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Relationships among stress-induced Raman shifts for isotropic and uniaxially oriented polymers

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It is shown that, although the shifts of Raman lines observed when random or uniaxially oriented polymers are uniaxially stressed depend on the polarization directions of the incident and scattered radiation, the shifts are not all independent. For a random sample, there is a very simple relationship between the four measurable shifts for small stresses, which is independent of the nature of the polymer or of the vibrational mode involved, so that only three of the shifts are independent. If the form of the Raman tensor is known, a further relationship exists between the shifts, so that only two of them are independent. For a uniaxially oriented polymer, the products of the shifts and corresponding intensities are related in such a way that, if the form of the Raman tensor is known, only three of the four measurable values are independent. The predictions are compared with experimental results on poly(ethylene terephthalate) and are confirmed within experimental uncertainty. For a random sample, it is possible to deduce the form of the function $f(\theta)$ that describes the average contribution to the shift produced by a chain making angle θ to the axis of stress. This function is found to have a form somewhere between that expected if the shift were proportional to the resolved stress parallel to the chain and that expected if the shift were proportional to the resolved strain.

(Keywords: Raman shift; oriented polymers; stress)

INTRODUCTION

A considerable number of papers have appeared in recent years reporting the effect of applied stresses on the infra-red and Raman spectra of oriented polymers. If a tensile stress is applied parallel to the axis with respect to which the chains are preferentially oriented, certain modes, particularly those associated with the stretching of the polymer backbone, are found to shift, generally to lower frequency, and the corresponding peaks broaden (see for example refs. 1–16). This has been interpreted in terms of stresses (or strains) transferred to individual molecules or crystals and the consequent changes in bond force constants.

Almost all the studies have been concerned with highly or very highly oriented polymers, and the effect of the polarization of the incident and scattered light on the shift observed in Raman studies has generally not been considered. Fina *et al.*[12] have, however, studied moderately oriented samples of poly(ethylene terephthalate) (PET) using Raman spectroscopy, and have shown that for such samples the observed shifts depend on the polarization directions. The reason is that, for polymers of low orientation, observations with different polarization combinations are selectively sensitive to chains oriented in different directions, and these chains are in different states of stress (or strain). This leads to the possibility of obtaining information about the distribution of stress or strain on chains at different orientations to the draw direction.

The present paper is, however, limited to presenting some very general considerations for random and uniaxially oriented samples, which show that certain relationships must exist between the shifts observed with different polarization conditions. The predictions are compared with experimental data on PET, which include the results of measurements for both uniaxial loading parallel to the draw direction and loading in a direction transverse to the draw direction.

THEORY

Introduction

Consider the simplest form of uniaxially oriented polymer, where the chains are preferentially oriented towards the draw direction but have no preferred orientation around the draw direction or around their own axes. The distribution of orientations is then fully specified by a function $N(\theta)$, where θ is the angle between a typical chain axis and the draw direction and $N(\theta)\,\mathrm{d}\omega$ represents the fraction of chains oriented within any infinitesimal solid angle $\mathrm{d}\omega$ at angle θ to the draw direction.

Let a set of orthogonal axes $OX_1X_2X_3$ be chosen in the sample so that OX_3 is parallel to the draw direction. Let I_{ij} be the intensity of Raman scattering observed for a particular mode when the incident light is polarized parallel to OX_j and the scattered light is observed through an analyser with its transmission direction parallel to OX_i, and let S_{ij} be the corresponding shift in the line frequency when a tensile stress is applied to the sample parallel to OX_3. It follows from the symmetry of

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the Raman tensor that $I_{ij} = I_{ji}$ and that $S_{ij} = S_{ji}$, and it follows from the uniaxial nature of the sample that $I_{11} = I_{22}$, $I_{31} = I_{32}$, $S_{11} = S_{22}$ and $S_{31} = S_{32}$. It may, however, be shown[17] that, if the intensities are correctly normalized and the Raman tensor components or their ratios are known, only three of the intensities I_{11}, I_{31}, I_{21} and I_{33} are independent, since they can all be expressed in terms of an absolute intensity factor and the two quantities $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$, where $\langle P_n(\cos\theta)\rangle$ is the average of the nth-order Legendre polynomial over the function $N(\theta)$. For a random sample, only two of the intensities are independent in the limit of zero applied stress, viz. $I_{11} = I_{22} = I_{33}$ and $I_{12} = I_{23} = I_{31}$, and if the ratios of the Raman tensor components are known the ratio of these intensities can be predicted.

For an initially random sample under stress it cannot, however, be concluded that $S_{33} = S_{11}$ or that $S_{31} = S_{12}$ (we assume that the OX_3 axis is chosen parallel to the tensile stress for a random sample), since the stress breaks the symmetry. It will nevertheless be shown that, in the limit of small shifts, only three of the shifts S_{11}, S_{33}, S_{12} and S_{31} are independent, and if the ratios of the Raman tensor components are known, only two. It will also be shown that for a uniaxially oriented sample there is a relationship among the four products of the shift and corresponding intensity if the ratios of the tensor components are known. If these ratios are not known, all four products are independent.

General considerations

It follows from equations given previously[17] that, for a uniaxial sample of the simplest type described above, the Raman scattering intensity for a particular mode is given by:

$$I = I_0[A_0 + A_2\langle P_2(\cos\theta)\rangle + A_4\langle P_4(\cos\theta)\rangle] \quad (1)$$

where I stands for any of the I_{ij}, I_0 is independent of i and j, and A_0, A_2 and A_4 depend only on the ratios of the Raman tensor components and on i and j. This equation can more usefully be written in its differential form:

$$dI = I_0(A_0 + A_2P_2^\theta + A_4P_4^\theta)N(\theta)\sin(\theta)\,d\theta \quad (2)$$

where

$$P_2^\theta = P_2(\cos\theta), \qquad P_4^\theta = P_4(\cos\theta) \quad (3)$$

and $N(\theta)$ is assumed to be normalized to unity in the range 0 to $\pi/2$. (A factor of 2π has been incorporated into I_0.)

Suppose that, when a unit stress is applied to the sample, a chain at angle θ to the draw direction experiences on average a stress that produces a shift $f(\theta)$. If the shifts are small, the observed shift S is the intensity-weighted average over all angles θ and equation (2) leads to:

$$S = \frac{\int_0^{\pi/2}(A_0 + A_2P_2^\theta + A_4P_4^\theta)N(\theta)f(\theta)\sin(\theta)\,d\theta}{\int_0^{\pi/2}(A_0 + A_2P_2^\theta + A_4P_4^\theta)N(\theta)\sin(\theta)\,d\theta} \quad (4)$$

For each shift S_{ij} the denominator in equation (4) is proportional to the intensity observed for the corresponding values of i and j. Equation (4) can thus be replaced by:

$$IS = I_0\int_0^{\pi/2}(A_0 + A_2P_2^\theta + A_4P_4^\theta)N(\theta)f(\theta)\sin(\theta)\,d\theta \quad (5)$$

Writing

$$\alpha = \int_0^{\pi/2}N(\theta)f(\theta)\sin\theta\,d\theta$$

$$\beta = \int_0^{\pi/2}P_2(\cos\theta)N(\theta)f(\theta)\sin\theta\,d\theta \quad (6)$$

$$\gamma = \int_0^{\pi/2}P_4(\cos\theta)N(\theta)f(\theta)\sin\theta\,d\theta$$

leads to:

$$IS = I_0(A_0\alpha + A_2\beta + A_4\gamma) \quad (7)$$

and explicitly to:

$$I_{33}S_{33} = I_0(A'\alpha - 8B'\beta + 16C'\gamma) \quad (8a)$$

$$I_{11}S_{11} = I_0(A'\alpha + 4B'\beta + 6C'\gamma) \quad (8b)$$

$$I_{21}S_{21} = I_0(D'\alpha + 4E'\beta + 2C'\gamma) \quad (8c)$$

$$I_{13}S_{13} = I_0(D'\alpha - 2E'\beta - 8C'\gamma) \quad (8d)$$

where A' to E' are essentially the functions of the Raman tensor components tabulated in ref. 18. The only differences between the present A' to E' and those of ref. 18 arise from differences in normalization of the generalized spherical harmonics previously used and the present 'unnormalized' Legendre polynomials. Replacing $\alpha I_0A'$ by α', $\beta I_0A'$ by β' and $\gamma I_0A'$ by γ' leads to:

$$I_{33}S_{33} = \alpha' - 8\frac{B'}{A'}\beta' + 16\frac{C'}{A'}\gamma' \quad (9a)$$

$$I_{11}S_{11} = \alpha' + 4\frac{B'}{A'}\beta' + 6\frac{C'}{A'}\gamma' \quad (9b)$$

$$I_{21}S_{21} = \frac{D'}{A'}\alpha' + 4\frac{E'}{A'}\beta' + 2\frac{C'}{A'}\gamma' \quad (9c)$$

$$I_{13}S_{13} = \frac{D'}{A'}\alpha' - 2\frac{E'}{A'}\beta' - 8\frac{C'}{A'}\gamma' \quad (9d)$$

If the ratios of the Raman tensor components are known, these equations contain only three unknown quantities, α', β' and γ' (which depend on the value of I_0, on the absolute values of the Raman tensor components and on the forms of $f(\theta)$ and $N(\theta)$), so that the four products of intensity and shift are not independent. The intensities I_{ij} may more conveniently be replaced by I_{ij}/I_{33}, since this is merely equivalent to scaling α', β' and γ' by the same factor I_{33}.

Random sample

For a randomly oriented sample, in the limit of small stresses, $N(\theta) = 1$, so that $I_{33} = I_{11} = A'I_0$ and $I_{21} = I_{13} = D'I_0$. Equations (8) can then be written:

$$S_{33} = \alpha - 8\frac{B'}{A'}\beta + 16\frac{C'}{A'}\gamma \quad (10a)$$

$$S_{11} = \alpha + 4\frac{B'}{A'}\beta + 6\frac{C'}{A'}\gamma \quad (10b)$$

$$S_{21} = \alpha + 4\frac{E'}{D'}\beta + 2\frac{C'}{D'}\gamma \qquad (10c)$$

$$S_{13} = \alpha - 2\frac{E'}{D'}\beta - 8\frac{C'}{D'}\gamma \qquad (10d)$$

It may be shown by the following argument that for a random sample the four shifts of equations (10) must satisfy the relationship:

$$S_{33} + 2S_{11} = S_{21} + 2S_{13} \qquad (11)$$

Assume, as above, that the uniaxial loading of the isotropic sample is initially in the OX_3 direction. Now imagine loading instead in the OX_2 direction. The new values of S_{ij}, called S'_{ij}, will be:

$$S'_{33} = S_{22}(= S_{11}), \qquad S'_{21} = S_{13}(= S_{31} = S_{23} = S_{32}) \qquad (12)$$

Similarly, if the stress were applied parallel to OX_1 the new values would be:

$$S'_{33} = S_{11}(= S_{22}), \qquad S'_{21} = S_{32}(= S_{31} = S_{23} = S_{13}) \qquad (13)$$

Assuming linearity, the simultaneous application of all three stresses would give:

$$S''_{33} = S_{33} + 2S_{11}, \qquad S''_{21} = S_{21} + 2S_{13} \qquad (14)$$

But application of all three stresses simultaneously is the same as the application of a hydrostatic tension, and since the chains are randomly oriented there can be no difference, on average, between the shifts produced by chains in different orientations. Thus the shift observed (but not the intensity) must be independent of the polarization conditions, and we must have $S''_{33} = S''_{21}$, which leads directly to equation (11).

Applying equation (11) to equations (10) leads to:

$$3\alpha + 28\frac{C'}{A'}\gamma = 3\alpha - 14\frac{C'}{D'}\gamma \qquad (15)$$

This equation must hold for any values of A', C' and D', so that γ must be zero. It can also be seen more directly that γ must be zero by the following argument. Apply the tensile load simultaneously in three directions at right angles. The function that describes the mean shift produced by a chain at angles θ_1, θ_2 and θ_3 to the three axes must now be $f(\theta_1) + f(\theta_2) + f(\theta_3)$, assuming linearity. But this must be independent of θ_1, θ_2 and θ_3 for an unoriented sample, and the only functions that have this property[19] are $f(\theta) =$ constant and $f(\theta) = P_2(\cos\theta)$. Thus $f(\theta)$ must take the form:

$$f(\theta) = a' + b'P_2(\cos\theta) = a\cos^2\theta + c \qquad (16)$$

which implies that $\gamma = 0$ in equations (10), since γ is directly proportional to $\langle P_4(\cos\theta)\rangle_f$, the average value of $P_4(\cos\theta)$ over $f(\theta)$, when $N(\theta) = 1$.

The four shifts thus depend on only the three quantities α, $B'\beta/A'$ and $E'\beta/D'$ and are related by equation (11). If the ratios of the Raman tensor components are known, B'/A' and E'/D' are known and the shifts depend only on α and β, so that only two of them are independent.

These predictions will now be tested using data recently obtained for shifting of the 1616 cm^{-1} Raman line due to tensile loading of random and uniaxially oriented samples of PET.

EXPERIMENTAL TEST OF THEORY

Reduction of the general equations to appropriate form

If δ represents the angle (19°) between the C1–C4 direction in the phenylene ring and the chain axis and the assumption that there is no preferred orientation around the chain axes is made, it follows from the Legendre addition theorem that P_2^θ and P_4^θ in equations (2)–(6) can be replaced by $P_2^\theta P_2^\delta$ and $P_4^\theta P_4^\delta$, where $P_n^\delta = P_n(\cos\delta)$, provided that in calculating A' to E' the Raman tensor is referred to axes fixed in the phenylene ring so that the principal reference axis is parallel to C1–C4. It has been shown previously that it is a good approximation to assume that the Raman tensor for the 1616 cm^{-1} line is cylindrically symmetric around the C1–C4 direction. If the ratio of the Raman tensor components perpendicular and parallel to the C1–C4 direction is r, equations (8) are then replaced (with adjustment of I_0 by a constant factor) by:

$$I_{33}S_{33} = I_0(A\alpha - 2B\beta + 8C\gamma) \qquad (17a)$$

$$I_{11}S_{11} = I_0(A\alpha + B\beta + 3C\gamma) \qquad (17b)$$

$$I_{21}S_{21} = I_0(D\alpha + 2E\beta + C\gamma) \qquad (17c)$$

$$I_{13}S_{13} = I_0(D\alpha - E\beta - 4C\gamma) \qquad (17d)$$

where A to E are given in terms of r by Jarvis *et al.*[20]. It is easily shown from their equations (18) that:

$$I_0 = (I_{33} + 2I_{11} + 2I_{21} + 4I_{13})/(3A + 6D) \qquad (18)$$

The value of −0.122 has been used here for the ratio r and leads to the values of A to E shown in *Table 1*. This value of r is different from those used previously[20,21]; the justification for using it here is that it was determined[22] on the undrawn material from which most of the present samples were made and that it corresponds to a lower depolarization ratio than the values previously determined. The undrawn material was carefully examined for evidence of orientation and none was found. Any polarization scrambling could only raise the observed depolarization ratio. Huijts and Peters[23] have recently also obtained the value $r = -0.122$.

For a random sample equations (10) reduce to:

$$S_{33} = \alpha - \frac{2B}{A}\beta \qquad (19a)$$

$$S_{11} = \alpha + \frac{B}{A}\beta \qquad (19b)$$

$$S_{21} = \alpha + \frac{2E}{D}\beta \qquad (19c)$$

$$S_{13} = \alpha - \frac{E}{D}\beta \qquad (19d)$$

The experimental data

We have recently made measurements of the shifts and intensities of the 1616 cm^{-1} Raman line for a random sample and three uniaxially oriented samples of PET.

Table 1 Values of A to E

$A = 0.1754$	$B = -0.2684$
$C = 0.0360$	$D = 0.0839$
$E = -0.0599$	

For two of the uniaxial samples, measurements were made with the load applied both parallel to the draw direction, OX_3, and parallel to the direction OX_1, perpendicular to the draw direction. The experimental details of this work will be described elsewhere[22].

When the load is applied parallel to the OX_1 direction, the shifts S_{22} and S_{23} become distinct, in addition to S_{33}, S_{11}, S_{21} and S_{13}. The stress tensor

$$\begin{pmatrix} \sigma_1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

can be represented as the sum of a pure shear (a) and a 'uniaxial dilation' (b):

$$\begin{pmatrix} \sigma_1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} \sigma & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$= \begin{pmatrix} \frac{1}{2}\sigma & 0 & 0 \\ 0 & -\frac{1}{2}\sigma & 0 \\ 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} \frac{1}{2}\sigma & 0 & 0 \\ 0 & \frac{1}{2}\sigma & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

(a) (b)

The shear (a) can have no first-order effect on S_{33} or S_{21}, but it will have equal and opposite effects on S_{11} and S_{22} and on S_{13} and S_{23}. One can thus calculate the shifts S_{ij}^{d} for a pure uniaxial dilation (b) as follows:

$$S_{33}^{d} = S_{33}, \qquad S_{11}^{d} = \tfrac{1}{2}(S_{11} + S_{22})$$
$$S_{21}^{d} = S_{21}, \qquad S_{13}^{d} = \tfrac{1}{2}(S_{13} + S_{23}) \qquad (20)$$

where S_{ij} is the measured value for the applied stress parallel to OX_1. These values of S_{ij}^{d} give a second set of data for testing equations (17), since they correspond to a second type of uniaxial stress parallel to the draw direction.

Comparison of data with theory

All the experimental shifts reported are shifts in the position of the maximum of intensity in the 1616 cm^{-1} peak, determined by fitting Lorentzian curves to the peaks. Although it would probably be preferable to use shifts of the centre of gravity of the peak in comparisons with the theory, such shifts cannot be reliably obtained[22]. *Table 2* shows the results of performing a weighted least-squares fit of the shifts for the random sample, expressed as stress sensitivities (cm^{-1} GPa^{-1}), to equations (19); the fit is very good. The experimental data in *Table 2* may also be tested against the simple prediction of equation (11). The value of the left-hand side is $-6.0 \pm 1.5\,cm^{-1}$ GPa^{-1} and that of the right-hand side $-8.5 \pm 3.4\,cm^{-1}$ GPa^{-1}. The agreement is satisfactory and leads to a mean value of $-6.4 \pm 1.4\,cm^{-1}$ GPa^{-1}; the best-fit value is $-6.5\,cm^{-1}$ GPa^{-1}.

Table 2 Fits of shifts for random sample to constraining equations (19). Values of shifts in cm^{-1} GPa^{-1}; fitted $\alpha = -2.16$, $\beta = -1.33$

Shift	Experiment	Fit
S_{33}	-6.19 ± 0.56	−6.24
S_{11}	0.08 ± 0.68	−0.12
S_{21}	-0.72 ± 1.31	−0.25
S_{13}	-3.90 ± 1.57	−3.11

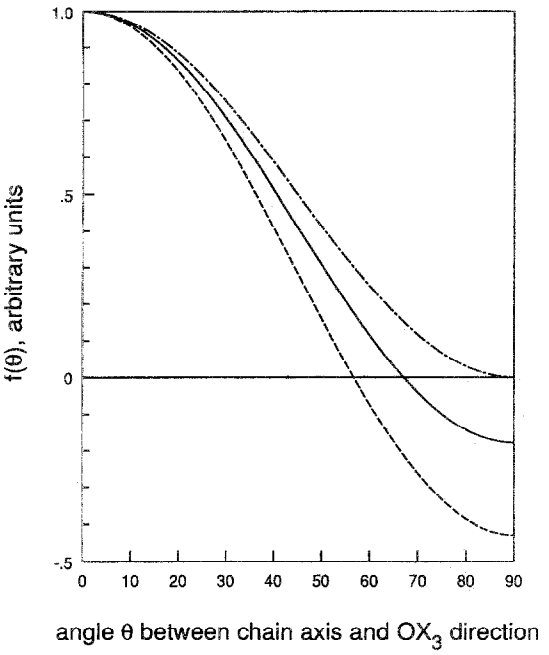

Figure 1 The shift function $f(\theta)$ for the random sample with tensile stress applied parallel to OX_3: (——), as deduced from the fit of the experimental shifts to equations (19); (– · – · –), assuming $f(\theta)$ is proportional to the macroscopic stress resolved parallel to the chain; (– – –), assuming $f(\theta)$ is proportional to the macroscopic strain resolved parallel to the chain. All curves are arbitrarily normalized to 1 at $\theta = 0$, whereas $f(\theta)$ as fitted is negative at $\theta = 0$, since the shift for chains parallel to the stress axis is negative for a positive tensile stress

Figure 1 shows the form of $f(\theta)$ deduced from the fit to equations (19), together with curves representing the expected forms of $f(\theta)$ if it were proportional to (i) the tensile component of the macroscopic stress or (ii) the tensile component of the macroscopic strain, both resolved parallel to the chain axis. The three curves have been arbitrarily normalized to the same value at $\theta = 0$ and the third curve was calculated for a Poisson's ratio[24] of 0.43. The fitted form of $f(\theta)$ is seen to lie very close to the mean of the values suggested by the macroscopic stress and strain curves. It has been shown[25] that the elastic constants of an isotropic aggregate of anisotropic units must lie between those calculated on the extreme assumptions that the sample is in uniform stress or uniform strain, and the present result is consistent with this.

The quantity represented by both sides of equation (11), and found to have the value $-6.4 \pm 1.4\,cm^{-1}$ GPa^{-1}, is the shift expected for a uniform hydrostatic tension, or negative pressure. Measurements of the shift of the 1616 cm^{-1} line for the random sample under hydrostatic pressure have recently been made[26], where the shifts were again determined by fitting Lorentzian peaks to the lineshape. Within experimental error, the shift was linear with pressure for pressures below 500 MPa and was equal to $5.6 \pm 0.3\,cm^{-1}$ GPa^{-1}, in good agreement with that predicted for positive pressures from the simple uniaxial loading data by assuming no change of slope at the origin. It should, however, be noted that the stress used in the determination of the shifts for uniaxial loading was only ~24 MPa.

Table 3 Fits of shifts for uniaxial tension parallel to draw direction to constraining equations (17). Values of shifts in cm^{-1} GPa^{-1}

	Draw ratio					
	3.38		4.71		3.9	
Shift	Experiment	Fit	Experiment	Fit	Experiment	Fit
S_{33}	-5.49 ± 0.57	−5.48	-6.05 ± 0.18	−6.04	-4.66 ± 0.22	−4.64
S_{11}	0.77 ± 0.65	0.42	0.00 ± 0.52	−0.36	-0.10 ± 0.38	−0.43
S_{21}	-0.35 ± 0.60	0.14	-0.34 ± 0.27	−0.14	-0.40 ± 0.22	−0.28
S_{13}	-3.60 ± 0.68	−3.65	-3.08 ± 0.17	−3.09	-3.04 ± 0.27	−3.07

Table 4 Fits of shifts for uniaxial dilation to constraining equations (17). Values of shifts in cm^{-1} GPa^{-1}

	Draw ratio			
	3.38		4.71	
Shift	Experiment	Fit	Experiment	Fit
S_{33}	2.95 ± 1.05	2.98	4.64 ± 0.55	4.65
S_{11}	-4.63 ± 1.22	−5.34	-7.08 ± 1.37	−7.57
S_{21}	-4.57 ± 1.19	−3.48	-5.05 ± 1.60	−3.64
S_{13}	-0.63 ± 1.43	−0.76	2.23 ± 0.08	2.18

For the uniaxially oriented samples the data were fitted by dividing both sides of equations (17) by the appropriate I_{ij} and performing a weighted least-squares fit of the shifts by varying only α, β and γ. The values of I_{ij} used were those of the unstressed sample and their uncertainties were not taken into account in the fitting. The fits, shown in *Table 3* for the shifts under uniaxial tension and in *Table 4* for the shifts under uniaxial dilation, are again good.

Unfortunately it is not possible to deduce the form of $f(\theta)$ directly from the fits to the data for uniaxial samples, as it is for the random sample, since the fitted parameters α, β and γ are now proportional to averages of $P_l(\cos\theta)N(\theta)f(\theta)$ over all angles θ. In order to interpret the data fully, it will be necessary to consider models for predicting the forms of both $N(\theta)$ and $f(\theta)$, from which either the shifts or α, β and γ can be calculated for comparison with the experimental values. The results do, however, show that even for a random sample $f(\theta)$ is not simply proportional to the resolved stress or strain parallel to the chain axis, so that more complicated models will certainly be required. This goes beyond the scope of the present paper but will be considered in a future paper[22].

CONCLUSIONS

The results of experiments on PET support the theoretical conclusion that, although the Raman shifts observed on stressing uniaxial or random samples are different for different combinations of the polarization directions of incident and scattered radiation, these shifts are not independent and their relationship can be predicted provided that information is available about the form of the Raman tensor. For a random sample a universal relationship is predicted and confirmed that is independent of any knowledge of the Raman tensor. In order to interpret the shifts in detail, models will be required that go beyond the assumption that the shift contributed by a given chain is proportional to either the resolved stress or resolved strain parallel to the chain axis.

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