

Vibrational spectra in the C—H stretching region and the structure of the polymethylene chain

R. G. SNYDER,* S. L. HSU† and S. KRIMM

Midland Macromolecular Institute, Midland, MI 48640, U.S.A.
Harrison M. Randall Laboratory of Physics and Macromolecular Research Center,
University of Michigan, Ann Arbor, MI 48104, U.S.A.

(Received 18 March 1977)

Abstract—The C—H stretching regions of both the Raman and i.r. spectra of the extended polymethylene chain have broad secondary maxima. In the case of the Raman spectrum, line shapes are dependent on the environment of the chain, a fact which has been previously exploited in the study of biosystems. We have explained this phenomenon in terms of Fermi resonance interaction between the methylene symmetric C—H stretching mode and appropriate binary combinations involving the methylene bending mode. It is emphasized that appropriate binary states are to be found throughout the Brillouin zone and not just at its center. It is the resulting continuum of binary states which leads to broad secondary bands. The shapes of these bands depend on the dispersion of the bending mode fundamental. For the isolated chain only parallel dispersion is involved, but in the case of the crystal perpendicular dispersion is equally important and leads to the observed dependence on crystal structure. All secondary bands have been accounted for in these terms. The ratio of the Raman intensities of the symmetric C—H stretching fundamentals to the antisymmetric is found to be about 5 and is independent of environment. The relevance of these results to studies on biosystems is briefly discussed.

INTRODUCTION

The C—H stretching region of the Raman and i.r. spectra of the extended polymethylene chain is inadequately understood. Interpretations of this region have long been unsatisfactory in that unresolved contradictory assignments have appeared in the literature [1–3]. A better understanding is also needed in order to utilize Raman spectra to investigate the structure of the lipid component of biomembranes [4–7], since in recent studies conclusions have been based on observed changes in the C—H stretching band intensities. In this paper we review what is known about the C—H stretching vibrations of the extended chain, present new Raman spectra illustrating their sensitivity to chain packing, and offer an explanation of how the observed differences between the Raman spectra are related to packing structure.

Until recently it has been assumed that, since the C—H stretching modes are highly localized and involve nearly pure hydrogen motion, they are essentially insensitive to the molecular conformation and environment, in sharp contrast to the skeletal modes at lower frequencies. This belief appeared intuitively sound and was supported by a half century of evidence from i.r. spectroscopy, essentially none of it to the contrary. It is therefore initially surprising to find that changes in the C—H stretching region of Raman spectra can be

correlated with polymethylene chain conformation and chain environment [4–7]. In fact this correlation has now become the basis for an important technique for investigating lipid structure in biological membranes.

Basically what is observed, is that the ratio of the peak heights of the two strongest Raman lines (2880 and 2845 cm^{-1}) in the C—H stretching region is sensitive both to the conformation of the chain and, in the case of the extended chain, to the packing of chains. Attempts to explain this phenomenon have exposed some superficiality in previous assignments for the isolated extended polymethylene chain. Recently some long overdue clarification has appeared in two papers, one by SPIKER and LEVIN [8] on the methylene and methyl group mode assignments and another by GABER and PETICOLAS [9] on the role of intermolecular effects.

Nevertheless we find the present state of understanding unsatisfactory. For example, although the two strongest Raman lines can be associated [8] with symmetric and antisymmetric C—H stretching modes of the methylene group, the origin of the intense broad structure which pervades this region for these ordered systems remains to be explained. Although the peak height ratios change with structure, this does not necessarily apply to the ratio of the intensities. We would like to know what the real intensity ratio is, what shapes the lines have, and why they change as they do. Among other things we would also like to know why it is that Raman spectra are much more sensitive to structural change than i.r. spectra.

To help answer these questions we have measured and identified characteristic features in the Raman spectra of the extended polymethylene chain in several

* To whom correspondence should be addressed at Western Regional Research Center, 800 Buchanan Street, Albany, California 94710, U.S.A.

† Present Address: Allied Chemical, Morristown, New Jersey, U.S.A.

Table 1. Mode designations, species, and assignments for methylene and methyl groups of the extended polymethylene chain

	Raman			Infrared			Description
	Mode	Species	ν_{obs} (cm^{-1})	Mode	Species	ν_{obs} (cm^{-1})	
CH ₂ modes	$\left\{ \begin{array}{l} d^-(0) \\ d^+(0) \\ \delta(0) \end{array} \right.$	B_{1g}	2880	$d^-(\pi)$	B_{2u}	2920	Antisym. C—H stretch
		A_g	2850	$d^+(\pi)$	B_{3u}	2850	Sym. C—H stretch
		A_g	1443	$\delta(\pi)$	B_{3u}	1467	HCH bend
					$P(\pi)$	B_{2u}	720
CH ₃ modes (<i>n</i> -paraffins)	$\left\{ \begin{array}{l} r_a^- \\ r_b^- \\ r^+ \end{array} \right.$		2964	r_a^-		2962	Asym. C—H stretch (in-skeletal plane)
			2952	r_b^-		2953	Asym. C—H stretch (out-of-skeletal plane)
			2871	r^+		2873	Sym. C—H stretch

known crystal structures. In our interpretation we consider both i.r. and Raman spectra since the same complicating factors underlie both. In this work we rely heavily on our present understanding of the inter- and intramolecular dynamics of the *n*-paraffins and polyethylene [1, 3, 10–12].

ASSIGNMENT OF THE C—H STRETCHING MODE FUNDAMENTALS

In this section we describe the C—H stretching region of the i.r. and Raman spectra of extended polymethylene chains and consider the assignment of the fundamental modes. We will defer until later a discussion of the origin of the secondary structure, which is prominent in the Raman, and present but obscured in the i.r.

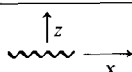
It will be convenient for our purposes to designate modes in an abbreviated manner. Thus for the methyl group we use r^- and r^+ to indicate degenerate and symmetric C—H stretching. For the methylene group we use d^- , d^+ , δ , and P to indicate antisymmetric C—H stretching, symmetric C—H stretching, HCH

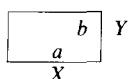
bending, and CH₂ rocking. These symbols follow the conventions of [3] and [10]. When applicable, vibrations of the chain will be described in terms of the phase angle, ϕ , between vibrations of adjacent CH₂ groups, whose value at the zone center is 0 or π . Conventions regarding the symmetry species of the isolated chain are those of [10] while the conventions regarding ϕ and the symmetry species of the orthorhombic crystal will follow those of [11]. A summary of these designations will be found in Tables 1 and 2.

Previous analyses of the vibrational spectra of the polymethylene chain have tended to ignore the details of the C—H stretching and HCH bending regions. In the earlier stages of interpretation such neglect was understandable since a greater uncertainty and hence challenge seemed to lie in the analyses of the more highly coupled modes, i.e. the methylene rocking, twisting, and wagging vibrations as well as those of the carbon skeleton. Furthermore, on the basis of the i.r. evidence it appeared that the interpretation of C—H stretching and methylene bending modes was almost trivial. Thus the i.r. spectrum of the extended polymethylene chain was always found to exhibit two very intense absorption bands, near 2920 and 2850 cm^{-1} , which could be confidently assigned to antisymmetric and symmetric C—H stretching vibrations, respectively; with equal certainty, the strong band near 1465 cm^{-1} could be assigned to methylene bending. Even the small perturbations arising from intermolecular interactions between two chains in a unit cell can be understood at least qualitatively: in the case of orthorhombic polyethylene the effect of the interaction is to split into two components the i.r. band assigned to bending [13, 14]. The narrowness of the components and the magnitude of the separation ($\sim 13 \text{ cm}^{-1}$) permit the splitting to be easily observed. Although predicted, this splitting is not easily observed in the case of C—H stretching, for these bands are broader and the separation of their components is less. The separation of components for methylene bending, C—H stretching, and other fundamentals of the chain can be accounted for reasonably well using a model based on atom-atom potentials [11]. In summary, except for some relatively minor features to be dis-

Table 2. Correlation of vibrational modes of the polymethylene chain with modes of orthorhombic polyethylene

	Species* (chain)	Species† (cryst.)
$d^-(0)$	$B_{1g}(yz)$	$A_g + B_{3g}(XY)$
$d^+(0)$	A_g	
$\delta(0)$		
$d^-(\pi)$	$B_{2u}(y)$	$B_{1u}(X) + B_{2u}(Y)$
$P(\pi)$		
$d^+(\pi)$	$B_{3u}(z)$	
$\delta(\pi)$		

* Chain axes definition 

† Crystal axes definition 

cussed later, the interpretation of the i.r. spectrum appears entirely satisfactory.

By contrast, the earliest Raman spectra [15, 16] of the extended chain exhibited complexities in the C—H stretching and methylene bending regions. These were difficult to explain, and they were essentially ignored. The development of laser Raman techniques has resulted in obvious exposure of these complexities, which are the focus of our present analysis. We will first consider the i.r. spectrum in more detail, and then will turn our attention to the complexities in the Raman spectrum.

THE INFRARED ACTIVE MODES

In this section the observed C—H stretching region in the i.r. will be examined. We include the methyl group since it also occurs in many of the systems of interest.

As mentioned earlier, methylene C—H stretching modes have long been considered to be group frequencies in the i.r. Standard references [17] list 2925 and 2855 cm^{-1} for $d^-(\pi)$ and $d^+(\pi)$ respectively. A range of ± 10 cm^{-1} from these values encompasses the frequencies observed for the extended chain in nearly all environments and includes the frequencies observed for the chain in solution and in the melt.

An estimated value of 3.0 ± 0.4 for the ratio of the integrated intensities of $d^-(\pi)$ to $d^+(\pi)$ is found by averaging the values for crystalline *n*-hexane, *n*-heptane and *n*-octane [18]. This average is in satisfactory agreement with the value of 2.0 which is calculated from a simple bond moment model with tetrahedral geometry.*

The C—H stretching vibrations, r^+ and r^- , of the methyl group occur in i.r. spectra at nearly the same frequencies as in the Raman. In the case of the crystalline *n*-paraffins the i.r. bands have been previously assigned [3] from spectra similar to those in Fig. 1. The symmetric stretch r^+ occurs near 2873 cm^{-1} . The components of the asymmetric stretch r^- occur at 2963 and 2953 cm^{-1} . Single crystal measurements [2] show that the higher frequency mode is polarized parallel to the skeletal plane while the lower frequency component is perpendicular.

Correlation splitting for both $d^-(\pi)$ and $d^+(\pi)$ occurs for the orthorhombic structure of polyethylene and for the orthorhombic and monoclinic structures of the *n*-paraffins [14, 19]. It is very difficult to separate and identify the components experimentally because the high intensity of the fundamentals makes it necessary to employ very thin crystals for the polarization measurements. In one i.r. study [14] on a single crystal

* The model assumes $\partial\bar{\mu}/\partial r$ is along the C—H bond. Then the ratio $I(d^-)/I(d^+) = \tan^2 \alpha/2$ where α is the angle between the C—H bonds.

† For the orthorhombic and monoclinic structures the skeletal planes of the two chains are nearly perpendicular to one another. Thus the two components should be nearly equal in intensity.

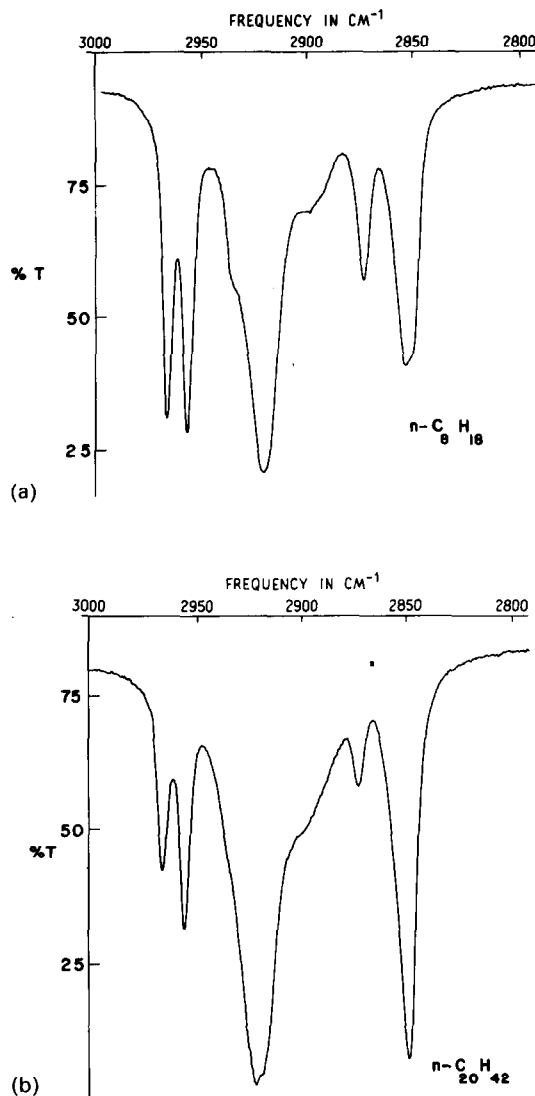


Fig. 1. C—H stretching region of the i.r. spectra of crystalline (a) $n\text{-C}_8\text{H}_{18}$ and (b) $n\text{-C}_{20}\text{H}_{42}$ at -180°C .

of $n\text{-C}_{36}\text{H}_{74}$ the splitting of both $d^-(\pi)$ and $d^+(\pi)$ was reported. In the case of $d^-(\pi)$ the very strong band at 2920 cm^{-1} is accompanied by a second, much weaker, band at 2898 cm^{-1} of a different polarization. However, the great disparity in intensity between the two components is not consistent with the expectation that they should be nearly equal,† as is indeed observed [19] for the correlation split fundamentals $\delta(\pi)$ and $P(\pi)$. Furthermore, the 2898 cm^{-1} band appears in the spectrum of the triclinic form of $n\text{-C}_{20}\text{H}_{42}$ (Fig. 1), where correlation splitting cannot occur because the structure has only one molecule per unit cell. On the other hand, the case for observed correlation splitting of the $d^+(\pi)$ fundamental is convincing. The observed band at 2850 cm^{-1} consists of an unresolved doublet whose components have about the same peak heights. The higher frequency component is polarized along the *b* axis and the lower frequency component along *a*.

The estimated separation is about $+7\text{ cm}^{-1}$, consistent with the small value ($+3\text{ cm}^{-1}$) estimated from theory [11].

Two bands remain to be explained. Both are relatively broad and weak, and both are obscured by the 2920 cm^{-1} band. The one near 2898 cm^{-1} has just been mentioned. Another near 2930 cm^{-1} is less obvious in the spectra of the longer chains. However, it can be seen clearly in the spectrum of *n*-octane (Fig. 1). The polarizations of both bands have been determined from measurements on a crystal of triclinic $n\text{-C}_{20}\text{H}_{42}$ [2]. They are found to be the same as that of the $d^+(\pi)$ fundamental. In that study the higher frequency band was placed at 2922 cm^{-1} , and we shall use this frequency here. A discussion concerning the origin of these bands will be deferred until after the observed Raman spectra have been discussed. Since certain of the Raman bands are of a similar origin, it will be appropriate to discuss both kinds of spectra together.

THE RAMAN ACTIVE MODES

This region appears more complex in the Raman than in the i.r., and its features are clearly dependent on chain packing, as the spectra displayed in Fig. 2 show. The spectra of polyethylene, and of the orthorhombic and monoclinic forms of the *n*-paraffins are essentially identical, in keeping with the fact that for all three cases the chain packing is essentially the same [20–22]. However, the triclinic form of the *n*-paraffins has a different structure [23] as does the hexagonal form [24], and these differences are reflected in the Raman spectra.

The above spectra share some common features. There is an intense and consistently narrow line near 2879 cm^{-1} which can be identified with $d^-(0)$. There is another intense, but broader, line (or lines) near 2845 cm^{-1} which can be associated with $d^+(0)$. In addition there is a very broad and asymmetric band which underlies the 2879 cm^{-1} line and which extends with diminishing intensity to about 2960 cm^{-1} . Finally there is a broad, less intense band near 2933 cm^{-1} . Most of the integrated intensity, as we shall see, is under the broad bands.

The differences between the spectra are most pronounced in the 2845 cm^{-1} region. For the orthorhombic and orthorhombic-related structures, there is a single broad line at 2846 cm^{-1} ; for the triclinic structure there are two maxima, at 2855 and 2846 cm^{-1} ; and for the hexagonal structure there is a single, narrower line at 2846 cm^{-1} . In all cases the 2879 cm^{-1} line is narrow, though it is least narrow for the higher temperature hexagonal structure.

When methyl groups are present, there are lines at 2964 and 2952 cm^{-1} . These are very near the i.r. bands observed at 2962 and 2953 cm^{-1} , and therefore, as in the i.r., they are assigned to r_a^- and r_b^- respectively. We assign the weak shoulder observed at 2871 cm^{-1} to r^+ , again in keeping with the i.r. assignment of r^+ to a band at 2873 cm^{-1} . We believe the assignment

of r^+ to 2935 cm^{-1} , as proposed in [8] to be incorrect since it is not compatible with the i.r. assignment [3]. Furthermore, we will show that the broad 2935 cm^{-1} band is part of the structure of the $d^+(0)$ fundamental.

The lines associated with $d^+(0)$ have been separated from those associated with $d^-(0)$ by means of appropriate polarized Raman measurements on oriented extended chains. The oriented chains in our experiment are in an orthorhombic crystal. As a consequence the analysis is complicated by the correlation splitting that results from the presence in this structure of two chains per unit cell. As indicated in Table 2, each fundamental is split into two components: one component belongs to symmetry species A_g and the other to B_{3g} . However, in spite of the fact that pairs of the components of $d^+(0)$ and $d^-(0)$ have common symmetry, it turns out that they can still be separated. The argument focuses on the form of the derived polarizability tensors for the various vibrational components, under the assumption that d^+ and d^- do not mix in the crystal. That d^+ and d^- modes do not mix significantly as a result of crystal interaction is a reasonable assumption since higher frequency intramolecular modes in non-polar crystals are ordinarily not significantly affected by intermolecular forces. In our case there is no experimental evidence for mixing. The fact that the observed frequencies of the C—H stretching fundamentals in the i.r. and Raman spectra are insensitive to crystal structure is experimental evidence against mixing.

Crystal symmetry dictates that the A_g tensor must be diagonal and that the B_{3g} tensor must have only one non zero element, α'_{XY} . Under the assumption that $d^+(0)$ and $d^-(0)$ do not mix, the only non zero elements of the derived polarizability tensor are

$$\begin{array}{l} d^+(0) \quad \begin{array}{l} A_g: \alpha'_{XX}, \alpha'_{YY}, \alpha'_{ZZ} \\ B_{3g}: \alpha'_{XY} \end{array} \\ d^-(0) \quad \begin{array}{l} A_g: \alpha'_{XX} = -\alpha'_{YY} \\ B_{3g}: \alpha'_{XY} \end{array} \end{array}$$

a result which follows when the tensors for $d^+(0)$ and $d^-(0)$ of two isolated chains are transformed into the orthorhombic crystal.

Of the above four derived tensors only that which is the A_g component of $d^+(0)$ has a non zero α'_{ZZ} element. Thus the spectrum of an oriented sample measured under ZZ polarization will not show the $d^-(0)$ fundamental. Also $d^+(0)$ will essentially have the same band shape as it does in the Raman spectrum of a randomly oriented polycrystalline sample. The reason for the latter is that the B_{3g} component of $d^+(0)$, which might have a structure different from that of the A_g component, is expected to have a very low intensity relative to the A_g component and consequently will contribute little to the spectrum of the polycrystalline sample. It is our estimate that the B_{3g} component contributes less than 5% to the total $d^+(0)$ intensity. This value is based on an oriented gas model calculation of the Raman intensities of the orthorhombic crystal [25] in

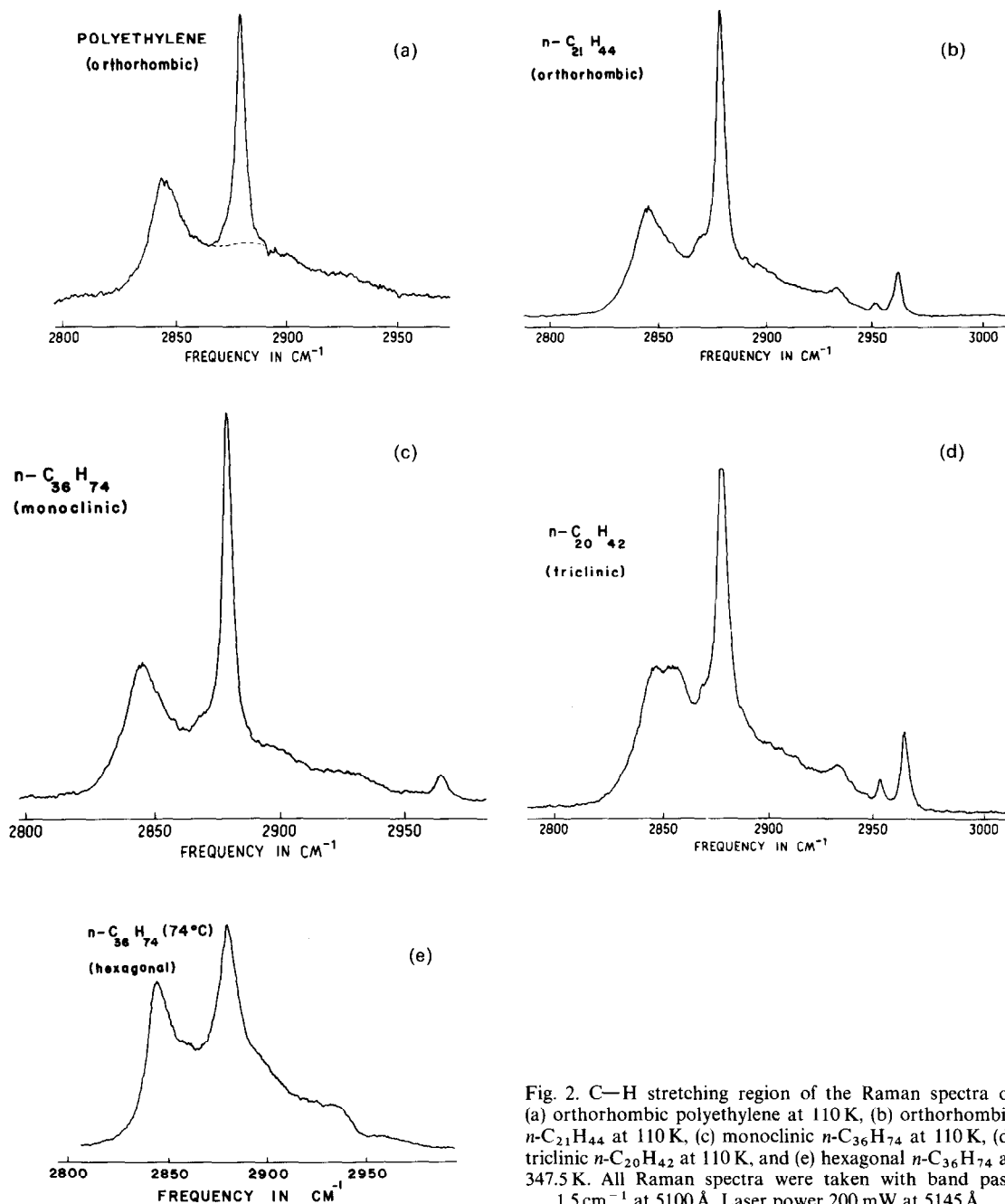


Fig. 2. C—H stretching region of the Raman spectra of (a) orthorhombic polyethylene at 110 K, (b) orthorhombic $n\text{-C}_{21}\text{H}_{44}$ at 110 K, (c) monoclinic $n\text{-C}_{36}\text{H}_{74}$ at 110 K, (d) triclinic $n\text{-C}_{20}\text{H}_{42}$ at 110 K, and (e) hexagonal $n\text{-C}_{36}\text{H}_{74}$ at 347.5 K. All Raman spectra were taken with band pass 1.5 cm^{-1} at 5100 \AA . Laser power 200 mW at 5145 \AA .

which the bond polarizability parameters used were derived from cyclohexane and previously used with success to calculate the Raman intensities for an isolated chain [26].

The Raman polarization measurements were made on a "solid-state" extruded sample of polyethylene. Such a sample is cylindrical in shape, with the extended chains of the polymer parallel to the axis of the cylinder. Orientation in the plane perpendicular to this long axis is random. The direction of the incident exciting radiation was perpendicular to the long axis of the

sample, and the polarizations of the incident and scattered radiation were parallel to this axis, corresponding to a ZZ measurement. Collection was at right angles. The observed spectrum is shown in Fig. 3.

The intensity of the line at 2880 cm^{-1} is greatly reduced relative to the rest of the spectrum. As seen in the figure, a residual intensity does persist, but this can be reduced further by narrowing the collection angle. Thus, this line can be confidently assigned to $d^-(0)$ and the remainder of the spectrum to $d^+(0)$. Associated with the latter, a previously hidden maxi-

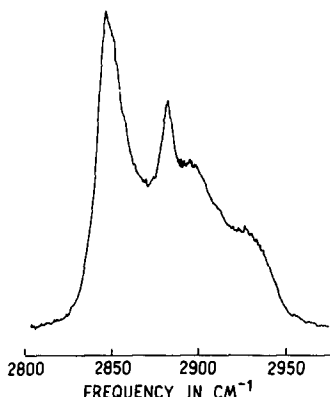


Fig. 3. Polarized Raman spectrum of uniaxially oriented "transparent" polyethylene at 110 K. $y(zz)x$ geometry employed with chain axes aligned with z axis. Band pass 2.5 cm^{-1} at 5100 \AA . Laser power 250 mW at 5145 \AA .

imum near 2890 cm^{-1} is revealed. The structure of the $d^+(0)$ line appears to be the same as that observed for a randomly oriented sample.

It is now possible to measure the ratio of the integrated intensities of the C—H stretching fundamentals, i.e. $\int I(d^+(0))/\int I(d^-(0))$. As a result of identifying the broad Raman bands associated with $d^+(0)$, we know their shapes and, therefore, can separate $d^+(0)$ and $d^-(0)$ in the spectra of polycrystalline samples such as those represented in Fig. 2. (The dotted line in Fig. 2(a) shows a typical separation.) We find this ratio to have a value of 5.1 ± 0.5 . This value is derived from measurements on six different spectra. The error appears related to experimental uncertainties such as are involved in drawing baselines and in separating $d^+(0)$ from $d^-(0)$, and probably masks any variations which might be related to differences in chain packing. This result is in accord with the expectation that this ratio should be characteristic of the isolated chain and should not be greatly affected by intermolecular effects.

We note that our finding, namely that the intensity of $d^+(0)$ is about $5 \times$ greater than $d^-(0)$, is in conflict with the impression conveyed when the intensity ratio is based on peak height measurements. In this case $d^-(0)$ is reported [9] to be more intense than $d^+(0)$. The much larger intensity of $d^+(0)$ compared with $d^-(0)$ is in accord with Raman intensity calculations based on bond polarizability parameters [26] and is also in accord with our observation that the Raman spectrum of the polymethylene chain in the liquid state is highly polarized over most of the C—H stretching region.

INTRA- AND INTERMOLECULAR EFFECTS ON INFRARED AND RAMAN BAND SHAPES

The observed complexities in the i.r. and Raman spectra of the C—H stretching region of extended polyethylene chains are largely the result of Fermi resonance interactions involving double excitations of fundamentals at lower frequencies. In fact, complica-

tions of this nature in the C—H stretching region for hydrocarbons are the rule rather than the exception [27]. An earlier interpretation of the Raman spectrum based on Fermi resonance [10], which seemed at the time to be supported by normal coordinate calculations but which, in view of the present results is certainly incorrect, associated the 2933 cm^{-1} line with $d^-(0)$ and both of the lines at 2879 and 2845 cm^{-1} with $d^+(0)$, the doubling in this latter case being explained as the result of Fermi resonance interaction with the overtone of $\delta(0)$.

As before, we invoke Fermi resonance in analyzing this region. However, it is clear that resonance involving a single binary combination will not adequately explain the many observed complexities, especially in the Raman spectrum. To describe the interaction properly, it will be necessary to consider the continuum of binary combination states resulting from frequency dispersion in the lower branch or branches that are involved in the combinations. Much of the spectral structure can be explained by considering only parallel dispersion, i.e. dispersion parallel to the chain axis.

If we assume that combinations no higher than binary are involved in the resonance, then only methylene bending modes need be considered. Although binary combinations between methylene bending and methylene wagging (w) modes have frequencies near the C—H stretching region, their symmetry is unfavorable for interaction. Thus, in an isolated chain approximation the zone center combination $\delta(0) + w(\pi)$ has a frequency near 2810 cm^{-1} and has B_{2g} symmetry. Similarly, $\delta(0) + w(0)$ is near 2840 cm^{-1} and has B_{1u} symmetry. Neither B_{2g} nor B_{1u} are of the proper symmetry for interaction since $d^+(0)$ and $d^-(0)$ are of A_g and B_{1g} symmetry. Although forbidden for the isolated chain, the possibility of such interaction cannot be strictly ruled out for the crystalline state since the lower symmetry of the crystal tends to lower the molecular symmetry and relax selection rules. However, we have found no evidence that bending-wagging combinations contribute to the spectra.

A detailed and quantitative treatment of Fermi resonance interaction between d^+ and the binary combinations of $\delta(\phi)$ is at present not possible since the dispersion of the bending modes is not completely understood, even for the isolated chain. Interpretation of the methylene bending mode region is complex for two reasons. First, these modes are involved in strong intermolecular interactions. For example for the orthorhombic structure, which is the only case studied in any detail, we believe that the perpendicular dispersion spans about 35 cm^{-1} at $\phi = 0$. At this value of the phase angle the perpendicular dispersion is greater than the parallel dispersion for the isolated chain, the latter spanning about 24 cm^{-1} ($1467 - 1443\text{ cm}^{-1}$). A second complication exists because the Raman active fundamental, $\delta(0)$, interacts with $2P(\pi)$, and results in a doubling of bands in this region.

Some of these complexities can be reduced by isotopic isolation. It is well known that intermolecular

coupling can often be virtually eliminated by isolating the molecule of interest in a matrix consisting of its deuterated analogue. Fermi resonance will, of course, persist, but the contribution of intermolecular effects through Fermi resonance to line broadening in the C—H stretching region will be largely eliminated.

We will first discuss the C—H stretching spectrum of the isotopically isolated molecule. An approximated dispersion curve for methylene bending modes of the isolated molecule will be used to interpret the C—H region in terms of Fermi resonance interaction involving binary combinations of $\delta(\phi)$. We will then consider the chain in the crystal.

THE ISOTOPICALLY ISOLATED CHAIN

The C—H stretching region

The i.r. spectrum in the C—H stretching region of the isotopically isolated chain ($n\text{-C}_{36}\text{H}_{74}$ in $n\text{-C}_{36}\text{D}_{74}$, 1:20), shown in Fig. 4(a), is little different from that of the chain in an undiluted crystal. The band maxima

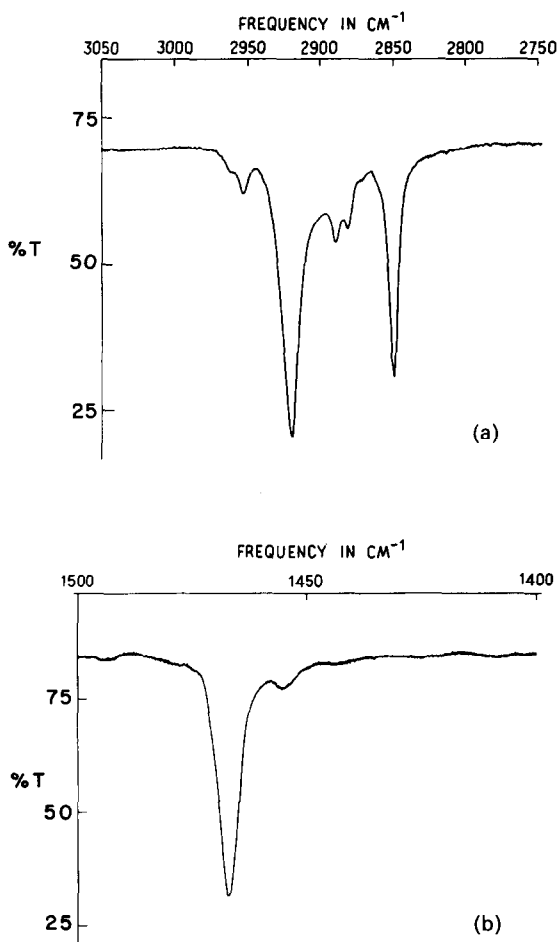


Fig. 4. Infrared spectrum of 1H/20D $n\text{-C}_{36}\text{H}_{74}$ at room temperature: (a) CH_2 stretching region; (b) CH_2 bending region. The spectra were taken at 1.5 cm^{-1} resolution.

assigned to $d^-(\pi)$ and $d^+(\pi)$, as well as those of r_a^- , r_b^- , and r^+ , are all within a few cm^{-1} of those for the pure crystal; the relative intensities of these bands also appear little changed.

The two bands at 2889 and 2881 cm^{-1} are associated with $n\text{-C}_{36}\text{D}_{74}$, and are due to the C—H stretching mode of a CHD group impurity in this matrix. There are two bands probably because the two C—H bonds of the methylene group have non equivalent sites in the crystal. The mean position of these two bands, 2885 cm^{-1} , is the frequency of an inter- and intramolecularly uncoupled C—H stretching vibration of the extended polymethylene chain.

The CHD bands obscure the broad shoulder previously observed at 2898 cm^{-1} . That the band is still there is apparent from the high background absorption.

The Raman spectrum of the same sample, shown in Fig. 5(a), exhibits significant changes in the C—H stretching region. The line at 2845 cm^{-1} has sharpened considerably, its half-width being reduced from about 22 cm^{-1} (its value in the monoclinic or orthorhombic structure) to about 10 cm^{-1} . The 2880 cm^{-1} line is relatively unaffected, its half-width remaining about 7 cm^{-1} . As a result the peak heights of the $d^+(0)$ and $d^-(0)$ bands are now nearly the same. There is considerable depletion in intensity on the low frequency side of the broad band underlying the 2880 cm^{-1} line. It is important to note, however, that this broad band is still largely unaffected at frequencies higher than 2880 cm^{-1} . This persistence may be explained in terms of intramolecular Fermi resonance interaction. The remaining features are attributable to r_a^- , r_b^- , r^+ and CHD, and may be identified respectively at 2964 , 2952 , 2971 and 2889 cm^{-1} .

Isotopic decoupling should not significantly change the integrated intensity ratio $\int I(d^+(0))/\int I(d^-(0))$ from its value for the isotopically undiluted crystal, since the observed differences between the spectra are presumably due to changes in intermolecular Fermi resonance interaction. This turns out to be the case. For the decoupled case we find that the value for this ratio is 5.2 , in good agreement with that of 5.1 ± 0.5 found earlier for the undiluted crystals.

Dispersion curve for CH_2 bending

Figure 4(b) shows the i.r. spectrum in the methylene bending region of crystalline $n\text{-C}_{36}\text{H}_{74}$ diluted in $n\text{-C}_{36}\text{D}_{74}$. The strong band at 1467 cm^{-1} is assigned to $\delta(\pi)$ since it is by far the strongest feature in this region and is midway between the two components (1474 and 1461 cm^{-1}) found for the undiluted crystal. The much weaker band at 1455 cm^{-1} probably belongs to the methyl asymmetric bending mode.

The Raman spectrum in the same region for this sample is shown in Fig. 5(b). There are two lines: the stronger is at 1431 cm^{-1} and the weaker and broader is at 1458 cm^{-1} . These two lines probably result from resonance between $\delta(0)$ and $2P(\phi)$ for ϕ near π . The dispersion curve for methylene rocking [1] is very flat near the zone center at $\phi = \pi$ so that for

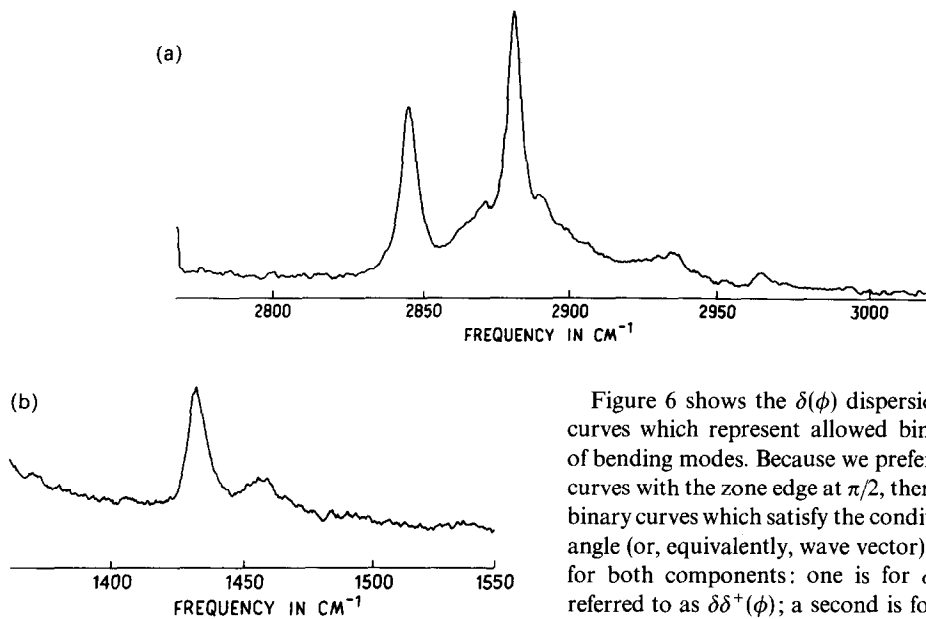


Fig. 5. Raman spectra of 1H/20D $n\text{-C}_{36}\text{H}_{74}$ at 110 K: (a) CH_2 stretching region; (b) CH_2 bending region. Band pass 2.5 cm^{-1} at 5100 Å. Laser power 250 mW at 5145 Å.

$n\text{-C}_{36}\text{H}_{74}$ we estimate [3] that there are 10 rocking fundamentals whose frequencies are essentially degenerate at 722 cm^{-1} . At higher frequencies the density of modes rapidly diminishes: thus only two rocking fundamentals fall in the interval between $723\text{--}735\text{ cm}^{-1}$. The proper binary combination state for interaction with $\delta(0)$ may be formed from a symmetric combination of these nearly degenerate states. From the observed frequencies and the observed intensity ratio of the two lines the positions of the unperturbed states may be calculated [28]. From integrated areas, $\int I(1431)/\int I(1458) = 1.4 \pm 0.1$ we calculate the unperturbed frequency of $\delta(0)$ to be $1442 \pm 1\text{ cm}^{-1}$.

As already pointed out, there are serious vibrational complications in this region which make it impractical to derive the shape of $\delta(\phi)$ from band progressions as can be done for most other types of polymethylene modes [3]. Instead we have used the shape derived from calculations using force constants from n -paraffins [29]. This calculated shape, adjusted slightly to be compatible with frequencies for the isolated chain, is shown in Fig. 6.

Interpretation

Most of the features in the C—H stretching region of the spectra can be explained in terms of Fermi resonance interaction between the symmetric methylene C—H stretching fundamental at the zone center ($\phi = 0$ or π) and binary combinations involving the methylene bending vibrations of the extended chain, not just at the zone center, but rather over the whole Brillouin zone. In the case of the crystal, which we consider later, dispersion of $\delta(\phi)$ perpendicular to the chain axis must be considered as well.

Figure 6 shows the $\delta(\phi)$ dispersion curve and two curves which represent allowed binary combinations of bending modes. Because we prefer to use dispersion curves with the zone edge at $\pi/2$, there are two possible binary curves which satisfy the condition that the phase angle (or, equivalently, wave vector) must be the same for both components: one is for $\delta(\phi) + \delta(\phi)$, to be referred to as $\delta\delta^+(\phi)$; a second is for $\delta(\phi) + \delta(\pi - \phi)$, to be referred to as $\delta\delta^-(\phi)$. The former, which has line symmetry A_g , may interact with $d^+(0)$, and the latter, which has line symmetry B_{3u} , may interact with $d^+(\pi)$. On the other hand, neither curve is of correct symmetry to interact with either of the antisymmetric stretching modes: $d^-(0)$ or $d^-(\pi)$.

The actual degree of interaction, if symmetry allowed, will depend on the frequency interval between the fundamental and the binary state and on the magnitude of the Fermi resonance matrix element [28]. In the i.r. this interaction is weaker than in the Raman, partly because of the consistently larger frequency separation between $d^+(\pi)$ and $\delta\delta^-(\phi)$ relative to that between $d^+(0)$ and $\delta\delta^+(\phi)$. There is some interaction, as is manifest in the two broad bands observed near 2922 and 2898 cm^{-1} . These may be identified with critical

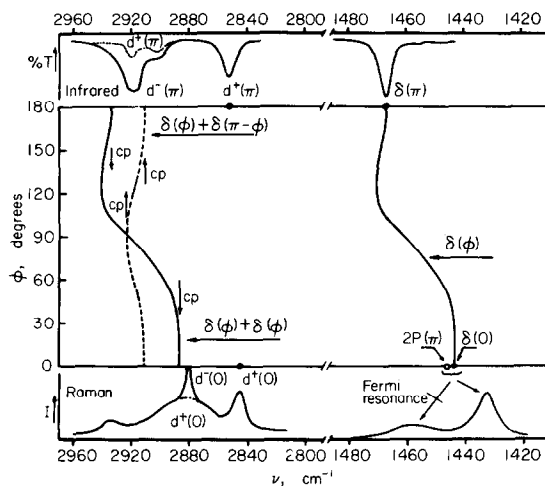


Fig. 6. C—H stretching and CH_2 bending Fermi resonance interaction scheme for the extended isolated polymethylene chain. (All the spectra except the C—H i.r. region are for the isotopically isolated chain. The C—H i.r. region is based on measurements on $n\text{-C}_{20}\text{H}_{42}$ in [2]).

points in the $\delta\delta^-(\phi)$ curve at $\phi = \pi/2$ (2921 cm^{-1}) and at $\phi = 0$ and π (2910 cm^{-1}). As discussed earlier, it has been found [2] that both these bands have the correct symmetry required for this assignment, namely that of $d^+(\pi)$. Unfortunately, most of this region is obscured by the strong $d^-(\pi)$ fundamental at 2920 cm^{-1} . Finally, we note that because this resonance overlaps $d^-(\pi)$, an undetermined and quite possibly significant part of the apparent intensity of this fundamental may actually belong to $d^+(\pi)$, and this should be taken into account in i.r. intensity studies.

The binary curve $\delta\delta^+(\phi)$ spans a considerably greater frequency interval than does $\delta\delta^-(\phi)$, and this is one reason for the more extended complexity in the Raman spectrum relative to the i.r. Fermi resonance interaction may be assumed to be strongest near $\phi = 0$ where $\delta\delta^+(\phi)$ makes its closest frequency approach to $d^+(0)$. This, combined with the high density of states in this region, assures an intensity maximum near 2890 cm^{-1} , as is indicated in Fig. 6. Moving from the maximum towards higher frequencies we find the band intensity decreasing both because interaction is diminishing and because the density of states is decreasing. Finally another critical point is reached at a calculated frequency of 2934 cm^{-1} ($\phi = \pi$), and a broad Raman line is observed near 2935 cm^{-1} . The calculated shape of $\delta\delta^+(\pi)$ exhibits another maximum near 2942 cm^{-1} , which may account for the Raman intensity observed beyond 2935 cm^{-1} .

THE CHAIN IN A CRYSTAL

As we noted earlier, one marked difference between the Raman spectrum of the isolated chain and the Raman spectrum of the coupled chain in a crystal is the greater breadth of the 2845 cm^{-1} line in the latter case. Related to this, there is also more intensity apparent on the high frequency side of this line, which tends to fill in the trough between the lines at 2879 and 2845 cm^{-1} . This broadening can be understood in a qualitative way by taking into account the perpendicular dispersion of the methylene bending modes, i.e. dispersion resulting from interchain coupling. Unfortunately, what we know about such coupling is confined primarily to the orthorhombic structure, and then is limited largely to modes that can be observed, i.e. those at the zone center. What we know, however, is adequate to enable us to propose a plausible explanation for the observed broadening.

Orthorhombic and monoclinic structures

The range of methylene bending mode frequencies dispersed in the perpendicular direction, plotted as a function of ϕ , is indicated in Fig. 7. The curve is based on the results of TASUMI and SHIMANOUCHI [11] who used the observed frequency separations of the crystal split components of the fundamentals ($\phi = 0$ and $\phi = \pi$) together with a model based on a hydrogen atom-atom repulsive potential to calculate separations as a function of ϕ . For the methylene bending mode

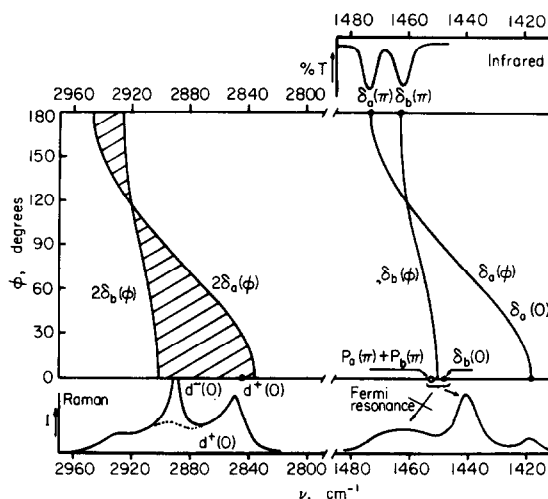


Fig. 7. C—H stretching and CH₂ bending Fermi resonance interaction scheme for the polymethylene chain in the orthorhombic structure.

the separation is largest at $\phi = 0$ (Raman active), diminishes to zero near $\phi = 0.6\pi$ and increases again with a reversed sign. The separation at $\phi = \pi$ (i.r. active) is about one third that at $\phi = 0$. We have adjusted the calculated curve slightly in order to account for a revised frequency assignment of the $\phi = 0$ components. On the basis of polarized Raman studies on extruded polyethylene and other supporting evidence we assign the 1418 cm^{-1} band to the A_g component. The two B_{3g} bands observed at 1462 and 1440 cm^{-1} we interpret as the result of Fermi resonance interaction between the B_{3g} component of $\delta(0)$ and the sum of the two components of $P(\pi)$. An estimate of the intensity ratio of the two B_{3g} bands leads to an unperturbed frequency near 1449 cm^{-1} for the fundamental.

An important point is that the effect of crystal coupling is to extend the frequency range covered by $\delta\delta^+(\phi)$ (Fig. 7) to about 2830 cm^{-1} so that it overlaps the $d^+(0)$ fundamental at 2845 cm^{-1} . Provided the Fermi resonance interaction is relatively weak, the consequence will be a broadening of the $d^+(0)$ line. According to this scheme, the effects of intermolecular coupling will be less at the higher frequency end ($\phi > \pi/2$) since the perpendicular dispersion in frequency in this region is less. Again this is in keeping with the observation that little change in the Raman spectrum is found above 2900 cm^{-1} as a result of isotopic dilution.

Triclinic structure

The same arguments are applicable to the triclinic crystal. However, this structure has a single chain in a unit cell, and little is known regarding its perpendicular dispersion since there is only one zone center component. A priori, there is no reason not to expect significant coupling and, hence, a dispersion of the same magnitude as that found in the case of the orthorhombic structure. In a preliminary study we have

found evidence for dispersion from a comparison of the spectra of triclinic $n\text{-C}_{20}\text{H}_{42}$ with the spectra of $n\text{-C}_{20}\text{H}_{42}$ diluted in $n\text{-C}_{20}\text{D}_{42}$. The $\delta(0)$ and $P(\pi)$ bands show significant frequency shifts in going from the undiluted to the diluted case. These shifts are comparable in magnitude to what we observed earlier in an analogous experiment for orthorhombic $n\text{-C}_{36}\text{H}_{74}$. Although at the present we cannot interpret these observed shifts in detail, it is clear that appreciable dispersion occurs for both the δ and P vibrations in the triclinic structure.

The characteristic feature of the Raman spectrum of the triclinic form is the doubling of the $d^+(0)$ fundamental to give components at 2855 and 2846 cm^{-1} . If we assume that $\delta(0)$ occurs near 1427 cm^{-1} , then the 2855 cm^{-1} component could be explained as the critical point at $\delta\delta^+(0)$ while the 2846 cm^{-1} would correspond to $d^+(0)$. This would account for the doubling of $d^+(0)$ for the triclinic form, a doubling which does not occur in the orthorhombic case since here this critical point and $d^+(0)$ are nearly coincident.

Hexagonal structure

The C—H stretching region of the Raman spectrum of $n\text{-C}_{36}\text{H}_{74}$ in the hexagonal phase (74°C) is shown in Fig. 2(e). Its overall appearance is intermediate between that of the orthorhombic form and that of the isotopically isolated chain. The half-widths of the 2845 and 2880 cm^{-1} lines of the hexagonal form are about 13 and 9 cm^{-1} respectively, and are thus comparable to those of about 10 and 7 cm^{-1} for the isolated chain. For the orthorhombic form, these half-widths are 22 and 7 cm^{-1} . On the other hand, unlike the case of the isolated chain, the 2845 cm^{-1} line is asymmetric, and there is considerable "filling in" of the trough between this line and the 2880 cm^{-1} line. In this respect the situation is similar to the orthorhombic structure, in which case the strong secondary $d^+(0)$ band at 2890 cm^{-1} extends to lower frequencies.

From these observations we would infer a "loose" structure, but one which still permits significant intermolecular coupling and hence, to some degree, perpendicular dispersion. This is consistent with what little is known about the structure [24]: the chains are extended and, though the unit cell is hexagonal, there is insufficient room in the lateral direction to allow free rotation of the chains about their long axis.

CORRELATION OF THE RATIO I_{2890}/I_{2850} WITH STRUCTURE

The ratio of peak heights I_{2890}/I_{2850} , which had been observed to be sensitive to the state of the polymethylene chain, has found use in studying structure and structural changes in such systems as cholesteric liquid crystals [4] and biomembranes [5, 6]. It has been shown that this ratio is sensitive both to the environment (lateral packing) of the extended chains and to conformational disorder [7]. A quantitative measure of lateral order (S) has been defined [9] in terms of this ratio (r) as follows:

$$S = \frac{r - 0.7}{1.5}$$

so that $S = 1$ for a chain in a crystal ($r = 2.2$) and $S = 0$ for a chain in the liquid state ($r = 0.7$) with intermediate values to be expected for other systems. This parameter is a useful guide in studying complex systems, so that it is appropriate to examine it in the light of our results. We find that it is not a simple quantity and, as implied in [9], it does not have the same meaning for the conformationally disordered chain as for the extended chain.

We note that r is a ratio of peak heights I_{2890}/I_{2850} rather than a ratio of integrated intensities $\int I_{2890}/\int I_{2850}$. As we have shown, the ratio of integrated intensities of Raman fundamentals does not depend on the environment of the extended chain and that the symmetric stretch is about five times as intense as the antisymmetric stretch: thus $\int I_{2890}/\int I_{2850} = 0.2$ and is nearly independent of environment. However, r is a hybrid quantity. When its value is about 2.0 the peak intensity of the antisymmetric mode is about equal to that of the symmetric mode since in the solid $d^-(0)$ is superimposed on a broad intense background that is part of a complex of bands belonging to $d^+(0)$. Approximately half of the peak height of I_{2890} belongs to the $d^+(0)$ fundamental.

Differences in the value of r for the extended chain result from several causes. At a given temperature, differences in r for different packing situations result primarily from changes in I_{2850} rather than from I_{2890} . Since changes in I_{2850} are related to changes in the shapes of the complex of $d^+(0)$ bands, another indication of lateral interaction is the half-width of the 2850 cm^{-1} line.

We have observed variations in r with temperature for a given crystal structure. Upon cooling a sample, r increases and approaches a value of 3.0 near 100 K. This temperature dependence is a result of I_{2890} increasing more rapidly than I_{2850} , a result of a significant narrowing of the 2890 cm^{-1} line.

The situation for the polymethylene chain in the liquid state is also complex. The Raman spectrum of $n\text{-C}_{36}\text{H}_{74}$ is shown in Fig. 8. The symmetric stretching mode (d^+) persists as a relatively narrow, intense, strongly polarized line near 2850 cm^{-1} . In breadth, shape and position it much resembles its $d^+(0)$ counterpart in the spectrum of the chain in the hexagonal crystal. There is a second somewhat less intense, broader, polarized line centered near 2925 cm^{-1} . It probably originates in Fermi resonance interaction between d^+ and 2δ . In between these two polarized d^+ lines, and obscured by them, is a weaker, depolarized line near 2890 cm^{-1} . Its position, polarization and intensity identify it as the antisymmetric stretching mode, d^- . This line is clearly revealed in the depolarized spectrum where it is found to be quite symmetric in shape and to have a half-width of about 25 cm^{-1} . Relative to the spectrum of the solid, the principal changes upon melting are some broadening of the

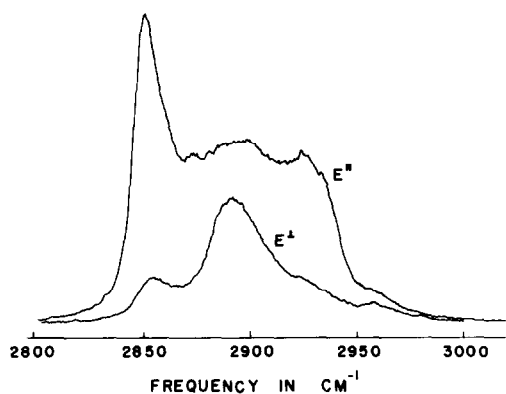


Fig. 8. Polarized Raman spectra of $n\text{-C}_{36}\text{H}_{74}$ in the melt. E^\perp and E^\parallel denote the exit electric vector is perpendicular and parallel to the incident electric vector. Band pass 2.0 cm^{-1} at 5100 \AA . Laser power 250 mW at 5145 \AA .

2890 cm^{-1} line and a displacement to higher frequency of the broad band which in the case of the extended chain was associated with Fermi resonance between $d^+(0)$ and $2\delta(\phi)$.

Whatever are the causes of these changes, it is clear that I_{2890} decreases in the liquid relative to the solid. There are two reasons for this: [1] the half-width of the 2890 cm^{-1} line has increased by a factor of between 2 and 3 with a consequent decrease in peak height; and [2] most of the underlying intensity from d^+ is now gone so that I_{2890} is now more nearly a measure of the true peak height of the d^- line. Thus, the ratio I_{2890}/I_{2850} measures something different in the liquid than in the solid, and as cautioned in [9] the parameter S can be used only in the domain where there is no appreciable conformational disorder.

SUMMARY AND CONCLUSIONS

In this study we have attempted to explain why the C—H stretching region of both the i.r. and especially the Raman spectra of the polymethylene chain is unexpectedly complex. We have been able to account for all of the major features in these spectra in terms of Fermi resonance interaction. The relevance of these results to spectral studies of biosystems is discussed briefly.

The observed complexities are associated with the methylene symmetric stretching mode, d^+ . The anti-symmetric mode, d^- at 2890 cm^{-1} in the Raman and at 2920 cm^{-1} in the i.r., is forbidden by symmetry from entering into Fermi resonance interaction and is therefore insensitive to environmental changes of the extended chain.

The complexities associated with d^+ are manifest in the appearance of broad, sometimes intense secondary maxima. These secondary bands are most prominent in the Raman, but they also appear in the i.r. where, however, they tend to be obscured by the strong absorption band of the d^- fundamental. The origin of these complexities is in a strong Fermi resonance

interaction between the i.r.- or Raman-active symmetric stretching fundamental and appropriate binary combinations involving the methylene bending modes.

The secondary bands are all characteristically broad. This is a consequence of the fact that the resonance involves a virtual continuum of binary combination states and not just those few (zone center) which are normally invoked and which involve only i.r.- and Raman-active bending fundamentals. Thus an important factor is the density of binary states. For the isolated chain these can be approximated from the calculated bending mode dispersion curve. Maxima occur only at the critical points, which are usually but not always at the zone center. Of course, the actual intensity distribution depends also on other factors such as the frequency separation between the fundamental and the binary states, and the matrix elements between them. The situation may be described in terms of two-phonon i.r. absorption [30] or Raman scattering, intensified by Fermi resonance. However, an important point is that a continuum of bending mode binary combinations is involved.

We distinguish two levels of Fermi resonance interaction. The first is intramolecular and involves dispersion of the bending modes parallel to the chain axis. This interaction occurs in the completely isolated chain. The second level, whose effects are similar but distinguishable, is intermolecular and involves perpendicular dispersion of the bending modes, and hence is crystal structure dependent.

The effects of intramolecular Fermi resonance can be seen in the spectrum of the isotopically isolated chain. On the basis of the shape of the bending mode dispersion curve we have assigned the secondary bands to critical points. We can in this way account for the number, position, and polarization of all bands which appear in this region of the i.r. and Raman spectra.

The effects of intermolecular Fermi resonance are seen in the differences between the Raman spectrum of the chain in a crystal and the spectrum of the isotopically isolated chain, as well as in the less marked differences between the Raman spectra of different crystal modifications. Those observed differences can be understood in a qualitative way in terms of the perpendicular dispersion which results from intermolecular coupling of bending vibrations.

Although such resonance may affect the distribution of intensity, i.e. the band structure, in dramatic ways, it is not expected to significantly affect the total integrated intensity of the fundamentals themselves. We have measured the ratio of the integrated Raman intensities $\int I_{d^+}/\int I_{d^-}$, and for the extended chain we find its value, 5.1 ± 0.5 , to be independent of state, and thus supportive of our interpretation.

Our results are in agreement with those of [9] concerning the significance of the ratio of peak heights I_{2890}/I_{2850} : this ratio (r) is dependent on the lateral order of extended chains; its use as a qualitative measure of lateral order is appropriate only in the absence of significant conformational disorder. The value

of the ratio is found to depend on different factors according to whether or not the chain is extended. In the case of the extended chain I_{2890} consists of approximately equal contributions from $d^-(0)$ and $d^+(0)$; the dependence of r on packing is a result of changes in the contribution of $d^+(0)$ while $d^-(0)$ remains nearly constant. However, in the liquid state where there is conformational disorder the 2890 cm^{-1} band consists primarily of $d^-(0)$ with only a small contribution from $d^+(0)$.

Acknowledgement—One of us (R. G. S.) wishes to thank Dr. W. L. PETICOLAS for bringing this problem to his attention. This research was supported in part by National Science Foundation grant MPS75-05239, and by National Institutes of Health grant HL 18737. One of us (S. L. H.) is indebted to the Macromolecular Research Center for fellowship support.

REFERENCES

- [1] M. TASUMI, T. SHIMANOUCI, and T. MIYAZAWA, *J. Mol. Spectrosc.* **9**, 261 (1962).
- [2] R. F. HOLLAND and J. R. NIELSEN, *J. Mol. Spectrosc.* **8**, 383 (1962).
- [3] R. G. SNYDER and J. H. SCHACHTSCHNEIDER, *Spectrochim. Acta* **19**, 85 (1963).
- [4] B. J. BULKIN and N. KRISHNAN, *J. Am. Chem. Soc.* **93**, 5998 (1971).
- [5] B. J. BULKIN and K. KRISHNAMACHARI, *J. Am. Chem. Soc.* **94**, 1109 (1972).
- [6] K. G. BROWN, W. L. PETICOLAS, and E. BROWN, *Biochem. Biophys. Res. Commun.* **54**, 358 (1973).
- [7] K. LARSSON and B. P. RAND, *Biochim. Biophys. Acta* **326**, 245 (1973).
- [8] R. C. SPIKER and I. W. LEVIN, *Biochim. Biophys. Acta* **388**, 361 (1975).
- [9] B. P. GABER and W. L. PETICOLAS, *Biochim. Biophys. Acta* **465**, 260 (1977).
- [10] J. H. SCHACHTSCHNEIDER and R. G. SNYDER, *Spectrochim. Acta* **19**, 117 (1963).
- [11] M. TASUMI and T. SHIMANOUCI, *J. Chem. Phys.* **43**, 1245 (1965).
- [12] R. G. SNYDER, *J. Chem. Phys.* **47**, 1316 (1967).
- [13] R. S. STEIN and G. B. B. M. SUTHERLAND, *J. Chem. Phys.* **22**, 1993 (1954).
- [14] S. KRIMM, C. Y. LIANG and G. B. B. M. SUTHERLAND, *J. Chem. Phys.* **25**, 549 (1956).
- [15] S. MIZUSHIMA and T. SHIMANOUCI, *J. Am. Chem. Soc.* **71**, 1320 (1949).
- [16] J. R. NIELSEN and A. H. WOOLLETT, *J. Chem. Phys.* **26**, 1391 (1957).
- [17] N. B. COLTHUP, L. H. DALY, and S. E. WIBERLEY, *Introduction to Infrared and Raman Spectroscopy*, (edited by N. L. ALPERT), Academic Press, New York (1975). W. E. KEISER and H. A. SZYMANSKI, *IR—Theory and Practice of Infrared Spectroscopy*, Plenum, New York (1973). L. J. BELLAMY, *The Infrared Spectra of Complex Molecules*, John Wiley, New York (1975).
- [18] R. G. SNYDER, *J. Chem. Phys.* **42**, 1744 (1965).
- [19] R. G. SNYDER, *J. Mol. Spectrosc.* **7**, 116 (1961).
- [20] C. W. BUNN, *Trans. Faraday Soc.* **35**, 482 (1939).
- [21] A. E. SMITH, *J. Chem. Phys.* **21**, 2229 (1953).
- [22] H. M. M. SHEARER and V. VAND, *Acta Crystallogr.* **9**, 379 (1956).
- [23] T. HAYASHIDA, *J. Phys. Soc. Japan* **17**, 306 (1962).
- [24] A. MÜLLER, *Proc. R. Soc. (London)* **A138**, 514 (1932).
- [25] R. G. SNYDER and J. R. SCHERER, to be published.
- [26] R. G. SNYDER, *J. Mol. Spectrosc.* **36**, 204 (1970); *J. Mol. Spectrosc.* **36**, 222 (1970).
- [27] J. C. LAVALLEY and N. SHEPPARD, *Spectrochim. Acta* **28A**, 2091 (1972); D. C. MCKEAN, *Spectrochim. Acta* **29A**, 1559 (1973).
- [28] G. HERZBERG, *Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand, New York (1945).
- [29] R. G. SNYDER, *J. Mol. Spectrosc.* **23**, 224 (1967).
- [30] R. G. SNYDER, *Bull. Am. Phys. Soc.* **21**, 348 (1976).

NOTE ADDED IN PROOF

Since the completion of this work we have modified our assignment for r^+ . We now believe this fundamental is split by Fermi resonance into two components at 2935 and 2875 cm^{-1} . Earlier we had associated only the latter with r^+ , but now are in agreement with [8] that the 2935 cm^{-1} band also belongs to r^+ . However, it should be noted that the CH stretching region of the Raman spectrum of crystalline polyethylene which contains no methyl groups displays a broad band near 2935 cm^{-1} . Thus the assignment of this feature to a critical point is unaffected.