectrum using a nonlinear least squares fitting program with 4 free parameters: the height and slope of the H₂ translational band baseline; the parameter *a* which is related to the Lorentzian linewidth; and a line strength multiplier applied to $g(\omega)$ from which the integrated area



Figure 5.2: The fit to the measured spectra over the R(0) line. The solid curves are the interpolated curves of Figure 5.1, and the dotted curves are the fits obtained by assuming the HD line is an instrument broadened Lorentzian superimposed on a linear continuum.

of the HD line is found [93]. The frequency of the HD line is input by hand to the fitting routine.

The results of fitting the measured spectra are shown in Figure 5.2 by the dashed line. The fit is good over the central maximum of the HD line and it even reproduces the first few ripples of the measured spectrum. The D₂ spectrum at the bottom of Figure 5.2 demonstrates that for narrow linewidths (low densities) the measured spectrum strongly resembles a sin x/x curve which is given by $g(\omega)$ if $a \to 0$ and $x = \Delta \omega T$.

5.3 The HD Dipole Moment

5.3.1 The Density Dependence of the Dipole Moment

The area under the HD line equals $r_m \rho \alpha_0 l$, where r_m is the HD/H₂ mixing ratio (1/3165), ρ is the sample density in amagat, α_0 is the integrated absorption coefficient and l is the pathlength. The dipole moment is then calculated from α_0 using equation 5.1, and the results of 10 spectra are plotted in Figure 5.3 as a function of density. In previously reported experiments, the integrated absorption coefficient of the HD rotational spectrum was shown to be density dependent, and the free-molecule dipole moment was derived from the integrated intensity extrapolated to zero density [90]. α_0 is temperature dependent and since the present work involves HD line intensities which are not measured at the same temperature, the dipole moment, which is independent of the temperature, is plotted as a function of the density.

The density dependence of the integrated absorption is caused by an interference between the permanent dipole moment and the collision-induced dipole moment [94],[95]. There exists some controversy, however, as to whether the interference is constructive or destructive. Previous work has shown that the integrated intensity of low J rotational lines decreases as a function of density at room temperature [88],[87]. At 77 K, the integrated intensity of R(0) increases slightly as a function of density [86],[87], but the present results show a slight decrease as a function of density. The R lines of the HD vibrational band have a marked density dependence, where these lines are described by a Fano lineshape [96]. The HD pure rotational lineshape is, however, not strongly affected

5.3.2 The Measured HD Dipole Moment

by density and the Lorentzian approximation is valid [86].

The uncertainty of the HD dipole moment is estimated by finding the dipole moment from a given sample spectrum using both background data sets, and the variation of these measurements is represented by the error bars of Figure 5.3. This variation is larger than the $\pm 1\%$ uncertainty in the density measurement, and it reflects the systematic transmission errors of the spectrometer-cell system when measuring weak absorptions. An additional error owing to the fitting procedure may exist for the highest and lowest density points. A least squares fit of a straight line to the data, weighted by the reciprocal of the square of the error bar height, gives the zero density intercept, $\mu = (0.82 \pm$ $0.04) \times 10^{-3}$ debye. The negative slope of this line is caused entirely by the extreme high and low density points, and the weighted average of μ , excluding these points, is $(0.78 \pm 0.02) \times 10^{-3}$ debye. A value of μ which includes both interpretations of the data is therefore $(0.81 \pm 0.05) \times 10^{-3}$ debye.

The present value of the dipole moment of the R(0) transition is consistent with the best theoretical calculation of 0.8463×10^{-3} debye [97], and with the previous measurement at 77 K by McKellar of $(0.818 \pm 0.026) \times 10^{-3}$ debye [86]. The present measurement is inconsistent, however, with the work of Ulivi et al. where μ has the following values at the various temperatures: 0.719 ± 0.003 at 77 K; 0.803 ± 0.012 at 195 K; 0.883 ± 0.028 at 295 K (all $\times 10^{-3}$ debye) [87]. No explanation is given in this latter work for the unexpected variation of μ with temperature.

Chapter 5. HD



Figure 5.3: The upper graph shows the density dependence of the HD dipole moment obtained from fitting the spectra. The dashed lined is the least squares fit to the data. The lower graph shows the R(0) linewidth (FWHM) as a function of density. The triangle denotes the deuterium spectrum. The dashed line is a linear fit to the hydrogen data, excluding the extreme density points.

5.3.3 The Density Dependence of the HD Linewidth and Frequency

Figure 5.3b shows the dependence of the HD linewidth on density. The data points are rather scattered across this plot, which is not surprising since the linewidths are inferred from unresolved spectral lines. A straight line fit to the data gives a broadening parameter of 0.01 cm⁻¹ amagat⁻¹ and this compares favorably with the earlier result of 0.006 cm⁻¹ amagat⁻¹ for HD in an unspecified mixture of H₂ at 77 K [87].

A frequency shift of the R(0) line of -0.03 cm⁻¹ is observed for the three highest density spectra (and the spectrum at 8.33 amagat). Previously measured frequency shifts at 77 K are: for HD mixed with H_2 , +0.16 × 10⁻³ cm⁻¹ amagat⁻¹ [87], and for pure HD 9 × 10⁻⁵ cm⁻¹ amagat⁻¹ [86]. The largest frequency shift predicted for the highest density spectrum measured in the present work is therefore +0.004 cm⁻¹, which is much smaller than the frequency step size of 0.030 cm⁻¹.

5.3.4 A Determination of the HD Concentration in D₂

The R(0) line is also present in the D_2 spectrum shown in Figures 5.1 and 5.2, where the line is much stronger and narrower than the H_2 spectra. The concentration of HD in the D_2 sample is measured using the integrated area of the R(0) line obtained from the fitting procedure and the HD dipole moment derived above. The HD/D₂ ratio is measured to be 1/339, in good agreement with the manufacturer's specification that the HD content is less than 1/250.

5.4 Future Investigations of HD Dimers

Under the low temperature conditions of these investigations, $HD-H_2$ dimers may form, and the dimer spectrum is predicted to show small 'satellite' lines near the R(0) line [98]. A measurement of the dimer spectrum requires obtaining high resolution spectra
of samples with high dimer concentrations. A 1% HD/H₂ gas mixture at a density of 3-6 amagat should exhibit 70-80% absorption at the R(0) peak using the present spectrometer-cell apparatus. This measurement would consume only 1-2 atm-liters of HD and the increased absorption should permit a more precise determination of the HD dipole moment. In order to observe the dimer spectrum it may be necessary to saturate the R(0) peak and measure spectra of 10 to 50% HD/H₂ mixtures.

Chapter 6

Experimental Errors

The systematic errors in these experiments fall into 4 categories: (1) errors associated with measuring the sample gas temperature and density; (2) errors associated with optical problems such as the alignment of the cell mirrors, and cell window distortions; (3) errors in the spectrum due to water ice impurities; and (4) errors due to detector nonlinearities. The dominant problem with the H₂ absorption spectra reported herein is the 5–10% mismatch between the LF and HF spectra (see Figures 4.12–4.17). The errors of the first 3 categories are too small to be responsible for the intensity mismatch, and this is is presumed to be due to detector nonlinearities.

6.1 Temperature, Pressure, and Density Errors

The method of measuring the sample gas temperature and density is discussed in the experimental chapter. In brief, the error in measuring the gas temperature results from using resistors mounted on the exterior of the cell (not in the gas itself), where the cell is non-uniform in temperature. The maximum temperature drift, or temperature gradient across the cell, is ± 1 K during data collection. Averaging the temperatures of the 4 cell resistors, 3 times during a sample data collection run, yields a temperature measurement with an estimated accuracy of ± 0.25 K.

The accuracy of the pressure transducer is two times worse than the manufacturer's stated accuracy, or about $\pm 1\%$ for the 1-3 atm pressures used in these experiments. The pressure sensor is at room temperature, whereas the sample is at low temperatures,

however, no significant pressure gradient exists along this density gradient since the sensing tube is 1" in diameter.

The gas density is obtained from the temperature and pressure measurements using the 2nd order virial coefficients and the error in the determination of the gas density is $\pm 1.5\%$ from the above considerations. The standard deviation of a set of density measurements of a 16.00 amagat gas sample sealed in the cell, over the temperature range 25-35 K, is 0.15 amagat, or an uncertainty of $\pm 1\%$.

6.2 Optical Errors

6.2.1 Spectrometer Calibration

The spectrometer frequency calibration has been established to better than 0.0025 cm⁻¹ by measuring the frequencies of CO, O₂, and H₂O lines. A spectrum of saturated CO lines is presented in Figure 7.5 where the infinite absorption level of the LF spectra is demonstrated to be accurate to better than 1% of the spectrum peak, for high resolution spectra. The infinite absorption level for the lower resolution H₂ spectra should be more accurate than the above case by a factor of 4, however, the residual baseline discussed in chapter 4 persists at a level of 0.5% of the spectrum peak.

6.2.2 The Reproducibility of Background Spectra

The estimated accuracy of the translational absorption spectra is based on the repeatability of background spectra taken at the beginning and end of a data collection run, a span of about 16 hours. Figure 6.1 shows the natural logarithm of the ratio of two such backgrounds, where ideally this 'absorption spectrum' should equal zero at every frequency. The reproducibility is quite good and the difference between the LF backgrounds corresponds to a 2% transmission error across the LF spectral region (omitting



Figure 6.1: An 'absorption spectrum' of LF backgrounds taken before and after the sample spectra which demonstrates the repeatability of the LF spectra.



Figure 6.2: An 'absorption spectrum' of HF backgrounds taken before and after the sample spectra which demonstrates the repeatability of the HF spectra.

the region of the beamsplitter null, $100-120 \text{ cm}^{-1}$), and a 1% transmission error between $40-90 \text{ cm}^{-1}$.

The repeatability of the HF background spectra is demonstrated in Figure 6.2. Over the region 50-200 cm⁻¹, the difference between the backgrounds corresponds to a transmission error of $\sim 3\%$, and over the region 200-320 cm⁻¹ a conservative estimate of the transmission error is $\sim 5\%$. The background ratio near 135 and 263-273 cm⁻¹ is anomalous owing to the absorption bands of the crystal quartz cold filter.

The repeatability of successive H₂ spectra, under the same conditions, is better than the background repeatability, and it corresponds to a 1% transmission variation across both spectral bands. For this reason, H₂ spectra at moderate densities are used as backgrounds for H₂ spectra at higher densities. The time interval between the high and moderate density spectra is about 1 hour, and the transmission error of these spectra is estimated to be about $\pm 1.5\%$ for the LF and HF cases.

The minimum transmission of the H₂ spectra at 25 K is 52%, where the absorption is limited by the maximum allowable gas density before the sample liquefies. The minimum transmission of the spectra at 35 K is 33%, where absorption is restricted by the 3 atm. pressure limit of the gas handling system. The uncertainty of the H₂ translational absorption band measurements, based on repeatability considerations, is conservatively estimated to be $\pm 2\%$ of the peak absorption from 40–90 cm⁻¹, $\pm 3\%$ across the LF region, and $\pm 5\%$ from 200–320 cm⁻¹.

6.2.3 Sources of Repeatability Errors

The background repeatability errors are caused by a number of systematic problems which are listed below. The sensitivity of the bolometer drifts owing to the temperature variation of the helium reservoir, but this problem has been minimized by pumping on the detector overnight before acquiring data. In a number of HF spectra, the detector sensitivity drifted due to a voltage drop of the preamplifier batteries. The intensity of the mercury arc source is stable and it is not a contributor to the repeatability error.

Pressurizing the cell with the sample gas slightly affects the mirror alignment, and the multipass cell has to be realigned between initial backgrounds, sample spectra, and final backgrounds. As a result, the optical paths of the various spectra do not intersect exactly the same regions of the absorption cell mirrors and windows and the cell transmission changes; this is a significant problem.

The AC detector signal increases as the cell is cooled since the reflectivity of the mirrors increases as the temperature decreases; however, efforts have been made to acquire spectra and backgrounds at nearly the same temperature. The problems of changes in the cell optical path, and the changes in reflectivity with temperature become even more significant if ice coats the mirrors.

6.2.4 Additional Sample Spectra Errors

The above suggestions as to the origin of transmission errors pertain to both background and sample spectra; however, some errors occur only with the sample gas in the cell. Density fluctuations in the optical path due to sample gas turbulence cause a low frequency variation of the transmitted light intensity. The fluctuations occur below 1 Hz, but the spectrum below 25 cm⁻¹ may be perturbed. The addition of the fluctuations to the sample spectra may slightly lower the absorption spectra, but this effect is not obviously noticeable. Turbulence has been previously discussed in the experiment chapter.

Pressurizing the cell with the sample gas can cause ripples in the absorption spectrum since a slight change in the cell window's thickness or position results in the failure of the sample and background 'channel' spectra to exactly cancel (see background spectra Figure 3.8). The window distortion effect is illustrated by the oscillating curve in Figure 6.3 which is the LF spectrum of helium at 2087 Torr at room temperature over a path



Figure 6.3: The absorption spectrum of helium demonstrating the error due to window distortions. The oscillating curve is He at 294 K and 2087 Torr. The flat curve is He at 78 K and 2010 Torr. The pathlength is 52 m.

of 52 m. The zero crossings of this curve correspond to the peaks and troughs of the background spectrum, and the magnitude of the effect depends upon the gas pressure. The flat curve of Figure 6.3 is the spectrum of He at 78 K at a similar pressure, it demonstrates that the windows are far less flexible at low temperatures (see also Figure 6.8). Low temperature window distortions cause at most a $\pm 1\%$ transmission error, and the deviation of this helium spectrum from zero absorption is another indicator of the accuracy of the absorption measurements.

6.2.5 Pathlength Errors

The cell mirrors are located on each other's centers of curvature and the error in the mirror spacing is less than 1 mm. The mirror adjustment mechanism is designed to minimize any spacing changes as the folding mirrors are rotated, and the mirror spacing is determined by invar bars which change in length by only 5 parts in 10⁴ as the temperature is lowered

to 20 K. It is possible that the number of spots along the field mirror has been miscounted resulting in a pathlength error of ± 4 m, or 7%. This miscounting error might account for the LF/HF intensity mismatch, but the pathlength was adjusted with great care, and the LF spectra measured over 52 and 60 m paths overlap appropriately. The pathlength error is estimated to be 0.1% of the optical path.

The overlap of neighbouring spots at the cell exit aperture allows radiation propagated over a path of $n\pm 4$ meters to be detected along with the desired optical path of n meters. The intensity distribution at the cell exit is unknown, and hence the contribution to the detected signal from pathlengths other than the desired one is also unknown. On the basis of the cell optical tests discussed in Appendix 1, the contamination of the 60 m signal by other paths is estimated to be less than 5%; at 52 m the contamination is negligible.

6.3 Water Ice

6.3.1 Ice Absorption

A spectral feature at 230 cm⁻¹ is noticeable in all the HF hydrogen spectra, particularly in the 25.5 K spectra. In addition, a band of excess absorption is observed over the frequency range 180-300 cm⁻¹ in the 25.5 K spectra. These features are due to very small quantities of ice in the multi-pass cell, where this this conclusion is based on the comparison of the present spectra to previously reported ice spectra [99],[100],[101].

Over the $\sim 3-4$ week course of a low temperature data collection run, the background spectra are observed to change. Figure 6.4 shows the absorption spectrum of a background at the end of a run with respect to a background near the beginning. Note that negative absorption indicates that the IR source intensity was higher in the later spectrum. Figure 6.6 shows the far-infrared absorption spectrum of conventionally formed ice I, where the broad peak demonstrates that it is an orientationally disordered phase. Figure 6.5 shows the multi-peaked absorption spectrum of ice II, an orientationally ordered phase, which is formed under high pressures (2 Kbar) at -50° C. Starting at the high frequency end of the spectra, every feature of Figure 6.4 corresponds to a line of ice II, except the strong peak at 230 cm⁻¹ and the dip at 180 cm⁻¹ which correspond to ice I features (an additional peak at 70 cm⁻¹ is possibly due to ice IX). The frequency correspondence between these spectra is not exact, but frequency shifts are expected since Figure 6.4 was obtained at a much lower temperature.

The source of the ice is probably the 5 ppm residual water vapour content of the UHP sample gases. The sample gas passes through a molecular sieve and liquid nitrogen traps en route to the the cell, but appears that the water vapour is not entirely frozen out. A typical gas sample uses about 5-700 atm-liters of gas which are flowed into the cell over 1-2 hours, and the entire experimental run involves over 5000 atm-liters of gas. If all the the water vapour content of this gas enters the cell and uniformly coats the walls and mirrors, then an ice film ~ 25 nm thick is formed. The infrared beam reflects off the mirrors up to 59 times and absorption by the ice film alters the background spectrum.

In addition to the water content of the sample gases, leaks or outgassing of the vacuum system could coat the cell entrance and exit windows with an ice film. In fact, the pyrex viewing window on the inner radiation shield slightly fogs with ice over the course of an experimental run, but this is presumably caused by minor vacuum leaks which occur as the mirror adjustment rods are turned.

6.3.2 Phase Effects

Ice has more solid phases than any other known substance and Figure 6.7 shows the phase diagram of ice. The phase boundary between ice I and ice II is of particular interest here, since it may be extrapolated to zero pressure at zero temperature. Apparently ice II is



Figure 6.4: The 'absorption spectrum' of HF backgrounds near 30 K over a 60 m path taken at the end, with respect to the beginning, of a low temperature run.



Figure 6.5: The absorption spectrum of ice II, from [99].



Figure 6.6: The absorption spectrum of ice I, from [101].

formed when the cell is pressurized to 1-3 atm at 20-30 K and it remains ice II, in a metastable state, even when the pressure is relieved [99]. Other forms of solid water exist and ice forms in a vitreous phase and in a form with voids filled with entrained gases; the latter form is certainly a possibility in the present case.

An interesting effect is observed when measuring the spectrum of helium at low temperatures. Figure 6.8 shows the spectrum of helium taken near the middle of a data collection run (not too much ice in the cell). The He spectrum is expected to be the same as an empty cell background, and the 2% transmission error reflects the repeatability error referred to above. If a straight line is drawn across this graph at the 2% level, a lump of excess absorption from 180 to 260 cm⁻¹ is seen along with a negative absorption dip at 230 cm⁻¹. The shape of this excess absorption strongly resembles the excess intensity of the H₂ translational spectra at 25.5 K (Figures 4.15 and 4.16). The negative dip has reached over -13% in the latter stages of the experiment when observing He at 3 atm pressure.

The negative absorption is possibly due to a change in the ice film absorption or reflection which occurs as the phase boundary between ice I and II is crossed when the



Figure 6.8: The absorption spectrum of helium at 760 Torr and 25.5 K over a 60 m path. The ice features above 180 cm⁻¹ resemble the distortion of the H_2 average spectra.

cell is pressurized. The dip is not observed when comparing backgrounds taken at the beginning and end of a day of data collection (see Figure 6.2), although a disturbance of the spectrum does occur here. Apparently, a change in the optical properties of the ice film occurs and then reverts to the initial state, perhaps with a time delay, as the cell is pressurized and evacuated. The behaviour of low temperature ice films would be an interesting project for further investigations.

The H₂ translational band average spectra are derived from helium, or lower density H_2 , backgrounds whenever possible to avoid the ice features. This procedure works well for the 36 K spectra, but the 25.5 K spectra exhibit ice absorption unless the spectra which compose the average are carefully selected. The ice features may be more prominent at 25.5 K because these spectra have been obtained late in the run when there is more ice in the cell, or perhaps the ice properties are particularly dependent on temperature. It is not possible to simply remove the excess ice absorption of the spectra because the quantity of ice which coats the mirrors is unknown, and the absorption coefficient per unit length of ice II has not been reported [100].

6.4 Detector Non-Linearities

The previous uncertainties are all substantially smaller than 10%, and it is believed that the discrepancy between the LF and HF spectra is caused by nonlinearities of the germanimum bolometer. The evidence for the detector nonlinearity consists of a measured increase in the interferogram contrast as a function of a decrease in the optical signal amplitude, and the correspondence between the H_2 spectra and simulated absorption spectra involving a hypothetical nonlinearity. Attempts have been made to measure the detector nonlinearity directly, but these have not been successful, and the exact origin of the intensity mismatch between the LF and HF spectra remains unknown.



Figure 6.9: The interferogram contrast as a function of the detector signal amplitude. The circles are measurements, the triangles are estimates based on a nonlinearity constant of $\epsilon = 0.5 \times 10^{-6}$ and a contrast of 0.8.

6.4.1 Interferogram Contrast

The optical bandpass of the HF spectrum is roughly twice that of the LF spectra, and to obtain similar detector operating conditions for the two cases, the interferometer output aperture and source intensity have been reduced for the HF spectra. Despite these alterations, the amplitudes of the chopped detector signals of the HF spectra are 1.4–1.6 times greater than the LF cases. The anomalously low absorption of the HF spectra may be caused by a detector nonlinearity since the HF background spectra, in particular, would be reduced in intensity. Note that the signal processing electronics of the lock-in amplifier, low pass filter, and A-D converter are all tested to be linear over the signal range of the LF and HF spectra.

A detector nonlinearity would be most apparent in the interferogram peak height, since the detector signal is roughly doubled in amplitude as the interferometer passes through zpd. An experiment has been conducted after the hydrogen experiments to examine the interferogram peak height as a function of the DC level, the lock-in output signal when the interferometer is far from zpd. The interferogram contrast

contrast =
$$\frac{\text{peak-DC level}}{\text{DC level}}$$
 (6.1)

increases as the DC level decreases. Figure 6.9 shows the measured contrast as a function of the DC level, where the signal is attenuated by shifting the output spot of the multipass cell across the field mirror edge. The effect demonstrated in Figure 6.9 may not be entirely related to a detector nonlinearity, but it is possibly due to the nonuniformity of the interference fringes across the beamsplitter.

6.4.2 A Computer Simulation of Detector Nonlinearity

A computer simulation has been performed to test the hypothesis that the detector signal V_m , is related to the applied optical power P, and a gain g, by

$$V_{\rm m} = g(P - \epsilon P^2) \tag{6.2}$$

where ϵ is the strength of a simple nonlinearity term. The triangles of Figure 6.9 simulate the contrast as a function of the DC level for $\epsilon = 0.5 \times 10^{-6}$ (in 16 bit A-D units) and an assumed contrast of 0.80. The spectrum obtained from the Fourier transform of an interferogram recorded by the above detector response consists of two terms,

$$H(\sigma) = (1 - 2\epsilon I_{o}) S(\sigma) - \epsilon C(\sigma)$$
(6.3)

where I_o is the interferogram DC level, $S(\sigma)$ is the true spectrum, and $C(\sigma)$ is the autocorrelation function of the true spectrum [102]. The simulated spectrum equals the true spectrum multiplied by a factor less than unity, and it is reduced further in intensity at low frequencies where the autocorrelation function is largest. The measured cosine background spectra and simulated background spectra are both slightly negative at high frequencies. At frequencies below 20 cm⁻¹, the simulated spectra are even more negative than at high frequencies, but the measured cosine spectra are positive; in this regard the simulation does not represent the measurements. The absorption of hydrogen is derived from power spectra, and at least for high frequencies, the residual baseline of the spectra discussed in chapter 4 may be related to squaring the negative cosine coefficients.

Absorption spectra derived from the simulated nonlinear spectra are lower in intensity than the true absorption, and simulated absorption spectra droop significantly below the true absorption over spectral regions where the background has low intensity. The measured H₂ absorption spectra exhibit a similar drooping over the region of the LF beamsplitter null (see Figure 4.1) and below 65 cm^{-1} in the HF spectra. The reproduction of this absorption droop suggests that the measurements have been affected by a detector nonlinearity.

6.4.3 Corrected Interferograms

The effect of the nonlinearity on the measured interferograms can be corrected provided that ϵ and the true interferogram contrast are known. By assuming $\epsilon = 0.5 \times 10^{-6}$ and a contrast of 0.8, corrected interferograms yield LF background spectra which are zero at high frequencies, and LF absorption spectra which no longer droop near the beamsplitter null. However, the residual baseline of a corrected background spectrum is raised near 100 cm^{-1} , and below 10 cm^{-1} , regions where it seems reasonable to expect zero intensity.

If the ϵ used to correct the LF spectra is now applied to the HF spectra, the 10% intensity discrepancy between the two spectral regions remains unaffected. An ϵ four times greater than the LF case is required to raise the HF high frequency cosine terms to zero. The HF absorption spectra obtained using this larger ϵ have a higher absorption,

but the droop of the HF spectra below 65 cm^{-1} is not affected by either correction.

The correction of the interferograms using this simple model of the detector nonlinearity has proven unsatisfactory since the same nonlinearity factor does not apply to both frequency regions. The LF and HF spectra are not brought into coincidence by this correction and the the low frequency portions of the HF spectra remain anomalously low. The removal of the residual baseline, however, does somewhat correct the low frequency droop of the HF spectra, and this procedure is described in chapter four.

6.4.4 Detector Nonlinearity Tests

Measurements of the nonlinearity of the detector have been conducted by changing the distance r between the detector and a source. The nonlinearity was expected to appear as a diminished signal at small r with respect to a $1/r^2$ detector signal dependence. A mercury arc source, with a water cooled shroud and a chopper, was mounted on an optical bench slide and the distance to the detector was varied from 53 to 135 cm. The chopper frequency was 162 Hz, the detector low-pass filter was crystal quartz, and the detector signal amplitude was varied over the same range as the hydrogen experiments. The optical bench was enclosed by a plexiglass box and a polyethylene tent which were purged with both nitrogen gas from a cylinder and the boil-off gas of liquid nitrogen.

A nonlinearity has been repeatably detected, but as a *larger* signal than expected at close distances. This nonlinearity is due to residual water vapour in the optical path, despite thorough nitrogen purging. In fact, over the ~ 24 hour course of the tests, the detector signal at a given source distance continuously rose as the water vapour content diminished.

The data has been fitted by a function which includes an e^{-kr} water vapour absorption term, and still the detector signal at small r exceeds the value of the fit. The anomalous high signal at small detector-source distances may be caused by fitting data which includes a small offset, so that the signal at an infinite source distance is not zero. This situation can arise if the detector signal is not zero even though the source is off.

The measurement of the detector nonlinearity turned out to be surprisingly difficult. The present tests are too imprecise to observe the suspected nonlinearity.

6.4.5 Detector Nonlinearity Comments

The bench top tests measure the response of the detector to slow changes in optical power; however, as the interferometer passes through zpd, the optical power increases and decreases rapidly. The frequency response of the bolometer depends upon a number of temperature dependent properties such as the heat capacity of the absorber and the thermal conductivity of the wires to the helium reservoir. The sensitivity and time constant of the detector can therefore change as the bolometer warms in response to an increase in the optical power. In the present case, the 162 Hz chopping frequency is comperable to the detector time constant, and the detector response to a rapid change of optical power is complicated.

A new test needs to be performed which measures the detector response at the chopping frequency, to rapid changes in optical power. The contrast tests previously mentioned have done this, but not very precisely. If the source is chopped at 162 Hz, and the source intensity is varied using 2 polarizers, and a third polarizer is spun at 2-4 Hz, then the amplitude modulation of the chopped detector signal can be examined as a function of the source intensity. This proposal simulates the dynamic interferogram signal, and the optical path and water vapour absorption would remain constant during such a test.

Chapter 7

Other Spectroscopic Studies

During the course of measuring the translational band of hydrogen, a number of other problems have been studied. The main emphasis of these projects has been the search for dimer spectral features in the far-infrared. Highlights of these projects and particularly interesting absorption spectra are presented in this section. In general these spectra demonstrate the capabilities of the spectrometer-cell apparatus when applied to the measurement of weakly absorbing gases. It is also notable that these low temperature spectra are not contaminated by water vapour lines, a common problem in far-infrared spectroscopy.

The gases used in these studies were supplied by Linde and the grades and purities are: D₂, CP, 99.5%; H₂, UHP, 99.999%; He, UHP, 99.999%; Ar, UHP, 99.999%; Ne, UHP, 99.996%; N₂, Medical, 99.998%; CH₄, UHP, 99.97%; CO, CP, 99.5%; O₂, UHP, 99.995%.

7.1 The Deuterium S(0) line

The translational absorption band of D_2 is shown in Figure 5.1, and the frequency region of the S(0) line (179 cm⁻¹) from this data set is shown in Figure 7.1. The peak of the D_2 translational band has the same absorption as the lowest point of Figure 7.1; this comparison demonstrates yet again the extremely weak absorption of the translational band. The spectral structure due to D_2 dimer bound state transitions superimposed on the collision-induced S(0) line is evident, and it matches the structure found in previous low temperature D₂ spectra reported by McKellar [28]. A marked increase in the intensity of the dimer lines is observed as the temperature is lowered only 10 degrees. D₂ dimer transitions should also be present in the translational band below 20 cm⁻¹, but observing this spectral region requires a low frequency polarizing interferometer. In the early phases of the present work, observations were also made of the S(0) frequency region of H₂ (354 cm⁻¹) from 20-40 K.

7.2 Hydrogen-Rare Gas Mixtures

A pure monoatomic gas exhibits no collision-induced absorption at low densities. However, adding a monoatomic gas to hydrogen, or other diatomic gases, will enhance the measured absorption spectrum. The absorption of radiation by a gas mixture takes place via transient dipoles induced in both H_2 - H_2 collisions and H_2 -rare gas collisions. H_2 - H_2 absorption is dominated by the quadrupole induced dipole, and the H_2 quadrupole moment acting on a polarizable rare gas atom will also induce a dipole moment. During H_2 -rare gas collisions additional absorption occurs due to an isotropic overlap induced dipole moment, where this mechanism is absent in pure H_2 - H_2 collisions due to their symmetry.

The absorption coefficient for a gas mixture (per unit pathlength) at a given frequency is

$$A = \alpha_{\rm H_2} \rho_{\rm H_2}^2 + \alpha_{\rm H_2-X} \rho_{\rm H_2} \rho_{\rm X}$$
(7.1)

where α_{H_2} is the absorption coefficient of H_2 (per unit density squared of H_2), α_{H_2-X} is the absorption coefficient of the H₂-rare gas enhancement (per unit density H₂, per unit density rare gas), and ρ_{H_2} and ρ_X are the densities in amagat units of the H₂ and rare gas components of the sample [12],[1]. There is an alternative definition of the mixture absorption coefficient in terms of the absorption coefficient, per collision pair per unit



Figure 7.1: The absorption spectrum of D_2 near S(0). The density is 2.93 amagat, the pathlength is 52 m, and the curves from highest to lowest correspond to temperatures of: 23.1, 26.7, 28.9, 33.3 K. Note the strong dependence of the dimer lines on temperature.



Figure 7.2: The absorption spectra of H_2 and a H_2 -He mixture for a path of 60 m. The density and temperature of the lower H_2 spectrum is: 9.03 amagat, 25.8 K, and 8.66 amagat of He is added to obtain the upper spectrum at 25.3 K. The He enhancement of the H_2 spectrum is mainly due to the isotropic overlap induced dipole moment.

density, of the H₂ and H₂-X sample components [103]. Using either definition, if the rare gas atom has the same polarizability as H₂, and no isotropic overlap induction occurs, a 50/50 mixture at the same density as a pure H₂ sample has 1/2 the absorption.

If the overlap induced dipole moment is insignificant, the shape of the spectrum remains unchanged by the addition of the rare gas to the hydrogen sample. However, the A(0001) isotropic overlap component of the induced dipole moment allows pure translation transitions only (and Q branch vibrational transitions), and it can strongly enhance and alter the translational spectrum.

The absorption of H₂-Ar mixtures has been studied over a pathlength of 52 m at 78 and 88 K by flowing liquid nitrogen or argon through the heat exchanger tubing of the multipass cell. The LF spectrum of H₂ and the LF spectrum of a 50/50 mixture of H₂-Ar, where both samples are at 88 K and 1.62 atm pressure, have similar bandshapes and intensities. The absorption maxima and frequencies are: H₂, 0.052 at 65 cm⁻¹; and H₂-Ar, 0.054 at 65 cm⁻¹. The similarity of the spectra demonstrates that the polarizability of argon is roughly two times larger than H₂, and that overlap induction is not significant.

The LF absorption spectrum of H₂-Ne mixtures has been observed using a 52 m pathlength at temperatures near 32 K, and the peak of the spectrum is dramatically shifted. The gas pressure, absorption maxima and peak frequencies are: H₂, 1.35 atm., 0.3 at 57 cm⁻¹; H₂-Ne, 1.02 atm., 0.1 at ~100 cm⁻¹. This simple comparison suggests that isotropic overlap must be significant in order to shift the the peak of the spectrum, and that the polarizability of neon is smaller than H₂ (it is 1/2 that of H₂). Bound state transitions of H₂-rare gas complexes are expected to occur in the very low frequency regions of these spectra, but no obvious structure has been observed.

The absorption of H_2 -He is the most significant mixture spectrum from an astrophysical point of view. The concentration of He in the gaseous planets has been established by modelling the the Voyager far-infrared spectra using laboratory measurements of H_2 and H_2 -He absorption spectra [12],[104]. H_2 rotational line absorption is dominated by the H_2 - H_2 interaction with a small He enhancement, as the polarizability of He is 1/4 that of H_2 . Over the translational band, however, H_2 -He collisions strongly enhance the absorption spectrum due to the isotropic overlap interaction.

The lower curve of Figure 7.2 shows the HF spectrum of H_2 at a density of 9.03 amagat at 25.8 K over a 60 m path, and the upper curve shows the enhanced absorption obtained at 25.3 K by adding 8.66 amagat of He to the gas sample. The shift of the peak frequency and the altered and enhanced bandshape are apparent and demonstrate primarily the effect of the isotropic overlap interaction. Given the astrophysical importance of H_2 -He mixtures and the unique low frequency measurement capability of the spectrometer-cell apparatus, this topic is worthy of further investigation.

The observations of the translational spectra of H_2 -rare gas mixtures are consistent with previous studies of the H_2 -rare gas collision-induced rotational spectra by Kiss, Gush, and Welsh [9]. This earlier work also demonstrates that the isotropic overlap induced dipole moment is significant for H_2 mixed with He and Ne, but not with Ar. The present observations are also consistent with the values of the polarizabilities reported in the literature [52].

7.3 Nitrogen-Argon Mixtures

Figure 7.3 shows the translational-rotational spectra of various N_2 and N_2 -Ar mixtures at 78 and 88 K over a pathlength of 52 m. These spectra are the highest sensitivity, highest resolution, and lowest density spectra of the translational-rotational band yet reported and are the first to show structure superposed on this collision-induced band. It is notable that the minima of the ripples occur at the frequencies of the N_2 free molecule S lines. This structure suggests that a band of unresolved dimer rotational lines is associated with



Figure 7.3: The absorption spectra of N_2 and N_2 -Ar mixtures. The pathlength is 52 m, the mixing ratio N_2/Ar , pressures and temperatures are: a, 100/0, 538 Torr, 78 K; b, 48/52, 1219 Torr, 88 K; c, 25/75, 729 Torr, 88 K; d, 51/49, 361 Torr, 88 K; e, 50/50 267 Torr, 78 K. Note the dimer structure superposed on the translational-rotational band.



Figure 7.4: The absorption spectra of CH_4 and CH_4 -Ar mixtures. The pathlength is 60 m, and the mixing ratio CH_4/Ar , pressures and temperatures are: a, 50/50, 1629 Torr, 115.5 K; b, 100/0, 794 Torr, 113.5 K; c, 50/50, 1138 Torr, 116 K; d, 50/50, 822 Torr, 117 K. The sharp centrifugal distortion dipole lines are observed on top of the collision-induced band.

each N_2 S line, where these dimer bands are analogous to unresolved P and R branches of the vibrational spectrum of a diatomic molecule. The maxima of such a spectrum would then appear offset from the frequencies of the N_2 S lines, as shown in Figure 7.3. At low frequencies the dimer ripples have a more complex shape; this indicates that intermolecular interactions involving N_2 molecules in low J states are anisotropic. Note that the overall intensity of curve a is roughly twice that of curve b indicating that the polarizability of Ar is roughly the same as N_2 , as is expected.

The structure of these spectra is very similar to structure observed in recent measurements of the fundamental vibrational band of N₂-Ar. [105]. The broad collision-induced rotational spectrum of N₂ has been measured many times, most recently reported in [106], and recent theoretical analysis is given in [47]. The present high resolution measurements are potentially valuable in assessing the validity of recent theoretical spectra [107],[108],[109]. The study of low temperature N₂-Ar mixtures is also relevant to the interpretation of the spectrum of Saturn's moon Titan which has an atmosphere composed of 82% N₂ and 15% Ar [110].

7.4 Methane-Argon Mixtures

Figure 7.4 shows the far-infrared absorption spectrum of CH_4 and CH_4 -Ar mixtures at various pressures near 115 K over a pathlength of 60 m. This work was motivated by the possibility that CH_4 -Ar dimer transitions might be observed at very low frequencies, or as 'satellite' lines on the wings of the sharp methane absorption lines. The present spectra are among the highest quality, highest resolution, and lowest density spectra yet reported, but in spite of this, no immediately obvious dimer features are observed.

The CH_4 molecule has no permanent dipole or quadrupole moments, and the broad

collision-induced baseline of Figure 7.4 results from the octopole and hexadecapole moments of the CH_4 molecule inducing transient dipole moments in CH_4 or Ar collision partners. Recently a low resolution, high density, experimental study of the CH_4 -Ar collision- induced spectrum has been reported [103]. The sharp lines in Figure 7.4 arise from the centrifugal distortion dipole moment, where analysis of these lines has been previously reported by Rosenberg and Ozier [111].

7.5 Carbon Monoxide-Argon Mixtures

Figure 7.5 shows the far-infrared transmission spectrum of the spectrometer-cell system, where the cell contains CO at a pressure of 7.4 Torr at 294 K, and the absorption path is 52 m. The electric dipole allowed rotational transitions of $^{12}C^{16}O$ are saturated, and this high resolution spectrum demonstrates the accuracy of the infinite absorption level and frequency calibration of the spectrometer. This spectrum is obtained from one sample and one background interferogram, where each requires about 60 min. integration time.

Figure 7.6 shows an expanded portion of the far-infrared absorption spectrum of a CO-Ar 27/73 mixture at a pressure of 30 Torr at 78 K over a 52 m. path. This investigation was motivated by McKellar's observation of CO-Ar dimer 'satellite' lines in the wings of the P and R lines of the CO fundamental vibrational band [112]. The present spectra are obtained from 4 sample interferograms, an observation time of 120 minutes. The ${}^{12}C^{16}O$ rotational lines are saturated and the other lines, in order of diminishing intensity, are due to ${}^{13}C^{16}O$, ${}^{12}C^{18}O$, and perhaps a ${}^{12}C^{17}O$ line at 41.2 cm⁻¹. Although the spectrum is quite good, the signal-to-noise is insufficient to observe any definite dimer structure. The dimer binding energy is likely to be dependent on the rotational state of the CO molecule and investigation of very low frequency CO lines is probably necessary to observe dimer structure.



Figure 7.5: The sample spectrum of CO at 7.4 Torr and 294 K over a pathlength of 52 m. The CO lines are saturated and this spectrum demonstrates the intensity and frequency calibration of the spectrometer.



Figure 7.6: The absorption spectrum of a 23/73 CO-Ar mixture at 30 Torr and 78 K over a pathlength of 52 m. The rotational lines of ${}^{12}C^{16}O$, ${}^{13}C^{16}O$, and ${}^{12}C^{18}O$, are observed, in order of diminishing intensity.

7.6 Oxygen

The low temperature spectrum of O_2 is shown in Figure 7.7, where the temperature, pressure, and pathlength are: 88 K, 241 Torr, and 52 m. O_2 demonstrates collision-induced absorption at high densities, but the sharp lines observed here are due to magnetic dipole allowed transitions. The electronic ground state of the oxygen molecule has 2 unpaired electrons with a net spin S=1. Coupling between the spin and the molecular rotation N splits the rotational energy levels into triplets, where the total angular momentum J=N+S. The selection rules for transitions within the triplets are: $\Delta N = 0$, $\Delta J = \pm 1$, and these transitions are observed in the microwave region near 2 cm⁻¹. Transitions between the triplets with the selection rules $\Delta N = 2$, $\Delta J = 0$, +1 [113], are responsible for the far-infrared absorption spectrum shown in Figure 7.7.

This spectrum demonstrates the performance of the spectrometer-cell system at high resolution, where the sample spectrum is obtained from 2 interferograms, requiring 90 minutes of observation time. The central lines of the two lowest triplets are nearly saturated, and this spectrum is notable for the absence of strong water lines which can easily overwhelm the O_2 spectrum at room temperature. Since this spectrum was obtained, a mercury arc source has been installed in the spectrometer and the signal-to-noise below 40 cm⁻¹ has been improved by at least a factor of 2.

The spectrum of the O_2 collision-induced vibrational band exhibits dimer structure similar to the N_2 dimer ripples of Figure 7.3 [114]. Again, evidence of dimer formation is expected to appear in the present spectrum, but it is not obviously apparent. The rotational spectrum of O_2 has previously been studied at room temperature [113], but the low temperature, magnetic dipole allowed rotational spectrum of O_2 is presented here for the first time.



Figure 7.7: The absorption spectrum of O_2 at 241 Torr and 88 K over a pathlength of 52 m. The lines are due to magnetic dipole rotational transitions.

Chapter 8

Conclusion

The far-infrared absorption spectrum of normal hydrogen gas has been measured over the frequency range 20-320 cm⁻¹, the temperature range 21-38 K, at pressures from 0.6-3 atmospheres. Since observations are performed on very low temperature gas samples, the collision-induced translational band of H_2 is better isolated from the rotational lines than previous higher temperature measurements; in fact, the translational band is isolated to practically the greatest extent possible. The H_2 translational spectrum is measured using new temperature and pressure conditions at a spectral resolution 10 times higher than previous studies.

These spectra comprise the best available measurements of an extremely weak absorption phenomenon. By comparison, the weak collision-induced absorption peak of the S(0) line of normal H₂ is over 15 times, and the S(1) peak over 50 times, greater than the peak of the translational band at these low temperatures. In addition, the present low temperature, low pressure spectra are the first experiments to search for dimer structure across the translational band.

Although dimer structure is not observed in these translational spectra (it may yet appear below 10 cm⁻¹), the R(0) dimer line of HD is observed as a sharp feature superposed on the translational continuum at 89.2 cm⁻¹. The analysis of the integrated area of this line yields a measurement of the HD electric dipole moment of $(0.81 \pm 0.05) \times 10^{-3}$ debye. This value corresponds to previous theoretical predictions and measurements made at higher temperatures and pressures.

The low temperature multi-reflection absorption cell developed for these experiments performs well, and optical pathlengths of 60 m are obtained even for wavelengths as long as 0.5 mm. The cell temperature instabilities and gradients are reasonably small and sample spectra are reliably acquired at very low temperatures. The absolute accuracy of the present spectra is comparable to previous measurements made in more convenient temperature regions.

The present spectra confirm the predictions of the Poll and Van Kranendonk theory of collision-induced absorption, and the measured integrated absorption coefficient is consistent with that calculated using the quantum mechanical pair distribution function obtained from the Lennard-Jones intermolecular potential. The low temperature results provide a closer correspondence between measurement and theory than all previous experiments over the temperature range 77-300 K. The temperature variations of the spectral invariants α_{1tr} and γ_{1tr} are extended to new temperature regimes, and new information is obtained regarding the H₂ intermolecular potential. The detailed shape of the present spectra should also provide a valuable test of modern ab-initio models of the H₂ intermolecular potential.

The low temperature spectra demonstrate the validity of fitting the H_2 translational band with the B-C lineshape function, where previous experiments have emphasized fitting the S(0) and S(1) rotational lines. The temperature variations of the B-C lineshape parameters are also extended to new temperatures, and this work may be applied to modelling the H_2 component of planetary spectra at very low temperatures.

Additional studies of H₂-rare gas, N₂-rare gas, and CH₄-Ar, CO-Ar, and O₂ have been undertaken in an effort to observe dimer structure in the far-infrared. Of these studies, the N₂ and N₂-Ar spectra most clearly demonstrate structure across the translationalrotational band.

The work presented in this thesis is also relevant to the longstanding astronomical

problem of detecting interstellar molecular hydrogen. A particularly important feature of these experiments is the demonstration that the D/H ratio of planetary atmospheres can be determined from the intensities of the HD R(0) line and the underlying H₂ translational band.

Appendix A

The Absorption Cell Optical Tests

Tests of the cell optical system were made on an optical bench using visible laser light and during the absorption measurements using far-infrared radiation. The visible tests establish the cell pathlength limits due to the aberrations of diffraction and astigmatism and these limits correspond well to calculated aberrations. The cell performance in the far-infrared is consistent with the limits determined from the bench top tests.

The diffraction spot size does not grow with successive reflections [66]. This was demonstrated by a test in which the cell mirrors were aligned on an optical bench and a 3 mm diameter aperture was placed over one of the folding mirrors. Laser light was introduced to the system such that the beam passed through this aperture many times. The Airy pattern at the cell exit was magnified and photographed. It was observed that the patterns corresponding to passage through the aperture 1,2,3,4,5, and 9 times were equivalent, and the same as predicted by the Airy disk diameter to better than 10%.

Diffraction is an aberration which is wavelength dependent, and in the visible, were no other aberration present, the maximum cell optical path would be 116 m, for an input spot of 6 mm diameter. The cell image also suffers from the optical aberration of astigmatism, where in this case, the image distortions accumulate with successive reflections.

The amount of image distortion due to astigmatism was calculated by following the appendix of Horn and Pimental [115]. Rays which reflect from one side of the field mirror to the other have the largest angle of incidence with respect to a folding mirror. The images on the field mirror associated with these paths therefore suffer the largest astigmatism as compared to smaller reflection angles. The distance between the sagittal and tangential focii is calculated by adding up the contributions to distortion from all of the reflection angles present in the multiple reflection cell. The diameter of the circle of least confusion is

$$d = \frac{s-t}{2f} \tag{A.1}$$

where s - t is the difference between the two focii and f is the f number of the beam. The results of calculating the distance between the sagittal and tangential focii and the astigmatic circle of least confusion from a point source input are tabulated below. Included in the table are measurements obtained from bench top tests of the White cell optics. The tests were made by focussing a laser at the field mirror edge such that the beam then fills the folding mirrors. Measurements of spot diameters were then made with a ruler.

s	pots	path (m)	s - t (cm)	diam(cm)	measured diam(cm)
	23	48	12.9	0.65	
	25	52	14.0	0.70	
	27	56	15.1	0.76	
	29	6 0	16.2	0.81	0.83
	45	92	24.8	1.24	1.25

Table A.1: The calculated and measured cell spot size as a function of pathlength due to astigmatism

The diffraction spot diameter for a 30 cm⁻¹ point source input to the multipass cell is 0.85 cm (see Table 3.1). For low frequency radiation, the table above shows that diffraction and astigmatism over long optical paths yield comparable distortions of the image. The effect of astigmatic distortion may be slightly reduced by defocussing the input image so that the spots on the field mirror are slightly elliptical, thereby allowing a longer path before spot overlap. Obviously at higher frequencies image distortion is due primarily to astigmatism.

The actual performance of the cell is very similar to the limits imposed by astigmatism and diffraction. During the operation of the cell in the low frequency far-infrared (20– 180 cm^{-1}), the overlap of spots was examined by comparing the intensity of a signal maximum to the neighbouring minimum as the pathlength is changed and spot images sweep across the field mirror exit. Note that these tests were conducted when the cell was at room temperature; the AC signal increases by about 10% when the cell is cold. The table below lists the number of field mirror spots, the corresponding pathlength, the ratio of a signal maximum to the neighbouring minimum, and the AC voltage of the detector signal which is proportional to the optical intensity.

spots	path (m)	ratio max/min	V _{AC}
23	48	19.2	1.227
25	52	9.4	1.198
27	56	5.9	1.164
29	60	3.5	1.119
31	64	2.6	1.057

Table A.2: The measured ratio of the cell far-infrared output signal maximum/minimum as a function of pathlength

The table above is only an indicator of the spot overlap as it uses the intensity of light at the midpoint between spots and not the contribution of the neighbouring spot at the center of the output image. Therefore, the estimates above are worst cases of overlap contamination, and the cell operates with virtually no pathlength ambiguity at 52 m and acceptable overlap up to \sim 60 m.

Bibliography

- H. R. Welsh. In MTP International Review of Science-Physical Chemistry, Volume 3, page 33, London, 1972. Butterworths.
- [2] G. Birnbaum. Phenomena Induced by Intermolecular Interactions NATO ASI Series, volume 127. Plenum Press, New York, 1985.
- [3] A. Borysow, L. Frommhold, and P. Dore. Int. Journal of Infrared and Mm Waves, 8(4), 1987.
- [4] J. Van Kranendonk. Physica, 23:825, 1957.
- [5] J. Van Kranendonk. Physica, 24:347, 1958.
- [6] J. Van Kranendonk Z. K. Kiss. Can. J. Phys., 37:1187, 1959.
- [7] J. D. Poll and J. Van Kranendonk. Can. J. Phys., 39:189, 1961.
- [8] D. R. Bosomworth and H. P. Gush. Can. J. Phys., 43:729, 1965.
- [9] Z. J. Kiss, H. P. Gush, and H. L. Welsh. Can. J. Phys., 37:362, 1959.
- [10] Z. J. Kiss and H. L. Welsh. Can. J. Phys., 37:1249, 1959.
- [11] Z. J. Kiss and H. L. Welsh. Phys. Rev. Lett., 2:166, 1959.
- [12] G. Birnbaum. J.Q.S.R.T., 19:51, 1978.
- [13] P. Dore, L. Nencini, and G. Birnbaum. J.Q.S.R.T., 30:245, 1983.
- [14] G. Bachet, E. R. Cohen, P. Dore, and G. Birnbaum. Can. J. Phys., 61:591, 1983.
- [15] L. M. Trafton. Ap. J., 147:765, 1967.
- [16] L. M. Trafton and G. Munch. J. Atm. Sci., 26:813, 1969.
- [17] R. Hanel, B. Conrath, M. Flasar, V. Kunde, P. Lowman, W. Maguire, J. Pearl, J. Pirraglia, R. Samuelson, D. Gautier, P. Gierasch, S. Kumar, and C. Ponnamperuma. Science, 204:972, 1979.
- [18] R. Hanel, B. Conrath, M. Flasar, L. Herath, V. Kunde, P. Lowman, W. Maguire, J. Pearl, J. Pirraglia, R. Samuelson, D. Gautier, P. Gierasch, L. Horn, S. Kumar, and C. Ponnamperuma. *Science*, 206:952, 1979.
- [19] R. Hanel, B. Conrath, M. Flasar, V. Kunde, W. Maguire, J. Pearl, J. Pirraglia,
 R. Samuelson, L. Herath, M. Allison, D. Cruikshank, D. Gautier, P. Gierasch,
 L. Horn, R. Koppany, and C. Ponnamperuma. Science, 212:192, 1981.
- [20] R. Hanel, B. Conrath, M. Flasar, V. Kunde, W. Maguire, J. Pearl, J. Pirraglia,
 R. Samuelson, D. Cruikshank, D. Gautier, P. Gierasch, and C. Ponnamperuma. Science, 215:544, 1982.
- [21] R. Hanel, B. Conrath, M. Flasar, V. Kunde, W. Maguire, J. Pearl, J. Pirraglia,
 R. Samuelson, D. Cruikshank, D. Gautier, P. Gierasch, L. Horn, and P. Schulte.
 Science, 233:70, 1986.
- B. Conrath, F. M. Flasar, R. Hanel, V. Kunde, W. Maguire, J. Pearl, J. Pirraglia,
 R. Samuelson, P. Gierasch, A. Weir, B. Bezard, D. Gautier, D. Cruikshank, L. Horn,
 R. Springer, and W. Shaffer. Science, 246:1454, 1989.
- [23] D. Gautier, A. Marten, J. P. Baluteau, and G. Bachet. Can. J. Phys., 61:1455, 1983.

- [24] R. Hanel, B. Conrath, D. Gautier, P. Gierasch, S. Kumar, V. Kumar, P. Lowman,
 W. Maguire, J. Pearl, J. Pirraglia, C. Ponnamperuma, and R. Samuelson. Space Science Reviews, 21:124, 1977.
- [25] V. Kunde, R. Hanel, W. Maguire, D. Gautier, J. P. Baluteau, A. Marten, A. Chedin, N. Husson, and N. Scott. Ap. J., 263:443, 1982.
- [26] B. E. Carlson, A. A. Lacis, and W. B. Rossow. Ap. J., 393:357, 1992.
- [27] A. R. W. McKellar. Ap. J., 326:L75, 1988.
- [28] A. R. W. McKellar and J. Schaefer. J. Chem. Phys., 95:308, 1991.
- [29] P. S. Parmar, J. H. Lacy, and J. M. Achtermann. Ap. J., 372:L25, 1991.
- [30] G. B. Field, W. B. Sommerville, and K. Dressler. Ann. Rev. Astron. Astro., 4:207, 1966.
- [31] J. M. Shull and S. Beckwith. Ann. Rev. Astron. Astro., 20:163, 1982.
- [32] S. Drapatz. In R. Lucas, A. Omont, and R. Stora, editors, The Birth and Infancy of Stars. Elsevier Science B. V., 1985.
- [33] J. Schaefer and W. Meyer. In J. Eichler, I. V. Hertel, and N. Stolterfoht, editors, Electronic and Atomic Collisions: invited papers of the XIII International Conference on the Physics of Electronic and Atomic Collisions, page 529, Amsterdam, 1984. North Holland.
- [34] H. P. Gush. Phys. Rev. Lett., 47:745, 1981.
- [35] H. P. Gush. In Gamow Cosmology, Bologna Italy, 1986. Soc. Italiana di Fisica.
- [36] H. P. Gush, M. Halpern, and E. H. Wishnow. Phys. Rev. Lett., 65:537, 1990.

- [37] J. Mather, E. Cheng, R. Eplee Jr., R. Isaacman, S. Meyer, R. Shafer, R. Weiss,
 E. Wright, C. Bennett, N. Boggess, E. Dwek, S. Gulkis, M. Hauser, M. Janssen,
 R. Silverberg, G. Smoot, and D. Wilkinson. Ap. J., 354:L37, 1990.
- [38] E. Wright, J. Mather, C. Bennett, E. Cheng, R. Shafer, D. Fixsen, R. Eplee Jr.,
 R. Isaacman, S. Read, N. Boggess, S. Gulkis, M. Hauser, M. Janssen, T. Kelsall,
 P. Lubin, S. Meyer, S. Moseley Jr., T. Murdock, R. Silverberg, G. Smoot, R. Weiss,
 and D. Wilkinson. Ap. J., 381:200, 1991.
- [39] E. H. Wishnow, I. Ozier, and H. P. Gush. Ap. J., 392:L43, 1992.
- [40] E. Bussoletti and G. Stasinska. Astron. and Astro., 39:177, 1975.
- [41] A. M. Boesgaard and G. Steogmann. Ann. Rev. Astron. Astro., 23:319, 1985.
- [42] B. Bezard, D. Gautier, and A. Marten. Astron. and Astro., 161:387, 1986.
- [43] J. D. Poll. PhD thesis, University of Toronto, 1960.
- [44] G. Birnbaum, B. Guillot, and S. Bratos. Adv. in Chem. Phys., 51:49, 1982.
- [45] J. Schaefer and A. R. W. McKellar. Z. Phys. D., 15:51, 1990.
- [46] G. Birnbaum and E. R. Cohen. Can. J. Phys., 54:593, 1976.
- [47] J. D. Poll and J. L. Hunt. Can. J. Phys., 59:1448, 1981.
- [48] J. D. Poll and J. L. Hunt. Can. J. Phys., 54:461, 1976.
- [49] R. N. Zare. Wiley-Interscience, New York, 1988.
- [50] H. P. Gush. Unpublished notes. On the Static Field Effect.

- [51] K. D. Moller and W. G. Rothschild. Far-Infrared Spectroscopy. Wiley Interscience, New York, 1971.
- [52] C. G. Grey and K. E. Gubbins. Theory of Molecular Fluids. Oxford Univ. Press, Oxford, 1984.
- [53] J. D. Poll and L. Wolniewicz. J. Chem. Phys., 68:3053, 1978.
- [54] J. D. Poll and M. S. Miller. J. Chem. Phys., 54:2673, 1971.
- [55] C. Kittel. Thermal Physics. Wiley, New York, 1969.
- [56] A. Watanabe and H. L. Welsh. Phys. Rev. Lett., 13:810, 1964.
- [57] L. M. Trafton. Ap. J., 146:558, 1966.
- [58] V. F. Sears. Can. J. Phys., 46:1163, 1968.
- [59] J. L. Hunt and J. D. Poll. Can. J. Phys., 56:950, 1978.
- [60] J. I. Steinfeld. Molecules and Radiation. MIT Press, 1981.
- [61] J. Schaefer. Astron. and Astro., 182:L40, 1987.
- [62] W. Meyer, L. Frommhold, and G. Birnbaum. Phys. Rev. A., 39:2434, 1989.
- [63] W. Meyer. In G. Birnbaum, editor, Phenomena Induced by Intermolecular Interactions NATO ASI series, volume 127, New York, 1985. Plenum Press.
- [64] J. Borysow, L. Trafton, L. Frommhold, and G. Birnbaum. Ap. J., 296:644, 1985.
- [65] A. R. W. McKellar and H. L. Welsh. Can, J. Phys., 50:1459, 1972.
- [66] E. H. Wishnow. Far-infrared absorption by liquid nitrogen and liquid oxygen. Master's thesis, University of British Columbia, 1985.

- [67] J. U. White. J. O. S. A., 32:285, 1942.
- [68] M. Born and E. Wolf. Principles of Optics. Pergammon, London, 1959.
- [69] H. P. Gush and M. Halpern. Rev. Sci. Inst., 63:3249, 1992.
- [70] G. K. White. Experimental Techniques in Low Temperature Physics. Oxford, London, 1968.
- [71] R. H. Sinclair, H. G. Terbeck, and J. H. Malone. In H. H. Plumb, editor, Temperature its Measurement and Control in Science and Industry, volume 4, Pittsburg, 1972. Inst. Soc. of Am.
- [72] J. J. Dymond and E. B. Smith. The Virial Coefficients of Pure Gases and Mixtures: A Critical Compilation. Clarendon, Oxford, 1980.
- [73] D. R. Bosomworth and H. P. Gush. Can. J. Phys., 43:729, 1965.
- [74] H. L. Buijs and H. P. Gush. Journal de Physique, Colloque C2, Supplement 3-4:C2-105, 1967.
- [75] N. Moazzen-Ahmadi, H. P. Gush, M. Halpern, A. Leung, and I. Ozier. J. Chem. Phys., 88:563, 1988.
- [76] J. Van Kranendonk. Solid Hydrogen. Plenum Press, New York, 1983.
- [77] E. R. Grilly. Rev. Sci. Inst., 24:72, 1953.
- [78] A. Farkas. Orthohydrogen, Parahydrogen and Heavy Hydrogen. Cambridge University Press, London, 1935.
- [79] R. G. Gordon and J. K. Cashion. J. Chem. Phys., 44:1190, 1966.

- [80] G. Danby and D. R. Flower. J. Phys. B.: At. Mol. Phys., 16:3411, 1983.
- [81] L. Frommhold, R. Samuelson, and G. Birnbaum. Ap. J., 284:L79, 1984.
- [82] A. R. W. McKellar. Can. J. Phys., 62:760, 1984.
- [83] K. M. Evenson, D. A. Jennings, J. M. Brown, L. R. Zink, K. R. Leopold, M. D. Vanek, and I. G. Nolt. Ap. J., 330:L135, 1988.
- [84] G. C. Wick. Atti R. Accad. Naz. Lincei, Mem. Cl. Sci. F.3. Mat. Nat., 21:708, 1935.
- [85] M. Trefler and H. P. Gush. Phys. Rev. Lett., 20:703, 1968.
- [86] A. R. W. McKellar, J. W. C. Johns, W. Majewski, and N. H. Rich. Can. J. Phys., 62:1673, 1984.
- [87] L. Ulivi, Z. Lu, and G. C. Tabisz. Phys. Rev. A., 40:642, 1989.
- [88] P. Essenwanger and H. P. Gush. Can. J. Phys, 62:1680, 1984.
- [89] L. Ulivi, P. DeNatale, and M. Ignuscio. Ap. J., 378:L79, 1991.
- [90] J. D. Poll. In G. Birnbaum, editor, Phenomena Induced by Intermolecular Interactions NATO ASI Series, volume 127, page 677, New York, 1985. Plenum Press.
- [91] H. Craig. Science, 133:1833, 1961.
- [92] C. H. Townes and A. L. Schalow. *Microwave Spectroscopy*. Dover, New York, 1975.
- [93] H. P. Gush. Unpublished notes. The Fitting of the Unresolved HD Line.
- [94] R. H. Tipping, J. D. Poll, and A. R. W. McKellar. Can. J. Phys., 56:461, 75.
- [95] R. M. Herman. Phys. Rev. Lett., 42:1206, 1978.

- [96] N. H. Rich and A. R. W. McKellar. Can. J. Phys., 61:1648, 1983.
- [97] W. R. Thorsen, J. H. Choi, and S. K. Knudson. Phys. Rev. A., 31:22, 1985.
- [98] J. Schaefer. Private communication. The Predicted HD-H₂ Dimer Spectrum, 1992.
- [99] J. E. Bertie, H. J. Labbe, and E. Whalley. J. Chem. Phys., 49:775, 1968.
- [100] J. E. Bertie, H. J. Labbe, and E. Whalley. J. Chem. Phys., 50:4501, 1969.
- [101] E. Whalley. In N. Reihl, B. Bullemer, and H. Engelhardt, editors, Physics of Ice, New York, 1969. Plenum Press.
- [102] H. P. Gush. Unpublished notes. A Model of the Detector Nonlinearity.
- [103] P. Dore and A. Filabozzi. Can. J. Phys., 68:1196, 1990.
- [104] G. Birnbaum, G. Bachet, and L. Frommhold. Phys. Rev. A., 36:3729, 1987.
- [105] A. R. W. McKellar. J. Chem. Phys., 88:4190, 1988.
- [106] I. R. Dagg, A. Anderson, S. Yan, W. Smith, and L. A. A. Read. Can. J. Phys., 63:625, 1985.
- [107] G. Brocks and A. van der Avoird. Molecular Phys., 55:11, 1985.
- [108] G. Brocks. PhD thesis, Katholieke Universiteit de Nijemegan, Nijemegan, Netherlands, 1987.
- [109] A. G. Ayllon, J. Santamaria, S. Miller, and J. Tennyson. Molecular Phys., 71:1043, 1990.
- [110] W. R. Thompson and C. Sagan. Icarus, 60:236, 1984.
- [111] A. Rosenberg and I. Ozier. J. Mol. Spect., 56:125, 1975.

- [112] A. R. W. McKellar. Chem. Phys. Lett., 186:58, 1991.
- [113] R. T. Boreiko, T. L. Smithson, T. A. Clark, and H. Wieser. J.Q.S.R.T., 32:109, 1984.
- [114] C. A. Long and G. E. Ewing. J. Chem. Phys., 58:4824, 1973.
- [115] D. Horn and G. C. Pimental. Applied Optics, 10:1983, 1971.