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Molecular biaxiality and reorientational correlation functions in nematic phases: Infrared spectroscopy

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In this paper we apply the theoretical results presented in the preceding paper to the case of infrared spectroscopy. A theoretical evaluation of the correlation functions connected with spinning and tumbling molecular fluctuations and comparison with the experimental correlation functions obtained from band-shape analysis of infrared dichroic spectra in ordered nematic phases allows us to evaluate the effect of molecular biaxiality (i.e., deviations from cylindrical symmetry) on polarized ir absorption spectra. From the fitting of our data we are able to recover the "true" behavior of the spinning diffusion coefficients (the tumbling coefficients are not affected by molecular biaxiality as predicted by the theory) and obtain a semiquantitative estimate of the strength of the biaxial term in the nematic potential.

I. INTRODUCTION

In paper I[1] the effect of a non-negligible biaxial term in the nematic potential on the spinning (rotations about the main molecular axis) and tumbling (rotations of the main molecular axis) reorientational correlation functions was calculated, in the framework of the small-step rotational diffusion model[2] and in the short-time limit. In particular, the tumbling correlations were shown to be unaffected by molecular biaxiality, whereas for the spinning motion additional correlation functions were seen to have a substantial role in determining the total correlation functions, especially at high values of the order parameter $\langle P_2 \rangle$.

Recently we have shown that Fourier band-shape analysis could be used to determine the decay of the orientational correlation functions in the picosecond time scale both for infrared[3] and Raman[4] spectra. The results of paper I indicate that, for tumbling motion in a strongly anisotropic system such as a nematic liquid crystal (where $D_\parallel \gg D_\perp$), cross correlations due to the biaxial term in the nematic potential have a negligible effect on the global correlation function. Thus the infrared and Raman band shapes associated with tumbling reorientations, i.e., those due to vibrations whose induced dipole moment is essentially parallel to the molecular axis (ir) or whose induced polarizability tensor is strongly uniaxial (Raman), should yield to a good approximation the true self-correlation function even in the presence of a non-negligible biaxial term in the nematic potential $U(\Omega)$. For vibrations which probe the spinning motion the situation may be quite different. Let us consider for simplicity the ir case: A vibrational band shape will be sensitive to the molecular spinning if the corresponding induced dipole moment makes a reasonably large angle with the main molecular axis. The maximum effect on the band shape will be obtained when the induced dipole points at the "magic angle" ($\theta \simeq 54°$), which corresponds to the first zero of the second-order Legendre polynomial $P_2(\cos\theta)$. As θ increases, the effect should decrease, although for reasons which are quite different from those which make the $\theta \simeq 0$ case insensitive to spinning. In fact, for $\theta \simeq 90°$, both the parallel $[a_z(t)]$ and perpendicular $[a_x(t)]$ normalized Fourier transforms of the corresponding ir absorption bands $A_z(\omega)$ and $A_x(\omega)$ will be strongly affected by the rotational motion; however, for a cylindrically symmetric nematic distribution function $f(\Omega)=f(\beta)$, the dependence of $a_z(t)$ and $a_x(t)$ on the spinning diffusion coefficient $D_\parallel$ is the same, and thus cancels out (see Sec. II for details). This very fact should make a "large angle" vibration particularly sensitive to the deviations of $f(\Omega)$ from cylindrical symmetry.

Therefore the theory of paper I and, more generally, the effects of molecular biaxiality on polarized ir and Raman band shapes may be studied by performing Fourier or—where possible—bandwidth analysis of ir or Raman bands connected with vibrations which are sensitive, to a greater or lesser degree, to spinning motion.

In this paper we present such a study, limited to the ir case, both because it is simpler to interpret and because the calculations presented in paper I were limited to $l=1$ correlation functions (theoretical and experimental work on the Raman case is in progress and will be reported elsewhere). In Sec. II we briefly summarize the relevant theory; then we present ir data taken using vibrations characterized by differing values for θ, and fit our results using the correlation functions calculated in paper I. From such fits we obtain the value of λ which parametrizes the intensity of the biaxial contribution to the nematic potential [Eq. (5), paper I], and the temperature behavior of the biaxial order parameter $\langle D^2_{02} \rangle$.

II. EFFECT OF $U(\Omega)$ BIAXIALITY ON ir BAND SHAPES

As mentioned in a recent paper,[3] we have developed an approach which enables us to obtain information about the decay of the orientational correlation functions in the dipicosecond time scale from ir band-shape analysis. This approach is based on the elimination of the large vibrational contribution to the band shape comparing the ir spectra taken in two different polarizations. In Ref. 3 we assume cylindrically symmetric distribution function $f(\Omega)=f(\beta)$ and we have

$$\frac{d}{dt}\frac{a_z(t)}{a_x(t)}=\frac{\phi_{00}^{11}(t)\cos^2\theta+\phi_{01}^{11}(t)\sin^2\theta}{\phi_{00}^{11}(0)\cos^2\theta+\phi_{01}^{11}(0)\sin^2\theta}\times\frac{\phi_{10}^{11}(0)\cos^2\theta+\phi_{11}^{11}(0)\sin^2\theta}{\phi_{10}^{11}(t)\cos^2\theta+\phi_{11}^{11}(t)\sin^2\theta}\ . \tag{1}$$

θ is the angle between the long molecular axis and the dipole moment of the transition and $a_i(t)$ is the Fourier transform of the normalized ir absorbance, where $i=z,x$ and z is chosen parallel to the nematic axis. Because of the cylindrical macroscopic symmetry of the phase, we have $a_x=a_y=a_\perp\neq a_\parallel=a_z$. The correlation functions $\phi(t)$ are defined in paper I.

In the framework of the small-step rotational diffusion model, we expand the correlation functions in a Taylor series which is then truncated at the terms proportional to t (a good approximation in the picosecond time domain). From Eqs. (26) and (27) of paper I we obtain

$$\frac{d}{dt}\frac{a_z(t)}{a_x(t)}=\frac{9D_\perp P_2(\cos\theta)\langle P_2\rangle+(D_\parallel-D_\perp)[1-P_2(\cos\theta)][1+2P_2(\cos\theta)]}{[1-\langle P_2\rangle P_2(\cos\theta)][1+2\langle P_2\rangle P_2(\cos\theta)]}\ . \tag{2}$$

If $\theta\cong0°$, Eq. (2) becomes

$$\frac{d}{dt}\frac{a_z(t)}{a_x(t)}=\frac{9\langle P_2\rangle}{(1-\langle P_2\rangle)(1+2\langle P_2\rangle)}D_\perp \tag{3}$$

and this enables us to calculate $D_\perp$ ($\langle P_2\rangle$ can be obtained from the dichroism of the integral intensity of the band). As mentioned, in this case the spinning diffusion coefficient $D_\parallel$ does not appear in the equation because the spinning motion of the molecule does not change the dipole moment coordinates in the laboratory frame. If $\theta\cong54°$,[3]

$$\frac{d}{dt}\frac{a_z(t)}{a_x(t)}=\langle P_2\rangle(D_\parallel-D_\perp) \tag{4}$$

and $D_\parallel$ can be calculated. If $\theta\cong90°$, we have

$$\frac{d}{dt}\frac{a_z(t)}{a_x(t)}=-\frac{9\langle P_2\rangle}{(1-\langle P_2\rangle)(2+\langle P_2\rangle)}D_\perp\ . \tag{5}$$

The physical reason for the disappearance of $D_\parallel$ in Eq. (5) is quite different from that in the case $\theta\cong0°$. For $\theta\cong90°$ both $a_z(t)$ and $a_x(t)$ depend strongly on the spinning motion, but if the distribution function $f(\Omega)$ is cylindrically symmetric as we have assumed in Ref. 3 the dependence of $D_\parallel$ is the same for $a_z(t)$ and $a_x(t)$ and it disappears in Eq. (5). As we shall see later, if $f(\Omega)$ is biaxial the compensation of the $D_\parallel$ dependence in Eq. (5) is not exact and Eq. (5) changes drastically.

For this reason the band with $\theta\cong90°$ are very sensitive to the cross-correlation functions $\phi_{l'1l'-1}^{11}(t)$ and they are a good tool for the investigation of the reorientations of the biaxial nematic molecules. Let us consider the case of biaxial ordering potential given by Eq. (5) of paper I. In this case Eq. (1) becomes

$$\frac{d}{dt}\frac{a_z(t)}{a_x(t)}=\frac{\phi_{00}^{11}(t)\cos^2\theta+\phi_{01}^{11}(t)\sin^2\theta-\phi_{010-1}^{11}(t)\sin^2\theta\cos(2\varphi)}{\phi_{00}^{11}(0)\cos^2\theta+\phi_{01}^{11}(t)\sin^2\theta-\phi_{010-1}^{11}(0)\sin^2\theta\cos(2\varphi)}\,\frac{\phi_{10}^{11}(0)\cos^2\theta+\phi_{11}^{11}(0)\sin^2\theta-\phi_{111-1}^{11}(0)\sin^2\theta\cos(2\varphi)}{\phi_{10}^{11}(t)\cos^2\theta+\phi_{11}^{11}(t)\sin^2\theta-\phi_{111-1}^{11}(t)\sin^2\theta\cos^2\varphi}\ , \tag{6}$$

where θ and φ are the polar angles of the transition dipole moment in the molecular frame. Expanding the correlation functions in Taylor series and using Eqs. (26) and (27) of paper I we obtain

$$\frac{d}{dt}\frac{a_z(t)}{a_x(t)}=\frac{9D_\perp[\langle P_2\rangle P_2(\cos\theta)+y]+(D_\parallel-D_\perp)\{\langle P_2\rangle[1-P_2(\cos\theta)][1+2P_2(\cos\theta)]+y[5-2P_2(\cos\theta)]\}}{[1-\langle P_2\rangle P_2(\cos\theta)-y][1+2\langle P_2\rangle P_2(\cos\theta)+2y]}\ , \tag{7}$$

where $y=(3/2)^{1/2}\langle D_{02}^2\rangle\sin^2\theta\cos(2\varphi)$. For $\theta\cong0°$ Eq. (3) remains the same, as it is expected. For $\theta\simeq54°$

$$\frac{d}{dt}\frac{a_z(t)}{a_x(t)}=\frac{18D_\perp x+(D_\parallel-D_\perp)(\langle P_2\rangle+10x)}{(1-2x)(1+4x)}\ , \tag{8}$$

where $x=\langle D_{02}^2\rangle\cos(2\varphi)\sqrt{6}$. Considering that $\langle D_{02}^2\rangle\ll\langle D_{00}^2\rangle$, the corrections are small. For $\theta\cong90°$ there is a drastic qualitative correction

$$\frac{d}{dt}\frac{a_z(t)}{a_x(t)}=\frac{-9D_\perp(\langle P_2\rangle-6x)+36(D_\parallel-D_\perp)x}{(1-\langle P_2\rangle+6x)(2+\langle P_2\rangle-6x)}\ , \tag{9}$$

since the new term depending on $D_\parallel-D_\perp$ can be rather large because $D_\parallel\gg D_\perp$. We note in particular that in some cases the right-hand side of Eq. (9) might change

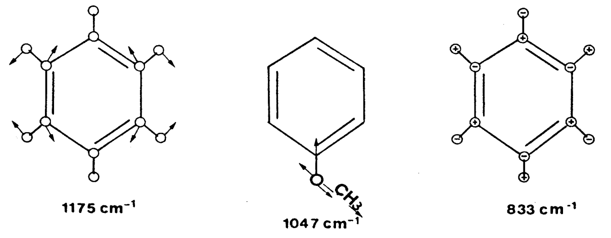

FIG. 1. Normal coordinates of the PMT 1175, 1047, and 833 cm^{-1} bands.

sign, leading to a correlation function which would appear to increase with time or, in the frequency domain, to a parallel absorption band which is broader than the perpendicular one. Such anomalous behavior thus would indicate strong molecular biaxiality.

III. EXPERIMENTAL RESULTS

In order to verify our theoretical model we have investigated the ir spectrum of 4,*n*-pentyl 4′-methoxytolane (PMT), with the nematic phase in the temperature interval 44–56C, and *N*-(4-pentyloxybenzylidene) 4′-toluidine (PBT) which is nematic between 54 and 67.3 C.

In the case of PMT, we selected the following bands: 1175, 1047, and 833 cm^{-1} (Fig. 1). The transition dipole moment of the mode at 1175 cm^{-1} (benzene ring inplane deformation) is essentially parallel to the long molecular axis (the dichroic ratio is $R=6$). The band at 1047 cm^{-1} is assigned to oxygen-alkyl tail stretching; it is weakly polarized ($R=1.8$). The 833 cm^{-1} band is due to the out-of-plane deformation of the hydrogen atoms on the benzene ring which involve also some ring-bending coordinates. It is strongly transversally polarized ($R=0.35$). Following paper I we choose the molecular frame to coincide with the principal axis system of the ordering matrix,[5] and we assume that the rotational diffusion tensor is diagonal in this frame (a reasonable approximation given the high anisotropy of nematic molecules). For tolane derivatives the planes of both the benzene rings are almost parallel to each other;[6] thus in paper I we chose the molecular axis to lie approximately in these planes. Due to the anisotropy of the benzene ring polarizability, the molecules can be expected to prefer an orientation such that their nematic director lies in the plane of the ring: This corresponds to $\langle D^2_{02} \rangle > 0$. The alkoxy group will then lie in the same plane and for the band 1047 cm^{-1} we expect $\varphi \cong 0°$. The origin of the 833 cm^{-1} band implies that for this mode $\varphi \cong 90°$.

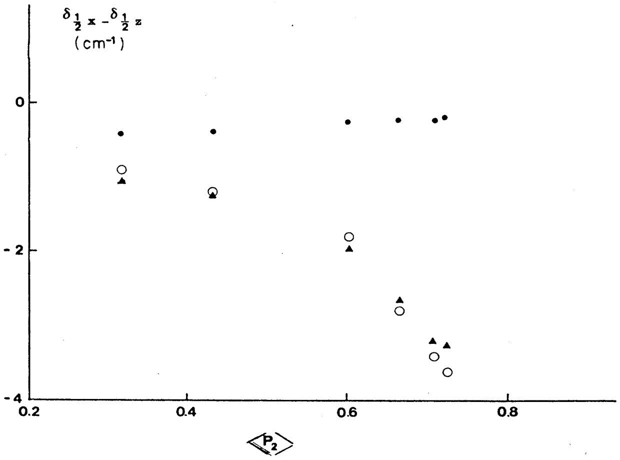

FIG. 2. Rotational contribution to the total FWHM of the 833 cm^{-1} mode as a function of orientational order parameter $\langle P_2 \rangle$; ○: experimental data; ●: calculated, with $\lambda=0$ (uniaxial model); ▲: calculated, with $\lambda=0.4$ (biaxial model).

Since all three bands are good Lorentzians, we do not need to Fourier transform the total band shape and we can directly work with the full width at half maximum (FWHM), as it is shown in Ref. 3,

$$\frac{d}{dt}\frac{a_z(t)}{a_x(t)} = \pi c\,(\delta_{(1/2)x} - \delta_{(1/2)z})\,, \tag{10}$$

where $\delta_{1/2}$ is the FWHM of the band measured in cm^{-1}. In Table I we present the experimental values of $\langle P_2 \rangle$, $\langle D^2_{02} \rangle$, $D_\perp$, $D_\parallel$ (Ref. 7) and the rotational FWHM's for the three bands. The reader is referred to Ref. 3 for details about the experimental set up and data analysis. In Fig. 2 we present the experimental data relative to $\delta_{(1/2)x} - \delta_{(1/2)z}$ for the 833 cm^{-1} band and the corresponding theoretical values calculated using Eqs. (3)–(5) [assuming cylindrical symmetry of $f(\Omega)$] and Eqs. (3),

TABLE I. Orientational order parameter, rotational contribution to the total band shape, $\langle D^2_{02} \rangle$, and rotational diffusion coefficients for PMT as a function of temperature.

T (C)	$\langle P_2 \rangle$	$\delta_{(1/2)x} - \delta_{(1/2)z}$ (cm^{-1}) 1175 cm^{-1}	1047 cm^{-1}	833 cm^{-1}	$\langle D^2_{02} \rangle$	$D^r_\perp$ (10^9 s^{-1})	$D^r_\parallel$ (10^9 s^{-1}) $\lambda=0$	$D^r_\parallel$ (10^9 s^{-1}) $\lambda\neq0$
41[a]	0.72	0.20	2.0	−3.6	0.045	2.1	270	230
43	0.71	0.25	1.9	−3.4	0.046	2.7	260	220
46	0.67	0.25	1.5	−2.8	0.052	3.2	220	180
51	0.61	0.30	1.0	−1.8	0.054	4.8	160	130
54	0.43	0.50	0.5	−1.2	0.066	13.5	100	70
55.8	0.32	0.55	0.4	−0.9	0.049	23.4	90	66

[a] Supercooled.

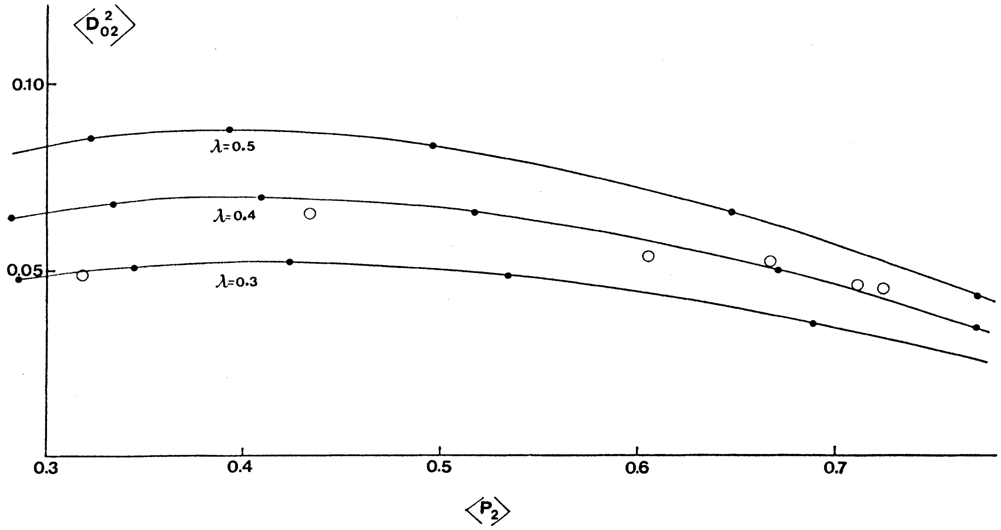

FIG. 3. $\langle D^2_{02}\rangle$ as a function of orientational order parameter $\langle P_2\rangle$; solid lines: theoretical data; open circles: experimental results. The "unphysical" $\lambda=0.5$ line has been shown solely to help demonstrate the resolution of our experiment with respect to the determination of λ.

(8), and (9) [assuming biaxial symmetry of $f(\Omega)$]. In this last case, the order parameter $\langle D^2_{02}\rangle$ was calculated using the potential given in Eq. (5) of paper I with the value $\lambda=0.4$ chosen to fit the experimental $\langle P_2\rangle$ data. For this we proceeded in the following way: From the experimental values of $\langle P_2\rangle$ and $\delta_{(1/2)z}-\delta_{(1/2)x}$ for the 1047 and 1175 cm^{-1} bands, we determined $D_\parallel$ and $D_\perp$ using Eqs. (3) and (4) or (8) and the calculated value of $\langle D^2_{02}\rangle$; then we calculated the value of $\delta_{(1/2)z}-\delta_{(1/2)x}$ for the 833 cm^{-1} band from Eqs. (5) or (9). One can see that the magnitude of the reorientational part of the half width calculated under the assumption $f(\Omega)=f(\beta)$ is much smaller and has a different temperature behavior. The curve calculated with $\lambda=0.4$ is close to the experi-

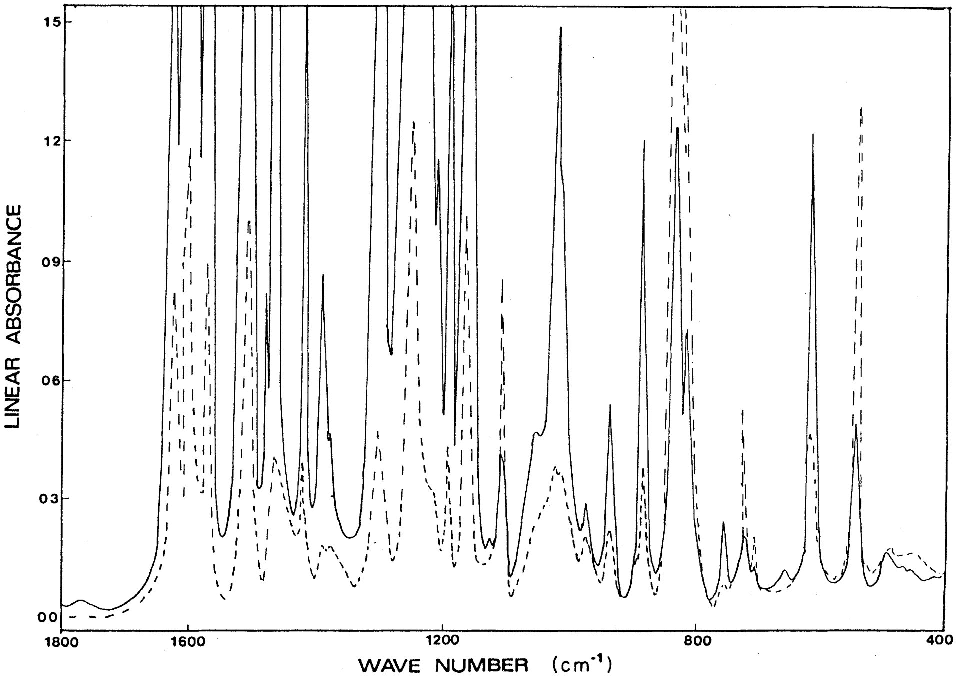

FIG. 4. ir spectra of *N*-(4-pentyloxybenzylidene) 4′-toluidine; solid line: **E**‖**n**; dashed line: **E**⊥**n**; cell thickness: 12 μm.

TABLE II. Analyzed ir bands of *N*-(4-pentyloxybenzylidene) 4′-toluidine, dichroic ratios, and their possible assignments.

Band (cm^{-1})	R	Possible assignment
1175	5.3	benzene ring in-plane deformation
935	1.5	benzene ring + CH aromatic out-of-plane deformation
888	2.2	benzene ring-nitrogen in-plane deformation
830	0.31	benzene ring + CH aromatic out-of-plane deformation
815	0.52	benzene ring + CH aromatic out-of-plane deformation
723	0.45	alkyl chain in-plane deformation (CH_2 rocking)
612	4	benzene ring out-of-plane deformation
540	0.37	benzene ring + pentyloxy group out-of-plane deformation

mental one. Taking into account the fact that Eq. (5) of paper I represents only approximately the potential $U(\Omega)$ together with the large uncertainties of the values of $\langle P_2 \rangle$, θ, φ, and the complicated origin of the ir bands, the coincidence should be considered reasonable. An alternative way to present our results is to eliminate $D_\parallel$ and $D_\perp$ using Eqs. (3) and (8) and then calculate $\langle D_{02}^2 \rangle$ from Eq. (9). In Fig. 3 we compare the experimental dependence of $\langle D_{02}^2 \rangle$ as a function of $\langle P_2 \rangle$ obtained in this way with the theoretical behavior[8] calculated for several values of λ. From the fit we obtain $\lambda = 0.4$ for PMT. From an experimental point of view, this value compares well with the result $\lambda = 0.2$ for 4,4′-dimethoxyazoxybenzene (PAA) (Ref. 6) and $\lambda \approx 0.5$ for 4,*n*-octyl-*d*-oxybenzoic acid and 4,*n*-heptyl-*d*-oxybenzoic acid (this value has been obtained by us comparing the experimental data given in Ref. 9 with the theoretical results from Ref. 8). The measured temperature dependence of $\langle D_{02}^2 \rangle$ has the same features (the presence of a maximum close to the clearing temperature as that observed by other investigators[9–11]). A more detailed comparison of the temperature dependence of $\langle D_{02}^2 \rangle$ with mean-field theories is under study, together with the theoretical implications of the high observed value for λ.

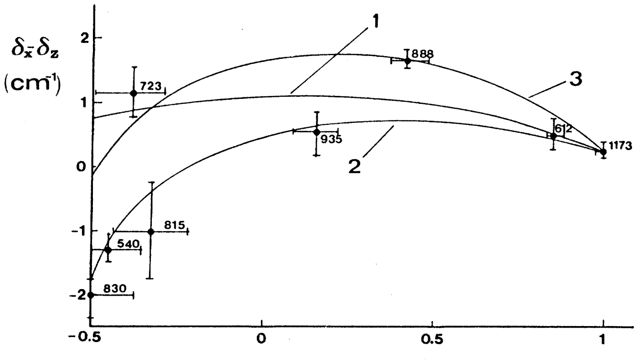

FIG. 5. Rotational contribution to the total halfwidth for in-plane and out-of-plane vibrations as a function of $P_2(\cos\theta)$, calculated by uniaxial ($\lambda = 0$) and biaxial ($\lambda = 0.4$) models: one-uniaxial model; two-biaxial model in-plane deformations; three-biaxial model out-of-plane deformations; circles: experimental data.

As regards PBT, we have selected it in order to study the effects of molecular biaxiality on the rotational contribution to the total ir band shape as a function of the direction of the vibrational transition dipole moment. Its ir spectra are presented in Fig. 4. Table II summarizes the possible assignment of the selected modes and the dichroic ratio $R = I_z(\omega)/I_x(\omega)$. Figure 5 gives the theoretically calculated rotational contribution to the in-plane and out-of-plane deformations for $\lambda = 0.4$ (biaxial model) and $\lambda = 0$ (uniaxial model), as a function of $P_2(\cos\theta)$ $[P_2(\cos\theta) = (R-1)/\langle P_2 \rangle (R+2)]$, i.e., the direction of the vibrational transition dipole moment. For strongly polarized modes ($\theta \cong 0°$) the effect of biaxiality is negligible, and the results obtained for PMT are a confirmation of this. For perpendicularly polarized modes, on the contrary, the biaxial contribution increases with increasing θ being more pronounced for out-of-plane vibrations. The coincidence between experimental and theoretical results is only semiquantitative: Two main sources of error can justify this discrepancy. The first one comes from the FWHM measurements. Only three bands are good Lorentzians—the 888, 612, 540 cm^{-1} ones. The others are characterized by complex contours, for which analytical curve-resolving methods are employed. The second and more important error arises from the nature of the vibrations of the mesomorphic molecules. Since PBT has 126 normal modes (all ir active) many of them—especially the lowest-frequency ones—are strongly coupled in the potential-energy distribution and usually big molecular fragments take part in the vibrational motion. For molecules as complex as PBT, the group frequency approach used by us for the assignment is too simple; a more correct attribution needs a normal coordinate analysis which is exceedingly difficult in this case. The results shown in Fig. 5 are important also from a spectroscopic point of view, since they allow for the first time to connect, and even to predict, the rotational contribution to the total band shape of different vibrations.

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