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THE INFRARED SPECTRA OF SINGLE CRYSTALS OF COMPOUNDS WITH LONG METHYLENE CHAINS

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BY
REDUS FOY HOLLAND
Norman, Oklahoma
1961

THE INFRARED SPECTRA OF SINGLE CRYSTALS OF COMPOUNDS WITH LONG METHYLENE CHAINS

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INTRODUCTION

Most of the molecular vibrational frequencies of compounds consisting of a long methylene chain terminated by single atoms or small groups of atoms may be expected to be characteristic of the chain and fairly independent of the end groups. Since these compounds have a great deal of practical importance, their vibrational spectra have been the subjects of numerous investigations. For no compound of this type, however, have all fundamental vibrational frequencies been assigned with certainty.

The complexity of the spectra make their interpretation very difficult. In the liquid phase, the molecules are generally bent or curled. Since each conformation is a different mechanical system, the number of vibrational frequencies is extremely large. In the crystalline phase the chains are extended and only one conformation is present. Even in this phase, however, because of the size of the molecules, the number of fundamental vibrations is very large.

The interpretation of the spectra has been aided greatly by many attempts to calculate the vibrational frequencies of n-paraffins and infinite polymethylene chains. In most of this work only the extended conformation was treated.

Because of the regular structure of the extended chain, the vibrational problem resembles that of a linear chain of coupled harmonic oscillators. The vibrations of the chain can be separated into sets, each of which is associated with a characteristic motion of a methylene group. If there are N such groups, there will be approximately N vibrations in each set. The frequency distribution and frequency range should be independent of N, provided N is sufficiently large. While the theoretical work has not led to accurate values of the frequencies, it has predicted more or less reliably the frequency ranges for the different types of vibrations and in a general way the distribution of the frequencies within these ranges.

By comparing the spectra of crystals of a series of homologous compounds with different chain lengths it has been possible to correlate many of the bands into sets arising from similar methylene vibrations. However, since the frequencies of some of these sets overlap, the assignments made have been beset with uncertainties.

From the molecular and crystal symmetry, the directions of the changes in dipole moment associated with the infrared-active fundamental vibrations may be predicted. Observations of the absorption of linearly polarized infrared radiation by oriented or single crystalline samples have made it possible in some cases to check these predictions and thus verify assignments.

When the methylene chains are extremely long the vibrational spectra are simpler. Not only do the end groups contribute less to the spectra, but the various sets of methylene vibrations are represented by only two of their members. The study of the highly crystalline polyethylenes, which have become available during the last five years, has been a great help in the interpretation of the spectra of compounds with chains of moderate length.

The present work is a continuation of an extensive investigation of the vibrational spectra of polyethylenes and related substances carried out in this laboratory by Nielsen and Woollett.[1] In particular, Nielsen and Woollett obtained the Raman spectrum of crystalline linear polyethylene and interpreted most of the weak infrared bands of polyethylene as linear combinations of a Raman-active and an infrared-active fundamental.

The earliest part of the present work was devoted to the problem of determining the infrared-active methylene wagging and twisting fundamentals of crystalline polyethylene. Since the results have already been published,[2] they will be mentioned only briefly.

The next part of the present work was a study of the dichroism of the infrared bands of oriented linear polyethylene. The information obtained was used to test and revise the interpretations of the many weak infrared bands of this polymer. The results appear in the current issue of the Journal of Molecular Spectroscopy and will therefore not be presented here.[3]

The third part of the present work has been devoted to a study, with polarized radiation, of the infrared spectra of single crystals of certain long-chain n-paraffins and of several polymorphs of stearic acid. The results of this work will be presented in the following chapters.

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[1] J. Rud Nielsen and A. H. Woollett, J. Chem. Phys. 26, 1391 (1957).

[2] J. Rud Nielsen and R. F. Holland, J. Mol. Spectroscopy 4, 488 (1960).

[3] J. Rud Nielsen and R. F. Holland, J. Mol. Spectroscopy 6, 394 (1961).

THE INFRARED SPECTRA OF SINGLE CRYSTALS OF COMPOUNDS WITH LONG METHYLENE CHAINS

CHAPTER I

PREVIOUS WORK ON THE CRYSTAL STRUCTURE AND VIBRATIONAL SPECTRA OF COMPOUNDS WITH LONG METHYLENE CHAINS

Crystal Structure

Crystals of compounds with long methylene chains have a remarkable variety of structures. Though most homologous series of these compounds have similar crystal forms, the stable structure may differ for different ranges of the chain length, and a particular compound usually has several polymorphic forms. The n-paraffins and n-fatty acids provide interesting examples.

Crystals of n-paraffins having hexagonal, orthorhombic, monoclinic, and triclinic structure have been observed.[4] The hexagonal structure seems to be possible for a wide range of chain lengths, but occurs only above a transition temperature a few degrees below the melting point. The transition temperature approaches the melting point for very short and very long chains.[5] Below this temperature, n-paraffins

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[4] V. Daniel, Adv. in Phys. 2, 450 (1953).

[5] W. M. Mazee, Rec. Trav. Chim. Pays-Bas 67, 197 (1948).

with an odd number of carbon atoms invariably have an orthorhombic form. The n-paraffins with an even number of carbon atoms, when pure, crystallize in a triclinic form when the chains are shorter than twenty-eight carbon atoms[6,7] but are monoclinic for longer chains,[8,6] at least up to forty-six carbon atoms.[3] Some long even-numbered chains have been observed to take an orthorhombic form,[9] and the shorter chains can also assume an orthorhombic form if they contain enough of the neighboring homologues.[7]

As in the case of the n-paraffins, the structures of crystals of the n-fatty acids are different for chains with even and odd numbers of carbon atoms. Two monoclinic and two triclinic forms of the even-numbered acids are commonly known.[10] In the present work, evidence for a third monoclinic form will be presented, and it will be shown that at least two of the n-fatty acids can assume four of the five forms.

In spite of this structural variety, crystals of these and other compounds with long methylene chains have several common features. X-ray determinations of structure have shown that in crystals, the methylene chains usually assume a configuration in which alternate carbon atoms lie along parallel straight lines, so that the carbon skeleton forms a planar zig-zag.[11] The hydrogen atoms of the methylene groups

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[6] A. E. Smith, J. Chem. Phys. 21, 2229 (1953).

[7] A. Müller and K. Lonsdale, Acta Cryst. 1, 129 (1948).

[8] H. M. M. Shearer and V. Vand, Acta Cryst. 9, 379 (1956).

[9] P. W. Teare, Acta Cryst. 12, 294 (1959).

[10] E. von Sydow, Arkiv Kemi 9, 231 (1956).

[11] A. Müller, Proc. Roy. Soc. (London) A, 120, 437 (1928).

are symmetrically placed with respect to the skeletal plane, and all interbond angles approximate the tetrahedral angles.[4,10]

The symmetry of an infinite extended chain can be described by a one-dimensional space group or line group. Tobin[12] has shown that the factor group giving the symmetry of a repeat unit, $-CH_2-CH_2-$, is isomorphic to the point group V_h. The symmetry of a finite segment of the chain is C_{2h} or C_{2v}, depending on whether the number of CH_2 groups is even or odd.

The symmetry of a molecule depends on the end groups. It is usually assumed that in the crystalline phase the n-paraffins have symmetry C_{2h} or C_{2v} for even- or odd-numbered chains, respectively.[13] A single molecule of a n-fatty acid in the crystalline phase has no strict symmetry. In some cases, however, the atoms of the carboxyl group are only slightly displaced from the skeletal plane of the chain,[14] so that the molecule has approximately the symmetry C_s.

Pure compounds with linear methylene chains generally crystallize in plane layers with the end groups at the surfaces of the layers. With some exceptions (crossed-chain soaps[15]), the axes of the methylene chains are parallel.[4] The relative orientation of the methylene groups in adjacent chains usually conforms to one of three common types of

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[12] M. C. Tobin, J. Chem. Phys. 23, 891 (1955).

[13] J. K. Brown, N. Sheppard, and D. M. Simpson, Trans. Roy. Soc. (London) A, 247, 35 (1954).

[14] V. Vand, W. M. Morley, and T. R. Lomer, Acta Cryst. 4, 324 (1951).

[15] V. Vand, T. R. Lomer, and A. Lang, Acta Cryst. 2, 214 (1949).

chain packing. The chain packing may be characterized by what would be the unit cell if the chain length were infinite. Such a unit cell will be called a subcell of the crystal.

The triclinic subcell represented in Fig. 1-1 was first observed by Vand and Bell[16] in crystals of the glycerol ester of lauric acid (trilaurin). It is thought to be characteristic of the triclinic form of the even-numbered n-paraffins, and has been observed in triclinic crystals of the n-carboxylic acids.[10] One methylene chain passes through the subcell, which includes two adjacent CH_2 groups of the chain. The triclinic subcell has an inversion center.

The orthorhombic subcell shown in Fig. 1-2 was first observed by Müller for orthorhombic crystals of n-$C_{29}H_{60}$.[11] It has since been observed in many other crystals, including the orthorhombic[9] and monoclinic[8] forms of the even-numbered n-paraffins, and the B [10] and C [14] forms of the n-fatty acids. Two chains, oriented so that the skeletal planes are nearly perpendicular, pass through the subcell. It includes two methylene groups of each chain.

Bunn[17] has found that the unit cell of an ideal polyethylene crystal is essentially identical to the orthorhombic subcell of the n-paraffins. The factor group of the space group of crystalline polyethylene which describes the symmetry of this unit cell is isomorphic to the point group V_h.

The third common type of chain packing is that characteristic

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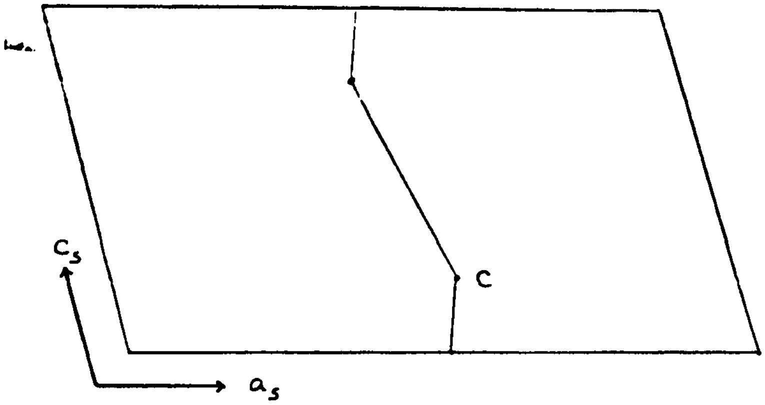
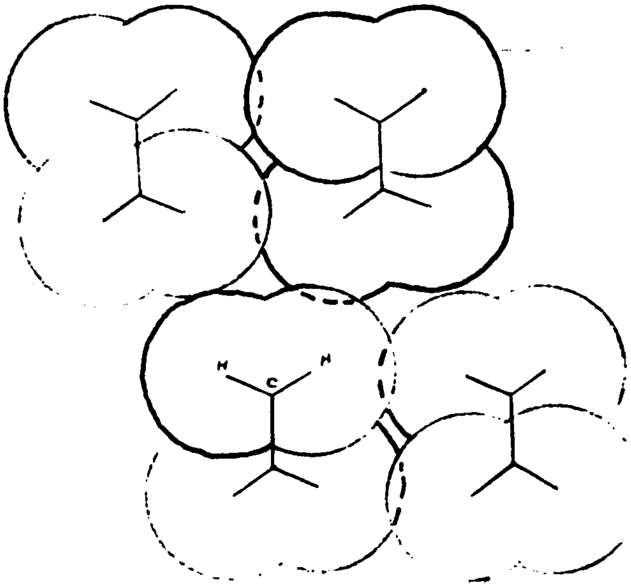
[16] V. Vand and I. P. Bell, Acta Cryst. 4, 465 (1951).

[17] C. Bunn, Trans. Faraday Soc. 35, 482 (1939).



Projection Along the b-axis

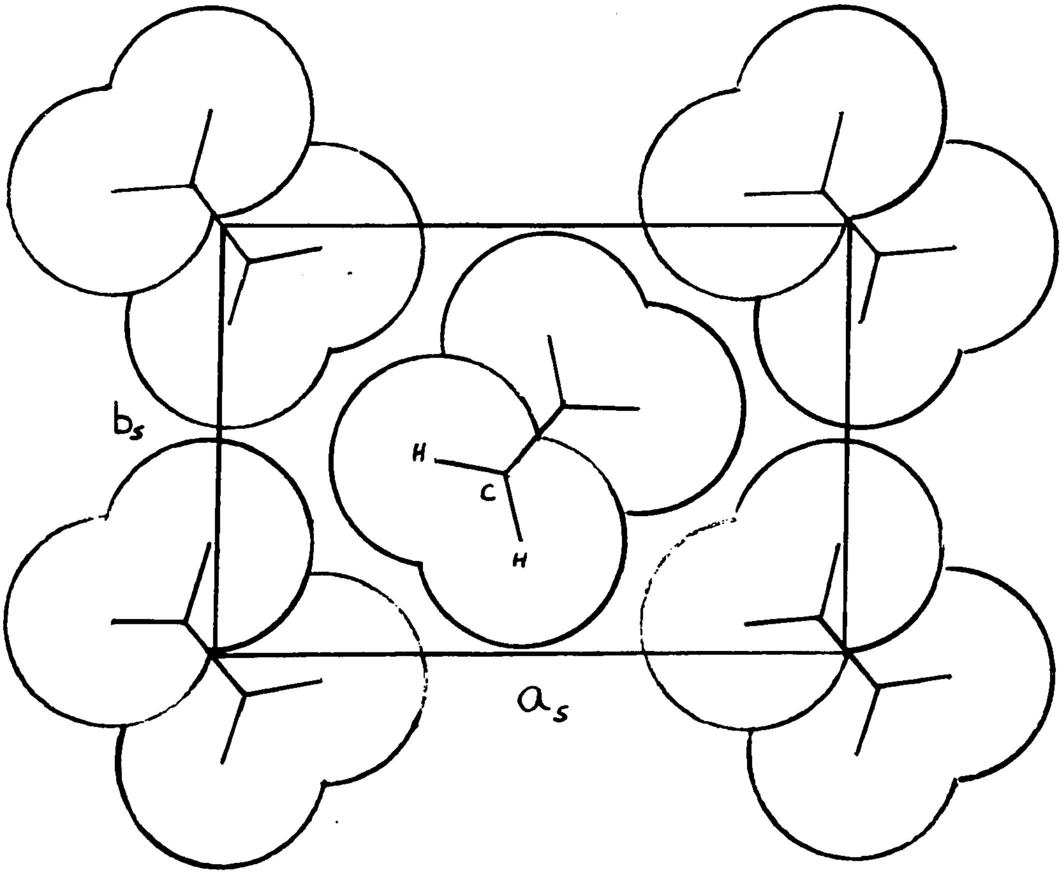


Side Packing of the Methylene Chains

Subcell
Dimensions: $a_s = 4.287$, $b_s = 5.40$, $c_s = 2.45$ Å

$\alpha_s = 74^\circ\ 25'$, $\beta_s = 108^\circ\ 2'$, $\gamma_s = 117^\circ\ 24'$

Fig. 1-1 The Triclinic Subcell



Projection Along the c_s-axis

$a_s = 7.42$ $b_s = 4.96$ $c_s = 2.54$ Å

Fig. 1-2 The Orthorhombic Subcell

of the hexagonal form of the n-paraffins.[4] Abrahamsson and Fischmeister[18] have described two less common orthorhombic subcells observed in crystals of monomethyloctadecanoic acids. No crystals having these types of packing will be treated in the present work.

The orientation of the molecular chains within a layer is only partly determined by the chain packing. For instance, both the orthorhombic and the monoclinic forms of the n-paraffins have the orthorhombic subcell. In the orthorhombic form, the chain axes are normal to the surface of the layer, while in the monoclinic form the chains are tilted with respect to this surface.

The structure of orthorhombic n-$C_{36}H_{74}$ has been determined by Teare.[9] The unit cell, shown in Fig. 1-3, extends through two molecular layers and includes four molecules. The unit cell group is isomorphic to the point group C_{2v}.

The structure of monoclinic n-$C_{36}H_{74}$ has been determined by Shearer and Vand.[8] The unit cell, shown in Fig. 1-4, includes two molecules. The unit cell group is isomorphic to the point group C_{2h}.

For none of the triclinic n-paraffins has the detailed structure been determined. However, the unit cell dimensions of triclinic n-$C_{18}H_{38}$ have been determined by Müller and Lonsdale.[7] They are as follows:

$$a = 4.28\text{Å}, \quad b = 4.82\text{Å}, \quad c = 23.07\text{Å}$$

$$\alpha = 91^\circ\, 6', \quad \beta = 92^\circ\, 4', \quad \gamma = 107^\circ\, 18'.$$

There is one molecule per unit cell and the chains are thought to have

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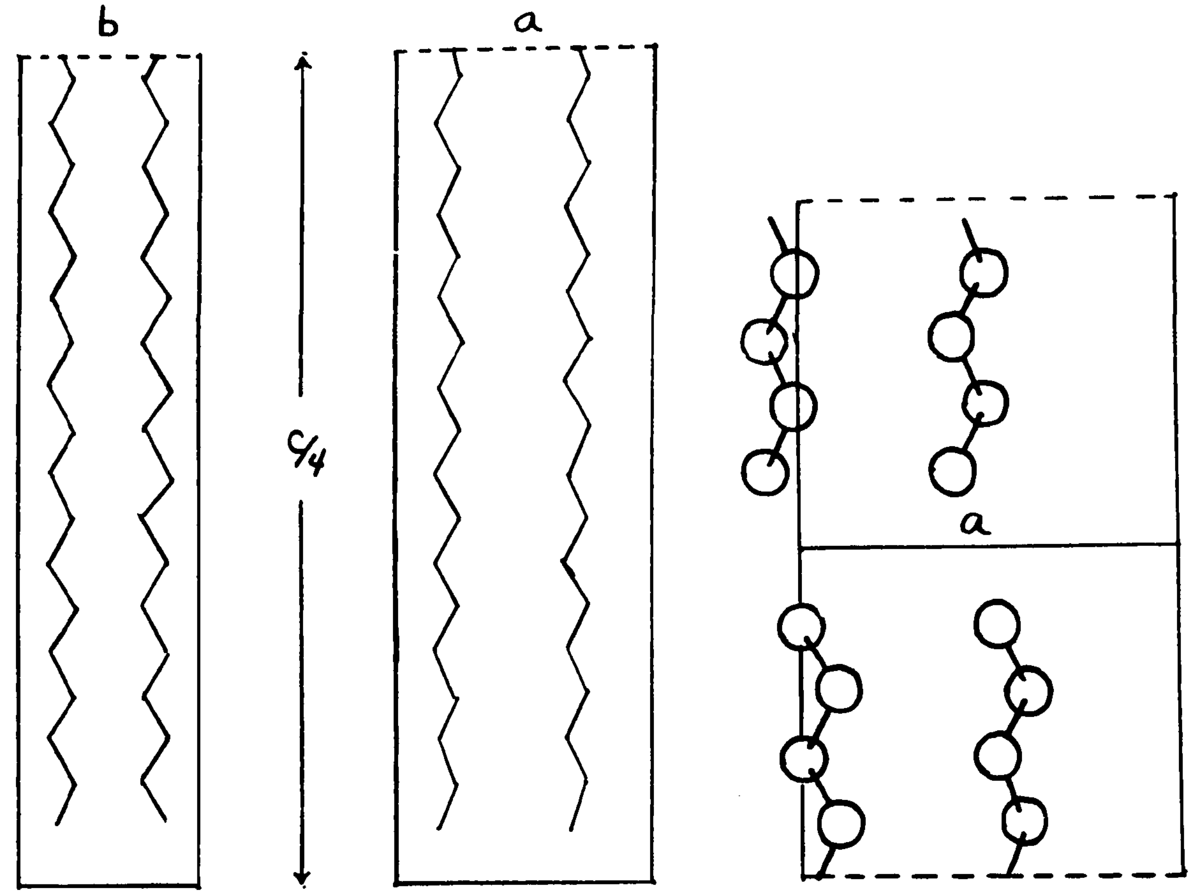
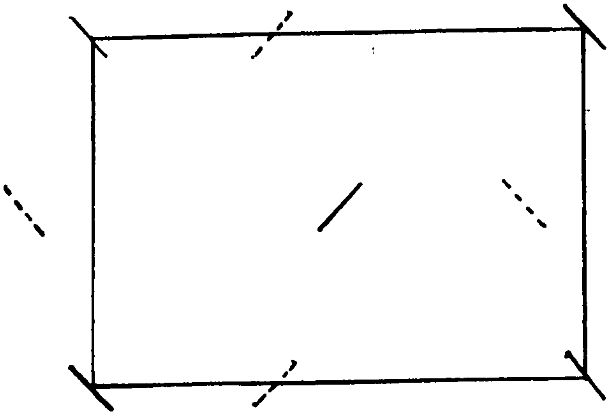
[18] S. Abrahamsson and I. Fischmeister, Arkiv Kemi 14, 57 (1959).



Projection Along the a-axis

Projection Along the b-axis

Boundary of the Molecular Layers



Projection Along the c-axis

a = 7.42 Å

b = 4.96

c = 95.14

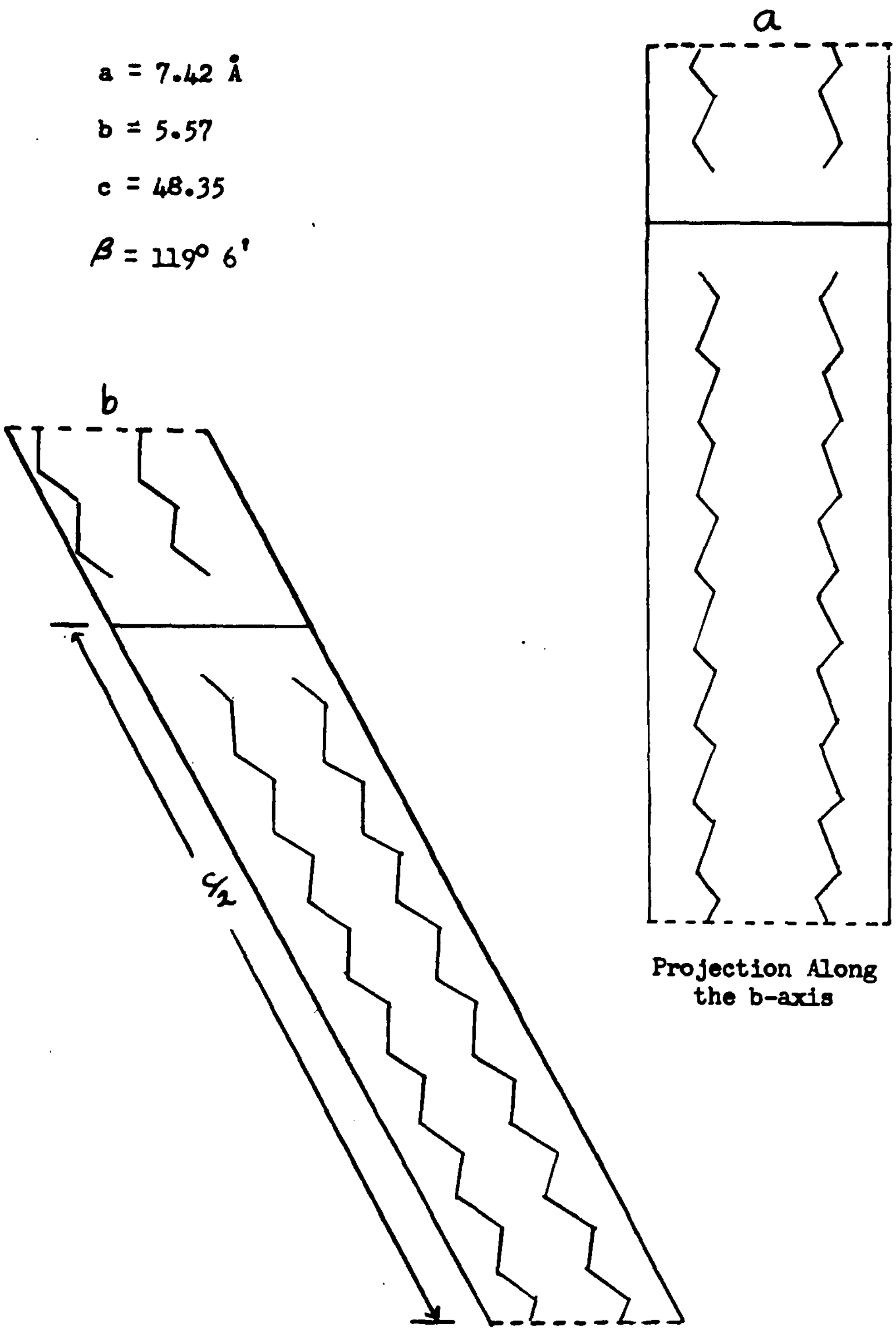
Fig. 1-3 Unit Cell of Orthorhombic n-$C_{36}H_{74}$

a = 7.42 Å

b = 5.57

c = 48.35

β = 119° 6'



Projection Along the b-axis

Projection Along the a-axis

Fig. 1-4 The Unit Cell of Monoclinic n-$C_{36}H_{74}$

the triclinic packing. The unit cell group is C_i.

The crystal structure of the monoclinic C-form of lauric acid, $CH_3(CH_2)_{10}COOH$, has been determined by Vand, Morley, and Lomer.[14] The unit cell, represented in Fig. 1-5, includes four molecules, two in each of two adjacent molecular layers. The molecules are paired in dimers, with hydrogen bonding between the hydroxyl hydrogen and the carbonyl oxygen atoms. The carboxyl carbon lies approximately in the plane of the carbon skeleton, and the oxygen atoms are displaced only slightly from this plane. The "ring" formed by the two carboxyl groups in a dimer is essentially planar, and the skeletal planes of the two chains in a dimer are parallel. The chains have the orthorhombic packing and the unit cell group is isomorphic to C_{2h}.

The structure of the monoclinic B-form of stearic acid, $CH_3(CH_2)_{16}COOH$, has been determined in part by von Sydow.[10] The projection of the unit cell along one of its axes is shown in Fig. 1-6. The unit cell includes four molecules, that is, two dimers. The chains have the orthorhombic packing. The chain skeletal planes in a dimer are parallel; however, in this case the carboxyl carbon does not lie in the skeletal plane. The carboxyl ring has an inversion center and is possibly planar, however, the orientation of the carboxyl groups with respect to each other and the skeletal plane is not certain. This unit cell group is again isomorphic to C_{2h}.

Two triclinic forms of even-numbered n-fatty acids have been reported. One, originally designated the A-form by Francis, Piper, and Malkin,[19] was distinguished from the other crystal forms by its

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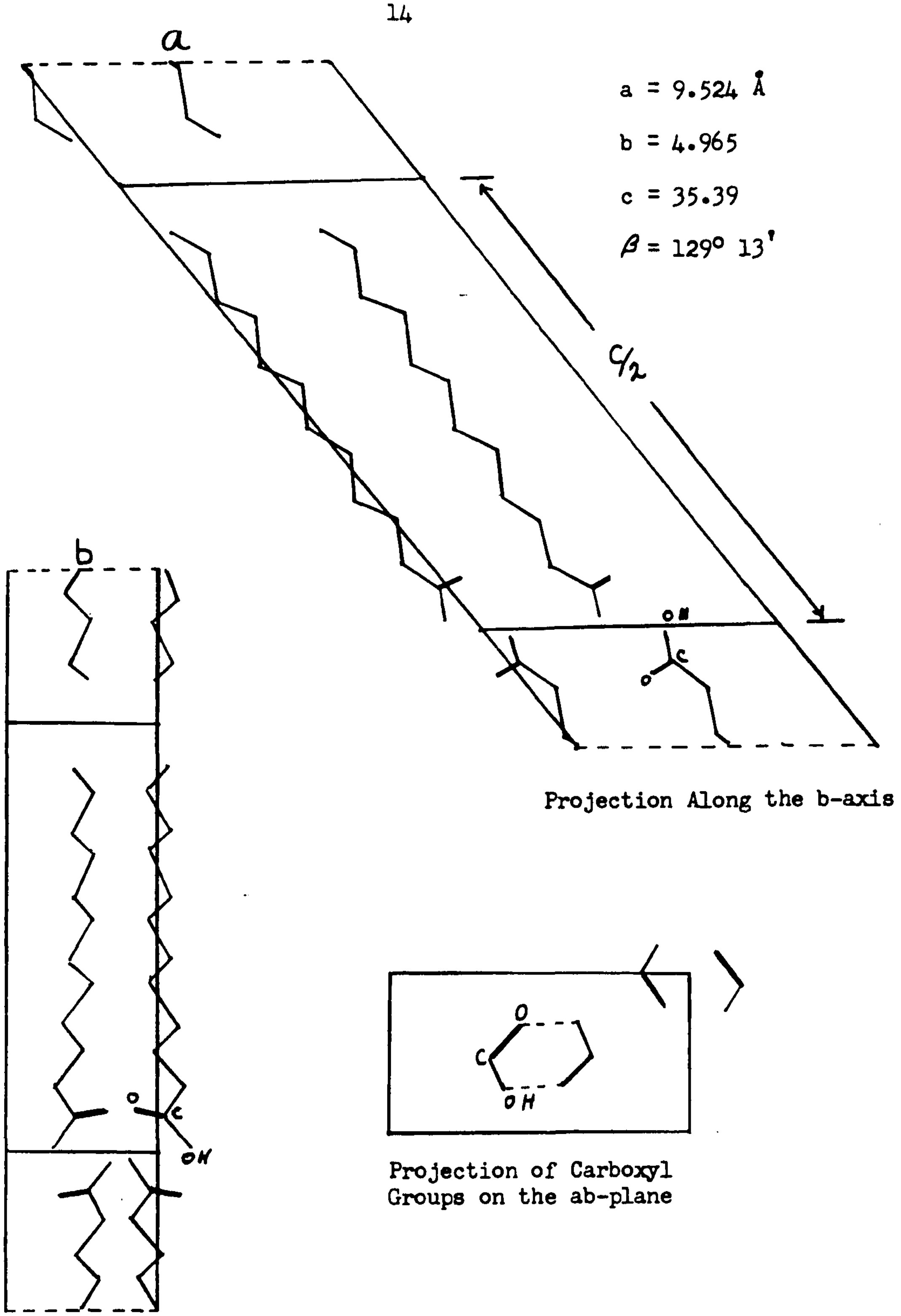
[19] F. Francis, S. H. Piper, and T. Malkin, Proc. Roy. Soc. (London) A, 128, 214 (1930).



a = 9.524 Å
b = 4.965
c = 35.39
β = 129° 13'

Projection Along the b-axis

Projection of Carboxyl Groups on the ab-plane

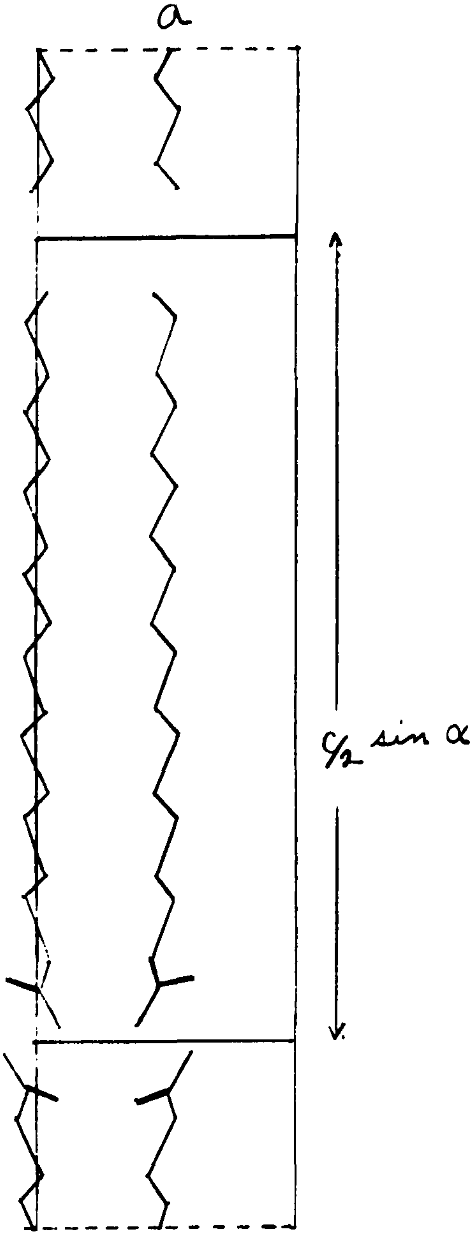
Projection Along the a-axis

Fig. 1-5 The Unit Cell of the C-form of Lauric Acid a = 7.404 Å

b = 5.591

c = 49.38

α = 117° 22'



Projection Along the b-axis

Fig. 1-6 The Unit Cell of the B-form of Stearic Acid greater "long spacing" (thickness of a dimer layer). This crystal form has one dimer per unit cell and almost certainly has the triclinic chain packing.[10] The unit cell has an inversion center.

Recently, von Sydow[10] has shown that another triclinic form exists, in which each boundary of a monomolecular layer includes both carboxyl groups and methyl groups, and which has no easily discernible long spacing. He has published a partial determination of the structure of this form of lauric acid. The unit cell includes six molecules (three dimers) and has an inversion center. For purposes of the structure determination, von Sydow has considered a twelve-molecule unit cell. A projection of half this cell along its shortest axis is shown in Fig. 1-7. The chain planes in a dimer are parallel and the chains have the triclinic packing. Von Sydow has observed this crystal form only for lauric acid, $CH_3(CH_2)_{10}COOH$, and myristic acid, $CH_3(CH_2)_{12}COOH$. He has reported that triclinic crystals of the acids with longer chains apparently have the form with long spacing.

Normal Vibrational Analyses

Most vibrational analyses of long methylene chains have not included the effects of the molecular environment. They have, however, generally assumed the extended conformation present in crystals. The first attempts dealt only with the skeletal vibrations of the chain. The CH_2 groups were treated as point masses and a valence-type potential was assumed. Bartholome' and Teller[20] investigated the effects of the

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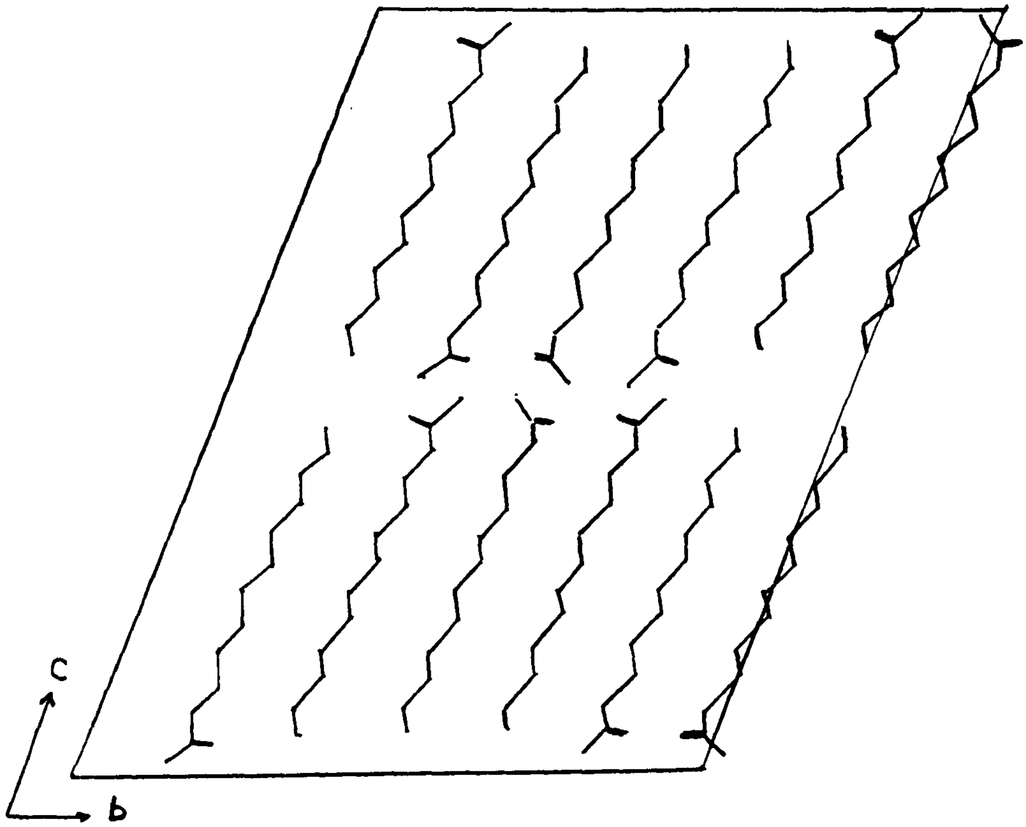
[20] E. Bartholome' and E. Teller, Z. physik. Chem. B. 19, 366 (1932).



Projection Along the a-axis

$a = 5.41$, $b = 26.2$, $c = 35.4$ Å

$\alpha = 74°$ $\beta = 109°$ $\gamma = 122°$

Fig. 1-7 The Unit Cell of the A-form of Lauric Acid end groups on the chain vibrations. They concluded that the skeletal frequencies lay within a range essentially independent of the chain length or type of end groups. Bartholomé and Teller, and Barriol,[21] and Parodi[22] determined frequency ranges for the skeletal vibrations.

Kirkwood,[23] Pitzer,[24] and more recently, Liang, Sutherland, and Krimm[25] attempted to calculate the frequencies of individual skeletal vibrations of the n-paraffins. Their approaches to the vibrational problem were not essentially different from those of the earlier workers.

Whitcomb, Nielsen, and Thomas[26] were the first to consider the motion of the hydrogen atoms in the methylene groups. Using a central force field, they calculated frequency ranges for the vibrations of the n-paraffins. They estimated the positions of the most intense bands and attempted a correlation with the spectrum of gaseous undecane. They did not explicitly consider the motion of the end groups in their analysis but did discuss these effects. They emphasized that the distinction between chain and end group vibrations was one of degree rather than kind.

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[21] J. Barriol <u>et al</u>., J. Phys. et Radium 10, 215 (1939); <u>8</u>, 8 (1947).

[22] M. Parodi, J. Phys. et Radium <u>2</u>, 58 (1941).

[23] J. G. Kirkwood, J. Chem. Phys. <u>7</u>, 506 (1939).

[24] K. S. Pitzer, J. Chem. Phys. <u>8</u>, 711 (1940).

[25] C. Y. Liang, G. B. B. M. Sutherland, and S. Krimm, J. Chem. Phys. <u>22</u>, 1468 (1954).

[26] S. E. Whitcomb, H. H. Nielsen, and L. H. Thomas, J. Chem. Phys. <u>8</u>, 143 (1940).

Mizushima and Shimanouchi[27] and Kellner[28] considered an infinite chain. They pointed out that, for a chain infinitely long, only those vibrations in which chain repeat units vibrate in-phase should be infrared or Raman-active. Both analyses included the hydrogen motion. Shimanouchi and Mizushima used a Urey-Bradley field, and Kellner used a strict valence force field.

Deeds[29] has made a complete normal coordinate analysis for chains of finite length. His approach to the vibrational problem is similar to that ~~of~~ Whitcomb et al.,[26] except that he used a strict valence force field and different symmetry coordinates.

Primas and Günthard[30] treated the normal vibrations of chains of the type $X(CH_2)_{2n}X$. They used the Wilson FG method[31] to arrive at symmetry coordinates. They assumed that the potential energy expressed in these coordinates had a diagonal quadratic form, and used an approximation method to diagonalize the secular determinant. The results were correlated with the spectra of the crystalline n-paraffins.

The most recent treatment of the vibrations of methylene chains

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[27] S. Mizushima and T. Shimanouchi, J. Am. Chem. Soc. 71, 1320 (1949). T. Shimanouchi and S. Mizushima, J. Chem. Phys. 17, 1102 (1949).

[28] L. Kellner, Proc. Phys. Soc. (London) A, 64, 521 (1951).

[29] W. E. Deeds, Ph. D. Thesis, Ohio State University (1951).

[30] H. Primas and H. H. Gunthard, Helv. Chim. Acta 36, 1659, 1791 (1953).

[31] E. B. Wilson, Jr., J. Chem. Phys. 7, 1047 (1939); 9, 76 (1941).

is that of Theimer.[32] He calculated frequencies and normal coordinates for the skeletal vibrations of finite chains, using a Urey-Bradley potential and taking terminal effects into account by a perturbation method. He concluded that in a chain with N carbon atoms, the effects of the perturbation on the frequencies are negligible for $N > 5$. A calculation of intensities showed that except for what were termed "physical boundary effects", such as the differences in the terminal and inner C-C bonds, none of the skeletal vibrations would be observable in the infrared spectra. He notes that the "mixing of CH vibrations and skeletal modes may activate the latter." Theimer also investigated the Raman and infrared intensities of the CH vibrations of solid n-paraffins. He concluded that the relative intensities of end-group vibrations are proportional to 1/N and that the intensities of chain vibrations in which all units in the chain vibrate in-phase are essentially independent of N. His results indicate that the other chain vibrations would be infrared-inactive except for the physical boundary effects.

The normal coordinate analyses have in most cases dealt with chains of indefinite length. By assuming as solutions vibrations which amount to travelling waves in the chain, the secular determinant may be reduced to a 9 x 9 block.[29,26] It is equal in dimension to the number of degrees of freedom of a methylene group.

The only strict symmetry operation common to extended methylene chains of any length is a reflection in the skeletal plane. If coordi-

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[32] O. Theimer, J. Chem. Phys. <u>27</u>, 408, 1041 (1957).

nates are chosen which take advantage of this symmetry, the 9 x 9 block can be factored into 5 x 5 and 4 x 4 blocks, corresponding to vibrations perpendicular and parallel to the skeletal plane, respectively.

The solutions of these secular equations are sinusoidal functions of the phase difference between the vibrations of adjacent chain units. Each solution defines a range of frequencies which is independent of the chain length. Particular solutions for chains of a given length are obtained by applying boundary conditions. This produces a series of frequencies corresponding to "standing waves", the normal vibrations of the chain. The distribution of this series over the frequency range depends upon the boundary conditions and the length of the chain. Boundary conditions of the sort usually applied require that for a finite chain with N methylene groups, the phase difference between adjacent vibrating units in a "travelling wave" have values $k\pi / N + 1$, where $k = 1, 2, \ldots, N$.

Each series is ordinarily associated with one of the following types of vibration of the methylene chain:

CH_2 symmetric stretching,
CH_2 deformation or "scissoring",
CH_2 wagging,
C-C stretching, and
C-C-C angle bending vibrations;
CH_2 asymmetric stretching,
CH_2 rocking,
CH_2 twisting, and
skeletal torsional vibrations.

The first five correspond to coordinates symmetric with respect to the skeletal plane, and the remaining four to coordinates antisymmetric with respect to this plane.

A chain with N methylene groups should have N of each type of CH_2 vibrations and (N-1) C-C stretching, (N-2) C-C-C angle bending, and (N-3) skeletal torsional vibrations. A normal paraffin will have two more of each of the last three types.[33] For an infinite chain, the solutions of the secular determinant represent branches rather than discrete sets of frequencies, since all values of the phase angle are allowed.

Selection Rules

The spectral activities of the vibrations of a methylene chain depend upon the symmetry of the molecule, and in the crystalline phase upon the crystal symmetry.

Methods developed by Bhagavantam and Venkatarayudu,[34] Halford,[35] Hornig,[36] and Winston and Halford[37] allow the use of the crystalline

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[33] N. Sheppard, "Rotational Isomerism About C-C Bonds in Saturated Molecules as Studied by Vibrational Spectroscopy," in Vol. I of Advances in Spectroscopy, ed. by H. W. Thompson. (New York: Interscience Publishers, Inc., 1959).

[34] S. Bhagavantam and T. Venkatarayudu, Theory of Groups and Its Application to Physical Problems (Bangalore City: The Bangalore Press, 1951).

[35] R. S. Halford, J. Chem. Phys. 14, 8 (1946).

[36] D. F. Hornig, J. Chem. Phys. 16, 1063 (1948).

[37] H. Winston and R. S. Halford, J. Chem. Phys. 17, 607 (1949).

space group to predict the symmetries and activities of the vibrations of molecular crystals. Only normal vibrations in which all unit cells vibrate in-phase are likely to be observed. These fundamentals are equal in number to the degrees of freedom of a unit cell, and they may be classified according to their behavior under the operations of the unit cell group.

Though the crystal symmetry is of the utmost importance in the present work, it is instructive first to consider the symmetry of, and the selection rules for, an extended methylene chain.

The symmetry of a finite methylene chain is the same as that of the corresponding normal paraffin molecule. The symmetry of an isolated n-paraffin in the extended configuration is C_{2v} for an odd-numbered chain and C_{2h} for an even-numbered chain. Brown, Sheppard, and Simpson[13] have classified the vibrations of all types according to symmetry species, except the low-frequency skeletal and the C-H stretching vibrations. This information, extended to include C-H stretching, is given in Table 1-I.

It may be noticed that the chain vibrations of each type are divided about equally between two symmetry classes in both even and odd-numbered chains. If discrete values $k\pi / N + 1$ are assumed for the phase angles between adjacent chain units, one of the two species will correspond to k even and the other to k odd. If a set of vibrations form a series in which the frequencies progressively increase or decrease with the phase angle, alternate members of the series will belong to the same species.

TABLE 1-I

CLASSIFICATION ACCORDING TO SYMMETRY SPECIES OF THE FUNDAMENTAL VIBRATIONS OF n-PARAFFINS WITH N METHYLENE GROUPS

Approximate Motion	Number of Fundamentals for							
	N even (C_{2h})				N odd (C_{2v})			
	A_g	B_g	B_u	A_u	A_1	A_2	B_1	B_2
CH_2 Symmetric Stretching	$\frac{N}{2}$		$\frac{N}{2}$		$\frac{N+1}{2}$		$\frac{N-1}{2}$	
CH_2 Deformation	$\frac{N}{2}$		$\frac{N}{2}$		$\frac{N+1}{2}$		$\frac{N-1}{2}$	
CH_2 Wagging	$\frac{N}{2}$		$\frac{N}{2}$		$\frac{N-1}{2}$		$\frac{N+1}{2}$	
C-C Stretching	$\frac{N+2}{2}$		$\frac{N}{2}$		$\frac{N+1}{2}$		$\frac{N-1}{2}$	
CH_2 Rocking		$\frac{N}{2}$		$\frac{N}{2}$		$\frac{N-1}{2}$		$\frac{N+1}{2}$
CH_2 Twisting		$\frac{N}{2}$		$\frac{N}{2}$		$\frac{N+1}{2}$		$\frac{N-1}{2}$
CH_2 Asymmetric Stretching		$\frac{N}{2}$		$\frac{N}{2}$		$\frac{N-1}{2}$		$\frac{N+1}{2}$
CH_3 Asymmetric Deformation and Stretching	1	1	1	1	1	1	1	1
CH_3 Symmetric Deformation and Stretching	1		1		1		1	
CH_3 Rocking	1	1	1	1	1	1	1	1
Activity	R.	R.	i.r.	i.r.	R.,i.r.	R.	R.,i.r.	R.,i.r.

R. Raman-active i.r. Infrared-active

For n-paraffins with an even number of carbon atoms, vibrations belonging to the infrared-active species B_u and A_u are associated with changes in dipole moment parallel and perpendicular to the plane of the carbon skeleton, respectively. For n-paraffins with an odd number of carbon atoms, vibrations belonging to species A_1, B_1, and B_2 are associated with changes in dipole moment parallel to the chain axis, perpendicular to the chain axis but parallel to the skeletal plane, and perpendicular to the skeletal plane, respectively.

To each type of chain vibration for an infinite chain there corresponds a continuous distribution of frequencies. However, actually only those vibrations in which adjacent CH_2 units have a phase difference of 0 or π, corresponding to $k = 1$ and $k = N$ in the finite chains, may be observed in the spectra. This was postulated by Shimanouchi and Mizushima,[27] who applied both symmetry groups C_{2h} and C_{2v}. It was later justified by Tobin in a more elaborate treatment based on the line group of an infinite chain.[12] In this treatment, which is equivalent to that derived for crystals, it is shown that vibrations can be analyzed in terms of the factor group of the line group which describes the symmetry of a single $-CH_2-CH_2-$ repeat unit.

Nielsen and Woollett[1] have classified the vibrations of crystalline polyethylene according to symmetry species of the unit cell group of an ideal polyethylene crystal. They have correlated this classification with that of Tobin. The information relevant to the present work is presented in Table 1-II. The approximate nature of the motions is given in the first column. The species of each of the factor group modes of an isolated polyethylene chain is given in the second column. The classification of the unit cell group vibrations of crystalline polyethylene is given in the third column. Corresponding to each normal vibration of a single chain, there will be two vibrations of the crystal, one in which the two chains in the unit cell vibrate in-phase, and one in which they vibrate out-of-phase.

In the line group analysis, a vibration of species a_u^F is inactive, and those of species b_{2u}^F, b_{3u}^F, and b_{1u}^F are associated with changes in dipole moment perpendicular to the skeletal plane, parallel to the skeletal plane but perpendicular to the chain axes, and parallel to the chain axes, respectively. Vibrations of the other species are Raman-active.

In the analysis based on the space group, the vibrations of species b_{2u}^F and b_{3u}^F each split into two infrared-active vibrations of species b_{2u} and b_{3u} with change in dipole moment parallel to the b- and a-axes of the polyethylene unit cell, respectively. The vibrations of species a_u^F or b_{1u}^F each split to produce an inactive vibration of species a_u and one of species b_{1u} which has a change in dipole moment parallel to the c-axis of the unit cell.

The space group analysis of the vibrations of the monoclinic n-paraffins predicts splitting similar to that in the polyethylene crystal. The unit cell group of the monoclinic crystals is isomorphic to C_{2h}. The unit cell is shown in Fig. 1-4. Since the inversion center of a molecule is also a center of symmetry of the unit cell, those vibrations which belong to the Raman-active species of the group C_{2h} of a single molecule are split into two Raman-active vibrations corresponding to in- and out-of-phase motions of the two molecules in

TABLE 1-II

CLASSIFICATION OF THE UNIT CELL GROUP MODES OF POLYETHYLENE ACCORDING TO THE LINE GROUP OF AN INFINITE CHAIN AND THE SPACE GROUP OF A POLYETHYLENE CRYSTAL

Approximate Motion	Line Group	Space Group
Asymmetric CH Stretching	b_{1g}^F	$a_g + b_{1g}$
Symmetric CH Stretching	a_g^F	$a_g + b_{1g}$
CH_2 Deformation	a_g^F	$a_g + b_{1g}$
CH_2 Rocking	b_{1g}^F	$a_g + b_{1g}$
Skeletal Deformation	a_g^F	$a_g + b_{1g}$
CH_2 Wagging	b_{2g}^F	$b_{2g} + b_{3g}$
CH_2 Twisting	b_{3g}^F	$b_{2g} + b_{3g}$
Skeletal Deformation	b_{2g}^F	$b_{2g} + b_{3g}$
CH_2 Wagging	b_{1u}^F	$a_u + b_{1u}$
CH_2 Twisting	a_u^F	$a_u + b_{1u}$
Asymmetric CH Stretching	b_{2u}^F	$b_{2u} + b_{3u}$
Symmetric CH Stretching	b_{3u}^F	$b_{2u} + b_{3u}$
CH_2 Deformation	b_{3u}^F	$b_{2u} + b_{3u}$
CH_2 Rocking	b_{2u}^F	$b_{2u} + b_{3u}$

a unit cell. Vibrations belonging to the infrared-active species of the group C_{2h} of a single molecule produce two infrared-active unit cell group modes associated with changes in dipole moment either parallel or perpendicular to the a-axis of the unit cell.

On the other hand, in the triclinic form of the n-paraffins, which has only one molecule per unit cell, no splitting is expected. The unit cell has an inversion center which, since there is only one molecule per unit cell, must also be an inversion center for the molecule, insuring that the sets of infrared- and Raman-active vibrations are mutually exclusive. Provided the crystal matrix does not greatly perturb the molecular vibrations, their other symmetry properties should be similar to those predicted from the symmetry of a single molecule.

The symmetry and selection rules of these and other crystals treated in the present work are discussed in more detail in Chapters III and IV.

Vibrational Spectra

The Raman spectra of several n-paraffins ranging from n-butane to n-cetane ($C_{16}H_{34}$) have been reported by Shimanouchi and Mizushima.[27] The Raman spectra of crystalline n-$C_{28}H_{58}$, n-$C_{36}H_{74}$, stearic acid, and highly crystalline linear polyethylene were obtained by Nielsen and Woollett.[1] Their Raman data on polyethylene were confirmed by Tobin.[38]

Previous work on the infrared spectra of n-paraffins and other compounds with long methylene chains is much more extensive. References

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[38] M. C. Tobin, J. Opt. Soc. Am. 49, 850 (1959).

are given by Jones and Sandorfy,[39] Bellamy,[40] Sheppard,[33] Elliott,[41] Krimm,[42] and Woollett.[43]

The article by Jones and Sandorfy and Bellamy's book are very general and only in part devoted to the spectra of the long-chain compounds. However, they touch on nearly all phases of the work done up to 1955. Elliott's article is concerned with the spectra of polymers in general and, though it is rather brief, contains references to most publications on the n-paraffins and polyethylene. Krimm's article deals with the spectra of polymers and includes a detailed discussion of the infrared spectrum of polyethylene. Sheppard's paper, though devoted primarily to rotational isomerism, includes a section on the spectra of compounds of the type $X(CH_2)_nY$ which is essentially a review of his own work on the n-paraffins and n-alkyl halides. Woollett's thesis contains a concise but comprehensive review of previous work on long-chain n-paraffins and polyethylene.

To references in these articles should be added the excellent recent work of Snyder on the infrared spectra of crystalline n-paraffins

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[39] R. N. Jones and C. Sandorfy, "The Application of Infrared and Raman Spectrometry to the Elucidation of Molecular Structure," in Vol. IX, Chapter IV of Technique of Organic Chemistry, ed. by A. Weissberger (New York: Interscience Publishers, Inc., 1956).

[40] L. J. Bellamy, The Infrared Spectra of Complex Molecules (London: Methuen and Co. Ltd., 1954).

[41] A. Elliott, "The Infrared Spectra of Polymers," in Vol. I of Advances in Spectroscopy, ed. by H. W. Thompson (New York: Interscience Publishers, Inc., 1959).

[42] S. Krimm, "Infrared Spectra of High Polymers," in Vol. 2 of Fortschritte der Hochpolymeren-Forschung (Berlin: Springer-Verlag, 1960).

[43] A. H. Woollett, Ph. D. Thesis, University of Oklahoma (1956).

from $C_{20}H_{42}$ to $C_{30}H_{62}$[44] and the work on the low-frequency skeletal vibrations of the n-fatty acids by Crisler and Fenton.[45]

The number of Raman bands which have been observed in the spectra of the crystalline n-paraffins is much less than that predicted by the theory. For all but the smaller molecules, the number of observed bands is essentially the same, and each band is a member of a "band sequence" which may be traced through the spectra of the n-paraffins, its frequency remaining constant or varying gradually with chain length. In some sequences, intensities vary little with the chain length, and bands which appear to be members of the sequences are observed in the Raman spectrum of crystalline polyethylene. In other sequences the bands decrease in intensity with increasing chain length and do not appear in the spectrum of polyethylene. The Raman spectrum of crystalline stearic acid obtained by Woollett is little different from that of the n-paraffins.

In the infrared spectra of crystalline compounds having methylene chains of moderate length, the number of bands observed is nearer that predicted by the theory. In the infrared spectra of homologous series of compounds, as in the Raman spectra, sequences of bands may be seen. In contrast to the Raman spectra, the number of sequences is not constant, new ones appearing as the chain lengths increase. Some of the band sequences are grouped together, their members in the spectrum of a particular compound forming regularly spaced "band series". The

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[44] R. G. Snyder, J. Mol. Spectroscopy 4, 411 (1960).

[45] R. O. Crisler and A. J. Fenton, paper given at the Tenth Annual Symposium on Spectroscopy, American Association of Spectrographers, Chicago, June 1-4, 1959.

number of bands increases and their separation decreases with increasing chain length, the range of frequencies in such a series remaining about the same.

Relative to a few strong bands, intensities decrease with increasing chain length. In the infrared spectrum of extremely long-chain n-paraffins and polyethylene, as in the Raman spectrum, few bands are observed. The most intense of these appear to be members of sequences which include the stronger bands in the spectra of shorter chains.

In some cases, the band series and sequences have been correlated with the sets of vibrations predicted by the theory.

The n-Paraffins and Polyethylene

In infrared spectra of the n-paraffins, a strong, persistent band sequence is observed near 720 cm^{-1}. In crystals having the orthorhombic packing, there is a doublet at this position. A strong doublet at 720 and 730 cm^{-1} is also observed in the spectrum of crystalline polyethylene. In the n-paraffins, a series of weaker bands extending toward higher frequencies are observed, each of which is a member of a sequence converging toward the strong 720-730 cm^{-1} bands as the chain lengths increase.

Brown, Sheppard, and Simpson[13] have assigned these bands as methylene rocking vibrations. The assignment is based on their number, frequency distribution, and the fact that the strong band sequence appears to originate in a propane band at 748 cm^{-1} assigned as CH_2 rocking. The splitting of the strong doublet has been attributed to in-phase and out-of-phase motion of adjacent chains in crystals having the orthorhombic chain packing.[46,47] Snyder has observed splitting also in the higher frequency members of this series.[48]

Though all infrared-active rocking vibrations of some of the n-paraffins with shorter chains have been accounted for by Brown *et al.*,[13] the upper end of the series appears to overlap another group of bands beginning around 1000 cm^{-1} in the spectra of the larger molecules.[44] In n-paraffins with an odd number of carbon atoms, all rocking fundamentals should be Raman-active;[13] however, no corresponding Raman series has been observed. Nielsen and Woollett[1] observed a weak Raman band at 1168 cm^{-1} which they assigned as CH_2 rocking. Presumably, this band indicates an upper bound for the rocking series of the n-paraffins.

A strong band sequence near 1470 cm^{-1} in the infrared spectrum has been ascribed to methylene scissoring or deformation vibrations. It is a doublet in those crystals having the orthorhombic chain packing. The fact that no obvious series is associated with this sequence is interpreted to mean that the interaction between adjacent methylene groups in this type of vibration is small, so that the entire set of vibrations predicted by theory have approximately the same frequencies. The doublet splitting is attributed to interactions between adjacent molecules.[46] A medium intensity band sequence near 1440 cm^{-1} in the Raman spectra of crystalline n-paraffins and polyethylene has been

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[46] R. S. Stein and G. B. B. M. Sutherland, J. Chem. Phys. 22, 1993 (1954).

[47] R. S. Stein, J. Chem. Phys. 23, 734 (1955).

[48] R. G. Snyder, J. Chem. Phys. 27, 969 (1947).

assigned as CH_2 deformation.[1]

A nearly constant-frequency sequence of very intense bands near 2850 cm^{-1} in both the infrared and Raman spectra of crystalline n-paraffins and polyethylene has been assigned as CH_2 symmetric stretching. Two sequences, near 2880 and 2920 in the Raman and infrared spectra, respectively, have been assigned as CH_2 asymmetric stretching vibrations.[49,50,1]

The torsional vibrations of the methylene chain are expected to have very low frequencies. No bands have been observed in the infrared or Raman spectra which could be associated with these vibrations. Mizushima <u>et</u> <u>al</u>.,[27] have associated a sequence of bands in the Raman spectra of crystalline n-paraffins with C-C-C angle bending. This sequence begins in a band at 425 cm^{-1} of butane and progresses to 150 cm^{-1} in the spectrum of $C_{16}H_{34}$.

Several sequences between 1000 and 1150 cm^{-1} in both spectra of the crystalline n-paraffins have been assigned as skeletal stretching vibrations.[13] Two, near 1060 and 1140 cm^{-1} in the spectrum of $C_{19}H_{40}$, have been assigned by Sheppard[33] as the skeletal stretching vibrations of limiting phase. The corresponding vibrations of the infinite polymethylene chain have been identified by Nielsen and Woollett with Raman bands of polyethylene at 1061 and 1131 cm^{-1}.[1]

Groups of very weak bands with frequencies between 1170 and 1370 cm^{-1} in the infrared spectra of the crystalline n-paraffins have

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[49] J. J. Fox and A. E. Martin, Proc. Roy. Soc. (London) A <u>175</u>, 208 (1940).

[50] S. Krimm, C. Y. Liang, and G. B. B. M. Sutherland, J. Chem. Phys. <u>25</u>, 549 (1956).

been attributed to methylene wagging and twisting vibrations. Brown *et al.*[13] have observed band sequences in the spectra of the shorter chains and have attempted to distinguish between wagging and twisting vibrations. The observed low-frequency limit of the bands identified as wagging vibrations was at 1189 cm^{-1} and the observed upper limit was at 1337 cm^{-1}. For the bands ascribed to twisting vibrations, the observed lower limit was 1175 cm^{-1}, and the upper limit was near 1300 cm^{-1}.

Snyder[44] has observed sequences in the infrared spectra of the n-paraffins from $C_{20}H_{42}$ to $C_{30}H_{62}$ which he has identified with members of CH_2 wagging series. The highest frequency bands lie at about 1360 cm^{-1} and the lowest near 1180 cm^{-1}.

Nielsen and Woollett assigned bands at 1295 and 1415 cm^{-1} in the Raman spectrum of polyethylene as the Raman-active methylene twisting and wagging unit cell fundamentals. A band at 1367 cm^{-1} in the infrared spectrum of crystalline polyethylene was assigned as the infrared active wagging fundamental by Krimm, Liang, and Sutherland,[50] Tobin and Carrano,[51] and by Nielsen and Woollett.[1] However, evidence obtained in the initial phase of the present work[2] indicated that the band at 1367 cm^{-1} is due to the amorphous, rather than the crystalline, phase of polyethylene. Two weak infrared bands at 1050 and 1176 cm^{-1} were assigned as the methylene twisting and wagging fundamentals of polyethylene.[2] Sheppard,[33] Snyder,[44] and Krimm[42] have concurred in this assignment of the wagging fundamental.

Band sequences in the infrared spectra near 2870 and 2960 cm^{-1}

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[51] M. C. Tobin and M. J. Carrano, J. Chem. Phys. 25, 1044 (1956).

have been attributed to CH_3 symmetric and asymmetric stretching vibrations, respectively.[49] Infrared bands near 1375 and 1455 cm^{-1} have been assigned as symmetric and asymmetric methyl deformation. Band sequences in both Raman and infrared spectra near 890 cm^{-1} have been attributed to rocking vibrations of the methyl groups,[33,44] though there is some uncertainty as to whether the rocking is parallel or perpendicular to the skeletal plane.

The n-Fatty Acids

Infrared spectra of polycrystalline samples of stearic acid obtained by Sinclair, McKay, and Jones[52] showed some bands which could be associated with vibrations of the methylene chains. For instance, strong bands near 720 cm^{-1} (CH_2 rocking) and 1465 cm^{-1} (CH_2 deformation) and several between 2800 and 3000 cm^{-1} (CH stretching) were observed. Other very broad, intense bands were attributed to vibrations of the carboxyl groups. A spectrum of one crystal form, called the β -polymorph (the C-form), was compared with that of a mixture of β and α -polymorphs (the C and B-forms). The spectra of the two forms are markedly different.

One feature of the spectrum of the C-form aroused considerable interest. A series of bands between 1180 and 1300 cm^{-1}, because of their regularity of spacing, were taken to be caused by chain vibrations. A subsequent paper[53] was devoted to the discussion of these and similar

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[52] R. G. Sinclair, A. F. McKay, and R. N. Jones, J. Am. Chem. Soc. 74, 2570 (1952).

[53] R. N. Jones, A. F. McKay, and R. G. Sinclair, J. Am. Chem. Soc. 74, 2575 (1952).

series in other crystalline n-fatty acids and related compounds. It was noted that the number of bands in the series in the n-fatty acids was about equal to half the number of methylene groups per molecule. The series were attributed to "wagging and/or twisting" vibrations of CH_2 groups.

Jones and Sandorfy[39] showed that members of the series formed sequences in the spectra of the n-fatty acids from $CH_3(CH_2)_{10}COOH$ to $CH_3(CH_2)_{19}COOH$, and assigned the bands as coupled wagging and twisting vibrations. Aranovic[54] and Meiklejohn et al.[55] published spectra of the acids from $CH_3(CH_2)_8COOH$ to $CH_3(CH_2)_{34}COOH$ which showed that the band series remain regular and the sequences continue in the spectra of the higher members of the homologous series of n-fatty acids.

Hadži and Sheppard[56] compared the spectra of several ordinary and deuterated carboxylic acids, including stearic and lauric acids, and assigned the carboxyl vibrations between 500 and 1500 cm^{-1}. Bratoz, Hadži and Sheppard[57] extended the results to include bands up to 3700 cm^{-1}. The assignments of Hadži and Sheppard, which are based in part on earlier work, will be presented in Chapter IV.

Crisler and Fenton[45] have observed a number of infrared band sequences in the region from 300 to 500 cm^{-1}, and have attributed them to low-frequency skeletal vibrations of the methylene chains and the

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[54] S. M. Aranovic, Ph. D. Thesis, University of Wisconsin (1957).

[55] R. A. Meiklejohn et al., Analyt. Chem. 29, 329 (1957).

[56] D. Hadži and N. Sheppard, Proc. Roy. Soc. (London) A 216, 247 (1953).

[57] S. Bratoz, D. Hadži, and N. Sheppard, Spectrochimica Acta 8, 249 (1956).

carboxyl groups.

Von Sydow[58] has published partial infrared spectra of Nujol mulls of the A and C forms of palmitic acid, and the B and C forms of stearic acid and has compared these spectra.

Infrared Dichroism

Ambrose, Elliott, and Temple[59] and Krimm, Liang, and Sutherland,[50] from observations of the dichroism of the bands in the spectrum of stretched polyethylene, have concluded that the crystal vibrational species b_{2u} and b_{3u} include the vibrations which produce the bands at 720 and 730, 1460 and 1470, and 2853 and 2925 cm^{-1}. This is consistent with the interpretation of these bands as caused by CH_2 rocking, deformation, and stretching, respectively.

The assignments of the weak bands at 1050 and 1176 cm^{-1} as CH_2 twisting and wagging fundamentals of crystalline polyethylene was based largely on the fact that their infrared dichroism in oriented polyethylene is that expected for vibrations of species b_{1u}.[2] These assignments and others mentioned earlier were supported in the early part of the present work by a study of the dichroism of an oriented sample of highly crystalline polyethylene.[3]

Krimm _et_ _al_.[50] have studied the dichroism of the most intense infrared bands in the spectra of single crystals of monoclinic n-$C_{36}H_{74}$ and orthorhombic n-$C_{29}H_{60}$. They have found that, in the doublets

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[58] E. von Sydow, Acta Chem. Scand. _9_, 1119 (1955).

[59] E. J. Ambrose, A. Elliott, and R. B. Temple, Proc. Roy. Soc. (London) A _199_, 183 (1949).

at 720 and 730 cm^{-1} and at 1463 and 1473 cm^{-1}, the two components belong to species b_u and a_u or b_{2u} and b_{3u} of the monoclinic and orthorhombic unit cell groups, respectively. This provided rather conclusive proof that the two bands in each doublet are produced by in- and out-of-phase motion of adjacent molecules.

To distinguish between vibrations parallel and perpendicular to the chain axes, Brown et al.[13] compared the spectrum of an unoriented sample of n-$C_{19}H_{40}$ with that obtained with radiation incident parallel to the chains in a partially oriented film. Their results aided in the assignment of several of the band sequences in the spectra of the n-paraffins with shorter chains.

In his study of the n-paraffins from $C_{20}H_{42}$ to $C_{30}H_{62}$, Snyder has applied a similar technique with $C_{25}H_{52}$ and $C_{29}H_{60}$.[44] The results lend strong support to his interpretation of a number of band sequences between 1180 and 1360 cm^{-1} as CH_2 wagging vibrations.

Cole and Jones[60] used polarized radiation to obtain the infrared spectrum of a single crystal of eicosanoic acid, $CH_3(CH_2)_{18}COOH$. The two components of each of the doublets near 720 and 1470 cm^{-1} appear to have changes in dipole moment at right angles to each other, as do the corresponding bands in the orthorhombic and monoclinic n-paraffins. The intensity of the band series between 1180 and 1300 cm^{-1} is strongly dependent on the direction of polarization of the radiation.

To use the infrared dichroism in the interpretation of crystal

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[60] A. R. H. Cole and R. N. Jones, J. Opt. Soc. Am. 42, 348 (1952).

vibrational spectra, one must be able to predict characteristic directions for the changes in dipole moment of the vibrations and control to some extent the directions of propagation and polarization of the radiation inside the crystal.

In some cases this is fairly easy. The infrared-active vibrations of crystalline polyethylene of species b_{1u}, b_{2u}, and b_{3u} are associated with changes in dipole moment parallel to the c, b, and a-axes, respectively. When polyethylene is stretched, the crystallites tend to be aligned so that the c-axes are parallel to the direction of stretch. A stretched sample is optically uniaxial, with the optic axis parallel to the direction of stretch. Radiation incident normal to a surface parallel to the axis and polarized either parallel or perpendicular to the stretch direction will not be refracted and will remain polarized in the same direction. Bands corresponding to vibrations of species b_{1u} will have maximum intensity when the radiation is polarized parallel to the stretch direction, and those of species b_{2u} and b_{3u} will be most intense when the radiation is polarized perpendicular to the stretch direction. The dichroic ratio should become very large as the alignment of the c-axes becomes more nearly perfect. Though the orientation is never complete, extremely high dichroic ratios have been observed for some of the polyethylene bands.[2] Such bands are said to be "polarized" in the directions for which they have maximum intensity.

In the orthorhombic n-paraffins, each of the three infrared-active vibrational species is associated with a change in dipole moment parallel to one of the three axes of the unit cell. The principal axes of the dielectric tensor are also parallel to these axes (see Chapter II).

Radiation incident normal to a surface perpendicular to one axis, and polarized parallel to another axis, will continue with the same direction and polarization inside the crystal. A spectrum obtained with this arrangement will show bands corresponding to vibrations of only one species.

A situation which arises frequently is that in which a monoclinic crystal has one symmetry axis, and two infrared-active vibrational species whose transition moments are parallel and perpendicular to this axis, respectively. One of the principal axes is parallel to the axis of symmetry, and two plane crystal surfaces are parallel to this axis. Radiation incident normal to a surface and polarized parallel or perpendicular to the axis of symmetry will not be doubly refracted and will retain its polarization. Spectra obtained in either case will include bands belonging to only one vibrational species.

In such a monoclinic crystal, though two of the principal axes must be normal to the symmetry axis, their directions are not in general independent of frequency. Likewise, though the change in dipole moment of the vibrations of one species has no component parallel to the axis, it is not necessarily associated with a definite direction perpendicular to the axis. In a triclinic crystal, the directions of neither the principal axes nor the moments of the vibration can in general be predicted. However, the molecular symmetry or other local symmetry in monoclinic and triclinic crystals sometimes allows approximate directions to be determined both for the principal axes and the transition moments.

If a crystal is cut normal to a principal axis, radiation incident parallel to this axis, polarized parallel to one of the other principal axes will continue in the same direction and will remain polarized, or nearly so. If a vibration has a transition moment whose component normal to the direction of propagation makes an angle θ with one of the principal axes, the absorptions observed at the vibrational frequency for radiation polarized parallel to the two principal axes are approximately given by an equation

$k_1/k_2 = \cos^2\theta / \sin^2\theta$, where k_1 and k_2 are the absorption coefficients.

If the vibration has a change in dipole moment parallel to one of the principal axes the absorption will be a maximum when the radiation is polarized parallel to that axis and zero when it is polarized parallel to the other. If the vibration involves a large change in dipole moment in a direction other than a principal axis, and if the difference in the magnitude of the two principal axes is slight, the absorption observed will be a maximum when the incident radiation is polarized parallel to the transition moment.

Though in these cases, the polarization of the radiation for maximum absorption indicates the direction of the transition moment, this simple relationship does not always hold.

Ward[61] has shown that if a band is weak and the difference between the indices great, extrema of absorption will be observed when the radiation is polarized parallel to the principal axes, regardless of the direction of the transition moment. When the direction of the transition

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[61] J. C. Ward, Proc. Roy. Soc. (London) A 228, 205 (1955).

moment is very different from the direction of the principal axes, however, the absorption will vary little with the direction of polarization of the radiation, so that if a large variation is observed, it may be assumed that the direction of polarization of the incident radiation for maximum absorption approximates the direction of the transition moment of the vibration.

CHAPTER II

THE GROWTH AND PROPERTIES OF SINGLE CRYSTALS OF THE n-PARAFFINS AND n-FATTY ACIDS

Crystal Growth Habits

The n-paraffins and n-fatty acids ordinarily crystallise from solution as thin flakes. The planar layers bounded by the methyl groups are parallel to the surfaces of the flakes, indicating that molecules are added more readily at the edges of a layer than at its surface.

Crystals in which the methylene chains have the orthorhombic packing often have well-defined edges which form a parallelogram. The crystals are shaped like thin lozenges. On the surface, lines may be observed which are parallel to the edges and which form spiral patterns. These lines are edges of growth terraces. Electron micrographs and interferometric studies of thin crystals have shown that the heights of the steps at the terrace edges are integral multiples of the thickness of a monomolecular layer.[62,63,64] This was interpreted to mean that the crystals grow in a direction normal to the layers by means of a

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[62] I. M. Dawson *et al.*, Proc. Roy. Soc. (London) A *206*, 55 (1951); *228*, 539 (1955); *239*, 349 (1957).

[63] S. Amelinckx, Acta Cryst. *8*, 530 (1955); *9*, 16, 217 (1956).

[64] A. R. Verma and P. M. Reynolds, Proc. Phys Soc. (London) B *66*, 414 (1953).
A. R. Verma, Proc. Roy. Soc. (London) A, *228*, 34 (1955).

screw dislocation, so that successive layers are deposited in a shallow spiral.

In crystals of some of the n-paraffins and n-fatty acids, more than one relative orientation of the chains in succeeding layers is likely to occur.[63] Fairly common cases are those in which successive layers are parallel or rotated 180° about an axis normal to the layers.

From a study of interlaced spirals on the surfaces of crystals of this type, Amelinckx has concluded that the alternation of the orientation is not always random, but that a particular stacking sequence present in initially deposited layers may be propagated throughout the crystal by a screw dislocation.[63]

In studies of the monoclinic form of n-$C_{34}H_{70}$ and the B and C (monoclinic) forms of docosanoic acid, $CH_3(CH_2)_{20}COOH$, Amelinckx observed that the surfaces of about five to ten percent of the crystals of the n-paraffin and the B-form of the acid exhibited interlaced spirals which were taken as an indication of a repeated stacking sequence. From measurements of the step heights he was able to determine the sequence. Results indicated that the most common type was that in which each succeeding layer was rotated 180° with respect to the neighboring layer, both in the n-paraffin and the B-form of the acid. Amelinckx observed no interlacing for crystals of the C-form of docosanoic acid, however.

Of the crystals of the n-fatty acids and n-paraffins whose structures have been determined, all which have the lozenge shape have the orthorhombic packing of the chains. In each case, the edges of the large face of the lozenge are parallel to the diagonals of a rectangle formed by the a- and b-axes of the unit cells, thus if ϕ is an interedge angle,

(1) $\tan \phi / 2 = b/a$ or a/b.

These crystals are either monoclinic or orthorhombic, and in each case the projections of the a- and b-axes upon a plane normal to the chain axes have the dimensions of the a_o and b_o axes of the orthorhombic subcell. Thus if θ is the angle between the chain axes and the normal to the ab-plane, either

(2) $\cos \theta = a_o/a$ and $b = b_o$ or

$\cos \theta = b_o/b$ and $a = a_o$.

The values which θ may take are limited to those which allow fitting of adjacent chains into the subcell, so that

(3) $\sin \theta = n\, c_o/a$ or $n\, c_o/b$, where n is an integer and c_o is the distance between next nearest carbon atoms in a chain.

From (1) and (2), one can get equations of the type

(4) $\tan \phi/2 = b/a = b_o/a = b_o \cos \theta/a_o$.

Though the dimensions a_o and b_o are not precisely the same for all crystals having the orthorhombic packing, a good approximation to a, b, and θ may be inferred from a known value of ϕ. Of course, equation (4) is not the only one which may be derived from (1) and (2); however, equation (3) helps make the choice unique.

Nowhere in the preceding discussion was the c axis of the unit cell mentioned. The direction and magnitude of this axis depend on the chain length and the orientation and separation of adjacent layers.

The magnitude of the interedge angles are thought to provide a rather specific identification of the crystal form. It will be shown in Chapter IV that the correspondence between the crystal form and these angles is not unique. Nevertheless, the interedge angles do indicate the arrangement of the chains, which helps in identifying the crystal form.[64]

Triclinic crystals of the n-fatty acids have been described as rectangular rods,[65] as thick parallelopipeds, and as plates with irregular edges.[58] Müller and Lonsdale[7] have noted that triclinic crystals of n-$C_{18}H_{38}$ take the form of flakes in which the chain axes are slightly tilted away from the normal to the surface of the flakes. Little else has been published about the relationship between the crystal structure and the growth habits of crystals which have the triclinic chain packing.

Optical Properties

Because of the rodlike shape of an extended methylene chain, it is fairly certain that crystals of the long-chain n-paraffins and n-fatty acids in which the chain planes are parallel will have one principal dielectric axis either precisely or approximately parallel to the chain axes.[66]

This is required by the crystal symmetry in the orthorhombic n-paraffins, where one symmetry axis is parallel to the chain axes and thus also parallel to the c-axis of the unit cell. There are reflection planes of symmetry normal to the a- and b-axes, which requires that the other two principal dielectric axes be parallel to these two crystallographic

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[65] E. von Sydow, Acta Cryst. 7, 529 (1954).

[66] See for example N. H. Hartshorne and A. Stuart, Crystals and the Polarizing Microscope, Third Edition (London: Edward Arnold, Ltd., 1960).

axes. The monoclinic forms of the even-numbered n-paraffins and n-fatty acids each have a screw rotation axis parallel to one axis of the unit cell. In the monoclinic n-paraffins and the B-form of the acids, this axis is parallel to the a-axis which is therefore parallel to one of the principal axes. In the C-form of the fatty acids, the axis of rotation is parallel to the b-axis, thus the b-axis is parallel to a principal axis in this form. If one axis is parallel to the chains, since the symmetry axis in each case is perpendicular to the chain axes, all the principal axes in these crystals should be frequency-independent. This conclusion is supported by the fact that the orthorhombic subcell which describes the chain packing would for infinitely long chains have a screw axis of rotation parallel to the chain axes.

The unit cells of the triclinic n-paraffins and n-fatty acids have at best a center of symmetry. However, all chain axes and chain planes are parallel. The finite chains have a reflection in the skeletal plane, and if the chains were infinite they would have one screw axis of symmetry parallel to the chain and two ordinary rotation axes parallel and perpendicular to the skeletal plane. It seems fairly certain that these three directions are the directions of the principal axes in the triclinic crystals.

The optical properties help in the determination of the crystal form and in the selection of crystals suitable for study. When the crystals are examined between crossed polarizers, the directions for extinction of white light are useful in determining directions of crystallographic axes and chain axes. Macroscopic twinning can often be detected by the failure to obtain complete extinction of visible light.

In most cases, twin boundaries can be thrown into relief by extinguishing light passing through one of the twins, so that homogeneous portions can be selected for use. For a particular crystal form and orientation, the color of the transmitted radiation depends upon the path length in the crystal. This property helps in selecting crystals of a desired thickness.

Crystal Growing; General Techniques

One reason that there have been so few attempts to study the spectra of single crystals of compounds having long methylene chains is that it is difficult to grow single crystals of the proper size and quality for spectroscopic study. Ideally, a sample should be a perfect single crystal with smooth surfaces, large enough to admit the beam from the spectrometer and thick enough to have sufficient absorbance.

The development of the reflecting microscope for use with the Perkin-Elmer spectrometer greatly reduced the area requirement for samples. A crystal one millimeter square can take advantage of the entire beam. For the materials treated in the present work, it has ordinarily been easy to select samples which are essentially single crystals. The problem has usually been that of getting crystals thick enough. Though some strong bands may be observed with crystals 1-10 microns in thickness, observation of many of the bands require samples 0.1 to 1.0 mm thick.

Three common crystal growing techniques were used: crystallization by cooling a melt, evaporation of solvents from solution, and the cooling of a solution.

Good crystals of materials which melt near room temperature, such as the n-paraffins $C_{18}H_{38}$ and $C_{20}H_{42}$ were obtained by cooling a melt. Crystals of the larger molecules obtained from the melt were generally inferior to those grown from a solution.

Of the two solution techniques, evaporation of the solvent gave more satisfactory results than the cooling of a solution. Controlling the evaporation rate at a constant temperature is easier than controlling the cooling rate. Also, a change in temperature is often accompanied by a change in the growth habits and sometimes even in the structure of the crystals being deposited. This may be prevented by using a narrow cooling range, but to get thick crystals then requires a solvent in which the material is highly soluble. This increases the probability that the crystals will be redissolved or grow too rapidly with small temperature fluctuations. Also, if crystals are removed from a concentrated solution, the surfaces become clouded with tiny crystallites produced by evaporation. This can sometimes be prevented if the crystals are quickly drained on absorbent tissue or washed in a poor solvent.

When crystals are produced by evaporation at a constant temperature, there are essentially only three control factors, the choice of solvent, the temperature, and the evaporation rate. The first two are perhaps more critical, since they sometimes determine the crystal form. All three factors affect the size and quality of the crystals.

Ordinarily, the slower the evaporation rate the bigger and better the crystals. Since the growing process is time-consuming at best, it is desirable to choose a favorable solvent and temperature before attempting to grow large crystals. This is largely a matter of trial and error. The procedure used here consisted of forming small crystals by rapidly cooling solutions in a variety of solvents. The crystals formed were examined under a microscope, often during crystallization. When the small crystals grown under these conditions were of good quality the deposition temperature was varied by changing the concentration until an optimum range characteristic of the solvent (and solute) was determined. Only then was an attempt to grow large crystals made.

Though slowing the evaporation usually results in better crystals, it should not proceed so slowly that temperature fluctuations in the thermostat cause unsaturation. If the crystals are partially dissolved during growth they are invariably imperfect. Their presence will prevent new crystals from forming, and the whole lot will be ruined.

The procedures used for growing crystals of particular compounds follows. Unless otherwise specified, the conditions described are those under which the best crystals were produced.

Procedures for Particular Materials

Monoclinic crystals of n-$C_{36}H_{74}$ up to 1/2 cm^2 in area and up to 0.1 mm in thickness were produced by cooling a xylene solution saturated at 30° C down to 27° overnight. Smaller, but thicker (up to 0.5 mm) crystals were grown by evaporation to dryness of a solution in isopropyl ether at 25° C. The evaporation took about three days for 20 cm^3 of solution.

Monoclinic crystals of n-$C_{46}H_{94}$ up to 80 microns in thickness were produced by evaporation of a xylene solution at 48° C. The evaporation took two days for 15 cm^3 of solution.

Orthorhombic crystals of n-$C_{24}H_{50}$ up to 1 mm in thickness were grown by evaporation in an acetone solution at a temperature of 35° C. Thinner but more regular crystals were obtained by evaporation of a solution in 30°-60° C petroleum ether at a temperature around 25° C.

Triclinic crystals of n-$C_{18}H_{38}$ and n-$C_{20}H_{42}$ were obtained by cooling melts.

The monoclinic C-forms of stearic and palmitic acid were crystallized by evaporation of an isopropyl ether solution at 27° C. Crystals up to 1 mm in thickness were obtained.

Crystals of stearic and palmitic acid having the monoclinic B-form were produced by evaporating solutions in CS_2 at 18° C. Both the B- and A-forms of palmitic and stearic acid crystallized when a solution in CS_2 was evaporated at -9° C. In both of these cases it was possible to select crystals up to about 0.1 mm in thickness, which was sufficient for the spectroscopic work.

Deuterated stearic acid, $CH_3(CH_2)_{16}COOD$, was made by first dehydrating stearic acid with acetic anhydride and then melting the stearic anhydride in contact with D_2O. In solution in ordinary organic reagents, the deuterium was rapidly replaced by hydrogen. Crystals of the C-form in which the acid was nearly completely deuterated were produced by evaporation of a solution in ethyl ether which had been dehydrated with metallic sodium. Solution and evaporation were carried out with the ether floating on a layer of D_2O.

Though the B-form was thought to crystallize most readily from a non-polar solvent, it was noticed that crystals which had the inter-edge angle of 74° thought to be characteristic of the B-form were formed when an isopropyl ether solution of stearic acid was evaporated at 0° C.

In an attempt to grow deuterated crystals of the B-form using the experimental arrangement already prepared, some of the crystals of the deuterated acid were redissolved, and the solution evaporated over D_2O at a temperature a few degrees above 0° C. Crystals of the deuterated acid which appeared to have the B-form were grown.

CHAPTER III

THE INFRARED SPECTRA OF SINGLE CRYSTALS OF THE n-PARAFFINS

The Monoclinic Form of n-$C_{36}H_{74}$

The unit cell of monoclinic n-$C_{36}H_{74}$ is described in Chapter I. There are two molecules per unit cell, and the chains have the orthorhombic packing. The two shorter axes of the unit cell are orthogonal and have been designated by the letters a and b, the a-axis being the longer of the two. The methylene chains are nearly parallel to the c-axis, which is normal to the a-axis but makes an angle of 61° with the b-axis.

Monoclinic crystals of n-$C_{36}H_{74}$ grown here had the common lozenge shape with the acute interedge angle of 74° characteristic of this crystal form.[8] The a- and b-axes of the unit cell lie in a plane parallel to the large face of the lozenge and are parallel to the bisectors of its acute and obtuse interedge angles, respectively. The c-axis is therefore tilted 29° away from the normal to the crystal surface, toward the b-axis. The axes of the methylene chains are parallel to the bc-plane and make an angle of about 27° with a normal to the surface.

The monoclinic unit cell has an inversion center, a twofold screw rotation axis parallel to the a-axis, and a glide reflection plane perpendicular to this axis. The unit cell group is isomorphic to the point group C_{2h}. The unit cell group fundamentals are Raman- or infrared-active according to their symmetry or antisymmetry with respect to the inversion. The infrared-active vibrations that are symmetric with respect to a screw rotation belong to species a_u. Those that are antisymmetric with respect to such a rotation belong to species b_u. In vibrations of one species, the motions of the two molecules in a unit cell are in-phase, while in vibrations of the other, the two move out-of-phase. Vibrations of species a_u are polarized parallel to the a-axis and those of species b_u are polarized perpendicular to the a-axis.

The spectrum of a monoclinic crystal of n-$C_{36}H_{74}$ between 700 and 1500 cm^{-1} is shown in Fig. 3-1. To obtain this spectrum, a crystal was mounted in the infrared microscope so that the axis of the cone of radiation was normal to the surface of the crystal. The solid and broken curves represent records obtained with radiation polarized parallel to the a- and b-axes, respectively. Bands appearing in the solid curves are therefore caused by vibrations of species a_u, and those in the broken curves represent vibrations of species b_u.

Though the a_u vibrations are polarized strictly parallel to the a-axis, the change in dipole moment associated with vibrations of species b_u may have components both parallel to the b-axis and normal to the ab-plane. In order to study the polarization of the b_u bands, a crystal was sliced parallel to the bc-plane. A slice was mounted in the infrared microscope so that the axis of the beam of polarized radiation was parallel to the a-axis. Spectra obtained with the electric vector making angles of 0°, ±15°, ±30°, ±45°, ±60° and 90° with the b-axis showed that

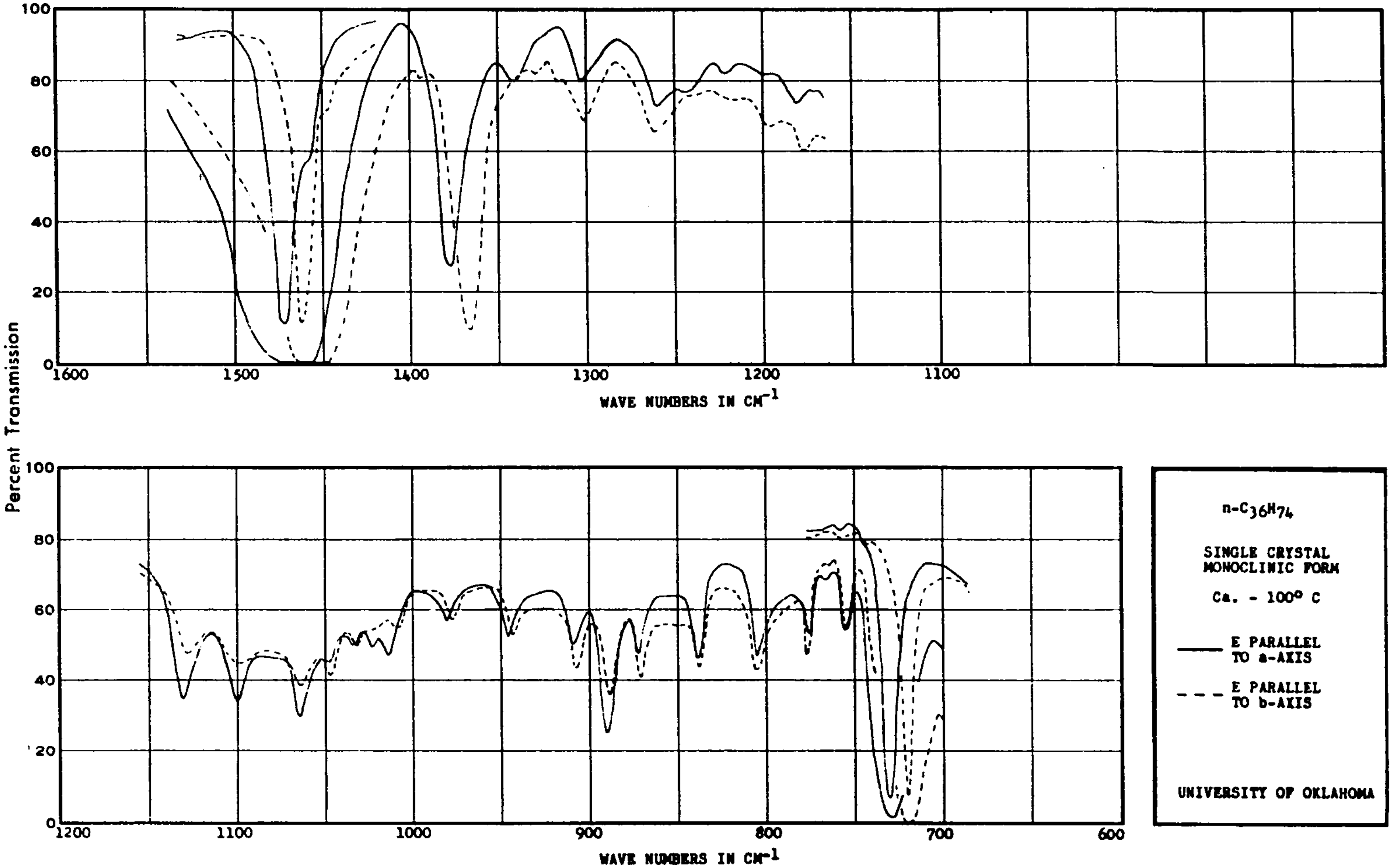

Fig. 3-1. Infrared Spectrum of Monoclinic n-$C_{36}H_{74}$; Radiation Incident Normal to the ab-Plane

the absorption depends on the magnitude of the angle, but not on its sign.

An examination of the crystal slices between crossed polarizers revealed that white light incident parallel to the a-axis was extinguished when the electric vector was parallel or perpendicular to the b-axis. Light incident normal to the ab-plane was extinguished when the electric vector was parallel to the a- or b-axes. These observations were interpreted to mean that about half the molecular layers in the crystal are rotated 180° with respect to the others about an axis normal to the ab-plane. The a- and b-axes of unit cells in each layer would then still be parallel, but the tilt of the chain axes away from the normal would alternate between ±27°.

Twinning of this sort has been reported by Shearer and Vand[8] for n-$C_{36}H_{74}$, and Amelinckx has proposed such variations to explain patterns on the surface of monoclinic crystals of n-$C_{34}H_{70}$.[63]

Whether this alternation of chain tilt is random twinning or the regular structure proposed by Amelinckx is not known. It is certain that all crystal slices examined here showed no evidence of a predominance of either tilt direction. Band maxima and minima in the spectra of the crystal slices were always observed when the electric vector of the radiation was aligned either parallel or perpendicular to the b-axis.

In Fig. 3-2 is shown the absorption observed for these two orientations of the crystal slices. Since the angle between the b-axis and the chain axes is 63°, bands corresponding to vibrations primarily perpendicular to the chain axes should be most intense when the radiation is polarized parallel to the b-axis. Bands corresponding to vibrations

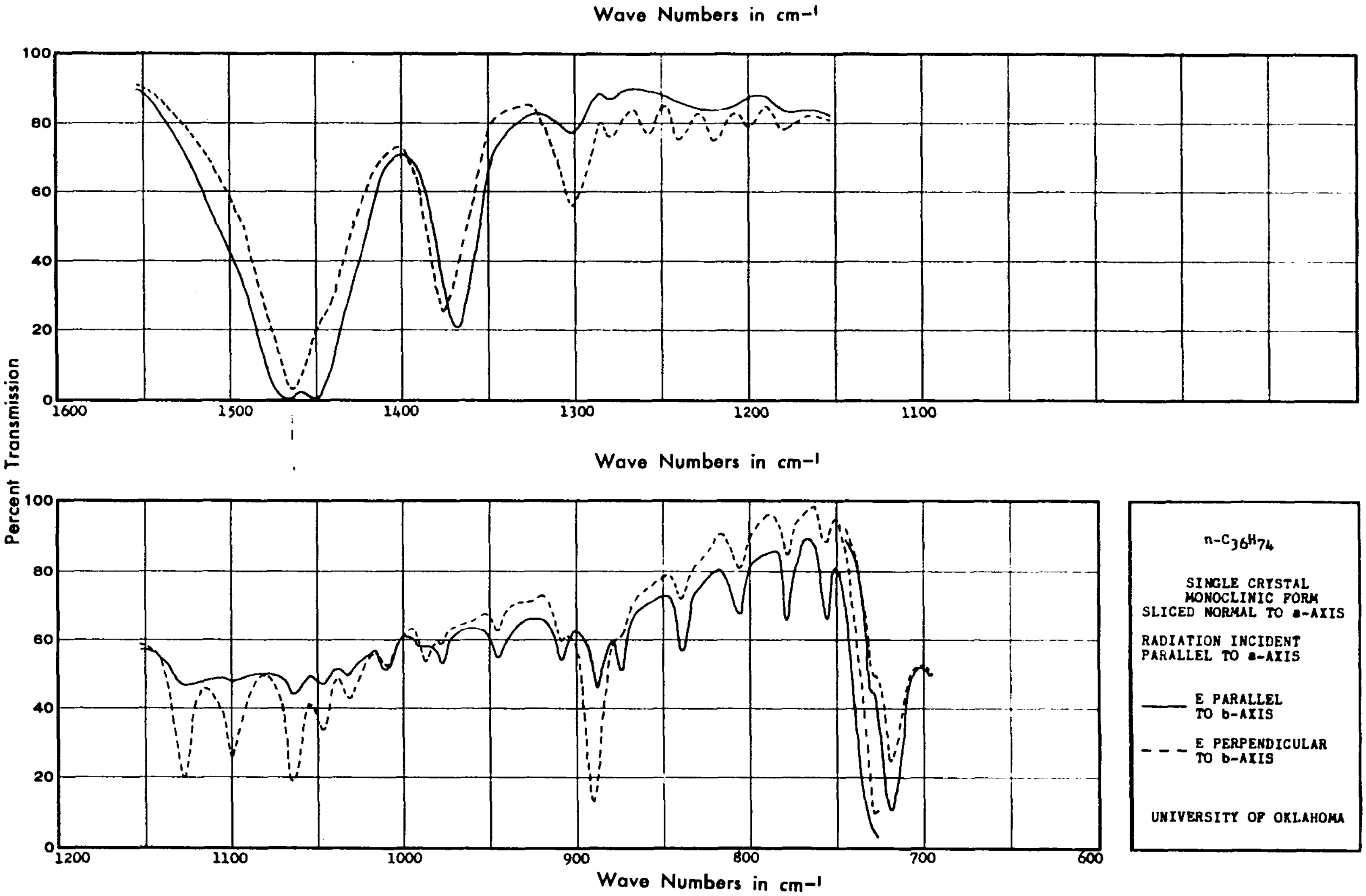

Fig. 3-2. Infrared Spectra of Monoclinic n-$C_{36}H_{74}$; Radiation Incident Normal to the bc-Plane

TABLE 3-I

INFRARED SPECTRUM OF MONOCLINIC n-$C_{36}H_{74}$

Wave Number	Intensity[(a)]	Symmetry[(b)] Species	Polarization[(c)]	Interpretation
719	vs	b_u	b	R (CH_2 Rocking)
729	vs	a_u		
741	w	b_u	b	R
744	w	a_u		
754	w	b_u	b	R
755	w	a_u		
776	w	a_u		R
777	w	b_u	b	
805	w	b_u, a_u	b	R
837	w	b_u	b	R
838	w	a_u		
872	w	b_u	b	R
873	w	a_u		
890	w	a_u		CH_3 Rocking Parallel to the Skeletal Plane
	m	b_u	⊥ ab	
907	w	b_u	b	R
909	w	a_u		
943	w	b_u	b	R
946	w	a_u		
977	vw	b_u	b	R
982	vw	a_u		

TABLE 3-I (Continued)

Wave Number	Intensity(a)	Symmetry Species(b)	Polarization(c)	Interpretation
994	vw		ab	S (C-C Stretching)
1009	vw	b_u	b, ⊥ab	R, S
1013	w	b_u, a_u	⊥ab	S
1023	w	b_u, a_u	⊥ab	S
1032	vw	b_u	b, ⊥ab	R
1034	vw	a_u		
1047	w	b_u, a_u	⊥ ab	S
1064	m-w	b_u, a_u	⊥ ab	S
1100	m-w	b_u, a_u	⊥ ab	S
1130	m-w	b_u, a_u	⊥ab	S
1176	vw	b_u		T (CH_2 Twisting)
1182	vw	b_u, a_u	⊥ ab	W (CH_2 Wagging)
1200	vw		⊥ ab	W
1219	vw	b_u, a_u	⊥ab	W
1238	vw		⊥ ab	W
1243	vw	b_u, a_u		T
1257	vw		⊥ab	W
1261	vw	b_u, a_u	⊥ ab	T
1273	vw	b_u, a_u	⊥ ab	W
1300	vw	b_u, a_u	⊥ab	W
1340	vw	a_u		
1368	m	b_u	b	CH_3 Symmetric Deformation
1378	w	a_u	⊥ ab	

TABLE 3-I (Concluded)

Wave Number	Intensity(a)	Symmetry(b) Species	Polarization(c)	Interpretation
1447	w	b_u	b	CH_3 Asymmetric Deformation
1457	w	a_u		
1463	vs	b_u	b	CH_2 Deformation
1473	vs	a_u		

(a) The abbreviations v,s,w,m, mean very, strong, weak, and medium, respectively.

(b) Vibrations of species a_u are polarized parallel to the a-axis, those of species b_u are polarized perpendicular to the a-axis.

(c) The symbols b, $\perp$ab indicate that the b_u bands are polarized predominantly parallel to the b-axis or perpendicular to the ab-plane.

parallel to the chain axes should have maximum intensity when the radiation is polarized normal to the b-axis.

The frequencies, relative intensities, and symmetry species of the bands which appear in Figs. 3-1 and 3-2 are listed in Table 3-I. The polarization of the b_u bands observed in Fig. 3-2 is indicated by the symbols b or $\perp$ab, showing that the bands have maximum intensity when the radiation is polarized parallel to the b-axis or perpendicular to the ab-plane.

Also included in Table 3-I are the assignments, which in the following pages will be related to the polarization observed and compared with previous work.

Consistent with the work of Brown <u>et</u> <u>al</u>.[13] and Snyder[44] on n-paraffins with shorter chains, a series of doublets in Fig. 3-1 with a_u and b_u components about equal in intensity have been attributed to methylene rocking vibrations. The series originates in the strong doublet at 719 and 729 cm^{-1}, and apparently terminates with the bands at 1032 and 1034 cm^{-1}. In Fig. 3-2, the b_u components of most of the doublets are more intense in the solid curve, which would be expected for rocking vibrations, since the motion is perpendicular to the chain axes. The assignments of the last two members of the series, at 1009 and at 1032 and 1034 cm^{-1} were based on their frequencies (see the section of this Chapter on the rocking frequencies of n-$C_{18}H_{38}$) and appearance in Fig. 3-1 and cannot be justified by their polarization in Fig. 3-2. Both are near stronger bands polarized perpendicular to the ab-plane.

By comparing the frequencies of members of the series with those of band sequences observed in the spectra of shorter chains,[13,44] the number of rocking fundamentals overlapping the strong doublet was found to be six. With the eleven remaining doublets, all seventeen infrared-active rocking doublets of n-$C_{36}H_{74}$ are accounted for.

Both the separation and the order of the a_u and b_u components of the rocking doublets vary over the series. Beginning with the strong bands at 719 and 729 cm^{-1}, the b_u component of each doublet has a frequency lower than that of the a_u component, and the separation decreases with increasing frequency in the first two higher doublets. In the next doublet, at 776 and 777 cm^{-1}, the a_u component has lower frequency. The separation is essentially zero at 805 cm^{-1}. In the higher frequency doublets, the order of a_u and b_u components is again the same as for the strong doublets, and throughout most of the series the splitting increases with increasing frequency. This behavior of the rocking doublets is related to the crystal structure and is discussed in Appendix III.

A band at 890 cm^{-1} is easily distinguished from the rocking series by its intensity and polarization. It must be regarded as a doublet, since it appears in both curves shown in Fig. 3-1, though the separation of the a_u and b_u components is negligible. Bands at this position have been attributed to rocking of the methyl groups either parallel[33] or perpendicular[44] to the skeletal plane. If it were out-of-plane it should be polarized perpendicular to the chain axes, like the methylene rocking vibrations, and its intensity would be expected to show about the same dependence on the direction and polarization of the radiation. In Fig. 3-1 the a_u and b_u bands at 890 cm^{-1} do not have the same intensities, as do the two components of the rocking doublets. The a_u band is more intense. Also, in the spectrum obtained with the radiation incident parallel to the a-axis (Fig. 3-2), the b_u component has a higher intensity when the radiation is polarized normal to the ab-plane. These results show that the vibration has a change in dipole moment neither strictly parallel nor strictly perpendicular to the chain axes. If the band is produced by methyl rocking, it must therefore be in-plane rocking, as suggested by Sheppard.[33]

The bands between 1000 and 1140 cm^{-1} not ascribed to methylene rocking are assigned as skeletal stretching vibrations. None of these bands show any appreciable separation of a_u and b_u components, which indicates that the vibrations involve little motion of hydrogen atoms perpendicular to the chain axes. Also, at each frequency, the absorption of radiation polarized parallel to the a-axis is about equal to that for radiation polarized normal to the ab-plane. This indicates that the vibrations are probably parallel to the skeletal plane. The interpretation given is therefore consistent with the behavior of these bands.

The strong a_u-b_u doublet at 1463 and 1473 cm^{-1} has been ascribed to methylene deformation.[46,50] Though it was difficult to get slices thin enough to study the polarization of the b_u components, the band at 1463 cm^{-1} (see Fig. 3-2) appears to be more intense in the record obtained with the radiation polarized parallel to the b-axis. The comparison of intensities is made more difficult by the presence of the shoulder at 1447 cm^{-1}. The origin of the latter band will be discussed later.

Between 1130 and 1350 cm^{-1} in Fig. 3-1, several weak bands may be seen. Bands in this frequency range in the spectra of the n-paraffins with shorter chains have been attributed to methylene wagging and twisting.[13,44] No regularly spaced series such as those assigned by Snyder as CH_2 wagging can be discerned. In the spectrum of the sliced crystal shown in Fig. 3-2, however, a series of bands are seen which are polarized normal to the ab-plane. Though the methylene wagging vibrations may have components both parallel and perpendicular to the chain axes, the twisting vibrations should be perpendicularly polarized. This series of bands is therefore ascribed to methylene wagging.

The remaining bands between 1100 and 1350 cm^{-1} have been somewhat arbitrarily assigned as methylene twisting modes. They are so weak that it has not been possible to determine their polarization precisely.

In Fig. 3-1, a band of about medium intensity, polarized parallel to the b-axis, is seen at 1368 cm^{-1}, and a weaker band, polarized parallel to the a-axis, is at 1378 cm^{-1}. Krimm et al.[50] have observed the polarization of these two bands. They assigned the band at 1378 cm^{-1} as symmetrical methyl deformation and that at 1368 cm^{-1} as the most intense wagging fundamental. It was thought that the latter, which should be polarized parallel to the chain axes, appeared b-polarized because of the tilt of the chains toward the b-axis.

In Fig. 3-2, the band at 1368 cm^{-1} does not appear in the record obtained with the radiation polarized normal to the ab-plane. It cannot, therefore, be a parallel band, and its assignment as the CH_2 wagging mode must be discarded.

In the spectrum of a monoclinic crystal of n-$C_{46}H_{94}$, obtained in the same manner as that of n-$C_{36}H_{74}$ shown in Fig. 3-1, two bands appear at 1370 and 1374 cm^{-1} which are similar to those at 1368 and 1378 cm^{-1} in n-$C_{36}H_{74}$.[2] The ratio of "base line" absorbances for the two bands in n-$C_{36}H_{74}$ is 2.72 and in n-$C_{46}H_{94}$ is 2.68. Relative to the two nearby methylene fundamentals, both bands in n-$C_{46}H_{94}$ are less intense than those in n-$C_{36}H_{74}$. The intensity difference is almost precisely that expected if both bands in each compound are attributed to methyl vibrations.

It seems reasonable, therefore, to assign the 1368 and 1378 cm^{-1} bands as the b_u and a_u components of a doublet produced by in- and out-of-phase symmetric deformation of adjacent methyl groups. However, this interpretation does not account for two significant facts. In the first place, the band at 1368 cm^{-1}, which from Fig. 3-1 should belong to species b_u, would be expected to have a component normal to the ab-plane. However, in Fig. 3-2 this band appears to be rather precisely polarized parallel to the b-axis. Secondly, though the band at 1378 cm^{-1} is definitely polarized parallel to the a-axis in Fig. 3-1, a band appears at or very near this frequency in the record obtained with the radiation polarized normal to the ab-plane in Fig. 3-2. Since a_u bands must be polarized strictly parallel to the a-axis, this cannot be the same band that appears in Fig. 3-1.

A possible explanation of these observations can be given if one assumes that the number of layer boundaries across which the chain tilt changes is comparable with the number of ordinary boundaries. This probably would not appreciably affect the frequencies of the methylene vibrations. It could, however, affect the methyl group modes.

In a crystal having only the ordinary boundaries, the symmetric deformation of the methyl groups produces two infrared-active vibrations, one of species a_u, polarized parallel to the a-axis, and one of species

b_u, polarized perpendicular to the a-axis. According to Amelinckx,[63] a crystal in which all boundaries are of the type across which the tilt changes would be orthorhombic. The space group describing the symmetry of the crystal would then be isomorphic either to V, C_{2v}, or V_h,[66] each of which has three, rather than two, infrared-active species. The infrared-active vibrations should be polarized in directions corresponding to the a-axis, b-axis, and a normal to the ab-plane of the ordinary unit cell. One would expect three infrared bands caused by CH_3 symmetric deformation, polarized parallel to these three axes.

Though this explanation is highly speculative, several facts may be cited in support of it.

(1) In Snyder's spectra of polycrystalline samples of monoclinic n-$C_{28}H_{58}$ and n-$C_{30}H_{62}$,[44] obtained at low temperatures with a high resolution instrument, three bands are observed between 1360 and 1380 cm^{-1}.

(2) The work of Amelinckx[63] indicates that the most common form of polytypism in monoclinic n-paraffins is that in which the tilt angle alternates from layer to layer.

(3) In the spectra of the B-form of stearic acid (see Chapter IV), in which the arrangement of the chains is similar to that in the monoclinic n-paraffins except that there appears to be no alternation of the chain tilt, two bands similar in frequency, polarization and relative intensity to those at 1368 and 1378 cm^{-1} are observed. In this case, however, the a-polarized band at the higher frequency has no component normal to the ab-plane, while that of lower frequency has components both parallel to the b-axis and normal to the ab-plane, as would be expected for a vibration of species b_u.

The Orthorhombic Form of n-$C_{24}H_{50}$

The tilt of the chains and the twinning or "polytypism" in monoclinic n-$C_{36}H_{74}$ made the use of the polarization of the bands in the interpretation of the spectra difficult. It was supposed that better results could be obtained with crystals which had the orthorhombic form.

n-Paraffins having an odd number of carbon atoms crystallize in the orthorhombic form.[4] Unfortunately, none of these compounds were available except in amounts too small to permit the growing of single crystals large enough for use.

A n-paraffin with an even number of carbon atoms will crystallize in the orthorhombic form if a few percent of n-paraffins with slightly longer or shorter chains are present as impurities. Attempts to grow orthorhombic crystals of n-$C_{36}H_{74}$ were unsuccessful, presumably because of the purity of the sample. However, thick lozenge-shaped crystals of n-$C_{24}H_{50}$ were grown which had the interedge angles of about 67° characteristic of the orthorhombic form.

The unit cell of orthorhombic n-$C_{36}H_{74}$ determined by Teare[9] is described in Chapter I. If the crystals of n-$C_{24}H_{50}$ have a similar structure, the unit cell includes four molecules, two in each of two adjacent layers, and the chains have the orthorhombic packing. All layers are identical, and the orientation of successive layers differs by a rotation of 180° and a displacement in the plane of the layer. Though the unit cell group is isomorphic to C_{2v}, the symmetry of a single layer is given by a two-dimensional space group which has a factor group isomorphic to C_{2h}. This group describes the symmetry of the half of the crystal unit cell lying in a single layer. Except possibly for the end group vibrations, this half unit cell should be adequate for the discussion of the spectrum of orthorhombic n-$C_{24}H_{50}$.

As in the crystals of the monoclinic form, the a- and b-axes of the unit cell are parallel to the lines bisecting the acute and obtuse interedge angles on the surface of the lozenge. The chain axes are parallel to the c-axis, and thus are normal to the lozenge surface.

Fig. 3-3 shows a spectrum obtained with the radiation incident normal to the ab-planes, polarized parallel to the b-axis (dotted curve) and the a-axis (solid curve). Fig. 3-4 is the spectrum of a crystal slice, obtained with the radiation incident parallel to the ab-plane and polarized parallel (dotted curve) or perpendicular (solid curve) to the axes of the chains.

The screw rotation associated with the layer unit cell group is in this case parallel to the b-axis, the vibrations of species a_u are polarized parallel to the b-axis, and those of species b_u are polarized normal to this axis. Thus the bands in the dotted curve in Fig. 3-3 belong to species a_u, and those in the solid curve belong to species b_u. The two curves in Fig. 3-4 indicate the relative magnitudes of the changes in dipole moment parallel and perpendicular to the axes of the chains.

In Table 3-II, the frequencies and relative intensities of the bands of n-$C_{24}H_{50}$ are listed, together with their polarization. The symbols a, b indicate that the bands, as shown in Fig. 3-3, are polarized parallel to the a- or b-axes, respectively. The symbols $\parallel$, $\perp$ distinguish between bands polarized primarily parallel or perpendicular to the chain axes. Assignments also are included in Table 3-II.

In the discussion which follows, attention will be limited to

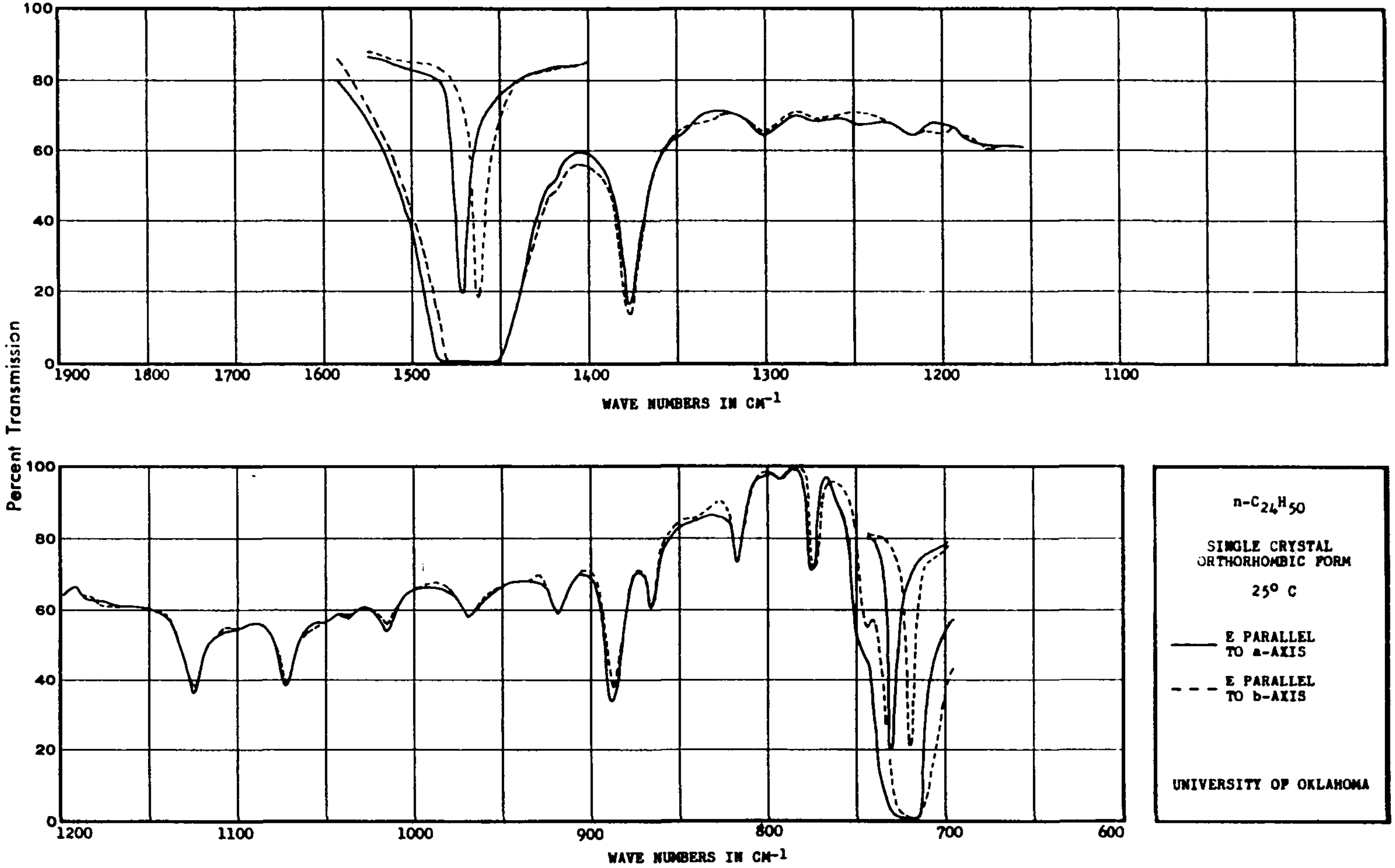

Fig. 3-3. Infrared Spectrum of Orthorhombic n-$C_{24}H_{50}$; Radiation Incident Normal to the ab-Plane

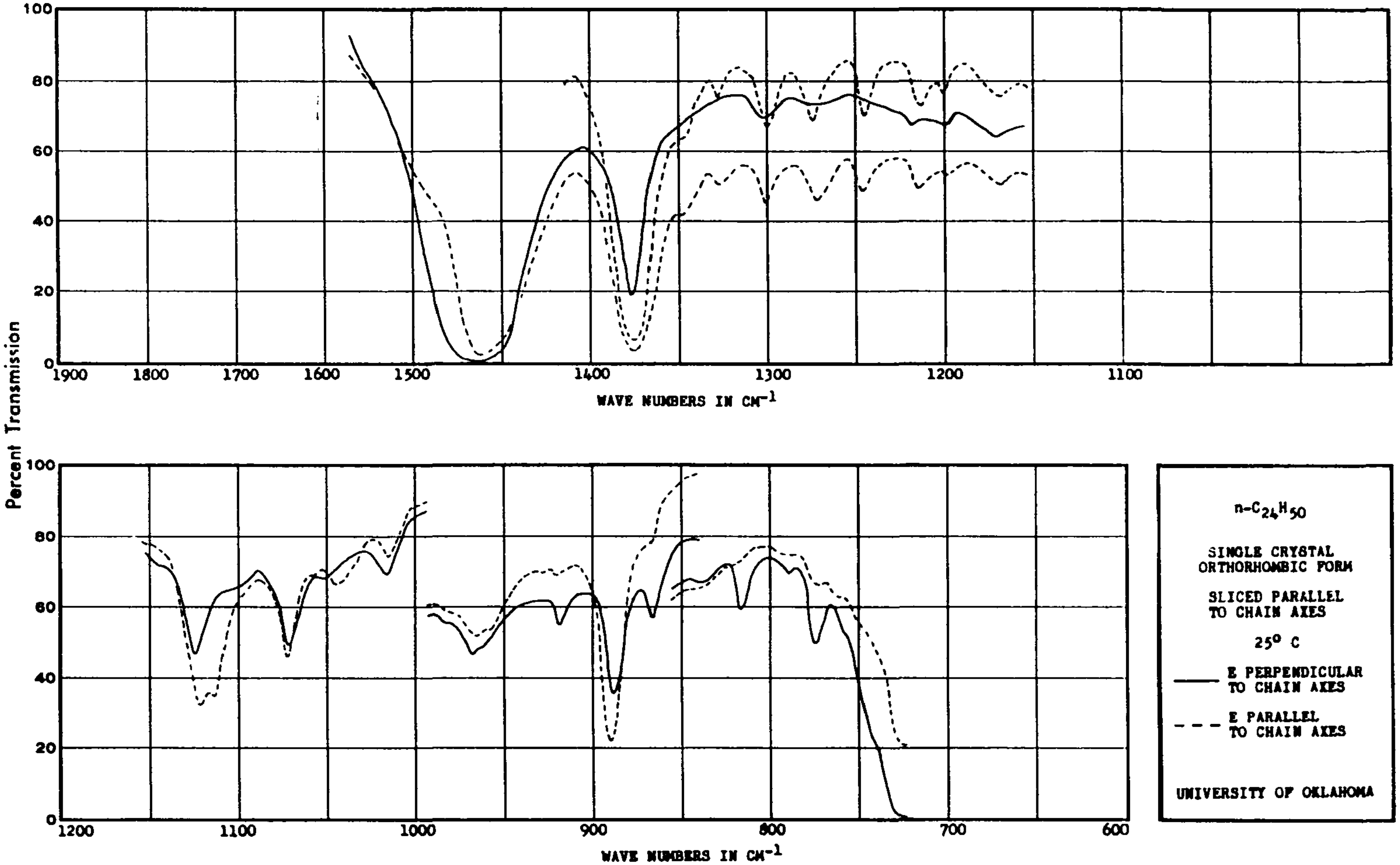

Fig. 3-4. Infrared Spectrum of Orthorhombic n-$C_{24}H_{50}$; Radiation Incident Parallel to the ab-Plane

TABLE 3-II

INFRARED SPECTRUM OF THE ORTHORHOMBIC FORM OF n-$C_{24}H_{50}$

Wave Number	Intensity[(a)]	Polarization[(b)]	Interpretation
720	vs	b	R (CH_2 Rocking)
730	vs	a ⊥	
744	w	b	R
747	w	a ⊥	
773	w	b	R
775	w	a ⊥	
816	w	b,a ⊥	R
866	w	b,a ⊥	R
887	m	b,a ∥,⊥	CH_3 Rocking Parallel to the Skeletal Plane
919	w	b,a ⊥	R
969	w	b,a ⊥	R
1013	w	b,a ⊥	R
1038	vw	∥	S (C-C Stretching)
1044	vw	∥	S
1051	vw	⊥	S
1071	w	b,a ∥,⊥	S
1112	w	∥	S
1121	w	b,a ∥,⊥	S
1168-1172	vw	b,a ∥,⊥	
1200	vw	b,a ∥	
1215	w	∥	W (CH_2 Wagging)

TABLE 3-II (Concluded)

Wave Number	Intensity[a]	Polarization[b]	Interpretation
1244	w	//	W
1274	w	//	W
1301	w	b,a //	W
1328	w	//	W
1348	w	//	W
1376	m	b,a //,⊥	CH_3 Symmetric Deformation
1395	w	//	W
1454	m	a ⊥	CH_3 Asymmetric Deformation
1462	vs	b	CH_2 Deformation
1473	vs	a ⊥,//	

(a) The abbreviations vs, s, w, etc. have the same meaning as in Table 3-I

(b) Bands marked b, a, //, ⊥ appear in the spectrum obtained with the radiation polarized:

b - parallel to the b-axis.

a - parallel to the a-axis.

// - parallel to the chain axes.

⊥ - perpendicular to the chain axes.

those features of the spectra which appear to support or contradict previous interpretations, or which appear to be characteristic of the crystal structure. Snyder[44] has published a good infrared spectrum of a polycrystalline sample of triclinic n-$C_{24}H_{50}$, together with a partial interpretation. Frequent reference to his work will be made.

The perpendicular polarization of the CH_2 rocking vibrations allows all members of the series to be identified, confirming Snyder's assignments and adding a final infrared-active rocking band at 1013 cm^{-1}. Except for the strong doublet at 720 and 730 cm^{-1}, the separation of the a_u and b_u components of the rocking doublets in Fig. 3-3 is very slight. In spectra obtained at lower temperatures, the splitting of the weaker bands is observable. The variation of the splitting over the series is similar to that observed by Snyder for orthorhombic crystals of the odd-numbered n-paraffins, that is, the splitting decreases with increasing frequency to zero for the band at 816 cm^{-1}, and becomes observable again in the higher frequency bands. In all doublets below 816 cm^{-1}, the low-frequency components are polarized in the b-direction, consistent with the conclusions reached in Appendix III, and the order of a- and b-polarized components appears to be reversed for the doublets at higher frequencies. The splitting of the higher frequency members of the series does not appear to be so great as that recorded by Snyder for the orthorhombic odd-numbered n-paraffins. The reason for this difference is not known.

The band at 887 cm^{-1}, like that near this frequency in n-$C_{36}H_{74}$, has a strong component parallel to the chain axes, which again shows that if it is to be assigned to methyl rocking, the rocking must be in-plane, since out-of-plane rocking should be perpendicular to the chain axes.

Six bands, at 1215, 1244, 1274, 1301, 1328, and 1348 cm^{-1} are shown in Fig. 3-4 to be polarized parallel to the chain axes. This supports Snyder's assignment of bands near these frequencies in triclinic n-$C_{24}H_{50}$ as CH_2 wagging vibrations. However, no parallel band corresponding to that at 1183 cm^{-1}, which he associated with the low-frequency limit of this series, is observed. Though it is not obvious in Fig. 3-4, a weak shoulder polarized parallel to the chain axes has been observed at 1395 cm^{-1}. This is also assigned as CH_2 wagging.

The doublet splitting and polarization of the two strong bands at 1462 and 1473 cm^{-1} is similar to that observed for bands near these frequencies in the monoclinic form and is consistent with the interpretation of these bands as caused by methylene deformation.

A medium intensity band at 1376 cm^{-1} is shown in Fig. 3-4 to have a stronger component parallel to the chain axes than perpendicular to it. This is consistent with its interpretation as symmetric deformation of the methyl groups. The change in dipole moment associated with this vibration should be approximately parallel to the C-CH_3 bond, which makes an angle of about 35° with the chain axis. The frequency of this band is 8 cm^{-1} higher than that reported by Snyder for the corresponding band in triclinic n-$C_{24}H_{50}$, and is almost precisely the same as that of a similar band of orthorhombic n-$C_{25}H_{52}$. The band at 1376 cm^{-1} shows no doublet splitting, though it appears in both curves of Fig. 3-3. Krimm, Liang, and Sutherland reported similar behavior for a band at 1375 cm^{-1} in orthorhombic n-$C_{29}H_{60}$. It seems that a single band near

1375 cm^{-1} is characteristic of the orthorhombic crystal forms, both for odd- and even-numbered chains, even though the relative orientation of the end-groups in adjacent layers is different in the two cases.

The Triclinic Form of n-$C_{18}H_{38}$

In the extended conformation, a molecule of a n-paraffin with an even number of carbon atoms has the symmetry C_{2h}. Vibrations of the infrared active species b_u and a_u are symmetric and antisymmetric, respectively, under reflection in the skeletal plane.

The unit cell of the triclinic n-paraffins contains only one molecule, and the chain packing is believed to be similar to that observed by Vand and Bell for trilaurin.[16] If this is true, the chains are extended, and the axes and skeletal planes of all molecules in the crystal are parallel.

Provided the intermolecular interaction is not too great, the symmetry of the unit cell group modes should be about that predicted for a single molecule in the extended conformation. It should therefore be possible to distinguish between vibrations of species b_u and a_u by their polarization parallel and perpendicular to the skeletal plane.

Crystals of n-$C_{18}H_{38}$ expected to have the triclinic form were plates with irregular edges. Parallel lines on the surfaces indicated cleavage planes nearly normal to the surfaces. A portion of a thick crystal was obtained by cleaving it at two adjacent lines. It had the form of a rod whose cross-section was a nearly rectangular parallelogram. Examination between crossed polarizers showed no evidence of twinning.

The crystal was mounted in the infrared microscope with polarized radiation incident normal to the original platelet surface. A quick scan of the spectrum showed a single strong band at 718 cm^{-1} rather than a doublet, indicating that the crystal has the monomolecular unit cell of the triclinic crystal form. The crystal was then rotated about a normal to the surface while the absorption of the band at 718 cm^{-1} was observed. At one position, the band was nearly absent. The spectrum in the range from 700 to 1500 cm^{-1} was recorded at this position. The crystal was then rotated 90^o about the normal and the spectrum recorded again. The percent transmission curves are shown in Fig. 3-5.

It may be seen that nearly every band in the spectrum shows a marked dependence on the orientation. Most of them are very weak in one of the two curves. The significance of this dependence may be revealed by comparing the strong bands at 718 and 1472 cm^{-1}. If these bands are attributed to CH_2 rocking and deformation, as bands at these frequencies generally are, both should be polarized perpendicular to the chain axes, with the CH_2 deformation parallel and the CH_2 rocking perpendicular to the skeletal plane. The two curves in Fig. 3-5 appear to distinguish between vibrations that are perpendicular and parallel to the skeletal planes.

The crystal was then oriented so that the radiation was incident normal to a surface of cleavage. Again, the absorption at 718 cm^{-1} was observed while the crystal was rotated about the normal. One of the curves shown in Fig. 3-6 was obtained in the position for which the intensity of the 718 cm^{-1} band was a maximum and the other where it was a minimum. The bands at 718 and 1472 cm^{-1} have maxima for the same

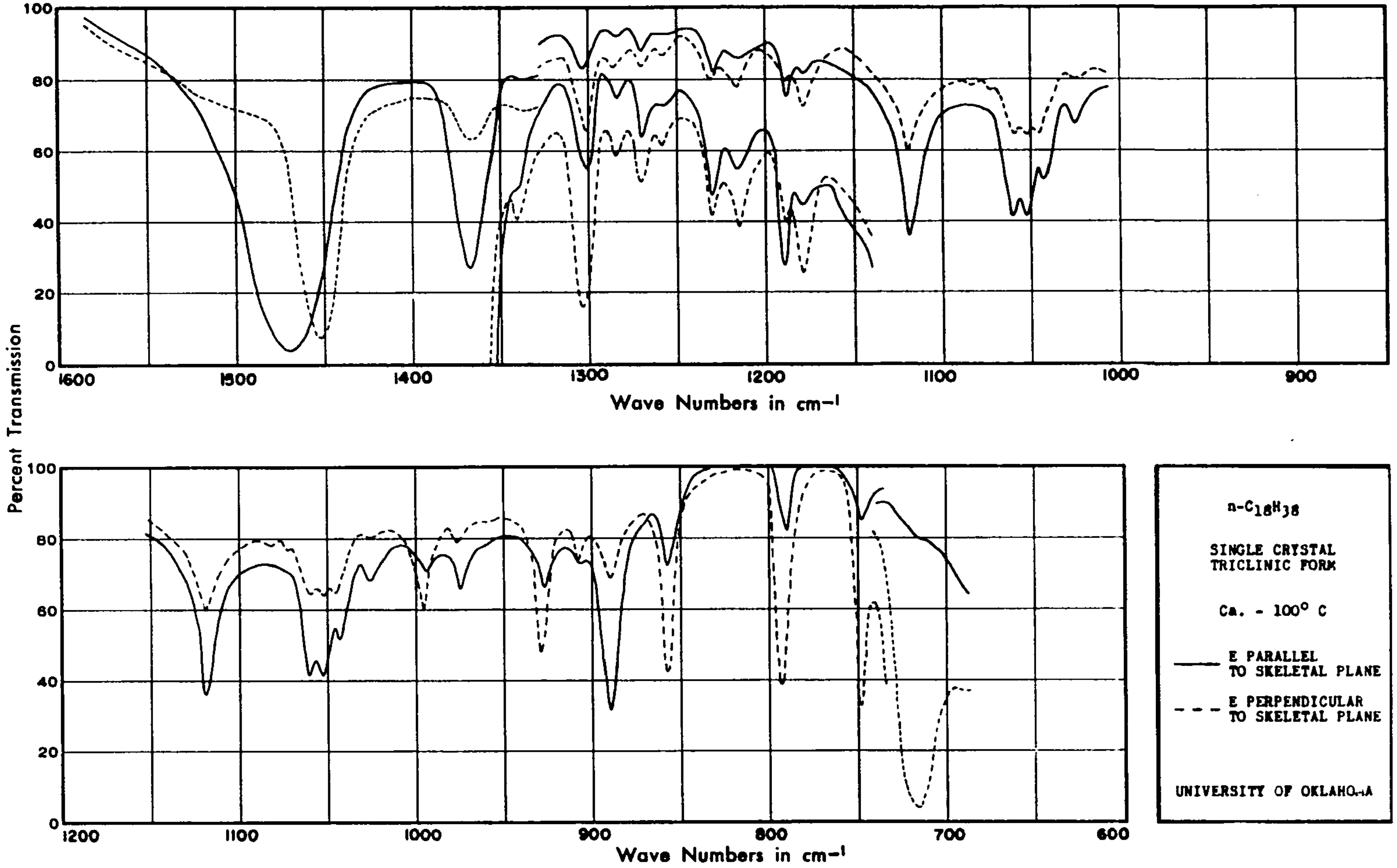

Fig. 3-5. Infrared Spectrum of Triclinic n-$C_{18}H_{38}$; Radiation Incident Approximately Parallel to the Chain Axes

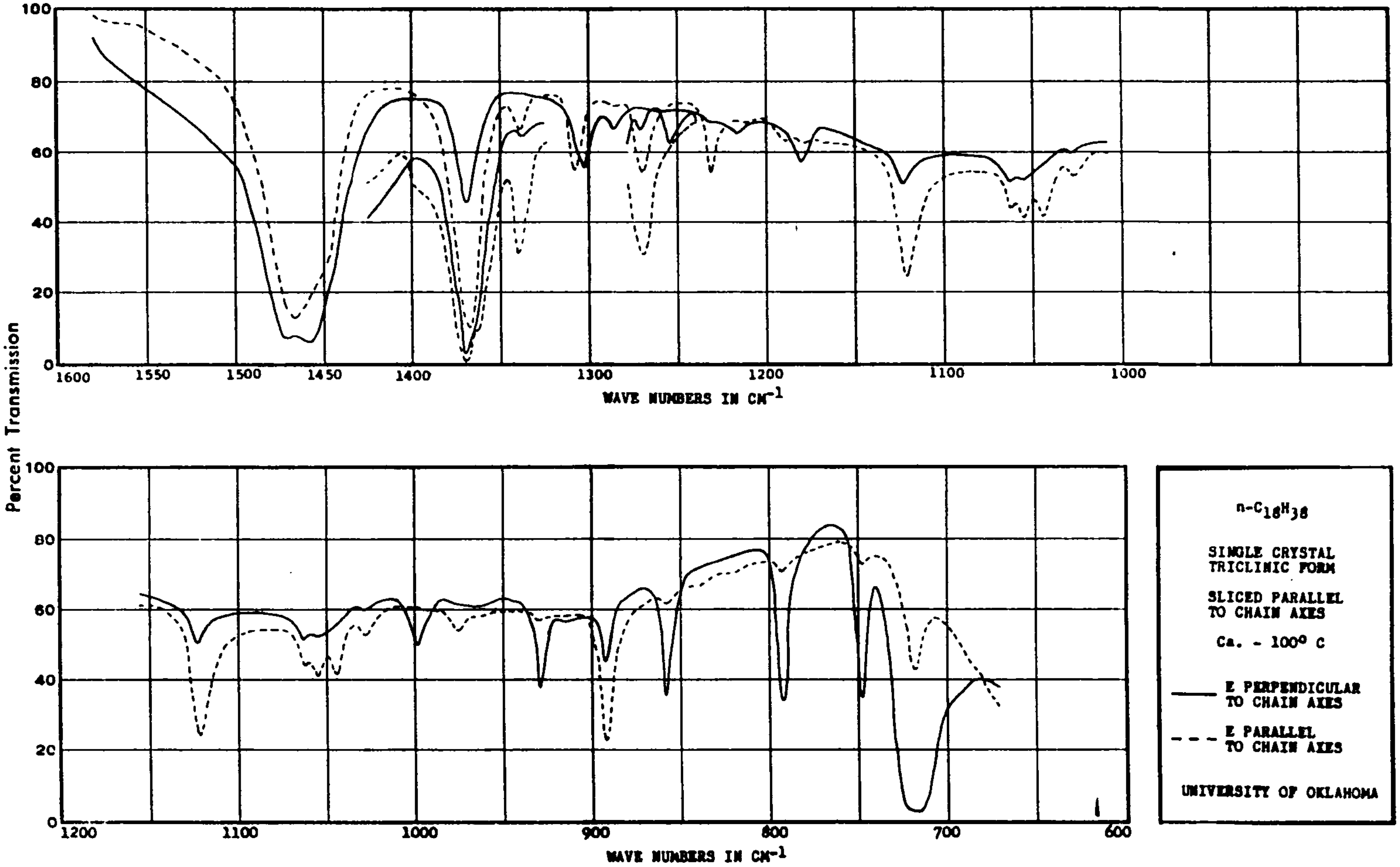

Fig. 3-6. Infrared Spectrum of Triclinic n-$C_{18}H_{38}$; Radiation Incident Approximately Perpendicular to the Chain Axes

TABLE 3-III

INFRARED SPECTRUM OF THE TRICLINIC FORM OF n-$C_{18}H_{38}$

Wave Number	Intensity(b)	Polarization(a)	Interpretation
718	vs	OP	R (CH_2 Rocking)
726	w	OP	R
746	w	OP	R
790	w	OP	R
860	w	OP	R
890	m	IP	CH_3 Rocking Parallel to the Skeletal Plane
926	w	OP	R
961	vvw	OP	
976	vw	IP	S (C-C Stretching)
991	vw	OP	R
1027	vw	IP	S
1044	w	IP	S
1054	w	IP	S
1061	w	IP	S
1120	w	IP	S
1179	vw	OP	T (CH_2 Twisting)
1188	vw	IP	W (CH_2 Wagging)
1217	vw	OP	T
1230	vw	IP	W
1255	vvw	OP	T
1268	vw	//	W

TABLE 3-III (Concluded)

Wave Number	Intensity(b)	Polarization(a)	Interpretation
1287	vw	OP	T
1301	vw	OP	T
1307	vw	//	W
1339	vw	//	W
1361	w	//	W
1368	m	IP	CH_3 Symmetric Deformation
1395	vw	//	W
1453	vs	OP	CH_3 Asymmetric Deformation
1466	s	//	CH_3 Asymmetric Deformation
1472	vs	IP	CH_2 Deformation

(a) OP polarized perpendicular to the skeletal plane.

IP polarized parallel to the skeletal plane.

// polarized parallel to the chain axes.

(b) The abbreviations vs, s, w, etc. have the same meaning as in Table 3-I.

orientation and have minima when the crystal is rotated 90°. It was concluded that the curves in Fig. 3-6 permit the distinction between bands polarized perpendicular or parallel to the chain axes.

The absorption frequencies, the polarization of the bands, and their assignments are listed in Table 3-III. In the following pages, the assignments will be discussed and compared with those made in preceding sections.

The series of bands beginning at 718 and terminating at 991 cm^{-1}, all of which have essentially the same polarization, is attributed to CH_2 rocking. A comparison with the assignments of Brown et al.[13] shows that they have correctly identified the rocking frequencies of nonadecane and the n-paraffins with 14 carbons or less. Though Snyder has not attempted to assign the highest-frequency infrared bands in the rocking series, the band at 991 cm^{-1} is a member of a sequence in his spectra which includes the perpendicular band of n-$C_{24}H_{50}$ at 1013 cm^{-1} and a doublet of n-$C_{30}H_{62}$ near 1028 cm^{-1}, and which may be extrapolated to the doublet near 1033 cm^{-1} believed to be the upper limit of the infrared active rocking series of n-$C_{36}H_{74}$.

Eight infrared-active skeletal stretching vibrations are expected for n-$C_{18}H_{38}$. Six bands between 976 and 1120 cm^{-1} which show the expected polarization have been assigned as skeletal vibrations. Two of the stronger bands, at 1061 and 1120 cm^{-1}, are members of sequences which by comparison with Snyder's spectra can be shown to include the bands of n-$C_{36}H_{74}$ at 1100 and 1130 cm^{-1}. Sheppard[33] has assigned both sequences to infrared-active vibrations of limiting phase. This seems reasonable, in view of the nearly constant frequencies in the sequences.

A series beginning at 1188 cm^{-1} and extending toward higher frequencies has been assigned as CH_2 wagging vibrations. The lower-frequency members of the series were recognized by their polarizations parallel to the skeletal planes, as shown in Fig. 3-5. The higher-frequency members were identified by their pronounced polarization parallel to the chain axes (see Fig. 3-6). If it is assumed that one member of the series is masked by the intense band at 1368 cm^{-1}, all the remaining infrared-active bands have been identified, the parallel band at 1395 cm^{-1} representing the highest-frequency infrared-active wagging vibration.

A series of very weak bands, the lower members of which are shown in Fig. 3-5 to be polarized perpendicular to the skeletal planes and all of which appear to be polarized perpendicular to the chain axes in Fig. 3-6, have been attributed to CH_2 twisting. The series overlaps that of the wagging modes, but the two are fairly easily differentiated by their polarization. Only five bands were observed, whereas there should be eight. The lowest-frequency band is at 1179 cm^{-1}, and the highest frequency band lies at 1301 cm^{-1}.

Jones, McKay, and Sinclair[53] have published a spectrum of octadecane in the region between 1170 and 1370 cm^{-1}. They assigned bands in this region as "wagging and/or twisting." Brown *et al*. made more specific assignments for the eight bands between 1170 and 1307 cm^{-1} which agree with results presented here. The perpendicular band at 1301 cm^{-1} and the parallel band at 1307 cm^{-1} were not resolved in the spectrum of Jones *et al*., and the higher frequency bands in the wagging series were not observed. The results obtained for n-$C_{18}H_{38}$ correlate well with Snyder's[44] assignments for the wagging modes of n-$C_{20}H_{42}$.

The band at 890 cm^{-1} is polarized parallel to the skeletal planes, which is consistent with its interpretation as planar methyl rocking. No band was observed which could be identified with the rocking of methyl groups perpendicular to the skeletal plane.

The fact that no band was observed at 1472 cm^{-1} when the band at 718 cm^{-1} had an intensity maximum was taken as an indication that the spectra recorded with the two orientations of the n-$C_{18}H_{38}$ crystal distinguish between vibrations parallel or perpendicular to the skeletal planes. The relative intensities at these two frequencies for the other direction of the beam was interpreted to mean that the radiation was incident perpendicular to the chain axes.

Actually, for no orientation was the absorption in the region 1450 to 1475 cm^{-1} completely eliminated. Three absorption peaks appear at 1453, 1466, and 1472 cm^{-1}. These three, together with the band at 1368 cm^{-1}, can be interpreted as methylene and methyl deformation vibrations.

Of all methylene and methyl-deformations active in the infrared, only the asymmetric methyl deformations perpendicular to the skeletal planes can be separated by their symmetry from the others. The band at 1453 cm^{-1}, which is polarized like the rocking vibrations has been attributed to such asymmetric methyl deformation. This type of vibration probably also accounts for the shoulders at 1447 and 1457 cm^{-1} on the CH_2 deformation bands of monoclinic n-$C_{36}H_{74}$.

In the spectrum shown in Fig. 3-6, there is still considerable absorption at 1466 cm^{-1} when the radiation is polarized parallel to the chain axes. This may be attributed to asymmetric methyl deformation parallel to the skeletal planes. The perpendicular band at 1472 cm^{-1} then accounts for the methylene deformation and both bands probably contribute to the strong, broad band at about 1470 cm^{-1} in Fig. 3-5.

The polarization of the band at 1368 cm^{-1}, which indicates that it is caused by a vibration parallel to the skeletal planes and is associated with a change in dipole moment more nearly parallel than perpendicular to the chain axes, is consistent with its assignment as symmetric methyl deformation.

CHAPTER IV

THE INFRARED SPECTRA OF FOUR POLYMORPHS OF STEARIC ACID

The C-Form of Stearic Acid

The C-form of the normal fatty acids is monoclinic, with two dimers per unit cell.[14] The chains have the orthorhombic packing. The unit cell group is isomorphic to the point group C_{2h}.

Normal modes are classified as Raman- or infrared-active according to their symmetry or antisymmetry with respect to an inversion. An inversion center is a symmetry center for a dimer. The infrared-active modes are therefore those in which the two molecules in a dimer execute the same vibration out-of-phase.

The infrared-active vibrations belong to species a_u or b_u depending on their symmetry or antisymmetry with respect to a twofold screw rotation about an axis parallel to the b-axis. This operation interchanges the two dimers, but leaves the same molecules side-by-side. In vibrations of one species, adjacent molecules move in-phase, and in vibrations of the other, they move out-of-phase. For each molecular degree of freedom, one would therefore expect to observe an a_u-b_u infrared doublet. The change in dipole moment associated with a vibration of species a_u is in the direction of the b-axis, and that associated with a vibration of species b_u is perpendicular to the b-axis.

The lozenge-shaped crystals having the form C may be identified by their interedge angles of 56°. The ab-planes of the unit cell are parallel to the face of the lozenge. The a- and b-axes are parallel to the bisectors of the acute and obtuse interedge angles, respectively. The chains are tilted away from the normal to the crystal face toward the a-axis. The angle of tilt in the C-form of lauric acid is only about 35°. The axes of the chains in stearic acid should be nearer the c-axis, which is tilted 38°.[67]

Crystals of stearic acid having the C-form were mounted so that the axis of the spectrometer beam was normal to the ab-plane. The spectrum was recorded with the radiation polarized parallel to the a- and b-axes, respectively. Fig. 4-1 shows this spectrum for the range 650 to 1750 cm^{-1}. Bands resulting from a_u vibrations, polarized parallel to the b-axis, appear in the dotted curve. Those of species b_u, polarized perpendicular to the b-axis, appear in the solid curve. A spectrum of the C-form of palmitic acid, obtained in a similar manner, is shown in Appendix I.

To study the polarization of the b_u bands, which may have components both parallel and normal to the ab-plane, crystals of the C-form were sliced perpendicular to the b-axis. These slices were examined between crossed polarizers with white light incident in the b-direction. The transmitted radiation was extinguished when the electric vector of the incident radiation made angles of about 45° with the a-axis. This indicates that the alternation of the chain tilt observed in monoclinic

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[67] S. Abrahamsson and E. von Sydow, Acta Cryst. 7, 591 (1954).

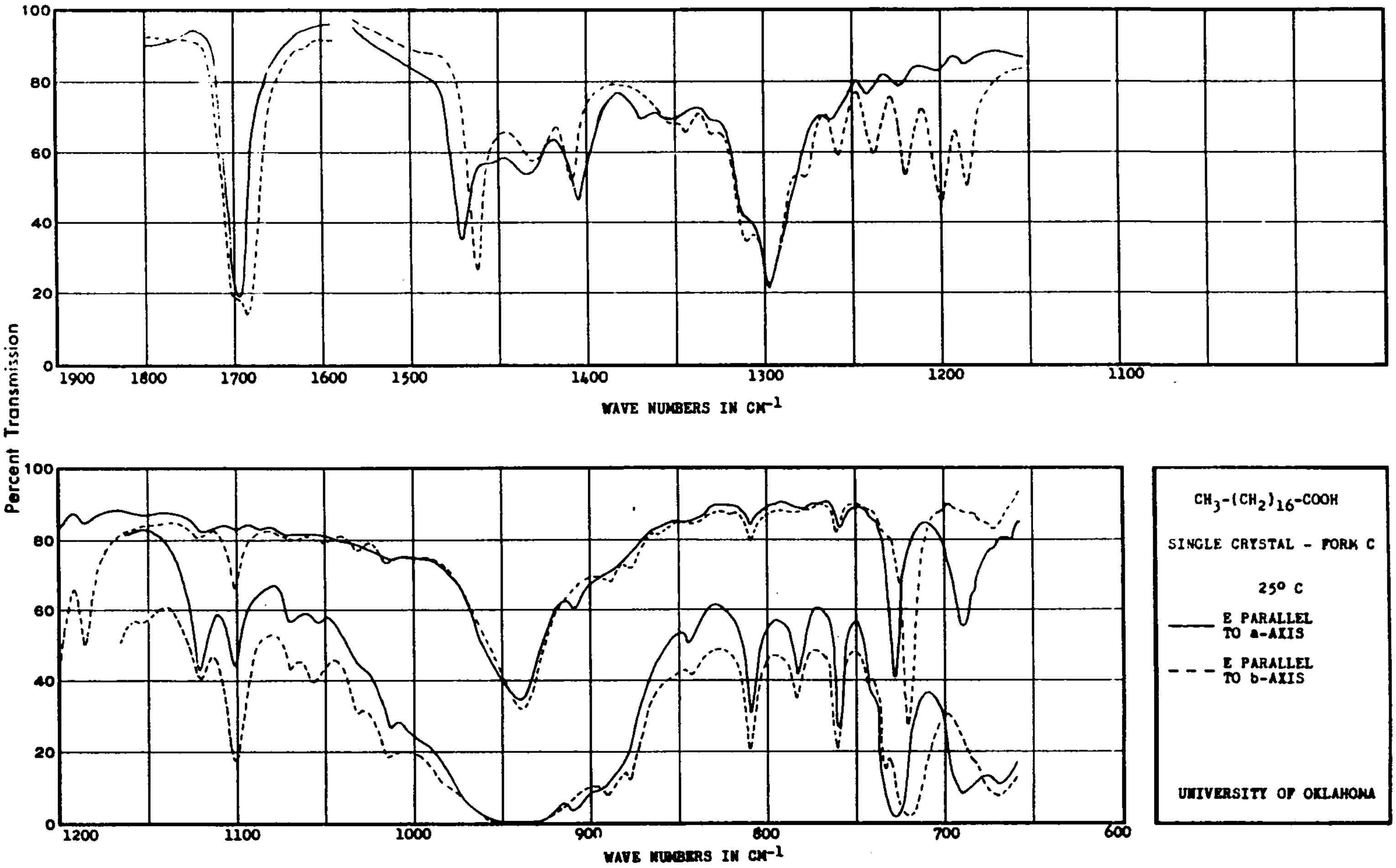

Fig. 4-1. Infrared Spectrum of the C-Form of $CH_3(CH_2)_{16}COOH$; Radiation Incident Normal to the ab-Plane

n-paraffins apparently does not occur in the C-form of the fatty acids.

Spectra obtained with the polarized beam incident parallel to the b-axis support this conclusion. The crystal slices were rotated about the b-axis and their spectra recorded at intervals of 15°. Most of the bands had well-defined minima (with zero or very weak absorption) and maxima separated by 90°. The orientation of the crystal slices corresponding to maximum absorption was different for different bands. Spectra recorded when the electric vector made angles of ± 45° with the a-axis are shown in Fig. 4-2. As nearly as could be determined from the extinction of visible radiation, these directions are parallel to two of the principal axes. As the caption of Fig. 4-2 indicates, they are also approximately parallel and perpendicular to the chain axes, which make an angle of about 52° with the a-axis.

The spectrum of a crystal of deuterated stearic acid, $CH_3(CH_2)16$-COOD, obtained with the axis of the beam normal to the crystal surface, is presented in Fig. 4-3. This crystal had the lozenge shape with an interedge angle of 56°, and so was assumed to have the C-form. This assumption was supported by an examination of a spectrum obtained a year later, when about half the deuterium had been replaced by hydrogen.

A comparison of Figs. 4-1 and 4-3 with the spectra of the n-paraffins shows that many features of the spectra of the acids have almost identical counterparts in the spectra of the normal paraffins. Also, several bands appear which have been attributed by earlier workers[52,56] to motions of the carboxyl end groups. Frequencies and interpretations given by Hadži and Sheppard for some of the carboxyl vibrations of crystalline samples of ordinary and deuterated stearic acid are shown in

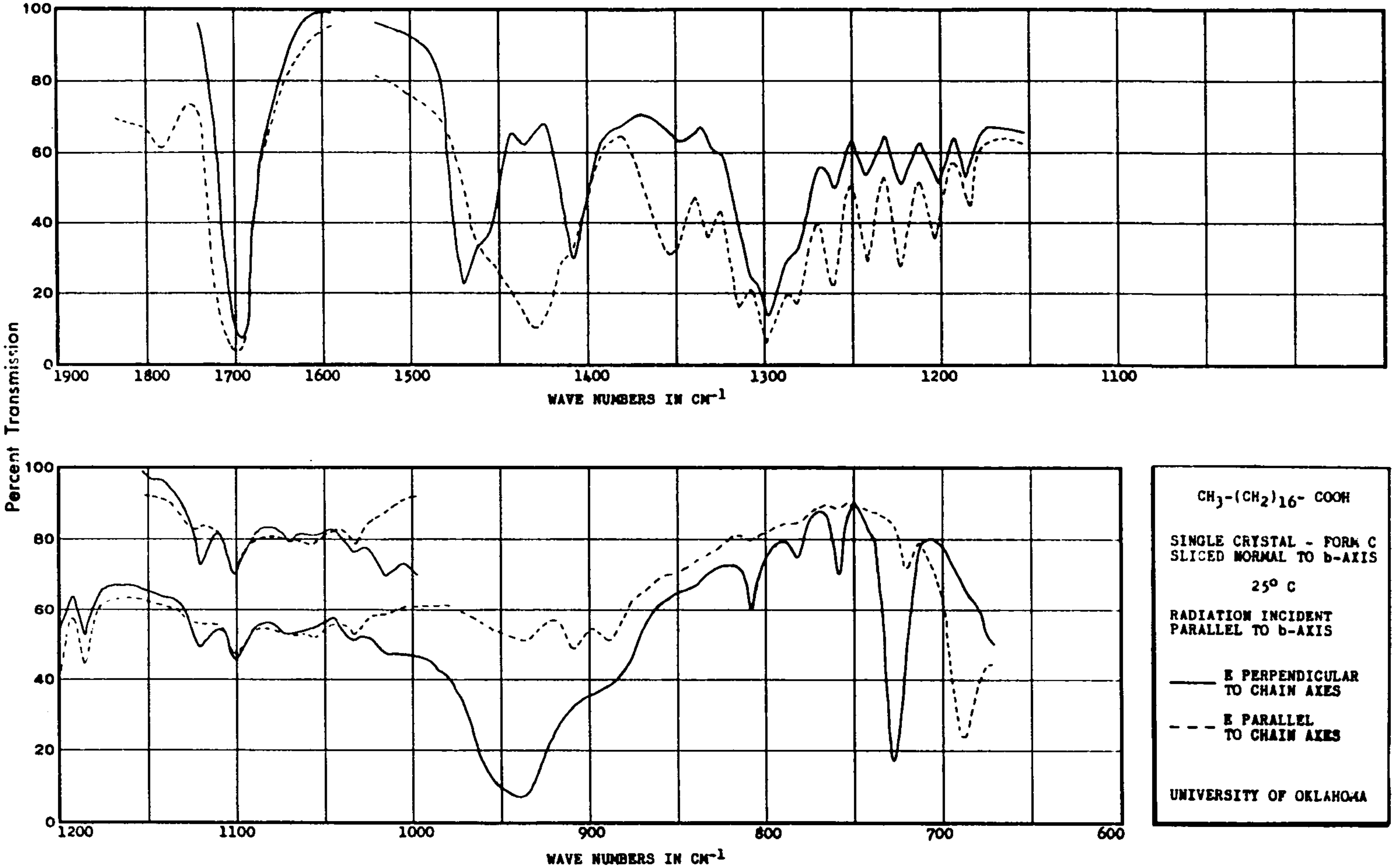

Fig. 4-2. Infrared Spectrum of the C-Form of $CH_3(CH_2)_{16}COOH$; Radiation Incident Normal to the ac-Plane

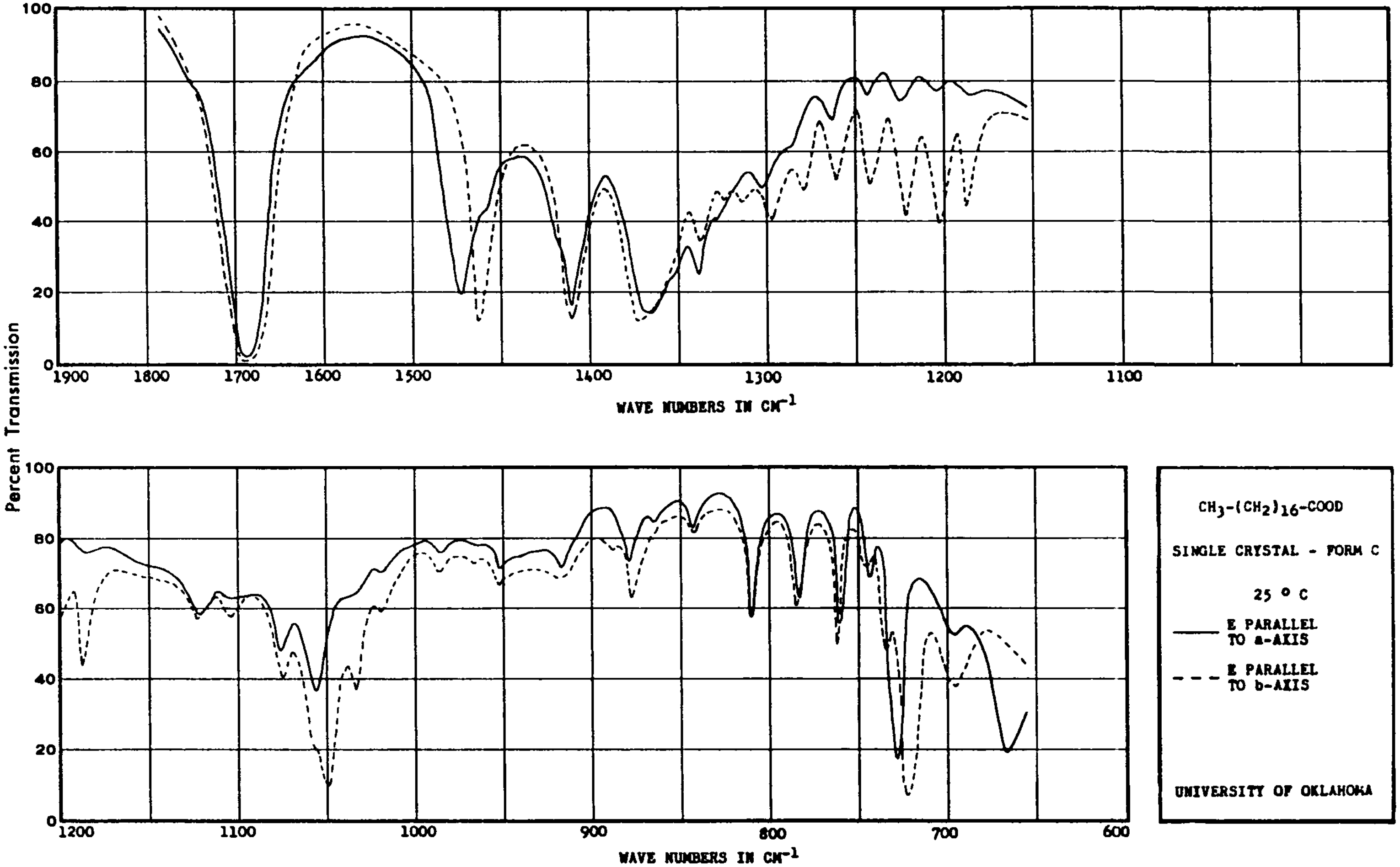

Fig. 4-3. Infrared Spectrum of the C-Form of $CH_3(CH_2)_{16}COOD$; Radiation Incident Normal to the ab-Plane

TABLE 4-I

FREQUENCIES OF CARBOXYL VIBRATIONS OF ORDINARY AND DEUTERATED STEARIC ACID

Ordinary Acid		Deuterated Acid	
Wave Number	Approximate Motion	Wave Number	Approximate Motion
675	O-C = O Angle Deformation	666	O-C = O Angle Deformation
940	O-H Bending Perpendicular to the Plane of the COOH Group		O-D Bending Perpendicular to the Plane of the COOD Group
1300 1435	Mixed C-O Stretching and O-H Bending Parallel to the Plane of the COOH Group	1058	O-D Bending Parallel to the Plane of the COOD Group
		1366	C-O Stretching
1700	C = O Stretching	1700	C =O Stretching

TABLE 4-II

INFRARED SPECTRA OF THE C-FORMS OF ORDINARY AND DEUTERATED STEARIC ACID

$CH_3(CH_2)_{16}COOH$					$CH_3(CH_2)_{16}COOD$			
Wave Number	Intensity & Polarization in Fig. 4-1		θ(a)	Intensity in Fig.4-2	Wave Number	Intensity & Polarization		Interpretation
689	s	a	45°	vs	667	m	a	O-C = O Angle Deformation
					696	m	b	O-D Bending
						w	a	
720	s	b			720	s	b	R (CH_2 Rocking)
727	s	a	120°	vs	725	s	a	
733	vw	b			735	w	b	R
741	vw	a	120°	vw	743	vw	a	R
744	vw	b			745	vw	b	
759	w	a	120°	w	760	w	a	R
760	w	b			761	w	b	
782	vw	a	120°	vw	783	w	a	R
783	vw	b			784	w	b	
809	w	a,b	120°	w	809	w	a,b	R
842	vw	b			842	vw	b	R
	vw	a			843	vw	a	
877	w	b			876	vw	b	R
	vw	a			878	vw	a	
889	w	b	0°	w	887	vvw	b	CH_3 Rocking Parallel to the Skeletal Plane
908	w	a	90°	w				
					915	vvw	b,a	R

TABLE 4-II (Continued)

$CH_3(CH_2)_{16}COOH$					$CH_3(CH_2)_{16}COOD$			
Wave Number	Intensity & Polarization in Fig. 4-1		$\theta^{(a)}$	Intensity in Fig.4-2	Wave Number	Intensity & Polarization		Interpretation
938	s	b						O-H Bending
940	s	a	135°	vs				
					951	vvw	b,a	R
985	vvw	b,a			985	vvw	b,a	R
1015	vw	b			1016	vw	b	R
	vvw	a	120°	vw		vvw	a	
1031	vw	b			1032	w	b	S (C-C Stretching)
	vvw	a				vvw	a	
					1049	s	b	O-D Bending
					1056	m	a	
1055	vw	b			1056	w	b	S
	vvw	a						
1070	vw	b			1074	w	b	S
	vvw	a				vw	a	
1101	m	b			1101	w	b	S
	vvw	a				vw	a	
1121	vw	b			1122	w	b	S
	vw	a			1123	w	a	
1186	m	b			1185	w	b	W (Mixed CH_2 Wagging and COH or COD Vibration)
	w	a	15°	m	1186	vvw	a	

TABLE 4-II (Continued)

$CH_3(CH_2)_{16}COOH$					$CH_3(CH_2)_{16}COOD$			
Wave Number	Intensity & Polarization in Fig. 4-1		$\theta^{(a)}$	Intensity in Fig.4-2	Wave Number	Intensity & Polarization		Interpretation
1201	m	b			1203	w	b	W
1205	vw	a	15°	m	1204	vvw	a	
1219	m	b			1222	w	b	W
1223	w	a	15°	m	1223	vvw	a	
1240	m	b			1240	w	b	W
1242	w	a	15°	m	1243	vw	a	
1258	m	b			1259	w	b	W
1263	w	a	15°	m	1263	vw	a	
1277	w	b			1278	vw	b	W
1281	w	a	15°	m	1281	vw	a	
1298	s	b	75°	s				Primarily O-H Bending
	s	a						
1300			15°	m	1296	vw	b	W
					1300	vw	a	
1310	w	b			1313	vvw	b	W
1312	w	a						
					1318	vvw	a	—
					1323	vvw	b	
1329	w	b			1326	vvw	a	W
1331	w	a	15°	m				
					1336	w	b	COH-COD?
					1337	w	a	

TABLE 4-II (Concluded)

$CH_3(CH_2)_{16}COOH$					$CH_3(CH_2)_{16}COOD$			
Wave Number	Intensity & Polarization in Fig. 4-1		$\theta^{(a)}$	Intensity in Fig.4-2	Wave Number	Intensity & Polarization		Interpretation
1346	w	b			1350	vvw	a,b	W
1350	w	a	15°	m				
1356	w	b,a	15°	m				W
					1365	m	a	C-O Stretching
					1371	m	b	
1371	w	a	90°	w				CH_3 Symmetric Deformation
1379	vvw	b						
1406	m	a	120°	s	1409	m	a,b	CH_2 Deformation
1410	m	b						
					1421	w	a	COH-COD?
1429	w	b						Primarily C-O Stretching
1438	w	a	30°	s				
1462	s	b			1462	s	b	CH_2 Deformation
1472	s	a	120°	s	1472	s	a	
1684	s	b			1682	vs	b	C=O Stretching
1695	s	a			1691	s	a	

(a) θ = The angle indicating the polarization of the radiation for maximum absorption, measured from the normal to the ab-plane in the direction of smallest rotation to the c-axis.

Table 4-I.[56]

The absorption frequencies of single crystals of the C-form of the ordinary and deuterated stearic acid are listed in Table 4-II. The polarization and relative intensities of bands shown in Figs. 4-1 and 4-3, obtained with the radiation incident normal to the ab-plane are indicated in the Table. Also given are relative values of the maximum intensities of the b_u bands of ordinary stearic acid as observed with the crystal slices, together with the angles indicating the direction of the electric vector for which the intensity was a maximum. The angles are measured from the normal to the ab-plane in the direction of smallest rotation to the c-axis. All are multiples of 15°, since only at this interval were spectra recorded. It was assumed that these angles give the approximate directions of the changes in dipole moment associated with the b_u vibrations.

Assignments, based in part upon the polarization of the bands and in part upon the previous interpretations, are included in Table 4-II. A discussion of the spectra and assignments follows.

Methylene Rocking Vibrations

The series of a_u-b_u doublets assigned as CH_2 rocking fundamentals begins with the strong doublet near 720 cm^{-1} and extends to 1016 cm^{-1} in the spectrum of the deuterated stearic acid. An identical series is observed for the ordinary acid, except in the region near 940 cm^{-1}, where it is masked by carboxyl vibrations.

The number of doublets in this series is approximately twice the number of methylene rocking bands in the spectrum of octadecane, which has the same number of methylene groups as stearic acid. Presumably bands appear which would be Raman-active but not infrared-active in the n-paraffin. The doublets alternate in intensity. If it is assumed that the stronger bands correspond to the infrared-active vibrations of the n-paraffin, the frequencies are nearer those expected for a n-paraffin with fifteen, rather than sixteen, CH_2 groups. This may indicate that the methylene group nearest the carboxyl group does not participate in these vibrations. If this is so, the band at 1016 cm^{-1} would be the upper limit of the series.

Since the b-axis of the unit cell is parallel to the b_o-axis of the orthorhombic subcell, the polarization of the two strong methylene rocking bands near 720 cm^{-1} is consistent with that observed for the corresponding bands of the monoclinic and orthorhombic n-paraffins. The splitting and polarization of the higher members of the series differs from those observed for the n-paraffins. In both Figs. 4-1 and 4-3, the low-frequency component of the doublet near 740 cm^{-1} is polarized in the a-direction, whereas the low-frequency member of the strong doublet at 720 cm^{-1} is polarized in the b-direction. The splitting decreases with increasing frequency until it becomes negligible for the band at 809 cm^{-1}. In the deuterated acid, the lower components of the next two doublets at 842 and 843 cm^{-1} and at 876 and 878 cm^{-1} are polarized in the b-direction. The splitting of the remaining bands in the series is slight. In spectra obtained at temperatures of about -100° C, the splitting of these bands is more pronounced, and the polarization of the doublets reverses again at 951 cm^{-1}. In Appendix III are listed the frequencies and polarization of the rocking doublets of the C-form of deuterated stearic acid observed at low temperatures.

Their behavior is shown to be consistent with that for other crystal forms.

In the spectra shown in Figs. 4-1 and 4-3, the b-polarized a_u band near 720 cm^{-1} is more intense than the a-polarized b_u band near 727 cm^{-1}. A difference in intensity is also observed with polycrystalline samples. Abrahamsson and Fischmeister[18] have suggested that such an intensity difference may be produced by a distortion of the usual orthorhombic chain packing. Whatever its origin, the effect is not limited to the strong doublet, but continues throughout the CH_2 rocking series.

Skeletal Stretching Vibrations

Between the final rocking mode at 1016 cm^{-1} and the series beginning at 1186 cm^{-1}, five bands are observed which may be assigned to chain skeletal vibrations. These bands have components both parallel and perpendicular to the b-axis and may therefore be considered a_u-b_u doublets whose splitting is not great enough to be observed.

In the spectrum of the deuterated acid, a strong additional b-polarized (a_u) carboxyl band is observed at 1049 cm^{-1}. The intensities of the skeletal modes, particularly the a_u-components, are greater than in the ordinary acid, presumably because of interaction with the carboxyl group. It is not certain whether the band at 1056 cm^{-1} represents a skeletal or a carboxyl vibration. Its polarization and intensity favors its interpretation as a b_u carboxyl mode. The skeletal vibration observed near this frequency in the ordinary acid is probably responsible for the shoulder on the a_u band at 1050 cm^{-1}.

The 1186 - 1350 cm^{-1} Band Series

The series of medium intensity bands having its lower limit at 1186 cm^{-1} has been variously attributed to methylene wagging, methylene twisting, and to coupled wagging and twisting vibrations.[33,39,53]

Ferguson[68] has criticized the assignment of these bands as methylene wagging modes, since in the spectrum of a single crystal of eicosanoic acid published by Cole and Jones,[60] the series appears polarized in the same direction as the 720 cm^{-1} component of the strong rocking doublet. Sheppard[33] has suggested that, since alternate members of the CH_2 wagging modes of a normal paraffin with an odd number of carbon atoms should be polarized perpendicular to the chain axes, these bands in the fatty acids may correspond to the perpendicular members of the wagging series. As support for this suggestion he observed that the number of bands observed is about half the number of CH_2 groups in the chain. Jones[39] has tentatively assigned this group of bands to coupled CH_2 wagging and twisting vibrations, citing the theoretical work of Primas and Gunthard.[31]

In the spectra of the C-form of stearic acid, eleven bands may be identified with the series in question. Ten can be easily discerned in the spectrum of the ordinary acid. The eleventh, which is masked by the carboxyl band at 1298 cm^{-1} in Fig. 4-1, appears in the spectrum of deuterated acid and in that of the crystal slices.

Actually, each band is an a_u-b_u doublet. In the spectra shown

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[68] E. E. Ferguson, J. Chem. Phys. <u>24</u>, 1115 (1956).

in Figs. 4-1 and 4-3, obtained with the radiation incident normal to the ab-plane, the a-polarized b_u components are much less intense than the b-polarized a_u components. The spectrum shown in Fig. 4-2, obtained with radiation incident parallel to the b-axis, only includes the b_u modes. The record shows that they are polarized more nearly parallel than perpendicular to the chain axes. These bands are about as strong as the a_u bands. Apparently, they are weak in Fig. 4-1 because their changes in dipole moment make an angle of only about 15° with the normal to the ab-plane.

The number and regular spacing of the bands in the series make it almost certain that they are caused by vibrations whose frequencies are determined primarily by motion of the methylene chains. However, the intensities of these bands in the spectra of the acids are much greater than any near these frequencies in the spectra of the n-paraffins. If the carboxyl end groups can so greatly affect the intensities of these bands, they may also influence their polarization.

The highly polar carboxyl groups may be expected to have some effect on the electrical properties of adjacent methylene groups, and will be coupled mechanically with the vibrating chain. The extent of the mixing of chain and end group vibrations will depend on their frequencies and symmetries.

Two carboxyl bands lie near the series in the spectra of the C-form, at 1298 and near 1435 cm^{-1} in the ordinary stearic acid and near 1050 and 1365 cm^{-1} in the deuterated acid. These bands have been ascribed to C-O stretching and C-O-H or C-O-D angle deformation.[56]

In the three diagrams of Fig. 1-5, the carboxyl groups of the

C-form of lauric acid are projected on the ab-, the ac-, and the bc-planes. The projection of the C-OH bond upon the ac-plane makes an angle of about 10° with the normal to the ab-plane. According to Table 4-II, the b_u components of the band series have maximum intensity when the electric vector of the radiation makes an angle of 15° with the normal to the ab-plane. The projection of the C-OH bond upon the ab-plane makes an angle of only about 11° with the b-axis. In the spectrum obtained with the radiation incident normal to the ab-plane, the b-polarized (a_u) bands in the series are more intense than the a-polarized (b_u) bands.

It has already been mentioned that the absorbance of the a_u and b_u components of the band series are approximately equal. The a_u component is strictly b-polarized, and the b_u component is polarized very nearly normal to the ab-plane. It is shown in Fig. 1-5 that the projection of the C-OH bond upon the bc-plane has nearly equal components parallel and perpendicular to the b-axis. Thus, coupling with the stretching of the C-OH bond could account for the observed polarization of the bands in the series.

On the other hand, the chain vibrations could equally well be coupled with the O-H or O-D bending motion. Since the positions of the H- and D-atoms are not precisely known, it is not possible to predict the direction of the change in dipole moment associated with this vibration. It can be seen in the spectrum of Fig. 4-3 that the band near 1050 cm^{-1} attributed by Hadzi and Sheppard to O-D bending in the carboxyl plane is polarized in the same direction as the bands in the series. In either case, it seems very likely that if the high intensities of the bands in the series are produced by coupling with carboxyl motion, it is with a COH vibration in the carboxyl plane.

The question then arises as to which type of methylene vibrations would be more likely to mix with a COH vibration in the carboxyl plane. Though the carbon skeleton is essentially planar, the atoms of the carboxyl groups do not lie quite in the skeletal plane. However, the displacements of the atoms from the chain plane are not great. The C=O bond and the C-OH bond makes angles of about 5° with the plane of the three end carbon atoms in the C-form of lauric acid.[14] The wagging vibrations of the CH_2 groups, which are symmetric with respect to a reflection in the skeletal plane should couple more readily with a COH vibration in the carboxyl plane than should the twisting modes, which are antisymmetric. Also, the displacement of the skeletal carbon atoms will be greater for wagging than for twisting modes, so that the coupling through the last carbon-carbon bond should be greater.

The lowest frequency band at 1186 cm^{-1} is very near the limit of the wagging series of octadecane, and the series extends past the upper limit observed for the twisting modes of octadecane. All these factors support the assignment of the bands in the series as essentially wagging modes.

Since the spacing of the bands in the series is about half that in the octadecane wagging series, and since the number of doublets observed is greater than half the number of methylene groups, it may be concluded that all the wagging modes are active. The higher frequency bands are either too weak to be observed or are masked by stronger bands. The fact that the number of bands usually observed is approximately half the number of CH_2 groups must then be considered fortuitous.

The CH_2 twisting modes are apparently masked by the strong wagging series. However, some indication of a contribution to the absorption of the B-form of stearic acid by twisting vibrations has been observed (see the section on the B-form of stearic acid).

Methyl Group Vibrations

Three bands in the spectrum of the C-form of stearic acid may be ascribed to vibrations of the methyl end groups. The band near 890 cm^{-1} has about the same frequency as that assigned to methyl in-plane rocking in octadecane.

Two bands similar in frequency and relative intensity to bands of n-$C_{36}H_{74}$ attributed to methyl deformation are observed in ordinary stearic acid at 1371 and 1379 cm^{-1}. The polarizations of these two bands, however, are just the reverse of those of the bands at 1368 and 1379 cm^{-1} in n-$C_{36}H_{74}$. In the spectrum of the C-form of stearic acid, the stronger band at the lower frequency is polarized in the a-direction, while the higher-frequency weaker band is polarized in the b-direction when the radiation is incident normal to the ab-plane. This is presumably due to the fact that the chain tilt it toward the a-axis rather than toward the b-axis as in the monoclinic normal paraffins.

Methylene Deformation

In the spectra shown in Figs. 4-1 and 4-3, the strong doublets with components at 1462 and 1472 cm^{-1} may be assigned as methylene deformation fundamentals. It is shown in Table 4-II that the change in dipole moment of the b_u component is approximately perpendicular to the chain axes. This is what would be expected.

In the spectrum of the ordinary acid an a_u-b_u doublet appears at 1406 and 1410 cm^{-1}. A corresponding band at 1409 cm^{-1} is observed in the deuterated acid. Though its splitting is negligible, it must also be considered a doublet, since it has components in both a- and b-directions. Bands near these positions have previously been attributed to deformation of methylene groups adjacent to the carboxyl groups.[52,56] It is shown in Table 4-I that the polarization of the b_u band at 1406 cm^{-1} is the same as that of the 1472 cm^{-1} band. This supports the previous interpretation.

The lack of splitting of the 1409 cm^{-1} band is not fully understood. However, the separation of a_u and b_u components of this and the corresponding doublet in the ordinary acid should be less than that of the 1462 - 1472 cm^{-1} doublets, since the methylene group causing the absorption is adjacent only to two methylene groups of neighboring chains.

Carboxyl Group Bands

The band at about 689 cm^{-1} in the spectrum of the C-form of ordinary stearic acid (Fig. 4-1) has a strong component in the a-direction. Table 4-II shows that it is actually polarized in a direction which makes an angle of about 45° with the a-axis. Hadzi and Sheppard[56] have interpreted this band as resulting from deformation of the O-C$\overset{-}{=}$O bond angle. Since this vibration would be expected to have a change in electric moment roughly parallel to the chain axes, their interpretation is consistent with the observed polarization.

The strong broad band at 940 cm^{-1} must be interpreted as an a_u-b_u doublet, though no splitting is observed in Fig. 4-1. Hadzi, Sheppard and others[56] have attributed bands near this position to vibrations of the hydrogen atom out of the carboxyl plane. The polarization of the b_u component, shown in Fig. 4-2 to be approximately perpendicular to the chain axes, supports this assignment.

According to Hadzi and Sheppard, the strong bands near 1298 and 1435 cm^{-1} are caused by mixed C-OH stretching and C-O-H angle deformation. A well-defined doublet is observed at 1429 and 1438 cm^{-1}, but though the band at 1298 cm^{-1} must be interpreted as an a_u-b_u doublet, the splitting is negligible.

Table 4-II shows that the b_u bands at 1438 cm^{-1} and 1298 cm^{-1} are polarized in directions which make angles of about 30° and 75°, respectively, with the normal to the ab-plane. Since the band at 1438 cm^{-1} is polarized more nearly in the direction of the projection of the C-OH bond on the ac-plane, it may be caused primarily by C-OH stretching. However, the fact that its polarization deviates about 20° from the direction of the C-OH bond indicates that the vibration involves an appreciable deformation of the C-O-H angle.

The absorption near 1700 cm^{-1} has been ascribed to stretching of the C=O bond. In the spectrum shown in Fig. 4-1, obtained with the radiation incident normal to the ab-plane, two bands appear. That at 1684 cm^{-1}, polarized in the b-direction, is slightly more intense than the band at 1695 cm^{-1}. This is consistent with the fact that the projection of the C=O bond on the b-axis is greater than its projection on the a-axis (see Fig. 1-5).

A band at 1695 cm^{-1} appears in the record obtained with radiation polarized in the a-direction, but at the same frequency a shoulder appears on the b-polarized band at 1684 cm^{-1}. In the spectra of the crystal slices, the intensity of the 1695 cm^{-1} band varies little with rotation of the plane of polarization. This fact is not understood.

Hadzi and Sheppard[56] have observed that strong bands near 900 cm^{-1} in the spectra of ordinary carboxylic acids are less intense, or not observed at all, in the spectra of acids in which the carboxyl hydrogen is replaced by deuterium. This supported their identification of these bands with motions of the carboxyl hydrogens. The corresponding vibrations in the deuterated acid were associated with bands near 700 cm^{-1}. In the spectra of the normal fatty acids these bands were thought to be superposed on the band resulting from deformation of the O-C=O angle.

In the spectrum of deuterated stearic acid shown in Fig. 4-3 the absorption near 700 cm^{-1} is resolved into a band at 667 cm^{-1} polarized in the a-direction, and an a_u-b_u doublet at 696 cm^{-1}. The band ascribed to O-C=O deformation in the ordinary acid is polarized in the a-direction; hence, it is reasonable to assume that the band at 667 cm^{-1} is caused by a similar vibration. Its frequency is slightly lower than in the ordinary acid because of the increased mass of the hydroxyl group. The doublet at 696 cm^{-1} can then be attributed to O-D out-of-plane bending.

A strong band near 1050 cm^{-1} in the spectra of several deuterated acids has been ascribed by Hadzi and Sheppard to a vibration involving primarily O-D bending in the plane of the carboxyl group. The two strongest bands near this frequency in the spectrum of the

C-form of deuterated stearic acid are the band at 1049 cm^{-1} polarized in the b-direction and that at 1056 cm^{-1} polarized in the a-direction. These bands have been assigned as the a_u and b_u components of in-plane O-D bending.

For each doublet assigned to skeletal stretching vibrations of ordinary stearic acid, there is a doublet at essentially the same frequency in the spectrum of the deuterated acid. However, the intensities of these bands, particularly the components polarized in the b-direction, are considerably greater in the deuterated acid. Since there is presumably no appreciable difference in the geometry of the deuterated and ordinary crystals, the increased intensity of the skeletal bands must be attributed to coupling with the O-D bending motion. Apparently, the motion of the end-group is sufficient to largely determine the intensities and polarization of the skeletal vibrations without altering their frequencies appreciably. This lends some support to assumptions made earlier regarding the mechanism by which the intensities of chain vibrations are enhanced by carboxyl groups.

In the spectrum of the deuterated stearic acid shown in Fig. 4-3, a strong, broad doublet appears at about 1370 cm^{-1}. A band at this position has been ascribed to C-OD stretching by Hadži and Sheppard. If this doublet is caused by C-OD stretching, it is surprising that its components are so nearly equal in intensity, for the projection of the C-O bond on the ab-plane is nearly parallel to the b-axis (see Fig. 1-5).

It is unfortunate that crystals grown of the C-form of the deuterated acid were not thick enough to allow the cutting of suitable slices. No doubt an examination of the polarization of the b_u bands, particularly those between 1000 and 1500 cm^{-1}, would result in a better understanding of the interactions between the carboxyl groups and the methylene chains.

The B-Form of Stearic Acid

Crystal structure data for the B-form of the normal fatty acids are not so complete as for the C-form. The information available is summarized in Chapter I.

Like the C-form, the B-form is monoclinic, having two dimers per unit cell, with the methylene chains packed as in the orthorhombic normal paraffins. The unit cell group is again isomorphic to the point group C_{2h}. As in the C-form, the dimers are centrosymmetric, and the symmetry center of a dimer is an inversion center for the unit cell. Unit cell group fundamentals are Raman- or infrared-active according to their symmetry or antisymmetry with respect to an inversion.

In other respects, the B- and C-forms are quite different. The twofold screw rotation axis of the B-form is parallel to the a-axis rather than to the b-axis, so that infrared-active normal modes of species a_u in this case are polarized in the direction of the a-axis, while those of species b_u are polarized perpendicular to the a-axis.

In the B-form, the chain axes are tilted only 24° away from the normal to the ab-plane, and toward the b-axis.[10] This small tilt implies that the separation of the carboxyl groups of the two dimers in the unit cell is less than in the C-form.

There is also some difference in the molecular configuration in the two crystal forms. In the B-form, the carboxyl carbon-methylene carbon bond is rotated out of the skeletal plane, while in the C-form all of the carbon atoms lie fairly accurately in the plane.

Crystals of the B-form have the lozenge shape characteristic of the orthorhombic chain packing. The interedge angle is about 74°. The ab-plane is parallel to the lozenge face and the a and b axes are parallel to bisectors of the acute and obtuse interedge angles, respectively. The chain axes therefore make an angle of 24° with a normal to the crystal face.

A lozenge-shaped crystal of stearic acid having an interedge angle of 74° was mounted so that the infrared radiation was incident normal to the surface of the lozenge. Its absorption was recorded with the plane of polarization of the radiation bisecting the acute and obtuse angles, respectively. This spectrum is shown in Fig. 4-4. The spectrum of a similar crystal of palmitic acid, obtained by an identical procedure, is included in Appendix I (Fig. A 1-2).

It will be shown in a later section that an interedge angle of 74° is not conclusive proof that a fatty acid crystal has the B-form. However, von Sydow has published a partial spectrum of a Nujol mull of stearic acid crystals whose B-form structure was determined from X-ray measurements.[58] The similarity of this spectrum to that of Fig. 4-4 provides a quite certain identification of the latter as the spectrum of a B-form crystal.

The solid curve in Fig. 4-4 was therefore obtained with the electric vector of the incident radiation parallel to the a-axis, and the broken curve with the electric vector parallel to the b-axis. The

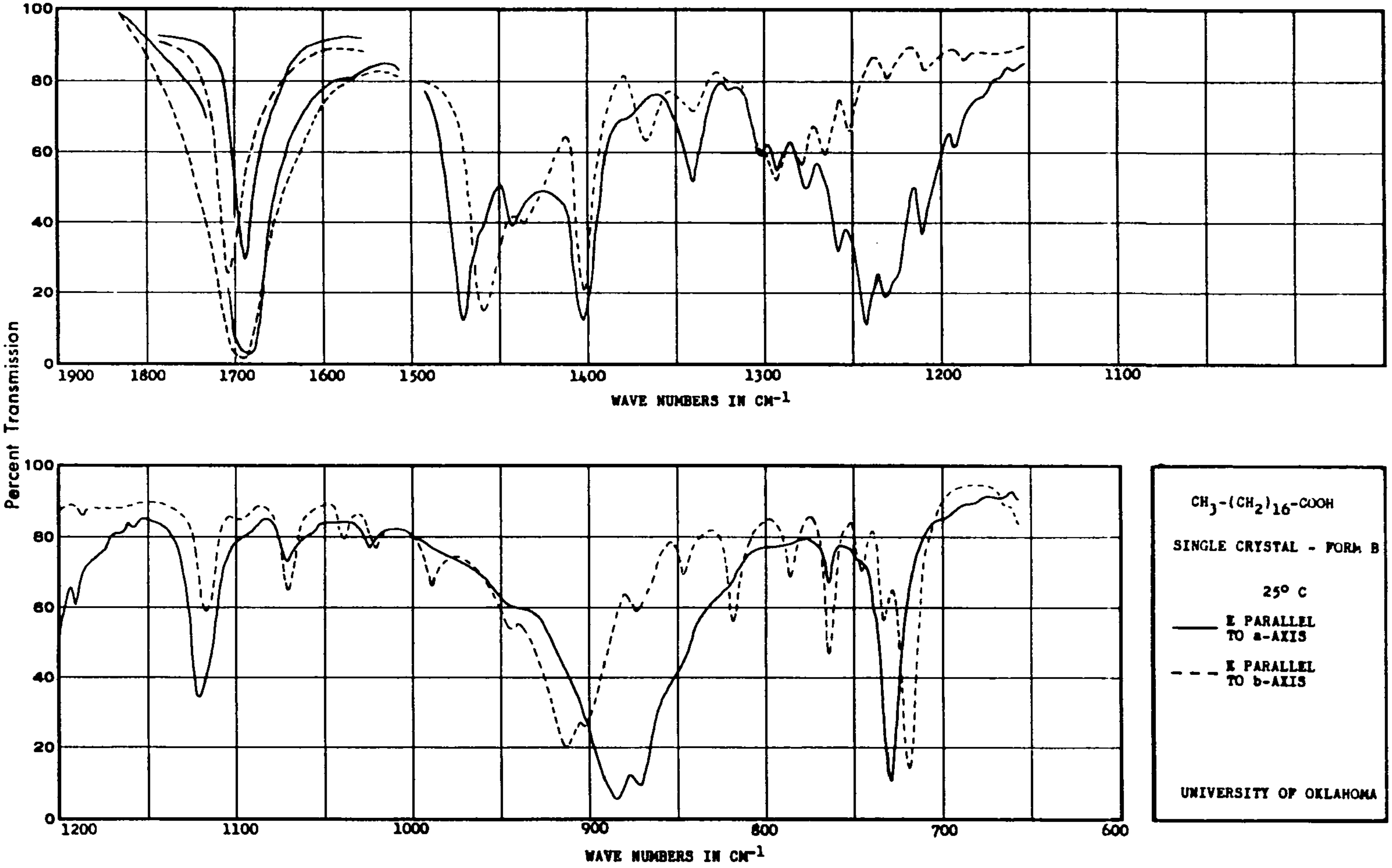

Fig. 4-4. Infrared Spectrum of the B-Form of $CH_3(CH_2)_{16}COOH$; Radiation Incident Normal to the ab-Plane

bands appearing in the solid and broken curves correspond to vibrations of species a_u and b_u, respectively.

Though the a_u modes are polarized strictly parallel to the a-axis, the change in dipole moment associated with the b_u vibrations may have components both parallel to the b-axis and normal to the ab-plane. To study the polarization of the b_u vibrations, crystals of the B-form of stearic acid were sliced perpendicular to the a-axis. The slices were examined visually between crossed polarizers. The light was extinguished when the electric vector of the incident radiation made angles of about 112° and 22° with the b-axis. It was assumed that for these two directions, the electric vector was approximately parallel and perpendicular, respectively, to the chain axes.

The crystal slices were then mounted so that the infrared radiation was incident in the direction of the a-axis. Spectra were recorded with the radiation polarized first parallel then perpendicular to the chain axes. The two curves in Fig. 4-5 represent the spectra obtained in these two positions.

In Table 4-III are given the frequencies and indications of the relative intensities of the bands shown in Fig. 4-4. The letters a and b refer to the a- and b-axes of the unit cell and indicate the direction of the electric vector for which the band was observed.

The bands marked b belong to species b_u and appear in both Figs. 4-4 and 4-5. The symbols ($//$) and ($\perp$) in the Table indicate whether the change in dipole moment in a b_u vibration is essentially parallel to or perpendicular to the chain axes. Included in the Table are the relative intensities of these bands as shown in Fig. 4-5.

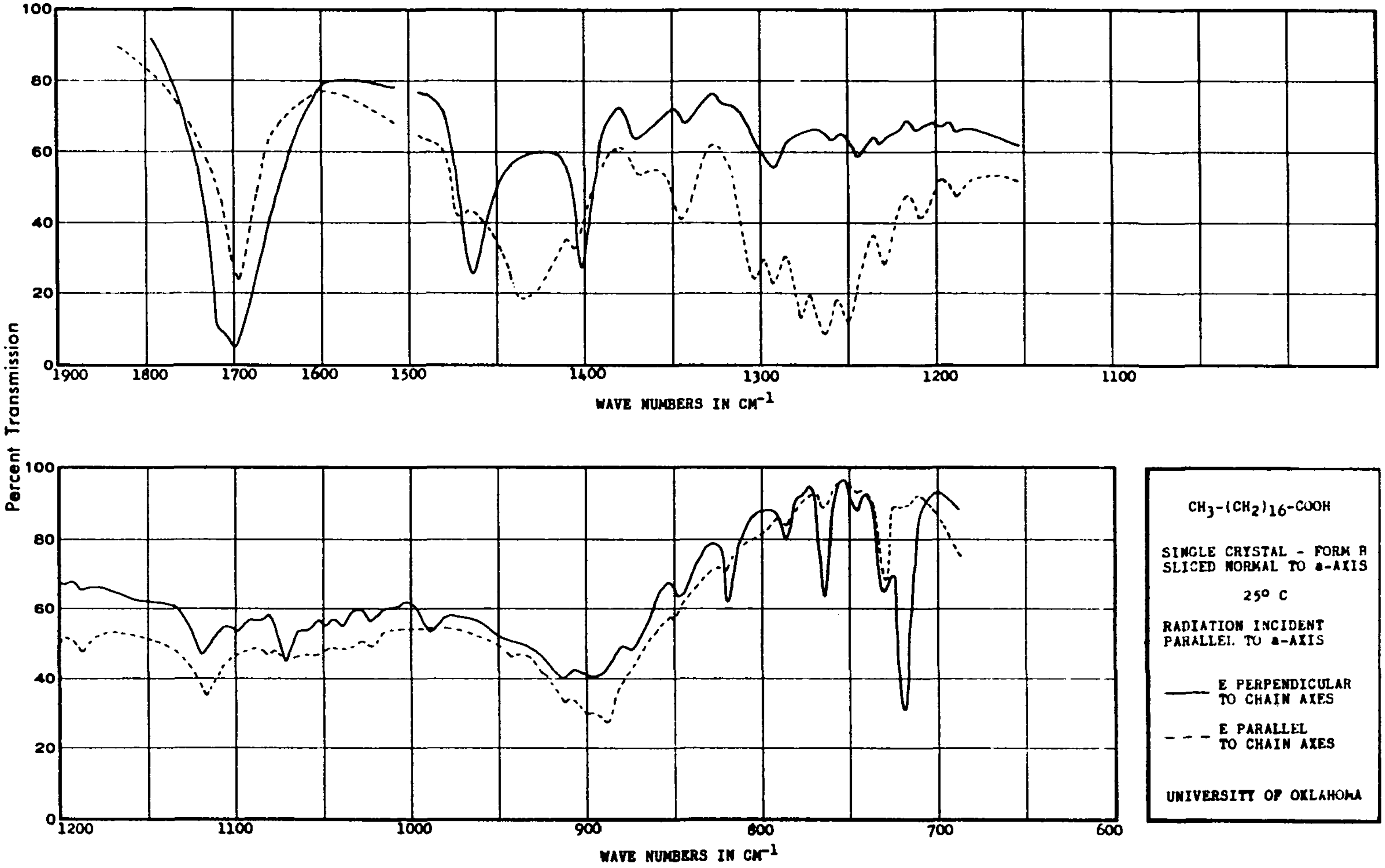

Fig. 4-5. Infrared Spectrum of the B-Form of $CH_3(CH_2)_{16}COOH$; Radiation Incident Normal to the bc-Plane

TABLE 4-III

INFRARED SPECTRUM OF THE B-FORM OF STEARIC ACID

Wave Number	Intensity & Polarization in Fig. 4-4		Intensity & Polarization in Fig. 4-5		Interpretation
719	s	b	⊥	s	R (CH_2 Rocking)
729	s	a			
733	w	b	⊥	w	R
745	w	b	⊥	w	R
764	w	b	⊥	w	R
765	vw	a			
786	w	b	⊥	w	R
817	w	b	⊥	w	R
847	w	b	⊥	w	R
866	vw	b	⊥	vw	
874	w	b	⊥	w	
894			//	w	CH_3 Rocking Parallel to the Skeletal Plane
871	s	a			Mixed O-H Bending and CH_2 Rocking
884	s	a			
908	m	b	//, ⊥	m	
918	m	b			
943	vw	b			R
	vvw	a			
989	vw	b		w	R
991	vvw	a			

TABLE 4-III (Continued)

Wave Number	Intensity & Polarization in Fig. 4-4		Intensity & Polarization in Fig. 4-5		Interpretation
1021	vw	a			S (C-C Stretching)
1022	vw	b	⊥, //	vw	
1039	vw	b	⊥	vw	S
1058	vw	a			S
1070	w	b, a	⊥	w	S
1097	vw	b, a			S
1117	w	b	//	m	S
1121	m	a			
1172	vvw	b			
1181	vw	a			
1189	vw	b	//	w	
1193	vw	a			
1209	vw	b	//	w	
1211	w	a			
1225	w	a			
1231	vw	b	//	m	
1231	m	a			
1243	s	a			
1251	w	b	//	s	
1260	w	a			
1266	w	b	//	s	
1277	w	a			

TABLE 4-III (Concluded)

Wave Number	Intensity & Polarization in Fig. 4-4		Intensity & Polarization in Fig. 4-5		Interpretation
1279	w	b	$\parallel$	s	
1293	w	b	$\parallel$	m	
1294	w	a			
1303	w	b, a	$\parallel$	m	
1318	vw	b, a			
1340	w	a			
1344	vw	b	$\parallel$	w	
1368	w	b	$\perp, \parallel$	w	CH_3 Symmetric Deformation
1373	vw	a			
1402	m	b	$\perp$	m	CH_2 Deformation
1403	m	a			
1435	w	b	$\parallel$	s	C-O Stretching
1443	w	a			
1462	s	b	$\perp$	s	CH_2 Deformation
1472	s	a			
1690	vs	b	$\perp$	vs	C=O Stretching
1710	vs	a			

Many features of the spectra of the B-form shown in Figs. 4-4 and 4-5 are similar to those of the spectrum of the C-form. The bands near 1410 and 1465 cm^{-1} may again be attributed to methylene deformation; a series of bands between 700 and 1000 cm^{-1} may be associated with methylene rocking, and several bands in the region from 1000 to 1150 cm^{-1} can be assigned as skeletal deformation bands. Also, as in the spectrum of the C-form, a series of bands is observed between 1170 and 1350 cm^{-1}.

The bands of the B-form at about 1700 and 1435 cm^{-1}, and also the strong bands near 1250 and 900 cm^{-1}, may be ascribed to carboxyl vibrations, as were bands near these frequencies in the spectrum of the C-form.

Despite these similarities, the spectrum of the B-form differs greatly in many ways from that of the C-form. No band having a frequency between 650 and 700 cm^{-1} is observed in the B-form. The relative intensities of the a_u and b_u components of the methylene rocking and deformation doublets are different from those observed in the C-form. The separation of the two components of the doublet near 1700 cm^{-1} is nearly twice that for the doublet in the C-form.

Perhaps the greatest difference is in the appearance of the bands near 900 cm^{-1} and in the region between 1170 and 1350 cm^{-1}. In the C-form, strong carboxyl doublets near 900 and 1250 cm^{-1} may easily be distinguished from bands attributed to methylene vibrations. For each of these doublets, the difference in frequency of the a_u and b_u components is negligible. In the spectrum of the B-form shown in Fig. 4-4, the absorption near 900 and 1250 cm^{-1} appears as broad bands with one or more strong shoulders or submaxima. The maximum of intensity of the broad a_u band is in each case separated in frequency from that of the b_u band.

The remainder of this section will be devoted to a discussion of these and other aspects of the spectrum of the B-form.

In the spectrum of the C-form the band at 689 cm^{-1} was attributed to a deformation of the O-C=O angle. Since this is essentially a skeletal vibration, its frequency may be lower in the B-form because of the different orientation of the carboxyl group relative to the methylene chain. Hadzi and Sheppard have reported that the frequencies of bands in this region vary considerably among different carboxylic acids.[56]

In the spectrum shown in Fig. 4-4, obtained with the radiation incident normal to the ab-plane, the intensities of the two components of the strong methylene rocking doublet at 719 and 729 cm^{-1} are nearly equal. The b_u components of the higher frequency members of the rocking series are much more intense relative to other bands in this region than in the C-form, so that the series can be more easily traced. The frequencies of bands in this series lie near those observed for the C-form, but are somewhat higher. The last band which may definitely be identified as a rocking mode lies at 989 cm^{-1}, while the observed upper limit was 1015 cm^{-1} for the C-form.

The fact that the frequencies of the rocking bands are higher and the upper limit of the series is lower in the B-form than in the C-form may be due to the displacement of the carboxyl carbon out of the skeletal plane. This will probably cause the nearest CH_2 group not to be symmetric with respect to the skeletal plane, so that there is one less CH_2 group in the regular portion of the chain.

The high intensities of the b_u rocking bands above 719 cm^{-1} is not understood. Since only the higher-frequency series members are enhanced, it cannot be caused by a distortion of the orthorhombic packing. If it is caused by mechanical coupling with the end-group vibrations, this coupling does not appear to alter the polarization. The spectrum shown in Fig. 4-5, obtained with the radiation incident in the direction of the a-axis, shows that the b_u components of the rocking doublets are polarized perpendicular to the chain axes, as they are in the C-form.

The b_u-a_u doublet at 1021 and 1022 cm^{-1} was not included in the rocking series because the change in dipole moment associated with the b_u band has a component parallel to the chain. The band at 1039 cm^{-1} is believed to have too high a frequency to be a member of the rocking series. The remaining bands up to 1121 cm^{-1} have frequencies very near those of bands ascribed to skeletal vibrations in the C-form, though their relative intensities are different. All these bands were attributed to skeletal vibrations.

The strong doublet at 940 cm^{-1} in the C-form of stearic acid was attributed to vibrations of the hydrogen atom out of the carboxyl plane. The doublet at 1298 cm^{-1} was ascribed to a C-O-H angle deformation involving primarily motion of the hydrogen atom in the carboxyl plane. These bands may easily be distinguished from neighboring methylene bands because of their high intensity.

It was mentioned earlier that the absorption of the B-form of stearic acid near 900 and 1250 cm^{-1} appears to consist of broad bands with one or more submaxima. An examination of the spectra of thinner crystals shows that these broad bands are produced by the overlapping of several sharp bands of comparable intensity. The most intense bands in these regions in the B-form of palmitic acid are shifted with respect to those in the B-form of stearic acid. (Compare Fig. 4-4 in this chapter with Fig. A 1-2 in Appendix I). This indicates a stronger interaction between chain and carboxyl vibrations in the B than in the C-form. It is probable that the bands near 1250 and 900 cm^{-1} in the B-form are caused by carboxyl and chain motions, mixed to such an extent that individual bands cannot be ascribed to either chain or carboxyl vibration.

Nevertheless, since the high intensity of these bands must be caused by the polar carboxyl groups, the separation between the most intense a_u and b_u bands may still result from interaction between carboxyl groups of different dimers. This interaction is greater than in the C-form because of the greater proximity of the carboxyl groups in the B-form. This would also account for the increased splitting of the C=O stretching doublet near 1700 cm^{-1}.

In the region between 1170 and 1350 cm^{-1}, two rather irregular series occur. The bands of one are polarized in the a-direction and those of the other are polarized essentially parallel to the chain axis. The lowest frequency b_u band lies at 1172 cm^{-1} and the lowest a_u band at 1181 cm^{-1}. The highest frequency bands in each series appear to be at 1340 cm^{-1}.

Only for a few bands near the upper limit of each series can corresponding a_u and b_u components be definitely identified. Though the number of bands in each series is roughly equal to the number observed in this region in the C-form, no definite correlation between bands of the two crystal forms has been found.

Since the molecule is not planar, it is possible that both wagging and twisting modes are represented in these series. This may be the cause of the appearance of bands below the lower limit observed for the C-form. The a_u bands at 1225 and 1231 cm^{-1}, which are more closely spaced than nearby a_u bands, may result from different types of vibrations.

The arrangement of the chains in the B-form of stearic acid is similar to that in the monoclinic n-paraffins, except that there appears to be no alternation in the tilt of the chains. It is reasonable to assume that the packing of the end groups, at least within a layer, is not greatly different in the two forms. The bands at 1368 and 1373 cm^{-1} have about the same relative intensities and similar polarization (except for the difference mentioned in Chapter III) as the bands near these positions in the spectrum of n-$C_{36}H_{74}$ shown in Fig. 3-1. They are therefore both ascribed to symmetric deformation of the methyl groups.

In the spectrum shown in Fig. 4-5, obtained with radiation incident in the a-direction, it may be seen that the b_u bands at 1402 and 1462 cm^{-1} are both polarized perpendicular to the chain axes. This again is consistent with the interpretation of these bands as methylene deformation vibrations.

The b_u component of the carboxyl doublet at 1436 cm^{-1} is polarized parallel to the chain axes, as in the spectrum of the C-form. If the interpretation of these bands as caused primarily by C-OH stretching is correct, the polarization indicates that the C-OH bond is approximately parallel to the axes of the chains. The largely perpendicular polarization of the band at 1690 cm^{-1} is therefore consistent with its assignment as C=O stretching.

The A-Form of Stearic Acid

Of the three common crystal forms of the even-numbered normal fatty acids, least is known about the structure of the A-form. The information available is summarized in Chapter I.

The original basis for the designation "A" was the long spacing obtained by X-ray diffraction, which was greater for the A-form than for the B- and C-forms. Von Sydow has associated the letter "A" also with a crystal form which exhibits no definite long spacing.[10] His determination of the structure of this latter form of lauric acid showed that the chains are packed as in the triclinic normal paraffins. No long spacing is observed because carboxyl and methyl groups are packed side by side. This crystal form is triclinic, with three dimers per unit cell. The A-form with long spacing is triclinic, with one dimer per unit cell, and according to von Sydow, also has the triclinic chain packing.

Triclinic crystals of stearic acid grown here were first recognized by their superficial resemblance to the triclinic n-paraffins. The crystals are thin sheets with irregular edges. The sheets were marked by parallel lines similar to those in the octadecane crystals.

A spectrum of stearic acid was recorded by a procedure analogous to that used to get the spectrum of octadecane shown in Fig. 3-5.

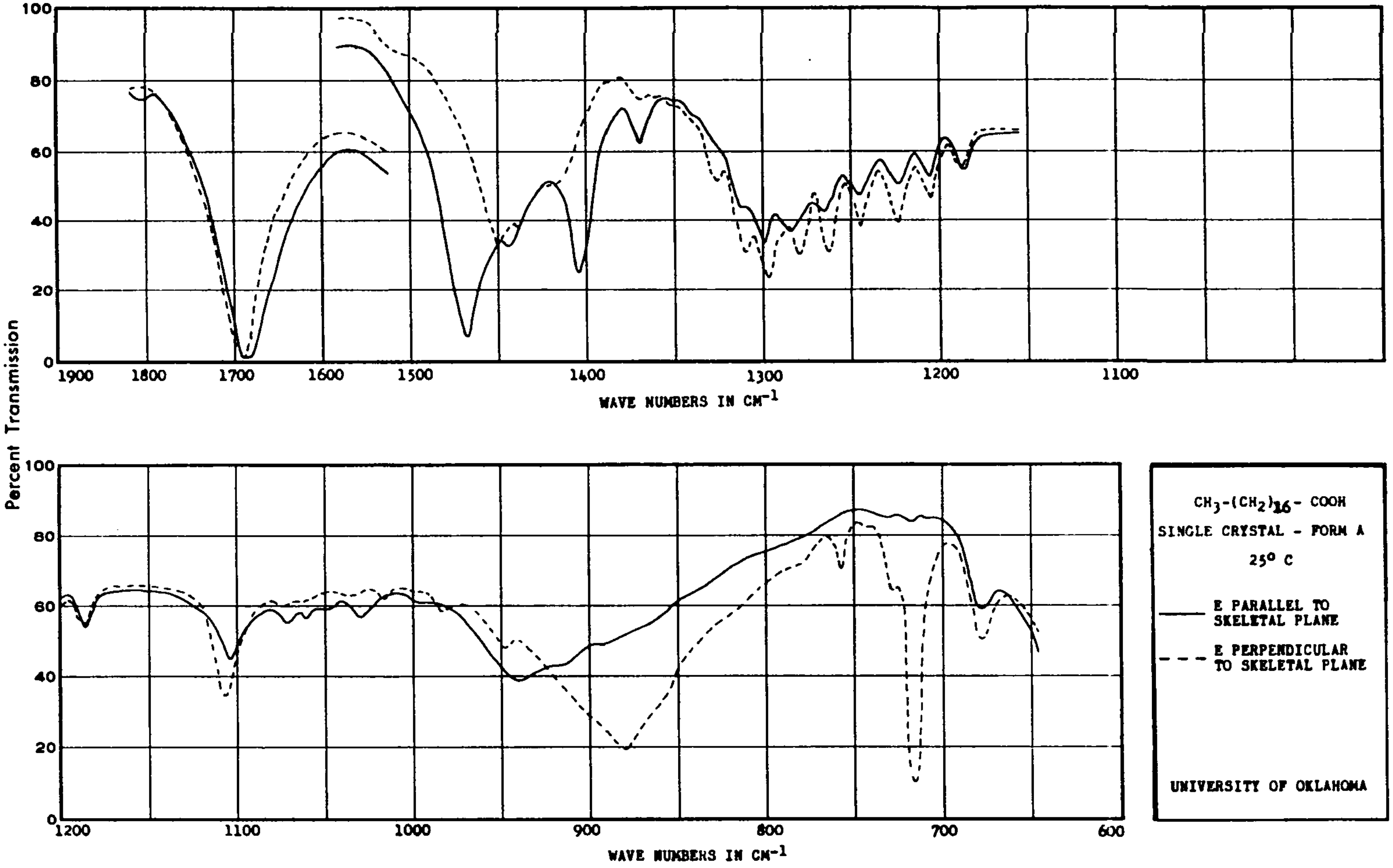

Fig. 4-6. Infrared Spectrum of the A-Form of $CH_3(CH_2)_{16}COOH$; Radiation Incident Approximately Parallel to the Chain Axes

The crystal was mounted so that the polarized radiation was incident normal to the large surface. A single strong rocking band was observed at 717 cm^{-1}. It was seen to vary in intensity as the crystal was rotated about the normal. The spectrum represented by the broken curve in Fig. 4-6 was recorded with the orientation for which this band had maximum intensity. The crystal was then rotated 90° about the normal and the spectrum shown by the solid curve in Fig. 4-6 was obtained. Spectra of palmitic acid, obtained in a similar manner, are included in Appendix I.

The appearance of single bands rather than doublets at 717 and 1468 cm^{-1}, and the fact that these bands are polarized at right angles to each other, as are the corresponding bands in the spectrum of the triclinic n-paraffins, strongly indicates that the chains have the triclinic packing. This resemblance extends also to several bands near 3000 cm^{-1}. In Appendix II, assignments of the bands of triclinic n-$C_{20}H_{42}$ in this region are discussed. The polarization and frequencies of these bands are compared with those of similar bands of palmitic acid. The comparison leaves little doubt that the crystals of stearic and palmitic acid whose spectra are shown in Figs. 4-6 and A 1-3 have one of the two triclinic forms. Whether the crystals have the form with long spacing or that having no long spacing is not certain.

Von Sydow has published a portion of the spectrum of a polycrystalline sample of palmitic acid, $CH_3(CH_2)_{14}COOH$, which he states has the A-form.[58] He later states that the form which has no long spacing was observed only for lauric acid, $CH_3(CH_2)_{10}COOH$, and myristic acid, $CH_3(CH_2)_{12}COOH$.[10] Presumably, then, the palmitic acid crystals whose spectrum he presented have the form with long spacing.

Von Sydow's spectrum was obtained with a sample suspended in a Nujol mull and does not include the regions near 720 and 1470 cm^{-1} where the absorption of the mineral oil is greatest. The portions included differ considerably from those shown in Fig. A 1-3, Appendix I. Though this difference may be due in part to orientation effects, the difference in frequency of the strong bands near 900 cm^{-1} is probably too great to be accounted for by anything but a difference in crystal structure.

Von Sydow observed a single broad band with a maximum at 935 cm^{-1}. The strongest of the two bands observed near this frequency in the spectrum of triclinic palmitic acid shown in Fig. A 1-3 lies at approximately 880 cm^{-1}. If the spectrum obtained by von Sydow is that of the form with long spacing, then the form studied here is probably that with no long spacing. Two objections to this conclusion may be raised. Von Sydow has observed the form with no long spacing only for lauric acid, $CH_3(CH_2)_{10}COOH$, and myristic acid, $CH_3(CH_2)_{12}COOH$, while the form with long spacing has been reported for several acids with longer chains, including stearic and palmitic acids.[19] Also, von Sydow has reported that the crystals with no long spacing were thick, while those grown here were thin flakes.

In Table 4-IV, the frequencies and relative intensities of the bands shown in Fig. 4-6 are given. Assignments are also included in the Table. Since the structure of the crystals is not precisely known, the assignments are based on interpretations made previously for other crystal forms rather than on the polarization observed in Fig. 4-6.

TABLE 4-IV

INFRARED SPECTRUM OF THE A-FORM OF STEARIC ACID

Wave Number	Intensity	Polarization	Interpretation
677	w	OP,IP	O-C$\simeq$O Angle Deformation
717	s	OP	R (CH_2 Rocking)
729	w	OP	R
744	vw	OP	R
757	w	OP	R
778	vw	OP	R
809	vw	OP	R
881	vs	OP	O-H Bending Perpendicular to the Carboxyl Plane
891	vw	IP	CH_3 Rocking Parallel to the Skeletal Plane
911	vw	IP	
938	m	IP	O-H Bending?
948	vw	OP	R
983	vw	OP	R
1016	vw	OP	R
1030	vw	IP	S (C-C Stretching)
1047	vw	IP	S
1061	vw	IP	S
1071	vw	IP	S
1074	vvw	OP	
1104	w	IP	S

TABLE 4-IV (Continued)

Wave Number	Intensity	Polarization	Interpretation
1108	m	OP	S
1186	w	OP,IP	W (CH$_2$ Wagging coupled with COH Vibrations)
1205	w	OP,IP	W
1223	w	OP,IP	W
1243	w	OP,IP	W
1262	m	OP	W
	w	IP	
1279	m	OP	W
	w	IP	
1286	w	IP	W
1298	m	OP,IP	W
1310	m	OP	W
	w	IP	
1325	w	OP	W
	vw	IP	
1361	vw	OP?	
1369	w	IP	CH$_3$ Symmetric Deformation
1404	s	IP	CH$_2$ Deformation
1416	m	OP,IP	
1436	m	OP	Primarily C-OH Stretching
1445	m	IP	

TABLE 4-IV (Concluded)

Wave Number	Intensity	Polarization	Interpretation
1450	m	OP	CH_3 Asymmetric Deformation
1468	s	IP	CH_2 Deformation
1684	vs	IP	C = O Stretching
1688	vs	OP	

Nevertheless, since the chain packing is triclinic, some features of the spectrum can be related to the crystal structure.

The strong methylene rocking band at 717 cm^{-1} and the methylene deformation bands at 1468 cm^{-1} should be polarized perpendicular to the chain axes. The change in dipole moment for a rocking vibration should be perpendicular to the chain skeletal plane and that for a methylene deformation vibration should be parallel to it. It was therefore assumed that the spectrum shown in Fig. 4-6 was obtained with the radiation incident nearly parallel to the chain axes, the dotted curve with the electric vector of the radiation parallel to the skeletal planes, and the solid curve with the electric vector perpendicular to the planes of the carbon skeletons. Conclusions regarding the polarization of the bands, indicated by IP (in-plane) or OP (out-of-plane) in Table 4-IV, were based on this assumption.

The weaker bands observed in the rocking series all appear to be polarized out-of-plane. All the bands ascribed to skeletal vibrations except that near 1108 cm^{-1} appear to be polarized in-plane, as do the bands at 1404 cm^{-1} and 1369 cm^{-1} ascribed to methylene deformation and symmetric methyl deformation, respectively.

The band at 881 cm^{-1} is polarized out-of-plane, consistent with its interpretation as O-H bending perpendicular to the carboxyl plane. It should be noticed that this band is apparently split, with another component lying at 938 cm^{-1}. This, and the apparent splitting of the C=O stretching band, at 1684 and 1688 cm^{-1} indicates that the crystal may have the form with no long spacing, since no splitting would be expected if there were only one dimer per unit cell.

The absorption in the region 1410 - 1460 cm^{-1} is relatively weak, as it is in the spectra of the B- and C-forms obtained with the electric vector perpendicular to the chain axes (see Figs. 4-1 and 4-4, also the solid curves in Figs. 4-2 and 4-5). Most of the absorption in this region may be attributed to C-OH stretching. The fact that there are several bands rather than one again indicates that the crystal has the form with no long spacing. The peak at 1450 cm^{-1}, like the band of octadecane near this frequency, may be interpreted as asymmetric methyl deformation.

As in the spectrum of the C-form, a band appears at 677 cm^{-1}. Also the bands in a regularly spaced series between 1186 and 1360 cm^{-1} have almost exactly the same frequencies as those of the corresponding series in the C-form. The irregularity of a band series of the B-form between 1170 and 1350 cm^{-1}, and the fact that no band appears near 689 cm^{-1} in the B-form, have been attributed to the displacement of the carboxyl group out of the skeletal plane of the chain. If this conclusion is correct, the presence of the regular series and the band at 678 cm^{-1} indicate that the carboxyl groups are not displaced in this crystal form. Since the band of the C-form at 689 cm^{-1} was assigned as O=C-OH angle deformation and the band series ascribed to methylene wagging coupled with a COH vibration parallel to the carboxyl plane, one would expect these bands to be polarized more nearly parallel to the skeletal plane than perpendicular to it. On the contrary, in Fig. 4-6, these bands are more intense in the spectrum obtained with the radiation polarized perpendicular to the skeletal planes.

It should be remembered, however, that the dipole moment changes associated with the corresponding bands of the C-form have strong components parallel to the chain axes. Though the intensities of the perpendicular 718 and 1468 cm^{-1} bands indicate that the radiation is incident more nearly parallel than perpendicular to the chain axes, a tilt in the chains could greatly influence the direction in which a parallel band appears to be polarized. Thus, until the structure of these crystals is better known, the observed polarization of the bands in question cannot be regarded as a serious objection to the interpretation given.

A New Crystal Form

In the discussion of the B-form of stearic acid, it was mentioned that a lozenge-shaped crystal with an interedge angle of 74° does not necessarily have this form.

When an ether solution of stearic acid was evaporated at 18° C, most of the crystals in the residue had the C-form, but some crystals with an interedge angle of 74° were also present. These crystals were assumed to have the B-form, and at first little attention was paid to them, since good crystals of the B-form had already been grown from a solution in carbon disulfide.

Later, after crystals of the C-form of deuterated stearic acid had been produced by evaporating an ethyl ether solution at room temperature over a layer of heavy water, some of these crystals were dissolved again, and the solvent was evaporated at 9° C in an attempt to grow crystals of deuterated stearic acid having the B-form. Some crystals with an interedge angle of 74° were produced. Though a spectrum of the crystals showed some similarity to that of the B-form of the ordinary acid, differences were observed which seemed too great to be accounted for by the deuteration.

Attention was then directed to the crystals of the ordinary acid with an interedge angle of 74° which had been precipitated along with crystals of the C-form from the ether solution. The spectrum of one of these crystals was obtained. It not only is unlike the spectrum of the B-form but is also different from those of the A- and C-forms. It seems certain that this crystal has a structure different from that of any of the polymorphs of stearic acid studied in preceding sections.

The letters A, B, and C have been applied to forms of both the even and odd-numbered normal fatty acids. The letter D has been associated with a form of the odd-numbered fatty acids.[19] The new form will therefore be designated by the letter E in what follows.

The spectrum of a crystal of stearic acid having the E-form is shown in Fig. 4-7. The spectrum of a crystal of the deuterated acid having an interedge angle of 74° is shown in Fig. 4-8. The procedure for obtaining these spectra was the same as that for the spectrum of the B-form shown in Fig. 4-4. The crystal was oriented so that the radiation was incident normal to its surface. The solid and broken curves were obtained with the electric vector parallel to the bisectors of the acute and obtuse interedge angles, respectively. In analogy to the notations used for the B- and C-forms, where the bisectors of the angles are parallel to the a- and b-axes of the unit cells, these are called the a- and b-axes in the captions of Figs. 4-7 and 4-8.

In Table 4-V are listed the frequencies and relative intensities of the bands shown in Figs. 4-7 and 4-8. The letters a and b distinguish

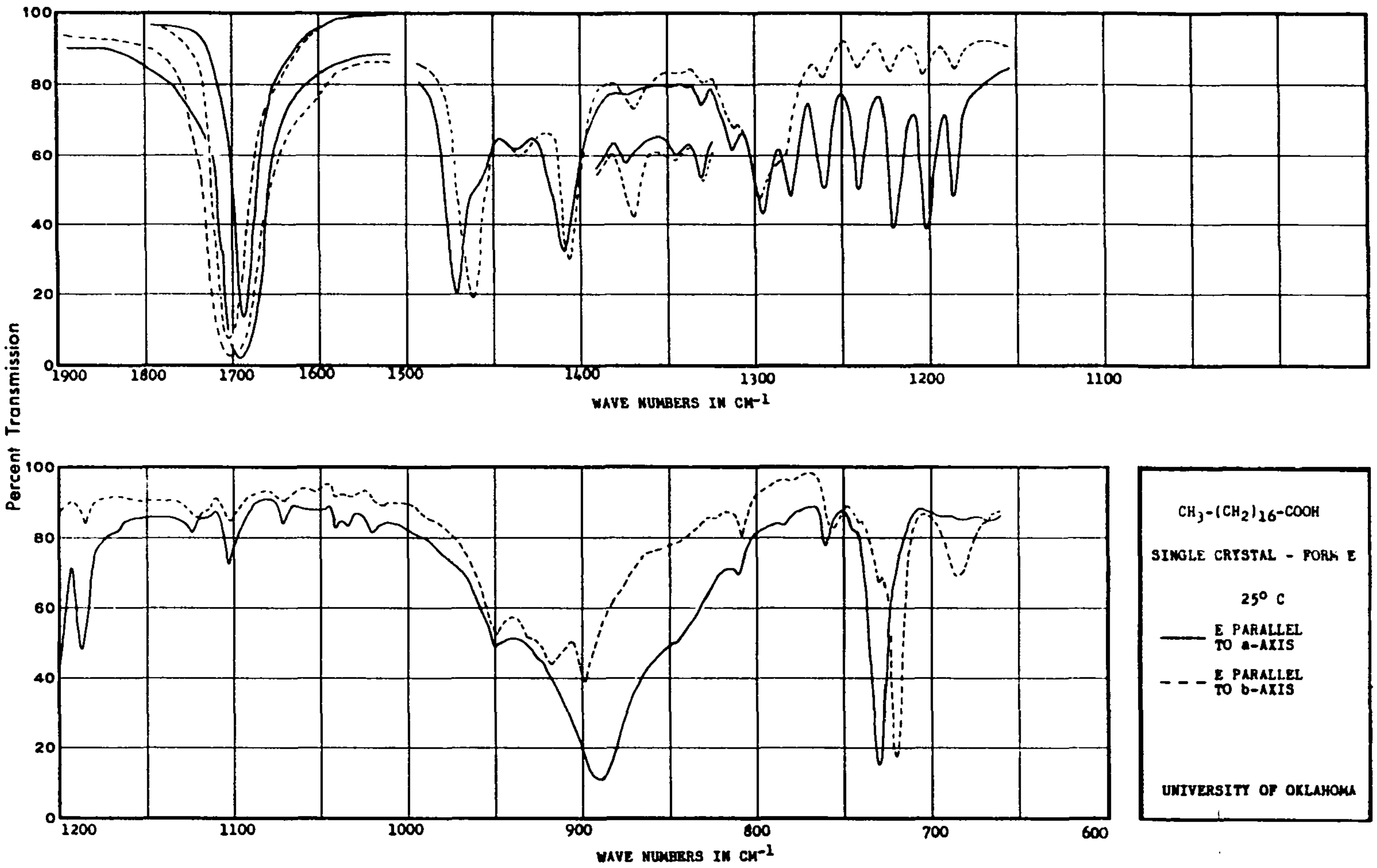

Fig. 4-7. Infrared Spectrum of the E-Form of $CH_3(CH_2)_{16}COOH$; Radiation Incident Normal to the ab-Plane

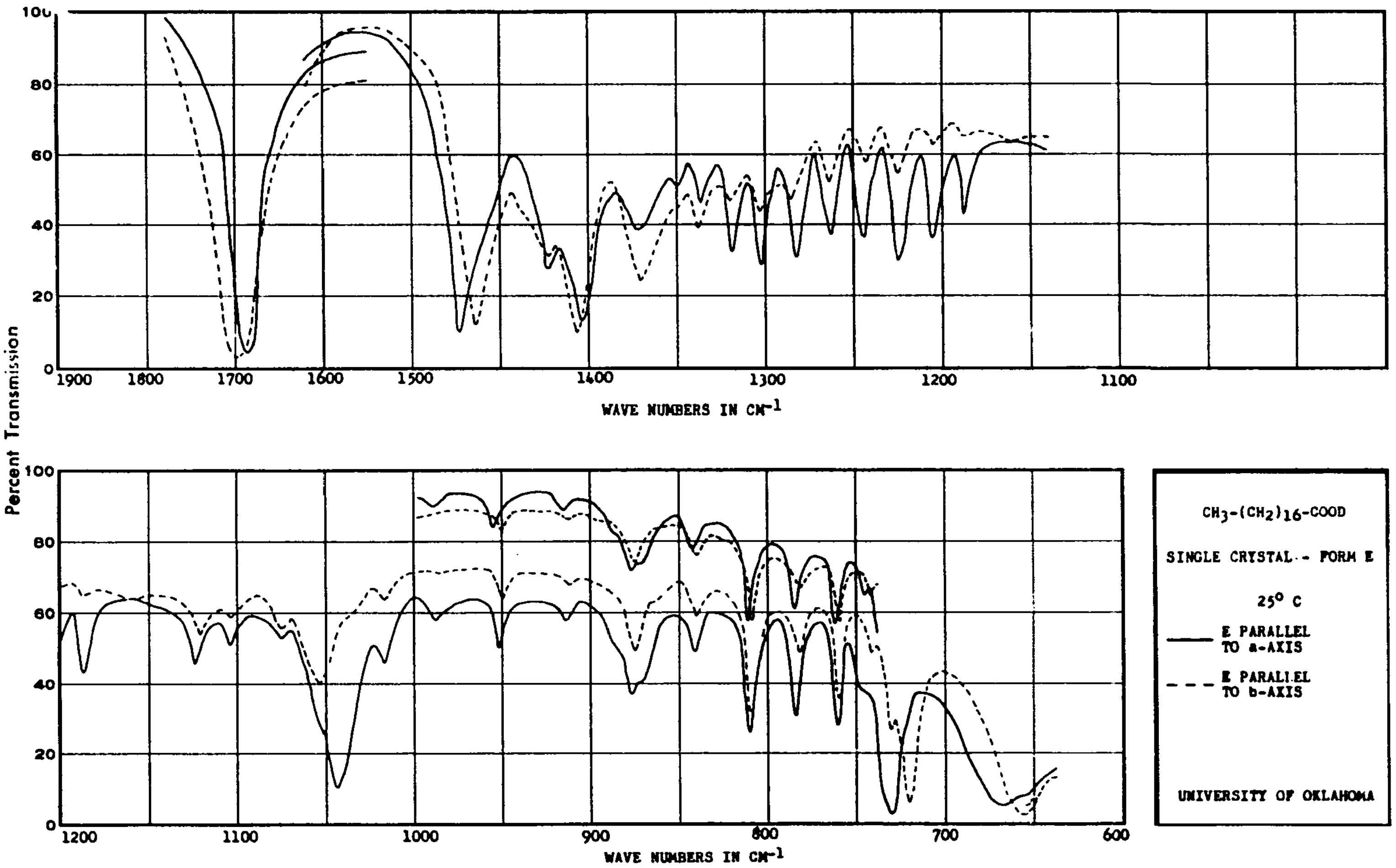

Fig. 4-8. Infrared Spectrum of the E-Form of $CH_3(CH_2)_{16}COOD$; Radiation Incident Normal to the ab-Plane

TABLE 4-V

INFRARED SPECTRA OF THE E-FORMS OF ORDINARY AND DEUTERATED STEARIC ACID

$CH_3(CH_2)_{16}COOH$			$CH_3(CH_2)_{16}COOD$			
Wave Number	Intensity & Polarization		Wave Number	Intensity & Polarization		Interpretation
686	w	b	656	m	b	O-C=O Angle Deformation
			670			O-D Bending
720	s	b	719	s	b	R (CH_2 Rocking)
729	s	a	730	s	a	
741	vw	b	741	vw	b	R
744	vw	a	744	vw	a	
759	w	b	759	w	b	R
761	w	a	760	w	a	
782	vw	b	782	vw	b	R
784	vw	a	784	w	a	
809	w	b	809	w	b	R
810	w	a	810	w	a	
848	vw	a	840	vw	b	R
			841	vw	a	
			870	w	a	COOH-COOD
877	vw	b	875	w	b	R
			877	w	a	
			888	w	a	CH_3 Rocking?

TABLE 4-V (Continued)

$CH_3(CH_2)_{16}COOH$			$CH_3(CH_2)_{16}COOD$			
Wave Number	Intensity & Polarization		Wave Number	Intensity & Polarization		Interpretation
890	vs	a				OH Bending
898	m	b				
917	m	b				
			911	vw	b	R
			914	vw	a	
949	m	b	949	vw	b	R
951	w	a	953	vw	a	
986	vw	a	987	vw	a	R
1015	vw	b	1014	vw	b	R
1019	vw	a	1015	vw	a	
1033	vw	a	1033		b,a	S (C-C Stretching)
1039	vw	b				S
1040	vw	a				
			1043	w	b	O-D Bending
			1053	m	a	
1071	vw	b,a	1074	vw	b	S
				vw	a	
1102	vw	b	1102	vw	b	S
1103	vw	a		vw	a	
1120	vw	b	1120	vw	b	S
1123	vw	a	1123	vw	a	

TABLE 4-V (Continued)

$CH_3(CH_2)_{16}COOH$			$CH_3(CH_2)_{16}COOD$			
Wave Number	Intensity & Polarization		Wave Number	Intensity & Polarization		Interpretation
1185	w	b	1186	vw	b	W (CH_2 Wagging Coupled with a COH or COD Vibration)
1186	m	a		w	a	
1202	w	b	1204	vw	b	W
1203	m	a		w	a	
1220	m	a	1223	vw	b	W
1222	w	b	1224	w	a	
1240	m	a	1243	w	a	W
1241	w	b		vw	b	
1260	m	a	1262	vw	b	W
1261	w	b	1263	w	a	
1279	m	a	1282	vw	b	W
1281	w	b		w	a	
1295	m	a				W, Superposed on a COH Vibration
1297	m	b				
			1302	w	a	W
				vw	b	
1312	w	b	1317	w	a	W
	w	a	1318	vw	b	
1329	vw	b	1333	vw	a	W
1330	w	a	1337	vw	b	

TABLE 4-V (Concluded)

$CH_3(CH_2)_{16}COOH$			$CH_3(CH_2)_{16}COOD$			
Wave Number	Intensity & Polarization		Wave Number	Intensity & Polarization		Interpretation
1345	vvw	a	1348	vvw	a	W
1346	vvw	b	1350	vvw	b	
1369	w	b				CH_3 Symmetric Deformation
1373	vw	a				
1370	w					C-O Stretching
1406	m	b	1402	s	a	CH_2 Deformation
1409	m	a	1405	s	b	
			1423	w	b,a	COOH-COOD
1435	w	b				COH Vibration
1437	w	a				
1462	s	b	1462	s	b	CH_2 Deformation
1471	s	a	1472	s	a	
1686	vs	a	1684	vs	a	C=O Stretching
1705	vs	b	1696	vs	b	

between bands in the solid and broken curves, respectively. Assignments, essentially similar to those in previous sections, are also included in Table 4-V.

In Fig. 4-8, the effects of the deuteration are manifest in the presence of carboxyl bands near 1370 and 1050 cm^{-1}, and in the absence of strong carboxyl bands from the vicinity of 1300 and 900 cm^{-1}. The deuteration may not be as complete as in the C-form, however. Bands which are probably caused by carboxyl vibrations in COOH - COOD dimers are seen at 870 and 1423 cm^{-1}.

The remainder of the spectrum of the deuterated acid resembles that of the ordinary acid shown in Fig. 4-7. Because of this similarity, it was concluded that the crystals of the deuterated acid also had the E-form. This was verified by examining the spectrum of a crystal of the deuterated acid a year after it was grown, when about half the deuterium had been replaced by hydrogen.

In Chapter II, the relationship between the interedge angles and the structure of lozenge-shaped crystals was discussed. Of the crystals of the n-paraffins and normal fatty acids whose structure have been determined, all which have the lozenge shape have orthorhombic packing of the chains. To the extent that the dimensions of the orthorhombic subcell are the same for these crystals, the interedge angles indicate the orientation of the methylene chains relative to the surfaces of the crystals.

Crystals of the B-form of stearic acid and the monoclinic form of n-$C_{36}H_{74}$ usually are lozenge-shaped with an interedge angle of 74°. Both have orthorhombic packing of the chains. The a- and b-dimensions of the unit cell are very nearly the same in both, and the orientation of these axes with respect to the crystal surfaces is also the same. The directions of the chain axes differ in the two cases only by about 3°.

If the superficial resemblance of the E- and B-forms indicates a similar arrangement of the chains, the two forms must differ only in the shape or arrangement of the end-groups. This conclusion appears to be borne out by the spectra of the E-form crystals.

The splitting and polarization of the strong doublets near 720 and 1465 cm^{-1}, ascribed to methylene rocking and methylene deformation, respectively, show that the chains have the orthorhombic packing in the E-form. If the polarization of these bands has its usual significance, the a_o axis of the orthorhombic subcell is parallel to a plane normal to the crystal surface and bisecting the acute angle, and the b_o axis is parallel to a plane perpendicular to the former and bisecting the obtuse angle. The chain axes are then normal to the surface or are tilted in one of these planes.

Two bands at 1369 and 1373 cm^{-1} are similar to the bands at 1368 and 1373 cm^{-1} ascribed to symmetric methyl deformation in the B-form. The splitting shows that methyl groups in neighboring chains are adjacent, rather than separated by a chain length as in one of the triclinic forms. The polarization and intensity of these two bands indicate that the relative orientation of the methyl groups is similar in the E- and B-forms.

The C=O stretching doublet near 1700 cm^{-1} and the broad O-H stretching doublet near 900 cm^{-1} resemble the bands near these frequencies in the B-form. The splitting indicates that the carboxyl groups in neighboring dimers are adjacent, which implies that the chain tilt is small, as in the B-form.

The remaining portions of the spectrum of the E-form are very different from the corresponding regions of the spectrum of the B-form. The band at 686 cm^{-1} has no obvious counterpart in the B-form. The CH_2 rocking bands above 730 cm^{-1} are less intense, and lie at slightly lower frequencies than in the B-form. The series of regularly spaced bands between 1185 and 1350 cm^{-1} is unlike the irregular group of bands in this region in the B-form.

The band at 686 cm^{-1}, the CH_2 rocking doublets, and the band series between 1185 and 1350 cm^{-1} all have frequencies very near those of similar bands in the C-form.

The differences between the B- and C-forms in these spectral regions were attributed to a difference in the orientation of the carboxyl groups with respect to the methylene chain. The similarity of these bands in the E- and C-forms therefore indicates that the molecular configuration in the E-form is like that in the C-form.

If this is accepted, the relationship between the spectra and the structures of the E-, C-, and B-forms is clear. Except for the splitting of the bands near 900 and 1700 cm^{-1}, caused by the proximity of the carboxyl groups, the spectrum of the E-form is about that which would be expected if the dimers of stearic acid have the molecular configuration characteristic of the C-form, but have the chains arranged as in the B-form.

In the region between 650 and 700 cm^{-1}, the relationship between the three crystal forms is particularly well demonstrated. The band at 689 cm^{-1} in the C-form, ascribed to deformation of the O=C-OH angle, is shown in Fig. 4-2 to be polarized approximately parallel to the chain axes. It appears polarized in the a-direction in Fig. 4-1, obtained with the radiation incident normal to the ab-plane, because of the tilt of the chains toward the a-axis. The fact that no band is observed near this frequency in the B-form is attributed to the displacement of the carboxyl carbon from the skeletal plane.

The presence of a band at 686 cm^{-1} in the E-form, at almost precisely the same frequency as the band of the C-form, indicates that the orientation of the carboxyl group with respect to the methylene chain is similar in the two forms. In Fig. 4-8, the band at 686 cm^{-1} appears in the record obtained with the electric vector of the radiation parallel to the bisector of the obtuse interedge angle. If the vibration is polarized parallel to the chain axes as in the C-form, its appearance in this record indicates that the chains are tilted in the plane bisecting the obtuse angle, as they are in the B-form.

The band at 686 cm^{-1} is less intense relative to the nearby rocking vibrations than the band at 689 cm^{-1} in the C-form. This indicates that the tilt angle is smaller in the E-form, consistent with the assumption that the chains are arranged as in the B-form, where the tilt angle is only 24° as compared to 38° in the C-form.

The polarizations of the rocking doublets above 730 cm^{-1} in the E-form are similar to those observed for monoclinic n-$C_{36}H_{74}$. The relationship of the polarization and splitting of these doublets to the crystal structure, discussed in Appendix III, provides further support for the conclusion that the chains are arranged as in the monoclinic n-paraffins and in the B-form.

Though the reason for the intensity difference in the two components of the doublet near 1050 cm^{-1}, assigned as O-D bending, is not known, the fact that the stronger band is polarized oppositely in the E and C-forms indicates a difference in the relative orientation of the carboxyl groups in the two cases. It can be seen that in the E-form of the deuterated acid, as in the C-form, the polarization of the stronger bands in the series between 1185 and 1350 cm^{-1} is like that of the stronger components of the O-D bending doublet, which in this case also indicates that the vibrations which produce the series may be coupled with O-D bending parallel to the carboxyl plane.

The features of the structure of the E-form of stearic acid which have been inferred from the spectrum and shape of the crystals may be summarized as follows:

(1) The molecules are dimeric and the molecular configuration is like that in the C-form.

(2) The dimers are arranged in planar layers parallel to the surface of the lozenge-shaped crystal.

(3) The methylene chains have the orthorhombic packing, and their orientation is like that in the B-form and in monoclinic n-$C_{36}H_{74}$.

Further, it seems probable that the dimers are centrosymmetric, since there is no evidence of an increase in the number of infrared bands over that observed in the C-form. There are at least two dimers per unit cell, and if the doublet splitting of both carboxyl and chain bands indicates two infrared-active species, it is likely that the unit cell group is isomorphic to the point group C_{2h}. One would then expect a screw rotation axis parallel to the a_o axis of the orthorhombic subcell and a glide reflection normal to this axis, as in the B-form and in the monoclinic n-paraffins.

After it was recognized that crystals having an interedge angle of 74° might have more than one crystal form, the crystals of the ordinary acids grown previously were reexamined. It was found that a few crystals having the E-form were usually present when B-form crystals were grown. The two forms were so nearly identical that they had to be distinguished by their spectra. The spectrum of a crystal of palmitic acid having the E-form is shown in Fig. A 1-4 of Appendix I.

When a solution of stearic acid in ethyl ether was evaporated at 0° C, all crystals grown apparently had the E-form, though not all had the lozenge shape. Many took the form of long, thin ribbons. Attempts to produce the B-form of docosanoic acid, $CH_3(CH_3)_{20}COOH$, by evaporation of a carbon disulfide solution at 25° C yielded only crystals of the E-form.

Since the E-form is easily grown, it seems certain that it has been observed before. The fact that only two common monoclinic forms have been recognized is understandable. The spectra of polycrystalline samples of the C- and E-forms are not very different. The B- and E-forms are identical in appearance, and it is probable that the a- and b-axes of their unit cells are nearly equal. It may also be that the X-ray long spacings of these two forms are so nearly equal that they are difficult to distinguish.

After the section of this chapter dealing with the C-forms of ordinary and deuterated stearic acid had been completed, it was found that similar work on the C-form of the ordinary acid had been done by H. Susi.[69]

Stearic acid crystallizes in the C-form from a melt. By cooling a melt between two salt plates, Susi obtained an oriented film. He inferred the directions of the crystallographic axes from the absorption observed with polarized radiation.

Susi obtained a spectrum with the radiation incident normal to the ab-plane and with the electric vector first parallel to the a-axis, then parallel to the b-axis. This spectrum is similar to that of eicosanoic acid published by Jones <u>et</u> <u>al</u>.,[39] and to the spectra of stearic and palmitic acids shown in Figs. 4-1 and A 1-1 of the present work. Susi also observed the absorption with radiation polarized parallel to the ac-plane, and incident at angles of ± 45° to a surface parallel to the ab-plane. The spectrum obtained in this manner is analogous to that shown in Fig. 4-2.

Susi's experimental results and assignments are essentially in agreement with those presented here. He was not able to resolve the weaker CH_2 rocking doublets nor the CH_3 deformation doublet at 1371 and 1379 cm^{-1}. He observed all members of the 1187 - 1357 cm^{-1} series which were observed here, but concluded that the polarization of the bands varied over the series, contrary to results obtained in the present work.

The oriented film technique has the advantage that the samples

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[69] H. Susi, J. Am. Chem. Soc. <u>81</u>, 1535 (1959).

apparently are so large that it is not necessary to use the reflecting microscope. It has the disadvantage, however, that only the polymorph which crystallizes from the melt may be studied.

APPENDIX I

THE INFRARED SPECTRA OF FOUR POLYMORPHS OF PALMITIC ACID.

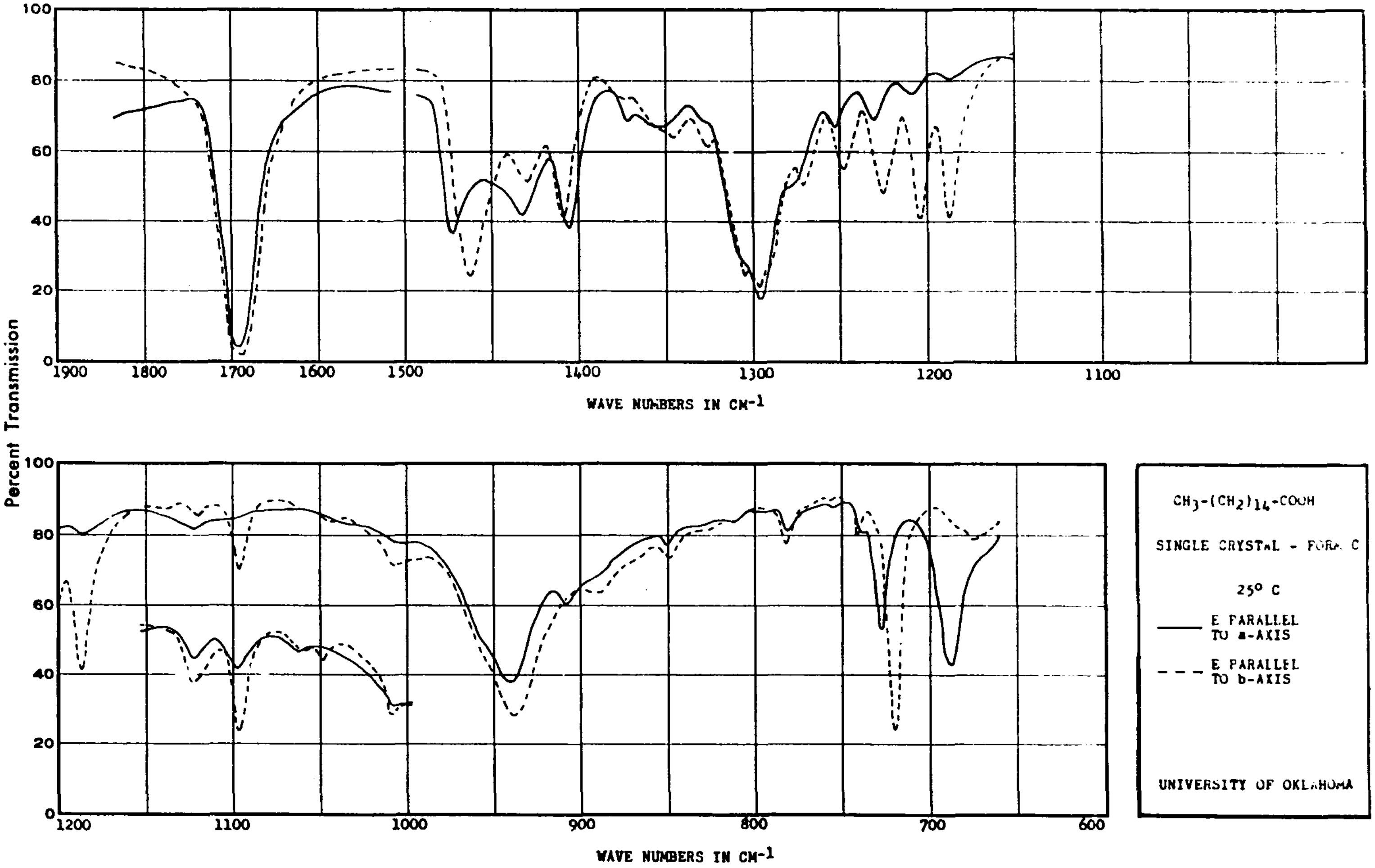

Fig. A 1-1. Infrared Spectrum of the C-Form of $CH_3(CH_2)_{14}COOH$; Radiation Incident Normal to the ab-Plane

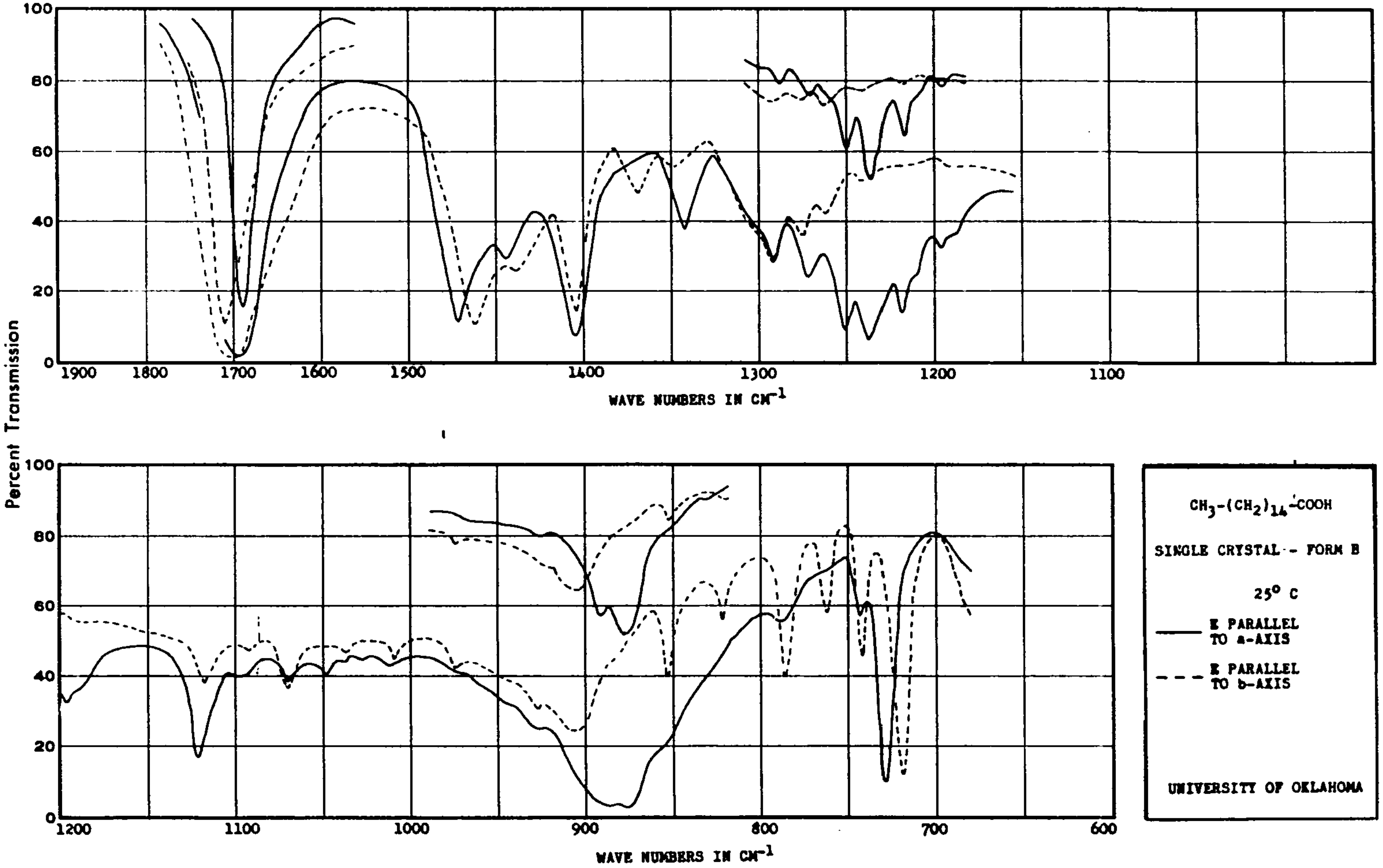

Fig. A 1-2. Infrared Spectrum of the B-Form of $CH_3(CH_2)_{14}COOH$; Radiation Incident Normal to the ab-Plane

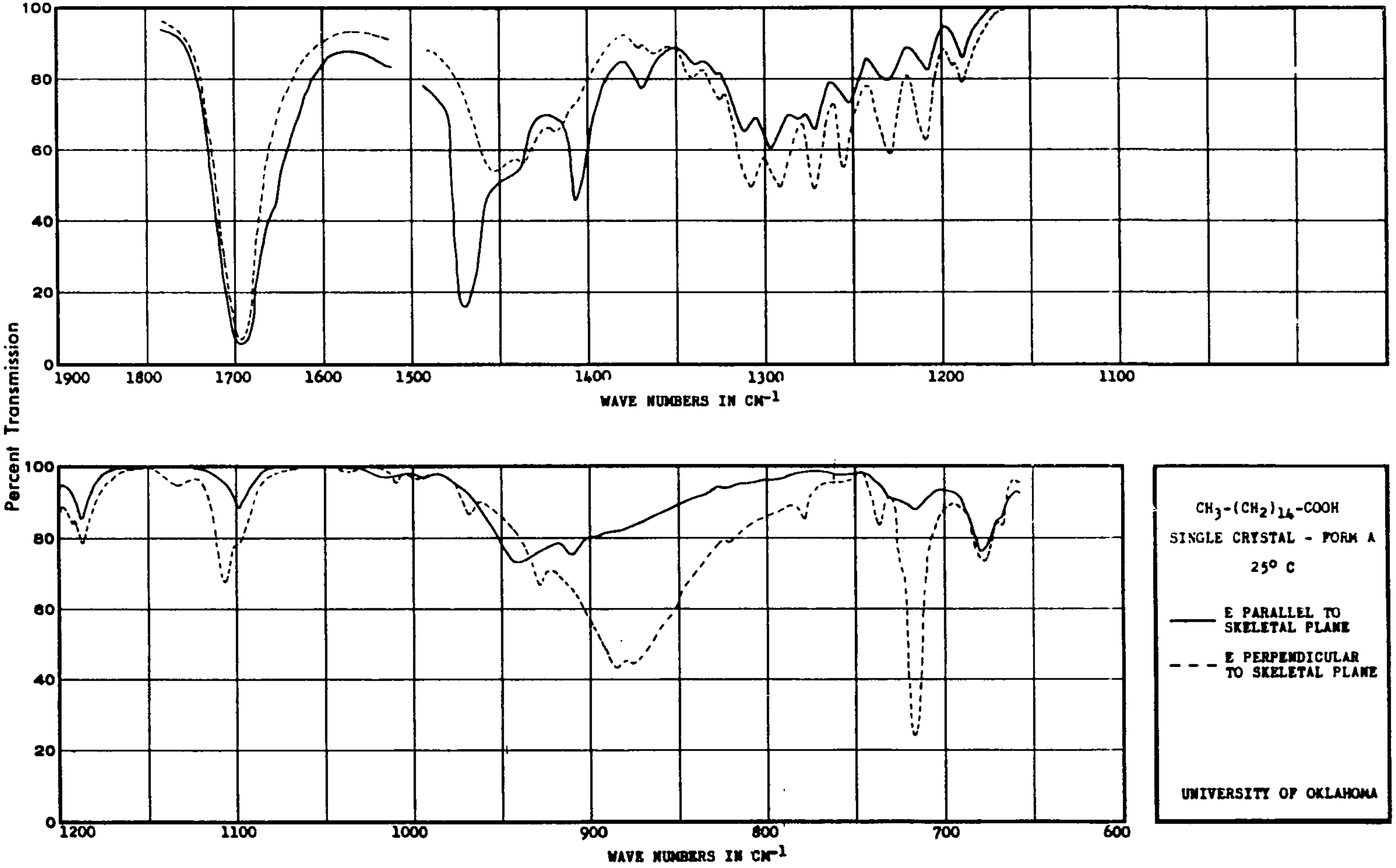

Fig. A 1-3. Infrared Spectrum of the A-Form of $CH_3(CH_2)_{14}COOH$; Radiation Incident Approximately Parallel to the Chain Axes

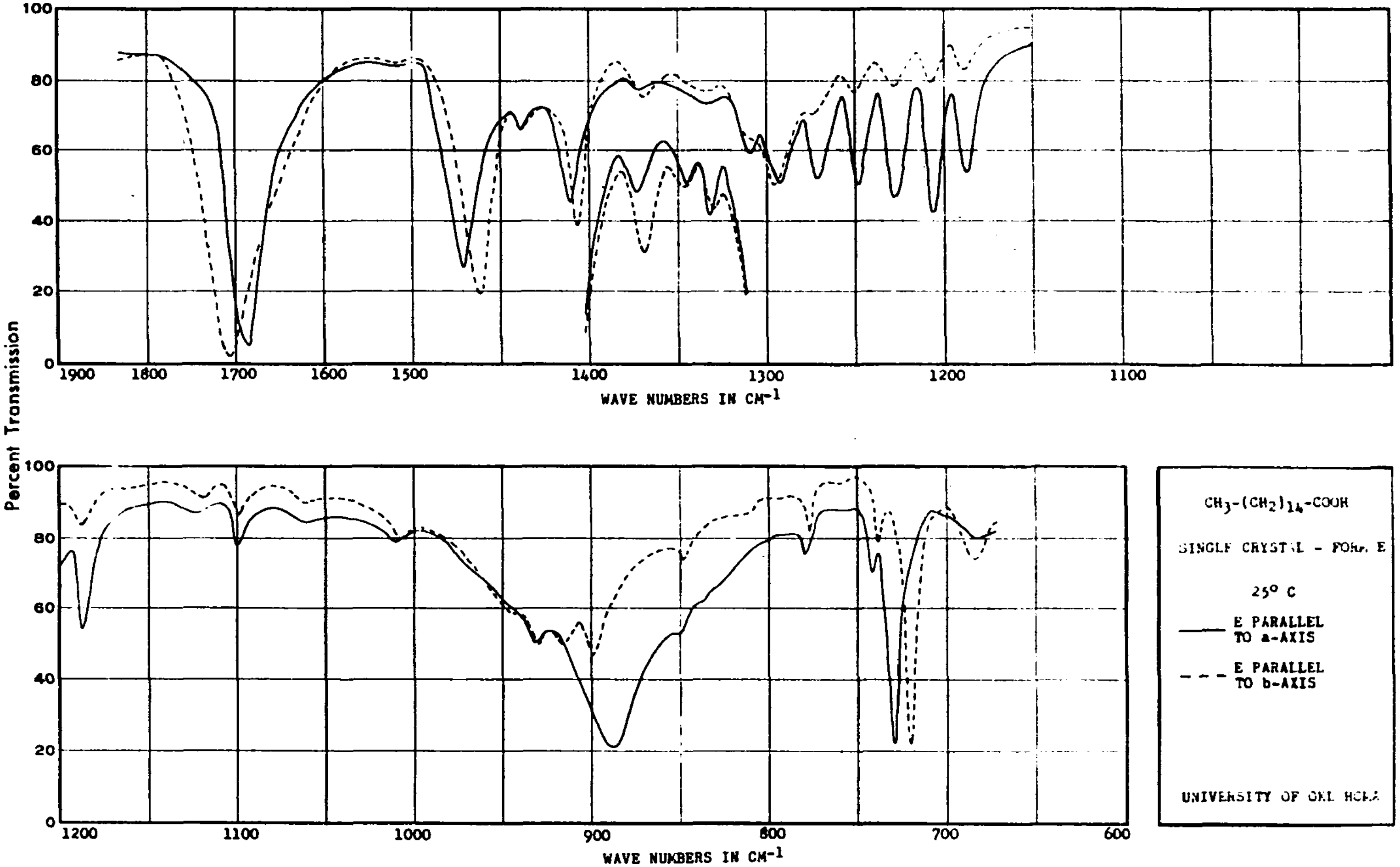

Fig. A 1-4. Infrared Spectrum of the E-Form of $CH_3(CH_2)_{14}COOH$; Radiation Incident Normal to the ab-Plane

APPENDIX II

THE C-H STRETCHING VIBRATIONS

In the infrared spectra of liquid n-paraffins, four bands between 2800 and 3000 cm^{-1} have been attributed to vibrations involving stretching of the C-H bonds. The symmetric and asymmetric stretching vibrations of the CH_3 groups have been associated with bands at 2872 and 2962 cm^{-1}, respectively. Bands at 2853 and 2926 cm^{-1} have been assigned as symmetric and asymmetric stretching of the CH_2 groups.[39] The corresponding bands of the crystalline n-paraffins are very near the same frequencies.

In the rest of this work, little attention was given the C-H stretching vibrations, since their assignments for the n-paraffins and related compounds are fairly well established. The spectra in the region 2800 to 3000 cm^{-1} of two crystals having the triclinic chain packing will be presented in this appendix, however. They provide some support for the assumptions regarding the polarization of lower-frequency bands appearing in the two curves of Figs. 3-5 and 4-7. Also, they give some additional information about the bands between 2800 and 3000 cm^{-1}.

The triclinic crystal form of the even-numbered n-paraffins has one molecule per unit cell. As discussed in Chapter III, the infrared-active vibrations should produce bands polarized either parallel or perpendicular to the skeletal plane. The symmetric stretching of the CH_2 and CH_3 groups, and one asymmetric stretching vibration of the CH_3 groups should be parallel to this plane. The asymmetric stretching of the CH_2 groups and one asymmetric CH_3 stretching vibration should be perpendicular to the plane.

The stronger bands in the spectrum of a triclinic crystal of n-$C_{20}H_{42}$ are shown in Fig. A 2. The spectrum was obtained in the same manner as that of n-$C_{18}H_{38}$ shown in Fig. 3-5. If it is assumed that the solid and broken curves distinguish between bands associated with changes in dipole moment parallel and perpendicular to the skeletal planes, the polarization of the bands in Fig. A 2 are consistent with most previous interpretations. The strong band at 2851 cm^{-1} is caused by symmetric CH_2 stretching, the weaker band at 2872 cm^{-1} represents symmetric CH_3 stretching, and the two bands at 2953 and 2962 cm^{-1} may be assigned as asymmetric stretching of the CH_3 groups perpendicular and parallel to the skeletal plane, respectively.

In the spectra of thinner crystals, obtained after Fig. A 2 was prepared, three bands are seen near 2900 cm^{-1}. A band at 2916 cm^{-1}, which is polarized perpendicular to the skeletal plane, may be assigned as asymmetric methylene stretching. What appears as a single broad band in the solid curve shown in Fig. A 2 is resolved into two bands, at 2898 and 2922 cm^{-1}, both polarized parallel to the skeletal plane. These bands may be interpreted as combination bands as follows. Mizushima and Shimanouchi[27] have reported Raman bands at 1442 and 1471 cm^{-1} in solid n-$C_{16}H_{34}$. If these bands represent vibrations of the totally symmetric species a_g of the group C_{2h} of the single molecule, the corresponding vibrations in n-$C_{20}H_{42}$, which may be expected to have very nearly the

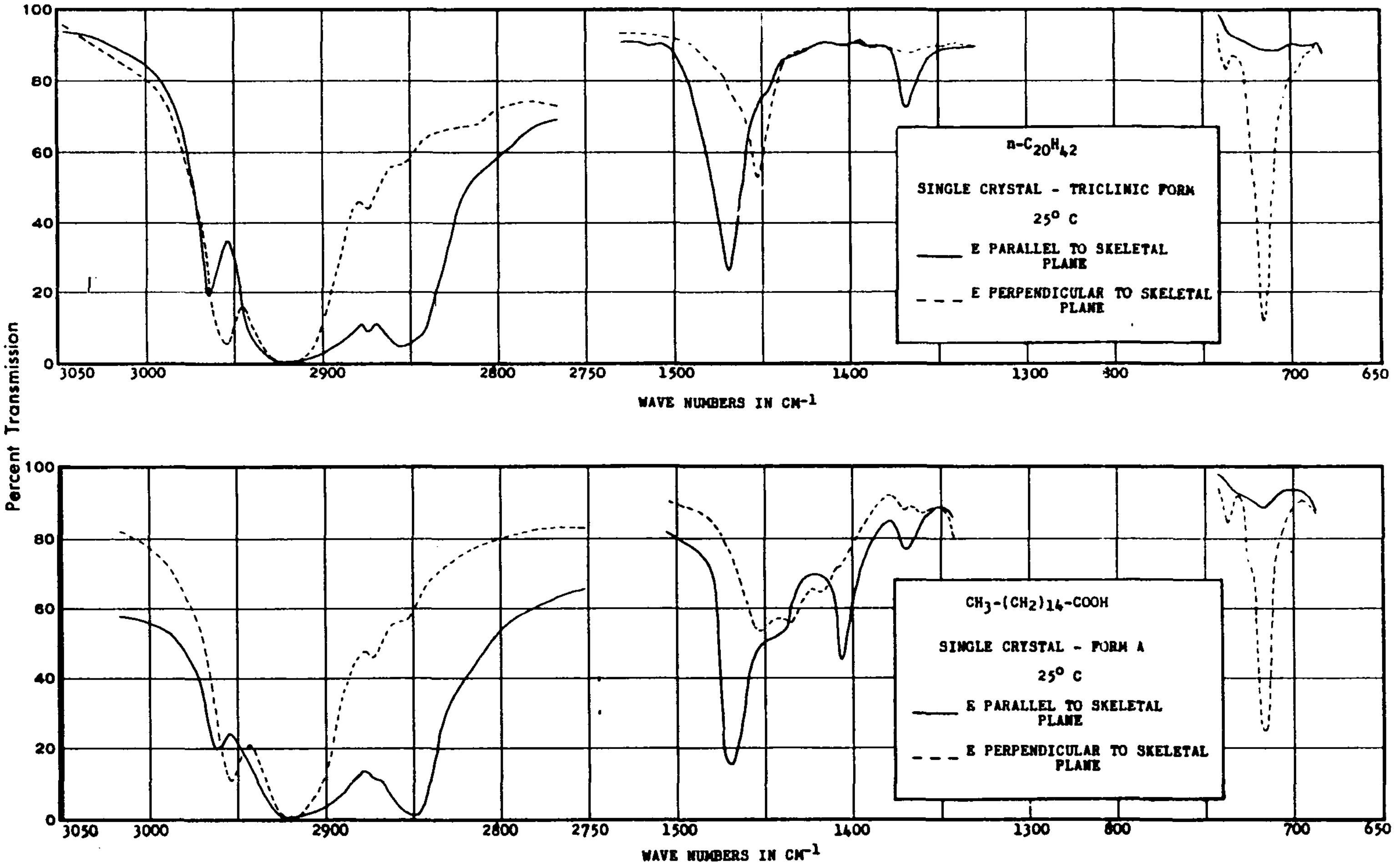

Fig. A 2. Infrared Spectra of Triclinic Crystals of $n-C_{20}H_{42}$ and $CH_3(CH_2)_{14}COOH$; Radiation Incident Approximately Parallel to the Chain Axes same frequencies, may combine with the strong infrared-active fundamental at 1470 cm^{-1} to produce the two bands at 2898 and 2922 cm^{-1}.

The fact that a band polarized parallel to the skeletal plane appears at 2898 cm^{-1} in the spectrum of the triclinic crystals, where no intermolecular doublet splitting occurs, casts some doubt on the assignment of a band near this position of polyethylene and monoclinic n-$C_{36}H_{74}$ [50] to the b-polarized component of the CH_2 asymmetric stretching doublet. It is more likely that both components of this doublet in the spectra of crystals having the orthorhombic chain packing lie very close to 2920 cm^{-1}.

In Fig. A 2, the spectrum of n-$C_{20}H_{42}$ is compared with that of a crystal of palmitic acid like the one whose spectrum is shown in Fig. A 1-3, and like the stearic acid crystal whose spectrum is shown in Fig. 4-6. The C-H stretching bands in the acid are superposed on a very broad absorption band which has been attributed primarily to stretching of the carboxyl O-H bond.[57] The latter is shown in Fig. A 2 by the lowering of the base line of the solid curve. Except for this difference and other differences caused by the carboxyl groups, the pattern of absorption is similar to that of the triclinic n-paraffin, indicating that the crystal of palmitic acid has the triclinic A-form.

APPENDIX III

THE SPLITTING AND POLARIZATION OF THE METHYLENE ROCKING DOUBLETS

Snyder[44,48] has shown that, when doublet splitting is disregarded, the frequency distribution in the series of infrared-active methylene rocking vibrations of the crystalline normal paraffins with chains twenty to thirty carbons long may be approximately described by the equation

(1) $w^2_{k,m} = a_o + 2a_1 \cos \phi_{k,m} + 2a_2 \cos 2\, \phi_{k,m}$,

where m is the number of CH_2 groups,

$\phi_{k,m} = \frac{k\pi}{m+1}$ $(k = 1, 3, 5, \cdots, \leqslant m)$, and a_o, a_1, and a_2 are constants. The low frequency limit of the series at 720 cm^{-1} was associated with w_{1m}. The remaining members of the series were associated with progressively higher values of k in order of increasing frequency, allowing for the bands masked by the intense band or doublet at the low frequency limit.

Snyder also has reported that the splitting of the rocking doublets observed in spectra of odd-numbered n-paraffins at -160° C can be represented by an equation

(2) $\Delta(w^2_{k,n}) = a + 2b \cos \phi_{k-2,n}$,

where $\phi_{n,k} = \frac{k\pi}{n-1}$, $(k = 1, 3, 5, \cdots, \leqslant n-2)$,

and n is the number of carbon atoms.[48]

Equation (1) has a form typical of the solution of the problem of a linear chain of m identical coupled simple harmonic oscillators.[29,30,48] Discrete values of the argument ϕ are obtained by imposing the proper boundary conditions.

Equations for w^2 from which $\Delta(w^2)$ may be derived can be obtained by considering two such chains side-by-side and including in the potential function quadratic terms for the interaction between an oscillator in one chain and its nearest and next-nearest neighboring oscillators in the adjacent chain.

In this Appendix, it will be demonstrated that results obtained with such a model, suitably modified for the various crystal forms, agree at least qualitatively with the splitting and polarization of the rocking doublets observed in the present work for crystals having the orthorhombic chain packing. The polarization of the rocking doublets in the odd-numbered n-paraffins is also predicted.

In this simple treatment, several assumptions are implicit. It is assumed that methylene rocking coordinates are defined for which the kinetic energy matrix is diagonal (perhaps of the type defined by Deeds[29]). It will be assumed that there are no terms in the potential function representing interactions between these coordinates and those of other types. The interaction between CH_2 groups in the rocking vibrations is assumed to be limited to nearest and next-nearest neighbors in the same and adjacent chains, and end-group effects are neglected in the calculations. It is assumed that the orthorhombic chain packing is the same for the crystals studied. Also, though there are four molecules per unit cell in some of the crystals, only two adjacent chains will be considered.

Finally, in comparing the spectral data with the results of the calculation, ϕ will be assumed to take on the values given in (1), and the values of k associated with particular doublets will be those which are most nearly consistent with the results of Snyder[44] and with the band sequences observed by Brown, Sheppard, and Simpson.[13]

Orthorhombic n-Paraffins

The contribution of the rocking vibrations to the kinetic energy of the two chains may be written

$$2\,T = \sum_n a\,(\dot{x}_n^2 + \dot{y}_n^2),$$

where the coordinates x_n belong to one, y_n to the other of two chains which pass through the orthorhombic subcell, and where n ranges from 1 to m (the number of methylene groups in a single chain).

A symmetric form of the corresponding potential function for the orthorhombic n-paraffins is

$$(3)\quad 2\,V = \sum_n k\,x_n^2 + k'(x_n - x_{n+1})^2 + k''(x_n - x_{n+2})^2$$
$$+ k\,y_n^2 + k'(y_n - y_{n+1})^2 + k''(y_n - y_{n+2})^2$$
$$+ 2e(x_n - y_n)^2 + 2e'(x_n - y_{n+1})^2 + 2e'(y_n - x_{n+1})^2,$$

where k is the force constant for the displacement of a methylene group from its equilibrium position, and k' and k'' are coefficients of terms representing the interaction between nearest and next-nearest neighbors, respectively, in the same chain. The constants e and e' are the coefficients of the interaction terms between nearest and next-nearest neighbors in adjacent chains.

The classical equations of motion then have the form

$$a\,\ddot{x}_n + (k + 2k' + 2k'' + 2e + 4e')\,x_n - k'(x_{n+1} + x_{n-1})$$

$$- k''(x_{n+2} + x_{n-2}) - 2ey_n - 2e'(y_{n+1} + y_{n-1}) = 0$$

$$a\,\ddot{y}_n + (k + 2k' + 2k'' + 2e + 4e')y_n - k'(y_{n+1} + y_{n-1})$$

$$- k''(y_{n+2} + y_{n-2}) - 2ex_n - 2e'(x_{n+1} + x_{n-1}) = 0.$$

If one assumes that

$x_n = x_o\, e^{i(wt - n\phi)}$ and $y_n = y_o\, e^{i(wt - n\phi)}$, then

$$(- a\,w^2 + k + 2k' + 2k'' + 2e + 4e' - 2k' \cos\phi - 2k'' \cos 2\phi)\, x_n$$

$$- (2e + 4e' \cos\phi)y_n = 0, \text{ and}$$

$$(- a\,w^2 + k + 2k' + 2k'' + 2e + 4e' - 2k' \cos\phi - 2k'' \cos 2\phi)y_n$$

$$- (2e + 4e' \cos\phi)x_n = 0.$$

The vanishing of the secular determinant requires that

$$(4)\quad w^2 = \frac{1}{a}\,(k + 2k' + 2k'' + 2e + 4e' - 2k' \cos\phi - 2k'' \cos 2\phi)$$

$$\pm \frac{1}{a}\,(2e + 4e' \cos\phi).$$

The first term corresponds to the right side of equation (1). The second term accounts for the doublet splitting and is similar to the right-hand side of equation (2). The transformation $\xi_n = x_n + y_n$, $\eta_n = x_n - y_n$ factors the secular determinant. Frequencies corresponding to ξ are given by the upper sign and those corresponding to η by the lower sign in (4). Solutions belonging to one of the two branches correspond to vibrations polarized parallel to the a-axis of the unit cell, and those belonging to the other are polarized parallel to the b-axis.

Monoclinic n-Paraffins

In the monoclinic n-paraffins and in the B-form (and presumably the E-form) of the n-fatty acids, corresponding methylene groups in the two adjacent chains in the unit cell are not nearest but next-nearest neighbors. Assuming that the packing of the chains is identical to that in the orthorhombic n-paraffins, the same coefficients for the interaction terms may be used, and the potential function has the same form as (3), except that the last three terms of (3) are replaced by

$$2e'\,(x_n - y_n)^2 \;+\; e\,(x_n - y_{n+1})^2 \;+\; e\,(y_n - x_{n+1})^2$$

$$+\; e'\,(x_n - y_{n+2})^2 \;+\; e'\,(y_n - x_{n+2})^2.$$

If ξ and η are defined as before, the solutions again separate into perpendicularly polarized branches which satisfy the equations

$$(5)\qquad \left.\begin{matrix} w_\xi^2 \\ \\ w_\eta^2 \end{matrix}\right\} = \begin{matrix} \frac{1}{a}\,(k \mp 2k' \mp 2k'' + 2e + 4e' - 2k'\cos\phi - 2k''\cos 2\phi) \\ \\ \pm\,\frac{1}{a}\,(2e' + 2e\cos\phi + 2e'\cos 2\phi) \end{matrix}$$

One branch corresponds to solutions belonging to the species b_u and the other to solutions belonging to species a_u of the unit cell group (isomorphic to C_{2h}).

The C-Form of the Normal Fatty Acids

In the C-form of the normal fatty acids, corresponding methylene groups in the two chains adjacent in the unit cell are so widely separated that their interaction need not be considered. The potential function for these crystals then has the form

$$\begin{aligned} 2\,V = \sum_n k\,x_n^2 &+ k'(x_n - x_{n+1})^2 + k''(x_n - x_{n+2})^2 + k\,y_n^2 \\ &+ k'(y_n - y_{n+1})^2 + k''(y_n - y_{n+2})^2 + e'(x_n - y_{n+1})^2 \\ &+ e'(y_n - x_{n+1})^2 + e(x_n - y_{n+2})^2 + e(y_n - x_{n+2})^2 \\ &+ e'(x_n - y_{n+3})^2 + e'(x_n - y_{n+3})^2. \end{aligned}$$

The usual procedure gives the two branches

$$(6) \quad \left.\begin{matrix} w_\xi^2 \\ \\ w_\eta^2 \end{matrix}\right\} = \begin{matrix} \frac{1}{a}\,(k + 2k' + 2k'' + 2e + 4e' - 2k'\cos\phi - 2k''\cos 2\phi) \\ \\ \pm\,\frac{1}{a}\,(2e'\cos\phi + 2e\cos 2\phi + 2e'\cos 3\phi) \end{matrix}$$

corresponding to the species a_u and b_u of the unit cell group.

For the three types of crystals considered,

$$(7) \quad w_\xi^2 - w_\eta^2 = \frac{4}{a}\begin{cases} e + 2e'\cos\phi \\ e' + e\cos\phi + e'\cos 2\phi \\ e'\cos\phi + e\cos 2\phi + e'\cos 3\phi \end{cases}$$

If $\phi = k\pi/m+1$, and $k = 1$ at the lower limit of the rocking series, $\phi \cong 0$ at this limit, and $w_\xi^2 - w_\eta^2 \cong 4(e + 2e')/a$. The sign of $w_\xi^2 - w_\eta^2$ depends on the phase relationship between x and y, which is not yet defined. If $e + 2e'$ is positive, w_ξ $(k = 1)$ is the frequency of the higher member of the strong doublet, and ξ corresponds to vibrations polarized nearly or precisely parallel to the a_0-axis of the orthorhombic subcell.

Comparison with Experiment

In the spectra of orthorhombic crystals of the odd-numbered n-paraffins, Snyder has observed that the splitting of the rocking doublets decreases with increasing frequency toward a minimum near the middle of the series and then increases again. From the spectra of n-$C_{21}H_{44}$ and n-$C_{23}H_{48}$ at -160° C, he obtained values $a = -0.005 \times 10^5\ \text{cm}^{-2}$ and $b = 0.092 \times 10^5\ \text{cm}^{-2}$ for the coefficients in (2). The second term in (2) dominates the splitting and its variation over the series.

The values which he allows ϕ to take in (2) differ from those assigned to ϕ in (1). In the treatment given here, however, no such difference is implied. A fairly good correlation with Snyder's results may still be obtained if it is assumed that $2\,e = e'$, and $e/a = 1000\ \text{cm}^{-2}$. If these values apply to the other crystals as well, (7) becomes

$$(8)\qquad w^2_{\xi} - w^2_{\eta} = 4000\ \text{cm}^{-2} \times \begin{cases} 1 + 4 \cos \phi \\ 2 + \cos \phi + 2 \cos 2\phi \\ 2 \cos \phi + \cos 2\phi + 2 \cos 3\phi \end{cases}$$

These functions for $0 \leqslant \phi \leqslant \pi$ are represented by the curves in Fig. A 3.

In Fig. A 3(a), $\Delta(w^2)$ for orthorhombic n-$C_{21}H_{44}$, n-$C_{23}H_{48}$, and n-$C_{25}H_{52}$ are plotted against ϕ defined as in (1). The frequencies and k values taken from Snyder's paper are listed in Table A 3-I. Also included in the Table are the values of ϕ/π and $\Delta(w^2)$. The latter are rounded off to correspond to the number of significant digits in the

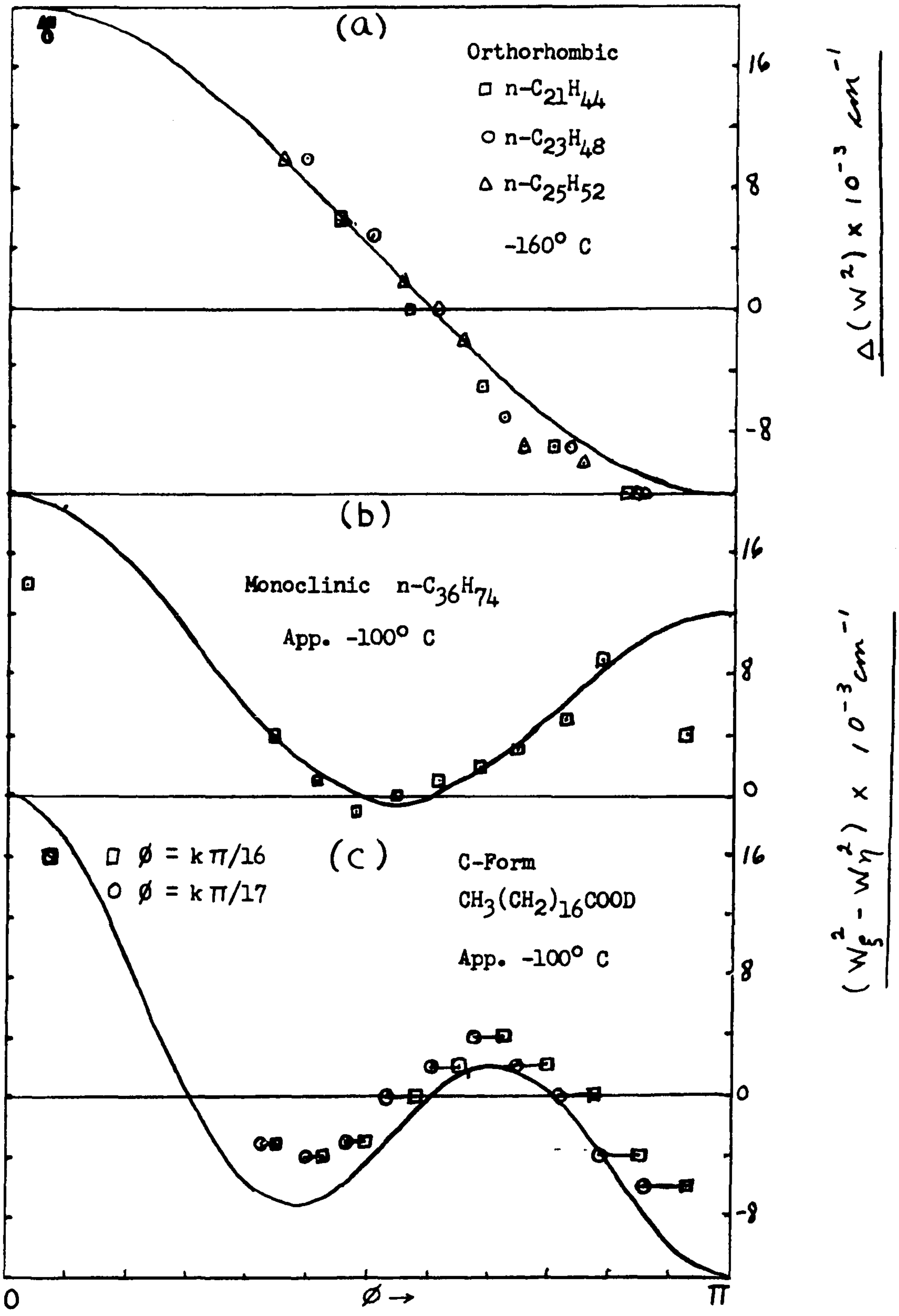

Fig. A 3 Correlation of Observed Splitting and Polarization of CH_2 Rocking Modes with Predictions Based on a Simple Model

TABLE A 3-I

THE SEPARATION OF THE CH_2 ROCKING DOUBLETS OF ORTHORHOMBIC n-$C_{21}H_{44}$, n-$C_{23}H_{48}$, AND n-$C_{25}H_{52}$ AT -160° C

	w (Wave Number)	$w^2 \times 10^{-3}$	$\Delta(w^2) \times 10^{-3}$	k	ϕ/π
$C_{21}H_{44}$	722	521	19	1	0.05
	735	540			
	761	579	6	9	0.45
	765	585			
	807		0	11	0.55
	862	743	5	13	0.65
	865	748			
	922	850	9	15	0.75
	927	859			
	980	960	12	17	0.85
	986	972			
$C_{23}H_{48}$	722	521	18	1	0.45
	734	539			
	748	560	10	9	0.41
	755	570			
	782	611	5	11	0.50
	785	616			
	831		0	13	0.59
	883	780	7	15	0.68
	887	787			

TABLE A 3-I (Concluded)

	w (Wave Number)	$w^2 \times 10^{-3}$	$\Delta(w^2) \times 10^{-3}$	k	ϕ/π
	938	880	9	17	0.77
	943	889			
	990	980	12	19	0.86
	996	992			
$C_{25}H_{52}$	722	521	19	1	0.04
	735	540			
	740	548	10	9	0.37
	747	558			
	765	585	6	11	0.46
	769	591			
	804	646	2	13	0.54
	805	648			
	851	724	2	15	0.62
	852	726			
	900	810	9	17	0.71
	905	819			
	951	904	10	19	0.79
	956	914			
	998	996	12	21	0.87
	1004	1008			

TABLE A 3-II

THE SEPARATION AND POLARIZATION OF THE CH_2 ROCKING DOUBLETS OF MONOCLINIC n-$C_{36}H_{74}$ AT APPROXIMATELY -100° C

w (Wave Number)	Polarization	$w^2 \times 10^{-3}$	$(w_\xi^{\ 2} - w_\eta^{\ 2}) \times 10^{-3}$	k	ϕ/π
719	b	517	14	1	0.03
729	a	531			
741	b	550	4	13	0.37
744	a	554			
754	b	569	1	15	0.43
755	a	570			
776	a	602	-1	17	0.49
777	b	603			
805	b,a		0	19	0.54
837	b	701	1	21	0.60
838	a	702			
872	b	760	2	23	0.66
873	a	762			
907	b	824	3	25	0.71
909	a	827			
943	b	890	5	27	0.77
946	a	895			
977	b	954	9	29	0.83
982	a	963			
1032	b	1066	4	33	0.94
1034	a	1070			

TABLE A 3-III

THE SEPARATION AND POLARIZATION OF THE CH_2 ROCKING DOUBLETS IN THE C-FORM OF DEUTERATED STEARIC ACID AT APPROXIMATELY -100° C

w (Wave Number)	Polarization	$w^2 x 10^{-3}$	$(w_\xi{}^2 - w_\eta{}^2) x 10^{-3}$	k	k/16	k/17
722	b	521	16	1	0.06	0.06
733	a	537				
742	a	551	-3	6	0.37	0.35
744	b	554				
758	a	575	-4	7	0.44	0.41
761	b	579				
782	a	611	-3	8	0.50	0.47
783	b	614				
808	b,a		0	9	0.56	0.53
840	b	705	2	10	0.62	0.59
841	a	707				
876	b	767	4	11	0.69	0.65
878	a	771				
913	b	833	2	12	0.75	0.70
914	a	835				
951			0	13	0.81	0.76
993	a	986	-4	14	0.87	0.82
995	b	990				
1015	a	1030	-6	15	0.94	0.88
1018	b	1036				

frequencies, and the sign assumed for $\Delta (\nu^2)$ is that consistent with (8).

In Figure A 3(b), values of $\nu_\xi^2 - \nu_\eta^2$ calculated for the rocking doublets of n-$C_{36}H_{74}$ at about -100° C are plotted against $\phi = k\pi/35$. The k values were obtained by extrapolation from the band sequences observed by Snyder.[44] The significant data are given in Table A 3-II.

In Figure A 3(c), the values of $\nu_\xi^2 - \nu_\eta^2$ for the C-form of deuterated stearic acid at about -100° C are plotted. Frequencies and other pertinent data are included in Table A 3-III. Since the distribution of the rocking doublets in the n-fatty acids corresponds roughly to that in a n-paraffin with one less CH_2 group, points are plotted both for $\phi = k\pi/17$ and $\phi = k\pi/16$. Points for the same k-values are connected by a bar.

In both Figs. A 3(b) and (c), the sign and magnitude of the observed values of $\nu_\xi^2 - \nu_\eta^2$ show fairly close agreement with the curves obtained from the simple model. The consistent results in (a), (b) and (c) indicate that the signs assumed for values of $\Delta (\nu^2)$ plotted in (a) are correct, so that the rocking doublets of the orthorhombic n-paraffins with frequencies below that for which the splitting is a minimum have low frequency components polarized in the b-direction, while in doublets above the minimum, these components are polarized in the a-direction.

When one considers the differences in molecular composition, temperature, and chain lengths of the compounds for which splittings are plotted in Fig. A 3, it may seem surprising that the points fit the curves so well. It should be pointed out that the fit is not extremely sensitive to changes in the ratio e/e', in fact, a rough approximation to the experimental data may be obtained for all values of e/e' between 0 and 1, provided $4(e + 2e')/a = 15{,}000$ to $20{,}000\ \mathrm{cm}^{-2}$. Any attempt to determine precise values for these interaction constants will require a better knowledge of the frequencies. The range of values indicated, however, has some significance.

Stein,[47] in his treatment of the splitting of the strong rocking doublet at 720 - 730 cm^{-1} and the methylene deformation doublet at 1465 cm^{-1}, neglected the interaction between next-nearest neighbors. If e/e' lies in the range indicated above, then e' is of the order of magnitude or greater than e , which implies that the interaction between next-nearest CH_2 groups in adjacent chains is at least as great and possibly greater than that between nearest neighbors in the rocking vibrations.

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