Infra-red bandshapes of methylene-d$_2$ bending vibrations in n-hexatriacontane-n-hexatriacontane-d$_{74}$

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Infra-red spectra in the CD$_2$ bending vibration region (1080–1100 cm^{-1}) have been analysed for mixtures of deuterated and hydrogenated hexatriacontane. The i.r. data analyses are based on lattice dynamical calculations of guest deuterated molecules in the host n-C$_{36}$H$_{74}$ and infrared intensities calculated using the electro-optical parameter method. The calculated band profiles as a function of the deuterated molecule concentration compare favourably to experimental spectra taken at 80K. The high resolution, low temperature spectra reveal features heretofore only observed at much higher concentrations of deuterated species. Self deconvolution procedures were used to further resolve the spectra. Excellent agreement was found between calculated and experimental ratios of the i.r. intensity of certain dimer arrangements to that of singlet molecules. This intensity ratio was found to be a better measure of deuterated species concentration than the halfwidth of the CD$_2$ bending vibration band that had been previously used.

INTRODUCTION

Mixtures of hydrogenated polyethylene (PEH) and its deuterated isotope (PED) have been used extensively in both small angle neutron scattering (SANS)[1−7] and infra-red (i.r.) spectroscopic studies[5,8−15] of the organization of polyethylene molecules in the solid state. The two experimental techniques are sensitive to chain organization at somewhat different levels, and the models of chain organization that have emerged to date have not been in full accord[6,7,14−16]. A possible cause that will be explored in the present work is that the methods previously used[1,5,13] to interpret the i.r. data may not be entirely satisfactory.

The infra-red method is based on the well-accepted concept that the infra-red spectra of crystals containing two or more nonequivalent molecules per unit cell may exhibit band splittings which result from intermolecular interactions between the nonequivalent molecules. The splittings are significant only if the vibrational frequencies of nearest neighbour molecules occupying nonequivalent sites are identical, so that if the lattice sites were occupied by different isotopes the splittings would be greatly diminished. The nature of the intermolecular interactions in polyethylene is such that the predominant effect on bandsplittings derives from nearest neighbour pairs[17]. Thus, the infra-red spectra are sensitive to the occupation of adjacent nonequivalent lattice sites by isotopically similar molecules.

The implications of this for polyethylene is that from i.r. spectra of mixtures of low concentrations of guest deuterated polyethylene in host hydrogenated polyethylene it should be possible to determine whether chain folding is adjacent along planes such as the (110) that places portions of the same molecule at nonequivalent nearest neighbour lattice sites. Although it has been substantiated by both i.r.[9,14] and SANS[4] that adjacent reentry folding occurs in dilute solution crystallized polyethylene the extent of its occurrence has not been completely resolved. This may be due in part to the methods previously used to analyse the infra-red data. Improved methods are developed in the present investigation that will be applied to polyethylene mixtures in future investigations.

In the present work, a method that is based on lattice dynamical calculations has been developed for analysing infra-red data of mixtures of hydrogenated and deuterated chains situated on the polyethylene lattice. Infra-red intensities of the CD$_2$ bending vibrations were calculated from the eigenvectors using the electro-optical parameter (EOP) method[18]. Random arrangements of deuterated molecules in a host of hydrogenated molecules were considered and applied to interpretation of data from mixtures of n-C$_{36}$D$_{74}$ and n-C$_{36}$H$_{74}$. Regular chain folding has been also considered by taking finite arrays of PED chains in the PEH host as models in the lattice dynamical calculations. The results of these calculations and comparisons to experimental results for both melt and solution crystallized polyethylene will be presented in a subsequent publication.

Values for parameters in the calculations either were taken from the literature[17,19] or, if not heretofore available, were derived from experimental studies of mixtures

of deuterated and hydrogenated hexatriacontanes. In this manner, the only additional information needed to analyse polyethylene blends was the contribution due to noncrystalline material.

Recently, Spells *et al.*[5] had compared bandwidths obtained from mixtures of n-dotriacontane and n-dotriacontane-d_{66} with those obtained from melt and dilute solution crystallized polyethylene mixtures. Their data on both mixtures of hydrogenated and deuterated dotriacontane and PEH–PED were taken at room temperature and at spectral resolutions comparable to and in excess of the natural bandwidth. For these reasons and because a dispersive i.r. system was used they were unable to resolve bandsplittings. Also, no frequencies or vibrational intensities calculations were performed in conjunction with their analysis[5]. We found in our studies that overall bandwidths were not as sensitive to the arrangement of deuterated and hydrogenated molecules as were ratios of intensities at specific frequencies.

Mixtures of deuterated and hydrogenated hexatriacontane were investigated by Bank and Krimm[9] as a model system upon which to deduce from spectroscopic studies of PED–PEH mixtures, the nature of chain folding in the crystalline polymer. To interpret the spectroscopic results on mixtures of hexatriacontanes, Bank and Krimm[9] used the frequencies calculated by Tasumi and Krimm[8] on lattice models in which regular arrays of planes of deuterated molecules were situated in the host hydrogenated molecules. Thus, in their work a 50–50 mixture was envisaged as composed of alternating planes of deuterated and hydrogenated molecules. For the 50% mixture the agreement between the observed and calculated infra-red bandsplittings of the bending vibration of the CD_2 group was reasonable, especially in view of the nearly random nature that mixtures of deuterated and hydrogenated n-alkanes must assume in the solid state. However, calculations based on a plane of deuterated molecules surrounded by planes of host molecules would not be expected to yield meaningful fits to experimental bandshapes of host species in low concentration.

In the earlier infra-red work on solid state mixtures of n-alkanes, measurements were conducted at room temperature[5,9]. It is well known that infra-red band profiles narrow at low temperature while bandsplittings increase. Both of these spectral effects with decreasing temperature mean that more information could be obtained from low temperature data. Subsequently, Krimm and his colleagues have made low temperature infra-red measurements on PED–PEH mixtures[13–15]. These experimental results have been modelled in terms of aggregates of deuterated chains in the hydrogenated host as this was thought to better represent the actual arrangement of deuterated chains when low concentrations were co-crystallized with the hydrogenated polymer.

Whereas the first mentioned work utilized lattice dynamic calculations[8], the latter work used an interacting dipole model to predict frequency shifts and factor group splittings[13]. To date, no calculations have treated the question of infra-red intensities except to assign all the intensity to the highest and lowest frequency modes of systems of interacting dipoles[13].

The dipole approximation can lead to significant errors in both frequencies and intensities and the current work is aimed at calculating these quantities for randomly mixed systems using lattice dynamic calculations for frequencies

and eigenvectors. The eigenvectors are used to calculate infra-red intensities using the electro-optical parameter (EOP) method[18]. As this method had been applied to hydrocarbons, including both PEH and PED, parameter values were available to determine infra-red vibrational intensities[19].

APPROACH

Lattice dynamics calculations

Lattice dynamics calculations were carried out on infinite polyethylene lattices in which the translational unit cell contained from 2 to 18 ethylene repeat units depending on the number and arrangement of the deuterated molecules. The total number of atoms in our unit cells ranged from 12 to 108. The arrangements of deuterated chains in a host of hydrogenated chains and the corresponding unit cells were selected in the following manner. All possible configurations of deuterated stems in the hydrogenated host were selected such that from one to four deuterated stems were contained in the unit cell and the minimum distance between deuterated molecules in nearest neighbour unit cells was 0.5 nm. A summation radius of 0.45 nm was used for non-bonded interactions based on previous work[17] which showed that lattice frequencies and factor group splittings were accurately calculated by summation over interactions within this radius. Interactions between non-nearest neighbour deuterated molecules were of a second order nature. The size and shapes of the unit cells were selected so that each deuterated chain within the unit cell was within 0.5 nm from at least one other deuterated stem in the same unit cell with the exception of the cell containing a single deuterated stem. A total of 24 different unit cells, containing from 1 to 4 deuterated stems, were generated, consistent with the above criteria. One of the two unit cells having a pair of deuterated molecules is shown in *Figure 1*. In the other unit cell the pair of deuterated molecules occupy equivalent polyethylene unit cell sites along the short i.e. *b*, axis.

At a given concentration of deuterated molecules their arrangement in the host lattice was represented by these 24 unit cells. The probabilities were determined for each of the unit cells and these were functions of the concentration of deuterated molecules and site degeneracy. Site degeneracy is the number of ways the deuterated molecules can be positioned to have the same arrangement and, hence, the same calculated frequencies. The probabilities are related to the initial concentration of guest species with the lower aggregates more important at low concentrations and higher aggregates at higher concentrations. The sum of the probabilities over all configurations provides an indication of the limitation due to treating aggregates only up to tetramers. We were primarily interested in the concentration range 0 to 10% deuterated molecules. Configurations up to and including tetramers account for 99.9% of the deuterated molecules for a 1% deuterated mixture and 98.8% for a 5% deuterated sample. At 10% deuterated, the percentage drops to 93.9%. Therefore, we did not include aggregates beyond 4 deuterated stems since at least 94% of the molecules are accounted for in the concentration range of interest.

As an example of configurations and unit cell geometry consider the case of two deuterated molecules within

0.5 nm of each other and separated by more than this distance from all other deuterated molecules. There are two possible configurations and one of these was illustrated in *Figure 1* along with the unit cell used in the vibrational calculations.

The molecular geometry and lattice parameters assumed in the calculation were taken from the X-ray diffraction study of n-octane[20], and low temperature neutron diffraction investigations of polyethylene[21], respectively. Low temperature values were selected since the spectroscopic measurements to be compared to calculations were carried out at low temperature. In addition, the vibrational force field of Barnes and Fanconi[17] was used with slightly modified force constants to better fit the observed CD_2 bending and rocking mode frequencies. The force field of Barnes and Fanconi[17] had been derived from a least squares refinement of vibrational frequency data at low temperature, including refinement of the Williams's IV intermolecular nonbonded parameter set[22], to better fit low frequency modes. The valence and central force field parameters that were changed, are listed in *Table 1*. The valence force field parameters that were
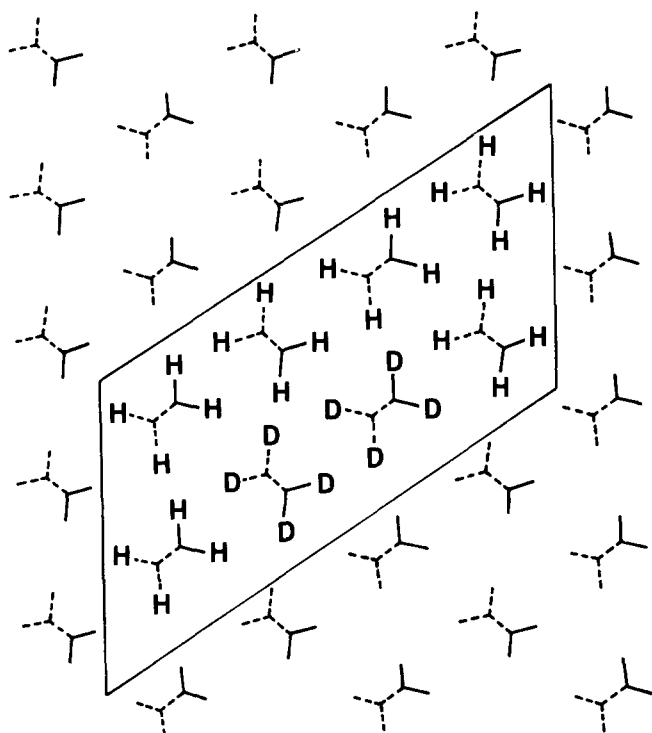
varied involved methylene bending and rocking internal coordinates. Only the pre-exponential terms of the H...H, or equivalently (D...D), were changed in the refinement procedure.

The summation radius for non-bonded intermolecular interactions was taken to be 0.45 nm. Calculations were carried out on deuterated–hydrogenated mixtures to determine the effect of non nearest neighbour interactions between deuterated molecules. In these calculations a deuterated molecule was separated from other deuterated molecules by successive layers of hydrogenated molecules. Unless the deuterated molecules occupied adjacent lattice sites no frequency shifts or splittings of the CD_2 bending vibrations were found from the calculations. Thus, the second order interactions of the CD_2 bending vibrations through intervening hydrogenated stems are negligible.

Calculated CD_2 bending frequencies and their intensity ratio are compared to experimental values in *Table 2* for the fully deuterated lattice. The calculated frequency of an isolated deuterated stem was low by about 2 cm^{-1}, but this was not deemed critical since the experimental values of interest were bandsplittings, bandwidths, and infra-red intensities rather than absolute frequencies. The calculated bandsplitting was low by 0.4 cm^{-1} and 0.9 cm^{-1} compared to the experimental values of n-$C_{36}D_{74}$ and PE-d_4, respectively. Variation of force constant parameters to improve the agreement produced

Figure 1 One of the two unit cells used in mixed crystal lattice dynamical calculations for a pair of deuterated stems. D and H label deuterated and hydrogenated molecules, respectively

Table 1 Force field parameters

Type[a]	Internal coordinates* Chemical repeat unit	Value[b]
1,5	0	−0.25
5,5	0	0.563
7,7	0	0.832
5,5	1	−0.028
5,5	2	−0.022

* Changes in parameters reported in Ref. 17
[a] 1, symmetric C—H stretch, 5 methylene bending 7, methylene rock
[b] The units are millidyne. Angstrom (10^{-18} N.m) for bend-bend terms and millidynes (10^{-8} N) for stretch bend terms

Type	Central force field[t] $V(r) = ar^{-6} + be^{-Cr}$ $a \text{(mdyn Å}^7)$	$b \text{(mdyn Å)}$	$c \text{(Å}^{-1})$
H...H	0.250	25.33	3.74
H...C	2.014	99.49	3.67
C...C	3.716	1036.4	3.60

[t] Identical to that reported in Ref. 17 except for b term of H...H type

Table 2 CD_2 bending frequencies

		I.r. frequencies (cm^{-1}) Fully deuterated lattice		Single deuterated stem	Intensity ratio
Calculated		1093.7	1084.4	1089.6	0.76
	n—$C_{36}D_{74}$	1093.7	1084.0	1087.7*	
Observed					0.7−1.4
	PE—d_4	1094.6	1084.4		

*Mixture of 0.4% n—$C_{36}D_{74}$ in n—$C_{36}H_{74}$

unacceptable calculated frequencies for other normal modes.

In normal mode calculations there are practical limits on the dimensions of the dynamical matrix that can be diagonalized due to computer size and speed. The following steps were taken to minimize the size of the dynamical matrix in the present calculations. The structures used in the calculations were assumed to be infinite in the chain axis direction so that the number of atoms in the translational unit cell was $6 \times$ the number of molecular stems. Such structures have at least one symmetry operation, a plane perpendicular to the chain axis, in addition to the identity operation. The symmetry operations were used to reduce the size of the dynamical matrix to 2/3 of its value as only vibrational displacements perpendicular to the chain axis were treated. The net result is that the size of the dynamical matrix is reduced from 18 to 12 times the number of molecules in the unit cell.

A further reduction in the size of the dynamical matrices was achieved for the larger unit cells as follows. The Raman active modes of an isolated polyethylene chain do not interact with its i.r.-active modes when placed in the polyethylene lattice owing to the common inversion symmetry operation of the line and space group. In general, this symmetry operation is not preserved in the mixed crystal unit cells and Raman and i.r. active modes of the isolated chain can interact. For PED the i.r. and Raman active CD_2 bending vibrations are separated by approximately 65 cm^{-1} that leads to exceedingly small perturbation effects in the mixed crystal unit cells. Thus, it was assumed that these modes do not interact which led to a further reduction in the size of the dynamical matrices by a factor of 2. The validity of neglecting the Raman-active modes was verified by comparing i.r. intensities and frequencies calculated for several mixed crystal unit cells with and without this assumption. It should be noted that for mixed crystals in which PEH is the minor species this approximation is not as sound owing to the closeness of the Raman and i.r. active CH_2 bending frequencies, e.g. 10 cm^{-1}. This was also verified by calculations.

A final comment on the calculations performed is concerned with the assumption that each site in the polyethylene (or n-alkane) lattice is equally probable for deuterated or hydrogenated molecules. The validity of this assumption has been questioned by Stehling et al.[23] who measured phase separation, melting temperature and crystallization rates on mixtures of deuterated and hydrogenated hydrocarbons. They reported selective partitioning of $n-C_{36}H_{74}$ and $n-C_{36}D_{74}$ when mixtures of the two n-alkanes were crystallized from the melt and from solution. Owing to the difference in the melting temperature of the pure n-alkane and its deuterated isotope ($\Delta T = 3.8°C$ for hexatriacontane) they concluded that the concentration of deuterated species varied in the solid during crystallization, being higher than the initial melt concentration in the beginning and less in the latter stages of crystallization. This result was substantiated by experiment[23]. We assumed both an equal probability of deposition in the crystal (no fractionation) as well as fractionation to the extent found in the work of Stehling et al.[23].

Infrared intensities

Infra-red intensities of the CD_2 bending vibrations

were calculated using the electro-optical parameter (EOP) method. The infra-red intensity of the band due to the normal mode Q_i is proportional to the square of the dipole moment M with respect to Q_i. This derivative is given by:

$$\frac{\partial M}{\partial Q_i} = \sum_l^{3N} \sum_j^m \sum_k^K \frac{\partial \mu^k}{\partial R_j} \underline{e}^k B_{jl} L_{li}^x + \mu^k \frac{\partial \underline{e}^k}{\partial R_j} B_{jl} L_{li}^x$$

where μ^k is the dipole moment of the k-th bond approximated by its equilibrium value, $\underline{e}^k$ is the normalized displacement of the k-th bond, $\overline{B}_{jl}$ is the B-matrix coefficient of the R_j internal coordinate with respect to the l-th cartesian displacement, and L_{li}^x is the l-th component of the eigenvector of the i-th normal mode in cartesian displacement space. The summation l is over all cartesian displacements, j over all internal coordinates, and k over all bonds. The quantities $\partial \mu^k / \partial R_j$ are parameters of the EOP method and their values as well as the equilibrium dipole moment values used in the calculations were taken from Table VIa of Ref. 19. The calculated intensity ratio is given in *Table 2* along with the observed range for the quantity from PE-d_4 and $n-C_{36}D_{74}$ spectra. The band profiles calculated from the frequencies and intensities given in *Table 2* had more intensity in the band component to the low frequency side of the isolated CD_2 bend frequency than in the high frequency side band. Our experimental results on PE-d_4 and $n-C_{36}D_{74}$ suggested that the ratio is sensitive to the sample preparation method. Preferred crystalline orientation and changes in the setting angle are possible causes of variability in the observed intensity ratio.

Experimental

The n-alkanes, $n-C_{36}H_{74}$ and $n-C_{36}D_{74}$, were obtained from Humphrey Chemicals, Inc.* and Merck, respectively, and used without further purification. Specimens for infra-red analysis were prepared by dissolving known amounts of the deuterated and hydrogenated n-alkanes in warm n-pentane and casting films at room temperature on CsI windows. The CsI windows with attached films were placed in the 80°C oven until the film melted, removed from the oven, and the molten n-alkanes allowed to solidify at room temperature. In this manner, low light scattering specimens suitable for i.r. analysis were obtained. In addition, a few specimens were prepared by placing the films as cast from solution in a vacuum to drive off the excess solvent. The i.r. bandshapes of these specimens were identical to those from the melt crystallized samples although the spectra of the vacuum dried films which scattered appreciably more light were of somewhat poorer quality.

The specimens were mounted at the tip of a cryostat that was operated at 77 K. The cryostat was placed in the sample compartment of a Nicolet Model 7199 Fourier transform spectrometer that was operated at a resolution of 0.24 cm^{-1}. Typically, 500 scans of the interferometer were co-added to obtain good signal-to-noise ratios.

RESULTS

Experimental

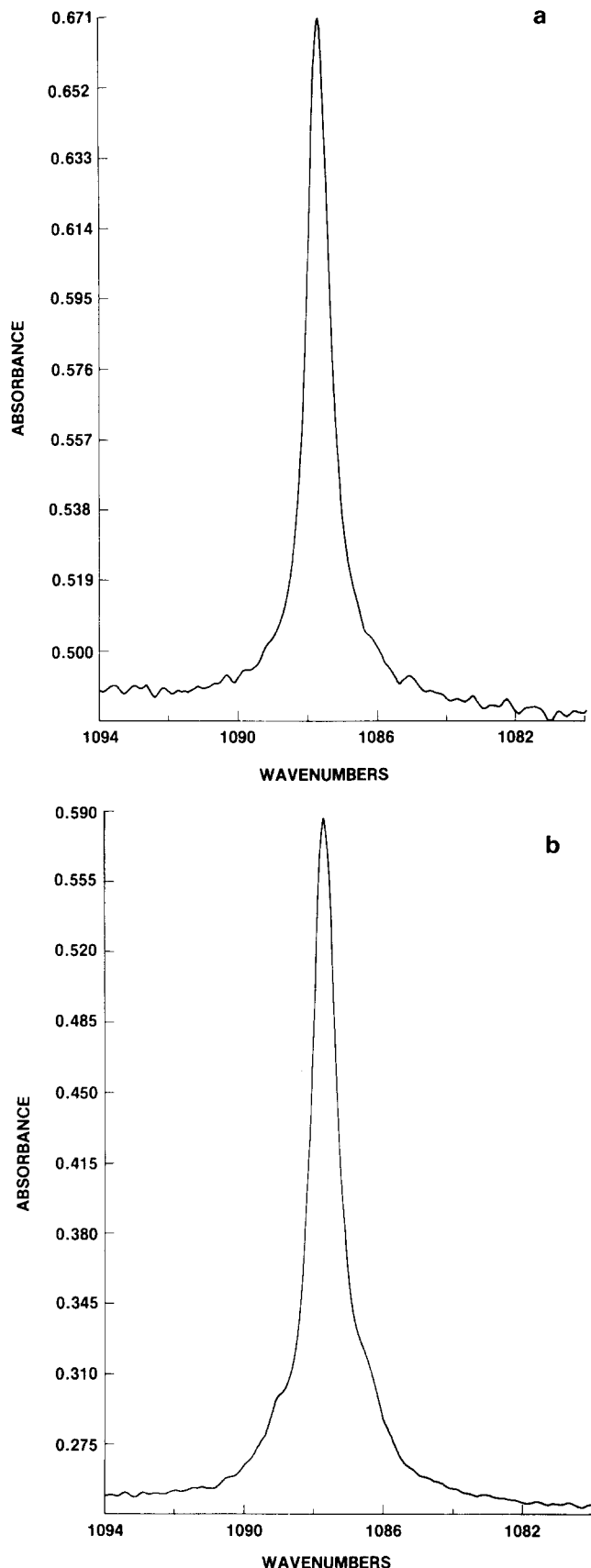Selected spectra in the frequency range of the CD_2 bending vibration are shown in *Figures 2a* and *b*. The

Figure 2 I.r. spectra of the CD_2 bending vibrations in mixtures of n-hexatriacontane and n-hexatriacontane-d_{74}, (a) 0.7% and (b) 4.0% D

in the spectra in addition to the central peak. At 4% deuterated species concentration the side bands appear as shoulders to the main band, *Figure 2b*. These can be assigned to pairs of deuterated molecules at adjacent non-equivalent lattice sites. As more of the adjacent sites are occupied, the splitting of the side bands increases to the limiting value of 9.7 cm^{-1} (see *Table 2*) which is the value for fully deuterated n-alkane. The side band intensity developes at the expense of the central band intensity, and the latter completely disappears in the fully deuterated sample.

Of particular interest in the current investigation is to identify spectral features that can be directly correlated with the local concentration of guest molecules. The two measures investigated were bandwidth and the intensity ratio of side bands to the central band. The ratio of the integrated intensity of the CD_2 bending band to that of an appropriate CH_2 vibration does establish the overall concentration of deuterated species. However, in polyethylene mixtures the guest molecules form clusters of stems even in the absence of fractionation. Segregation may also occur as clearly established by neutron scattering. For both reasons the local concentration may deviate significantly from the overall concentration.

Melt crystallized mixtures of deuterated and hydrogenated polyethylene in which the deuterated species is present in low concentrations exhibit a single CD_2 bending vibration band[15] and the width of the band may be reflective of the extent the perdeuteropolyethylene stems are isolated from one another. Spells *et al.*[5] had examined the relationship between CD_2 bending vibration bandwidth and the concentration of deuterated species for n-alkanes and polyethylenes. A linear relationship was found for the n-alkane mixtures. Our experimental bandwidths of mixtures of hexatriacontanes are plotted against concentration of deuterated species in *Figure 3*. There is considerable scatter in the bandwidth
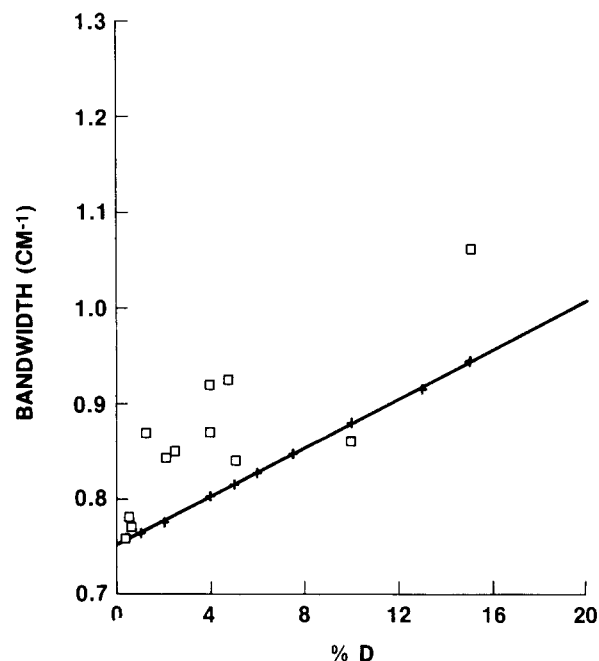

Figure 3 Observed (squares) and calculated (crosses) bandwidths (full width at one-half height) for CD_2 bending vibration plotted against concentration. The straight line is the relationship between bandwidth and concentration determined by calculations

spectra of low concentration of deuterated n-alkane contain a single band at 1087.7 cm^{-1} which is assignable to the CD_2 bending vibration of an isolated deuterated n-alkane chain. At higher concentrations, side bands appear

(full width at one-half height) data that militates against its use as a measure of local concentration, especially at low overall concentration. Although a detailed investigation of the origin of this scatter has not been made it appears from limited observations that the bandwidth is sensitive to the sample preparation method. Bandwidths determined from room temperature spectra are larger by a factor of about 3 and small variations are not as significant. In the n-alkane data of Spells et al.[5] the zero concentration intercept of the bandwidth vs. concentration plot yielded a bandwidth of approximately 3 cm^{-1}. This can be interpreted as the CD_2 bending vibration bandwidth of a molecule completely isolated from other deuterated molecules. Extrapolation of the bandwidth data (*Figure 3*) to zero concentration yields a width of approximately 0.75 cm^{-1} for the isolated deuterated molecule and by deconvolution with the instrument function the corresponding natural linewidth is 0.65 cm^{-1}.

Jing and Krimm[15] recently used a bandwidth of 2.5 cm^{-1} for the singlet band of a 5% deuterated mixture of hexatriacontanes. This value obtained from low temperature data is larger by a factor of 3 than our value for the same concentration. The spectral resolution of 1 cm^{-1} used in Jing and Krimm's work[15] accounts for some of the additional bandwidth, although Cream and Krimm had obtained a bandwidth of 1.9 cm^{-1} for the same n-alkane mixture under similar experimental conditions[13]. This further supports the notion that bandwidth data cannot be reliably used as a measure of local concentration.

The investigations of Spells et al.[5] and Cheam and Krimm[13] report no discernible splitting of the CD_2 bending vibration band at 5% deuterated species concentration. In fact, Spells et al.[5] reported that concentrations in excess of 50% had to be used before additional spectral features could be resolved. It is evident from *Figure 2* that even for concentrations less than 5% deuterated species the CD_2 bending vibration spectrum contains side bands. This is in contrast to previous observations[5,13] and results from the higher spectral resolutions and lower sampling temperatures used to acquire the spectra of *Figure 2*. However, even with higher spectral resolution the side band peaks are not completely resolved from the wings of the much more intense central band. To better resolve these spectra the method of self-deconvolution was employed[24]. Through use of this data manipulation procedure the spectra are stripped of their natural line-widths and multiplet structure, if present, are revealed. Important to the application herein, relative intensities of the component bands making up a complex band profile are retained. By means of self-deconvolution, resolution is enhanced at the expense of the signal-to-noise ratio and bandshape information. An example of self-deconvolution of a 15% deuterated mixture of hexatriacontane is shown in *Figure 4*. In addition to the resolved central band, two sets of side bands are discernible, although the lowest frequency side band appears only as a shoulder. The side bands whose frequencies lie closest to the central band were assigned to pairs of deuterated molecules occupying nearest neighbour non-equivalent lattice sites, and the remaining bands were attributed to higher aggregates in which at least one deuterated molecule has two nearest neighbour deuterated molecules occupying nonequivalent sites. That the side band frequency shifts from the central peak of the

calculated spectrum are less than the observed values can be attributed to the lower calculated CD_2 bending vibration bandsplitting of PED, *Table 2*. The smaller calculated bandsplittings are consistent with previous calculations[13,17].

The second spectral feature investigated for correlation with concentration of deuterated molecules was the intensity ratio of the side band whose frequency is 1.1 cm^{-1} less than that of the main peak to the main peak intensity. Self-deconvoluted spectra were used since the side bands were better resolved. Intensity ratios could not be determined over the full concentration range of interest. At concentrations less than 2% the side band intensity was of the order of the spectral noise which is increased by the self-deconvolution calculation. Over the concentration range for which intensity ratios could be determined the plot of this quantity against concentration, *Figure 5*, showed less scatter than the bandwidth plot. The intensity ratio for the 10% deuterated mixture fell well below the curve for the other values, and the measured bandwidth was also low for this spectrum as evident from *Figure 3*. We have no explanation for either observation.

Calculated spectra

The i.r. frequencies and intensities were calculated for the 24 configurations that contained from 1 to 4 deuterated stems. In *Table 3* the calculated frequencies, i.r. intensities, and bandsplittings are presented for 4 different configurations. Comparison is made to the predictions of the coupled oscillator model[13] using parameters generated in the present calculation. The comparison is in terms of bandsplitting, that is, the frequency difference between the maximum and minimum frequency bands. According to the coupled oscillator model the i.r. intensity is distributed among the highest and lowest modes for each of the configurations of *Table 3*. This is not the case for two of the configurations of *Table 3*, in which approximately 6% of the intensity is distributed among intermediate frequency bands. For other arrangements of
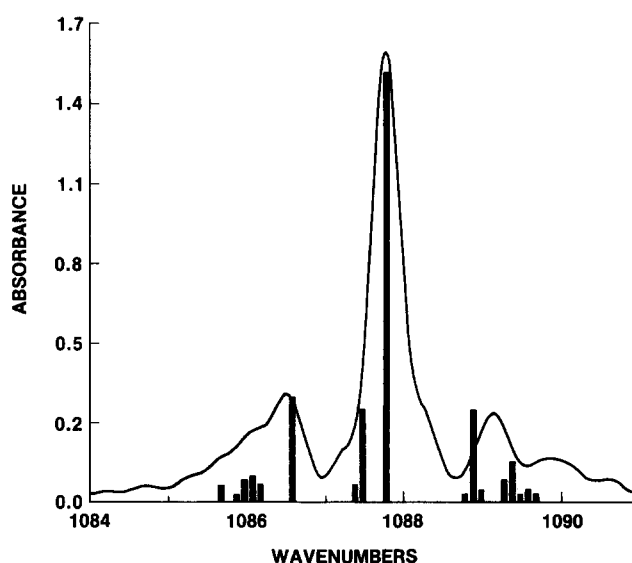

Figure 4 Effect of self-deconvolution of i.r. spectrum from a 15% deuterated mixture of n-hexatriacontanes. The bar spectrum results from the lattice dynamical calculations with i.r. intensities determined by the EOP method

deuterated molecules the spread of intensities over intermediate frequencies was even more pronounced. The bandsplittings are also at variance, differing by about $0.3\ \mathrm{cm}^{-1}$ for two of the configurations. Variations in frequencies and i.r. intensities of the sort illustrated in *Table 3* can lead to differences in the interpretation of the CD_2 bending vibration spectra.

The i.r. intensities as a function of frequency and fraction of deuterated species were determined by summation over the calculated intensities for each configuration multiplied by the probability of that configuration. This produced line spectra, an example of which is shown in *Figure 4*. Calculated spectra with
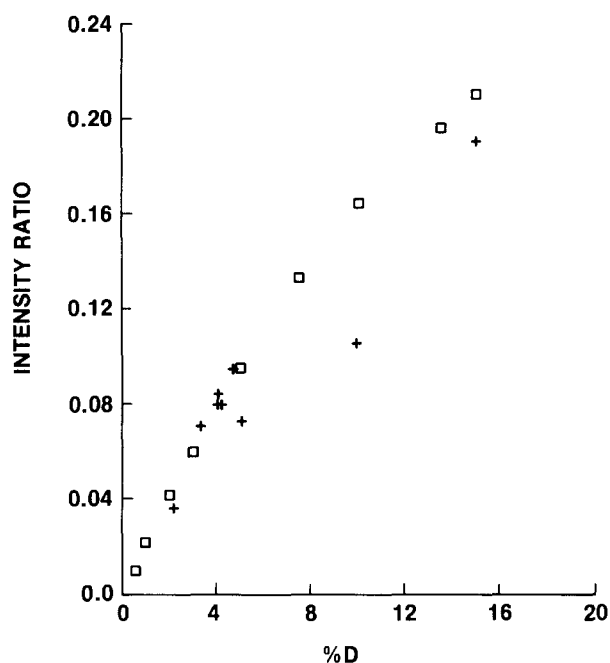

Figure 5 Comparison of calculated (squares) and observed (crosses) i.r. intensity ratios determined from side band nearest to central peak on the low frequency side and the central peak. Experimental values were determined from self-deconvolution spectra

lineshapes were also determined by using calculated frequencies and intensities, an assumed bandshape, and instrument function. The instrument function used in these calculations was the Fourier inversion of the Happ–Genzel apodization function[25] since this is the apodization function used to calculate the Fourier transform of the interferograms to obtain the spectra.

The natural bandshapes of the CD_2 bending vibrations were assumed to be Lorentzian with a bandwidth found by extrapolating the experimentally determined bandwidths, corrected for instrument broadening, to infinite dilution. The effect of using a resolution of $0.24\ \mathrm{cm}^{-1}$ to collect the spectra increased these bandwidths by approximately $0.1\ \mathrm{cm}^{-1}$. These bandwidths are considerably less than the values used in the previous work.

The calculated CD_2 bending vibration band profile for a particular concentration of deuterated molecules was determined by summing the Lorentzian bandshapes for each of the calculated frequencies. Each Lorentzian was weighted by the product of the calculated i.r. intensity for the mode and the concentration of the particular configuration from which the frequency was calculated. The configurational concentrations were calculated in two different ways and resultant spectra determined. In the first case, equal probability of site occupation was assumed for deuterated and hydrogenated molecules. In the second case, fractionation during crystallization was assumed according to the findings of Stehling *et al.*[23]. In the latter case the concentration of the deuterated molecules varies with the extent of crystallization, being higher than the initial melt concentration at first and approaching zero as the extent of crystallization becomes 100%. The variation of the concentration of the deuterated molecules with the extent of crystallization was computed by formulas of Skeist[26] and the calculated vibrational band profiles with fractionation was treated by partitioning the specimen into ten equal parts with the concentration of deuterated molecule in the j-th part given by $1.47\ C_j$ where C_j is the concentration in the melt at the midpoint in the deposition of the j-th part.

As the probabilities of a particular configuration are

Table 3 Comparison of lattice dynamical calculations and coupled oscillator model

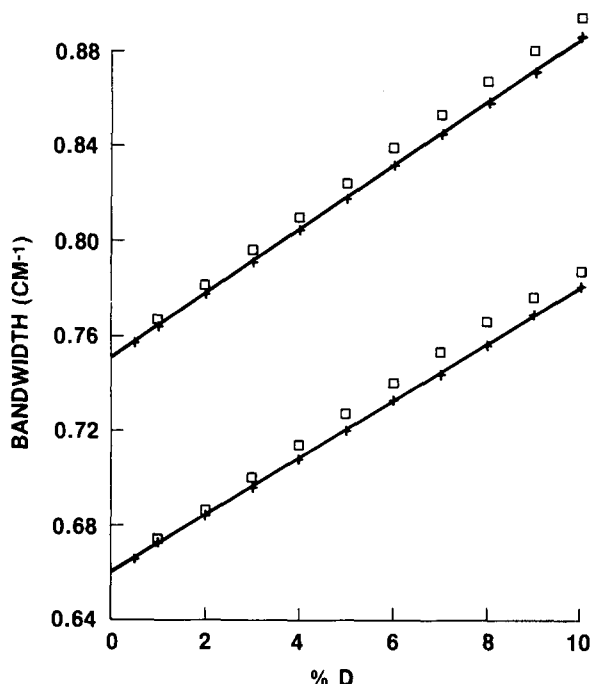| Configuration	Cal'c Freq.	Normalized intensity	Frequency splittings (cm⁻¹)	
			Lattice dynamics	Coupled oscillators
⋊ Ⳝ	1090.79	0.56	2.31	2.31
	1088.48	0.44		
Ⳝ ⋊ Ⳝ	1091.26	0.56	3.26	2.89
	1089.63	0.0		
	1088.0	0.44		
⋊ Ⳝ ⋊ Ⳝ	1091.50	0.53	3.74	3.47
	1090.34	0.03		
	1088.91	0.03		
	1087.76	0.41		
⋊ Ⳝ	1091.80	0.56		
Ⳝ ⋊	1089.91	0.0	4.62	4.62
	1089.63	0.0	1087.18	0.44
Ⳝ ⋊	1091.25	0.52		
	1090.61	0.02		
Ⳝ ⋊	1089.17	0.04	3.75	3.47
	1087.50	0.42		

Figure 6 Effect of fractionation (squares) and instrument broadening (upper two curves) on calculated bandwidths of n-hexatriacontane mixtures. The crosses are calculated values without fractionation

Figure 7 Comparison of calculated (crosses) and observed (solid curve) spectra of a 5% deuterated mixture of n-hexatriacontanes

functions of the initial n-$C_{36}D_{74}$ concentration the calculated band profiles are also a function of concentration. These band profiles were convoluted with the instrument function to obtain calculated spectra and bandwidths that could be compared to experimental values. The dependence of the calculated bandwidth on concentration with and without fractionation is shown in *Figure 6*. From *Figure 6* it is clear that the effect of fractionation on the bandwidth is more pronounced in the higher concentration spectra, but even at the higher concentrations it is minimal compared to the effect of instrumental resolution, even at 0.24 cm^{-1}. In *Figure 3* the dependence of calculated bandwidths on concentration is compared to experimental values. The calculated bandwidths vary linearly with concentration over the range adequately treated by assuming a maximum aggregate of 4 deuterated molecules. Although there is considerable scatter in the experimentally determined bandwidths the calculated values appear to be too low.

Using the calculated line spectra, e.g. *Figure 4*, intensity ratios of the side band to main band were determined and a comparison of this quantity with the corresponding experimental value is shown as a function of concentration in *Figure 5*. Over the limited concentration range for which self-deconvolution could be used the agreement between calculated and observed intensity ratios is quite good.

The calculated spectrum with Lorentzian lineshapes and the observed spectrum of a 5% mixture of n-$C_{36}D_{74}$ in n-$C_{36}H_{74}$ are shown in *Figure 7*. The appearance of side bands in the calculated spectrum agrees well with the experimental spectrum, although the side band frequency difference is slightly less than the observed value. It is evident from *Figure 4* that this is also true for comparisons of self-deconvoluted spectra with calculated spectra without lineshapes.
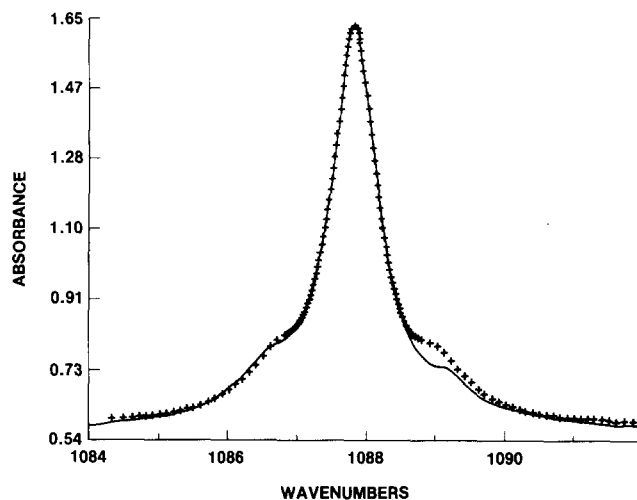
CONCLUSIONS

The infra-red spectra of mixed crystals of deuterated and hydrogenated hexatriacontane have been calculated from lattice dynamical calculations and electro optical parameters. The calculated spectra were in agreement with observed spectra taken at high resolution and liquid N_2 temperature. Under these experimental conditions structure in the form of side bands to the main CD_2 bending vibration peak were observed at deuterated species concentrations much lower than previously reported. Additional spectral details were revealed through the use of self-deconvolution which enhanced resolution. By this procedure features of the observed spectra could be assigned to clusters of two and three deuterated molecules.

The calculated spectra were compared to predictions of the coupled oscillator model that illustrated limitations of the latter model in describing bandsplittings and i.r. intensity distributions. The calculated spectra were determined for the models of either random deposition or fractionation of deuterated molecules during crystallization. It was shown that fractionation of deuterated molecules during crystallization had a negligible effect on the calculated spectra which supports the earlier findings of Krimm and Ching[27] concerning the effect segregation had on the i.r. spectra of mixed crystals of polyethylene.

The comparison of experimental and calculated bandwidths given in *Figure 3* demonstrated that this quantity cannot be reliably used as a measure of the local concentration of deuterated stems in a host of hydrogenated stems. For this reason the self-deconvoluted spectra of the sort shown in *Figure 4* were compared to the calculated spectra without lineshape. Analysis of these spectra indicated that a realistic measure of local concentration was the ratio of the intensity of the side band whose frequency is about 1.1 cm^{-1} less than the central peak frequency to the intensity of the central peak.

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