

polymer papers

Raman scattering activities for partially-oriented systems: the case of a unique molecular symmetry axis perpendicular to the uniaxial direction

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(Received 18 February 1983; revised 4 April 1983)

Raman scattering activities have been derived for the case where the system has uniaxial order imposed on it, but the molecular or factor group's axis of symmetry is perpendicular to the uniaxial direction. The symmetry axis has random ordering about the uniaxial direction around which orientation averaging is done. The expressions for the scattering activities in the molecular co-ordinate system are related to a fixed laboratory co-ordinate system. This is carried out for the three orthogonal orientations of the sample in right-angle and back-scattering geometries.

Keywords Raman spectroscopy; symmetry; uniaxial orientation; polarization; polymer; group theory

INTRODUCTION

In Raman scattering the ability to select subsets of the polarizability components by carrying out polarization experiments is modified by the degree to which a system is ordered. In principle for a perfect crystal all six of the independent polarizabilities may be available while for a liquid there are only two independent parameters. These invariants are called the spherical or isotropic part of the polarizability, α , and the anisotropy, β^1 . In the case to be investigated in this paper one axis is fixed in a unique direction and the other orthogonal axes are randomly positioned in the plane perpendicular to the fixed axis. In this case there are four independent parameters. The derivation of these independent terms and their separation in the various polarized Raman experiments is the subject of this paper. These results can be used in conjunction with polarized Raman measurements to assign the symmetry of the normal modes observed.

Previously, Snyder² presented the results for the case where the symmetry axis was parallel to the orientation axis in a uniaxially-oriented system or where it was randomly located in a fixed plane. These results have been applied to a number of different polymers, e.g., isotactic polypropylene³, polyethylene⁴, polytetrafluoroethylene⁵, and the helical model of an alternating copolymer of ethylene-tetrafluoroethylene⁶. In several cases Snyder's results have been rederived and applied to very specific cases of the general type presented in this work^{7,8}. These results are very useful but not all encompassing. In particular there are a number of polymer systems that have their unique symmetry axis perpendicular to the chain backbone and therefore perpendicular to the orientation axis in a uniaxially-drawn filament or film^{6,9,10,11}. As processing conditions for uniaxially-oriented polyvinyl alcohol, polyvinylidene fluoride (β form), and syndiotactic polypropylene, for example, are

improved, polarized Raman measurements will become possible thereby requiring the use of this group theoretical framework for analysis.

In addition the results of this work will find applicability in the study of molecules embedded in uniaxially-drawn host polymer films where frequently the guest molecule has its unique symmetry axis perpendicular to the orientation axis¹² and in the analysis of the local vibrational modes of a pendant side group oriented normal to the polymer backbone^{13,14}.

EXPERIMENTAL

The notation outlined in Wilson, Decius, and Cross¹ and in Snyder's work² will be followed in this paper in the interest of continuity. Therefore, the space-fixed co-ordinates are designated (*XYZ*) and the molecule-fixed co-ordinates are designated (*xyz*). These axes are shown in *Figure 1* with the three possible orientations of a uniaxial sample relative to the laboratory co-ordinate system. In all cases the *z*-axis corresponds to a unique molecular symmetry axis as determined by its being the highest-order rotation axis, or a rotation axis perpendicular to a reflection plane. Indeterminate cases follow the assignments in Wilson *et al.*¹ in the point group tables. The *x*-axis is arbitrarily chosen to be parallel to the orientation direction. The *y*- and *z*-axes are then free to be randomly positioned in a plane perpendicular to the *x*-axis.

The experimental geometry is shown in *Figure 2*. The laser beam is travelling in the positive *X* direction with an incident polarization parallel to either *Y* or *Z*. The Raman scattered light is collected in the positive *Z* direction and analysed for *Y* and *X* polarizations in the right-angle scattering experiment (RAS). In the back-scattering experiment (BS) the signal is collected in a negative *X* direction and the analyser (polarizer) positioned parallel

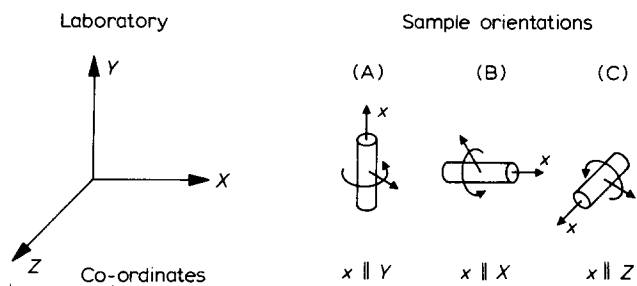


Figure 1 The laboratory-fixed co-ordinates are shown on the left (X, Y, Z). The sample co-ordinates (x, y, z) are attached to the uniaxially-oriented sample with x parallel to the uniaxial-orientation direction. The three orthogonal orientations of the sample in the laboratory co-ordinate system are shown and defined as: (A) x||Y; (B) x||X; and (C) x||Z

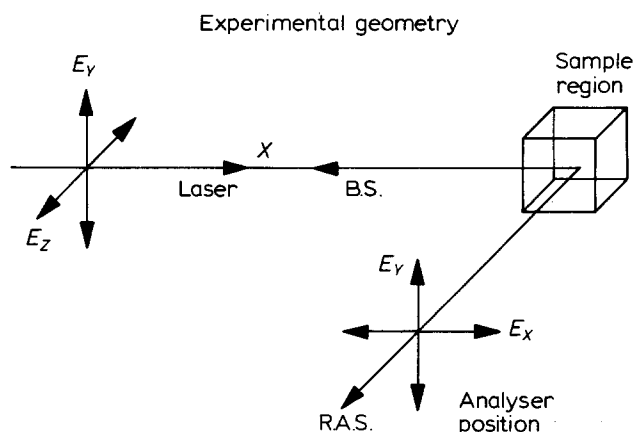


Figure 2 The experimental geometry in the laboratory-fixed co-ordinate system is shown. The laser travels in the X direction with polarizations E_y or E_z . In right-angle scattering (RAS) the scattered Raman signal is collected along Z and analysed for polarizations E_y and E_x . In back scattering (BS) the signal is collected in the $-X$ direction and analysed for polarizations E_y and E_z

to either the Y or Z direction. The sample orientations are A: x parallel to Y; B: x parallel to X; and C: x parallel to Z.

For arbitrary directions F and F' in the laboratory co-ordinate system (with the incident polarization in the F direction and the scattered radiation analysed in the F' direction) the intensity of the scattered Raman signal will be proportional to $\alpha_{FF'}^2$. Therefore, the polarizability elements in the molecular co-ordinate system must be related to the laboratory co-ordinate system to analyse the normal mode symmetries (microscopic) observed in the experiment (macroscopic). To relate the polarizability elements ($\alpha_{FF'}$) in the laboratory fixed co-ordinates to those (α_{gg}) in the molecule-fixed co-ordinates, a transformation can be derived. These two co-ordinate systems can be related by:

$$F = \Phi g \tag{1}$$

where the tensor Φ is formed from the direction cosines between the two co-ordinate systems. The polarizabilities are then related by the expression:

$$\alpha[F] = \Phi \alpha[g] \Phi^T \tag{2}$$

As the relation between the two systems is not fixed in a

uniaxially-oriented material, but varies about a shared axis, orientation averaging must also be done in the plane perpendicular to the unique axis. The final result for an individual component in the space-fixed frame is:

$$\langle \alpha_{FF'}^2 \rangle = \left\langle \left(\sum_{gg'} \Phi_{Fg} \Phi_{F'g'} \alpha_{gg'} \right)^2 \right\rangle \tag{3}$$

The matrices Φ for the three orientations are given in Table 1. The rows of these matrices are indexed by the laboratory co-ordinates while the columns are indexed by the molecule-fixed co-ordinates. The calculated results for the squared, orientation-averaged polarizabilities $\langle \alpha_{FF'}^2 \rangle$ in terms of the molecule-fixed polarizabilities are given in Table 2. The terms A_1 - A_4 are defined in Table 2 to facilitate their separation into irreducible representations in the various point groups. These can be explicitly expressed in terms of the molecule-fixed polarizabilities as:

$$A_1 = \alpha_{xx}^2 \tag{4}$$

$$A_2 = \frac{1}{8}(\alpha_{yy} - \alpha_{xx})^2 + \frac{1}{2}\alpha_{yz}^2 \tag{5}$$

$$A_3 = \frac{3}{8}(\alpha_{yy}^2 + \frac{2}{3}\alpha_{yy}\alpha_{zz} + \alpha_{zz}^2) + \frac{1}{2}\alpha_{yz}^2 \tag{6}$$

$$A_4 = \frac{1}{2}(\alpha_{yx}^2 + \alpha_{zx}^2) \tag{7}$$

RESULTS AND DISCUSSION

General results

The results of this analysis can be used in conjunction with the observed Raman spectra to elucidate molecular

Table 1 Transformation matrices Φ between the space and molecular co-ordinates used in the three orientations A, B, and C

Orientation A: $x \parallel Y$, θ is the angle between z and Z

$$\begin{pmatrix} 0 & -\cos \theta & \sin \theta \\ 1 & 0 & 0 \\ 0 & \sin \theta & \cos \theta \end{pmatrix}$$

Orientation B: $x \parallel X$, θ is the angle between z and Z

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & -\sin \theta \\ 0 & \sin \theta & \cos \theta \end{pmatrix}$$

Orientation C: $x \parallel Z$, θ is the angle between y and Y

$$\begin{pmatrix} 0 & -\sin \theta & -\cos \theta \\ 0 & \cos \theta & -\sin \theta \\ 1 & 0 & 0 \end{pmatrix}$$

Table 2 $\langle \alpha_{FF'}^2 \rangle$ in terms of the molecular polarizabilities^{a,b}

$$\langle \alpha_{FF'}^2 \rangle \begin{cases} A_1 = \frac{1}{4} [r + s]^2 \\ A_2 = \frac{1}{32} [r^2 + s^2 + 4p^2 + 16n^2 + 4sp - 4rp - 2rs] \\ A_3 = \frac{1}{32} [3r^2 + 3s^2 + 12p^2 + 16n^2 + 4rp - 6rs - 4sp] \\ A_4 = \frac{1}{2} [l^2 + m^2] \end{cases}$$

Orientation A			Orientation B			Orientation C		
A_3	A_4	A_2	A_1	A_4	A_4	A_3	A_2	A_4
A_4	A_1	A_4	A_4	A_3	A_2	A_2	A_3	A_4
A_2	A_4	A_3	A_4	A_2	A_3	A_4	A_4	A_1

^a See Figure 1 for the orientation geometries

^b $l^2 = \alpha_{xy}^2$, $m^2 = \alpha_{xz}^2$, $n^2 = \alpha_{yz}^2$, $p^2 = \alpha_{zz}^2$, $r^2 = (\alpha_{xx} + \alpha_{yy})^2$, $s^2 = (\alpha_{xx} - \alpha_{yy})^2$

structure. This is carried out by considering relative band intensities either within a single spectrum or among several different spectra and comparing to the predicted symmetry species expected (from Tables 4-8) for a particular molecular model structure and scattering geometry. In many instances this type of structure analysis has proven useful⁶ in identifying the correct structure from among a number of proposed models.

It is convenient, therefore, to have tabulated results that can be utilized simply by matching the experimental co-ordinate systems. These are provided in this paper for all the point groups that can have a unique axis. This excludes the point groups C_1 , C_i , T , T_d , T_h , O , O_h , G , and G_h . The remaining point groups listed in Wilson *et al.*¹ can be divided into five sets. The irreducible representations can be generalized as A for the totally symmetric representation and γ_i for the i th non-totally symmetric representation. This development follows Snyder² and the specific partitioning can be found in Table 3 which is included for completeness.

The results for the case where the orientation axis is perpendicular to the symmetry axis are presented in Tables 4-8. Results for both the right-angle and back-scattering geometries are given. In the left-hand columns the irreducible representation and the polarization of the incident laser beam are indicated. Listed in the top rows of the tables are the scattering geometries (A, B, or C) and the direction of polarization of the analysed radiation.

Resonance Raman results can be derived in a similar manner to that described previously with the additional complication of retaining the off-diagonal terms separately. This is due to the nonequivalence of the off-diagonal polarizabilities which result from preferred orientations of the transition moments of the molecular system. An application of this is given by Margulies and Stockburger¹² in their work on oriented diphenylpolyenes.

Table 4 $G_1: \{C_s, C_2, C_{2h}\}$
 $A: \alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}$
 $\gamma: \alpha_{yz}, \alpha_{zx}$

G_1 RAS	A		B		C	
	X	Y	X	Y	X	Y
A Y	$\frac{1}{2}I^2$	A1	$\frac{1}{2}I^2$	C1	B1	C1
Z	B1	$\frac{1}{2}I^2$	$\frac{1}{2}I^2$	B1	$\frac{1}{2}I^2$	$\frac{1}{2}I^2$
γ Y	$\frac{1}{2}m^2$	0	$\frac{1}{2}m^2$	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$
Z	$\frac{1}{2}n^2$	$\frac{1}{2}m^2$	$\frac{1}{2}m^2$	$\frac{1}{2}n^2$	$\frac{1}{2}m^2$	$\frac{1}{2}m^2$

G_1 BS	A		B		C	
	Y	Z	Y	Z	Y	Z
A Y	A1	$\frac{1}{2}I^2$	C1	B1	C1	$\frac{1}{2}I^2$
Z	$\frac{1}{2}I^2$	C1	B1	C1	$\frac{1}{2}I^2$	A1
γ Y	0	$\frac{1}{2}m^2$	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$	$\frac{1}{2}m^2$
Z	$\frac{1}{2}m^2$	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$	$\frac{1}{2}m^2$	0

$$A1 = \frac{1}{4} (r + s)^2$$

$$B1 = \frac{1}{32} [r^2 + s^2 + 4p^2 - 2rs - 4rp - 4sp]$$

$$C1 = \frac{1}{32} [3r^2 + 3s^2 + 12p^2 + 4rp - 6rs - 4sp]$$

Table 3 Classification of point groups according to their Raman activities

G_1	C_s	C_2	C_{2h}	G_2	C_3	D_3	C_{3v}	D_{3d}	S_6
A	A'	A	A_g	A	A	A_1	A_1	A_{1g}	A_g
γ	A''	B	B_g	γ	E	E	E	E_g	E_g

G_3	C_4	C_5	C_6	D_5	D_6	C_{5v}	C_{6v}	C_{3h}	C_{4h}	C_{5h}	C_{6h}
A	A	A	A	A_1	A_1	A_1	A_1	A'	A_g	A'	A_g
γ_1	B	E_2	E_2	E_2	E_2	E_2	E_2	E''	B_g	E_2''	E_{2g}
γ_2	E	E_1	E_1	E_1	E_1	E_1	E_1	E''	E_g	E_1''	E_{1g}

G_3	D_{3h}	D_{5h}	D_{6h}	D_{4d}	D_{5d}	D_{6d}	S_4	S_8	$C_{\infty v}$	$D_{\infty h}$
A	A_1'	A_1'	A_{1g}	A_1	A_{1g}	A_1	A	A	A_1	Σ_g
γ_1	E'	E_2'	E_{2g}	E_2	E_{2g}	E_2	B	E_2	E_2	Δ_g
γ_2	E''	E_1'	E_{1g}	E_3	E_{1g}	E_5	E	E_3	E_1	Π_g

G_4	D_4	C_{4v}	D_{4h}	D_{2d}	G_5	D_2	C_{2v}	D_{2h}
A	A_1	A_1	A_{1g}	A_1	A	A	A_1	A_g
γ_1	B_1	B_1	B_{1g}	B_1	γ_1	B_1	A_2	B_{1g}
γ_2	B_2	B_2	B_{2g}	B_2	γ_2	B_2	B_1	B_{2g}
γ_3	E	E	E_g	E	γ_3	B_3	B_2	B_{3g}

Ethylene-tetrafluoroethylene (E-TFE) alternating copolymer

As has been alluded to previously, a set of polarized Raman experiments can be designed to select out modes belonging to each of the Raman active symmetry species through a knowledge of the chain orientation with respect to the filament axis, the factor group symmetry and the Raman scattering activities. In the case of an alternating E-TFE copolymer conformational energy calculations¹⁵ on isolated chain and crystal lattice structures indicated that either a 3/2 helix or a planar zig-zag structure was possible. In a 3/2 helix the factor group of the line group is isomorphic to the C₃ point group the unique axis of which is parallel to the orientation direction of a uniaxially-oriented sample. In this case mode assignments to Raman active symmetry species are possible by specific choice of the input polarization and analyser directions using the theoretical framework for partially-oriented systems derived by Snyder².

In a planar conformation for E-TFE, the factor group is isomorphic to the C_{2h} point group and the unique axis (C₂) is perpendicular to the plane of the molecule and, therefore, perpendicular to the chain axis of uniaxial-orientation direction. For this case the orientation averages derived in this paper must be used and upon consulting Table 4 for the RAS case in orientation A they can be written:

Experiment	A _g	B _g
X(YY)Z	A1	0
X(YX)Z	$\frac{1}{2}l^2$	$\frac{1}{2}m^2$
X(ZY)Z	$\frac{1}{2}l^2$	$\frac{1}{2}m^2$
X(ZX)Z	B1	$\frac{1}{2}n^2$

Table 5 G₂: {C₃, D₃, C_{3v}, D_{3d}, S₆}
A: α_{xx} + α_{yy}
γ: (α_{xx} - α_{yy}, α_{xy}), (α_{yz}, α_{xz})

G ₂ RAS	A		B		C	
	X	Y	X	Y	X	Y
A Y	0	$\frac{1}{4}r^2$	0	E2	A2	E2
Z	A2	0	0	A2	0	0
γ Y	B2	D2	B2	F2	C2	F2
Z	C2	B2	B2	C2	B2	B2

G ₂ BS	A		B		C	
	Y	Z	Y	Z	Y	Z
A Y	$\frac{1}{4}r^2$	0	E2	A2	E2	0
Z	0	E2	A2	E2	0	$\frac{1}{4}r^2$
γ Y	D2	B2	F2	C2	F2	B2
Z	B2	F2	C2	F2	B2	D2

$$A2 = \frac{1}{32}(r^2 - 4rp + 4p^2), \quad B2 = \frac{1}{2}(l^2 + m^2)$$

$$C2 = \frac{1}{32}(s^2 - 2rs + 4sp + 16n^2), \quad E2 = \frac{1}{32}(3r^2 + 4rp + 12p^2)$$

$$D2 = \frac{1}{4}(s^2 + 2rs), \quad F2 = \frac{1}{32}(3s^2 - 6rs - 4sp + 16n^2)$$

Table 6 G₃: {C₄, C₅, C₆, D₅, D₆, C_{5v}, C_{6v}, C_{3h}, C_{4h}, C_{5h}, C_{6h}, D_{3h}, D_{5h}, D_{6h}, D_{4d}, D_{5d}, D_{6d}, S₄, S₈, C_{∞v}, D_{∞h}}
A: α_{xx} + α_{yy}, α_{zz}
γ₁: α_{xx} - α_{yy}, α_{xy}
γ₂: (α_{yz}, α_{xz})

G ₃ RAS	A		B		C	
	X	Y	X	Y	X	Y
A Y	0	$\frac{1}{4}r^2$	0	D3	A3	D3
Z	A3	0	0	A3	0	0
γ ₁ Y	$\frac{1}{2}l^2$	C3	$\frac{1}{2}l^2$	E3	B3	E3
Z	B3	$\frac{1}{2}l^2$	$\frac{1}{2}l^2$	B3	$\frac{1}{2}l^2$	$\frac{1}{2}l^2$
γ ₂ Y	$\frac{1}{2}m^2$	0	$\frac{1}{2}m^2$	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$
Z	$\frac{1}{2}n^2$	$\frac{1}{2}m^2$	$\frac{1}{2}m^2$	$\frac{1}{2}n^2$	$\frac{1}{2}m^2$	$\frac{1}{2}m^2$

G ₃ BS	A		B		C	
	Y	Z	Y	Z	Y	Z
A Y	$\frac{1}{4}r^2$	0	D3	A3	D3	0
Z	0	D3	A3	D3	0	$\frac{1}{4}r^2$
γ ₁ Y	C3	$\frac{1}{2}l^2$	E3	B3	E3	$\frac{1}{2}l^2$
Z	$\frac{1}{2}l^2$	E3	B3	E3	$\frac{1}{2}l^2$	C3
γ ₂ Y	0	$\frac{1}{2}m^2$	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$	$\frac{1}{2}m^2$
Z	$\frac{1}{2}m^2$	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$	$\frac{1}{2}m^2$	0

$$A3 = \frac{1}{32}[r^2 - 4rp + 4p^2]$$

$$B3 = \frac{1}{32}[s^2 - 2rs + 4sp]$$

$$C3 = \frac{1}{4}[s^2 + 2rs]$$

$$D3 = \frac{1}{32}[3r^2 + 4rp + 12p^2]$$

$$E3 = \frac{1}{32}[3s^2 - 6rs - 4sp]$$

where the scattering notation is of the form A(BC)D where A and D are the propagation directions of the incident (A) and scattered (D) radiation, while B and C refer to the direction of polarization of the incident (B) and analysed (C) radiation, respectively.

Comparison of these predictions for a planar zig-zag structure with those obtained for a 3/2 helix in conjunction with specially selected Raman polarization measurements have been the subject of a detailed study.⁶

Polyethylene (PE)

It should suffice to note that PE is an example where a

Table 7 $G_4: \{D_4, C_{4v}, D_{4h}, D_{2d}\}$
 $A: \alpha_{xx} + \alpha_{yy}, \alpha_{zz}$
 $\gamma_1: \alpha_{xx} - \alpha_{yy}$
 $\gamma_2: \alpha_{xy}$
 $\gamma_3: (\alpha_{yz}, \alpha_{xz})$

G ₄ RAS	A		B		C	
	X	Y	X	Y	X	Y
A Y	0	$\frac{1}{4}r^2$	0	D4	A4	D4
Z	A4	0	0	A4	0	0
γ_1 Y	0	C4	0	E4	B4	E4
Z	B4	0	0	B4	0	0
γ_2 Y	$\frac{1}{2}l^2$	0	$\frac{1}{2}l^2$	0	0	0
Z	0	$\frac{1}{2}l^2$	$\frac{1}{2}l^2$	0	$\frac{1}{2}l^2$	$\frac{1}{2}l^2$
γ_3 Y	$\frac{1}{2}m^2$	0	$\frac{1}{2}m^2$	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$
Z	$\frac{1}{2}n^2$	$\frac{1}{2}m^2$	$\frac{1}{2}m^2$	$\frac{1}{2}n^2$	$\frac{1}{2}m^2$	$\frac{1}{2}m^2$

G ₄ BS	A		B		C	
	Y	Z	Y	Z	Y	Z
A Y	$\frac{1}{4}r^2$	0	D4	A4	D4	0
Z	0	D4	A4	D4	0	$\frac{1}{4}r^2$
γ_1 Y	C4	0	E4	B4	E4	0
Z	0	E4	B4	E4	0	C4
γ_2 Y	0	$\frac{1}{2}l^2$	0	0	0	$\frac{1}{2}l^2$
Z	$\frac{1}{2}l^2$	0	0	0	$\frac{1}{2}l^2$	0
γ_3 Y	0	$\frac{1}{2}m^2$	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$	$\frac{1}{2}m^2$
Z	$\frac{1}{2}m^2$	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$	$\frac{1}{2}m^2$	$\frac{1}{2}m^2$	0

$$A4 = \frac{1}{32} [r^2 - 4rp + 4p^2]$$

$$B4 = \frac{1}{32} [s^2 - 2rs + 4sp]$$

$$C4 = \frac{1}{4} [s^2 + 2rs]$$

$$D4 = \frac{1}{32} [3r^2 + 4rp + 12p^2]$$

$$E4 = \frac{1}{32} [3s^2 - 6rs - 4sp]$$

unique axis cannot be unequivocally assigned due to the high symmetry exhibited in all three orthogonal directions. An ambiguity then results because a choice of this unique axis (of the D_{2h} point group) parallel to the direction of chain alignment in a uniaxial-oriented system requires group theoretical analysis using Snyder's tables. However, an equivalent choice of unique axis perpendicular to the direction of uniaxial orientation requires use of the orientation averages listed in Table 8. Different symmetry assignments result from either choice of the unique axis. For polyethylene the modes assigned to

Table 8 $G_5: \{D_2, C_{2v}, D_{2h}\}$
 $A: \alpha_{xx}, \alpha_{yy}, \alpha_{zz}$
 $\gamma_1: \alpha_{xy}$
 $\gamma_2: \alpha_{xz}$
 $\gamma_3: \alpha_{yz}$

G ₅ RAS	A		B		C	
	X	Y	X	Y	X	Y
A Y	0	B5	0	C5	A5	C5
Z	A5	0	0	A5	0	0
γ_1 Y	$\frac{1}{2}l^2$	0	$\frac{1}{2}l^2$	0	0	0
Z	0	$\frac{1}{2}l^2$	$\frac{1}{2}l^2$	0	$\frac{1}{2}l^2$	$\frac{1}{2}l^2$
γ_2 Y	$\frac{1}{2}m^2$	0	$\frac{1}{2}m^2$	0	0	0
Z	0	$\frac{1}{2}m^2$	$\frac{1}{2}m^2$	0	$\frac{1}{2}m^2$	$\frac{1}{2}m^2$
γ_3 Y	0	0	0	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$
Z	$\frac{1}{2}n^2$	0	0	$\frac{1}{2}n^2$	0	0

G ₅ BS	A		B		C	
	Y	Z	Y	Z	Y	Z
A Y	B5	0	C5	A5	C5	0
Z	0	C5	A5	C5	0	B5
γ_1 Y	0	$\frac{1}{2}l^2$	0	0	0	$\frac{1}{2}l^2$
Z	$\frac{1}{2}l^2$	0	0	0	$\frac{1}{2}l^2$	0
γ_2 Y	0	$\frac{1}{2}m^2$	0	0	0	$\frac{1}{2}m^2$
Z	$\frac{1}{2}m^2$	0	0	0	$\frac{1}{2}m^2$	0
γ_3 Y	0	0	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$	0
Z	0	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$	$\frac{1}{2}n^2$	0	0

$$A5 = \frac{1}{32} [(r-s)^2 - 4(r-s)p + 4p^2]$$

$$B5 = \frac{1}{4} (r+s)^2$$

$$C5 = \frac{1}{32} [3(r-s)^2 + 4(r-s)p + 12p^2]$$

$B_{1g}(B_{3g})$ when the unique axis is parallel to the chain become $B_{3g}(B_{1g})$ modes when the unique axis is perpendicular to the chain direction. To compare mode assignments for PE, equivalent geometries must be used or considerable confusion may result as also noted in the infrared assignments of the low-frequency lattice modes by Jones *et al.*¹⁰

CONCLUSIONS

With the advent of sophisticated polymer processing technology the availability of partially-oriented materials has increased significantly. Structural characterization by

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polarized Raman measurements is possible when these materials are transparent and a group theoretical framework for analysis of the observed bands is in place. Until recently, only one particular case⁶ in which the unique symmetry axis of the molecule is perpendicular to the orientation direction has been considered in detail. The results of this work in conjunction with that of Snyder² now allows routine analysis in cases where this unique axis is either parallel or perpendicular to the direction of the uniaxial orientation. In addition, investigation of the orientational relation of large pendant side groups to a partially oriented polymer backbone may now also be considered.

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