

It is proposed to continue to study this interesting reaction in greater detail, and to publish a full report elsewhere.

A. B. HART

Royal Naval Scientific Service,  
Fanum House,  
Leicester Square,  
London, W.C.2.  
Dec. 6.

<sup>1</sup> Baker and Ouellet, *Can. J. Res.*, **23** B, 167 (1945).

<sup>2</sup> Harris, *Proc. Roy. Soc.*, A, **175**, 254 (1940).

<sup>3</sup> Giguère, *Can. J. Res.*, **25** B, 135 (1947).

<sup>4</sup> Mackenzie and Ritchie, *Proc. Roy. Soc.*, A, **185**, 207 (1946).

<sup>5</sup> Midard, *C.R. Acad. Sci., Paris*, **222**, 1491 (1946).

### Vibrations of an Infinitely Long Chain of CH<sub>2</sub>-Groups and the Infra-red Spectrum of Polythene

THE vibrations of an infinitely long chain of CH<sub>2</sub>-groups have been calculated using a valence and angle force potential. It is assumed that the carbon atoms form a zigzag line in the  $x, y$ -plane, from which the two C—H linkages branch off symmetrically with respect to this plane, with the  $x$ -axis as molecular axis. This array can be considered as a crystal lattice the elementary cell of which consists of two CH<sub>2</sub>-groups (six particles in the cell) resulting in eighteen vibrations of the elementary cell. The potential function  $V$  has the form:

$$2V = f_C \sum_i \lambda_i^2 + f_H \sum_i (l_i'^2 + l_i''^2) + b^2 \varphi_H \sum_i \beta_i^2 + a^2 \varphi_C \sum_i \lambda_i^2 + ab \varphi_{CH} \{ \sum_i (\delta_i'^2 + \delta_i''^2) + \sum_i (\epsilon_i'^2 + \epsilon_i''^2) \} + 2 ab \sin \frac{\theta}{2} \tau \sum_i \Psi_i^2.$$

$$(\lambda_i = \beta_i - \delta_i' - \delta_i'' + \epsilon_i' + \epsilon_i''),$$

where  $l_i$  is stretching of C<sub>*i*</sub>—C<sub>*i+1*</sub> linkages;  $l_i'$  and  $l_i''$  are stretching of two C—H linkages attached to C<sub>*i*</sub>;  $\lambda_i$  is change of the angle C<sub>*i-1*</sub>—C<sub>*i*</sub>—C<sub>*i+1*</sub>;  $\beta_i$  is change of the angle H<sub>*i*</sub>'—C<sub>*i*</sub>—H<sub>*i*</sub>'';  $\delta_i'$ ,  $\delta_i''$  are changes of the angle C<sub>*i-1*</sub>—C<sub>*i*</sub>—H<sub>*i*</sub>;  $\epsilon_i'$  and  $\epsilon_i''$  are changes of the angle H<sub>*i*</sub>—C<sub>*i*</sub>—C<sub>*i+1*</sub>;  $\Psi_i$  is angle of twist of C—C linkages produced by a rotation of the two CH<sub>2</sub>-groups at the ends of the bond around it;  $a$  is the equilibrium distance of the carbon atoms,  $b$  of the C—H linkages and  $\theta$  the tetrahedral angle;  $f_C$ ,  $f_H$ , etc., are the force constants associated with these movements.

The vibrations can be split up into two groups, symmetric and antisymmetric with respect to the  $x, y$ -plane. There are five frequency branches in the symmetric group and four branches in the antisymmetric group. The eighteen vibrations (corresponding to the phase differences 0 and  $\pi$ ) have been evaluated as functions of the force constants and interatomic distances, and the dipole moments associated with them calculated on the assumption that only the C—H linkages carry a dipole moment. Five frequencies turn out to be zero (improper vibrations), and of the remaining thirteen only five are infra-red active. The inactivity of the other vibrations is due to the inner symmetry of the elementary cell (symmetry group  $S_2(i)$ ).

An attempt has been made to fit these vibrations to the observed infra-red spectrum of polythene<sup>1</sup> (molecular weight 13,000); the results of the cal-

Infra-red spectrum of C<sub>n</sub>H<sub>2n</sub>

Symmetry class	Frequencies in wave numbers		Relative intensities	
	Calc.	Obs.	Calc.	Obs.
A <sub>g</sub>	$\nu_2$ 1090 cm. <sup>-1</sup>	1080 cm. <sup>-1</sup> <sup>1</sup>	0	3.5
	$\nu_3$ 2880	2853 <sup>2</sup>	0	0.9
	$\nu_4$ 1560	—	0	—
	$\nu_5$ 890	890 <sup>1</sup>	0	2.0
	$\nu_6$ 1617	1640 <sup>1</sup>	0	1.0
	A <sub>u</sub>	$\nu_7$ 717	725 <sup>1</sup>	100 $M_x$
$\nu_8$ 2960		2960 <sup>2</sup>	0.7 $M_z$	0.6
$\nu_{12}$ 1710		1710 <sup>1</sup>	0	0.9
B <sub>g</sub>	$\nu_{13}$ 1490	1380 ? <sup>1</sup>	0	16 $\pi^4$
	$\nu_{14}$ 2980	—	0	—
	B <sub>u</sub>	$\nu_{16}$ 1307	1310 <sup>1</sup>	10 $M_x$
$\nu_{17}$ 2884		2925 <sup>2</sup>	1.7 $M_y$	0.5
$\nu_{18}$ 1460		1460 <sup>1</sup>	65 $M_y$	27 $\sigma^{3,4}$

culations are compared in the accompanying table with Thompson and Torkington's<sup>1</sup> and Fox and Martin's<sup>2</sup> observations.

The observed intensities refer to the absorption coefficient at maximum absorption; the calculated intensities are proportional to  $n^2 e_H^2$ , where  $n$  is the number of CH<sub>2</sub>-groups in the molecule and  $e_H$  the effective charge on the CH-dipole.  $M_x$ ,  $M_y$  and  $M_z$  are the non-vanishing components of the dipole moment; the observed polarization is indicated by  $\pi$  and  $\sigma$ .  $\pi$  and  $\sigma$  mean that the intensity of the band is stronger when the incident electric vector is parallel or perpendicular to the molecular axis ( $x$ -axis). The inactive bands are, with two exceptions, weakly active, possibly on account of the two CH<sub>2</sub>-groups at the ends of the molecule. Besides, any folding of the chain would destroy the  $S_2(i)$  symmetry, that is, alter the selection rules. The spectra of cracked polythene observed by Thompson and Torkington<sup>1</sup> seem to show that the case of molecular weight 7100 ( $n \sim 500$ ) must still be treated as a finite molecule, whereas the periodic structure is fully established for a molecular weight of 13,000 ( $n \sim 900$ ).

It is proposed to extend this treatment to more complicated polymers. A detailed report of the calculations will be published shortly.

L. KELLNER

Imperial College of Science and Technology,  
London, S.W.7.  
Dec. 3.

<sup>1</sup> Thompson, H. W., and Torkington, P., *Proc. Roy. Soc.*, A, **184**, 3 (1945).

<sup>2</sup> Fox, J. J., and Martin, A. E., *Proc. Roy. Soc.*, A, **175**, 208 (1940).

<sup>3</sup> Sutherland, G. B. B. M., and Vallance Jones, A., *Nature*, **160**, 567 (1947).

<sup>4</sup> Elliott, A., Ambrose, E. J., and Temple, R. B., *J. Chem. Phys.*, **16**, 877 (1948).

### Metallic Oxides as Barrier Treatments for Prevention of Attack by Light on Cellulose

ALTHOUGH the literature contains evidence of sporadic attempts to investigate various types of barrier treatments on cellulose for the prevention of attack by light<sup>1,2,3</sup>, no systematic work would appear to have been carried out to date on the subject. The evidence is often conflicting, as in the case of iron compounds<sup>1,2</sup>, and in any event the mechanism of protective action of such diverse barriers as have been studied is not clear. In the course of a wider investigation on the elucidation of the mechanism of attack by light on cellulose, which is in progress in this Laboratory, it was considered of immediate practical importance to study on systematic lines the influence of certain metallic oxides deposited on