

## Raman Effect of Dichlorohexafluorocyclobutane

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from the saturation value of the emitted fluorescence and by assuming the time of the elementary processes.

For both of these there can be found in the literature only very feeble and uncertain data, but they can still be relied upon for an approximate calculation that the necessary number of centers should lie between  $10^{14}$ – $10^{17}$  centers per gram of fluorescent material.

This means that if the  $10^{-4}$ th part of the present manganese atoms has a valency of six resp. seven, a sufficiently great number of manganate resp. permanganate ions is present to give rise to the measured fluorescence. It is to be noted that the estimated number of these colored anions per unit surface does not cause any perceptible discoloration even in aqueous solutions. Therefore these quantities of the activator anions cannot be detected in the powders by absorption measurements.

### Raman Effect of Dichlorohexafluorocyclobutane

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November 13, 1947

LATELY the question of the planarity of the ring in simple cyclic hydrocarbons has been of considerable interest. Recent work<sup>1</sup> indicates that the cyclopentane ring is puckered. On the other hand, Raman and infra-red spectroscopy<sup>2</sup> indicates that the cyclobutane ring is planar while the same seems to be true of the ring in perfluorocyclobutane.<sup>3</sup> This study of dichlorohexafluorocyclobutane was undertaken in connection with this laboratory's interest in this problem.

Dichlorohexafluorocyclobutane is a colorless liquid boiling at 60°C. The material used was furnished by the E. I. DuPont de Nemours and Company. It was further purified by vacuum distillation, dried over  $\text{CaCl}_2$  for twenty-four hours, and made optically clear by shaking with activated charcoal and filtration through a very fine sintered glass filter. The Raman tube, having a volume of 15 ml, was filled by vacuum distillation.

Exposures were made on Eastman spectrographic plates type 103-0 and type 103a-0, using an Adam Hilger E-2 spectrograph. The Raman tube was suspended in a vertical position with the scattered light being directed into the

spectrograph by a right-angle prism. Eight upright mercury arcs arranged in a circle about the Raman tube provided the exciting radiation. Each of these mercury arcs were mounted in front of an individual elliptical reflector which was focused upon the Raman tube. The 4358Å line was used as the exciting intensity. Inasmuch as fluorocarbons are notoriously poor light scatterers, exposure times varied from 48 to 172 hours by use of slit widths from 25 to 60 microns. A continuously circulating filter solution of 0.2 percent paranitrotoluene and 0.03 gram of DuPont Rhodamine 5 GDN Extra per liter, dissolved in alcohol, was used<sup>4</sup> to reduce general scattering in the region of 4358Å and to eliminate the Raman shifts excited by the 4047Å mercury line. The average temperature of the sample was 38°C during the exposures.

We have observed nineteen Raman shifts in dichlorohexafluorocyclobutane. The results are shown in Table I.

We wish to thank Dr. J. D. Park of the Jackson Laboratories of the E. I. DuPont de Nemours and Company for this substance. Further consideration of these results will be published later.

- <sup>1</sup> J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Am. Chem. Soc.* **69**, 2483 (1947); J. G. Aston, S. C. Schumann, H. L. Fink, and P. M. Doty, *J. Am. Chem. Soc.* **63**, 2029 (1941); J. G. Aston, H. L. Fink, and S. C. Schumann, *J. Am. Chem. Soc.* **65**, 341 (1943); E. J. Rosenbaum and H. F. Jacobson, *J. Am. Chem. Soc.* **63**, 2841 (1941).  
<sup>2</sup> T. P. Wilson, *J. Chem. Phys.* **11**, 369 (1943).  
<sup>3</sup> W. F. Edgell, *J. Am. Chem. Soc.* **69**, 660 (1947).  
<sup>4</sup> J. T. Edsall and H. Scheinberg, *J. Chem. Phys.* **8**, 520 (1940).

### Phases of Fourier Coefficients Directly from Crystal Diffraction Data

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July 14, 1947

THE intensity of an x-ray beam diffracted from a crystal can be used to find the absolute value of the "crystal-structure factor"  $|F_{hkl}|$ , but not its phase. However, it appears to be possible to place limits on the phase or, if  $F_{hkl}$  is real, to determine the sign, by combining the intensity data from several diffracted beams. The general methods for doing this are outlined in the following paragraphs; a detailed article on the subject will appear later.

Although not necessary, it is helpful in strengthening the method to assume that the "atomic-structure factors,"  $f_j$ , of the atoms in a crystal are related to one another by the relation  $f_j = Z_j f$ , where  $Z_j$  is the atomic number of the  $j^{\text{th}}$  atom and  $f$  is a function of  $(\sin \theta)/\lambda$  called "the unitary atomic-structure factor." If there are  $N$  atoms in the unit cell of a crystal and

$$Z = \sum_{j=1}^N Z_j$$

is the total number of electrons in a unit cell, then

$$\sum_{j=1}^N f_j = Z f.$$

TABLE I. Raman lines of dichlorohexafluorocyclobutane.

$\Delta\nu$ $\text{cm}^{-1}$	Estimated relative intensity	$\Delta\nu$ $\text{cm}^{-1}$	Estimated relative intensity
162	S	863	W
216	VW	910	W
270(b)	S	966	S
334(b)	S	1074	W
396(d)	VS	1111	W
465	S	1190	W
490	S	1243	M
561	W	1287	W
640(b)	VS	1392	M
810	VW		

S=strong; M=medium; W=weak; V=very; b=broad; d=diffuse.

Since

$$F_{hkl} = \sum_{j=1}^N f_j \exp [-2\pi i(hx_j + ky_j + lz_j)],$$

the introduction of the  $f$  assumption allows one to write

$$\hat{F}_{hkl} = \sum_{j=1}^N n_j \exp [-2\pi i(hx_j + ky_j + lz_j)],$$

where  $\hat{F}_{hkl} = (F_{hkl})/(Zf)$  and  $n_j = Z_j/Z$ .  $\hat{F}_{hkl}$  is called "the unitary crystal-structure factor" or "the unitary Fourier coefficient." This way of writing assumes that all the atoms in the crystal have the same "shape."

The relation

$$|\sum_{j=1}^N a_j b_j|^2 \leq (\sum_{j=1}^N |a_j|^2) \cdot (\sum_{j=1}^N |b_j|^2)$$

("Cauchy's inequality") can be applied to the expression for  $\hat{F}_{hkl}$ . Taking  $a_j = (n_j)^{1/2}$  and  $b_j = (n_j)^{1/2} \exp [-2\pi i(hx_j + ky_j + lz_j)]$ , one obtains

$$|\hat{F}_{hkl}|^2 \leq \left\{ \sum_{j=1}^N n_j \right\} \left\{ \sum_{j=1}^N n_j \exp [-2\pi i(2hx_j + 2ky_j + 2lz_j)] \right\}$$

or  $|\hat{F}_{hkl}|^2 \leq 1$ , since

$$\sum_{j=1}^N n_j = 1.$$

This result explains the use of the word "unitary" in the name of  $\hat{F}_{hkl}$ .

If the crystal has symmetry, more interesting relations are obtained from Cauchy's inequality. If, for instance, a center of inversion is present, one can write

$$F_{hkl} = 2 \sum_{j=1}^{N/2} n_j \cos 2\pi(hx_j + ky_j + lz_j)$$

and, noting that  $\hat{F}_{hkl}$  is real and applying Cauchy's inequality,

$$\hat{F}_{hkl}^2 \leq 4 \left\{ \sum_{j=1}^{N/2} n_j \right\} \left\{ \sum_{j=1}^{N/2} n_j \cos 2\pi(hx_j + ky_j + lz_j) \right\}.$$

By the use of  $2 \cos^2 a = 1 + \cos 2a$  and elementary rearrangements, it follows that  $\hat{F}_{hkl}^2 \leq \frac{1}{2} + \frac{1}{2} \hat{F}_{2h2k2l}$ . This important relation requires, for instance, that  $\hat{F}_{2h2k2l}$  be positive or zero if  $\hat{F}_{hkl}^2 \geq \frac{1}{2}$ , or, if  $|\hat{F}_{2h2k2l}| > \frac{1}{2}$ , then  $\hat{F}_{2h2k2l}$  must be positive if  $\hat{F}_{hkl}^2 \geq \frac{1}{4}$ , etc. Conversely, if this inequality is contradicted, the crystal cannot have a center of symmetry. (This does not invalidate Friedel's Law, which merely states that  $|F_{hkl}| = |F_{\bar{h}\bar{k}\bar{l}}|$ .)

The presence of other symmetry elements leads to other inequalities which are derived from the appropriate expressions for  $\hat{F}_{hkl}$  by using Cauchy's inequality as in the last paragraph. Inequalities for crystals having the several

TABLE I. The inequalities arising from the various axes of symmetry.

Symbol of Axis	Equivalent Symbol	Coordinates	Inequality
1	—	Triclinic	$ \hat{F}_{hkl} ^2 \leq 1$
$\bar{1}$	—	Triclinic	$\hat{F}_{hkl}^2 \leq \frac{1}{2} + \frac{1}{2} \hat{F}_{2h2k2l}$
2	—	Monoclinic	$ \hat{F}_{hkl} ^2 \leq \frac{1}{2} + \frac{1}{2} \hat{F}_{2h02l}$
$\bar{2}$	$m$	Monoclinic	$ \hat{F}_{hkl} ^2 \leq \frac{1}{2} + \frac{1}{2} \hat{F}_{02k0}$
$2_1$	—	Monoclinic	$ \hat{F}_{hkl} ^2 \leq \frac{1}{2} + \frac{(-1)^k}{2} \hat{F}_{2h02l}$
3	—	Hexagonal	$ \hat{F}_{HK \cdot L} ^2 \leq \frac{1}{2} + \frac{1}{2}  \hat{F}_{H-K \ H+2K \cdot O}  \cos 2\pi \alpha_{H-K \ H+2K \cdot O}^*$
3	$3+\bar{1}$	Hexagonal	$\hat{F}_{HK \cdot L}^2 \leq \frac{1}{2} + \frac{1}{2} \hat{F}_{H2K \cdot 2L} + \frac{1}{2} \hat{F}_{HK \cdot 2L} + \frac{1}{2} \hat{F}_{H-K \ H+2K \cdot O}$
$3_1$	—	Hexagonal	$ \hat{F}_{HK \cdot L} ^2 \leq \frac{1}{2} + \frac{1}{2}  \hat{F}_{H-K \ H+2K \cdot O}  \cos 2\pi \left( \alpha_{H-K \ H+2K \cdot O} + \frac{L}{3} \right)^*$
4	—	Tetragonal	$ \hat{F}_{hkl} ^2 \leq \frac{1}{2} + \frac{1}{2} \hat{F}_{2h2k0} + \frac{1}{2} \hat{F}_{h-k \ h+k0}$
$\bar{4}$	—	Tetragonal	$ \hat{F}_{hkl} ^2 \leq \frac{1}{2} + \frac{1}{2} \hat{F}_{2h2k0} + \frac{1}{2}  F_{h-k \ h+k2l}  \cos 2\pi \alpha_{h-k \ h+k}^*$
$4_1$	—	Tetragonal	$ \hat{F}_{hkl} ^2 \leq \frac{1}{2} + \frac{(-1)^l}{4} \hat{F}_{2h2k0} + \frac{1}{2} \left( \cos 2\pi \frac{l}{4} \right) \hat{F}_{h-k \ h+k0}$
$4_2$	—	Tetragonal	$ \hat{F}_{hkl} ^2 \leq \frac{1}{2} + \frac{1}{2} \hat{F}_{2h2k0} + \frac{(-1)^l}{2} \hat{F}_{h-k \ h+k0}$
6	—	Hexagonal	$ \hat{F}_{HK \cdot L} ^2 \leq \frac{1}{2} + \frac{1}{2} \hat{F}_{H2K \cdot O} + \frac{1}{2} \hat{F}_{H-K \ H+2K \cdot O} + \frac{1}{2} \hat{F}_{HK \cdot O}$
$\bar{6}$	$\frac{3}{m}$	Hexagonal	$ \hat{F}_{HK \cdot L} ^2 \leq \frac{1}{2} + \frac{1}{2} \hat{F}_{00 \cdot 2L} + \frac{1}{2}  \hat{F}_{H-K \ H+2K \cdot O}  \cos 2\pi \alpha_{H-K \ H+2K \cdot O} + \frac{1}{2}  \hat{F}_{H-K \ H+2K \cdot 2L}  \cos 2\pi \alpha_{H-K \ H+2K \cdot 2L}^*$
$6_1$	—	Hexagonal	$ \hat{F}_{HK \cdot L} ^2 \leq \frac{1}{2} + \frac{(-1)^L}{6} \hat{F}_{H2K \cdot O} + \frac{1}{2} \cos 2\pi \frac{L}{3} \hat{F}_{H-K \ H+2K \cdot O} + \frac{1}{2} \cos 2\pi \frac{L}{6} \hat{F}_{HK \cdot O}$
$6_2$	—	Hexagonal	$ \hat{F}_{HK \cdot L} ^2 \leq \frac{1}{2} + \frac{1}{2} \hat{F}_{H2K \cdot O} + \frac{1}{2} \cos 2\pi \frac{L}{3} \hat{F}_{H-K \ H+2K \cdot O} + \frac{1}{2} \cos 2\pi \frac{L}{3} \hat{F}_{HK \cdot O}$
$6_3$	—	Hexagonal	$ \hat{F}_{HK \cdot L} ^2 \leq \frac{1}{2} + \frac{(-1)^L}{6} \hat{F}_{H2K \cdot O} + \frac{1}{2} \hat{F}_{H-K \ H+2K \cdot O} + \frac{(-1)^L}{3} \hat{F}_{HK \cdot O}$

\* Note:  $\hat{F}_{hkl}$  may be expressed  $\exp(-2\pi i \alpha_{hkl}) |\hat{F}_{hkl}|$ .  $\alpha_{hkl}$  is the "phase" of  $\hat{F}_{hkl}$ .

rotation axes, screw axes and rotation-inversion axes are listed in Table I.

It is possible to obtain information on the signs of those  $\hat{F}_{hkl}$ 's not determined by the inequalities involving only one  $|\hat{F}_{hkl}|^2$ . For instance, for the case of a center of inversion, treatment of  $|\hat{F}_{hkl} \pm \hat{F}_{h'k'l'}|^2$  by the methods just described yields the relation  $|2\hat{F}_{hkl}\hat{F}_{h'k'l'} - \hat{F}_{h+h', k+k', l+l'} - \hat{F}_{h-h', k-k', l-l'}| \leq 1 + \frac{1}{2}(\hat{F}_{2h2k2l} + \hat{F}_{2h'2k'2l'}) - \hat{F}_{hkl}^2 - \hat{F}_{h'k'l'}^2$ . It is probable that further development of this method will provide sign or phase determinations for most of the  $\hat{F}_{hkl}$ 's of a crystal. That not all of the signs (or phases) can be determined by these methods follows from the ambiguities in crystal structure determination discussed by A. L. Patterson.<sup>1</sup>

It is essential, before using any of these inequalities, that the experimental  $F_{hkl}$ 's be expressed in absolute units. In the case of x-ray diffraction, the units are electrons per unit cell.

<sup>1</sup> A. L. Patterson, "Ambiguities in the x-ray analysis of crystal structures," *Phys. Rev.* **65**, 195 (1944).

## Infra-Red Dichroism in Aligned Polythene and "Parowax"

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November 6, 1947

**O**RIENTED specimens of polythene were examined for dichroism in the 0.6- to 2.7- $\mu$  region. These specimens had been very kindly given to us by Dr. Wilfried Heller, now at Wayne University, and his former co-worker at the University of Chicago, Hans Oppenheimer. They were plastic films which had been stretched until the alignment of the molecular chain axes was as closely parallel to the stretch direction<sup>1</sup> as possible. The planes of the carbon backbones had a random angular distribution about this direction.

The absorption bands which appeared with unpolarized light were as follows: (1) a weak band at 8237  $\text{cm}^{-1}$ ; (2) a well defined doublet at 5782 and 5671  $\text{cm}^{-1}$ ; (3) a very strong doublet at 4322 and 4271  $\text{cm}^{-1}$ ; (4) a comparatively weak but distinct band at 4216  $\text{cm}^{-1}$ ; (5), a shallow poorly defined region between roughly 4180 and 4080  $\text{cm}^{-1}$ .

The most interesting dichroism was exhibited by the 4216- $\text{cm}^{-1}$  band. All the bands were present to some extent for both *E*-components, vibrating respectively perpendicular and parallel to the stretch direction, but were considerably stronger in the former. The 4216- $\text{cm}^{-1}$  band, in contrast, appeared *only* for the *E*-vector parallel to the stretch direction. Its intensity was considerably stronger than that found with unpolarized light.

Since this band appears distinctly for films as thin as 50 $\mu$ , it probably involves displacements within the  $\text{CH}_2$  groups. It is quite likely an overtone of a fundamental

mode in which the change of dipole moment is completely parallel to the chain axis. In their mathematical treatment of an infinite  $>\text{CH}_2$  chain, Whitcomb, Nielsen, and Thomas<sup>2</sup> derive a fundamental mode in which all the hydrogens vibrate against all the carbons in a direction parallel to the chain axis. They attribute, we believe mistakenly, the 1460- $\text{cm}^{-1}$  hydrocarbon band to this mode.

The known strong bands of normal saturated hydrocarbons at approximately 2925, 2853, and 1460  $\text{cm}^{-1}$  are usually assigned, on the uncoupled oscillator approximation, to internal vibrations of the  $>\text{CH}_2$  units. They are considered to be, respectively, the  $\nu_a$ ,  $\nu_s$ , and  $\delta$  type modes of a triangular  $\text{YX}_2$  molecule. On this same naive approximation, the two pairs of doublets (2) and (3) can be readily assigned to  $2\nu_a$ ,  $2\nu_s$ ,  $\nu_a + \delta$ , and  $\nu_s + \delta$  in that order. In keeping with these assignments, the high frequency component of both doublets was considerably the stronger of the two.

The  $\text{CH}_2$  groups lie on planes perpendicular to the chain axis. For uncoupled oscillators it would be expected that harmonics and combinations of  $\nu_a$ ,  $\nu_s$ , and  $\delta$  type  $\text{CH}_2$  vibrations would be inactive for the *E*-vector parallel to the chain axis. Although appreciably diminished, both doublets definitely appeared for this *E*-component. Their intensity was greater than what can be accounted for by imperfect alignment of the polarizer and the fact that we used a converging beam. A reasonable explanation is that for coupled oscillators there is a component of these vibrations perpendicular to the  $\text{CH}_2$  planes. It is of interest that in both pairs of doublets the lower frequency (presumably "symmetrical") component showed considerably the lesser diminution for *E*-vibrations parallel to the stretch direction.

Unpolarized light spectrograms of thin films sliced from a block of "parowax" were essentially identical with those for polythene. The random molecular orientation in the sliced films made useless any polarization study.

Electron diffraction studies of very thin paraffin films, deposited from a drop of ether solution onto a water surface, have shown that the molecular chain axes are oriented normal to the surface.<sup>3</sup> We prepared semi-crystalline films of from 40- to 500- $\mu$  thickness by slow cooling of a melt on a hot water surface. To minimize disorientation owing to the heat of the beam, these films were placed at the exit rather than entrance slit of our instrument. Unpolarized light spectrograms gave convincing proof of an excellent alignment of the chain axes normal to the surface. The band at 4216  $\text{cm}^{-1}$  was completely missing, and the intensity ratios and general appearance of the observed bands were unmistakably like those of the spectrograms made for polythene when the *E*-vector was directed perpendicular to the stretch direction.

A detailed account will be published in the future. We intend to investigate the fundamental region with an instrument now under repair. An assignment in agreement with group theory selection rules will be attempted for the bands involving  $\text{CH}_2$  vibrations.

<sup>1</sup> W. Heller, *Phys. Rev.* **69**, 53 (1946).

<sup>2</sup> S. E. Whitcomb, H. H. Nielsen, and L. H. Thomas, *J. Chem. Phys.* **8**, 143 (1940).

<sup>3</sup> Trillat and Hirsch, *Comptes rendus* **195**, 215 (1932).