Calculation of the f.i.r. absorption frequencies of polyethylene using a proved semiempirical potential function

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A potential function successful in describing the properties of isolated chains of several polymers as well as crystal properties of polyethylene is applied to calculate frequencies of lattice modes of this polymer. The B_{1u} and B_{2u} frequencies are determined as 86 and 105 cm^{-1}, respectively, for the crystal at T = OK. These values are compared with the extrapolated frequencies from temperature dependent f.i.r. absorption spectrum of linear PE (6011 L) measured by Frank *et al.* The values are 83 and 108 cm^{-1}, respectively. An influence of the setting angle to the transition moment is discussed.

INTRODUCTION

The far infra-red spectrum of PE shows two absorption bands, one of them observable at room temperature at 73 cm^{-1}, the other observable only at low temperature near 108 cm^{-1}.

In recent work Frank *et al.*[1] have measured the complete temperature dependence of the f.i.r. absorption spectrum of PE. So one can extrapolate these frequencies to T = OK.

It would be interesting to test a theoretical crystal model, developed in 1974 by Scherr *et al.*[2], for its ability to reproduce these extrapolated frequencies. By moving neighbouring chains in this model in a manner in keeping with the band assignment one should produce potential functions, from which the intermolecular force constants can be calculated. In the past this type of calculation was carried out only considering the intermolecular H . . . H interaction[3,4]. In the present work a semi-empirical potential function considering the C–H as well as C–C intermolecular interaction is used.

BAND ASSIGNMENT

Calculations by Tasumi and Shimanouchi[3] and Tasumi and Krimm[4] give an assignment of the translatory lattice vibration B_{1u} to a vibration parallel to the b-axis (transition moment parallel to the a-axis). This gives rise to the well known 73 cm^{-1} band. The vibration B_{2u} perpendicular to B_{1u} was predicted[4] and the corresponding absorption band at 113 cm^{-1} at 100K was first observed by Dean and Martin[5] at 2K. From the frequencies observed the force constants can be determined provided there is no doubt about the vibrating masses. In *Figure 1* the absorption spectra of linear PE (6011 L) are shown at 296K, and 12K together with the spectrum of a 99% deuterated PE at 296K. Under the provision, that in both kinds of PE the force constants of the intermolecular interactions do not differ, the vibrating masses can be calculated:

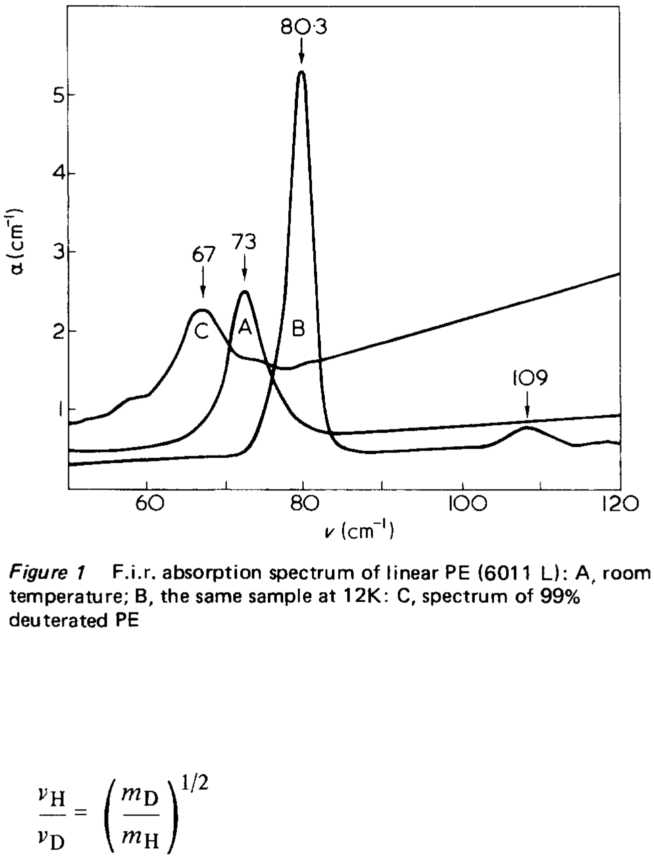

Figure 1 F.i.r. absorption spectrum of linear PE (6011 L): A, room temperature; B, the same sample at 12K: C, spectrum of 99% deuterated PE

$$\frac{\nu_H}{\nu_D} = \left(\frac{m_D}{m_H}\right)^{1/2}$$

where ν_D, ν_H are wavenumbers of the deuterated and undeuterated material, respectively and m_D, m_H are analogous to the vibrating masses.

From the frequencies of *Figure 1* we obtain:

$$\frac{\nu_H}{\nu_D} = 1.089 \approx \left(\frac{16}{14}\right)^{1/2}$$

(see also Dean and Martin[5]).

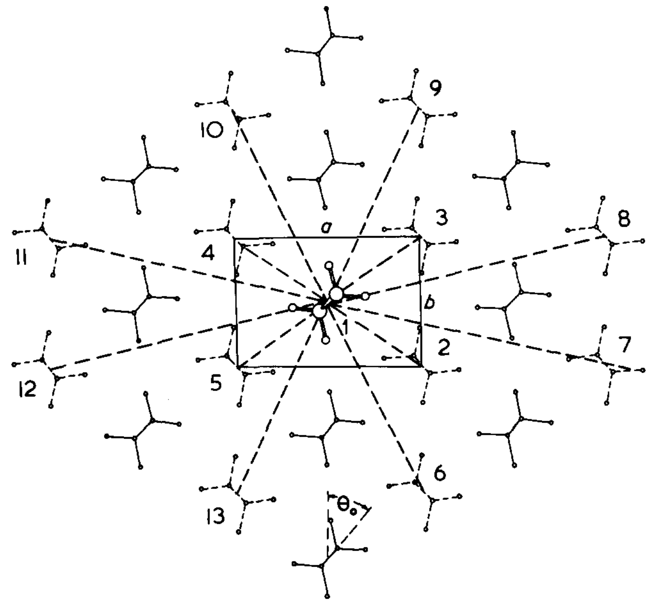

Figure 2 Projection of the *ab*-plane of the orthorhombic lattice of PE. Note the definition of Θ_0

THE CRYSTAL MODEL

Starting with an extended chain crystal of infinite dimensions, a unit cell was chosen with translatory symmetry determined by the crystal geometry. For practical calculations, the following interactions were taken into account.

(a) Intermolecular interaction between chains is as indicated in *Figure 2*. The chains connected by lines form a partial lattice vibrating towards the unconnected chains as a whole. By considering the lattice of unconnected chains as fixed, then each vibrating chain has 4 nearest neighbours in the first shell (*Figure 2*, chain 2–5) and an additional 8 (*Figure 2*, chain 6–13) in the second shell of the resting partial lattice. For the infinite crystal it is sufficient to consider only one chain moving against the fixed lattice. The calculations showed, that the second shell influences the force constants to less than 1%. Therefore we restricted our considerations to the first shell.

(b) Especially for a single CH_2 group the following interactions are taken into account (see *Figure 3*). Each atom of a CH_2 group interacts with each atom of 15 CH_2 groups on each neighbouring chain. More distant groups produce a negligible influence, as shown by calculations[6].

For the purpose described we have used the potential function developed by Wobser and Hägele, which has been proved in the meantime to give good values for the ideal chain structure, and for the defect structure by rotational isomers[7–9] and folds[10] of several polymers, such as PE, polypropylene, polyisobutylene, polybutadiene, polyisoprene and polystyrene.

For PE the model additionally gives the elastic constants of the crystal, the dimensions and angles of the unit cell and the cohesion energy[11,12]. The potential set in general is given by:

$$U_{\mathrm{total}} = U_{\mathrm{ster}} + U_{\mathrm{rot}} + U_{\mathrm{val}}$$

with

$$U_{\mathrm{ster}} = \sum_{\substack{\mathrm{H..H}\\ \mathrm{C..H}\\ \mathrm{C..C}}} -A\,r^{-6} + B\exp(-Cr)$$

$$U_{\mathrm{rot}} = \sum_{\mathrm{C-C}} \frac{U_0}{2}\,(1 - \cos 3\varphi)$$

$$U_{\mathrm{val}} = \sum_{\substack{\mathrm{C..C}\\ \sphericalangle\mathrm{C..H}\\ \mathrm{H..H}}} \frac{k}{2}\,(\vartheta - \vartheta_0)^2$$

In our case we assume that the chain backbone remains rigid which means that any coupling of intramolecular vibrations and rotations with the vibration under consideration is neglected. So we have only to consider the Buckingham term U_{ster}. In the expression for U_{ster} we have to put the following constants:

	H...H	C...H	C...C
A (kcal/mol Å^6)	33	128.5	500
B (kcal/mol)	3000	14 000	53 000
C (Å^{-1})	3.74	3.67	3.60

PROCEDURE

The calculation was carried out as follows. The central

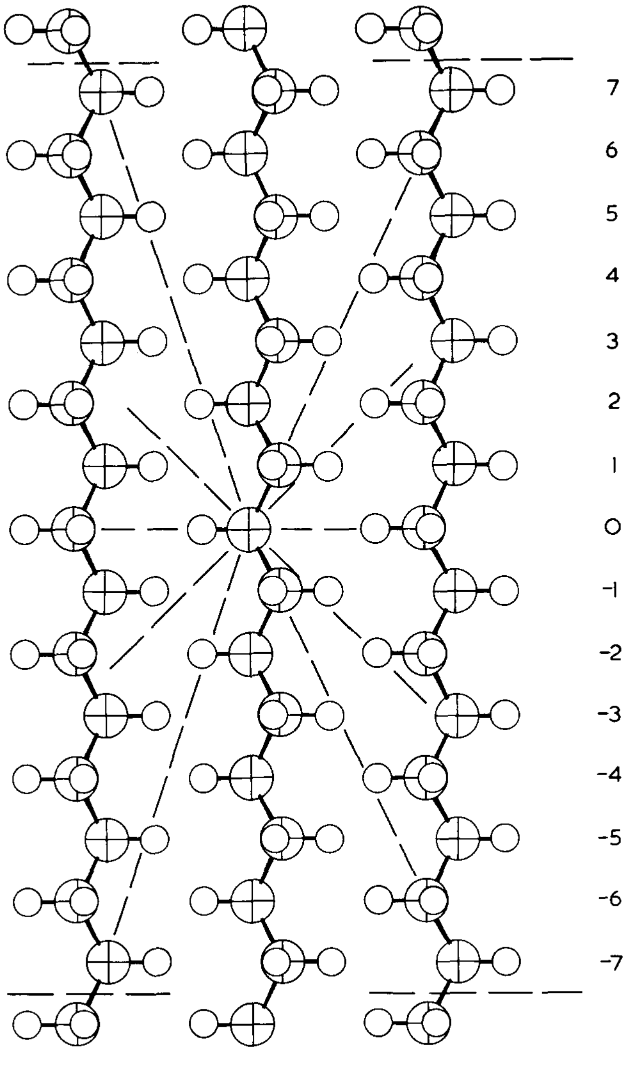

Figure 3 Projection of the chains 1, 2 and 5 in the direction of the *b*-axis

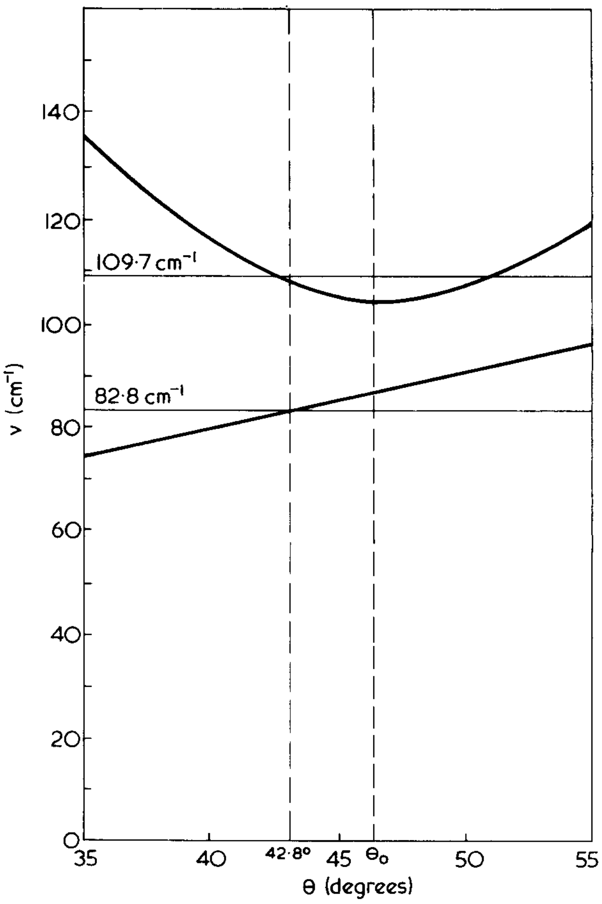

Figure 4 Dependence of the calculated frequencies from the setting angle Θ

chain of the unit cell was moved as a stick in *a*- and in *b*-directions in steps of 0.01 Å with a total displacement of ±0.2 Å. The region within ±0.1 Å of the equilibrium position was approximated by a parabola. The second derivative of this gives the relevant force constant. With the CH_2 group as the vibrating mass the frequencies were calculated under the condition, that the actual force constant is twice that calculated. These calculations were carried out for several setting angles between 35° and 55° (see *Figure 4*).

The lattice parameters (crystallographic distances a = 7.239 Å, b = 4.927 Å and setting angle ($\Theta_0 = 46.3°$) were taken from a minimization of the total crystal energy with the potential function mentioned above. Each chain interacts with its six nearest neighbours[2,12].

In order to prove the influence of the setting angle on the vibrational frequencies, the crystal axes were kept constant at the above values and the setting angle was varied between 35° and 55°.

RESULTS AND DISCUSSION

The experimental values are extrapolated to T = OK from the measured temperature dependence of the two absorption bands. They are shown in *Figure 5*. The extrapolation is carried out from the medium temperature range since the zero-point vibration, which gives rise to a softening of the force constant at T = OK, must be eliminated.

The values obtained are:

	Experimental	Calculated $\Theta = \Theta_0 = 46.3°$	Calculated $\Theta = 42°$
B_{2u}	109.7 ± 1 cm^{-1}	105 cm^{-1}	110 cm^{-1}
B_{1u}	82.8 ± 0.2 cm^{-1}	85.5 cm^{-1}	82.5 cm^{-1}

It is clear that the deviation of the calculated and measured values do not display the same trend. So we assumed an influence of the setting angle, which in the first calculation had the value fitted to the parameters of Zugenmaier for the extended chain crystal[13]. In an actual PE the angle has the well established values of θ 42° [14].

We have varied the angle from 35° to 55° with the result illustrated in *Figure 4*. If we plot the experimental frequencies into *Figure 4*, we see that they can be theoretically obtained with a Θ of 42.8°, a value which is close to that determined experimental. The difference between the value of Θ for the extended chain crystal and the measured values of real samples may be generated by the influence of surface defects, e.g. folds.

Small discrepancies in the frequencies are introduced by the use of cell parameters calculated by minimization of the crystal energy function considering 18 nearest neighbours per chain. These discrepancies would be decreased by admitting a torsion of the rigid chain during its movement, which gives an additional lowering of the potential energy of the crystal.

It is remarkable that the simple procedure – moving rigid chains with fixed setting angle – is able to reproduce the experimental frequencies.

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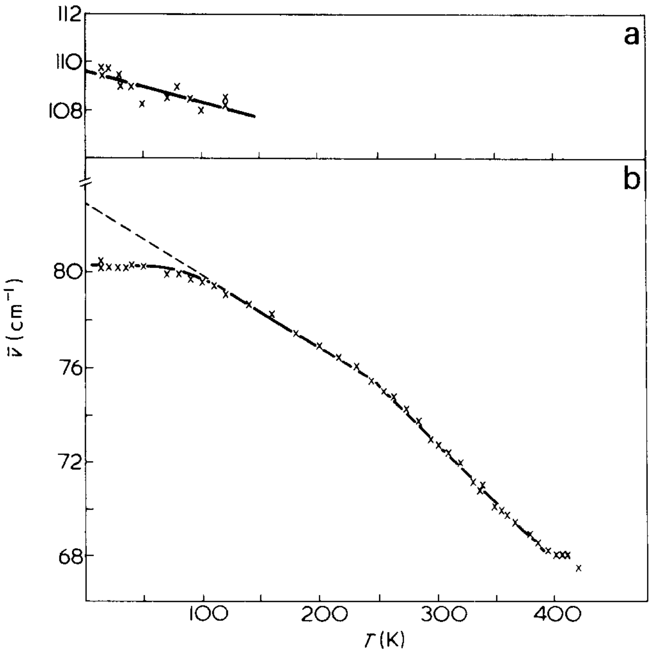

Figure 5 Temperature dependence of the maximum absorption frequencies of the B_{2u} (a) and B_{1u} (b) vibrations from Frank *et al.*[1]

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