

## InfraRed Dichroism in Aligned Polythene and "Parowax"

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Citation: [The Journal of Chemical Physics](#) **15**, 884 (1947); doi: 10.1063/1.1746415

View online: <http://dx.doi.org/10.1063/1.1746415>

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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).