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Coupling of Inter- and Intramolecular Vibrations in the p-Xylene Crystal

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The temperature effect on the low-frequency Raman bands of the four deuterated p-xylene crystals indicates that the coupling between the intramolecular torsional vibration of the CD_3 group and the intermolecular rotational vibrations takes place below about −80 °C.

The low-frequency Raman bands of the $[^1H_{10}]$- and $[^2H_{10}]p$-xylene crystals were observed at 0 °C and the bands were assigned to the intermolecular rotational vibrations based on the isotopic effect on the vibrational frequency in the previous work.$^{1)}$ The bands were classified into symmetry species through the observation of the polarization behavior of the individual band. The structure of the low-frequency Raman spectrum of the $[^1H_{10}]p$-xylene (p-xylene-d_0) crystal observed at −196 °C is essentially the same as that observed at 0 °C, while the structure of the spectrum of the $[^2H_{10}]p$-xylene (p-xylene-d_{10}) crystal observed at −196 °C is very complex and quite different from the structure observed at 0 °C. In order to clarify the complex spectral structure observed for the p-xylene-d_{10} crystal at −196 °C, the low-frequency Raman spectra of the p-xylene-d_4 (the four hydrogen atoms bonded to the benzene ring are all deuterated) and p-xylene-d_6 crystals (the six hydrogen atoms of the CH_3 groups are all deuterated) are studied through the measurement of the polarization behavior and temperature effect on the frequency of the Raman bands.

Experimental

Material. p-Xylene-d_0, -d_4, -d_6, and -d_{10} were obtained from Tokyo Kasei Chemical Co., Isotec Inc., Aldrich Chemical Co., and MSD Isotopes, respectively, and the samples were purified by repeated distillations under reduced pressure.

Optical Measurement. The polarized Raman spectrum was observed at 0 °C in single crystal. The single crystal was grown in a capillary tube of about 3 mm in diameter with a JEOL Model RS-VTC 41 cryostat. The direction of the crystal growth, which is nearly along the capillary tube, was found to be the crystal b axis$^{1)}$ and another crystal axis was found by rotating the capillary tube under the polarized light. The third axis was taken to be perpendicular to both the axes described above. The direction of the capillary tube and the other two axes are referred to as u, v, and w axes, respectively, in the same manner as taken in the previous work.$^{1)}$

The polarized Raman spectrum was observed with the right angle scattering method. The sample crystal was held in such a way that the polarization direction of the laser beam and the optical axis of the spectrophotometer were parallel to the u and w axes, respectively, and a pair of the polarized uu and uv spectra was observed. Then the polarization direction of the laser beam was turned to be parallel to the w axis using the half-wave plate, and a pair of the polarized uw and vw spectra was observed. Next the sample crystal was turned for 90 ° around the u axis so that the optical axis of the spectrophotometer was parallel to the v axis. This orientation of the sample and the two polarization directions of the laser beam gave two pairs of the polarized uu and uw spectra and of the uv and vw spectra. Comparing the relative intensity of the bands observed in the four pairs of the polarized spectra, the normalized polarized uu, uv, uw, and vw spectra were obtained.

The temperature effect on the Raman frequency was observed between 0 °C and −135 °C with the JEOL cryostat mentioned above. The spectra at −196 and −268.8 °C were observed by immersing the sample in liquid nitrogen and helium, respectively. The sample was excited with the 476.5, 496.8, and 514.5 nm lines from an Ar^+ ion laser of Spectra Physics 168B.

Results and Discussion

The crystal structure of p-xylene belongs to the space group C_{2h}^2 with two molecules in the unit cell$^{2)}$ and the six rotational intermolecular vibrations are distributed among the a_g and b_g symmetry species as $3a_g+3b_g$. The x axis is taken perpendicular to the molecular plane and the y and z axes in the plane with the z axis passing through the methyl groups. The Raman spectra of p-xylene-d_0, -d_4, -d_6, and -d_{10} observed at various temperatures are shown in Figs. 1 and 2.

The Raman spectra observed at 0 °C consist of three bands, which are referred to as bands I, II, and III. The main framework of the spectral structures of the p-xylene-d_0 and -d_4 crystals is unchanged with decreasing temperature except for the following points. (1) A broad band is clearly observed at about 140 cm^{-1} below about −100 °C. (2) A weak band and a shoulder band are resolved at −196 °C in the lower and the higher wavenumber sides of the bands I and III, respectively. These bands are referred to as bands I′ and III′. (3) A shoulder band is resolved in the higher wavenumber side of the band II in the p-xylene-d_4 crystal, which is referred to as band II′. On the other hand, the behavior of the change of the spectral structures of the p-xylene-d_6 and -d_{10} crystals due to decreasing temperature is much complex. The five bands are clearly resolved in the spectra observed below about −100 °C.

The frequencies observed at 0 and −196 °C for the four deuterated p-xylene crystals are given in Table 1, and the observed temperature effects on the vibrational frequencies for the p-xylene-d_0 and -d_{10} crystals are shown in Fig. 3. The temperature effects on the vibrational frequencies for the p-xylene-d_4 and -d_6 crystals are essentially the same as the effects for the p-xylene-d_0 and -d_{10} crystals, respectively. In the p-xylene-d_0 and -d_4 crystals the frequencies increase monotonically with decreasing temperature, while in the p-xylene-d_6 and -d_{10} crystals the frequency-temperature curves for the bands II and III become discontinuous at about −80 °C, although the frequency of the band I increases monotonically with decreasing temperature.

In order to clarify the complex behavior of the change of the spectral structure observed in the p-xylene-d_6 and -d_{10} crystals, the assignment given for the rotational intermolecular vibrations in the previous work[1] was reinvestigated. Since the frequency of the rotational

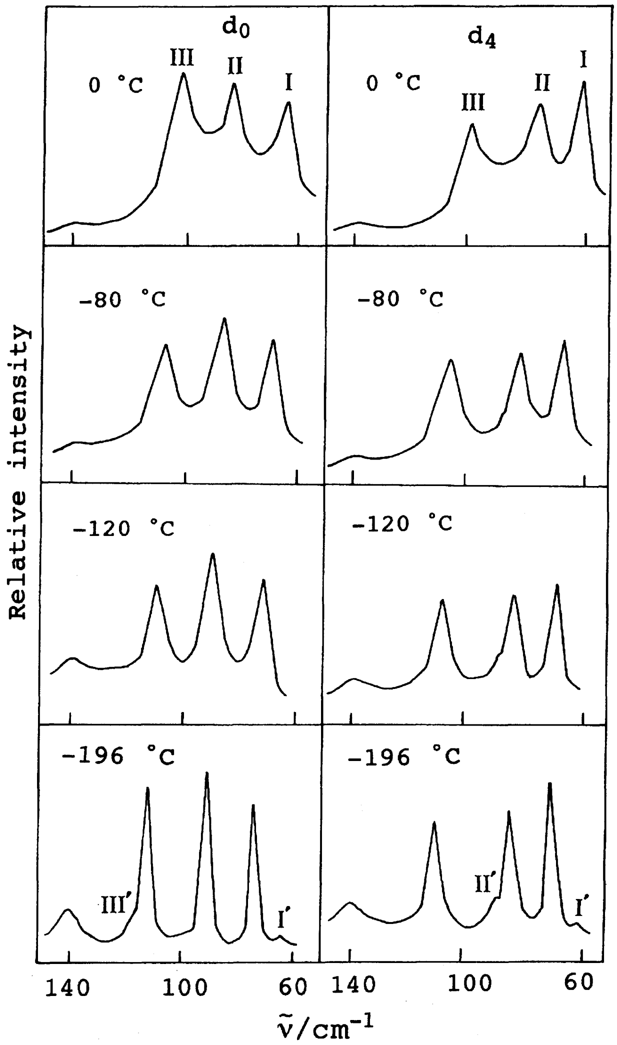

Fig. 1. The low-frequency Raman spectra of the p-xylene-d_0 and -d_4 crystals observed at various temperatures.

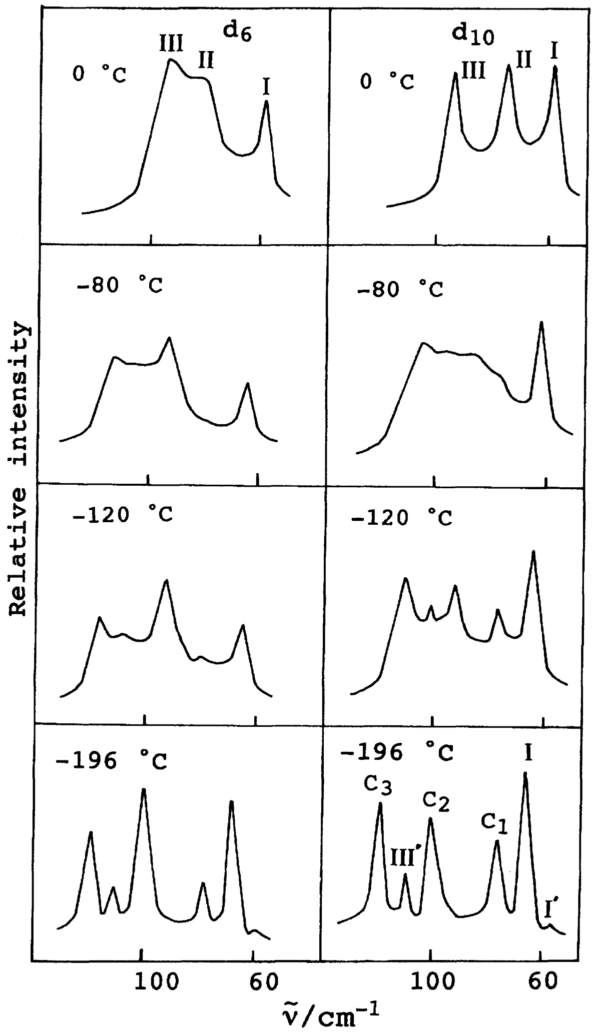

Fig. 2. The low-frequency Raman spectra of the p-xylene-d_6 and -d_{10} crystals observed at various temperatures.

Table 1. Raman Frequencies of the Rotational Lattice Vibrations of Four Deuterated *p*-Xylenes

Temp °C	Band	Xylene-d_0 $\tilde{\nu}/\mathrm{cm}^{-1}$	Xylene-d_4 $\tilde{\nu}/\mathrm{cm}^{-1}$	Xylene-d_6 $\tilde{\nu}/\mathrm{cm}^{-1}$	Xylene-d_{10} $\tilde{\nu}/\mathrm{cm}^{-1}$	Assign
0	I	63	61	58	57	$R_x(b_g)$
	II	83	76	81	76	$R_z(a_g)$
	II′		82			$R_y(b_g)$
	III	102	100	92	94	$R_y(a_g)$
−196	I′	63(64)[a)]	62	58	57(57)	$R_x(a_g)$
	I	72(76)	70	67	65(68)	$R_x(b_g)$
	C1			78	75(77)	Coupling(a_g)[b)]
	II	90(92)	83			$R_z(a_g)$
	II′	(94)	89		(87)	$R_y(b_g)$
	C2			99	98(100)	Coupling(a_g)[b)]
	III	112(117)	111			$R_y(a_g)$
	III′	118(125)	107	111	107(111)	$R_z(b_g)$
	C3			116	116(123)	Coupling(a_g)[b)]
		135(142)	135			$\tau_{\mathrm{C-CH3}}$[c)]
		140(147)	140			$\tau_{\mathrm{C-CH3}}$[c)]

a) Values in parentheses are observed at −268.8 °C. b) Coupling of the $R_z(a_g)$ and $R_y(a_g)$ intermoleccular rotational vibrations with the intramolecular torsional vibration of the CD_3 group belonging to a_g species. c) Intramolecular torsional vibration of the CH_3 group.

intermolecular vibration is inversely proportional to the square root of the moment of inertia, the square root of the relative moments of inertia about the *x*, *y*, and *z* axes for the four deuterated *p*-xylene crystals was calculated and the results are given in Table 2. The Raman tensors calculated based on the oriented gas model approximation are given in Table 3.[1)] The table indicates that (1) the rotational intermolecular vibrations about the *z* axis belonging to the symmetry species a_g and b_g are observed in the polarized aa and c′c′ spectra and in the ab and bc′ spectra, respectively, (2) the rotational intermolecular vibration about the *y* axis belonging to the symmetry species a_g is strongly observed in the bb spectrum, while the rotational intermolecular vibrations about the *y* axis belonging to the symmetry species b_g hardly observed in any polarized spectrum, and (3) the rotational intermolecular vibrations about the *x* axis belonging to the symmetry species a_g and b_g are observed in the aa and c′c′ spectra and in the ab and bc′ spectra, respectively.

The polarized Raman spectra of the *p*-xylene-d_4 crystal observed at 0 °C is shown in Fig. 4. This figure shows the following facts. The *uu* spectrum mainly consists of the bb polarized spectrum because the *u* axis is nearly along the crystal *b* axis, and the *uv* and *uw* spectra mainly consist of the polarized ab and bc′ spectra, respectively, (or vice versa).[1)] Since the *v* and *w* axes do not coincide exactly with the crystal *a* and *c*′ axis, respectively, (or vice versa), the *vw* spectrum contains the polarized aa, c′c′, and ac′ spectra.

The relative values of the moment of inertia and the observed polarization behavior of the bands lead to the

Table 3. Squares of Relative Values of the Elements of the Raman Tensor for *p*-Xylene Crystal

Crystal		Molecule		
		$b_{1g}(R_z)$	$b_{2g}(R_y)$	$b_{3g}(R_x)$
a_g	$(A_{aa})^2$	0.46	0.27	0.53
	$(A_{bb})^2$	0.00	0.99	0.00
	$(A_{c'c'})^2$	0.45	0.22	0.54
	$(A_{ac'})^2$	0.00	0.24	0.00
b_g	$(A_{ab})^2$	0.25	0.00	0.22
	$(A_{bc'})^2$	0.28	0.00	0.24

Table 2. Relative Values of the Moments of Inertia of Four Deuterated *p*-Xylenes

Axis	I_{d_0} 10^{-45} kg m^2	$(I_{d_4}/I_{d_0})^{1/2}$	$(I_{d_6}/I_{d_0})^{1/2}$	$(I_{d_{10}}/I_{d_0})^{1/2}$
x	7.21	1.026	1.076	1.099
y	5.80	1.008	1.093	1.101
z	1.49	1.090	1.027	1.114

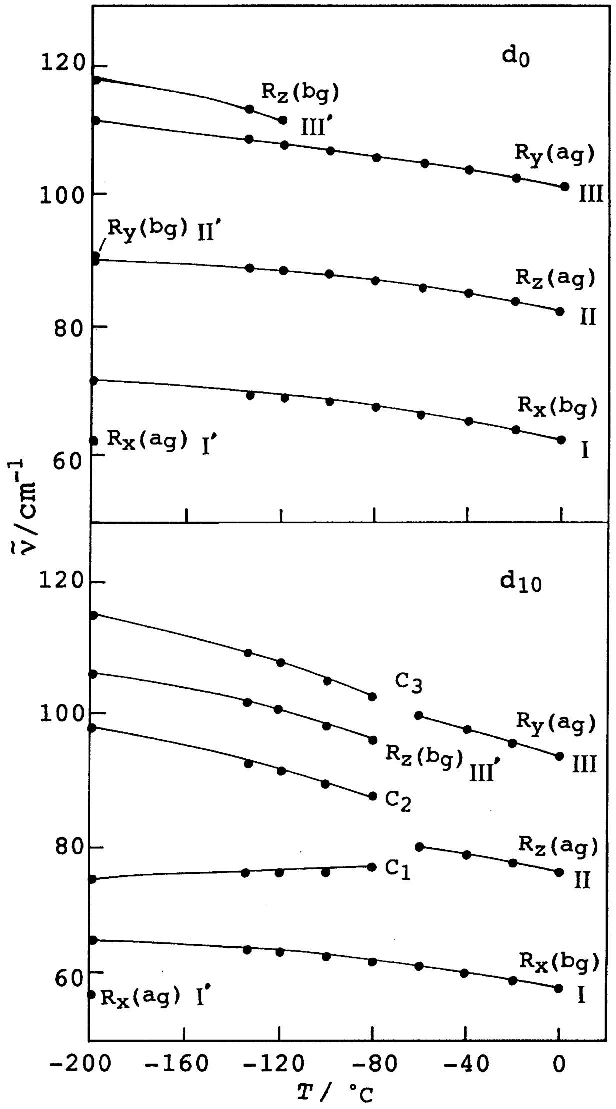

Fig. 3. Temperature effect on the frequencies of the Raman bands of the p-xylene-d_0 and -d_{10} crystals.

following conclusion. The band I observed strongly in the *uv* and *uw* spectra in the lowest wavenumber region can be assigned to the rotational intermolecular vibration about the x axis belonging to the symmetry species b_g, which will be referred to as $R_x(b_g)$ vibration. The band II observed strongly in the *vw* spectrum can be assigned to the rotational intermolecular vibration about the z axis belonging to the symmetry species a_g, ($R_z(a_g)$vibration). The band III observed strongly in the *uu* spectrum can be assigned to the rotational intermolecular vibrations about the y axis of the symmetry species a_g, ($R_y(a_g)$vibration). The band II′ observed weakly in the *uv* and *uw* spectra could be assigned to the rotational intermolecular vibrations about the y axis belonging to the symmetry species b_g, ($R_y(b_g)$vibration), which could be observed weakly through perturbations.

The bands I′ and III′ observed clearly at −196 °C can be assigned to the rotational intermolecular vibration about the x axis belonging to the symmetry species a_g, ($R_x(a_g)$vibration) and the vibration about the z axis belonging to the symmetry species b_g, ($R_z(b_g)$vibration), respectively. The frequencies of the bands I, I′, II, III, and III′ observed in the four deuterated p-xylene crystals are all well explained by the isotopic effect on the frequency of the rotational intermolecular vibrations. The reason why the band II′ was not resolved in the polarized Raman spectra of the p-xylene-d_0 and -d_{10} crystals in the pervious work[1)] is due to fact that the frequencies expected from the isotopic effect on the frequency of the band II′ in the p-xylene-d_4 crystal are 83 and 75 cm^{-1} in the p-xylene-d_0 and -d_{10} crystals, respectively, and these frequencies are almost equal to the frequencies of the strong band II.

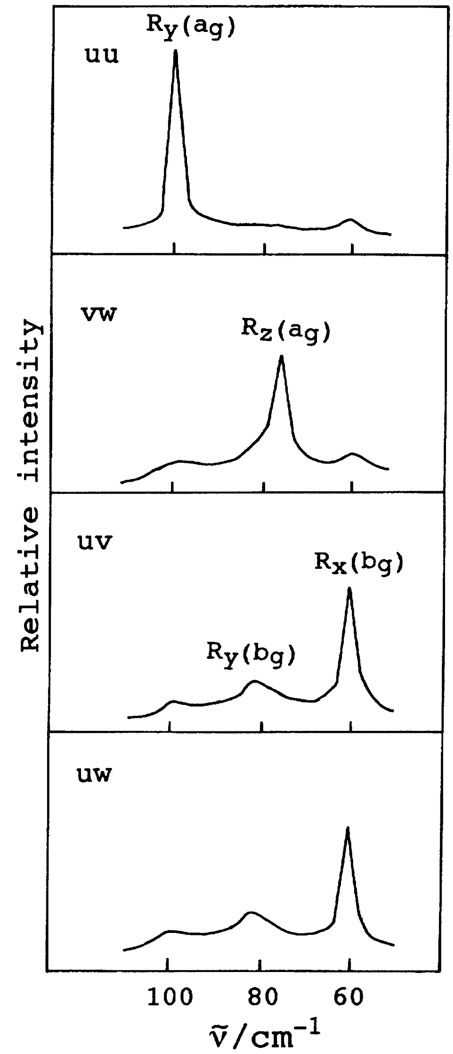

Fig. 4. The polarized low-frequency Raman spectra of the p-xylene-d_4 crystal observed at 0 °C.

The band, which was clearly detected around 140 cm^{-1} below about −100 °C and was observed very weakly as the very broad band above −100 °C in the p-xylene-d_0 and -d_4 crystals, may be assigned to the CH_3 torsional vibration according to the following reasons. The Raman active intramolecular vibration having the lowest frequency, except for the torsional vibration of the methyl group, is the methyl wagging vibration, whose frequency is 312 and 289 cm^{-1} for CH_3 and CD_3 groups, respectively.[1)] Breen et al.[3)] showed in the supersonic molecular jet experiment, where the *p*-xylene molecule is free from the molecular interaction, that (1) the potential barrier to internal rotation of the CH_3 group of *p*-xylene is small and the CH_3 rotor may be nearly free, and (2) the height of the CH_3 rotor potential barrier increases in the order of ortho>meta>para in the *o*-, *m*-, and *p*-xylenes due to the steric hinderance between two CH_3 rotors. In crystal the *p*-xylene molecule suffers from strong intermolecular interaction and thus the CH_3 rotor potential barrier may become quite higher in crystal than in supersonic molecular jet. If the frequency of the intramolecular torsional vibration of the CH_3 group in the *p*-xylene-d_0 and -d_4 crystals is taken to be about 140 cm^{-1}, the intramolecular torsional vibration of the CD_3 group in the *p*-xylene-d_6 and -d_{10} crystals is expected to be observed around 100 cm^{-1} from the relative value of the moments of inertia of the CH_3 and CD_3 groups. The base part of the strong band III in the *p*-xylene-d_6 and -d_{10} crystals spreads over around 100 cm^{-1} and thus the intramolecular torsional vibration of the CD_3 group in the *p*-xylene-d_6 and -d_{10} crystals could not be detected. The symmetry species of the Raman active intramolecular torsional vibration of the methyl group is b_{1g} in the molecule (D_{2h} point group) and a_g and b_g in the crystal (C_{2h}^2 space group with two molecules in the unit cell). The temperature effect on the frequencies of the strong bands II and III in the *p*-xylene-d_6 and -d_{10}, which are assigned to the $R_z(a_g)$ and $R_y(a_g)$ vibrations, respectively, shows monotonical change with decreasing temperature up to about −60 °C as can be seen in Fig. 3. While the spectral structure below about −80 °C becomes quite different from the structure observed above −60 °C.

These observations may lead to the following interpretation. The increase of the frequency of the intermolecular vibration due to decreasing temperature is expected to be quite larger than the increase of the frequency of the intramolecular vibration of the methyl group. Thus, the frequency of the rotational intermolecular vibrations approaches to the frequency of the intramolecular torsional vibrations of the CD_3 group with decreasing temperature, and as the results the coupling of the $R_z(a_g)$ and $R_y(a_g)$ intermolecular rotational vibrations with the intramolecular torsional vibrations of the CD_3 groups of a_g species may take place below about −80 °C.

The bands observed below −80 °C are referred to as bands C_1, C_2, and C_3, respectively, (see Fig. 2). As can be seen in Fig. 3, the frequency of the band C_1 decreases with decreasing temperature contrary to the general temperature effect on the frequency of the intermolecular vibration. This fact may support the increase of the coupling between the inter- and intramolecular vibrations with decreasing temperature. Thus the bands C_1, C_2, and C_3 are assigned to the bands resulting from the coupling of the $R_z(a_g)$ and $R_y(a_g)$ intermolecular rotational vibrations with the intramolecular a_g torsional vibration of CD_3 group.

In the *p*-xylene-d_0 and -d_4 crystals the frequency of the intramolecular torsional vibration of the CH_3 group is observed around 140 cm^{-1}, which is quite far from the frequency of the intermolecular rotational vibrations, and therefore, no coupling between the inter- and intramolecular vibrations takes place in the *p*-xylene-d_0 and -d_4 crystals. The quite monotonical temperature effect on the frequencies of the intermolecular rotational vibrations observed in the *p*-xylene-d_0 and -d_4 crystals is thus well understood. The coupling between the inter- and intramolecular vibrations of the symmetry species b_g was not detected in this work. The assignment given for the observed Raman bands are shown in Fig. 3 and Table 1.

It is concluded that (1) the intramolecular CD_3 torsional vibration interacts with the intermolecular rotational vibrations in the *p*-xylene-d_6 and -d_{10} crystals, and (2) the frequency of the intramolecular methyl torsional vibration and the potential barrier for the rotation of the methyl group are quite higher in crystal compared with those in vapor.[3)]

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References

1) S. Nakamura, Y. Sonoda, S. Tominari, Y. Nibu, H. Shimada, and R. Shimada, *Bull. Chem. Soc. Jpn.*, **65**, 280 (1992).

2) H. van Koningsveld and A. J. van den Berg, *Acta Crystallogr.*, **42**, 491 (1986).

3) P. J. Breen, J. A. Warren, and E. R. Bernstein, *J. Chem. Phys.*, **87**, 1917 (1987).