Frequency Distribution and Dispersion Curves of Crystal Vibrations of Perdeuterated Polyethylene

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ABSTRACT: Crystal vibrations of perdeuterated polyethylene were treated with interchain as well as intrachain potential functions. Degeneracies and compatibility relations of frequency dispersion curves were derived from irreducible representations of k groups. Frequency dispersion curves for boundaries of the first Brillouin zone were calculated and were assigned to symmetry classes of k groups on the basis of eigenvectors in symmetry co-ordinate space. Theoretical dispersion curves for the phase difference vector along the c axis agree closely with experimental data derived from coherent inelastic scattering of neutrons measured by Feldkamp, *et al.* The frequency distribution of crystal vibrations was calculated, in agreement with the experimental distribution derived from incoherent scattering of neutrons measured by Lynch, *et al.*

KEY WORDS Perdeuterated Polyethylene / Crystal Vibrations / Frequency Distribution / Frequency Dispersion Curve / Neutron Scattering / Normal Vibrations.

A group-theoretical method for treating lattice vibrations of orthorhombic polyethylene was worked out previously and, with irreducible representations of k groups, Cartesian symmetry co-ordinates of carbon atoms were constructed from translational-symmetry co-ordinates with non-integral index vectors.¹ Acoustic vibrations in the lowest frequency region are responsible for specific heat in the lowest temperature region. Accordingly a practical method was derived for calculating the frequency distribution of acoustic vibrations from the volume enclosed in constant-frequency surfaces in the three-dimensional phase-difference space.² The frequency distribution of optical as well as acoustic branches is responsible for specific heat in the intermediate temperature region. An efficient method was worked out for calculating the frequency distribution of chain-polymer crystals from vibrational frequencies associated with a number of phase-difference vectors in the first Brillouin zone.²

Elastic and inelastic scattering cross sections of thermal neutrons are due to the frequency distribution of crystal vibrations and vibrational displacements of scattering nuclei. For analyses of experimental data of neutron-scattering from

orthorhombic polyethylene, the frequency distribution⁴ and scattering cross sections^{5,6} were calculated and vibrational assignments were made of inelastic scattering peaks.

Inelastic scattering of thermal neutrons was also measured for the orthorhombic form of perdeuterated polyethylene.⁷ For an oriented sample, coherent inelastic scattering was measured and some dispersion relations were experimentally studied.⁸ Accordingly, for analyzing neutron scattering data of perdeuterated polyethylene, crystal vibrations were treated and the frequency distribution, frequency dispersion curves, their degeneracy and compatibility relations were treated in the present study.

CRYSTAL STRUCTURE AND FORCE CONSTANTS

The crystal structure of orthorhombic polyethylene was analyzed by Bunn⁹ with the X-ray diffraction method. The space group is $P_{21}am$ (D_{2h}^{16}) and there are four methylene groups per unit cell, and two molecular chains pass through a unit cell along the c axis (Figure 1). However, the setting angle (θ) of the skeletal plane with respect to the a axis is not yet

Figure 1. Crystal structure⁹ and inter-hydrogen contacts (P_1 — P_4)¹⁷ of orthorhombic polyethylene.

established by X-ray crystal analyses; thus the setting angle at room temperature was reported as $\theta = 48.7^\circ$ (Bunn⁹), $\theta = 42^\circ$ (Smith¹⁰ for orthorhombic $n\text{-C}_{23}\text{H}_{48}$), $\theta = 41^\circ 23'$ (Shearer and Vand¹¹ for monoclinic $n\text{-C}_{36}\text{H}_{74}$) or $\theta = 47.7^\circ$ (Teare¹² for orthorhombic $n\text{-C}_{36}\text{H}_{74}$). Snyder¹³ measured the relative infrared intensities of the B_{1u} and B_{2u} components of the CH_2 rocking bands at -180°C and reported the value of $\theta = 42^\circ$. The setting angle possibly depends upon temperature. In the present study on crystal vibrations at low temperatures, the lattice constants¹⁴ at 77°K were used ($a_0 = 7.155$, $b_0 = 4.899$, and $c_0 = 2.547 \text{ \AA}$) and the setting angle was taken as $\theta = 45^\circ$. As the intramolecular parameters, the bond lengths of $r(\text{C} - \text{C}) = 1.54$ and $r(\text{C} - \text{H}) = 1.09 \text{ \AA}$ and bond angles of $\phi(\text{C} - \text{C} - \text{C}) = 111^\circ 47'$ and $\phi(\text{H} - \text{C} - \text{H}) = 109^\circ 27'$ were used.

As for the intrachain potential function, the force constants refined by Schachtschneider and Snyder¹⁵ were used. However, the force constant for the internal rotation about $\text{C} - \text{C}$ bonds was adjusted as $0.075 \text{ md} \cdot \text{\AA} / \text{rad}^2$ with reference to the specific heat¹⁶ at $\sim 60^\circ\text{K}$. As the interchain potential, four types $P_1 - P_4$ in Figure 1) of $\text{H} \cdots \text{H}$ interaction terms¹⁷ were incorporated. The $\text{H} \cdots \text{H}$ force constants⁴ of $P_1 = 0.004_2$, $P_2 = 0.010_1$, $P_3 = 0.006_4$ and $P_4 = 0.011_2 \text{ md/\AA}$ yield the splitting of the infrared active CH_2 vibrations as $\Delta\nu(\text{bend}) = 10$ and $\Delta\nu(\text{rock}) = 10 \text{ cm}^{-1}$ as compared with the experimental values¹³ of $\Delta\nu(\text{bend}) = 13$ and $\Delta\nu(\text{rock}) = 13 \text{ cm}^{-1}$.

SYMMETRY CO-ORDINATES

Crystal vibrations are specified with phase-differences of vibrational displacements between corresponding atoms in adjacent unit cells. For the orthorhombic crystal of polyethylene, there are twelve atoms per unit cell and accordingly there are thirty-six Cartesian symmetry co-ordinates $[S(\delta)]$ associated with any given phase-difference vector (δ). The symmetry co-ordinates of hydrogen atoms may be constructed with the same transformation as the symmetry co-ordinates of carbon atoms¹, since hydrogen and carbon atoms of orthorhombic polyethylene are group-theoretically on the same special site (the mirror plane perpendicular to the c axis).

The symmetry-co-ordinate subvectors $S_j(\delta)$ may now be defined as

$$S_j(\delta)^\dagger = [S_{jH_1}(\delta) \quad S_{jH_2}(\delta) \quad S_{jC}(\delta)] \quad (1)$$

where the superscripts (H_1 , H_2 and C) characterize atoms (Figure 1) and the subscripts (j) denote symmetry co-ordinates as given in eq 26 of ref 1. Then, corresponding to eq 36 of ref 1, the Cartesian symmetry-co-ordinate vector $S(\delta)$, with thirty-six components, may be written as

$$\begin{aligned} S(\delta)^\dagger = & [S_1(\delta)^\dagger S_2(\delta)^\dagger S_3(\delta)^\dagger S_4(\delta)^\dagger \\ & S_5(\delta)^\dagger S_6(\delta)^\dagger S_7(\delta)^\dagger S_8(\delta)^\dagger \\ & S_9(\delta)^\dagger S_{11}(\delta)^\dagger S_{12}(\delta)^\dagger S_{10}(\delta)^\dagger] \quad (2) \end{aligned}$$

Similarly, for the i -th methylene group of a unit cell, the Cartesian co-ordinate vector $X(\rho_i)$, with nine components, may be defined as

$$X(\rho_i)^\dagger = [x(\rho_i)^\dagger y(\rho_i)^\dagger z(\rho_i)^\dagger] \quad (3)$$

and

$$\alpha(\rho_i)^\dagger = [\alpha^{H_1}(\rho_i) \alpha^{H_2}(\rho_i) \alpha^C(\rho_i)] \quad (4)$$

where $\alpha^k(\rho_i)$ is the component α ($= x, y$ or z) of the Cartesian co-ordinate vector of the atom κ ($= H_1, H_2$ or C) and ρ_i is the non-integral index vector of the i -th methylene group as given in eq 1 of ref 1. Accordingly, the elements (c_i , s_i , and 0) of the transformation submatrices (u_i^c and u_i^s) of eq 38 of ref 1 need to be substituted with three-dimensional constant matrices,

$$\begin{aligned}
 c_i &\rightarrow \begin{bmatrix} c_i & 0 & 0 \\ 0 & c_i & 0 \\ 0 & 0 & c_i \end{bmatrix} \\
 s_i &\rightarrow \begin{bmatrix} s_i & 0 & 0 \\ 0 & s_i & 0 \\ 0 & 0 & s_i \end{bmatrix} \\
 0 &\rightarrow \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}
 \end{aligned}$$

(5)

Finally, eq 37 of ref 1 applies for the transformation of the $X(\rho_1)$, $X(\rho_2)$, $X(\rho_3)$ and $X(\rho_4)$ vectors [eq 3] into the Cartesian symmetry-co-ordinate vector $S(\delta)$ [eq 2].

COMPATIBILITY

For special δ vectors (with components of $\delta = 0$ or π), dynamical matrices of crystal vibrations may be factored and frequency-dispersion curves may be assigned to symmetry species of the k group.¹⁸ However, vibrational frequencies change continuously with δ and the symmetry co-ordinates for a special δ vector can serve as symmetry co-ordinates for k groups of lower symmetry (see Table 12 of ref 1). These compatibility relations are derived from irreducible representation of k groups.

For the space group Pnam, the compatibility relations of frequency-dispersion curves were derived as shown in Table I, where symbols follow the BSW notation.²⁰ The two symmetry

Table I. Compatibility relations of frequency-dispersion curves of polyethylene crystal (Pnam)

Table I. Continued

(0,0,0)		(0,0, π)	($\pi,\pi,0$)	(π,π,π)
(0,0, σ_c)			(π,π,σ_c)	
Γ_1	Δ_1	Υ_1	U_1	F_1
Γ_4			U_2	
Γ_6	Δ_4	Υ_1	U_4	F_2
Γ_7			U_3	
Γ_2	Δ_3	Υ_2	U_5	F_3
Γ_3			U_6	
Γ_5	Δ_2	Υ_2	U_8	F_4
Γ_8			U_7	
				R_1
				R_2
(0,0,0)		($\pi,0,\pi$)	(0, $\pi,0$)	(0, π,π)
(0,0, σ_c)			(0, π,σ_c)	
X_1	D_1	S_1	Z_1	T_1
X_2			Z_2	
				T_2

species partitioned by a broken line in a block are degenerate pairs due to the time reversal symmetry, and accordingly the degeneracy of frequency dispersion curves is twice the degeneracy due to the space symmetry. The time reversal degeneracy (t_s) and space degeneracy (f_s) were derived previously (Table 10 of ref 1).

DISPERSION CURVES

Dynamical matrices of perdeuterated polyethylene ($-\text{CD}_2-$)_p for various $\mathbf{\theta}$ vectors were constructed on the basis of the Cartesian symmetry co-ordinate vector of eq 2 and were diagonalized. Frequency dispersion curves of crystal vibrations below 500 cm^{-1} are shown in Figures 3a—h. Since the dynamical matrix may be factored into blocks of symmetry species of the $\mathbf{k}$ group, the dispersion curves of different

Figure 2. Vibrational modes and calculated frequencies of lattice vibrations of the orthorhombic form of perdeuterated polyethylene.

species may intersect each other. Those of the same species, however, do not intersect each other.

Γ Point. At the origin $\Gamma(0, 0, 0)$ of the Brillouin zone, the k group is D_{2h} , the factor group of the space group. The vibrational modes and calculated frequencies of the five interchain vibrations are shown in Figure 2. The $B_{1u}(\Gamma_6)$ and $B_{2u}(\Gamma_8)$ vibrations are infrared active while the $A_g(\Gamma_1)$ and $B_{3g}(\Gamma_3)$ vibrations are Raman active. The B_{1u} vibration calculated

at 68 cm^{-1} was, in fact, observed²¹ at 66.7 cm^{-1} for $C_{100}D_{202}$.

Σ and Λ Points. At the $\Sigma(\delta_a, 0, 0)$ and $\Lambda(0, \delta_b, 0)$ points, the k group is C_{2v} , with four symmetry species ($\Sigma_1-\Sigma_4$ and $\Lambda_1-\Lambda_4$). Dispersion curves are shown in Figures 3a and b.

The highest Σ_1 and Σ_2 (also Λ_1 and Λ_4) vibrations are due to rotational modes about the chain axis and the next highest Σ_1 and Σ_2 (also Λ_1 and Λ_4) vibrations are due to translational modes in the c plane. The Σ_3 and Σ_4 (also Λ_2

Figure 3. Frequency-dispersion curves of the orthorhombic form of perdeuterated polyethylene in the region below 500 cm^{-1} .

Figure 3. (continued).

and A_3) vibrations are due to translational modes along the c axis.

Acoustic modes of the lowest-frequency branches (Σ_1 , Σ_2 , Σ_4 ; A_1 , A_4 , A_2) are classified into longitudinal and transverse modes. The Σ_1 and A_1 branches are longitudinal and their inclinations are given by elastic constants; $(\partial\nu/\partial\delta_a)_0 = (c_{11}/\rho)^{1/2}/2\pi a_0 c$, and $(\partial\nu/\partial\delta_b)_0 = (c_{22}/\rho)^{1/2}/2\pi b_0 c$, where ρ is the density, c is the velocity of light, and a_0 and b_0 are lattice constants. The Σ_2 and Σ_4 branches are transverse and are associated with the translatory modes along the

b and c axes; $(\partial\nu/\partial\delta_a)_0 = (c_{66}/\rho)^{1/2}/2\pi a_0 c$ and $(c_{55}/\rho)^{1/2}/2\pi a_0 c$, respectively. The A_4 and A_2 branches are also transverse and are associated with the translatory modes along the a and c axes: $(\partial\nu/\partial\delta_b)_0 = (c_{66}/\rho)^{1/2}/2\pi b_0 c$ and $(c_{44}/\rho)^{1/2}/2\pi b_0 c$, respectively.

As the phase difference δ_a approaches π , the Σ_1 and Σ_2 (or Σ_3 and Σ_4) branches approach each other and finally meet at the zone edge of $(\pi, 0, 0)$, to form doubly-degenerate X_1 (or X_2) vibrations. The inclinations $(\partial\nu/\partial\delta_a)_\pi$ of the Σ_1 and Σ_2 (or Σ_3 and Σ_4) branches are of same

magnitude as, but of opposite sign to, each other. Also at the zone edge of $(0, \pi, 0)$, the A_1 and A_4 (or A_3 and A_2) branches meet to form doubly-degenerate Z_1 (or Z_2) vibrations.

Δ Point. Dispersion curves for the $\Delta(0, 0, \delta_c)$ points were published previously by Tasumi and Krimm.²² In the present study, however, symmetry assignments were made. At the Δ points, the k group is C_{2v} , with four symmetry species (A_1 — A_4). Dispersion curves are shown in Figure 3c. As the phase-difference changes from $\delta_c = 0$ to π , interchain vibrations turn into intrachain vibrations and accordingly vibrational frequencies vary sensitively with δ_c .

Except for small values of δ_c , the higher A_1 and A_3 branches are largely due to C—C—C bending modes. If there were no interchain interactions, there should be a longitudinal branch of the isolated chain, starting from $\nu = 0$ at the Γ point. Actually, however, because of interchain interactions, the longitudinal branch is split into the A_1 and A_3 branches of the crystal. The lower A_1 and A_3 branches are largely due to internal-rotation modes about C—C bonds.

Recently, frequency-dispersion relations of perdeuterated polyethylene were experimentally studied from measurements of coherent inelastic scattering of thermal neutrons.⁸ The scattering vector was parallel to the c axis and accordingly inelastic scattering cross sections were proportional to squared displacements of scattering nuclei along the c axis. Inelastic scattering due to internal-rotation vibrations was hardly detected. As shown in Figure 3c, observed frequency-dispersion relations (open circles) agree fairly well with calculated relations (solid lines). The splitting of the A_1 and A_3 branches or of the A_2 and A_4 branches was not detected possibly because of the low resolution of scattering measurements. The maximum frequency of the higher A_1 and A_3 branches is observed at 452 cm^{-1} , slightly lower than the calculated frequency of 480 cm^{-1} . However, Raman lines due to accordion vibrations of $n\text{-C}_{94}\text{H}_{190}$ were observed²³ at 536 and 556 cm^{-1} , suggesting the maximum frequency of perdeuterated polyethylene higher than 470 cm^{-1} .

X , Z and Y Points. At the $X(\pi, 0, 0)$, $Z(0, \pi, 0)$

and $Y(0, 0, \pi)$ points, the k group is D_{2h} . Irreducible representations are two-dimensional and crystal vibrations are doubly degenerate, yielding four different frequencies in the region below 500 cm^{-1} (Figures 3a, b and c). The symmetry co-ordinates for the X point were discussed previously.¹

Inclinations of the dispersion curves at the Z point may be seen in Figure 3b: $(\partial\nu/\partial\delta_a)_0 = 0$ but $(\partial\nu/\partial\delta_b)_\pi \neq 0$. Generally at an edge of the irreducible zone of orthorhombic crystals, the inclinations of dispersion curves are always $(\partial\nu/\partial\delta) = 0$ if, the four-fold or two-fold degeneracy persists, but are $(\partial\nu/\partial\delta) \neq 0$ if the degeneracy is reduced.

G , A and U Points. For the $G(\pi, \delta_b, 0)$ and $A(\delta_a, \pi, 0)$ points, the k group is C_{2v} but for the $U(\pi, \pi, 0)$ point the k group is D_{2h} . However, for all these points, irreducible representations are one-dimensional. The time-reversal degeneracy appears (Table 10 of ref 1), and symmetry species form degenerate pairs: (G_1 and G_4), (G_2 and G_3), (A_1 and A_2), (A_3 and A_4), (U_1 and U_2), (U_3 and U_4), (U_5 and U_6) and (U_7 and U_8). Four dispersion curves are shown in Figures 3a and b. The symmetry co-ordinates for the U point were discussed previously.¹

F and R Points. For the $F(\pi, \pi, \delta_c)$ point, the k group is again C_{2v} and irreducible representations are one-dimensional. Because of the time-reversal degeneracy, symmetry species form degenerate pairs (F_1 and F_2) and (F_3 and F_4). Dispersion curves are shown in Figure 3d. Vibrational frequencies change sensitively with the phase-difference (δ_c) along the chain axis.

Finally, at the $R(\pi, \pi, \pi)$ point, the k group is D_{2h} , with the time-reversal degeneracy. Irreducible representations are two-dimensional and accordingly crystal vibrations are quadruply degenerate. Symmetry co-ordinates for the R point were discussed previously.¹

D and B Points. For the $D(\pi, 0, \delta_c)$ and $B(0, \pi, \delta_c)$ points, the k group is C_{2v} . There is only one symmetry species with the two-dimensional representation and accordingly crystal vibrations are doubly degenerate. Dispersion relations for the D (Figure 3e) and B (Figure 3f) points are similar to each other.

T and S Points. For the $T(0, \pi, \pi)$ and

$S(\pi, 0, \pi)$ points, the k group is D_{2h} and irreducible representations are two-dimensional. Crystal vibrations of the T point are doubly degenerate (Figure 3f). However, for the S point, the time-reversal degeneracy appears and crystal vibrations of the S point are quadruply degenerate (Figure 3e).

H , C , E and Q Points. For the $H(0, \delta_b, \pi)$, $C(\delta_a, 0, \pi)$, $E(\delta_a, \pi, \pi)$ and $Q(\pi, \delta_b, \pi)$ points, the k group is C_{2v} . Two-fold degeneracy of vibrations is due to the space symmetry (H and C) or to the time-reversal symmetry (E) (Figures 3g and h). Dispersion curves of the Q points are quadruply degenerate for any value of δ_b , owing to the space and time-reversal degeneracies (Figure 3h). Crystal vibrations of the H , C , E and Q points are associated with the phase difference of $\delta_e = \pi$ and the vibrational frequencies change little with the phase differences of δ_a and δ_b .

FREQUENCY DISTRIBUTION

Under the cyclic boundary condition, phase-difference vectors are distributed uniformly in the first Brillouin zone. However, for orthorhombic crystals with the factor group of D_{2h} , the irreducible volume is one-eighth of the first Brillouin zone. Vibrational frequencies of chain-polymer crystals change sensitively with the phase-difference (δ_e) along the chain axis but little with δ_a or δ_b . Accordingly, for perdeuterated polyethylene, the value of δ_a or

δ_b was taken as 10, 30, 50, ..., 150 or 170° while the value of δ_e was taken as 0.5, 1.5, 2.5, ..., 178.5 or 179.5°. Thus for a total of 14580 phase-difference vectors in the irreducible volume, 116,640 vibrations lying below 500 cm^{-1} were collected in a histogram of frequency distribution (Figure 4, frequency interval of 10 cm^{-1}).

The distribution peak at 480 cm^{-1} corresponds to the maximum frequency of C-C-C bending vibrations (Figure 3). The prominent peak at 160 cm^{-1} is due to internal-rotation modes about C-C bonds, while the peak at 120 cm^{-1} is due to overall rotatory modes (R_e) about the chain axis. These distribution peaks correspond to the inelastic scattering peaks of thermal neutrons⁷ at 440, 160 and 110 cm^{-1} . The distribution peak at 75 cm^{-1} is due to translatory modes (T_a and T_b) perpendicular to the chain axis. The weak scattering peak observed⁷ near 250 cm^{-1} does not correspond to any distribution peak (Figure 4) and is not due to the one-phonon process. This scattering peak is possibly due to the two phonon process [160 $\text{cm}^{-1}(R_e) + 75 \text{ cm}^{-1}(T_a \text{ and } T_b)$].

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Figure 4. Frequency distribution of the orthorhombic form of perdeuterated polyethylene.

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