A STUDY OF PREMELTING
IN THE
C-FORMS OF STEARIC, PALMITIC, MYRISTIC AND LAURIC ACIDS
BY
INFRARED SPECTROSCOPY
AND IN
ANHYDROUS SODIUM STEARATE
BY
HIGH RESOLUTION NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY
by
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B.Sc., University of British Columbia, 1960

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
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of
Chemistry

We accept this thesis as conforming to the required standard

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ABSTRACT

A general discussion of melting and premelting is given. Crystal structures and phase transitions in the C-forms of stearic, palmitic, myristic and lauric acids and in anhydrous sodium stearate are also discussed. Simple theories of infrared and nuclear magnetic resonance spectrometry are presented.

Experimental difficulties in the use of solid phase infrared spectra are discussed. A detailed study is made of the temperature behaviour of the infrared spectra of the fatty acids in the region from 750 to 700 cm$^{-1}$ and over the range from about 700$^\circ$ below the melting points to about 200$^\circ$ above them. Three overlapping peaks of different intensity are resolved - 720 cm$^{-1}$, about 727 cm$^{-1}$, and a peak at higher frequency the position of which varies in the different acids. The complete disappearance of the 720 cm$^{-1}$ band slightly below the melting point in each acid is taken to indicate a transition, not previously reported, to a disordered phase in which there is considerable molecular motion as evidenced by the phase's liquid-like spectra. The presence of three peaks in the region is discussed on the basis of a simple theoretical expression derived by Snyder for the position of fundamental methylene rocking vibrations. The crystallinities of the acids are estimated from an expression, based on the work of Stein and Sutherland, which involves the apparent integrated
absorption intensities of the resolved 720 and 727 cm\(^{-1}\) bands. The extent of premelting is determined. Extensive premelting giving the spectra a liquid-like, but not completely liquid character is found to take place within about 20\(^\circ\) of the melting point.

The high resolution nuclear magnetic resonance spectra of anhydrous sodium stearate were taken at the limit of their experimental application. The spectra show, however, that the subwaxy, waxy, superwaxy and subneat phases of anhydrous sodium stearate form a structurally similar group (from about 120 to 235\(^\circ\)C) with liquid-crystalline properties, while the neat and melt phases also form a structurally similar group (from 235\(^\circ\)C upwards) but with the properties of a liquid.

The information indicates extensive premelting beginning in the vicinity of 120\(^\circ\)C, below which temperature the salt is essentially crystalline, which reaches a climax at 235\(^\circ\)C, above which temperature the salt is essentially liquid.
ACKNOWLEDGEMENTS

Considerable thanks are due to Dr. B.A. Dunell who directed this research. His advice and cheerful good nature have been highly appreciated.

Thanks are also due to my colleagues Messrs. Allan, Janzen, Krakower and Ware who alternately coerced and cajoled the reluctant high resolution spectrometer into working condition during the last portion of this investigation.
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CHAPTER I

INTRODUCTION

In many compounds certain anomalous behaviour is observed close to but below the melting point. This behaviour, attributed to the phenomenon of premelting, is found in, among other substances, straight-chain paraffins (1) and similar compounds such as the fatty acids. As an extension of previous work (2), stearic acid was re-examined in more detail and palmitic, myristic and lauric acids also investigated.

In numerous cases of compounds containing four or more consecutive CH₂ groups, a doublet in the region of 720 cm⁻¹ is observed in the infrared spectrum. Previously it had been considered that under the above conditions the band in this region was always a doublet (3), however, more recently it has been shown that the appearance of the band as doublet or singlet is dependent on the sample's crystal structure (4)(5). The doublet (as will be noted later, there may be more than a single doublet) has been found by many investigators (6)(7)(8)(9). When present, the behaviour of the doublet - split at low temperature, single in the immediate vicinity of and above the melting point (8)(9) - suggests that it may be used as an indication of the premelting in fatty acids. This investigation was intended to explore that possibility and also to determine the possibility of correlating infrared results with results obtained in nuclear magnetic resonance studies of the acids (10)(11).
In addition to infrared work, high temperature (120°C and above) phase transitions were investigated in sodium stearate. These observations were made by high resolution nuclear magnetic resonance techniques in an extension of work begun in this laboratory with broad line methods (12).
CHAPTER II

MELTING AND PREMELTING

Premelting refers to changes in the solid as it approaches the melting point. These changes anticipate to a lesser degree the changes occurring in the actual solid to melt transition. There may be present thermodynamic anomalies such as enhanced specific heat, coefficient of thermal expansion, electrical conductance (of ionic crystals), or plasticity (13). Measurements of thermal conductivity (14) and elastic moduli (15) also show anomalies attributable to premelting as do infrared (2) and nuclear magnetic resonance spectra (10)(11).

Information about phase changes and premelting may be obtained in several ways. While heats and temperatures of fusion vary over a very large range, the entropies of fusion of all compounds are of the same order - about one to ten entropy units (16). The Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} \quad \ldots \ldots \ldots \ldots \ldots (1)$$

suggests that entropy and volume changes per unit mass are parameters that will give information concerning phase changes. Although there exists no generalization concerning the influence of volume, the Boltzmann relationship,

$$\Delta S = R \ln \frac{\omega_f}{\omega_i} \quad \ldots \ldots \ldots \ldots (2)$$
where $W_1$ and $W_2$ are the number of independent ways the higher and lower temperature phases respectively may be realized, suggests that the entropy change is a useful parameter.

Empirical correlation (16) shows that compounds consisting of simple units (atoms, ionic crystals such as NaCl) and some polyatomic molecules (such as CH$_4$, CCl$_4$, C(CH$_3$)$_4$) have low entropies of fusion - about 1.5 to 3 e.u. Some large molecules (such as camphor and cyclohexane) which possess compact shapes are also in this class. However, some molecules, even though in certain cases similar to the preceding ones, have entropies of fusion of the order of 10 e.u. (C$_2$H$_6$, CHCl$_3$). The difference is found to be in the method of heat intake before melting. The high-entropy substances show unbroken specific heat-temperature curves while the low-entropy substances show one or more specific heat maxima below the melting point. The maxima are related to transitions in the solid in which the molecules increase their average symmetry of orientation before melting. If there is only intermediate energy intake below the melting point there may be only rotation about certain axes in the crystal. The molecule does not acquire complete spherical symmetry of rotation in the solid and the entropy of fusion has an intermediate value. This may be the case when only part of a molecule rotates.

Considered on the grounds of classical theory, equilibrium between two phases is attained when the phases, say solid and liquid, possess the same Gibbs free energy per
unit mass. Transition from solid to liquid then should imply a discontinuous jump between two independent free energy surfaces which intersect along the transformation curve (16). Classically no singularities of behaviour near the melting point are expected. Classical theory, however, disregards the structure of the phases, but studies indicate (13)(16) (17)(18) that the relationship between solid and melt may in some cases be very close. For example, in the melt molecules of crystalline paraffins are found in roughly parallel alignment of chains and while long-range order is largely absent there is indication of short-range order (18). Other studies, specific heat and thermal expansion investigations (1)(16), confirm the similarity between solid and melt near the melting point. There may even be domains, analogous to magnetic domains, in the melt near the transition point (18). Marked hysteresis effects may also be present near the melting point (18).

Melts are of course in general considerably more disordered than their solids. The familiar Boltzmann relationship gives a measure of the increase in disorder upon melting. Some crystals may assume more than one kind of disorder, each type of which provides a possible melting mechanism, with the possibility of several types of disorder occurring simultaneously. The main mechanisms (13) are:

1. Positional melting - structure units are randomised with respect to their ideal lattice positions.

2. Orientational melting - mutual orientations of
asymmetric structure units are randomised with respect to the ideal lattice at low temperature.

3. Configurational melting - randomisation of flexible molecules (19) which by means of free rotation about valency bonds may take on more than one configuration. On freezing the configuration most easily packed into the lattice will be found, but in the melt if the energy differences are of the order of kT all configurations may be present. This mechanism is common in the polymethylene series and in many polymers.

4. Associational melting - in the case of certain inorganic salts the formation of association complexes increases the entropy of fusion. While all four mechanisms are important the most common are 1. and 2. Mechanisms 3. and 4. may, for the appropriate compounds, be found in combination with 1. and 2. That is in case 3. the total entropy of fusion would be

\[
S_{\text{fus}} = S_{\text{positional}} + S_{\text{orientational}} + S_{\text{configurational}} \quad \ldots \ldots \ldots (3)
\]

While premelting has been observed to influence many properties of solids, the most commonly observed influence has been that on specific heat. The rise in the specific heat - temperature curve as the melting point is approached from either direction has been termed a premelting phenomenon. It has been suggested (20), however, that a cause of the rise could be the presence, in the liquid, of small amounts of impurity not soluble in the solid phase. On freezing, the concentration of the impurity would become progressively increased in the liquid phase as solid crystallized out. Such segregation of
impurities in the first part of the solid to melt or the last part of the liquid to freeze could make a large numerical contribution to the specific heat and coefficient of expansion (16). However, experiment does not agree exactly with calculations derived from the above considerations and it is believed that there are other contributions to the anomaly. It must be remembered nonetheless that such trivial causes as impurities do exist and care should be taken to avoid such possibility. When feasible structural studies should also accompany the thermodynamic or other means by which premelting is investigated.

For some compounds, the premelting phenomenon is positively observed under conditions in which it cannot be attributed to heterophase separation of impurities in the liquid phase but must instead be homophase (sometimes called monophase) premelting. This may be found in the medium and long-chain paraffins where likely impurities would remain in solid solution and for which addition of known impurities did not affect the specific-heat curves (1)(21).

It may be suggested that premelting is a universal phenomenon but one which appears in greatly different degrees in different crystal structures (13). That is since a fraction of lattice defects

$$\frac{n}{N} = \exp(-\Delta E/kT) \quad \cdots \cdots \cdots \cdots \ \ (4)$$

will be present in all crystals below the melting point, all solids will exhibit premelting, centered about these defects, to some degree. In equation (4), n is the number of defects,
N the total number of lattice points, and $\Delta E$ the energy increase associated with the disordering process occurring. Only for a comparatively few compounds whose crystals are capable of undergoing extensive disorder (involving values of $\Delta E/k$ relatively small compared to $T_{\text{fusion}}$) will premelting exist to a marked degree.
CHAPTER III

CRYSTAL STRUCTURES AND PHASE TRANSITIONS

A. FATTY ACIDS

1. CRYSTAL STRUCTURE

Normal fatty acids are polymorphic. The particular crystal structure obtained depends on purity of acid, temperature and rate of crystallization, and solvent. There are three forms A, B, C of even-numbered (even number of carbon atoms) and three A', B', C' and possibly a fourth D' for the odd-numbered acids (22)(23)(24). The distinction between the forms A, B, C will be given later.

The two most important factors in determining the crystal form obtained are temperature and solvent. In a given solvent different polymorphs may be formed depending on the temperature of crystallization. The nature of the solvent (polar or nonpolar) influences the rate of crystallization and hence the polymorphic form (23).

The C-form may be obtained by crystallization at about 20 °C as follows: for stearic acid from ethyl alcohol and acetone; for palmitic acid from n-pentane; for myristic acid from ethyl acetate, ethyl alcohol, benzene and carbon tetrachloride and for lauric acid from n-pentane, diethyl ether, ethyl alcohol, ethyl acetate and acetone (23). The C-form may also be obtained by cooling from the melt (22).
The C-form fatty acid unit cells are long monoclinic prisms. Two acid molecules, associated at the carboxyl groups, lie along each of the four edges of the prism's cross-section with a fifth pair in the center. Two of the pairs belong to the unit cell and the remaining three pairs belong to adjacent cells (25).

Due to the great difficulty in obtaining satisfactory crystals for single crystal measurements (26) complete crystallographic data have been obtained for few fatty acids. Lauric acid has been reported, however, and the structures of the three other acids considered in the present investigation may be assumed from a knowledge of this and of the fairly complete powder x-ray studies. For lauric acid Vand gives the following data (27):

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>monoclinic crystal</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>9.524 ± 0.02Å</td>
</tr>
<tr>
<td>b</td>
<td>4.965 ± 0.01Å</td>
</tr>
<tr>
<td>c</td>
<td>35.39 ± 0.07Å</td>
</tr>
<tr>
<td>β</td>
<td>129°13' ± 1'</td>
</tr>
<tr>
<td>csinβ</td>
<td>27.42 ± 0.06Å</td>
</tr>
</tbody>
</table>

four molecules per unit cell

space group: \( \text{C}_{iA}^- \ - P_{2_1}/a \)

Figures I and II show the structure of this acid. The hydrocarbon chain was found to be not quite straight but bent in the a-axis projection. The average distance between alternate carbon atoms was found to be 2.521 ± 0.007Å and the angle of tilt \( \tau = 54°52' \). The
FIGURE 1

FOURIER PROJECTIONS

OF THE

C-FORM OF LAURIC ACID

FROM REFERENCE 27

PROJECTION ALONG THE $a$-AXIS

PROJECTION ALONG THE $b$-AXIS
FIGURE II
THE C-FORM OF LAURIC ACID
FROM REFERENCE 24

PROJECTION ALONG THE b-AXIS
molecules were joined in pairs by hydrogen bridges 2.56Å long.

Table I lists unit cell dimensions from various sources for the C-forms of lauric, myristic, palmitic and stearic acids.

Table I. Unit Cell Dimensions

<table>
<thead>
<tr>
<th>Acid</th>
<th>a ±0.002Å</th>
<th>b ±0.004Å</th>
<th>c ±0.008Å</th>
<th>d001 ±0.004Å</th>
<th>β ±6°</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric</td>
<td>9.63±4</td>
<td>4.96±6</td>
<td>35.58</td>
<td>27.43</td>
<td>129°35'</td>
<td>28</td>
</tr>
<tr>
<td>Myristic</td>
<td>9.50±9</td>
<td>4.96±8</td>
<td>40.71</td>
<td>31.58</td>
<td>129°7'</td>
<td>28</td>
</tr>
<tr>
<td>Palmitic</td>
<td>9.40</td>
<td>5.0</td>
<td>45.9</td>
<td>36.0±</td>
<td>129°</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>9.41</td>
<td>5.00</td>
<td>45.61</td>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>Stearic</td>
<td>9.35±7</td>
<td>4.95±6</td>
<td>50.76</td>
<td>39.87</td>
<td>128°12'</td>
<td>28</td>
</tr>
</tbody>
</table>

Estimates of error do not apply for palmitic acid.

*From reference (22)

The forms of the acids are distinguished by decreasing long spacing d in the crystal structure in the order A,B,C. For each form the long spacing and the c-axis are functions of the number n of carbon atoms in the chain. The function has different slopes and intercepts for series of different forms.

For the C-form the values are given in Table II (28).

Table II. C-Axis and Long Spacing Functions

<table>
<thead>
<tr>
<th>c-axis</th>
<th>long spacing d001</th>
</tr>
</thead>
<tbody>
<tr>
<td>c = pn+q</td>
<td>d001 = Pn+Q</td>
</tr>
<tr>
<td>p = 2.5378±0.0042Å</td>
<td>P = 2.0850±0.0024Å</td>
</tr>
<tr>
<td>q = 5.12±0.080Å</td>
<td>Q = 2.383±0.044Å</td>
</tr>
</tbody>
</table>
Summing up the crystal structures, it has been reported that the saturated n-chain fatty acids are found in the solid state with the hydrocarbon chain in an extended zigzag arrangement of the carbon atoms in one plane. The carbon bonds are believed to have angles of $109^\circ 28'$ and the distance between alternate carbon atoms is $2.52\AA$ (26)(27). The acids crystallize in dimers with the carboxyl groups hydrogen bonded. The $\text{O-H}$ bond length is taken as $1.04\AA$ from which the dimer interproton distance is about $2.40\AA$ (12) or the distance is more probably $2.56\AA$ (27). The carboxyl group packing determined by Vand was assumed to apply to all fatty acids (an assumption made for some other values also). The distance between planes passing through the carbon nuclei of the end methyl groups was taken to be $2.18\AA$ (12). The hydrocarbon chains are arranged with long axes parallel. The chains in general are not perpendicular to the parallel planes of carboxyl and methyl groups but are tilted at an angle $\tau$ with respect to them. A reasonably accurate value of $\tau$ may be obtained from the calculated increment per two carbon atoms and the observed long spacing increment and the assumption of tetrahedral C-C bond angles (31).

The periodicity in the fatty acid hydrocarbon chain causes small groups of strong reflections to be regularly distributed in the reciprocal lattice. The groups describe a large reciprocal lattice (and hence a smaller direct cell) and give the translations between equivalent groups in a chain and in adjacent chains. While the main advantage of
the smaller cell or subcell is in x-ray structure factor calculations, it is also useful in calculations such as those of infrared splittings due to intermolecular interactions. There are two kinds of subcells commonly used in normal fatty acids - orthorhombic and triclinic (24). The triclinic subcell is used in the acids having triclinic unit cells and causes no confusion. The C-form fatty acids, however, although they have monoclinic unit cells and subcells, also have very close to orthorhombic packing of their hydrocarbon chains. Figure III shows the orthorhombic subcell for an idealized C-form fatty acid in which the hydrocarbon chain axes are assumed parallel to the c-axis and to the a-c plane. Figure IV shows an enlarged view of an orthorhombic subcell.

2. PHASE TRANSITIONS

The phase transitions in the fatty acids are relatively simple. For the even-numbered acids C is the stable form, the transitions A → C and B → C not being reversible (22). However, it has been reported by Lomer that there is a spontaneous but very slow transformation to the A-form from the C-forms of lauric and myristic acids (32). A check, made on lauric acid some years after the above observation was made, suggested that coexisting with the powdered A-form were crystals whose unit cell dimensions bore a resemblance to both the A and B-forms. The cell dimensions did not agree closely with either A or B but were markedly different from the C-form. It appears that for
FIGURE III
METHYLENE CHAIN PACKING IN A C-FORM FATTY ACID

NOTE: A PERFECT SUBCELL IS NOT USUALLY PRESENT.
FIGURE IV
C-FORM FATTY ACID
ORTHORHOMBIC SUBCELL

CARBON
HYDROGEN IN i-th METHYLENE GROUP LAYER
HYDROGEN IN (i+1)th METHYLENE GROUP LAYER
lauric acid at least there may be possible a forth crystalline form. Study of Lomer's paper, however, suggests that perhaps the form is related to the A modification. 

Transitions in lauric, myristic, palmitic and stearic acids have been listed by von Sydow (22) and are reproduced in Table III. Since all the forms go to Table III. Previously Observed Transitions in Selected Fatty Acids

<table>
<thead>
<tr>
<th>Acid</th>
<th>Melting Point °C</th>
<th>Transition Point on Heating °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric</td>
<td>44.0</td>
<td>32</td>
</tr>
<tr>
<td>Myristic</td>
<td>54.2</td>
<td>44</td>
</tr>
<tr>
<td>Palmitic</td>
<td>62.9</td>
<td>59</td>
</tr>
<tr>
<td>Stearic</td>
<td>69.7</td>
<td>54</td>
</tr>
</tbody>
</table>

the C-form on heating, there is only one melting point for all the forms of an individual acid. There is some evidence that the transitions may be influenced by the rate of heating. For instance, the B → C transition reported at 52.9 °C (note: this is reported as B → C, not A → C as by von Sydow) for stearic acid takes place in a short time. But a B → C transition at 35.2°C takes about 400 hours in the range 30 to 35°C (33). It was noted in the paper reporting the 52.9 °C B → C transition that this value agreed with that of Thibaud and La Tour who found the B → C transition at 53.0 °C (34). It would appear then that there is some uncertainty about the transitions as to rate of heating and even as to which form is present. Fortunately this difficulty does not arise with the C-form investigated in this study.
E. SODIUM STEARATE

1. CRYSTAL STRUCTURE

The x-ray analysis of solid fatty acid salts (or soaps) shows that in general the salts have a layer structure in which the carboxyl ion ends are opposed in parallel planes. The parallel planes are held together by the positive ions. The hydrocarbon chains are parallel to each other with their longitudinal axes inclined to the plane of the carboxyl ion groups at an angle $\tau$ (35).

Evidence has been obtained that in certain projections the chains of the A-form in at least potassium caprate are not parallel to each other but form a criss-cross pattern (31).

Due to varying degrees of hydration, a number of different modifications of the structure of sodium stearate have been reported. While the forms may be distinguished by x-ray diffraction (36), it is not always made clear which form is being reported. The form studied by Grant (12) was anhydrous sodium stearate. A complete structural determination of sodium stearate has not yet been made (37). Available information reports the unit cell of the salt at room temperature to be a monoclinic prism with the following dimensions (35):
The density of the salt specifies two molecules per unit cell.

While sodium stearate is uncertain, the structure of silver stearate is well defined. The silver stearate unit cell is triclinic with two molecules per unit cell and the following dimension (38):

\[
\begin{align*}
s & = 4.16 \text{Å} \\
b & = 4.62 \text{Å} \\
c & = 4.83 \text{Å} \\
d_{001} & = 0.83 \\
t & = 61.53^\circ
\end{align*}
\]

The chains are arranged in the usual manner for these salts. The planes of the hydrocarbon chains are approximately parallel to the a-axis and the longitudinal axes of the chains are tilted in a plane perpendicular to the a-axis.

It will be mentioned under THEORY, A. INFRARED that the behaviour, doublet or singlet, of the 720 cm\(^{-1}\) methylene rocking band may be correlated with orthorhombic and monoclinic or triclinic packing respectively of the hydrocarbon chains. In the case of sodium stearate, this band is single (4). It is probable, then, that triclinic packing of chains occurs (that is, a triclinic subcell) and the arrangement of chains
In sodium stearate may be similar to that in silver stearate. Grant observes (12) that the cell cross sections of sodium and silver stearate are almost identical and concludes that the latter's crystal lattice is sufficiently similar to sodium stearate to serve as a model for the sodium soap.

From Vand's data (38) a unit cell model of silver stearate may be constructed. See Figure V taken from Grant (12). Bond angles were assumed tetrahedral throughout the hydrocarbon chain although there may (38) be slight deviations. The C-H bond lengths were taken as 1.094\(\text{Å}\) and the C-C distances as 1.54\(\text{Å}\). The hydrocarbon chains were arranged in the common zig-zag configuration. In Figure V it was assumed that the carbon zig-zag was parallel to the a-axis. Vand (38) could not determine this exactly but relied on comparison with other hydrocarbons. Calculations by Grant (12) suggest that Vand's assumption is correct. Once the silver stearate model has been constructed it is necessary to make the assumption that the sodium stearate molecules are packed in the crystal lattice with the same intermolecular distances as in the silver soap (12).

2. PHASE TRANSITIONS

The phase transitions in the fatty acid salts are much more complicated than those in the fatty acids. Stearic acid shows at the most transitions from the forms A or B to C, but sodium stearate possesses a formidable array of transitions. The extreme temperatures of the transitions as reported by different sources are given in Table IV. Numerous references for the transition temperatures are listed in Grant (12), from
FIGURE V

CROSS SECTION, SILVER STEARATE
HYDROCARBON CHAIN PACKING.

THE SUGGESTED PACKING FOR
SODIUM STEARATE

FROM REFERENCE 12

SECTION OF TRICLINIC UNIT CELL

CARBON
HYDROGEN
which the table was taken and will not be reproduced here.

Table IV. Phase Transitions in Sodium Stearate

<table>
<thead>
<tr>
<th>Name of Transition</th>
<th>Reported Extreme Temperatures of Transition °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Genotypic Point</td>
<td>65-70</td>
</tr>
<tr>
<td>Gurd to Supercurd</td>
<td>89-93</td>
</tr>
<tr>
<td>Supercurd to Subwaxy</td>
<td>110-117</td>
</tr>
<tr>
<td>Subwaxy to Waxy</td>
<td>125-134</td>
</tr>
<tr>
<td>Waxy to Superwaxy</td>
<td>165-175</td>
</tr>
<tr>
<td>Superwaxy to Subneat</td>
<td>198-209</td>
</tr>
<tr>
<td>Subneat to Neat</td>
<td>226-262</td>
</tr>
<tr>
<td>Melting Point</td>
<td>278-298</td>
</tr>
</tbody>
</table>

The genotypic point at about 70°C may be due to impurities (39).

The curd to supercurd transition at around 90°C is usually observed only by differential thermal analysis and there appears to be no abrupt change in density at the transition (40). The hydrocarbon chains have considerable freedom of motion in the supercurd phase. It is believed that the lattice expands in this phase to a degree sufficient to allow flexing and twisting of the hydrocarbon chains (4).

The supercurd to subwaxy transition occurs around 114°C. At this temperature there is an abrupt change in plasticity which is attributed to a loosening of the sodium stearate lattice at the methyl group ends of the hydrocarbon chains. This would provide easier slip planes (41)(42).
Infrared spectra indicate that there are now many more methylene groups free to move incoherently about the long axis than there were below the transition. All fine structure due to methylene wagging vanishes and methylene rocking becomes diffuse (4). There appears to be a significant change of structure at the transition and a large degree of motion is allowed the hydrocarbon chains (12).

The subwaxy to waxy transition around $130^\circ C$ represents a loss of crystalline properties. The soap becomes translucent (43), there is an abrupt change in density (44) and the infrared spectrum becomes very close to that for a molten fatty acid (4). There is still some structure, however, for sodium stearate appears fairly solid in the waxy phase (12). However, the above considerations suggest that a great decrease in short range order of the hydrocarbon chains occurs (12).

The waxy to superwaxy transition around $165^\circ C$ exhibits a further decrease in density and an increase in transparency (43)(40). A decrease in the cell long spacing suggests (45) that the hydrocarbon chains have more room to flail about than at lower temperatures.

The superwaxy to subneat transition around $200^\circ C$ appears to be similar to but of greater magnitude than the preceeding transition (40).

The subneat to neat transition around $250^\circ C$ is marked by further changes in density and transparency (43)(40). Above this transition sodium stearate will flow (46) and considerable changes are believed to be taking place at the
ionic layer at this transition (47).

In the vicinity of 280°C the remaining long range structure of the neat form disappears and sodium stearate melts to an isotropic liquid (46)(48).
CHAPTER IV

GENERAL THEORY

A. INFRARED SPECTRA

1. ORIGIN

The infrared region is the portion of the electromagnetic spectrum lying between visible light and radio waves. The region extends from about $12,500 \text{ cm}^{-1}$ to $10 \text{ cm}^{-1}$ but the most commonly used portion of the region is from $4000$ to $600 \text{ cm}^{-1}$.

The energy of a molecular state may be written as a sum of four terms

$$E = E_e + E_v + E_r + \epsilon \quad \cdots \cdots \cdots \cdots (5)$$

$$E_e \gg E_v \gg E_r$$

where the $E_e$, $E_v$, $E_r$ are the electronic, vibrational and rotational energies respectively of the molecule and $\epsilon$ is an interaction term between the energies. Band spectra which arise from transitions between $E_e$ levels are not found in the infrared ($\lambda \geq 4$). The infrared spectra have their origin in transitions between vibrational and rotational levels of the ground electronic states of molecules and are characterized by the frequencies or wavelengths of the transitions occurring and the intensities of those transitions. The frequencies are determined by
mechanical properties of the molecule and the intensities by electrical properties (49).

The vibrational energies of a molecule arise in the energies of nuclei oscillating about their equilibrium positions in the electrostatic field of the molecule (that is, of its electrons and nuclei). The nature of the field is known exactly only for simple molecules for which the quantum mechanical problem of the electronic energies may be solved. However, an approximate solution may be obtained by replacing the exact potential energy function by an approximation which holds for small displacements of the nuclei from their equilibrium positions.

The simplest approximation is the simple harmonic oscillator model (50). If a point mass is slightly displaced, in a direction \( r \), from its equilibrium position, it will carry out simple harmonic motion with a frequency

\[
\nu_k = \frac{1}{2\pi} \sqrt{\frac{k_r}{m}}
\]

where \( k_r \) is the force constant in the \( r \) direction. In this model the restoring force (for displacement \( r \),

\[
f_r = -k_r r
\]

is proportional to the first power of the displacement of the nucleus from its equilibrium position and the potential energy function is proportional to the square of the displacement (49).

The simple harmonic oscillator model accounts for the fundamental vibration from the nonvibrating state to the state with one vibrational quantum excited but does not account for overtones and combination frequencies where
the change in vibrational quantum number is greater than one (overtones) or where more than one vibration is excited by one or more quanta. These more complicated transitions may be explained by the use of a potential energy function containing higher terms than the square of the displacement (49). The potential energy $V$ may be expanded in a Taylor series for small displacements $r^k$ of the mass points (note the point approximation necessary for simplicity) about the nuclei's equilibrium positions.

$$V = V_0 + \sum_k \left( \frac{\partial^2 V}{\partial r^k} \right)_0 r^k + \frac{1}{2} \sum_k \sum_e \left( \frac{\partial^3 V}{\partial r^k \partial r^e} \right)_0 r^k r^e$$

$$+ \frac{1}{3} \sum_k \sum_e \sum_m \left( \frac{\partial^4 V}{\partial r^k \partial r^e \partial r^m} \right)_0 r^k r^e r^m + \cdots \cdots \cdots (7)$$

where the derivatives are evaluated at the equilibrium positions of the mass points of the nuclei. The first term is the value of $V$ when the molecule is at equilibrium where $V_0$ may be taken as zero for zero displacement. The second term is zero since the slope of the potential energy surface is zero at equilibrium. The third term is the usual potential energy term for the harmonic oscillator and the higher terms are anharmonicity terms. The terms $\left( \frac{\partial^j V}{\partial r^k \partial r^e} \right)_0$ may be regarded (48) as generalized force constants which may be determined so as to give the correct position of the fundamental bands in the spectrum.

The frequencies of pure rotational spectra correspond in the simplest approximation to transitions between quantized energy levels of a rigid rotator (51). The mechanical model depends only on the location of the
fixed mass points relative to the coordinate axes fixed in the molecule. In a linear molecule there is only one principal moment of inertia \( I = \sum m_i r_i^2 \) where \( r_i \) is the perpendicular distance of the mass point \( m_i \) from the axis; in a symmetrical-top molecule two of the three principal moments are equal; in the spherical-top molecule all three moments are equal; and in the asymmetrical-top molecule all three moments are different. When the above four models are considered as rigid with the energy states defined by angular momentum quantum numbers, the transitions between the lowest energy levels may be adequately accounted for by the rotator model. Transitions between higher energy states must be accounted for by introducing centrifugal stretching or distortion of a more rapidly rotating molecule (49).

Using the rigid rotator approximation one may write the kinetic energy of the molecule as (49)

\[
\mathcal{T} = \frac{1}{2}\left( I_{xx} \omega_x^2 + I_{yy} \omega_y^2 + I_{zz} \omega_z^2 \right)
\]

where the \( I_{aa} \) are the principal moments of inertia and the \( \omega_a \) the angular velocities. In terms of angular momentum \( \mathcal{P}_a = \partial \mathcal{T}/\partial \omega_a \) equation (8) becomes

\[
\mathcal{T} = \frac{1}{2}\left( \frac{\mathcal{P}_x^2}{I_{xx}} + \frac{\mathcal{P}_y^2}{I_{yy}} + \frac{\mathcal{P}_z^2}{I_{zz}} \right)
\]

and since \( \mathcal{P}_a = \mathcal{P}_x^1 + \mathcal{P}_y^2 + \mathcal{P}_z^2 \)

\[
\mathcal{T} = \frac{1}{2} \left\{ \mathcal{P}_x^2 \sqrt{I_{xx}} \left( \frac{1}{I_{xx}} + \frac{1}{I_{yy}} \right) + \mathcal{P}_y^2 \left[ I_{zz}^{-\frac{1}{2}} \left( \frac{1}{I_{xx}} \frac{1}{I_{yy}} \right) \right] \\
+ (\mathcal{P}_x^2 - \mathcal{P}_y^2) \frac{1}{2} \left( \frac{1}{I_{xx}} - \frac{1}{I_{yy}} \right) \right\}
\]
From quantum mechanics one may replace $P$, the value of $P$ by, $\hbar [j(\varepsilon + \varepsilon)]^{1/2}$ where $J$ is an integer $\geq 0$.

Now, for example, with a symmetric rotator the last term of equation (11) vanishes and $P_z$ is quantized as well as $J$. $P_z = \hbar \kappa$ where $0 \leq |\kappa| \leq J$ and the energy of the symmetric rotator where $I_{xx} = I_{yy}$ may be expressed as

$$\frac{T}{\hbar c} = J(j+1) \frac{\hbar}{8 \pi^2 I_{xx} c} + \frac{\kappa^2 \hbar}{8 \pi^2 c} \left( \frac{1}{I_{zz}} - \frac{1}{I_{yy}} \right) \quad (12)$$

or to a cruder approximation

$$\frac{T}{\hbar c} = J(j+1) \frac{\hbar}{8 \pi^2 I_{xx} c} \quad (13)$$

for the simple mechanical rigid rotator model.

For an asymmetric rotator $(I_{xx} - I_{yy}) \neq 0$ and a much more complicated expression arises. The asymmetric rotator may be approximated by limiting cases of the symmetric rotator – the prolate and the oblate rotators. For the prolate (cigar-shaped) rotator $I_B = I_C$ (if the moments of inertia $I_A$, $I_B$, $I_C$ of the molecule are such that $I \leq I_B \leq I_C$) and

$$\frac{1}{T} = J(j+1) \frac{\hbar^2}{8 \pi^2 I_{xx} c} + \frac{\kappa^2 \hbar^2}{8 \pi^2 c} \left( \frac{1}{I_A} - \frac{1}{I_C} \right) \quad (14)$$

and for the oblate (disc-shaped) rotator $I_A = I$ and

$$\frac{1}{T} = J(j+1) \frac{\hbar^2}{8 \pi^2 I_A} + \frac{\kappa^2 \hbar^2}{8 \pi^2 c} \left( \frac{1}{I_A} - \frac{1}{I_C} \right) \quad (15)$$

While the above discussion has treated the vibrational and rotational spectra as separate cases, the
observed fine structure of the rotation bands suggests that simultaneous vibration and rotation occurs. If the interaction between vibration and rotation could be neglected the energy of the vibrating rotator would be simply the sum of the vibrational energy of the anharmonic oscillator and the rotational energy of the nonrigid rotator. Hence a series of rotational levels would exist for each vibrational level. To an approximation this occurs, but for a precise description interaction terms must be included (51).

The foregoing discussion using mechanical properties of molecules may be used to explain the frequencies at which bands occur. Electrical and related properties must be used to explain the intensities of the bands. The intensities of transitions between two energy states i and j of a molecule are determined \(19\) by integrals of the form

\[
\vec{P}_{ij} = \int \Psi_i \vec{P} \Psi_j d\tau
\]

where the functions \(\Psi_i\) and \(\Psi_j\) are time independent wave functions of spatial coordinates. The functions are orthonormal and may be either real or complex. For the interpretation of infrared spectra, \(\vec{P}\) becomes the dipole moment \(\vec{M}\) of the molecule.

\[
\vec{M} = \sum_k e_k \vec{r}_k
\]

where \(e_k\) is the charge on mass point \(k\) and \(\vec{r}_k\) is the point's vector distance from an origin of coordinates in the molecule. In the cartesian system
\[ \mathbf{M}^r = M_x^r + M_y^r + M_z^r \]  
(18)

and in general

\[ M_q = \xi \epsilon_k q_k \]  
(19)

The infrared transitions are then dipole transitions whose intensities are proportional to

\[ \varepsilon \left| \int \psi_i \mathbf{M}_q \psi_j d\mathbf{r} \right|^2 \]  
(20)

where \( \psi_i \) and \( \psi_j \) are vibrational or rotational wave functions or products of such functions.

For pure rotational motion \( \mathbf{M} \) is a constant and the intensities of the transitions depend only on the permanent dipole moment of the molecule. However, for vibrational transitions the distances \( r_k \) will change and a changing dipole moment must exist. A Taylor series expansion may be used for small displacements to give

\[
\mathbf{M} = \mathbf{M}_0 + \frac{\xi}{\xi} \left( \frac{\partial \mathbf{M}}{\partial \xi} \right)_0 \xi + \frac{1}{2} \frac{\xi}{\xi} \left( \frac{\partial^2 \mathbf{M}}{\partial \xi \partial \xi} \right)_0 \xi_1 \xi_2 + \cdots
\]  
(21)

If the relation (21) is introduced into expression (20), it is seen that for the rigid rotator approximation only the first term of (21), the permanent dipole term, contributes to the intensity of pure rotational spectra. For vibrational transitions since the vibrational wave functions \( \psi_i \) and \( \psi_j \) are orthogonal the first term of (21) is zero in the harmonic oscillator approximation. In this case the second term determines the vibrational intensity and it follows that unless the dipole moment changes during the
vibration the intensity will be zero. The third and higher terms account for electrical anharmonicity and permit the appearance of overtones and combination frequencies.

Experimentally band intensity may be measured in terms of Beer's Law (53)

\[ I = I_0 \exp(-K_v c l) \]  

from which

\[ K_v = (1/c l) \ln(I_0/I) \]  

\( K_v \) is the absorption coefficient, \( c \) is the concentration of the absorbing species (in moles per liter in solution or molecules per \( \text{cm}^3 \) in the solid phase), \( l \) is the cell length or sample thickness in centimeters, \( I_0 \) the intensity of the incident radiation and \( I \) the intensity of the transmitted radiation. The molecular extinction coefficient \( \varepsilon_v \), or more simply extinction coefficient, defined as

\[ \varepsilon_v = (1/c l) \log_{10}(I_0/I) \]  

is more commonly used.

An infrared band is defined most precisely by a plot of \( \varepsilon \) against \( \nu \) and the maximum value of the extinction coefficient may be used to characterize the order of magnitude of the band intensity. Theoretically more significant (53) and experimentally more reproducible than the maximum extinction coefficient is the integrated absorption intensity, \( A \).

\[ A = \int K_v d\nu \]  

This is the area under the absorption curve and in the case of uncorrected values is closer to the true integrated intensity than the uncorrected extinction coefficient is to
the true coefficient.

2. CHARACTERISTIC BANDS

A non-linear molecule containing N atoms possesses 3N-6 fundamental vibrational modes. If the molecule has few symmetry elements there could be 3N-6 fundamental absorption bands all of which may be allowed in the infrared spectrum (48). Other bands would appear due to combinations of sums, differences and multiples of the fundamental frequencies and to resonance coupling between nearby frequencies. If the molecule is altered in any way each of the fundamental modes may be disturbed with a subsequent alteration in the whole spectrum. The infrared spectrum of a molecule is therefore a highly characteristic physical property. However, comparison has shown that infrared spectra are not as individual as might be believed. At frequencies above 1350 cm\(^{-1}\) the spectra of many compounds show comparatively few strong bands although below that point there may be a rather bewildering array. Fortunately it has proved possible to associate most of the bands and especially the more intense ones and those in the higher frequency range with specific bonds or groups which cause absorption at about the same frequency, depending on environment, in all molecules.

While the 720 cm\(^{-1}\) doublet is the only infrared band considered in the present study, many of the various frequencies, arising as indicated above, are characteristic of paraffin chain compounds. In particular the following bands are noted. In all of a large number of compounds
investigated by Fox and Martin (54) two strong bands corresponding to asymmetrical and symmetrical C-H stretching modes were observed at 2962 cm\(^{-1}\) and 2872 cm\(^{-1}\) respectively. The CH\(_2\) group gives (55) two bands, at 2926 cm\(^{-1}\) and 2853 cm\(^{-1}\), which correspond to in-phase and out-of-phase stretching vibrations of the hydrogen atoms.

It was found (54), using integrated absorption areas as a measure of intensity, that in long-chain n-paraffins the intensities of the CH\(_2\) and CH\(_3\) bands are directly related to the number of groups present. The CH\(_2\) absorption was found to change by a constant increment for each carbon unit increase in chain length. A definite CH\(_2\) band progression series was found in the region 1150-1350 cm\(^{-1}\). It was noted (56) that in lauric acid, (CH\(_2\))\(_{10}\), only three recognizable bands could be found. The band head was at 1195 cm\(^{-1}\). In heneicosanoic acid, (CH\(_2\))\(_{19}\), nine bands were found with the band head at 1184 cm\(^{-1}\). The high frequency end of the band was difficult to distinguish due to C-O perturbation.

Due to hydrogen bending vibrations CH\(_2\) deformation gives absorption near 1465 cm\(^{-1}\). CH\(_3\) deformation occurs at 1450 cm\(^{-1}\) (3).

The various methylene vibrations are illustrated in Figure VI. In the symmetrical stretching vibration the hydrogen atoms move towards and away from the carbon atom in unison altering the interatomic distance without changing the valence angle. In the asymmetrical stretching
FIGURE VI

METHYLENE VIBRATIONS

FROM REFERENCE 57

SYMMETRICAL STRETCHING

ASYMMETRICAL STRETCHING

WAGGING

TWISTING

DEFORMING

ROCKING
vibration one hydrogen approaches the carbon while the other moves away. In the wag vibration the hydrogens move in unison in and out of the plane of the methylene group. The twist involves movement of the hydrogens in and out of the plane in opposite directions. There is also the deformation in which the hydrogens move alternately towards and away from each other in the plane of the group thus deforming the valence angle. The rocking vibration involves movement of the hydrogen atoms together in the plane in the same direction thus maintaining the valence angle. The stretching and deformation modes are considered to be internal to the methylene group while the rock, wag and twist are external to the group and related to the rest of the molecule. Generally internal modes involve more energy and occur at higher frequency than external modes. Asymmetrical stretching gives rise to higher frequency and more intense absorption than symmetrical stretching (57).

In addition to the above paraffin-type vibrations, the fatty acids of course possess the very characteristic O-H stretching vibration. Carboxylic acids generally (58) exist in the dimeric form with strong hydrogen bonding between carboxyl and hydroxyl group. The acids are best run as solids or in the liquid state in order to avoid complication with the monomer O-H absorption. The O-H vibration gives a broad band near 3000 cm\(^{-1}\) and a satellite near 2650 cm\(^{-1}\).

The carboxyl absorptions for saturated
monocarboxylic acids are found (58) at 1725 cm\(^{-1}\) and 1705 cm\(^{-1}\) in the solid or liquid state.

Skeletal vibrations are frequently unreliable, that is difficult to assign, however, the \((\text{CH}_2)_n\) group where \(n \geq 4\) gives a strong band near 720 cm\(^{-1}\). It arises (3) from the \(\text{CH}_2\) rocking mode and is therefore not strictly a skeletal mode. Tuot and Lecomte (6) observed the band in some thirty alcohols in which at least four consecutive \(\text{CH}_2\) groups were present.

Thompson and Torkington (7) assigned the doublet at 721 cm\(^{-1}\) and 732 cm\(^{-1}\) in polythene to the presence of the methylene groups. It was shown (59)(60) that the vibrations where at right angles to the carbon chain. Sheppard and Sutherland (59) suggested the range 760 - 720 cm\(^{-1}\) for the band in various hydrocarbons.

The appearance of the band - double or single - has been correlated with orthorhombic for the doublet and hexagonal or triclinic crystal structure for the single band (61). Extensive recent work (5)(62) shows that the doublet is associated with orthorhombic and monoclinic crystal structure and the singlet with triclinic structure.

In the doublet, the high frequency component has been correlated with crystalline behaviour and the low frequency component partly with amorphous and partly with crystalline behaviour of the substance (8). Considering the \(\text{CH}_2\) rocking frequency as arising from perturbation of the vibrations of the free molecule by the crystal field,
it has been calculated (63) that the CH$_2$ rocking frequency at about 720 cm$^{-1}$ should be split into two components. The calculation by Stein, however, does not account for the presence of a third peak which he himself reported present in some of the compounds investigated (8). The third peak was observed for stearic acid in work (2) preceding this present investigation. Subsequent to Stein's work it has been reported (5)(64) that the strong doublet is believed to mask other doublets originating in higher normal vibrations of the CH$_2$ rocking mode. These vibrations may account for the third peak or shoulder on the high frequency side of the doublet. The band (5)(64) is the origin of a series of doublets, with lesser splitting, which terminates around 1013 cm$^{-1}$. 
B. NUCLEAR MAGNETIC RESONANCE

A descriptive approach to nuclear magnetic resonance theory may be obtained from a combination of the simplified vector model of the nucleus and elementary quantum mechanical concepts. The following discussion is from Gutowsky (65) unless specified otherwise.

The mass $M$ and charge $e$ of a nucleus are considered as being uniformly distributed over the surface of a spherical shell spinning with constant angular momentum $\vec{P}$ directed along the axis of rotation of the sphere. The moving charge generates a magnetic field cylindrically symmetrical about the axis of rotation with the field being represented by a magnetic moment $\vec{\mu}$ directed along the axis. The magnetic moment vector is colinear with and proportional to the angular momentum vector according to the equation

$$\vec{\mu} = \frac{e}{2Mc} \vec{P}$$

where $c$ is the velocity of light.

The above description is a crude approximation from which actual nuclei differ. A more accurate vector model would take into account orbital motions of components within the nucleus as well as spinning motions to give a resultant angular momentum for the nucleus. An unfortunate consequence of the coupling of spin and orbital moments is that nuclei with an even number of neutrons and protons
have zero angular momentum and magnetic moment and cannot be investigated by nuclear magnetic resonance (n.m.r). These include the chemically important nuclei $^{12}\text{C}$, $^{16}\text{O}$, and $^{32}\text{S}$. Fortunately the $^{1}\text{H}$ nucleus which cannot be conveniently examined by some other methods does possess a magnetic moment and can be studied by n.m.r. Indeed, hydrogen is the principal nucleus studied. To give a more accurate representation of the nuclear moment, equation (26) is modified by inclusion of the nuclear $g$ factor analogous to the Lande $g$-factor of atomic spectra, to give

$$\mu^* = \frac{e}{2Me} \mathbf{P}$$

In free space, the energy of a nuclear magnet is independent of its orientation. However, in the presence of a magnetic field $\mathbf{H}$ the nuclear magnet is subject to a torque

$$\mathbf{T} = \mu^* \times \mathbf{H}$$

which tends to align it parallel to the field. If the magnetic field is static and of uniform value $\mathbf{H}_0$ over the nuclear magnet, the magnetic interaction produces an energy of interaction

$$E = -\mu^* \cdot \mathbf{H}_0 = -\mu \mathbf{H}_0$$

where $\mu$ is the component of $\mu^*$ along $\mathbf{H}_0$.

From quantum mechanics elementary particles exist only in states with particular angular momenta (that is, angular momentum is quantized). From the proportionality between angular momentum and magnetic moment it is therefore seen that discrete magnetic energy levels occur.
When the interaction of $\vec{\mu}$ and $\vec{H}_0$ establish a direction in space for a nucleus, then $P_H$, the nuclear angular momentum along $\vec{H}_0$, has a maximum value of $I\hbar/2\pi$ where $I$ is the nuclear spin, a quantity having integral or half integral values, and $\hbar$ is Planck's constant. The allowed orientations are

$$P_H = m\hbar/2\pi \quad \quad \quad (30)$$

where $m$ is the magnetic quantum number which may take values $I, I-1, \ldots -I$.

By substituting components in equation (27) one may obtain

$$\mu_H = e\sigma_{2Mc} P_H \quad \quad \quad (31)$$

from which using equation (30) one gets

$$\mu_H = m\sigma \frac{\hbar e}{4\pi Mc} = m\sigma \mu_n \quad \quad \quad (32)$$

Hence the magnetic energy becomes

$$E = -mg\mu_n H_0 \quad \quad \quad (33)$$

The equation (33) describes a set of $2I + 1$ nuclear orientations and energy levels which are shown schematically for the $^1H$ nucleus in Figure VII. The selection rule for transitions between these levels is that $\Delta m = \pm 1$.

Therefore $\Delta E = \pm g\mu_n H_0$. Using the Bohr frequency condition $\Delta E = h\nu$, it is found that the frequency $\nu_0$ corresponding to an allowed nuclear magnetic energy change is

$$\nu_0 = \frac{g\mu_n H_0}{h} \quad \quad \quad (34)$$

The torque exerted on the nuclear magnetic moment by the field $H_0$ tends to align it with the field. From Newton's Law, the time rate of change of angular momentum
FIGURE VII

$^1$H NUCLEAR ORIENTATIONS AND ENERGY LEVELS

(A) QUANTIZATION OF THE NUCLEAR ANGULAR MOMENTUM $\vec{P}$ AND THE NUCLEAR MAGNETIC MOMENT $\vec{\mu}$ ALONG $\vec{H}_0$.

(B) NUCLEAR MAGNETIC ENERGY LEVELS. NOTE THAT ABSORPTION CORRESPONDS TO $\Delta m = -1$. 

\[
\begin{align*}
\vec{P} = & \frac{1}{2} \hbar \\
\vec{\mu} = & \frac{1}{2} g \mu_B n \\
\vec{P}_H = & -\frac{1}{2} \hbar \\
\vec{\mu}_H = & -\frac{1}{2} g \mu_B n
\end{align*}
\]
equals the torque
\[ \frac{d\vec{P}}{dt} = \mathcal{L} \] (35)

Using equations (27) and (28) one finds
\[ \frac{d\vec{P}}{dt} = g(e/2Mc)\vec{P} \times \vec{H}_0 \] (36)

This describes the precession of \( \vec{P} \) about \( \vec{H}_0 \) with angular velocity \( \omega_0 \) where
\[ \omega_0 = g(e/2Mc)\vec{P} \times \vec{H}_0 \] (37)

Hence, since \( \omega_0 = 2\pi\nu_0 \), the Larmor precessional frequency is
\[ \nu_0 = g(\hbar e/4\pi Mc)H_0/h = g\mu_n H_0/h \] (38)

as was derived from the Bohr frequency relation.

The precession of the nuclear spin axis about a magnetic field (see Figure VIII) provides a means to change the orientation and the magnetic energy of a nucleus. A small magnetic field \( \vec{H}_1 \) is generated perpendicular to \( \vec{H}_0 \).

The torque \( \vec{H}_1 \) exerts on \( \vec{P} \) will cause the spin axis to precess about \( \vec{H}_1 \) thus changing the orientation of the nucleus with respect to \( \vec{H}_0 \). Because the sense of this nutation changes with relative orientations of \( \vec{H}_1 \) and \( \vec{P} \), \( \vec{H}_1 \) must rotate about \( \vec{H}_0 \) synchronously with the nuclear precession about \( \vec{H}_0 \) in order that the net effect will not be cancelled out. Consequently, the rotation of \( \vec{H}_1 \) is in resonance with the Larmor precession about \( \vec{H}_0 \). Circularly polarized radiation of frequency \( \nu_0 \) is associated with such a rotating magnetic field. The circularly polarized radiation is generated with a radiofrequency (rf.) current which produces a magnetic field oscillating perpendicularly
FIGURE VIII
NUCLEAR REORIENTATION

FROM G.E. PAKE, SCIENTIFIC AMERICAN, AUGUST 1958, P58

(A) \( \vec{H}_i = 0 \). \( \vec{\mu} \) PRECESES ABOUT \( \vec{H}_o \).

(B) \( \vec{H}_i \neq 0 \). IF \( \vec{H}_i \) IS IN RESONANCE WITH THE LARMOR PRECESSION OF \( \vec{\mu} \) ABOUT \( \vec{H}_o \), THE NUCLEUS WILL PRECESS WITH A SPIRAL MOTION INTO THE OPPOSITE ORIENTATION.
to $\mathbf{H}_0$. If the rf. current produces a linearly oscillating field such that

$$H_x = 2H_1 \cos 2\pi vt, \quad H_y = 0, \quad H_z = 0 \quad \cdots \cdots \quad (39)$$

this is equivalent to two circularly polarized fields rotating in opposite directions in the plane perpendicular to $\mathbf{H}_0$.

Right circularly polarized field. Left circularly polarized field

$$\begin{align*}
H_x &= H_1 \cos 2\pi vt \\
H_y &= H_1 \sin 2\pi vt \\
H_z &= 0
\end{align*}$$

$$\begin{align*}
H_x &= H_1 \cos 2\pi vt \\
H_y &= -H_1 \sin 2\pi vt \\
H_z &= 0
\end{align*} \quad \cdots \cdots \quad (40)$$

The component having the correct sense for a given nucleus (the sense of the Larmor precession depends on the sign of the magnetic moment with a positive $\mathbf{\mu}$ requiring a left circularly polarized $\mathbf{H}_1$) satisfies the resonance condition while the other component has very minor effect.

When attention is turned from a single nucleus to an assembly of nuclei, one must consider the mechanism by which the nuclear spins attain and maintain thermal equilibrium with their surroundings. Nuclei are insulated from their environment (the lattice) by the atomic electrons and transfer of nuclear magnetic energy to the lattice is a comparatively slow process. In practice the electrons must provide some coupling with the lattice (66) or there could be no interaction. Since spontaneous emission is negligible and induced transitions require a magnetic field oscillating at the Larmor frequency, in order that there may be energy transfer from nuclei to
lattice the required fields must be produced at the nuclei by thermal energy of the lattice.

Since the probability of an induced transition up or down is the same (66), if there is to be a net absorption of rf. energy there must be an excess of nuclei in the lower energy states. A general analysis may be made (67), but it is simpler to consider only the most important case, that of \( ^{1}\text{H} \) where \( I = \frac{1}{2} \). For the hydrogen nucleus, it may be shown by use of the Boltzmann relation that at thermal equilibrium the ratio of the population \( N_{2} \) of the upper-energy state to the population \( N_{1} \) of the lower-energy state is (65)

\[
\frac{N_{1}}{N_{2}} = \exp \left( -\frac{\Delta E}{kT} \right) \quad \quad \quad \quad \quad (41)
\]

where \( k \) is Boltzmann's constant, \( T \) is the absolute temperature of the sample and \( \Delta E \) is the energy difference between the two states. Using equation (33) and (41) one finds that in a field of 10,000 gauss the ratio of the lower state to the upper state for the proton is

\[
\frac{N_{1}}{N_{2}} = 1 + \frac{g\mu_{n}H_{0}}{kT} + \cdots \approx 1 + 6 \times 10^{-6} \quad \quad \quad \quad \quad (42)
\]

This slight excess of nuclei in the lower state permits net absorption of energy in an rf. field. When rf. energy is absorbed by the system, some of the excess population in the lower level is transferred to the upper level thus giving rf. heating of the nuclear-spin system. Since the nuclear insulation is such that the nuclei are slow in losing their extra rf. energy to the lattice, the lower-state excess population steadily decreases until a steady state is
reached. If the insulation is good enough even weak rf.
fields may heat the spin system to saturation. If the rf.
field is then removed, relaxation processes cool the spin
system exponentially with a characteristic time $T_1$, the
spin-lattice relaxation time. The usual range of $T_1$ values
is $10^{-4}$ to $10^4$ seconds and they are dependent on
temperature, state and nature of the sample, and the
field $H_o$.

In addition to the spin-lattice interaction, there
exists the spin-spin interaction $T_2$ between the nuclei
themselves. The small magnetic fields associated with the
individual nuclei may be broken into two parts - the static
and rotating fields. For a nucleus in a rigid lattice the
nuclear magnetic moment $\mu$ produces at a nearby point $Q$
a local field $H_{Q}$ which is dependent on the distance $r$ and
the direction $\theta$ of $Q$ from the nucleus considered. The
local field is generally of the order of a few gauss but
reaches 28.2 gauss at a distance of 1 Å in the case of the
proton. When, as is usual, the external applied field $H_e$
is very much greater than $H_Q$, the net field is approximately

$$H_o \approx H_e + H_{\ell_2}$$  \hspace{1cm} (43)

where $H_{\ell_2}$ is the component of $H_{\ell}$ along $H_o$. Since it has
been found that

$$H_{\ell_2} = \pm \frac{\mu}{r^3} (3 \cos^2 \theta - 1)$$  \hspace{1cm} (44)

then

$$H_o = H_e \pm \frac{\mu}{r^3} (3 \cos^2 \theta - 1)$$  \hspace{1cm} (45).
From equation (45) it is apparent that there exists a splitting (spread) in the applied field \( \vec{H}_e \) which will give the resonant field \( \vec{H}_o \). For samples containing isolated pairs of nuclei with \( I = \frac{1}{2} \), the resonance at a fixed frequency would be split into two equal components separated by a distance of \( \frac{2J_f}{3}(3\cos^2 \theta - 1) \) gauss. For pairs oriented at random, as in a powder, a broadened resonance doublet occurs; while for many, interacting, randomly oriented nuclei a roughly bell-shaped absorption curve results.

If the nuclei are in motion rather than stationary, the internuclear distances and directions will vary with time. The z-component of the resulting magnetic field is given by

\[
\vec{H}_{zz}(t) = \pm \left[ \mu r^2 \right] \left[ 3 \cos^2 \theta(t) - 1 \right]
\]

The changing local fields produce motional narrowing by averaging out the spin-spin broadening. For example, for a pair of nuclei rotating with fixed \( r, \theta \) is a function of time. If the rotation occurs uniformly over all directions and occurs rapidly (that is, the frequency of motion is of the order of the frequency width of the resonance) the average value of \( \cos^2 \theta(t) \) is \( 1/3 \) and equation (46) reduces to zero and rotational narrowing has taken place with the result that

\[
\vec{H}_o \approx \vec{H}_e + \vec{H}_{zz}(t) = \vec{H}_e
\]

The rotating components of the local magnetic fields also add to broadening of the resonance. A pair of
identical nuclei, with \( I = \frac{1}{2} \), in the same field \( \mathbf{H}_0 \) precess at the same Larmor frequency. Each nucleus has a component (the component perpendicular to the field direction \( \mathbf{H}_0 \)), of the magnetic moment, which rotates in the x-y plane. These rotating components produce a spin-exchange or spin-spin collision between the nuclei in the pair by generating rotating local fields \( \mathbf{H}_{1\ell} \) at each nucleus. The fields produce a simultaneous reorientation of both nuclei by interchanging individual energies yet conserving total energy. The spin-exchange limits the lifetime \( \Delta t \) of the nuclear states and by the Heisenberg principle gives a related uncertainty \( \Delta E \) in the energy.

A nuclear spin will precess about \( \mathbf{H}_{1\ell} \) and have an energy in the field of

\[
\Delta E = - g \mu_n \mathbf{H}_{1\ell} \quad \cdots \quad (48)
\]

\( \mathbf{H}_{1\ell} \) is of the order of magnitude of \( \mathbf{H}_{2\ell} \) and gives a broadening in resonance comparable to that of the static fields. The spin-exchange effect is, however, only important between nuclei of the same species.

The generation of oscillations in the local magnetic field by lattice motions provides an important mechanism for spin-lattice relaxation. An exact analysis of the spin-lattice mechanism demands a knowledge of the time dependence of nuclear position. If this is known, then the oscillations at the Larmor frequency in the x-y plane local fields may be calculated and their effect on \( T_1 \) deduced (67).
Since the nuclear surroundings influence the width and shape of nuclear magnetic resonance lines (68), this may be used to provide structural information about the system investigated. Theoretical line shapes have been calculated and verified for two-spin (69), three-spin (70)(71), and four-spin (72) systems. However, the complexity of interactions in many-spin systems (the complexity of even the four-spin system is formidable) precludes calculation. It should be noted that even for few-spin systems the resonance line shape in powder samples is very much broadened (73) and only internuclear distance information may be obtained. For this reason, single crystal studies are often employed in n.m.r. structural analyses. Although quantitative information cannot always be obtained from the line shapes, valuable qualitative information can frequently be obtained. Line width, the measurement usually made on n.m.r. absorption lines, may be defined either as the distance between the maximum and minimum slope on the absorption curve or the width at one-half maximum amplitude on the curve.

Although it is difficult to determine theoretical line shapes for complex structures, Van Vleck has shown (74) that the second moment of the n.m.r. line can be related to a given structural model. The second moment is defined (75) as

$$\Delta H_2^2 = \frac{\int_{-\infty}^{\infty} f(H)(H-H_0)^2 dH}{\int_{-\infty}^{\infty} f(H) dH} \quad \cdots \cdots \cdots \cdots \cdots \cdots (49)$$
where $f(H)$ is the line-shape function at any value of the field $H$ and $H_0$ is the value of $H$ at the center of the absorption line. The relation between second moment of a powdered crystal and the distance $r_{jk}$ between resonating atoms was calculated theoretically by Van Vleck and rewritten by Gutowsky (75) as

$$\Delta H_k^2 = \frac{\mu}{\alpha} \sum_{j<k} \frac{\mu_j^2 \mu_k^2}{r_{jk}^6} + \frac{1}{\alpha} \sum_{j<k} N \mu_j^2 \mu_k^2 \sum_{l=1}^{3} \frac{b_l}{r_{jk}^l}$$

(50)

where the subscript $f$ refers to nuclei other than resonating nuclei which nonetheless contribute to broadening. $N$ represents the total number of resonating nuclei in the particular sub-group (unit cell, etc.) to which the broadening is attributed. Attached to this equation are the conditions (75) that the lattice must be rigid at the temperature at which the experiment is carried out; the nuclei must not move appreciably in time of order $T_2$ (that is the local configuration remains stationary for up to $10^{-4}$ to $10^{-5}$ seconds, zero point motion is ignored (7)) and that there must not be paramagnetic ions present in greater atomic ratio of paramagnetic ion to resonating ion than $10^{-6}$ to one. If it is assumed that interactions of magnetic nuclei other than protons are negligible, then the second moment reduces (74) to

$$\Delta H_k^2 = \frac{7/6}{N} \sum_{j<k} r_{jk}^{-6}$$

(51)

where $r_{jk}$ is the distance between any two protons $j$ and $k$. When the temperature dependence of n.m.r. phenomena is observed, abrupt changes in line width and second moment may often be found. When frequency of
rotation, which is influenced by temperature, is of the order of the n.m.r. line width, the line width and second moment decrease. Such changes frequently correspond to phase transitions (76) and second moments can be estimated for these transitions by the various second moment equations. In general, the changes in line width and second moment are useful in estimating the onset and extent of molecular motions and of determining the type of motion itself (76).
Ködak white label grade stearic, palmitic, myristic and lauric acids were purified by repeated low temperature crystallizations (77). Quantities ranging from 25 to 50 gms. of acid were dissolved in dilute solution in hot, freshly distilled reagent grade acetone. The beaker containing the acid solution was then placed in a dewar containing a dry ice-acetone bath at a selected temperature. The temperatures used for crystallization are listed in Table V.

Table V. Crystallization Temperatures

<table>
<thead>
<tr>
<th>Acid</th>
<th>Crystallization Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stearic</td>
<td>-20</td>
</tr>
<tr>
<td>Palmitic</td>
<td>-15</td>
</tr>
<tr>
<td>Myristic</td>
<td>-20</td>
</tr>
<tr>
<td>Lauric</td>
<td>-30</td>
</tr>
</tbody>
</table>

The solution was stirred mechanically for about an hour and then the acid was permitted to settle, the solvent filtered off and the acids pressed between filter paper to remove excess solvent before drying in a vacuum dessicator over P₂O₅. The process was repeated until the freezing points were found to be constant for successive recrystallizations
(preferably at least three successive constant freezing points). Purification of the acids depends on the quite different solubilities of the homologous acids at low temperatures. The least soluble acid (stearic) can be obtained with no difficulty. More soluble acids may also be obtained in a pure state if less soluble impurities are present in small amount as was the case with the relatively pure starting materials (less than 5% impurity) used.

As an index of purity, melting and freezing points were determined. Melting points were done on a hot-stage microscope heating at about 0.2°C per minute. Freezing points were taken from the plateaux of temperature-time cooling curves. The observed melting and freezing points are compared in Table VI to those listed by Markley (78)

Table VI. Melting and Freezing Points of Selected Fatty Acids

<table>
<thead>
<tr>
<th>Acid</th>
<th>Observed Melting Point °C</th>
<th>Observed Freezing Point °C</th>
<th>Reported Melting Point °C</th>
<th>Reported Freezing Point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stearic</td>
<td>69.5-69.8</td>
<td>69.4</td>
<td>69.6</td>
<td>69.3</td>
</tr>
<tr>
<td>Palmitic</td>
<td>63.0</td>
<td>62.7</td>
<td>63.1</td>
<td>62.8</td>
</tr>
<tr>
<td>Myristic</td>
<td>54.3-54.5</td>
<td>54.1</td>
<td>53.9*</td>
<td>54.1</td>
</tr>
<tr>
<td>Lauric</td>
<td>44.0-44.3</td>
<td>43.7</td>
<td>44.2</td>
<td>43.9</td>
</tr>
</tbody>
</table>

*54.4 listed by reference (79)
Spectra were run on a Perkin-Elmer Model 21B double beam infrared spectrometer. It was found that normal qualitative operating conditions (80) gave satisfactory resolution.

Preliminary studies were made of the spectra of the acids over the range 4000 to 600 cm\(^{-1}\) from about 30°C to about 90°C for stearic acid and at 30°C only for the other acids. Expanded spectra (50 cm per 100 cm\(^{-1}\)) were run from 750 cm\(^{-1}\) to 700 cm\(^{-1}\) to cover the region of interest. For expanded spectra a scanning rate of about 50 cm\(^{-1}\) in seven minutes was used. For all expanded spectra, the absorption was set at a suitable point (about 0.05 optical density at 750 cm\(^{-1}\), the point of minimum absorption) and left untouched for the duration of each set of experimental runs on an acid. Spectra were recorded on a logarithmic optical density grid chart and each curve was traced at least twice. Except when taken exactly on a transition point when equilibrium had not been fully established the curves always agreed very closely. Variation between curves was of the order of 0.005 optical density units about the magnitude of the noise fluctuations in the curves.

Preliminary runs in the 750 - 700 cm\(^{-1}\) range of samples both as films crystallized between sodium chloride plates and as solid solutions in potassium bromide discs were run from about 30°C (the approximate machine temperature) up past the melting point and back to 30°C.
Final runs, which were made with films between salt plates, were commenced at 30°C, taken down in successive steps to about 60°C below the melting point, then raised in successive steps to about 20°C above the melting point and then taken back by steps to 30°C.

Temperatures were changed by small increments - about 0.50°C when near the melting point. Since even for changes of the order of 15°C equilibrium was reached in about 15 minutes, it was considered adequate to allow some 20 to 25 minutes between runs. As a check some spectra were taken close to the melting point after the standard period at equilibrium and then left for several hours at the same temperature before repeating the spectra. No change was observed. Temperatures were measured at the beginning and end of each individual run and were found to vary by less than ±0.2°C.

Heating was done with a standard Perkin-Elmer electrical heating unit. The unit was designed for use in the temperature range 100 to 200°C and was difficult to control in the range required. However, by keeping the unit's heating control fixed, adequate control could be achieved with a variac into which the unit was plugged. For additional control a constant voltage transformer was used to supply the current. An electrically heated brass ring in a ceramic mounting held the salt plates or the brass KBr disc holder.

The cooling device consisted of a simple box, open at both ends, constructed to enclose the sample beam
path. Cold nitrogen vapour was allowed to flow over the sample plates from an inlet tube above the plates and just out of the beam path. Either tank nitrogen passed through a calcium chloride tower and cooled by being passed through a copper coil immersed in a acetone-dry ice or liquid nitrogen bath or nitrogen vapour boiled off from liquid nitrogen was used.

As noted above, spectra were run with samples both as films between salt plates and as solid solutions in KBr discs. Temperatures were recorded for the films by a copper-constantan thermocouple placed in a groove between the opposing faces of the salt plates. The couple was in the instrument beam and in contact with the sample. For the KBr discs a copper constantan thermocouple was soldered into the brass pellet-holder (couple and holder were calibrated as one unit). Because of temperature gradients in the KBr pellet holder temperatures were considered accurate to not better than 3°C, however, the temperatures for the films were considered to be good to not worse than ±0.5°C.

Films were prepared by melting the acid on a heated NaCl plate, pressing a second plate on top, and rapidly cooling the plates with a stream of dry compressed air. A double thickness NaCl plate was used in the reference beam to compensate for radiation scattering and reflection. In order to avoid excessive absorbance by too thick a sample, thin spacers of about 0.01 to 0.03 mm
thickness were used. However, uniform sample thickness was not achieved and the bother of handling the fragile spacers was such that samples were run without them. Due to difficulty in polishing the plates into plane, parallel surfaces, it proved impossible to obtain a film of constant thickness. In addition, as the film cooled from the melt, areas of crystal orientation were apparent between the plates with obvious inhomogeneities including the presence of some areas free of acid.

Very considerable error may be introduced due to inhomogeneity in the sample (53). When the absorbing material is composed of macro particles separated by regions of high transmittance and when there is no uniformity of sample thickness, the results do not follow closely the laws governing absorption of radiation by isotropic materials. For example, deviations from Beer's Law occur in inhomogeneously dispersed systems. The presence of the small, freely transmitting areas found in the samples would be expected to give rise to a considerable difference between true and observed optical density (53). With 10% freely transmitting space and an optical density of 1.0, deviations of 20-25% between true and experimental optical densities occur. However, below an optical density of about 0.3 there will be little difference for up to 20% clear space which is quite an extreme case. Sample thickness to give values of around 0.2 to 0.3 was generally used in this investigation.
To avoid the marked orientational effects noted in the films, samples were prepared in KBr discs as described by Kirkland (61). Pellets were prepared with dried, Harshaw optical grade KBr. Acids stored in a desiccator were melted under vacuum for up to 10 hours to remove any moisture or solvents that might be present (this was also done for the films) quickly solidified, ground in a mortar, shaken mechanically with KBr for 15 minutes, and pressed in a Perkin-Elmer die at 20,000 psi. This gave an inhomogeneously appearing (transparent and opaque regions) pellet. The pellet was ground up, reshaken and repressed to give a homogeneous, visually opaque pellet. To eliminate the possibility of moisture being picked up from the atmosphere, the procedure was carried out in a dry box, but the same type pellet was obtained and it was concluded that the appearance of the pellet was due to the sample, not moisture. Since the 720 cm\(^{-1}\) region is near the end of the KBr range, a pure KBr pellet was used in the reference beam to compensate for any change in absorption and to compensate for radiation scattering and reflection at the sample pellet's surface.

Although KBr disc samples are sometimes described as solid solutions, the linear dimensions of the individual absorbing particles are in excess of 100 Å and hence each contains several unit cells of crystal (53). Consequently even in KBr discs, one is dealing with solid phase spectra subject to orientational effects similar to but in
somewhat lesser extent than that in crystalline films between plates. As the spectra obtained in this work were quite similar whether as film or KBr disc, but since temperatures were more accurately known for the films, most, including the final runs, were with films.

Since adjusting the spectrometer's optical system for use with a horizontal cell required about one half a day's time both before and after runs, a vertical cell was used to avoid tying-up the spectrometer more than was absolutely necessary. This meant that the use of films did introduce one complication; the possibility of slumping after melting. In some cases slumping or perhaps reorientation of the sample on the plates on cooling from the melt has occurred, but this has merely produced a parallel displacement of the curve obtained. Repetition of runs was made on displaced curves for lauric acid to determine if the curves could be retraced. (See RESULTS, A. FATTY ACIDS.)
B. SODIUM STEARATE

The sodium stearate used was an anhydrous sample (M. pt. 275-280°C) prepared by Grant in an earlier investigation (12).

Spectra were run on a Varian Model V-4352 high resolution nuclear magnetic resonance spectrometer operating at 40 Mc. A minimum of six spectra were recorded at each temperature - three sweeps up field and three down field. Individual spectra at a constant temperature were not closely reproducible. The extent of the deviations will be noted under RESULTS, B. SODIUM STEARATE. Due to the construction of the sample dewar it was impossible to spin the sample to obtain the best possible field. The spectra were checked at each temperature for saturation broadening. The sweep rate was calibrated at each temperature by imposing side bands on the main signal with a Hewlett Packard Model 200 CD oscillator. The oscillation frequencies were measured with a Hewlett Packard Model 522B electronic counter. The absorption line shapes were recorded on a Leeds and Northrup Speedomax H recorder except for spectra taken at three temperatures. For the three temperatures a malfunction in the Varian V-K3506 super stabilizer made it impossible to sweep the field and spectra were photographed on a Dumont Type 304-AR oscilloscope with a Dumont oscillograph-record camera.
Spectra were recorded from about $120^\circ C$ to about $300^\circ C$. The spectra were not all recorded in sequence of increasing temperature, but the sample was always brought to thermal equilibrium by heating, never by cooling, in order to avoid any possible complications from hysteresis effects in the vicinity of phase transitions. A minimum of two hours was always allowed between runs in order to achieve thermal equilibrium. Due to restrictions on the availability of the equipment, it was not possible to leave the sample at equilibrium for several hours when near a transition point as was done by Grant (12). The possibility of non-equilibrium conditions near a phase transition was investigated in some cases by repeating spectra after different periods of time at a constant temperature. It was found that the two hour period was satisfactory except when exactly on a transition point where a four hour period was adequate. However, even within as close as $20^\circ C$ to a transition the two hour period was satisfactory. Hence at worst a transition would only be slightly displaced due to non-equilibrium conditions.

The sample was heated by a stream of compressed air flowing over a resistance wire element in a tin can heater constructed by a co-worker. The heated stream was passed through a dewar lead into the sample dewar. The stream passed down over the sample and out a return passage. The temperature was recorded by a copper-
constantan thermocouple placed in the return air stream about 12 cm above the coil in the sample insert. Due to the construction of the lead it was impossible to place the couple closer to the coil surrounding the sample. However, at the conclusion of the runs the temperature gradient between sample and thermocouple was determined by running a second couple through the air intake and into a sealed but empty sample tube. The presence of the couple in the air intake passage affected the rate of flow. Unfortunately, as will be noted below it was not feasible to put a pressure guage in the system and while it was attempted to maintain equivalent flow rates, the rates may have been different. Constancy of temperature when taking spectra was checked by graphical recording. Temperatures remained constant within ±0.5°C for the runs recorded. The reported temperatures are the average of readings taken on a precision potentiometer at the beginning and end of the set of spectra at each temperature. The electrical heater was controlled by a variac plugged into a constant voltage transformer. Using a needle valve and pressure guage it was impossible to get sufficient air flow to give adequate heating and it was necessary to take the air directly (with filtering) from the lines. Fluctuations in temperature greater than those noted above were observed due to air pressure change but in such cases the system was permitted to re-establish equilibrium before spectra were recorded.
A. FATTY ACIDS

The original intention in undertaking this infrared investigation of some selected fatty acids had been to carry out fairly precise quantitative measurements. However, a number of unsuccessful attempts showed that accurate control of orientation, sample thickness, reflectivity and scattering in solid films would be very difficult. This applies also but to a slightly lesser extent to samples run in KBr pellets. As noted earlier, sample thickness was chosen to give essentially equal true and apparent extinction coefficients. However, due to other factors, including non-parallel radiation and finite slit width as well as those above, the true and apparent coefficients may still differ by some 20%. Indeed, it has been stated (53) that the considerable labour involved in evaluating true extinction coefficients and integrated absorption intensities for solid samples is scarcely justified by the results obtained. Fortunately, however, in the optical density range from 0.2 to 0.7 the true and apparent integrated absorption intensities may differ by only about 5% and apparent intensity can be used quite satisfactorily. No attempt therefore was made in
this work to obtain true values but comparisons were made between apparent values. If care is taken reasonably good relative values may be obtained for solid phase infrared spectra.

Preliminary studies of the infrared spectrum of stearic acid from 4000 cm\(^{-1}\) to 600 cm\(^{-1}\) showed (Figures IX and X) a general broadening and loss of definition of the bands, particularly the CH\(_2\) bands, on heating. In the full spectrum the 727, 720 cm\(^{-1}\) doublet is barely resolved and rapidly loses its definition as the temperature increases.

Appendix I contains reproductions of representative expanded spectra of all four acids studied. The expanded spectra were transferred from the logarithmic grid on the chart paper to a linear plot of optical density against wave number. The behaviour of the spectra with changing temperature is shown in Figures XI, XII, XIII, XIV for samples run as crystalline films between salt plates. The behaviour when samples were run in KBr pellets was similar.

The total band between 750 and 700 cm\(^{-1}\) was resolved into its component bands by using the absorption in the vicinity of 750 cm\(^{-1}\) to fix the base line. Preliminary spectra had indicated that for all the acids, the absorption at 750 cm\(^{-1}\) was a convenient local minimum (it was in fact the absolute minimum for the entire range 4000 to 600 cm\(^{-1}\)) and that the minimum
FIGURE X
STEARIC ACID 80°C

OPTICAL DENSITY

FREQUENCY, CM⁻¹

0.00 0.10 0.20 0.30 0.40 0.50 0.60 0.70

0.00 2500 5000 7500 10000 12500 15000 17500 20000

TO FOLLOW PAGE 58
FIGURE XIII
MYRISTIC ACID EXPANDED SPECTRA
M.P.T. 54.3-54.5°C

The spectra marked "A" exhibit anomalous behaviour. The 727 cm⁻¹ band does not disappear, but becomes the principal peak above the transition range.

The spectrum marked "N" indicates the expected "normal" behaviour (observed for other myristic acid samples) of the corresponding temperature "anomalous" spectrum.
remained essentially constant (about \(\pm 0.01\) optical density change). Resolution of the bands was made using this baseline according to the following criteria (8):

(i) that the extinction coefficients of the bands were additive,

(ii) that the bands were symmetrical about their maxima,

(iii) that the bands possessed no appreciable portion of their areas in long tails extending far from their maxima,

and (iv) that the transmission losses due to scattering could be interpolated from transmission measurements on either side of the band where no absorbance was assumed to occur.

The resolution of spectra in the vicinity of 35°C is indicated in Figures XV, XVI, XVII, XVIII.

Two prominent peaks and a third peak which sometimes appears only as a shoulder were recognizable in the 750 to 700 cm\(^{-1}\) region. The peaks were resolved according to the procedure outlined above and their variation in integrated intensity with temperature plotted in Figures XIX, XX, XXI, XXII. The intensities given are in arbitrary units unrelated from one acid to the next. Accurate resolution was extremely difficult and errors in integrated intensities of 15% may easily be encountered. Because of the difficulty in resolution, it was decided
FIGURE XV
STEARIC ACID
RESOLUTION AT 34.2°C
FIGURE XVI
PALMITIC ACID
RESOLUTION AT 34.5°C
FIGURE XVII
MYRISTIC ACID
RESOLUTION AT 33.1°C
FIGURE XVIII
LAURIC ACID
RESOLUTION AT 33.6°C
FIGURE XIX
STEARIC ACID.
TEMPERATURE DEPENDENCE
OF THE APPARENT
INTEGRATED ABSORPTION
INTENSITIES OF THE
RESOLVED BANDS

- 720 CM⁻¹ BAND
- 727 CM⁻¹ BAND
- HIGH FREQUENCY BAND (~735 CM⁻¹)

• STARTING TEMPERATURE
■ DECREASING TEMPERATURE
□ INCREASING TEMPERATURE

TO FOLLOW PAGE 59
FIGURE XX
PALMITIC ACID
TEMPERATURE DEPENDENCE
OF THE APPARENT
INTEGRATED ABSORPTION
INTENSITIES OF THE
RESOLVED BANDS

STARTING TEMPERATURE
DECREASING TEMPERATURE
INCREASING TEMPERATURE
FIGURE XXI
MYRISTIC ACID ("ANOMALOUS")
TEMPERATURE DEPENDENCE
OF THE APPARENT
INTEGRATED ABSORPTION
INTENSITIES OF THE
RESOLVED BANDS

NOTES:
(1) FOR A NORMALLY BEHAVING MYRISTIC
ACID SAMPLE, THE 727 CM⁻¹ BAND IS NOT FOUND
IN THE TRANSITION OR MELT REGIONS AS IT IS IN
THIS PARTICULAR ANOMALOUSLY BEHAVING SAMPLE.
(2) THE PARALLEL DISPLACEMENTS OF THE
COOLING PORTIONS OF THE CURVES ARE DUE TO
CHANGES IN THE ORIENTATIONS IN THE POLYCRYSTALLINE
FILM AFTER REFREEZING FROM THE MELT.
FIGURE XXII
LAURIC ACID

TEMPERATURE DEPENDENCE
OF THE
APPARENT INTEGRATED ABSORPTION INTENSITIES
OF THE
RESOLVED BANDS

720 CM\(^{-1}\) BAND

727 CM\(^{-1}\) BAND

HIGH FREQUENCY BAND
(731 CM\(^{-1}\))

\(\bullet\), \(\square\) STARTING TEMPERATURE
\(\bullet\), \(\blacksquare\) DECREASING TEMPERATURE
\(\bigcirc\), \(\Box\) INCREASING TEMPERATURE

TEMPERATURE °C
that apparent integrated absorption intensities were all that were justified for computation.

In the four acids investigated the most intense band found in the 750 to 700 cm$^{-1}$ region is at 720 cm$^{-1}$. Reproducibility of band frequency is about ±0.5 cm$^{-1}$ but the band does seem to range from 719.5 cm$^{-1}$ for stearic acid to 720 cm$^{-1}$ for lauric acid. For palmitic and myristic acids the frequency is slightly below but close to 720 cm$^{-1}$. Within experimental error the band's frequency is unaffected by temperature until the melting point is approached. Then over a narrow temperature range (see Table VII) the band shifts slightly to between 720.5 and 721 cm$^{-1}$. The band intensity remains fairly constant for all the acids until the melting point is approached but then begins to drop and, in the same narrow temperature range (Table VII) referred to above, reaches a value constant within experimental error from that point upwards. Resolution and band position above the melting point is, however, a contentious issue which will be mentioned later.

The second most prominent band in the region is that at 727 cm$^{-1}$. Although for convenience this band will always be referred to as the 727 cm$^{-1}$ band, its frequency as seen in Table VII varies slightly with temperature. At low temperatures there is a clear splitting between this band and the 720 cm$^{-1}$ band, which overlaps it, and even within 5°C of the melting point it appears as a prominent
shoulder on the total band. Its intensity, which is relatively less than that of the 720 cm\(^{-1}\) band, is considerably affected by temperature. The band intensity either diminishes steadily from the lowest temperature observed (myristic and stearic acids) or at least begins to diminish much sooner before the melting point than for the 720 cm\(^{-1}\) band (lauric and palmitic acids). As indicated in Table VII, just below the melting point the band does not reach a constant value but seems to disappear entirely. Some samples of myristic acid exhibited an anomalous behaviour which will be reported later in this chapter.

In addition to the two distinct bands in the 750 to 700 cm\(^{-1}\) region, a third band was observed towards higher frequency. Its frequency range for the acids is shown in Table VII. This band, referred to hereafter as the high frequency band, appeared in lauric acid as a very distinct band of about equal shape and intensity to that of the 727 cm\(^{-1}\) band which it overlapped. In myristic acid it appeared as a barely recognizable shoulder but in palmitic acid it appeared as a separate peak clearly distinct from and not overlapping the others. For stearic acid the band is again a shoulder. In lauric and palmitic acids the band's frequency remains essentially unaffected by temperature. In lauric acid its intensity follows a behaviour with increasing temperature similar to that of the 727 cm\(^{-1}\) band with the exception that just below the
melting point it does not disappear but reaches a constant value as did the 720 cm\(^{-1}\) band. For palmitic acid the band may also reach a constant intensity just below the melting point. In stearic acid the high frequency band appears as a shoulder caused by a broad, low band. Its frequency and intensity are greatest between 60 and 67°C and are less towards room temperature. For myristic acid only an unresolvable shoulder can be found. The band's shape is probably similar to that in stearic acid. Due to the varying behaviour of the high frequency band in the different acids, it is not entirely clear if the same band is being referred to in each case. Certainly other shoulders in the region suggest that a number of weak bands overlapped by the stronger ones may be present.

Myristic acid requires special mention. Some samples of this acid behaved anomalously. Two samples at about 30°C showed 727 cm\(^{-1}\) peaks that were more intense than the 720 cm\(^{-1}\) peak. The intensity ratio assumed the normal relationship on rotating the sample 90° in the spectrometer beam or heating about 150°. In none of the other acids was a reversal of the relative intensities observed on rotation. In addition, for the anomalous myristic acid sample shown in Figure XXI, the 720 and 727 cm\(^{-1}\) bands were of equal intensity at low temperatures, remained so, and remained fairly constant with increasing temperature. Just below the melting point not only did the 727 cm\(^{-1}\) band not disappear but above the
melting point it appeared at about 729 cm\(^{-1}\) as a more intense band than the band found at about 721 cm\(^{-1}\) in all the melts. Other myristic acid samples, however, showed disappearance of the band in a manner similar to that for the other acids. For these other myristic acid samples, the high frequency shoulder is slightly more pronounced than in the so-called anomalous samples.

Figures XIX to XXII show that a slight decrease in intensity takes place through the melting point before constant intensity is reached. This is difficult to say with certainty due to the considerable scattering of points, however, the spectra unquestionably take on a liquid-like character a short distance below the melting point.

Figures XIX to XXII also show that the intensity-temperature curves possess hysteresis loops. There is some evidence that the width of these loops is dependent on the rate of cooling. The widths are in all cases wider than can be accounted for by the acids' freezing points being lower than their melting points (see Table VI). While the loops do not always rejoin the curve they usually lie within the scatter of points about it. In some cases the cooling portion of the curve was displaced vertically from the heating portion to a degree greater than could be accounted for by the difficulty in resolution. This could have been due to slumping of the films above the melting point but since the same phenomenon was also found in some
of the samples run in KBr discs, it was probably due to reorientation of the sample on cooling from above the melting point. This is indicated by the fact that the cooling and heating curves were co-incident below the melting point if the sample had not been melted. It was only when cooling from above the melting point that this phenomenon was sometimes observed. Repetition of runs on lauric acid showed that, until the hysteresis region was reached, the intensity of the curve on re-heating was, within experimental error, the same as that of the cooling curve on the previous run.

Resolution above the melting point deserves some consideration. At all temperatures resolution was fairly difficult, but above the melting point it is highly questionable and may be meaningless. For melt spectra a single asymmetric band was found. The upper and lower frequency ends of the band appeared to have broadened and overlapped with neighbouring bands. This may in part be due to different scattering and reflective properties of the melt. Compared to the total band at low temperatures, the total band's extinction coefficient and integrated absorption intensity were much diminished above the melting point. The integrated intensity was down by a factor of three in each case. The asymmetrical band had its maximum at about 721 cm$^{-1}$. Using this point as a center, a symmetrical band could be resolved and assigned to the 720 cm$^{-1}$ band in the melt. This left a single,
Table VII. Intensities and Frequencies of Resolved Bands

<table>
<thead>
<tr>
<th>Acid</th>
<th>Melting Point °C</th>
<th>Transition Range °C</th>
<th>Bands in Solid Frequency in cm⁻¹</th>
<th>Bands in Melt Frequency in cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stearic</td>
<td>69.5-69.8</td>
<td>67.2-67.8</td>
<td>719.5 S 729-726² M ™ 736-733.5³ W 721 M (735) W</td>
<td></td>
</tr>
<tr>
<td>Palmitic</td>
<td>63.0</td>
<td>61.3-63.0</td>
<td>720 S 729-726.5² M ™ 740.5 W 721 M (735) W</td>
<td></td>
</tr>
<tr>
<td>Myristic</td>
<td>54.3-54.5</td>
<td>52.6-53.8 ⁴</td>
<td>720 S 728.5-726.5² S-M (735) W 721 M (735) W</td>
<td></td>
</tr>
<tr>
<td>Lauric</td>
<td>44.0-44.3</td>
<td>43.9-43.7</td>
<td>720 S 727-724² M ™ 731 M 721 M (735) W</td>
<td></td>
</tr>
</tbody>
</table>

S, strong intensity; M, medium intensity; W, weak intensity. All values of intensity relative to that of the 720 cm⁻¹ band. The position of any bracketed band is tentative.

1 For a given acid the first temperature range in this column is that in which on heating the 720 cm⁻¹ and high frequency bands reach a constant minimum intensity and in which the 727 cm⁻¹ band disappears. In and above this range the bands can no longer be described as in column four but must be described as in column five. The second temperature range for each acid is that in which a reversal of the above takes place on cooling.

2 The frequency of this band decreases with increasing temperature for all the acids.

3 The frequency of this band in stearic acid appears to increase with increasing temperature.

4 One sample of this acid behaved anomalously in that instead of disappearing in the noted range, its 727 cm⁻¹ band merely changed shape between 52.7 and 53.4°C and assumed a constant intensity above the range. The reversal on cooling took place between 49.0 and 48.0°C. In this case in the melt the tentative 735 cm⁻¹ band was replaced by a band at 729 cm⁻¹ which was more intense than that at 721 cm⁻¹.
low and broad, irregularly shaped band which could not possibly be resolved into two bands. This band was centered in the vicinity of 735 cm\(^{-1}\) for all the acids and it seems possible that it may correspond to the position in the melt of the third, high frequency, band which was found in the solid. It appears that the 727 cm\(^{-1}\) band has disappeared in the melt. The procedure of resolution in the melts is rather arbitrary with the 721 cm\(^{-1}\) band being taken to contribute most to the total band. Based on the asymmetry of the total band this is probably justified however.

Finally visual observations were made on crystalline films of the acids as they were heated on a hot-stage microscope. The heating rate was about 0.2°C/min but an extremely slow rate of heating (1°C in 45 min) on a repeat of stearic acid confirmed that the effects reported below were not rate of heating phenomena. At the temperatures listed in Table VIII, the acids appeared to undergo a "jump" as though strains were being released. The interiors of the crystalline films appeared to become somewhat plastic although the exterior crystalline outlines were maintained. The observations are somewhat marginal but have been confirmed by Grant for stearic acid (82).

<table>
<thead>
<tr>
<th>Acid</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stearic</td>
<td>68.0</td>
</tr>
<tr>
<td>Palmitic</td>
<td>62.0</td>
</tr>
<tr>
<td>Myristic</td>
<td>53.7</td>
</tr>
<tr>
<td>Lauric</td>
<td>41.5</td>
</tr>
</tbody>
</table>
B. SODIUM STEARATE

The changing nuclear magnetic absorption line shape is illustrated in Appendix II which reproduces representative high resolution spectra. Only one spectrum of the several taken at a particular temperature is shown but a typical spectrum was always reproduced. Some spectra exhibited considerable base line drift. This drift was in some cases due to a shifting balance in the n.m.r. probe and could be corrected. However, the probe was malfunctioning during this series of runs and could not always be properly balanced.

Two series of runs on the same sodium stearate sample are shown in the line width (Figure XXIII) and second moment (Figure XXIV) against temperature plots. In the first set, marked O, a medium sweep rate was used while for the second set, marked ●, a rate twice that of the first set was used. In Appendix II the reproductions of the spectra are identified as to set by the appropriate symbols placed beside the spectra's temperatures. The faster sweep rate meant that the recorder traced a narrower line which could be measured less accurately than the broader line at the lower sweep rate. However, the faster rate appeared to give a signal whose wings generally were less affected by base line drift and noise than for the slower rate.
\[ \Delta H_{1/2} \text{ for water at } 25^\circ C \text{ under the same conditions as set one is } 0.02 \text{ gauss.} \]
FIGURE XXIV
SODIUM STEARATE
SECOND MOMENTS

$\Delta H^2$ for water at 25°C under the same conditions as Set One is $\sim 10^{-4}$ gauss$^2$.
The original intention in the investigation of sodium stearate had been to plot derivative curves from the absorption curves and hence determine the line widths between maximum and minimum slope. However, for the spectra between 120 and 235°C the line widths were essentially constant being between 0.06 and 0.09 gauss. Above 235°C the line width narrowed to about 0.01 or 0.02 gauss but could be measured even less accurately than at lower temperatures. The constancy of the line width between maximum and minimum slope indicates that the absorption line consists of a comparatively narrow spike superimposed on a broad pedestal. This is most apparent in the spectra taken at the faster sweep rate since in the slower sweep rate spectra the spike is partially masked by the wide signal. The line width at the same temperature is the same for both sets of course.

While the narrow spike did not change with temperature, the wings or pedestal did and the line width $\Delta H_{1/2}$ at one-half maximum amplitude gives a description of the behaviour of the signal. Below 120°C the line was too broad to be found on the spectrometer's oscilloscope and could not be recorded conveniently as an absorption curve. However, at 120°C the signal is narrow enough to be recorded on the high resolution spectrometer. At this temperature the wings are very prominent but they diminish steadily with increasing temperature until 235°C is reached. Between 235 and 237°C the wings disappear and the
absorption band takes on a shape, line width, and second moment comparable to that of a water sample the spectrum of which was taken in the same field for comparison.

The variation of line width with temperature is shown in Figure XXIII. The only transitions which are clearly indicated by the line width-temperature curve are between 119 and 120°C and between 235 and 237°C. In the former case the signal is too broad to be measured conveniently by high resolution techniques and an obvious change in line width takes place at this point even though line width cannot be measured below the transition (Grant (12) gives 2.8 gauss below the transition but places the transition at between 113 and 114°C). In the latter case the line width drops suddenly to a value comparable to that for a liquid but does this well before the melting point (275-280°C) of the sample is reached. The values reported here are at the limit of the experimental accuracy and the scattering of points makes it difficult to fix the transition points. Above 235°C, where the spectra have a completely liquid-like character, the base lines are better than at lower temperatures, but the line width in such a liquid-like region is governed by the field inhomogeneity. That the values given there are higher in the second set of runs than the first is believed to be due to the presence of a less homogeneous magnetic field in the former case.

The second moments were computed from the absorption signal by numerical integration. For numerical
integration of the absorption line, equation (49) becomes

\[ \Delta H^2 = (\text{scale factor})^2 \frac{\sum x^2 y}{\sum y} \]  \hspace{1cm} (52)

For calculation the base line is taken as the x-axis, which is divided into equal divisions, the y value for each division measured, a scale factor in gauss/division computed from the sweep rate calibration, and the sums computed.

In set one base line difficulties made it necessary to average the absorption lines by superimposing them on each other and drawing an average curve for each temperature. This was the only possible way to obtain values for that set. In set two the same procedure was followed but it was found in checking the second moment obtained from the averaged curve against moments obtained from individual curves, that the average curve's second moment was very sensitive to the manner in which the wings were drawn in. Consequently moments were computed from the individual spectra in set two. Unfortunately due to variations in wing area, individual second moments at the same temperature could differ by large amounts (100% in an extreme case). In set one there frequently was, as may be seen from Appendix II, the additional complication of a high noise level in the wings. The variable wings seriously affect the accuracy of the second moment calculations. The point of one-half maximum amplitude is well above the wings and due to the comparative narrowness of the spike the \[ \frac{\Delta H}{2} \] line width is relatively unaffected (differences between individual spectra
at the same temperature were of the order of 10% by differing base lines. The second moments, nonetheless, proved to be the more useful of the two measurements.

In spite of their seeming inaccuracy, the second moment calculations gave results which, as will be seen later, were readily interpretable. The second moment curve (Figure XXIV) in its lower temperature region agrees reasonably well with the values obtained by Grant (12) between 114 and 130°C. However, the transition reported by Grant as occurring between 113 and 114°C appears from this work to take place between 119 and 120°C. Grant determined the value of the second moment just below the transition as 6.7 gauss$^2$. This would be consistent with the low, too broad to be measured signal found below 120°C in the present work. No abrupt changes in second moment can be seen between 120 and 235°C. The second moment decreases gradually but remains, within experimental error, at about 0.1 gauss$^2$. Between 235 and 237°C a sudden change takes place. The second moment decreases to a value of the order of $10^{-4}$ gauss$^2$ comparable to the value found for a water sample at room temperature in the same field.
CHAPTER VII

DISCUSSION

A. FATTY ACIDS

The 720 cm\(^{-1}\) doublet has been observed in the infrared spectrum of very many although not all compounds containing four or more consecutive straight chain methylene groups. That the band was due to the CH\(_2\) rocking vibration was established by many investigators only some of whom (59)(60)(62)(83)(84) are mentioned here. Although the intense 720 cm\(^{-1}\) band was recognized as only the terminal band of a long series extending from 720 to about 1050 cm\(^{-1}\) (83)(84) most work has been concerned with it.

Snyder (64) has derived an expression

\[
\omega^2 = (61.41 - 21.7 \cos \phi + 107.2 \cos^2 \phi - 5.29 \cos^3 \phi + 6.85 \cos^4 \phi) 10^4 \tag{53}
\]

which gives, to an excellent approximation, the frequency in cm\(^{-1}\) of the methylene rocking bands in unperturbed, fully extended n-paraffins. The expression depends on a single parameter \(\phi_{k,m}\) the phase difference between adjacent oscillators (the CH\(_2\) groups).

\[
\phi_{k,m} = k\pi/(m+1) \tag{54}
\]

\(k = 1, 2, 3, \ldots, m\)

\(k = \) odd for an infrared active vibration
In the above expression \( m \) is the number of methylene groups. Equation (53) was found to be independent of chain length, except for the dependence on \( m \), and could be used to predict the \( 
{\text{CH}_2} \) rocking frequencies in compounds not yet investigated.

Since the frequencies with which we are concerned arise from \( n \)-paraffin chains the equation (53) may be expected to apply to the fatty acid methylene chain at least to an approximation. The expression does not account for splitting but gives only the position of the unperturbed band. Calculated values for the band observed at 720 cm\(^{-1}\) in the fatty acids were satisfactory giving about 718 to 720 cm\(^{-1}\) for \( k=1 \). Since the high frequency band could be tentatively resolved in the melt region, it was felt that it was probably one of the members of the series of fundamental bands. It proved difficult to fit the high frequency band, however. For lauric acid the band appeared to correspond to a \( k \) value between 3 and 5 and for myristic, palmitic and stearic acids, it corresponded to a value between 5 and 7. Although the expression may be a rather crude approximation for the fatty acids, it does indicate that beneath the 720 cm\(^{-1}\) doublet there may be other, less intense bands of the \( \text{CH}_2 \) rocking series (\( k=1 \) corresponds to the first band, \( k=3 \) to the second band, etc.). These weaker bands cannot be seen until, like the so-called high frequency band, they are far enough from the intense terminal band not to be overlapped. This provides,
unfortunately, an obvious uncertainty in the resolution of the 720 cm\(^{-1}\) doublet components.

It was thought that the cause of the so-called anomalous behaviour in certain of the myristic acid samples might be attributed to the presence of another member of the methylene rocking series. Indeed, calculation from equations (53) and (54) showed that for \(k=5\) a fundamental band should appear at 728 cm\(^{-1}\) in excellent agreement with the observed value of 727 cm\(^{-1}\). The 727 cm\(^{-1}\) component which arises due to doublet splitting is markedly affected by polarization (8). One might suggest then that at certain orientations in the spectrometer beam (the beam is polarized to a slight extent (53)), the 727 cm\(^{-1}\) component might be extinguished to such a degree that a previously submerged fundamental band at the same frequency might be seen. Fundamental bands do not disappear above the melting point and the band should therefore be seen in and above the transition region of the normally behaving sample if this explanation were correct. The band, however, is not found and the origin of the non-vanishing 727 cm\(^{-1}\) band in the anomalous myristic acid sample must be left unexplained.

Explanations for the appearance of a doublet in the 720 cm\(^{-1}\) region have been advanced by various investigators. Liang, Krimm and Sutherland (85)(86) pointed out in their discussion of the general theory and experimental behaviour of the infrared spectra of polymers
that while fundamental vibrational frequencies may be assigned without error by considering an isolated molecule, the splitting of frequencies arises from interactions with neighbouring chains. Prior to Liang et al, Stein and Sutherland (8) had attributed the 720 cm\(^{-1}\) doublet splitting to interactions between CH\(_2\) groups (it had been well established previously that this band was due to the CH\(_2\) rocking mode) and had discussed the splitting qualitatively on this basis. Krimm (87) demonstrated conclusively that the splitting was due to intermolecular interactions and Stein (63) on the basis of in-plane nearest neighbour hydrogen atom interactions derived expressions for the splitting and temperature dependence of the components of the 720-727 cm\(^{-1}\) doublet. He attributed the 727 cm\(^{-1}\) peak to in-phase CH\(_2\) rocking interactions and the 720 cm\(^{-1}\) peak to 180° out-of-phase interactions. Unfortunately Stein's calculations could not be extended to a correct explanation of the behaviour of the CH\(_2\) symmetrical deformation at 1460 cm\(^{-1}\). However, Snyder (5) has pointed out that by considering interactions in adjacent planes which had been overlooked by Stein a correct interpretation could be given. Chapman (88) pointed out that the doublet could be correlated with orthorhombic packing of hydrocarbon chains while the single band at the same position could be correlated with hexagonal or triclinic packing. Chapman (9) noted that when end groups are disregarded, a layer of chains may be considered as
being composed of repeating units or subcells. Then, reasoning from symmetry arguments similar to those of Krimm et al (86) and Tobin (89), he concluded that the two methylene chains in the orthorhombic subcell would make possible two components of the fundamental vibration. This would be the case in the C-forms of the fatty acids which all have this subcell. Since the magnitude of the splitting is due to intermolecular interactions, it is possible that if the dimensions of the cell are unusually large or if cell distortions are present no splitting may be observed (9) even though theoretically present. In the triclinic and hexagonal subcells only one chain is present and hence only the fundamental frequency exists. The work of Holland and Nielsen (62) has confirmed the correlation of orthorhombic chain packing with doublet splitting and triclinic and hexagonal packing with non-splitting.

The temperature dependence of the 720-727 cm\(^{-1}\) doublet in the infrared spectra of the fatty acids enables one to estimate the disorder and hence extent of premelting in the acids. Stein and Sutherland (8) have stated that for pure crystalline hydrocarbons both components of the doublet are of equal intensity (this is not necessarily so - see Snyder (5) below). This implies that the fatty acids possess some degree of amorphous character. This has been confirmed by Grant (12) who suggested from n.m.r. evidence that stearic acid has
crystalline and amorphous phases coexisting. If an amorphous phase exists there will be a superposition of amorphous and crystalline spectra to give a single spectrum in which the $720 \text{ cm}^{-1}$ component is more intense than the $727 \text{ cm}^{-1}$ one. Stein and Sutherland's work on polythene (8) showed that for a sample containing amorphous and crystalline phases the $727 \text{ cm}^{-1}$ peak was due solely to a contribution from the crystalline portion while the intensity of the $720 \text{ cm}^{-1}$ peak was due to contributions from both the crystalline and amorphous portions. Applying this reasoning to the fatty acids, an estimate may be made of their crystallinities.

Let $I_{720}$ represent the total, measured apparent integrated absorption intensity (for convenience integrated intensity or intensity is sometimes used in this thesis but apparent integrated absorption intensity is always meant) of the $720 \text{ cm}^{-1}$ component of the doublet and $I_{727}$ be that of the component about $727 \text{ cm}^{-1}$. Let $I_{720a}$ represent the intensity of the component at $720 \text{ cm}^{-1}$ if the sample were completely amorphous and $I_{720c}$ and $I_{727c}$ the intensities for the $720$ and $727 \text{ cm}^{-1}$ bands respectively if the sample were completely crystalline. Now, if $x$ is the fraction of crystalline material in the sample, then

\[
I_{727} = x I_{727c} \tag{55}\]

\[
I_{720} = x I_{720c} + (1-x) I_{720a} \tag{56}\]
\[ \frac{I_{727}}{I_{120}} = \frac{x I_{727c}/I_{120c}}{x + (1-x)I_{720a}/I_{120c}} \quad \cdots \cdots (57) \]

and solving for \( x \) one obtains

\[ x = \frac{\mathcal{P}}{\left[ \frac{I_{727c}/I_{120c}}{I_{727}/I_{120}} \right] + (\mathcal{P} - 1)} \quad \cdots \cdots (58) \]

where \( \mathcal{P} = I_{720a}/I_{120c} \).

In expression (58) the ratio \( (I_{727}/I_{120})_t \) may be readily obtained from a plot of the ratio against temperature. When the sample is completely crystalline \( x=1 \) and from equation (57) \( (I_{727c}/I_{120})_0 = \lim_{x \to 1} (I_{727}/I_{120})_t \).

Plots of \( (I_{727}/I_{120})_t \) against temperature (not shown here) indicate that the slope of the curve is zero at the lower temperatures studied in this work. If the constancy of the ratio may be taken to mean that the sample is completely crystalline, then \( (I_{727c}/I_{120})_0 \) may be safely evaluated some 60 to 900°C below the melting point. This cannot be stated with certainty from infrared data, but it seems a reasonable assumption.

Snyder (5) has obtained an expression for the relative intensities of the components in the \( \text{CH}_2 \) rocking doublets in crystalline paraffins. When applied to the 720-727 cm\(^{-1}\) doublet the expression gives

\[ \frac{I_{727}}{I_{120}} = \tan^2 \theta \quad \cdots \cdots \cdots \cdots (59) \]
where $\Theta$ is the angle which the plane of the hydrocarbon chain makes with the a-axis of the cell. Hence if $\Theta$ is less than $45^\circ$ at low temperatures, the intensity ratio will be less than one even though the sample is completely crystalline. Equation (59) gives values of $\Theta$ between 37 and $44^\circ$ for the four acids investigated. These values are in good agreement with the value of $42^\circ - 5^\circ$ found by Smith (90) for orthorhombic n-$C_{23}H_{48}$ and that of $38^\circ$ computed for C-form lauric acid from Vand's data (27). This suggests that the values of the $(I_{727c}/I_{720c})$ ratios used in the calculation of the crystallinity curves shown in Figure XXV are probably fairly correct.

The value of $\rho$ can only be estimated since it is dependent on measurements above the melting point which may be of doubtful accuracy. In the melt region not only is resolution difficult but also errors due to different scattering and reflectivity from that below the melting point may be encountered. Above the melting point $x = 0$ and $I_{720a} = I_{720}$ or, as it is then called, $I_{721}$. At low temperatures where $x = 1$, it is seen that $I_{720c} = I_{720}$. Evaluation of the ratio suggested that $\rho = \frac{1}{2}$ was a reasonable estimate. A check on the value of $\rho$ may be obtained by examining the behaviour of the 720 cm$^{-1}$ component. By rearranging equation (56) to give

$$I_{710} = I_{720a} + x(I_{720c} - I_{720a}) \quad (60)$$
FIGURE XXV
CRISTALLINITY OF THE FATTY ACIDS AS A
FUNCTION OF CLOSENESS TO THE
MELTING POINT

\[ T_m - T \] °C

TO FOLLOW PAGE 79

- x - STEARIC ACID
- • - PALMITIC ACID
- o - MYRISTIC ACID, "ANOMALOUS" SAMPLE
- □ - MYRISTIC ACID, "NORMAL" SAMPLE
- o - LAURIC ACID
one sees that if $\rho > 1$, $I_{720a} > I_{720c}$ and $I_{720}$ increases as $x$ decreases. If $\rho = 1$, $I_{720a} = I_{720c}$ and $I_{720}$ remains constant. If $\rho < 1$, $I_{720a} < I_{720c}$ and $I_{720}$ decreases as $x$ decreases. It is the last case which applies for the fatty acids thus confirming that $\rho = \frac{1}{2}$ is of the correct magnitude.

In Figure XXV, the crystallinity $x$ is plotted for each of the four fatty acids as a function of $T_m - T$ the temperature interval below the melting point $T_m$. Well below the melting point the acids show what might be considered a surprising lack of crystallinity. The lack of crystallinity is so great that one wonders if $x$ does indeed represent that quantity. Perhaps estimate of order might be a better designation for $x$. Comparison of these curves with similar curves derived from n.m.r. data presented in Barr, Grant and Dunell (11) shows that while qualitative behaviour is the same, with the same relative order of crystallinity being maintained, the infrared curves indicate much greater non-crystallinity for the samples. This might be attributed to errors in evaluating $\rho$ but even a value of $\rho = 2$, (not shown here), which cannot possibly be justified by the experimental results, while it gives a reasonably appearing crystallinity curve still shows less crystallinity than that indicated by the n.m.r. curves. Probably the infrared results are fairly good, at least to the extent of being a good qualitative representation, and the discrepancy may perhaps
be explained by a difference in the pictures "seen" by infrared and n.m.r.

Since one would expect n.m.r. to be more sensitive to molecular reorientation than is infrared spectroscopy, it is surprising, unless the results here are grossly in error, that the infrared data indicate a higher degree of disorder than the n.m.r. This may possibly be explained by noting that n.m.r. calculations show only those molecules which are reorienting. Perhaps as in form A of potassium caprate (31), there is not a perfectly repeating crystal pattern in the fatty acids and a partially random succession of chain inclinations and orientations from layer to layer may exist. Vand (27) has found that the hydrocarbon chain in C-form lauric acid is not fully extended in a zigzag but is bent. This may affect the phase relationships between the oscillators (methylene groups) in the chain and result in a partly amorphous character for the infrared spectra. If some chains are in disarray or even slightly twisted but still rigidly fixed, the infrared spectra, which for the 720-727 cm\(^{-1}\) doublet are dependent on ordered crystal interactions, could indicate a fairly high amorphous nature at a comparatively low temperature. The n.m.r. spectra, however, would not show this since the molecules although in some disorder (perhaps slightly twisted or not fully extended) would still not be reorienting.

The crystallinity curves in Figure XXV. show a
steadily increasing disorder from quite far below the melting point for stearic and myristic acids as the temperature is increased. Palmitic and lauric acids show the same behaviour but disorder does not become pronounced until higher temperatures are reached. It appears that an alternation of order may exist among the four fatty acids studied here. Lauric (C₁₂) and palmitic (C₁₆) acids fall in the same region in Figure XXV and behave similarly with changing temperature. Normally behaving myristic acid (C₁₄) and stearic acid (C₁₈) also fall together, but in a different region from the other two acids, and also behave similarly to each other with changing temperature.

Since the normal myristic sample was in a preliminary set which was not taken below 30°C its low temperature values were obtained by extrapolation and it consequently is the least reliable of the curves shown. It is felt, however, because of the general similarity of the behaviour of its spectra to that of stearic acid, that its position near the latter acid indicates that the curve lies in the correct general region. It probably should indicate, however, that myristic acid is more crystalline than stearic acid rather than the reverse. It is unfortunate that the run on myristic acid which included low temperatures was a sample that behaved anomalously. The comparatively high crystallinity exhibited by this sample may be due to the possibility expressed above that a fundamental rocking mode, which does not vanish in intensity above the melting point,
was contributing to the apparent 727 cm\(^{-1}\) band arising from intermolecular perturbations. Possibly the correct myristic acid curve is between the two showing fairly much more crystallinity than the normal curve, as is suggested by the anomalous curve, but having a shape similar to that of the normal curve.

The gradually increasing disorder exhibited by the fatty acids as the temperature is increased may be termed the approach to or perhaps beginning of premelting. There is some doubt as to how accurately the crystallinity curves in Figure XXV represent the true conditions. There is no doubt, however, about the disappearance of crystallinity in the transition region slightly below the melting point. The curves in Figure XXV and the transition range in Table VII show that crystallinity finally disappears fairly abruptly about 2\(^{\circ}\) below the melting point in stearic acid, about 1.5\(^{\circ}\) below in both normally and anomalously behaving myristic acid and about 1\(^{\circ}\) below in palmitic and lauric acids. Except for lauric acid, these temperatures correspond with those, listed in Table VIII, at which the crystals appeared to become somewhat plastic. In addition although infrared and n.m.r. techniques indicated different degrees of crystallinity over the range studied, they showed that the actual temperatures at which crystallinity vanished were the same by both methods (11). The infrared spectra take on a completely liquid-like appearance (as do the n.m.r. spectra) in the transition
region but seem to decrease in intensity a slight amount when the respective melting points are reached. This exhibition just below the melting point of an abrupt discontinuity in the crystallinity which clearly foreshadows actual melting exactly fits the definition of premelting.

Until the fatty acids' transition temperatures are reached the infrared results merely show a gradually increasing disorder. Probably, as suggested by Chapman for sodium soaps (4), as the temperature is increased the increasing lack of resolution between the band components is due to the hydrocarbon chains beginning to flex and twist. This will produce some rotational isomerism with each isomer having its own slightly different frequency in the region with a resultant smearing out of the spectrum. That is, as the chains twist and flex, it will no longer be possible to have all oscillators exactly in-phase and out-of-phase. Band intensity will diminish since there will be fewer oscillators at any one frequency and the bands will widen out since more vibrational frequencies will arise in the region due to the increased number of phase relationships between oscillators. Grant (12) has pointed out that lattice defects due to dislocations and impurities in the crystal might allow the hydrocarbon chains to rotate about their long axes and to flex and whip about while remaining in their lattice positions. Then as the temperature rose the zones of
motion and disorder would grow at the expense of the surrounding, ordered crystal structure until just below the melting point the structure was completely amorphous. The melting point then would correspond to the breakdown of the amorphous structure.

A transition below the melting point has not been reported in the fatty acids by previous investigators (8)(56)(91) except for one acid (91). This may possibly be due to the closeness of the transition point to the melting point and the fact that in unexpanded spectra (56)(91) the behaviour of the doublet components is difficult to observe. The one case in which a transition was found was in capric acid where Corish and Chapman (91) reported that, on cooling the sample the single 720 cm$^{-1}$ band split into a doublet somewhere between 24 and -78°C. Since this was in unexpanded spectra it is very likely that in expanded spectra the doublet could be distinguished considerably closer to the acid's melting point at 31.5°C. Corish and Chapman suggested that the capric acid transition was analogous to that observed (88) when long-chain hydrocarbons, esters and alcohols change from a higher temperature hexagonal form with rotating chains to a lower temperature more stable orthorhombic form. As noted earlier the hexagonal form will not show splitting, the orthorhombic form will.

It seems possible then that the transition in the fatty acids may be from an orthorhombic chain packing.
to a hexagonal chain packing. In support of this, one may note that Holland and Nielsen (62) have stated that the hexagonal form in paraffins occurs only above a transition and close to the melting point. Below the transition the form is orthorhombic as with the C-form fatty acids. Above the transition, in the hexagonal subcell, one may expect rotation of the hydrocarbon chains about their long axes (92). Crowe and Smyth (93), however, suggested from dielectric measurements on the C-form of stearic acid that there was no rotational phase below the melting point. This observation may again be due to the closeness of the transition to the melting point. The narrow component n.m.r. line width found (11)(12) in the acids near the melting points suggests molecules in rapid motion. Finally, for the somewhat analogous n-paraffins, Stein (8)(63) related the infrared transition with the discontinuities observed by Muller (95) in the x-ray diffraction patterns. The discontinuities correspond to the \( \lambda \)-points of the respective hydrocarbons. Above these points there is an onset of free rotation or randomness of orientation about the long axes of the molecules (96).

From the experimental evidence in this work, it appears that a change in crystal structure takes place fairly abruptly just below the melting points of the fatty acids when the 727 cm\(^{-1}\) or crystalline component of the doublet disappears. The transition is anticipated by a gradual decrease, over a long temperature range, of the
crystalline band. The gradual decrease indicates an increasing flexing and twisting and the beginning of rotation of the methylene chain portion of the molecule. The growing disorder may take place by a cooperative increase in lattice defects as noted above. That the fatty acids have transitions much closer to the melting point than in the n-paraffins (except for very long chain paraffins which will exhibit some amorphous nature) is reasonable. If one imagines the n-paraffins as being roughly analogous to cylindrical rods, they may be expected to pack quite regularly into an ordered, crystalline array and exhibit the accompanying infrared spectra. However, because the chains are held together only by Van der Waal's forces, it is reasonable to expect those forces to be sufficiently weak to permit the n-paraffins to exhibit amorphous character some degrees below the melting point. While it has been suggested earlier that the chains of fatty acid molecules may not be in as regular an array as in the paraffins, it is probable that the intermolecular attractions involving the acids' carboxyl groups contribute to holding the chains fairly firmly in their somewhat disordered array. Thus, although the chains may twist and flex as the temperature is increased, the attractive forces anchor the molecules and the transition indicating a very large degree of disorder cannot take place until quite near to the melting point. At this point one feels that the steadily increasing disorder culminates in rapid, random
reorientation about the chain axes accompanied by the breakdown of the carboxyl layers. At such close proximity to the melting point it is likely that the change is not to an ordered crystal form (hexagonal has been suggested for other cases (62)(88)) but to an amorphous form closely resembling the melt. In this region the carboxyl layers are being broken down, diffusion is probably beginning to occur, and the melting point merely corresponds to the final breakdown of the amorphous structure. This would appear to be substantiated by the closeness, almost indistinguishability, of the spectra in the transition region and in the melt.

The final picture then of the fatty acids studied is that of a gradually increasing disorder which culminates in a transition to a very amorphous form close to but below the melting point. Since the transition form behaves very similarly to the melt, it may clearly be termed a premelting phenomenon with the final, slight breakdown of the amorphous form corresponding to actual melting.
B. SODIUM STEARATE

Table IV lists a number of high temperature phase transitions which have been observed in sodium stearate. Some transitions are hinted at in Figure XXIII between the obvious transitions at 119 to 120°C and 235 to 237°C but these intermediate transitions are very ill-defined and require a lively imagination for their observation. In addition, the line shape is changing in this region and under such conditions (97), line width is not a completely reliable index to the nature of temperature phenomena. The second moment, which is a reliable index (98), shows (Figure XXIV) only the single transitions at each end of the range.

At the 119 to 120°C transition there is a change in second moment from a value too large to be conveniently measured by high resolution to a value of the order of 0.1 to 0.5 gauss². Such a change surely suggests a transition from a fairly crystalline state to a state in which some liquid-like character is present. Below this transition, which he placed at 113 to 114°C, Grant (12) has observed that twisting and rotation occurs about the hydrocarbon chains' long axes. Above the transition the chains are believed to be completely free to rotate about their long axes and very likely free to flail about as well. He believed the ionic layers to be maintained however.
This is exactly the picture of a transition from a fairly crystalline phase to a phase with liquid-like character as is suggested below.

The second moment determined from the present high resolution work remains nearly constant between the two observed transitions in the high temperature region. The intermediate phases observed by other methods but not by n.m.r. must then be structurally similar. The slight slope to the second moment curve indicates gradually increasing motion but not sharp phase changes. It has previously been suggested that the hydrocarbon chains possess considerable liquid-like behaviour in this region. A rather oblique confirmation of this is given by the fact that all the second moments of set two are larger than those of set one in Figure XXIV. The greater magnitude for set two values was ascribed to slightly greater field inhomogeneity in that case, a condition which would affect the spectra of a liquid-like sample but not a solid.

There is an abrupt transition between 235 and 237°C. Here the sample's second moment falls from a value of the order of 0.1 gauss$^2$, believed to indicate a liquid-like condition, to a value of the order of $10^{-4}$ gauss$^2$. This very small second moment was of the same order as that of a water sample in the same field (but at room temperature). This very small liquid type second moment must indicate diffusion of molecules through the sample (94). At this point the attraction of the ionic layers must be overcome
and the sample takes on a behaviour, as far as n.m.r. is concerned, indistinguishable from the isotropic melt.

The following picture of sodium stearate is obtained from the high resolution n.m.r. results. Below 120°C the soap is probably essentially crystalline. The subwaxy, waxy, superwaxy and subneat phases form a structurally similar group exhibiting liquid-crystalline properties. Finally the neat phase and the melt form a structurally similar group with the properties of a liquid.

There is some conflict between the view expressed above and that obtained by some other methods. Vold's (47) heat of transition measurements show the largest heat (5180 cal/mole) observed at any temperature for sodium stearate is that for the supercurd to subwaxy transition at about 114°C. This suggests that it is probably this transition that marks the departure from mostly crystalline properties. The subwaxy to waxy transition has a heat of transition only about 20% less than that of the previous transition but the sample does not show a change in second moment at this point in the high resolution results. Since the two transitions are only 15 to 20°C apart there may perhaps be a gradual transition as suggested by the gradual fall off of line width through the region 120 to 140°C (Figure XXIII). While the second moments in Figure XXIV do not indicate such a fall off Grant's (12) second moment curve does show it, but modulation broadening may be an influence there. While thermodynamic evidence
provides some confirmation for the interpretation of the supercurd to subwaxy transition, it provides none for the subneat to neat transition. The heat of transition for this change which is observed by n.m.r. is of virtually the same magnitude (about 1600 cal/mole) as that for the superwaxy to subneat transition which is not observed by n.m.r. However, the waxy to superwaxy transition is not observed at all by Vold for sodium stearate and possibly calorimetric measurements may not provide a completely accurate estimate of the magnitude of transitions taking place in this structurally complicated region.

Vold's work shows that sodium palmitate and stearate behave almost identically with respect to their transitions and the temperatures of those transitions. Therefore the detailed x-ray investigation of sodium palmitate by Nordsieck et al (99) may provide some information. They decided that below the subwaxy region the soap was essentially crystalline. The subwaxy, waxy and superwaxy regions they classified as a group with hydrocarbon chains in a loose hexagonal packing with a common average orientation of the polar end groups. Subneat and neat were also classified as a group, but one in which the common orientation of the end groups had disappeared. This would fit the second moment change at 120°C but not that at 235-237°C which corresponds to the subneat to neat transition. Their suggestion that the subneat to neat
transition may mark the change from a structure in which the chains were in a state of frozen rotation to a state of actual rotation would provide an explanation for the second moment change in this region.

The suggestion of frozen rotation in the subneat phase is incompatible, however, with the work of Grant (12), the observation by Powell and Pudington (46) that the phases in this region have the decidedly liquid-like ability to flow, and infrared data to be mentioned below. It is also in conflict with the x-ray work of de Bretteville and McBain (45), on sodium stearate itself, who point out that the hexagonal packing in that soap probably arises from the spinning of the hydrocarbon chains about their long axes in the superwaxy and higher temperature phases. In addition they disagree with the preceding grouping of structurally similar forms and state that the subwaxy and waxy forms are definitely crystalline while the superwaxy phase more nearly resembles the subneat and neat forms. They believe that in the last three phases the carboxylate groups are fixed with respect to each other with the paraffin chains spinning on their long axes.

So far other evidence has not confirmed the n.m.r. interpretation of the sodium stearate high temperature phases. Indeed the other evidence is even contradictory with respect to itself. It may be possible that the sodium stearate observed was not in every case an anhydrous sample such as that observed by n.m.r. This might account for
differences in apparent behaviour especially (36) in the x-ray diffraction results.

A recent x-ray investigation of anhydrous sodium stearate by Skoulios and Luzzati (100), however, provides strong confirmation of the n.m.r. interpretation. They classified the high temperature phases into the same groups as was done from n.m.r. evidence. The subwaxy, waxy, superwaxy and subneat phases were believed to form a group possessing a two-dimensional rectangular structure. This structure consisted of a set of parallel ribbons indefinite in length and packed in a rectangular array. The polar groups fit into the ribbons and the hydrocarbon chains, in a liquid-like state, fill up the rest of the cell. The neat phase was found to be in a lamellar structure with a decidedly liquid character with structure similar to that of the melt. This fits the n.m.r. interpretation of (1) considerable rotation and flailing of hydrocarbon chains in the subwaxy to subneat phase regions, (11) maintenance of the ionic layer in the foregoing regions followed by disruption of that layer at the subneat to neat transition, and (111) subsequent similarity of neat phase and melt. In addition they placed the subneat to neat transition at 238°C in excellent agreement with the 235-237°C transition found by n.m.r.

Final confirmation of the n.m.r. interpretation comes from Chapman's (4) study of the infrared spectra of sodium soaps. From the spectra of sodium palmitate and
stearate he deduced that in the vicinity of 100°C the hydrocarbon chains begin to twist and flex as evidenced by the loss of resolution of certain bands in the 1250 cm\(^{-1}\) region and the decrease in intensity of the methylene rocking band at 719 cm\(^{-1}\). (The band, incidentally, is single due to triclinic crystal structure and possible hexagonal packing in the high temperature phases.) On heating to about 120-130°C, the approximate range of the second moment change at 120°C, a further decrease in the intensity of the 719 cm\(^{-1}\) band combined with the disappearance of some other bands, suggests that many more methylene groups are spinning freely about the C-C bonds. This change from a fairly crystalline state to one possessing some liquid-like character agrees with the n.m.r. interpretation. Above 120-130°C the spectra are definitely liquid-like being analogous to those at the fatty acid transition from crystalline to liquid phase. Methylene groups are spinning freely and the paraffin chains are in a liquid-like condition with melting probably only being prevented by the strong sodium and carboxylate group attraction. This liquid-crystalline region extends at least to 200°C the highest reported temperature. This again is consistent with the n.m.r. results and it is not surprising that n.m.r. does not distinguish between a succession of similar, liquid-like phases until the breakdown of the ionic layer permits actual diffusion to take place about 400°C below the melting point.
Sodium stearate then consists of three general phases. There is a crystalline phase group below about 120°C, a liquid-crystalline phase group between about 120 to 235°C, and a liquid phase group from the last temperature upwards. The sodium soap does not therefore melt in a sudden catastrophic process but goes through an intermediate region between the essentially crystalline structure and the true melting point. Premelting may certainly be said to be occurring in this region. It may be considered as beginning in the vicinity of 120°C and reaching a climax around 235°C above which temperature the sample is essentially liquid although well below the melting point (275-280°C).
APPENDIX I

REPRODUCTIONS OF REPRESENTATIVE EXPANDED INFRARED SPECTRA
OF
STEARIC, PALMITIC, MYRISTIC AND LAURIC ACIDS
STEARIC ACID

- 1.3°C
- 67.8°C
- 61.0°C
- 1.3°C

OPTICAL DENSITY

CM⁻¹
MYRISTIC ACID

Graph showing the optical density at different temperatures: 56.1°C, 53.4°C, 45.5°C, and -30.1°C. The graph plots wavelength against optical density with a range of 740 to 710 cm⁻¹ on the x-axis and -0.30 to 0.10 on the y-axis.
APPENDIX II

REPRODUCTIONS OF REPRESENTATIVE
HIGH RESOLUTION NUCLEAR MAGNETIC RESONANCE SPECTRA
OF
SODIUM STEARATE

Single absorption spectra are shown in each of sets one and two, but in set one the indicated second moment is for the averaged spectrum (not shown) while in set two it is for the particular spectrum reproduced.
SET ONE

RELATIVE SCALE IS DENOTED BY THE ATTENUATION VALUE.

- 121°C
  \( \Delta H_x = 0.31 \) GAUSS
  \( \Delta H_y = 0.08 \) GAUSS
  ATTENUATION = 1.7

- 131.5°C
  \( \Delta H_x = 0.26 \) GAUSS
  \( \Delta H_y = 0.07 \) GAUSS
  ATT. = 1.7

- 176°C
  \( \Delta H_x = 0.22 \) GAUSS
  \( \Delta H_y = 0.11 \) GAUSS
  ATT. = 1.7
SET ONE CONTINUED

- **220°C**
  - $\Delta H_p = 0.15$ GAUSS
  - $\Delta H_2 = 0.06$ GAUSS$^2$
  - ATT. = 1.2

- **225.5°C**
  - $\Delta H_p = 0.12$ GAUSS
  - $\Delta H_2 = 0.07$ GAUSS$^2$
  - ATT. = 0.9

- **259°C ( & higher )**
  - $\Delta H_p \approx 0.02$ GAUSS
  - $\Delta H_2 \approx 10^{-4}$ GAUSS$^2$
  - ATT. = 1.5
SET TWO

RELATIVE SCALE IS DENOTED BY THE ATTENUATION VALUE

- 120°C
  $\Delta H^L = 0.32$ GAUSS
  $\Delta H^Z = 0.59$ GAUSS
  ATTENUATION = 2.0

- 140°C
  $\Delta H^L = 0.25$ GAUSS
  $\Delta H^Z = 0.18$ GAUSS
  ATT. = 1.5

- 171.5°C
  $\Delta H^L = 0.23$ GAUSS
  $\Delta H^Z = 0.20$ GAUSS
  ATT. = 1.5

- 197.5°C
  $\Delta H^L = 0.14$ GAUSS
  $\Delta H^Z = 0.37$ GAUSS
  ATT. = 1.0
• 226 °C
  \( \Delta H_2^2 = 0.10 \) GAUSS
  \( \Delta H_1^2 = 0.13 \) GAUSS
  ATT. = 1.0

• 235 °C
  \( \Delta H_2^2 = 0.050 \) GAUSS
  \( \Delta H_1^2 = 0.11 \) GAUSS
  ATT. \approx 0.7

• 237 °C ( & HIGHER )
  \( \Delta H_2^2 \approx 0.03 \) GAUSS
  \( \Delta H_1^2 \approx 10^{-4} \) GAUSS
  ATT. = 0.2
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