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Raman intensities of stretch oriented polyethylene and perdeuteropolyethylene. II. Electro-optical parameters for solid *N*-hydrocarbons

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In this paper use is made of the experimental Raman intensities of stretch-oriented polyethylene and perdeuteropolyethylene for the calculation of Raman electro-optical parameters (eop). The experimental data are reported in Paper I immediately before this paper. $\partial\alpha_{uv}/\partial Q_i$ are given as linear combinations of symmetrized and internal Raman eop's. From the experiments one set of eop's has been derived and compared with other sets obtained from the Raman spectra of chemically similar molecules. The problem of the transferability of eop's is discussed.

I. INTRODUCTION

This paper is a continuation of a previous one (here-after referred as I) which is published jointly.

In Paper I the results of experimental determinations on Raman intensities on stretch-oriented samples of polyethylene and perdeuteropolyethylene were presented and their reliability critically analyzed. The assignment of the fundamentals has been reasonably settled and the problem of the residual scattering due to the amorphous part has been discussed.

In this paper formulas are given for the calculation of electro-optical parameters from the experimental intensities of stretch-oriented PE and PDE, namely, we express the $\partial\alpha_{uv}/\partial Q_i$ in terms of linear combinations of symmetrized eop's; definitions of symmetrized eop's in terms of internal eop's are also presented.

While the numerical evaluation of symmetrized eop's from experimental data is fairly unequivocal, approximations and decisions must be introduced when internal eop's need to be evaluated numerically. The problems and difficulties in this numerical evaluation are discussed in detail in this paper.

The numerical values of the obtained internal eop's are compared with others derived from chemically similar molecules in various phases.

The increasing availability of experimental data allows one to test the transferability of eop's to chemically similar molecules, thus opening the way to the important problem of the dependency of eop's on the phase of the subtance. The example of the Raman intensities of liquid cyclohexane calculated from eop's of polyethylene is discussed.

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II. THEORY

In Paper I we have reported the numerical values of the Raman intensities I_{AB} of stretch-oriented PHE and PDE and given the relationship between the scattering activities $\bar{\alpha}'^2_{AB}$ and the $\partial\alpha_{uv}/\partial Q_i$ (u, $v = a$, b, c or x, y, and z; A, $B = X$, Y, Z). [As in Paper I, xyz is the system fixed in the chain, abc the system fixed in the crystallite ($\hat{a} \cdot \hat{x} = \cos\theta$, $\theta = $ setting angle), and XYZ the laboratory system ($X \cdot \hat{a} = \cos\phi$, $\phi = $ orientation angle). Averages on ϕ are discussed in Paper I.] We have previously shown[1,2] that most of the features of the observed spectra of PHE and PDE can be interpreted on the basis of the model of a single chain. For this reason in all the calculations discussed in this paper, without a loss of any essential information, we refer to *single chain quantities* (i.e., u, $v = x$, y, z; Q_i is the ith normal mode of the isolated chain; etc.).

We wish here to calculate $\partial\alpha_{uv}/\partial Q_i$ on the basis of the valence electrooptical theory.[3-6] This theory is based on the assumption that α can be expressed at any instant during the motion as the sum of K bond polarizability tensors:

$$\alpha = \sum_{k=1}^{K} \alpha^k . \tag{1}$$

Each bond tensor is assumed to have a principal axis along the bond direction and to be cylindrical around this direction at any instant. One can then write[5]

$$\alpha_{uv} = \sum_{k=1}^{K} [\alpha^{kL} e_u^{kL} e_v^{kL} + \alpha^{kT}(e_u^{kT} e_v^{kT} + e_u^{kT'} e_v^{kT'})] , \tag{2}$$

where α^{kL} and α^{kT} are the longitudinal and transversal principal values, respectively, of the polarizability of the kth bond; e_u^{kL}, e_u^{kT}, and e_u^{kT} are the uth components of the principal vectors of the polarizability of the kth bond.

In the case of the single chain polymers (where one dimensional translation symmetry exists) it has been shown[1] that for $k = 0$ phonons

$$\frac{\partial \alpha_{uv}}{\partial Q_i(0)} = \sqrt{N} \left[\delta_{uv} \tilde{1} \frac{\partial \bar{\alpha}}{\partial R}(0) + (\widetilde{e_u^{L0} e_v^{L0}} - \tfrac{1}{3} \delta_{uv} \tilde{1}) \frac{\partial \gamma}{\partial R}(0) \right.$$

$$\left. + \tilde{\Gamma}^0 \frac{\partial e_u^L e_v^L}{\partial R}(0) \right] L_i(0) , \qquad (3)$$

with

$$\frac{\partial \bar{\alpha}}{\partial R}(0) = \sum_{s=-p}^{p} \frac{\partial \bar{\alpha}}{\partial R(s)}$$

and

$$\frac{\partial \gamma}{\partial R(s)} = \sum_{s=-p}^{p} \frac{\partial \bar{\alpha}}{\partial R(s)} ,$$

where R are the M internal coordinates in the repeat unit and p measures the largest extent of the electro-optical interactions around the central unit; N is the number of translational units in the chain. Matrices $\partial \bar{\alpha}/\partial R(s)$, $\partial \gamma/\partial R(s)$, and Γ^0 collect the Raman electro-optical parameters (hereafter referred to as eop). The elements of the $\partial \alpha/\partial R(s)$ matrix are the bond mean polarizability derivatives

$$\frac{\partial \bar{\alpha}^k}{\partial R_m}(s) = \frac{\partial}{\partial R_m(s)} \tfrac{1}{3}(\alpha^{kL} + 2\alpha^{kT}) \qquad (4)$$

and the elements of the $\partial \gamma/\partial R(s)$ matrix are the anisotropy derivatives

$$\frac{\partial \gamma^k}{\partial R_m(s)} = \frac{\partial}{\partial R_m(s)} (\alpha^{kL} - \alpha^{kT}) . \qquad (5)$$

These two kinds of parameters are called "valence eop's." The elements of the Γ^0 column vector are the equilibrium bond antisotropies

$$\gamma^{k0} = \alpha^{kL0} - \alpha^{kT0} . \qquad (6)$$

In Eq. (3), δ_{uv} is the Kronecker symbol, 1 is a K vector of all unit entries, $e_u^{L0} e_v^{L0}$ a K vector containing the products of the direction cosines of the equilibrium bond vectors with respect to u and v axes. The term $\partial e_u e_v / \partial R(0)$ is a $K \times M$ matrix containing the so called "deformation coefficients" which can be calculated as described in Refs. 1 and 5. $L_i(0)$ is the ith $k=0$ eigenvector written in terms of internal phonon coordinates which is obtained from the dynamical treatment of the polymer chain.[7]

In the actual calculations made in this paper use is made of the methods and results already presented in Ref. 1 on PHE and PDE. In particular, the choice of the minimum set of internal electro-optical parameters derives from Table X of Ref. 1 and consists in this case of 24 valence eop's and 2 equilibrium eop's which are listed in Tables V and VI. The internal coordinates are defined in Fig. 1. In order to compute the coefficients of eop's in $\partial \alpha_{uv}/\partial Q_i(0)$ [Eq. (3)] one needs first the vibrational eigenvectors which have been obtained from a k-dependent normal coordinate calculation based on the geometry and the valence force field derived by Snyder.[8]

One can then write explicitly the expression of $\alpha_{uv}' = \partial \alpha_{uv}/\partial Q_i(0)$ in terms of eop's for all Raman active normal modes of PHE and PDE. Since normal modes of PHE and PDE belong to various symmetry species, the Raman intensity of each transition depends on particular symmetry combinations of internal eop's. We
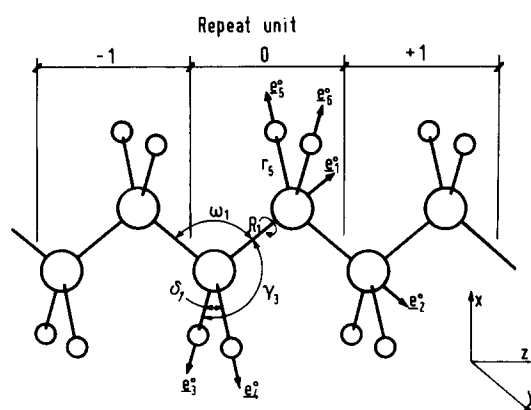

FIG. 1. Definition of internal coordinates and bond unit vectors.

found it convenient to examine the dependency of α_{uv}' upon these symmetry combinations, which we call "symmetry eop's." We list in the following the expression of α_{uv}' in terms of symmetry eop's:

Species B_{3g}, $\alpha_{yz}' = \alpha_{zy}' \neq 0$:

Mode: CX$_2$ twist (T):

PHE $\nu_{calc} = 1301$ cm^{-1}

$\alpha_{yz}' = 1.488 \gamma_{CH}^0$,

PDE $\nu_{calc} = 920$ cm^{-1} ,

$\alpha_{yz}' = 1.053 \gamma_{CH}^0$;

Species B_{2g}, $\alpha_{xz}' = \alpha_{zx}' \neq 0$:

Mode: CX$_2$ wag (W):

PHE $\nu_{calc} = 1385$ cm^{-1} ,

$\alpha_{xz}' = 1.644N - 0.241L + 1.006\gamma_{CH}^0 + 0.078\gamma_{CC}^0$,

PDE $\nu_{calc} = 1293$ cm^{-1} ,

$\alpha_{xz}' = 1.158N - 0.302L + 0.623\gamma_{CH}^0 + 0.100\gamma_{CC}$,

Mode: C–C antisymmetric stretch (sk^-):

PHE $\nu_{calc} = 1060$ cm^{-1} ,

$\alpha_{xz}' = -0.565N - 0.202L - 0.530\gamma_{CH}^0 + 0.065\gamma_{CC}^0$,

PDE $\nu_{calc} = 803$ cm^{-1} ,

$\alpha_{xz}' = -0.758N - 0.088L - 0.593\gamma_{CH}^0 + 0.029\gamma_{CC}^0$,

where

$$N = \frac{\partial \gamma^{CC}}{\partial \gamma} - \frac{\partial \gamma^{CC}}{\partial \gamma'} ,$$

$$L = \frac{\partial \gamma^{CC}}{\partial R} - \frac{\partial \gamma^{CC}}{\partial R'} ;$$

Species B_{1g}, $\alpha_{xy}' = \alpha_{yx}' \neq 0$:

Mode: CX$_2$ antisymmetric stretch (d^-):

PHE $\nu_{calc} = 2928$ cm^{-1} ,

$\alpha_{xy}' = -0.990I + 0.404M + 0.108\gamma_{CC}^0 + 0.070\gamma_{CH}^0$,

PDE $\nu_{calc} = 2207$ cm^{-1} ,

$\alpha_{xy}' = -0.731I + 0.575M + 0.155\gamma_{CC}^0 + 0.097\gamma_{CH}^0$,

Mode: CX_2 rocking (P):

PHE $\nu_{\text{calc}} = 1170 \text{ cm}^{-1}$,

$$\alpha'_{xy} = -1.310M - 0.049I - 0.494\gamma^0_{\text{CH}} - 0.216\gamma^0_{\text{CC}} ,$$

PDE $\nu_{\text{calc}} = 990 \text{ cm}^{-1}$,

$$\alpha'_{xy} = -1.087M - 0.078I - 0.330\gamma^0_{\text{CH}} - 0.219\gamma^0_{\text{CC}} ,$$

where

$$I = \frac{\partial \gamma^{\text{CH}}}{\partial r} - \frac{\partial \gamma^{\text{CH}}}{\partial r'} ,$$

$$M = \frac{\partial \gamma^{\text{CH}}}{\partial \gamma} - \frac{\partial \gamma^{\text{CH}}}{\partial \gamma'} ;$$

Species A_g, $\alpha_{xx} \neq \alpha_{yy} \neq \alpha_{zz} \neq 0$:

pattern of

$$\alpha'_{xx} = f(\overline{\alpha}) + a_1 \gamma^0_{\text{CC}} + a_2 \gamma^0_{\text{CH}} ,$$

$$\alpha'_{yy} = f(\overline{\alpha}) + g(\gamma) - a_2 \gamma^0_{\text{CH}} ,$$

$$\alpha'_{zz} = f(\overline{\alpha}) - g(\gamma) - a_1 \gamma^0_{\text{CC}} ,$$

Mode: CX_2 symmetric stretch (d^+):

PHE $\nu_{\text{calc}} = 2864 \text{ cm}^{-1}$,

$$f(\overline{\alpha}) = -2.044A + 0.131B - 0.714C - 0.862D ,$$

$$g(\gamma) = -0.681E - 0.044F - 0.238G - 0.287H ,$$

$$a_1 = 0.113 ,$$
$$a_2 = -0.180 ,$$

PDE $\nu_{\text{calc}} = 2117 \text{ cm}^{-1}$,

$$f(\overline{\alpha}) = -1.471A + 0.211B - 1.130C - 1.381D ,$$

$$g(\gamma) = -0.490E - 0.070F - 0.377G - 0.460H ,$$

$$a_1 = +0.182 ,$$

$$a_2 = -0.286 ,$$

Mode: CX_2 bending (δ):

PHE $\nu_{\text{calc}} = 1439 \text{ cm}^{-1}$,

$$f(\overline{\alpha}) = 0.057A + 0.154B - 9.270C - 4.385D ,$$

$$g(\gamma) = 0.019E - 0.052F - 3.090G - 1.463H ,$$

$$a_1 = 0.134 ,$$

$$a_2 = -1.801 ,$$

PDE $\nu_{\text{calc}} = 953 \text{ cm}^{-1}$,

$$f(\overline{\alpha}) = -0.057A - 0.185B - 4.962C - 1.168D ,$$

$$g(\gamma) = -0.020E + 0.062F - 1.654G - 0.389H ,$$

$$a_1 = -0.160 ,$$

$$a_2 = -0.871 ,$$

Mode: C–C symmetric stretch (sk^+):

PHE $\nu_{\text{calc}} = 1134 \text{ cm}^{-1}$,

$$f(\overline{\alpha}) = 0.086A + 0.426B + 1.164C - 1.411D ,$$

$$g(\gamma) = 0.028E - 0.142F + 0.388G - 0.470H ,$$

$$a_1 = 0.369 ,$$

$$a_2 = -0.142 ,$$

PDE $\nu_{\text{calc}} = 1158 \text{ cm}^{-1}$,

$$f(\overline{\alpha}) = -0.203A - 0.379B + 4.518C + 3.477D ,$$

$$g(\gamma) = -0.068E + 0.126F + 1.506G + 1.159H ,$$

$$a_1 = -0.328 ,$$

$$a_2 = 0.983 ,$$

where

$$A = \frac{\partial \overline{\alpha}^{\text{CH}}}{\partial r} + \frac{\partial \overline{\alpha}^{\text{CH}}}{\partial r'} + \frac{2\partial \overline{\alpha}^{\text{CC}}}{\partial r} ,$$

$$B = \frac{\partial \overline{\alpha}^{\text{CC}}}{\partial R} + \frac{\partial \overline{\alpha}^{\text{CC}}}{\partial R'} \frac{4\partial \overline{\alpha}^{\text{CH}}}{\partial R} ,$$

$$C = \frac{\partial \overline{\alpha}^{\text{CH}}}{\partial \gamma} + \frac{\partial \overline{\alpha}^{\text{CH}}}{\partial \gamma'} + \frac{\partial \overline{\alpha}^{\text{CC}}}{\partial \gamma} + \frac{\partial \overline{\alpha}^{\text{CC}}}{\partial \gamma'} ,$$

$$D = \frac{\partial \overline{\alpha}^{\text{CH}}}{\partial \omega} + \frac{\partial \overline{\alpha}^{\text{CC}}}{\partial \omega} ,$$

$$E = \frac{\partial \gamma^{\text{CH}}}{\partial r} + \frac{\partial \gamma^{\text{CH}}}{\partial r'} - \frac{2\partial \gamma^{\text{CC}}}{\partial r} ,$$

$$F = \frac{\partial \gamma^{\text{CC}}}{\partial R} + \frac{\partial \gamma^{\text{CC}}}{\partial R'} - \frac{4\partial \gamma^{\text{CH}}}{\partial R} ,$$

$$G = \frac{\partial \gamma^{\text{CH}}}{\partial \gamma} + \frac{\partial \gamma^{\text{CH}}}{\partial \gamma'} - \frac{\partial \gamma^{\text{CC}}}{\partial \gamma} - \frac{\partial \gamma^{\text{CC}}}{\partial \gamma'} ,$$

$$H = \frac{\partial \gamma^{\text{CH}}}{\partial \omega} - \frac{\partial \gamma^{\text{CC}}}{\partial \omega} .$$

Moreover, [1]

$$\frac{\partial \overline{\alpha}^{\text{CH(CC)}}}{\partial \delta} = -\frac{\partial \overline{\alpha}^{\text{CH(CC)}}}{\partial \omega} - 2\left(\frac{\partial \overline{\alpha}^{\text{CH(CC)}}}{\partial \gamma} + \frac{\partial \overline{\alpha}^{\text{CH(CC)}}}{\partial \gamma'}\right) ,$$

$$\frac{\partial \gamma^{\text{CH(CC)}}}{\partial \gamma} = -\frac{\partial \gamma^{\text{CH(CC)}}}{\partial \omega} - 2\left(\frac{\partial \gamma^{\text{CH(CC)}}}{\partial \gamma} + \frac{\partial \gamma^{\text{CH(CC)}}}{\partial \gamma'}\right)$$

III. APPROXIMATIONS

A close examination of the expressions above leads to the following observations:

(i) γ^0_{CH} enters all expressions, thus affecting to a different extent all the Raman intensities. At least within this model γ^0_{CH} is the only factor determining the intensity of the B_{3g} CX_2 twisting mode which is one of the strongest and most isolated bands in the Raman spectrum. It then follows that the value γ^0_{CH} could be easily determined if absolute intensities were available. Since we are forced to use relative intensities, the determination of γ^0_{CH} is affected not only by the unique intensity of CX_2 twisting but also by the intensity of the chosen standard.

(ii) The B_{1g} modes (CX_2 d^- and CX_2 P) are determined, in addition to γ^0_{CH} and $\gamma^0_{\text{C–C}}$, only by the combinations M and I of the anisotropy derivatives of the CH bonds. The B_{2g} modes (CX_2 W and C–C R^-) instead contain valence contributions only from combinations N and L of anisotropy derivatives of the C–C bonds. Combinations of internal eop's indicated as I, M, N, and L never occur in the A_g species.

(iii) The A_g modes are CX_2 d^+, CX_2 δ, and C–C R^+. From the expression of α'_{xx}, α'_{yy}, and α'_{zz} four independent quantities need to be calculated, namely, $f(\overline{\alpha})$,

$g(\gamma)$, $a_1\gamma_{CC}^0$, and $a_2\gamma_{CH}^0$, for each normal mode. From the expression of $\overline{\alpha}_{AB}'^2$ in terms of α_{uv}' reported in Paper I, Table I, one can see that the experiment $A(XY)B$ can provide information on $g(\gamma)$, γ_{CC}^0, and γ_{CH}^0. Since, as will become apparent later, the value of γ_{CC}^0 is unimportant and since we know γ_{CH}^0, $g(\gamma)$ can be calculated from the $A(XY)B$ geometry. From the geometry $X(ZZ)Y$ one can then calculate $f(\overline{\alpha})$. Data from the $A(YY)B$ geometry are also available but have been used only for checking the validity of the numbers obtained from the other geometries (which are not equivalent, and hence do not give redundant information).

(iv) From the values of $f(\overline{\alpha})$ and $g(\gamma)$ derived from several bands of A_g species values for A, B, C, D, E, F, G, and H could be determined. In an analogous way the values for I, M and N, L can be derived.

The calculations made in this paper have been simplified following the observations that in the expressions listed above only a few parameters play a dominant role where they appear with a large coefficient. For each normal mode it is seen that different symmetry parameters play the dominant role. Calculations have been simplified by dropping those symmetry parameters which appear with a small coefficient.

Calculations were developed from a starting set of symmetry eop's derived from our previous paper on the PHE and PDE. [1,5] By trial and error, guided by the relationships given above, the starting numerical values of the symmetry eop's have been modified to improve the fitting with the experimental values listed in Tables VI and VII of Paper I. The coefficients in the above expressions act in our guided trial and error calculations like the elements of a Jacobian matrix in a least squares fitting.

We are well aware that all these types of calculations suffer from a multiplicity of solutions. This problem has been variously discussed both in the case of normal coordinate calculations[9-11] or intensity calculations. We judge the validity of the set of parameters in two ways: (i) its capability of predicting the spectra of related compounds; (ii) the physical acceptability of the obtained numbers within the present knowledge of electro-optical parameters independently obtained from different molecules.

Once symmetry eop's have been obtained one is faced with the problem of defining the contributions of each internal eop. This problem is again well known both in dynamical calculations[9-11] and intensity calculations[6] and has been variously solved by the various authors according to their personal taste. The splitting of both force constants or eop's into contributions from internal coordinates is an arbitrary decision which can only be somehow justified by a physical and chemical common sense. On the basis of our previous experience in intensity calculations[6,12] we generally assume that the eop's related to the stretching of bonds are generally of one order of magnitude larger than the eop's related to bendings. Furthermore, the "off diagonal" terms are expected to be small or zero. From the discussion which follows it will become clear which decisions in the choice of the internal eop's were made.

We neglect in this paper the problem of sign indetermination in intensity calculation which has been already more thoroughly treated for the infrared intensities[13] and is being treated for the case of the Raman intensities.

IV. RESULTS

In this paper we report only one set of results out of the many which were obtained and examined during this work. Our main concern was the problem of Fermi resonances which are either known[14,15] or supposed to exist in PHE and n-alkanes. In intensity calculations nothing is lost in the C–H stretching region, where Fermi resonance does exist,[15] since we measure and fit the whole area. In the CH_2 bending region the situation becomes somewhat more complex. It has been suggested[14] and experimentally proven[16] that the B_{1g} component of the factor group splitting at 1440 cm^{-1} is in Fermi resonance with the combination of the infrared active CH_2 rocking correlation field components at 720 and 731 cm^{-1} (720 B_{2u} + 731 B_{3u} = 1451 B_{1g}). In our studies we have measured and fit the whole intensity I_{XY} from 1460 to 1440 cm^{-1}. Another Fermi resonance may occur between the A_g component of the factor group splitting at 1416 cm^{-1} with the first overtone levels of the rocking modes (2×720 B_{2u} = 1440 A_g, 2×731 B_{3u} = 1462 cm^{-1} A_g). In a previous paper[2] we neglected this Fermi resonance since the distance of the interacting levels made it less likely. However, in the measurements presented in Paper I in the ZZ geometry a non-negligible broad scattering has been observed between 1460 and 1440 cm^{-1}. Two possible explanations can be conceived for this observation: (i) This Raman band truly is of A_g symmetry and thus must come from the above mentioned Fermi resonance; (ii) the scattering is a residual due to the "amorphous" component of the sample; hence, it has to be neglected in the fitting procedure. For sake of completeness we have done two sets of calculations taking into account the two possibilities. The results turn out not to be strikingly different. Since the main purpose of this work is to show the usefulness in intensity calculations of the data from oriented samples, we then decided to neglect the above mentioned finer details on the Fermi resonance between A_g levels and decided to present only the results of the calculations in which no A_g Fermi resonance is considered.

Using the set of symmetry electro-optical parameters of Table I we have fit the experimental results as shown in Tables II and III. The set of symmetry electro-optical parameters of Table I has been obtained by fitting the experimental data listed in the first three columns of Table II for PHE and listed in Table III for PDE. The fitting obtained is very satisfactory and shows that it is indeed possible to find a set of eop's which is able to account simultaneously for the observed spectra of PHE and PDE. As a further check of the validity of the calculated parameters we have predicted the relative intensities $I_{XX} = I_{YY}$ for PHE which were measured in our experiments. The results reported in the fourth column of Table II show the reliability of the present calculations.

TABLE I. Symmetry electro-optical parameters (A from cyclohexane[5]; B present work).

		A	B	Units
A_g $(\bar{\alpha})$	A	1.300	1.200	Å^2
	B	0.920	0.800	Å^2
	C	0.0	-0.045	Å^3/rad
	D	0.060	0.078	Å^3/rad
A_g (γ)	E	2.200	1.500	Å^2
	F	1.460	1.000	Å^2
	G	0.050	-0.027	Å^3/rad
	H	0.0	0.065	Å^3/rad
B_{1g}	I	2.200	2.250	Å^2
	M	-0.200	-0.400	Å^3/rad
B_{2g}	L	1.460	1.100	Å^2
	N	-0.070	-0.121	Å^3/rad
	γ^0_{CC}	0.050	0.050	Å^3
	γ^0_{CH}	0.320	0.290	Å^3

A further check of the consistency of this kind of work has been made by calculating the relative integrated Raman intensities of powders of PHE and PDE. Using the correct expression for the Raman intensities of powder samples[2]

$$I + 45\bar{\alpha}^2 + 10\gamma^2 , \qquad (7)$$

we have obtained the results reported in Table IV. It is very pleasing to notice that the predicted intensities

TABLE III. Perdeuteropolyethylene: measured and calculated (set B of Table I) relative intensities. Numbers in parentheses refer to residuals.

Frequencies species, and assignments		ZZ (A_g)	XY (A_{1g}, B_{1g})	ZX = ZY (B_{2g}, B_{3g})
2250–2000 cm^{-1}				
$A_g + B_{1g}$	exp.	14.21	39.47	(16.45)
d^+, d^-	calc.	12.76	33.96	···
1250 cm^{-1}				
B_{2g}	exp.	(0.70)	(0.75)	1.36
W	calc.	···	···	···
1145 cm^{-1}				
A_g	exp.	12.36	1.55	(3.21)
sk^+	calc.	11.33	1.25	···
975–995 cm^{-1}				
$A_g + B_{1g}$	exp.	0.36	4.53	(0.89)
$\delta + P$	calc.	0.85	3.08	···
915 cm^{-1}				
B_{3g}	exp.	(0.81)	(0.66)	1.97
T	calc.	···	···	2.54
830 cm^{-1}				
B_{2g}	exp.	(0.43)	(0.33)	1
sk^-	calc.	···	···	1

TABLE II. Polyethylene: measured and calculated (set B of Table I) relative intensities. Numbers in parentheses refer to residuals.

Frequencies, species, and assignments		ZZ (A_g)	XY (A_g, B_{1g})	ZX = ZY (B_{2g}, B_{3g})	YY = XX (A_g, B_{1g})
2930–2850 cm^{-1}					
$A_g + B_{1g}$	exp.	10.68	26.65	(6.71)	33.70
d^+, d^-	calc.	9.12	18.43	···	63.65
1410–1460 cm^{-1}					
A_g	exp.	1.28	2.68	(0.89)	2.78
δ	calc.	1.28	1.81	···	2.76
1370 cm^{-1}					
B_{2g}	exp.	(0.06)	(0.02)	0.11	(0.05)
W	calc.	···	···	0.21	···
1295 cm^{-1}					
B_{3g}	exp.	(0.45)	(0.43)	1.48	(0.47)
T	calc.	···	···	1.52	···
1170 cm^{-1}					
B_{1g}	exp.	···	0.22	(0.035)	0.22
P	calc.	···	0.20	···	0.20
1130 cm^{-1}					
A_g	exp.	3.15	0.41	(0.303)	0.40
sk^+	calc.	3.19	0.98	···	1.05
1064 cm^{-1}					
B_{2g}	exp.	(0.28)	(0.26)	1	(0.30)
sk^-	calc.	···	···	1	···

TABLE IV. Experimental and calculated relative Raman intensities of powders of PHE and PDE: (A) electro-optical parameters from cyclohexane, (B) present work.

Observed frequencies (cm^{-1})	Exp.	A	B
	PHE		
2883	a	6.60	17.75
2848	a	17.25	25.02
1460	⎫		
1440	⎬ 3.34	0.99	2.63
1416	⎭		
1370	0.10	0.08	0.22
1295	1.56	0.99	1.56
1170	0.17	0.00	0.20
1130	0.96	1.46	1.39
1062	1	1	1
	PDE		
2198	a	10.75	33.05
2150	a	25.03	43.13
1250	1.38	0.81	1.49
1145	4.76	2.89	8.43
995	⎫	0.06 ⎫	1.0 ⎫
990	⎬ 3.98	2.57 ⎬ 2.63	2.44 ⎬ 3.44
975	⎭	⎭	⎭
915	2.38	1.39	2.56
830	1.0	1.0	1.0

^{a}Not measured because of strong overlapping.

are in very good agreement with the experimental ones both for PHE and PDE. A comparison of analogous data obtained by us from previous calculations (Table IV) shows that a definite improvement has been achieved in the search of Raman electro-optical parameters for PHE and PDE.

Let us first compare the numerical values of the symmetry electro-optical parameters in Table I obtained in our previous work (A) and in the present one (B). The largest differences are observed for two symmetry parameters of C–H stretching (E and I) and two symmetry parameters (F and L) of C–C stretching. The differences in the other parameters are not so meaningful.

TABLE V. Internal electro-optical parameters: bond mean polarizability parameters. (A) from cyclohexane; (B) present work; (C) from an overlay on methanes and ethanes.[17]

	A	B	C	Units
$\partial\bar{\alpha}_{CH}/\partial r$	1.300	1.200	1.099	Å^2
$\partial\bar{\alpha}_{CH}/\partial r'$	0.0	0.0	0.006	Å^2
$\partial\bar{\alpha}_{CH}/\partial R$	0.0	0.0	⋯	Å^2
$\partial\bar{\alpha}_{CH}/\partial\omega$	−0.017	0.039	⋯	Å^3/rad
$\partial\bar{\alpha}_{CH}/\partial\gamma$	0.0	−0.011	⋯	Å^3/rad
$\partial\bar{\alpha}_{CH}/\partial\gamma'$	0.0	−0.011	0.031	Å^3/rad
$\partial\bar{\alpha}_{CC}/\partial r$	0.0	0.0	⋯	Å^3/rad
$\partial\bar{\alpha}_{CC}/\partial R$	0.921	0.800	1.082	Å^3/rad
$\partial\bar{\alpha}_{CC}/\partial R'$	0.0	0.0	⋯	Å^3/rad
$\partial\bar{\alpha}_{CC}/\partial\omega$	0.079	0.039	⋯	Å^3/rad
$\partial\bar{\alpha}_{CC}/\partial\gamma$	0.0	−0.011	⋯	Å^3/rad
$\partial\bar{\alpha}_{CC}/\partial\gamma'$	0.0	−0.011	⋯	Å^3/rad

TABLE VI. Internal electro-optical parameters: bond anisotropy parameters. (A) from cyclohexane[5]; (B) present work; (C) from an overlay on methanes and ethanes.[17]

	A	B	C	Units
$\partial\gamma_{CH}/\partial r$	2.200	2.075	1.851	Å^2
$\partial\gamma_{CH}/\partial r'$	0.0	−0.575	−0.532	Å^2
$\partial\gamma_{CH}/\partial R$	0.0	0.0	⋯	Å^2
$\partial\gamma_{CH}/\partial\omega$	0.0	0.0	⋯	Å^3/rad
$\partial\gamma_{CH}/\partial\gamma$	−0.089	−0.050	⋯	Å^3/rad
$\partial\gamma_{CH}/\partial\gamma'$	0.109	0.055	⋯	Å^3/rad
$\partial\gamma_{CC}/\partial r$	0.0	0.0	⋯	Å^3/rad
$\partial\gamma_{CC}/\partial R$	1.459	1.050	1.790	Å^3/rad
$\partial\gamma_{CC}/\partial R'$	0.0	−0.050	⋯	Å^3/rad
$\partial\gamma_{CC}/\partial\omega$	0.0	−0.065	⋯	Å^3/rad
$\partial\gamma_{CC}/\partial\gamma$	−0.049	−0.0445	⋯	Å^3/rad
$\partial\gamma_{CC}/\partial\gamma'$	0.018	0.0765	⋯	Å^3/rad
γ_{CC}^0	0	0.050	⋯	Å^3
γ_{CH}^0	0.316	0.290	0.292	Å^3

It is important to point out that the physical meaning of of symmetry eop's (just as in the case of symmetry force constants) is difficult to judge whereas when transformed into internal eop's some physical insight can be found.

Using the explicit analytical expression of symmetry eop's given before and the results of Tables V and VI, it becomes clear which approximations have been taken in the transformation from symmetry to internal eop's. The values of internal eop's of Tables V and VI are also compared with the values previously obtained from the intensities of cyclohexane and used (in Ref. 1) for PHE and PDE.

One can notice that bond mean polarizability parameters do not change drastically, their differences not being meaningful at the present stage of intensity studies. More interesting differences are found for bond anisotropy parameters which reflect the changes of the symmetry parameters as mentioned above. The first noticeable difference is found in bond anisotropy parameters of CH stretching $\partial\gamma_{CH}/\partial r$ and $\partial\gamma_{CH}/\partial r'$. These parameters were held fixed in the least squares fitting of the Raman intensities of cyclohexanes[5] since at that time there were no experimental data which allowed their calculation. The values obtained in this work (2.075 and −0.575) nicely compare with those (1.851 and −0.532) independently refined in an "overlay" calculation on Raman intensities and depolarization ratios of methane, dueteromethanes, ethanes, and perdeuteroethane.[17]

The second difference is found for the pair of parameters $\partial\gamma_{CC}/\partial R$ and $\partial\gamma_{CC}/\partial R'$. They were refined in the case of cyclohexane,[5] while they were held fixed in the overlay calculation on methanes and ethanes.[17] We wish to point out that the determination of these parameters is difficult and becomes dubious since they enter with small coefficients every time they appear in an intensity combination. This fact can be seen numerically either in the expressions of α'_{uv} in terms of symmetry eop's reported before in this paper or in the Jacobian matrix

TABLE VII. Experimental and calculated relative Raman intensities of liquid cyclohexane from 1500 cm^{-1}. (A) Refined from C_6H_{12} and C_6D_{12} (data from Ref. 18); (B) from stretch oriented PHE and PDE.

	Assignment	$\nu_{obs}^{(18)}$ (cm^{-1})	$I_{obs}^{(18)}$	$\rho_{obs}^{(18)}$	$I_{obs}^{(20)}$	I_{calc}^{A}	I_{calc}^{B}	ρ_{calc}^{B}
A_{1g}	δ	1465	1.1	0.1	...	3.4	23.0	0.039
	P	1158	8.5	0.167	8.0	10.5	14.4	0.061
	R	802	100	0.036	100	100	100	0.017
	ω	386	5.6	0.080	6.2	5.2	9.1	0.228
E_g	δ, R	1444	31.3		45.2	32.1	38.6	
	W, R	1348	5.6		6.1	11.9	12.4	
	T, W	1267	26.9		40.5	25.1	26.2	
	T, R	1029	30.2		48.4	36.8	21.8	
	P	785	2.6		...	4.1	6.4	
	ω	427	4.0		6.6	4.0	4.5	

of our previous paper on PHE and PDE.[1] For this reason the seemingly large difference of our values (1.459, 0.0, and 1.050, −0.050) with the values (1.790 and 0.01) given by Snyder for cyclohexane[18] has no real physical meaning within the present knowledge since it affects only slightly the calculated intenisites. The other angle bending parameters of Tables V and VI are small and do not show meaningful differences.

V. CONCLUSIONS

In this paper we have presented the calculation of Raman electro-optical parameters for one of the few organic crystals for which so many experimental data are available. A critcal evaluation of the validity and accuracy of the experimental data has been presented in Paper I. In this paper we have shown that, because of the symmetry of crystalline orthorhombic PHE and PDE, these experiments allow the separation of the contributions to the intensity of mean polarizability parameters and of the anisotropy parameters. Measurements restricted to powders do not allow an independent determination of the above two kinds of parameters.

From these measurements a set of electro-optical parameters has been derived which fits satisfactorily both PHE and PDE in all scattering geometries and nicely predicts data from geometries which were not included

in the refinement. The Raman spectra of powders of PHE and PDE are also nicely accounted for by the same set of parameters. The parameters so obtained represent certainly an improvement with respect to previous calculations[1,5,17,19] toward the building up of a general set of eop for polyethylene and n-alkane molecules.

In spite of this success caution must be taken in transferring these parameters to chemically similar molecules or in attempting to give a sort of physical meaning to the calculated numbers. Several aspects of such a kind of calculations need to be developed further. We feel that the most important ones are the following: (i) uncertainty in sign choice; (ii) extension of electrical interactions to the neighboring unit within the chain; (iii) lack of enough experimental data on many n-alkane molecules for a simultaneous least squares refinement on many chemically similar molecules.

In our previous works in the field of Raman intensities on hydrocarbon molecules we were concerned with the problem of whether the eop's from substances in the gas, liquid, or solid phase where similar.[17] Because of the paucity of the experimental data available at that time, the calculations made before led us to observe that the phase of the substances seemed not to drastically affect the numerical values. At this stage of the work we can compare two sets of results derived from a fair-

TABLE VIII. Experimental and calculated relative Raman intensities of liquid cyclohexane-d_{12} from 1500 cm^{-1}. (A) Refined from C_6H_{12} and C_6D_{12} (data from Ref. 18); (B) from stretch-oriented PHE and PDE.

	Assignment	$\nu_{obs}^{(18)}$ (cm^{-1})	$I_{obs}^{(18)}$	$\rho_{obs}^{(18)}$	$I_{obs}^{(20)}$	I_{calc}^{A}	I_{calc}^{B}	ρ_{calc}^{B}
A_{1g}	δ	1120	12.7	0.04	11.85	7.1	74.4	0.011
	P	1015	5.9	0.007	5.91	26.0	19.8	0.088
	R	724	100	0.031	100	100	100	0.025
	ω	298	3.8	0.130	4.45	3.1	7.6	0.285
E_g	W, R	1214	6.4		11.59	11.4	10.8	
	δ, P	1071	10.6		15.45	16.9	24.1	
	W, T	937	33.5		57.76	29.9	35.9	
	T, W	796	21.6		36.36	22.0	16.9	
	P	637	0.8		1.62	2.0	4.0	
	ω	373	4.7		9.04	4.3	5.5	

ly large number of experimental data on (i) gases (methanes and ethanes[17,19]) and (ii) solids (this paper). From that discussed before in detail it seems that some of the parameters start being different in the two phases. Such differences may reflect a different physical situation of the electrical properties of bonds in gaseous or solid hydrocarbons. More work from independent techniques or from "ab initio" calculations are necessary to support or disclaim such observations.

The electrical properties of bonds in liquid hydrocarbons and their intermolecular interactions as probed by the molecular polarizability which gives rise to the Raman spectrum is a field still to be explored. We thought it worthwhile to test the applicability of the eop's obtained from solid PHE and PDE in this work by calculating again the Raman spectrum of liquid cyclohexane and perdueterocyclohexane. This is a process opposite to that followed in our previous work which consisted of using model molecules to calculate the intensities of PHE and PDE. This procedure is justified by the fact that from this work new experimental data became available and have been used to improve the set of Raman eop's, whose validity needs to be tested.

The results of the calculations of cyclohexane and cyclohexane-d_{12} are presented in Tables VII and VIII, respectively, compared with our previous theoretical results and with the experimental results of Snyder.[18] Recent experiments[20] show some discrepancy if compared with the data by Snyder. The trend of the calculated values is not too far from the experimental values for the E_g species but shows a dramatic discrepancy for the A_g bending modes both for C_6H_{12} and C_6D_{12}. The intensity of the A_g bending modes is mainly determined by the terms $\partial\alpha_{CH}/\partial\omega$, $\partial\alpha_{CC}/\partial\omega$, $\partial\alpha_{CH}/\partial\gamma'$, $\partial\alpha_{CC}/\partial\gamma$, and $\partial\alpha_{CC}/\partial\gamma'$: even if small, they are added together and enter the expression of the intensity with very large coefficients.

The main message we receive from the lack of good fitting on cyclohexanes is that either the above parameters are strongly intermolecular dependent (hence

phase dependent) or some essential intramolecular interactions have still been left out from the calculations. We plan first to focus our attention to the latter hypothesis and will consider in a future work the importance of electrical interactions between *trans* and *gauche* positions.

[1]S. Abbate, M. Gussoni, G. Masetti, and G. Zerbi, J. Chem. Phys. 67, 1519 (1977).

[2]S. Abbate, M. Gussoni, and G. Zerbi, J. Chem. Phys. 70, 3577 (1979).

[3]M. V. Wolkenshtein, L. A. Gribov, M. A. Elyashevich, and Y. Y. Stepanov, *Kolebanya Molekul* (Nauka, Moskow, 1972).

[4]L. M. Sverdlov, M. A. Kovner, and E. P. Koainov, *Vibrational Spectra of Polyatomic Molecules* (Wiley, New York, 1974).

[5]M. Gussoni, S. Abbate, and G. Zerbi, J. Raman Spectrosc. 6, 289 (1977).

[6]M. Gussoni, in *Advances in Infrared and Raman Spectroscopy*, edited by R. J. Clark and R. E. Hester (Heyden, London, 1979), Vol. 6.

[7]L. Piseri and G. Zerbi, J. Mol. Spectrosc. 26, 254 (1968).

[8]R. G. Snyder, J. Chem. Phys. 47, 1316 (1967).

[9]G. Zerbi, Appl. Spectrosc. Rev. 2, 193 (1969).

[10]G. Zerbi, in *Vibrational Spectroscopy: Modern Trends*, edited by A. J. Barnes and W. J. Orville-Thomas (Elsevier, Amsterdam, 1977).

[11]I. L. Duncan, *Force Constant Calculations in Molecules*, Specialist Report (Chemical Society, London, 1975), Vol. 3.

[12]M. Gussoni, S. Abbate, and G. Zerbi, in *Vibrational Spectroscopy Modern Trends*, edited by A. J. Barnes and W. J. Orville-Thomas (Elsevier, Amsterdam, 1977).

[13]S. Abbate and M. Gussoni, Chem. Phys. 71, 3428 (1979).

[14]M. J. Gall, P. J. Hendra, C. J. Peacock, M. E. Cubdy, and and H. A. Willis, Spectrochim. Acta Part A 38, 1485 (1972).

[15]R. G. Snyder, S. L. Hsu, and S. Krimm, Spectrochim. Acta Part A 34, 395 (1979).

[16]C. K. Wu and M. Nicol, J. Chem. Phys. 38, 5150 (1973).

[17]S. Abbate, M. Gussoni, and G. Zerbi, Indian J. Pure Appl. Phys. 16, 199 (1978), Raman Memorial volume.

[18]R G. Snyder, J. Mol. Spectrosc. 36, 204 (1970).

[19]S. Abbate, M. Gussoni, and G. Zerbi, J. Mol. Spectrosc. 73, 415 (1978).

[20]C. Schmid (private communication).