Effect of Intermolecular Interactions between CH Frequencies on the Infrared Spectra of *N*-Paraffins and Polythene*

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A systematic study has been made of the infrared absorption band near 725 cm^{-1} which arises from the rocking vibration of methylene groups in *n*-paraffins and in polyethylene. In unoriented crystals of *n*-paraffins, this band exhibits two components of equal intensity below the transition point; above the transition temperature and in the liquid state only the higher frequency component is found. In solid cold-drawn polyethylene the two components are of unequal intensity, the low frequency component being the stronger; in liquid polyethylene only the lower frequency component is found. Studies were made of polyethylene in various states of crystallinity and orientation, using both polarized and unpolarized radiation. The results obtained can be consistently interpreted, if the higher frequency component is attributed to crystallites in the polyethylene and the lower frequency component is assumed to be due partly to the crystalline and partly to the amorphous form of the polyethylene. It is concluded that the doubling of this frequency arises from some interaction between methylene groups which is peculiar to the crystalline state of long chain *n*-paraffins below their transition points.

INTRODUCTION

THERE are three main regions of intense absorption in the infrared spectrum of any *n*-paraffin and of polythene between 1 and 15μ. These are centered near 3.3μ (2920 cm^{-1}), 6.9μ (1470 cm^{-1}), and 13.8μ (725 cm^{-1}). The first two have long been known to be associated with internal modes of vibration of the CH$_2$ groups while the third has recently been proved[1,2] to be due to a deformation motion of the CH$_2$ groups as units which may be roughly described as a twisting of this group about the C-C-C skeletal axis. It was noticed by Thompson and Torkington[3] that this last band showed a doublet structure in solid polythene which disappeared when the polythene became molten. This phenomenon was further investigated by Elliott, Ambrose, and Temple,[4] who confirmed this finding. Using polarized radiation, they reported that when the incident radiation was polarized perpendicular to the chain axis (in stretched, partially oriented polythene) the doublet was present, but when the radiation was polarized parallel to the chain only a single broad band was observed. They attributed the higher frequency component (referred to as component *B*), which disappeared on changing the direction of polarization, to the mode of vibration mentioned above and remarked that the origin of the other component was obscure, suggesting that it might be due to amorphous regions in the material.

More recently King, Hainer, and McMahon[5] have studied the behavior of this band with unpolarized radiation as polythene is cooled to 77°K and 4°K. The higher frequency component sharpens very considerably and moves about 4 cm^{-1} to shorter wavelengths; the lower frequency component (component *A*) remains broad and moves only about 1 cm^{-1} in the same direction. The explanation offered by these workers is that component *B* arises from chains in the *gauche* configurations in the crystalline portions while component *A* is due to chains in the *cis* configuration in amorphous portions of the polythene.

The effect of heating on this doublet was also studied by Robert and Favre.[6] Rugg, Smith, and Atkinson[7] discuss the effect of cold drawing of polythene on the intensity of the components and indicate that they are affected by the degree of strain of the polythene crystallites.

One object of the present investigation was to try to elucidate this phenomenon, it being considered important to have a complete understanding of the spectrum of polythene which may, in many senses, be regarded as the basic polymer. Since the phenomenon was clearly related to orientation and crystallinity, it was desirable to study pure crystalline *n*-paraffins of varying chain length above and below the melting point. It was also desirable to see whether corresponding changes took place in any of the other CH frequencies. In the case of the internal deformation mode of the CH$_2$ groups at 1470 cm^{-1}, such changes were found, but time did not permit a careful examination of the CH stretching frequencies near 2920 cm^{-1}.[8] It was also desirable to investigate deuterated paraffins to see whether

* R. S. Stein and G. B. B. M. Sutherland, J. Chem. Phys. **21**, 370 (1953). This work was conducted while both authors were at the Department of Colloid Science, Cambridge, England.

[1] N. Sheppard and G. B. B. M. Sutherland, Nature **159**, 739 (1947).

[2] G. B. B. M. Sutherland and A. Vallance Jones, Nature **160**, 567 (1947).

[3] H. W. Thompson and P. Torkington, Proc. Roy. Soc. (London) **184A**, 3 (1945).

[4] Elliott, Ambrose, and Temple, J. Chem. Phys. **16**, 877 (1948).

[5] King, Hainer, and McMahon, J. Appl. Phys. **20**, 599 (1949).

[6] Louis Robert and Jean Favre, Compt. rend. **234**, 2270 (1952).

[7] Rugg, Smith, and Atkinson, J. Polymer Sci. **9**, 579 (1952).

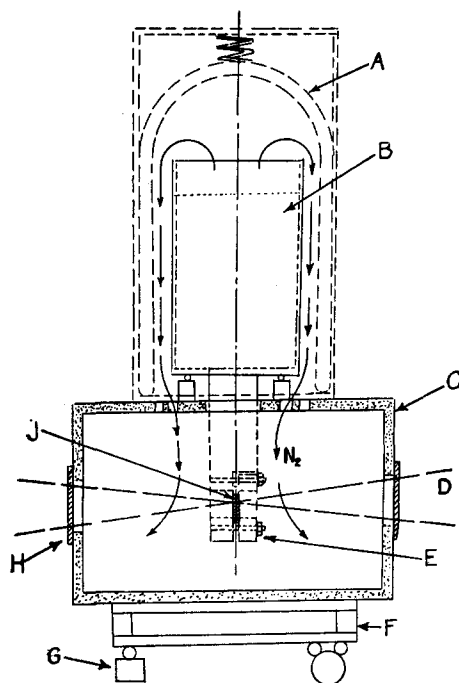[8] Private communication from Dr. Gilbert W. King.

FIG. 1. The low-temperature unit: (A) removable Dewar flask; (B) copper cup containing liquid nitrogen; (C) insulated box; (D) path of infrared radiation; (E) cylindrical copper rod; (F) carriage which rides on the track (G); (H) silver chloride window; and (J) sample or silver chloride liquid cell.

the effects could be attributed to vibrations involving only the hydrogen (or deuterium) atoms and were not due to combination frequencies involving vibrations of the carbon skeleton. It was hoped that investigations along these lines, in addition to throwing light on the polythene phenomenon, might give help in understanding changes in the infrared spectra of compounds in going from the solid crystalline state through a partially ordered solid state to the liquid state.

EXPERIMENTAL PROCEDURE

The experiments described here were mainly carried out with a Perkin-Elmer Model 12B Spectrometer using automatic recording. The measurements with polarized radiation were made using a 5-plate selenium pile transmission polarizer which was placed immediately in front of the entrance slit. The resolving power at 725 cm^{-1} was approximately 3 cm^{-1}. Measurements
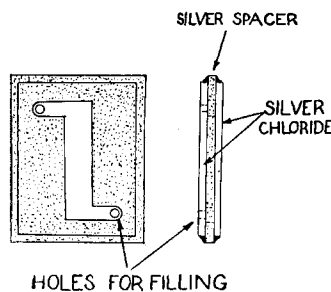

FIG. 2. The silver chloride liquid cell.

on polymer films at elevated temperatures were made by holding the sample between two rock salt plates in an electrically heated cell, the temperature of the sample being obtained by means of a thermocouple between the plates.

Measurements at liquid nitrogen temperatures were made in a special low temperature unit designed and constructed by Dr. A. V. Jones[9] (Fig. 1). The sample was held between silver chloride plates which were bolted between semicylinders of copper at the lower end of the copper rod (E of Fig. 1). Corrosion of the silver chloride by the copper was prevented by a covering of silver metal. Condensation of water on the silver chloride windows was prevented by flushing with a stream of dry nitrogen from the evaporating liquid nitrogen. Measurements by Dr. Jones indicated that the temperature of the sample was within 10°C of
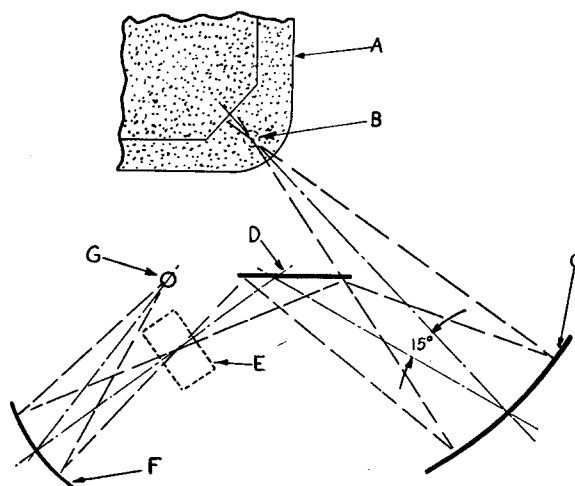

FIG. 3. The modified optical system: (A) the Perkin-Elmer spectrometer; (B) the former location of the globar; (C) a 15 cm diameter, 38 cm focal length front surface aluminized spherical mirror; (D) plane mirror; (E) sample cell; (F) 20 cm focal length front surface aluminized spherical mirror; and (G) the globar.

liquid nitrogen temperature, and that heating of the sample due to energy absorption from the infrared beam did not amount to more than 3° or 4°C.

Measurements on materials which were liquid at room temperature but solid at low temperatures were made by using the silver chloride transmission cell (Fig. 2) which was placed between the copper blocks E. The spacer was made of silver and the cell was bolted together. Arrangements were such that the cell could be filled after it was mounted on the copper rod. It was not possible to obtain a completely uniform layer of solid upon freezing the liquid and consequently impossible to obtain quantitative intensity measurements under these conditions.

In order to make room for the low temperature unit, it was necessary to have an extra focus in the radiation

9 A. Vallance Jones, Ph.D. dissertation, Cambridge University (1949).

path. This was done as shown in Fig. 3, the low temperature unit being mounted on a sliding platform which could be moved in and out from the optical path without upsetting alignments.

The polythene samples studied were both solvent cast and extruded samples of du Pont polythene[†] and ICI polythene.[‡] The solid pure n-paraffin samples studied were mostly those used in the investigations of Dr. Alex Müller[10-17] and were kindly made available to us by Professor Sir. E. K. Redeal, then at the Royal Institution. The remaining samples of n-paraffins were kindly supplied by Dr. J. W. Oldham of the Royal Institution and by the Anglo-Iranian Oil Company.

EXPERIMENTAL RESULTS

(a) Polythene

The effect of melting on the polythene doublet near 725 cm^{-1} was first reinvestigated using unpolarized radiation. At room temperature, the doublet consists of two peaks, one at 720 cm^{-1} (A) and the other at about 730 cm^{-1} (B) (Fig. 4). In all cases, the intensity of the lower frequency component (A) was observed to be greater than that of the higher frequency one (B). A general observation was that the more highly crystalline the sample, the more nearly were the two peaks equal in intensity. As the temperature was increased, the intensity of component B decreased continuously until at the melting point it had completely disappeared. Component A became lower and broader during this process, but the integrated extinction coefficient remained essentially constant. Upon cooling, the bands reversibly assumed their original shapes. No shift in the frequency of maximum absorption for either of the bands was observed.

An attempt was made to divide a plot of the extinction coefficient (Fig. 5) into two bands. This was done assuming (a) that the extinction coefficients of the bands are additive, (b) that the bands are symmetrical about their maxima, (c) that the loss in radiation due to scattering by the solid may be determined by interpolating from transmission measurements made on either side of the doublet where no absorption is believed to occur, and (d) that there is not an appreciable part of the absorption which is included in a long low tail extending far from the center of the band. The areas under the two bands were determined by measure-
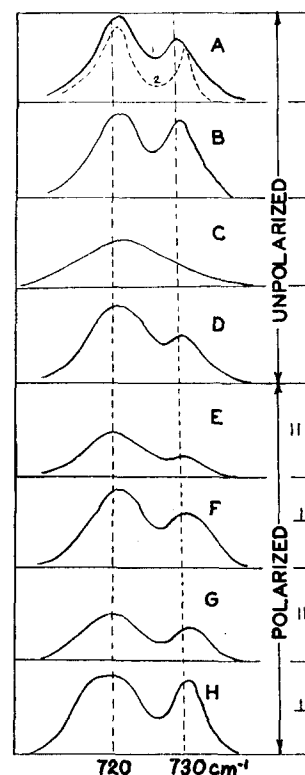
FIG. 4. The behavior of the 13.8μ doublet of polythene under various conditions: (A) general appearance at (1) room temperature and (2) $-185°C$; (B) appearance with a highly crystalline sample of polythene at room temperature; (C) at the melting point of polythene (about 110°C); (D) sample corresponding to (A) which has been stretched 500 percent at room temperature; (E) the preceding sample with radiation polarized parallel to the direction of stretching, and (F) perpendicular to the direction of stretching; (G) the preceding sample after annealing at a temperature slightly below the melting point with parallel polarization, and (H) with perpendicular polarization.

ment with a planimeter and were corrected for the finite slit width of the spectrometer using the method of Hardy and Young.[18] In making this correction, it was assumed that the bands had the shape described by the well-known Lorenz equation (1).

$$\ln\frac{I_0}{I} = \frac{c}{(\nu - \nu_0)^2 + b^2}. \tag{1}$$

The correction factor was
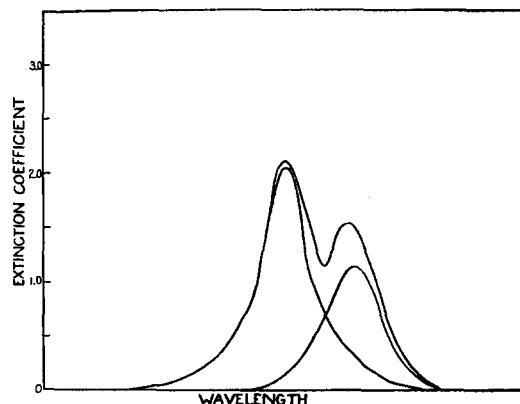
$$\text{percent error} = \frac{\ln(I_0/I)_{\max}}{11.08}\frac{a^2}{S^2}, \tag{2}$$

FIG. 5. The resolution of the doublet into two bands.

[†] Supplied through Dr. J. H. Dillon through the courtesy of Dr. F. F. Signaigo. E. I. du Pont de Nemours and Company, Rayon Department, Pioneering Research Station, Buffalo, New York.

[‡] Supplied through the courtesy of Dr. R. B. Richards, Imperial Chemical Industries, Ltd., Alkali Division, Winnington, Northwich, Cheshire, England.

[10] A. Müller, Proc. Roy. Soc. (London) A124, 317 (1929).
[11] A. Müller, Proc. Roy. Soc. (London) A127, 417 (1930).
[12] A. Müller, Proc. Roy. Soc. (London) A138, 514 (1939).
[13] A. Müller, Nature 129, 436 (1932).
[14] A. Müller, Proc. Roy. Soc. (London) A154, 624 (1936).
[15] A. Müller, Proc. Roy. Soc. (London) A158, 403 (1937).
[16] A. Müller, Proc. Roy. Soc. (London) A178, 227 (1941).
[17] A. Müller and K. Lonsdale, Acta Cryst. 1, 129 (1948).

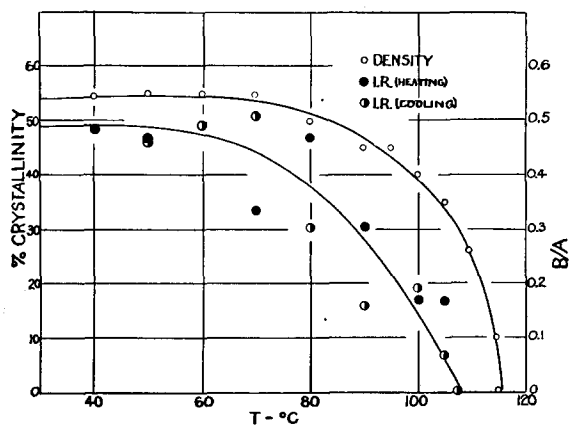[18] A. C. Hardy and F. M. Young, J. Opt. Soc. Am. 39, 265 (1949).

FIG. 6. A comparison of the ratio of the intensity of peak B to that of peak A with temperature with the variation of crystallinity (as determined by density methods).

where S is the half-width of the band and a that of the spectrometer slit. In no case did this correction amount to more than 10 percent.

The ratio of the integrated extinction coefficient under band B to that under A is plotted as a function of temperature in Fig. 6. For comparison, a typical plot of the crystallinity of polythene as a function of temperature[19] is also included. It is apparent that the relative integrated extinction coefficients and the degree of crystallinity are closely related.

A sample of the du Pont polythene 20μ thick was cold drawn as much as possible without tearing (about 500 percent) and spectra were determined. It was found that when stretched and examined with unpolarized radiation, band B became considerably weaker (Figs. 4a and 4d). For example, in the unstretched state the ratio of the extinction coefficient at the maximum of band B to that of A was about 0.7, while in the stretched state it appeared to be about 0.4. (These figures are rough because of the overlap of the bands.) With polarized radiation, band A gave a dichroism D

$$(\text{where } D = [\ln(I_0/I)_{max\perp}]/[\ln(I_0/I)_{max\|}])$$

of 6.5, while band B gave about 100. This indicates that whatever structural feature is responsible for band B is much more sensitive to orientation than that responsible for band A.

TABLE I. Transition points of C_nH_{2n+2}.

	Melting point			Transition point		
n	(This work)	(Müller)	(SPK)	(This work)	(Müller)	(SPK)
18	30°C	···	28.3°C	···	···	26.8°C
19	33°C	···	31.4°C	15°C	···	···
21	43°C	···	40.4°C	30°C	···	···
23	44°C	···	47.0°C	28°C	28–40°C	···
24	50°C	51.2°C	50.6°C	40°C	40–41°C	47.9°C
26	58°C	58.0°C	55.8°C	48°C	45–46°C	48.8°C
29	65°C	61.4°C	63.2°C	56°C	56.7–57.1°C	57.1°C
34	69°C	72.8°C	···	68°C	67–68.9°C	···
54	90°C (gradual)	···	···	80–92°C (gradual)	···	···

[19] R. B. Richards, Trans. Faraday Soc. 41, 127 (1945).

On annealing by heating for 1 hour at the melting point (without being held stretched) and then recooling quickly (5 minutes), the dichroism of each band was lost, and the intensity of band B relative to A regained its original value. There was, however, some indication that the relative intensities were restored at a lower temperature than that at which the dichroism vanished.

(b) Pure Hydrocarbons

In order to eliminate the complications arising from the coexistence of amorphous and crystalline components, the spectra of pure crystalline hydrocarbons were next studied. The latter were melted and crystallized on rock salt plates. It was found that for n-paraffins above $C_{16}H_{34}$, a doublet was present at temperatures well below their melting points, closely resembling that found for polythene except that the two peaks had equal intensity. However, on heating, peak B was observed to disappear sharply several degrees below the melting point, the transition range being less than a
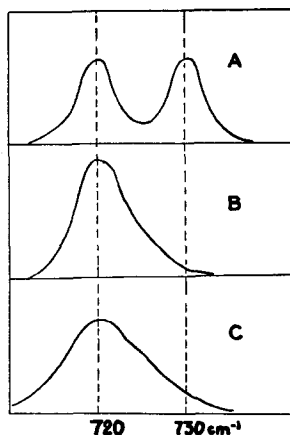

FIG. 7. The behavior of the 13.8μ doublet of n-paraffins at the transition point: (A) $\frac{1}{2}$°C below the transition point; (B) $\frac{1}{2}$°C above the transition point; and (C) above the melting point.

degree (Fig. 7). On cooling, the peak reappeared sharply at the same temperature. The transition temperature at which the peak disappeared is given for a series of n-paraffins in Table I. The melting points given in Table I were obtained by observing the temperature at which the edges of a small crystal of the material began to melt when placed on an electrically heated block on the stage of a polarizing microscope. These are compared with the values given by Müller[11] and Seyer, Patterson, and Keays (SPK).[20]

The transition temperatures may be compared (Table I) with transition temperatures ascribed to these same samples by Müller,[11] who observed a discontinuous change in the nature of the x-ray diffraction pattern. The transition points determined by Seyer, Patterson, and Keays came from discontinuities in the slope of the density-temperature curve. It is apparent that the various transition points are related to the same phenomenon. There seems little doubt that these transi-

[20] Seyer, Patterson, and Keays, J. Am. Chem. Soc. 66, 179 (1944).

tions are due to changes in crystal structure. The x-ray patterns indicate that on passing the transition point the longitudinal order of the chains in the crystal is preserved, but that there is an expansion of the unit cell perpendicular to the crystal symmetry in this plane. There appears to be some evidence to indicate that above the transition there is rotational disorder about the long axes of the chains.

(c) Deuteration

In a fully deuterated paraffin wax the absorption near 725 cm^{-1} is shifted to about 520 cm^{-1}.[1] Attempts to examine the behavior of this band on melting the deuterated paraffin led to inconclusive results because of lack of resolving power. However, this band was examined for us in another laboratory§ and the doublet separation in the solid phase was determined as 6 cm^{-1}, the individual peaks being at 518 cm^{-1} and 524 cm^{-1}. On heating to the melting point, the band at 524 cm^{-1} gradually disappears, as does the corresponding high-frequency component of this band in a normal paraffin wax.

The ratio of a hydrogenic frequency in an H compound to the corresponding frequency of the D compound should be approximately $\sqrt{2}$, and this same factor would be expected for doublet separations unless the doublet arises from combination with a low lattice mode due entirely to the nonhydrogenic atoms. The predicted separation for the doublet near 520 cm^{-1} would, therefore, be close to 7 cm^{-1} if the doubling phenomenon has no connection with the carbon vibrations. The observed value of 6 ± 1 cm^{-1} proves that the cause of the doubling must be sought entirely in motions of the hydrogen atoms.

The analog of the 1470 cm^{-1} band in n-paraffins is near 1090 cm^{-1} in the deuterated paraffin. This band is clearly a doublet in the original spectrum of Sheppard and Sutherland.[1] The maxima were carefully redetermined to be at 1086 cm^{-1} and 1093 cm^{-1}. On melting, the doublet disappears and is replaced by a single peak at an intermediate frequency.

(d) Splitting of Other Frequencies

The fact that the internal deformation frequency of the CD$_2$ group in solid deuterated paraffin is so clearly split at 1090 cm^{-1} led us to reexamine the band due to the corresponding frequency in CH$_2$ groups at 1470 cm^{-1} in C$_{24}$, C$_{26}$, C$_{34}$, and C$_{54}$ n-paraffins. Although the fine structure of the atmospheric water vapor is troublesome in this region, it was possible to establish two peaks in the solid state close to 1464 cm^{-1} and 1473 cm^{-1}. On melting, these are replaced by a single broader peak centered near 1466 cm^{-1}. We understand that this same splitting has more recently been observed by

§ We are much indebted to the late Dr. H. P. Koch of the British Rubber Producers Research Association for making these observations for us.

TABLE II. Absorption bands obtained with n-paraffins in the vicinity of 13.8μ at approximately liquid nitrogen temperature.

n	Frequencies of absorption maxima (cm^{-1})
Above 18	720 (strong), 733 (strong)
18	720
16	720 (strong), 733 (fairly strong)
15	720 (strong), 728 (very weak), 733 (fairly strong)
11	720 (strong), 728 (weak), 733 (fairly strong)
10	720 (strong), 730 (strong)
9	720 (strong), 737 (strong)
6	720 (strong), 733 (weak)

King[8] in polythene, where he also finds evidence for splitting in the CH stretching frequencies near 3.4μ.

(e) Effect of Low Temperatures

A sample of polythene was cooled to within 10°C of the liquid nitrogen temperature. It was found that the component B became appreciably sharper and shifted a little towards higher frequencies (about 3 cm^{-1}). Band A exhibited a similar but much smaller shift (about 0.5 cm^{-1}) and remained diffuse. This is in agreement with the observations of King, Hainer, and McMahon.[5]

(f) Stearic Acid and Paraffin Wax

The 13.8μ band is present in any compound containing a paraffinic chain $-(CH_2)_nCH_3$ where $n>3$. Observations were made on stearic acid ($n=17$) and a similar doubling was observed at room temperature. The high-frequency component disappeared on melting. In solution in CS$_2$ it was also found that only the lower-frequency component was present. Similar results were obtained for ordinary paraffin wax. Cole and Jones[21] have observed the dichroic doublet for single crystals of C$_{19}$H$_{39}$COOH.

(g) Multiple Splittings

Paraffins below C$_{18}$ which were normally liquid at room temperature were solidified by cooling to within 10°C of liquid nitrogen temperature in a silver chloride cell. Most of these exhibited splitting of the 13.8μ band, but not always in the simple manner found with the higher paraffins.

The results of these experiments are summarized in Table II. The resolving power was not so high in these cases as with the preceding measurements because of the scattering of the material and because of the difficulty of forming a uniform film of the solid.

It would be interesting to see whether these anomalies can be correlated with irregularities in crystal structure.

DISCUSSION OF RESULTS

In both of the explanations previously advanced for the doubling of the 13.8μ band in polythene[4,5] it was

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

assumed that the two components of the doublet were quite independent of one another. There was agreement that component B at 730 cm^{-1} must be due to the rocking frequency of the CH$_2$ group in the oriented crystalline portions of the polymer, while component A at 720 cm^{-1} was attributed solely to the amorphous part of the polymer. The experimental work described above shows that the components of the doublet are not independent of one another. The most important new fact is that in several purely crystalline n-paraffins the intensities of the components are equal. It is only reasonable to conclude that in polythene the crystalline portion must also contribute to the intensity of component A of the doublet. Confirmation of this conclusion comes from our polarization data which show that A does possess the same type of dichroism as B, but much less pronounced. Additional support is given by our observation that the more crystalline the sample of polythene, the more nearly equal are the intensities of A and B. We may now consider in some detail some of the consequences of this conclusion.

Let A_c be the integrated extinction coefficient for band A due to the crystalline material, B_c the contribution of the crystals to band B, and let A_a represent the contribution of the amorphous material to band A, and A_T and B_T the total integrated extinction coefficients, respectively, of bands A and B. It follows that

$$A_c = B_c,\tag{3}$$

$$A_T = xA_c + (1-x)A_a,\tag{4}$$

and

$$B_T = xB_c,\tag{5}$$

where x is the weight fraction of crystalline material in the sample. Let ρ be the ratio of the extinction coefficients for amorphous to crystalline material, i.e.,

$$\rho = A_a/A_c.$$

Then

$$\frac{B_T}{A_T} = \frac{x}{x+(1-x)\rho}.\tag{6}$$

It is clear that as x decreases with increasing temperature, the ratio (B_T/A_T) will decrease in a corresponding manner. In fact, if ρ can be determined, it would be possible to determine x from a measurement of (B_T/A_T).

In this connection, it should be mentioned that some observations were made on the intensity of the 13.8μ bands in crystalline C$_{21}$H$_{44}$ above and below the transition temperature. It was found that the total integrated intensity of the two bands observed below the transition temperature was equal to the integrated intensity of the single band observed above that temperature. From such an observation one might conclude that the value of ρ should be 2. However, it could be argued that A_a should be derived from measurements above the melting point. This is not easy to do experimentally as the scattering of radiation is so different
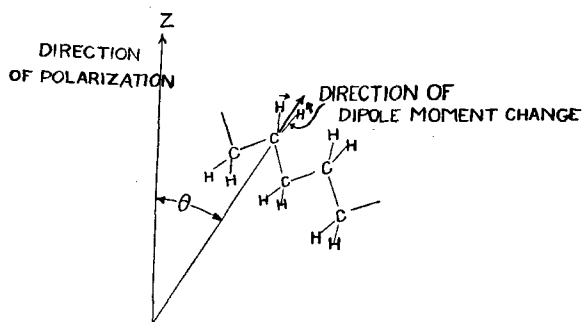

FIG. 8. The orientation of dipole moment change associated with the symmetrical CH$_2$ deformation frequency.

on the two sides of the melting point. Exploratory experiments seem to indicate that there is a decrease in the integrated extinction coefficient on melting which would reduce ρ to about 1.4.

The CH$_2$ rocking motion causes a varying component of dipole moment only perpendicular to the chain axis. Therefore, in a completely oriented crystalline paraffin, absorption due to this vibration occurs only with radiation polarized perpendicular to these axes. Assume for simplicity that no double orientation occurs upon stretching and let the extinction coefficient per CH$_2$ group for light polarized along the direction of maximum varying dipole be a. If the angle between this direction for a CH$_2$ group and the actual direction of the incident electric vector is θ (Fig. 8), the extinction for this CH$_2$ group is $a\cos^2\theta$. The total extinction coefficient for radiation polarized parallel to the z axis for a sample of polythene containing n CH$_2$ groups per cm^3 will be

$$E_{\parallel} = a\sum_i n_i \cos^2\theta_i\tag{7}$$

where n_i of the CH$_2$ groups are oriented at angle θ_i. If the sample is unoriented, all orientations are equally likely and

$$E_{\parallel} = \tfrac{1}{3}na,\tag{8}$$

since $\cos^2\theta = \tfrac{1}{3}$ averaged over a sphere. Similarly for an unoriented sample

$$E_{\perp} = \tfrac{1}{3}na\tag{9}$$

and thus for unpolarized radiation

$$E = E_{\parallel} + E_{\perp} = \tfrac{2}{3}na.\tag{10}$$

Now suppose the sample is completely oriented with the chain axis lying along the z axis and with the a and b axes randomly oriented in a direction perpendicular to this; clearly

$$E_{\parallel} = 0,\tag{11}$$

while for $E_{\perp}$, θ may assume any value around a circle with equal probability giving

$$E_{\perp} = \frac{na\int_0^{2\pi}\cos^2\theta\,d\theta}{2\pi} = \tfrac{1}{2}na\tag{12}$$

and, for unpolarized radiation,

$$E = \tfrac{1}{2} na. \tag{13}$$

It follows, therefore, that for unpolarized radiation, the extinction coefficient E will be less for an oriented sample than for an unoriented sample. Now band B is due entirely to the crystalline material, which orients quite highly on stretching.[22] This accounts qualitatively for the reduction in absorption for this band on stretching (Fig. 4). Band A is due to both amorphous and crystalline contributions. The amorphous material does not orient nearly so well as does the crystalline; consequently, the reduction in intensity for this band will not be so great. Thus the ratio (B/A) should decrease on stretching in agreement with observation (Fig. 4). There is some evidence that the reduction may be even greater than one would expect from this consideration, and that a further decrease in band B may occur as a result of a factor such as crystal deformation. However, better intensity measurements are necessary to establish this point.

The conclusion that in polythene component A is due partly to amorphous and partly to crystalline material, whereas component B is due entirely to crystalline material, also gives a satisfactory explanation of the behavior of these bands at very low temperatures. The considerable sharpening of band B is probably due to the depopulation of higher energy lattice modes, combination with which can be an important factor in broadening this band at room temperature. The increase in the B frequency at very low temperatures is also to be expected since the lattice contracts as the temperature is lowered. The doublet separation which is presumably due to the crystalline field is, therefore, increased. On the other hand, the greater width of component A at all temperatures may be attributed mainly to the amorphous polythene. It probably arises from two causes: (a) the configuration of the polymer molecule is very variable in the amorphous state and (b) the field in which the CH_2 groups oscillate is also very variable.[5] Both factors could be expected to cause small changes in the rocking frequency. Since these conditions persist at low temperatures the width and position of this band will be rather insensitive to temperature.‖

We conclude that the splitting of certain frequencies in the infrared spectra of n-paraffins and of polythene in the solid form arises only when these materials are in a certain crystalline state. The exact manner in which the crystalline field causes the observed splittings is discussed in a following paper.[23]

[22] C. W. Bunn, *Advances in Colloid Science* (Interscience Publishers, Inc., New York, 1940), Vol. 2, p. 146.

‖ Some recent observations by S. Krimm (J. Chem. Phys. **22**, 568 (1954)) demonstrate that the polarization of the components A and B is dependent upon the orientation of the a and b axes of the crystallites. This is further confirmation of the above observations, and is in agreement with predictions based upon an analysis of coupled vibrations within the crystal (see reference 23).

[23] R. S. Stein (to be published).