

TABLE I.

A*	B	$x_B$	mean $T$ ( $^{\circ}\text{C}$ )	$10^4 \cdot D'/D$
1 $\text{CCl}_4$	$\text{CCl}_2\text{CH}_3$	0.50	-2.8	0 $\pm$ 1
		0.46	12.0	3.5 $\pm$ 0.7
2 $\text{CCl}_4$	$\text{CCl}_2(\text{CH}_3)_2$	0.53	-2.8	2.4 $\pm$ 0.6
		0.50	-2.8	29 $\pm$ 1.5
3 $\text{CCl}_4$	$\text{C}(\text{CH}_3)_4$	0.28	-2.8	26 $\pm$ 1.5
		0.39	-2.8	0.5 $\pm$ 1
4 $\text{CCl}_2\text{CH}_3$	$\text{CCl}_2(\text{CH}_3)_2$	0.30	12.0	3 $\pm$ 0.7
		0.47	25.0	18 $\pm$ 1
5 $\text{CCl}_2\text{CH}_3$	$\text{C}(\text{CH}_3)_4$	0.30	-2.8	17.5 $\pm$ 1
		0.47	-2.8	17 $\pm$ 2

\* A becomes more concentrated in the cold part of the thermal diffusion cell.

The experiments were carried out with the apparatus described by G. Thomaes,<sup>3</sup> in which a system without convection is subjected to a vertical temperature gradient, the concentration gradient being measured continuously by an optical system. In order to test this method, we also measured the diffusion coefficient of the system  $\text{CCl}_4-\text{C}(\text{CH}_3)_4$  as a function of concentration by the diver method of B. Gerlach.<sup>8</sup> Both methods gave values of  $D$  of the same order of magnitude in the case of equimolecular solutions ( $D_{\text{therm}}=2.10^{-5}$ ,  $D_{\text{diver}}=1, 3.10^{-5}$ ) while dilute solutions of  $\text{C}(\text{CH}_3)_4$  in  $\text{CCl}_4$  studied in the thermal diffusion apparatus gave values of  $D$  much larger than expected. This might be explained by a slow convection of the liquid (see Table I).

As in all the former papers of this laboratory, the theory gives the correct sign of  $D'/D$ . Besides it is in good quantitative agreement with the experimental results for the system  $\text{CCl}_4-\text{C}(\text{CH}_3)_4$  ( $X=5$ ), but it cannot actually explain the rapid increase of  $D'/D$  with temperature in the case of systems 1 and 4.

We are much indebted to Professor de Brouckère and Professor Prigogine for constant advice and interest, and to the Institut Interuniversitaire des Sciences Nucléaires for financial aid.

\* Chercheur agréé de l'Institut Interuniversitaire des Sciences Nucléaires.

- Prigogine, de Brouckère, and Amand, *Physica* 16, 577 (1950).
- Prigogine de Brouckère, and H. Amand, *Physica* 16, 851 (1950).
- G. Thomaes, *Physica* 17, 885 (1951).
- R. Buess, *Bull. Soc. chim. Belg.* 61, 463 (1952).
- I. Prigogine, L. de Brouckère, and R. Buess, *Physica* 18, 915 (1952).
- Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).
- V. Mathot and A. Desmyter, *J. Chem. Phys.* 21, 782 (1953).
- B. Gerlach, *Ann. Physik* 5, 10, 437 (1931).

## Infrared Dichroism in the $13.8\mu$ Band of $n\text{-C}_{36}\text{H}_{74}$ Single Crystals and Polyethylene.

SAMUEL KRIMM

Department of Physics, University of Michigan, Ann Arbor, Michigan  
(Received January 11, 1954)

**S**TUDIES on the  $13.8\mu$  band in the infrared spectrum of  $n$ -paraffins and of polyethylene have established that this band is due to the  $\text{CH}_2$  rocking vibration in the plane perpendicular to the chain axis,<sup>1,2</sup> and that the splitting into two components, at about  $720\text{ cm}^{-1}$  and  $730\text{ cm}^{-1}$ , is probably a result of interaction between rocking modes on neighboring chains in the crystal.<sup>3,4</sup> In melted paraffins and in the amorphous regions of polyethylene this vibration occurs only at  $720\text{ cm}^{-1}$ , and, therefore, polarization measurements on cold-drawn polyethylene (in which both components exhibit perpendicular polarization) always show a higher dichroic ratio for the  $730\text{ cm}^{-1}$  band than for that at  $720\text{ cm}^{-1}$ . Theoretical considerations<sup>4</sup> indicate that the two components arise from in-phase and out-of-phase rocking motions of  $\text{CH}_2$  groups on neighboring chains. As a consequence, it is to be expected that each of the components will be polarized along a difference crystallographic axis. In order to check this, polarized spectra of single crystals of a  $n$ -paraffin  $\text{C}_{36}\text{H}_{74}$  were obtained; the results agree with this theoretical prediction.

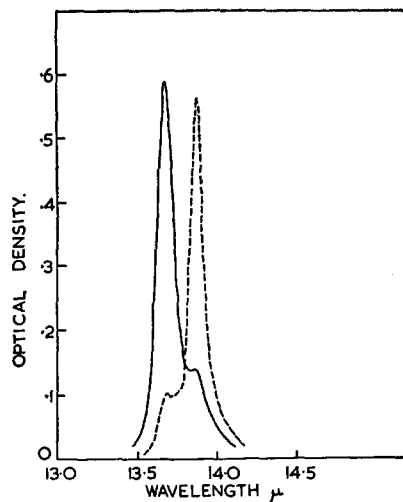


FIG. 1. Spectrum in  $13.8\mu$  region of  $n\text{-C}_{36}\text{H}_{74}$  single crystals, using polarized radiation: — electric vector parallel to  $a$  axis, ---- electric vector parallel to  $b$  axis.

Crystals of  $\text{C}_{36}\text{H}_{74}$  were grown from a di-isopropyl ether solution, being obtained as thin parallelepipeds. X-ray diffraction photographs showed that the  $c$  axis of the crystal was approximately perpendicular to the plane of the platelet and also established the orientation of the  $a$  axis and  $b$  axis. A  $b$ -axis length of  $5.56\text{ \AA}$  indicates that the crystal is a modification, different from the normal form,<sup>5</sup> in which the long chain axes are tilted at a small angle to the basal plane. The sample used consisted of a number of such single crystals oriented identically (as nearly as possible) on a rock salt plate. Using a silver chloride polarizer, spectra were obtained with the electric vector parallel to the  $a$  axis and to the  $b$  axis of the crystal.

The polarized spectrum in the  $13.8\mu$  region of the single crystals of  $\text{C}_{36}\text{H}_{74}$  is shown in Fig. 1. It is seen that each component is almost completely polarized along one crystallographic axis, the  $720\text{-cm}^{-1}$  band along the  $b$  axis and the  $730\text{-cm}^{-1}$  band along the  $a$  axis. The doublet at  $1460\text{ cm}^{-1}$  shows the same characteristics: the low-frequency component is polarized along the  $b$  axis and the high-frequency component along the  $a$  axis.

The perpendicular polarization of both components in cold-drawn polyethylene is a consequence of the fact that the alignment of the  $c$  axis along the stretching direction is accompanied by a random orientation of the  $a$  and  $b$  axes perpendicular to this direction. It has been found possible, however, by heat relaxation of a stretched sample, to disorient the crystallites in such a way that the  $a$  axis turns into the stretching direction.<sup>6</sup> On the basis

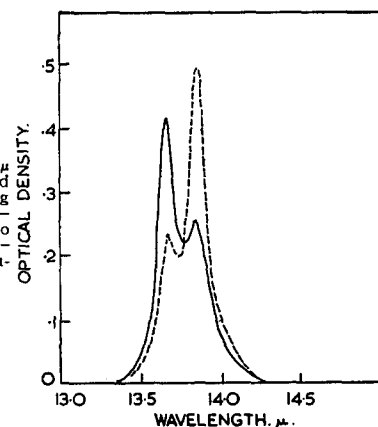


FIG. 2. Spectrum in  $13.8\mu$  region of machine-extruded polyethylene film, using polarized radiation: — electric vector parallel to machine direction, ---- electric vector perpendicular to machine direction.

of the above results on paraffin crystals, one would expect the 730-cm<sup>-1</sup> component to show parallel polarization; the spectrum of such a heat-relaxed sample showed this to be true. The same type of preferred orientation is also found in some machine-extruded films. The spectrum of such a polyethylene film is shown in Fig. 2; the parallel polarization of the 730-cm<sup>-1</sup> band is evident. The expected orientation of the crystallites, *viz.* with the *a* axis lying along the machine direction, was confirmed by x-ray photographs.

Knowing that in polyethylene the absorption at 730 cm<sup>-1</sup> is associated with *a* axes of crystals whereas that at 720 cm<sup>-1</sup> is attributable to *b* axes as well as to amorphous material, it is possible, assuming reasonable simplified crystallite distributions, to calculate readily the dichroic ratio of only the amorphous band at 720 cm<sup>-1</sup>. Such a calculation has indicated that the amorphous regions in cold-drawn and in machine-extruded specimens are indeed oriented, a result in agreement with previous x-ray studies.<sup>7</sup> The author wishes to express his appreciation to Dr. F. P. Reding of Carbide and Carbon Chemicals Company for making available the C<sub>36</sub>H<sub>74</sub>, and to Dr. P. H. Lindenmeyer of Visking Corporation for furnishing the machine-oriented polyethylene.

- <sup>1</sup> N. Sheppard and G. B. B. M. Sutherland, *Nature* **159**, 739 (1947).  
<sup>2</sup> G. B. B. M. Sutherland and A. Vallance Jones, *Nature* **160**, 567 (1947).  
<sup>3</sup> R. S. Stein and G. B. B. M. Sutherland, *J. Chem. Phys.* **21**, 370 (1953).  
<sup>4</sup> R. S. Stein (to be published).  
<sup>5</sup> A. Muller, *Proc. Roy. Soc. (London)* **A120**, 437 (1928).  
<sup>6</sup> A. Brown, *J. Appl. Phys.* **20**, 552 (1949).  
<sup>7</sup> S. Krimm and A. V. Tobolsky, *J. Polymer Sci.* **7**, 57 (1951).

### Dielectric Behavior of Methyl Bromide in 3-cm Region

KRISHNAJI AND PREM SWARUP

Department of Physics, University of Allahabad, Allahabad, India

(Received January 4, 1954)

THE dielectric behavior of the symmetric top methyl bromide molecules has been studied in gaseous state in the 3-cm microwave region at moderate pressures. The dielectric properties of a polar medium in which storage and dissipation of microwave energy are involved can be represented by complex dielectric constant  $\epsilon = \epsilon' - j\epsilon''$ , where  $(\epsilon' - 1)$  represents the electric susceptibility of the gas and  $\epsilon''$  is the dielectric loss factor which is related to the microwave absorption coefficient by the linear relation:

$$\alpha (\text{per cm}) = 2\pi\bar{\nu}\epsilon''$$

where  $\bar{\nu}$  is the frequency (cm<sup>-1</sup>) at which the absorption is measured.

The absorption of methyl bromide in the centimeter  $\nu$  region is due to a number of rotational lines<sup>1,2</sup> clustered about 0.63 cm<sup>-1</sup> and due to the inversion of the molecule in its ground vibrational state. The inversion frequency in this case is virtually zero but the absorption line is spread out to microwave region owing to the collision broadening effect. The absorption in the three-centimeter region is solely due to inversion, the contribution<sup>3</sup> of the resonant lines at 0.63 cm<sup>-1</sup> being negligible.

The theoretical value of the absorption coefficient is calculated by the quantum-mechanical expression of VanVleck and Weisskopf<sup>4</sup> for absorption:

$$\left. \begin{aligned} \frac{\alpha}{\bar{\nu}^2} &= \frac{4\pi^2 \sum_{JK} N_{JK} |\mu_{JK}|^2}{3kT} \left[ \frac{\langle \Delta\nu \rangle_{AV}}{\Delta\bar{\nu}^2 + (\bar{\nu} - \bar{\nu}_0)^2} + \frac{\langle \Delta\nu \rangle_{AV}}{\Delta\bar{\nu}^2 + (\bar{\nu} + \bar{\nu}_0)^2} \right] \\ &= \pi \cdot I \cdot \bar{\nu} \left[ \frac{\langle \Delta\nu \rangle_{AV}}{\Delta\bar{\nu}^2 + (\bar{\nu} - \bar{\nu}_0)^2} + \frac{\Delta\bar{\nu}}{\Delta\bar{\nu}^2 + (\bar{\nu} + \bar{\nu}_0)^2} \right] \\ &= 2 \cdot \pi \cdot I \cdot \bar{\nu} \left[ \frac{\langle \Delta\nu \rangle_{AV}}{\Delta\bar{\nu}^2 + \bar{\nu}^2} \right] \text{ for } \bar{\nu}_0 = 0, \end{aligned} \right\} \quad (1)$$

where  $\alpha$  (per cm) is the absorption coefficient;  $I$  is the intensity factor (per cm mercury);  $\bar{\nu}$  is the pressure (cm Hg);  $\langle \Delta\nu \rangle_{AV}$  is the line-width parameter (cm<sup>-1</sup>);  $\bar{\nu}_0$  (cm<sup>-1</sup>) is the resonance frequency. In the case when resonant frequency  $\bar{\nu}_0$  is zero, this expression (1) reduces to the well-known Debye expression (2). Table I gives

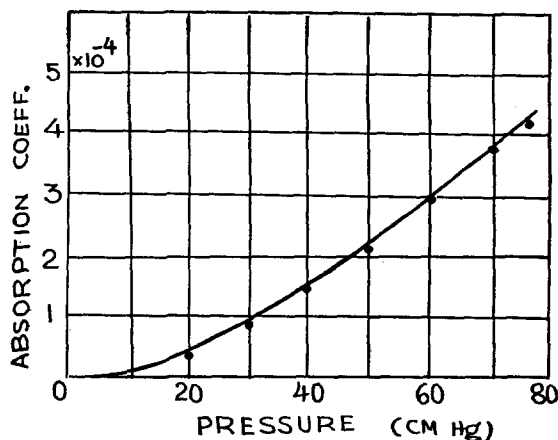


FIG. 1. Pressure variation of absorption coefficient of methyl bromide (— experimental, ··· theoretical).

the values of the parameters used for calculations. The values of these two parameters at atmospheric pressure are the same as given by Walter and Hershberger<sup>5</sup> and Bleaney and Loubser,<sup>1</sup> respectively.

The experimental techniques adopted in the measurements of absorption and susceptibility have already been reported.<sup>6-8</sup> The experimental values of the absorption coefficient in unbounded medium taken at room temperature and 3.3-cm wavelength have been plotted against pressure in Fig. 1 which also displays the theoretical points by small circles. There is a close agreement between the two sets of values. From the experimental curve of absorption *vs* pressure, we find that the curve follows  $\bar{\nu}^2$  law up to 35-cm pressure. It is, therefore, possible to represent accurately the data of the absorption coefficient tabulated in Table II for

TABLE I.

Parameters	Pressure in cm Hg					Atmos
	20	30	40	50	60	
$2 \cdot \pi \cdot I \cdot \bar{\nu} \times 10^4$	10	15	20	25	30	38
$(\Delta\nu)_{AV}$ (cm <sup>-1</sup> )	0.032	0.05	0.06	0.08	0.096	0.122

pressures up to 35 cm Hg by an equation:

$$\frac{\alpha}{\bar{\nu}^2} = (\text{const})\bar{\nu}^2$$

in which the constant comes out to be  $1.22 \times 10^{-6}$  cm per (cm Hg)<sup>2</sup>. From the absorption values we have calculated the values of the

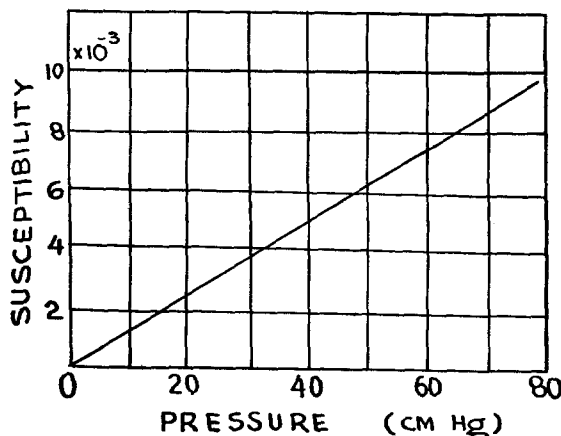


FIG. 2. Pressure variation of electric susceptibility of methyl bromide.