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Rotational Lattice Vibrations of Tetramethyl- and Tetramethyl-d_{12}-pyrazine Crystals

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The low-frequency Raman bands of the tetramethyl- and tetramethyl-d_{12}-pyrazine crystals and their hydrated crystals were studied at various temperatures between 4.2 and 298 K. The isotopic factors and the temperature effects on the frequencies of the Raman bands indicate that the low-frequency Raman bands observed in the crystal are to be ascribed to the rotational lattice vibrations. A smooth curve of the plot of the Raman frequency versus temperature suggests that no apparent temperature-induced phase transition takes place in the tetramethylpyrazine crystal. Classification of the rotational lattice vibrations into symmetry species was made based on the polarization behavior of the Raman bands. It was also observed that tetramethylpyrazine hydrates quite easily with a trace of moisture in the air.

The low-frequency Raman bands due to the lattice vibrations of the aromatic compounds in crystals have been studied by many workers.[1-6] Ito et al. observed the low-frequency Raman bands of the benzene and pyrazine crystals and calculated the mean square amplitudes of the rotational motions of the molecules in the crystals.[3,4] Suzuki et al.[5] and Bonadeo et al.[6] observed the polarized Raman spectra of the naphthalene and benzene crystals, respectively, and classified the Raman bands arising from the rotational lattice vibrations into symmetry species. Recently, Calvé et al. studied the temperature effects on the frequencies of the lattice vibrations of the 4-methylpyridine crystal and discussed about the phase transition.[7] They also observed the temperature dependence of the torsional vibration of the methyl group and showed that the rotation of the methyl group is free in the crystal phases above 100 K, while the rotation is hindered in the phase below 100 K.

Braam et al. determined the crystal structure of tetramethylpyrazine and showed that four molecules are involved in the unit cell.[8] Thus, based on the knowledge of the crystal structure, the lattice vibrations of the tetramethylpyrazine crystal can easily be distinguished from the torsional vibrations of the methyl group, which will be observed in the same low-frequency region, by measuring the temperature effects and isotopic factors of the frequencies of the Raman bands.

The intramolecular vibrations of tetramethylpyrazine were studied through the analyses of the polarized Raman and infrared spectra and the assignments of the normal vibrations were made based on the oriented gas model approximation.[9] It was known that when the tetramethylpyrazine crystal is grown in aqueous solution, one obtains the trihydrated crystal.[10] It is interesting to investigate whether the oriented gas model approximation can be applied to the assignments of the intermolecular vibrations or not, and to study how the lattice vibrations are affected by hydration.

In this paper the lattice vibrations of the tetramethyl- and tetramethyl-d_{12}-pyrazine crystals are discussed based on the isotopic factors and temperature effects on the Raman frequencies and the polarization behavior of the Raman bands, and then the effects of hydration on the lattice vibrations are studied.

Experimental

Material. Tetramethyl-d_{12}-pyrazine (TMP-d_{12}) was synthesized by the exchange reaction of tetramethylpyrazine (TMP-d_0) obtained from Aldrich Chemical Co. with D_2O. The isotopic purity of the product was confirmed by the nuclear magnetic resonance measurement. The samples were purified by zone refining of about 100 passages. The hydrated crystals were prepared by adjusting the amount of moisture adding to the TMP-d_0 and TMP-d_{12} crystals.

Optical Measurements. The sample was sealed in a glass tube of about 3 mm in diameter and was excited with the 514.5 nm line from an Ar^+ ion laser. The Raman spectra were observed with a JEOL 400 T Laser Raman Spectrophotometer at various temperatures between 298 and 155 K. The temperature was regulated with an automatic temperature controller of JEOL Model RS-VTC 41. The Raman scattering and excitation light beams were at right angles. The Raman spectra were also observed at 77 and 4.2 K. The preparation of the single crystal and the method of the measurement of the polarized Raman spectrum were exactly the same as those described previously.[9]

Results and Discussion

Tetramethylpyrazine crystallizes in the orthorhombic space group D_{2h}^{15} with four molecules in the unit cell, each molecules being located at the site of symmetry C_i.[8] There are twenty one optical branches of the lattice vibrations, of which nine are the vibrations of the translational modes and twelve are of the rotational modes. According to the group theory the six lattice vibrations of the nine translational modes are infrared active and the three of them are

inactive both in the infrared and Raman spectra, while the twelve lattice vibrations of the rotational modes are all Raman active. The twelve rotational lattice vibrations are classified into four symmetry species A_g, B_{1g}, B_{2g}, and B_{3g}, and three vibrations belong to each symmetry species. Each mode of the rotational lattice vibrations can be represented by a linear combination of the in-phase and out-of-phase rotational oscillations of the four molecules in the unit cell about the u, v, and w axes of the molecule. The u axis is taken perpendicular to the molecular plane and the v and w axes are in the plane with the w axis passing through the nitrogen atoms.

The Raman spectra of the TMP-d_0 and TMP-d_{12} crystals in the low-frequency region observed at 4.2 K are shown in Fig. 1. The twelve Raman bands were clearly observed and their frequencies are given in Fig. 1 and Table 1. If the low-frequency Raman bands are ascribable to the rotational lattice vibrations, the isotopic factor of the corresponding bands of the TMP-d_0 and TMP-d_{12} crystals is given by $\tilde{\nu}(d_0)/\tilde{\nu}(d_{12})=\{I_r(d_{12})/I_r(d_0)\}^{1/2}$, where $\tilde{\nu}$ is the Raman frequency and I_r the moment of inertia of the molecule about the axis r (=u, v, or w). The values of the moments of inertia of the TMP-d_0 and TMP-d_{12} molecules were calculated

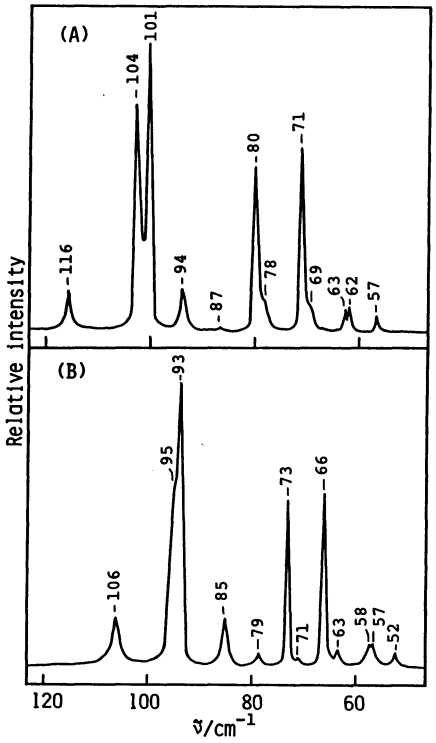

Fig. 1. The Raman spectra of the tetramethyl-(A) and tetramethyl-d_{12}-pyrazine(B) crystals in the low-frequency region observed at 4.2 K.

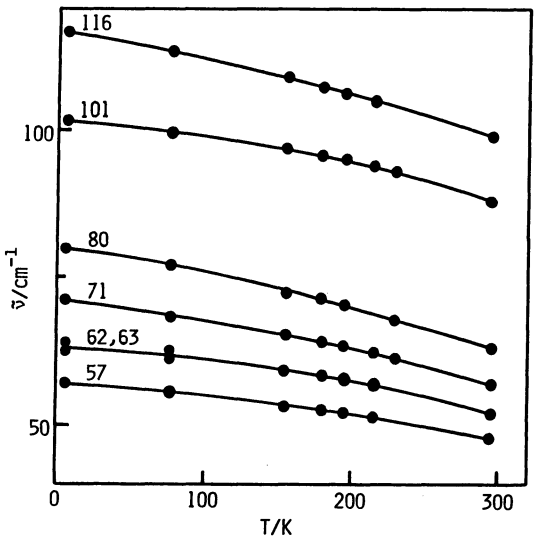

Fig. 2. Temperature effects on the frequencies of the Raman bands of the tetramethylpyrazine crystal.

Table 1. Raman Frequencies of Rotational Lattice Vibrations of Tetramethyl-d_0- and Tetramethyl-d_{12}-pyrazine Crystals

4.2 K				77 K				298 K				
TMP-d_0		TMP-d_{12}		TMP-d_0		TMP-d_{12}		TMP-d_0		TMP-d_{12}		Assign
$\tilde{\nu}$/cm^{-1}	I	$\tilde{\nu}$/cm^{-1}	I	$\tilde{\nu}$/cm^{-1}	I	$\tilde{\nu}$/cm^{-1}	I	$\tilde{\nu}$/cm^{-1}	Pol	$\tilde{\nu}$/cm^{-1}	Pol	
57	w	52	w	55	w	50	w	48	cc, aa	43	cc, aa	Ag
62	w	57	w	61	w							
						56	w	52	bc	47	bc	B_{3g}
63	w	58	w	62	w							
69	sh	63	sh	66	sh	60	sh	55	ac	50	ac	B_{2g}
71	s	66	s	68	s	63	s	57	aa, bb, cc	52	aa, bb, cc	Ag
78	sh	71	sh									
80	s	73	s	77	s	71	m	63	bc	58	bc	B_{3g}
87	vw	79	w					66	ab	60	ab	B_{1g}
94	w	85	w	92	w	83	w	82	ab	74	ab	B_{1g}
101	vs	93	vs	99	vs	91	vs	88	cc, aa, bb	80	cc, aa, bb	Ag
104	vs	95	vs	101	vs	92	vs	91	ac	83	ac	B_{2g}
116	w	106	w	113	w	104	w	99	bc	91	bc	B_{3g}

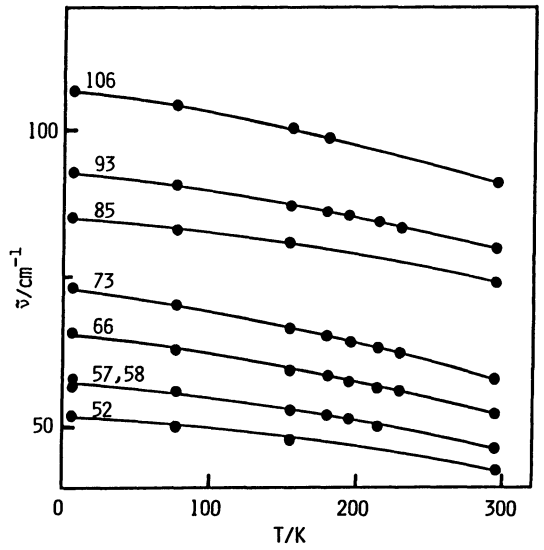

Fig. 3. Temperature effects on the frequencies of the Raman bands of the tetramethyl-d_{12}-pyrazine crystal.

using the molecular structure give by Braam.[8] The values are ranged in a order $I_u > I_w > I_v$. The isotopic factors were calculated to be 1.09, 1.09, and 1.10 at 100 and 300 K for the rotational lattice vibrations about the u, v, and w axes, respectively. The observed Raman frequencies for the TMP-d_0 and TMP-d_{12} crystals at 4.2, 77, and 298 K are given in Table 1 and the temperature effects on the frequencies of the Raman bands are shown in Figs. 2 and 3 for TMP-d_0 and TMP-d_{12}, respectively. The spectral structures observed at various temperatures are exactly the same as that observed at 4.2 K except for the width of the bands, which increases with increasing temperature. It is readily seen from Table 1 and Figs. 2 and 3 that (1) the observed isotopic factors are about 1.1 for all the corresponding Raman bands, (2) the frequencies increase with decreasing temperature, and (3) the observed Raman frequencies lie on a smooth curve against temperature within the experimental errors. These facts suggest that (1) the observed low-frequency Raman bands can be ascribed to the rotational lattice vibrations in the crystals and (2) no apparent phase transition takes place between 298 and 4.2 K in the TMP crystal. This is consistent with the fact that the crystal structure of TMP belongs to the space group D_{2h}^{15} at 300 and 100 K.[8] Calvé et al. observed the Raman bands arising from the torsional vibration of the methyl group in the 4-methylpyridine crystal at various temperatures between 4.2 and 100 K and pointed out that the isotopic factor of the torsional vibration of the methyl group is about 1.4 and the frequency increases with increasing temperature, unlike the behavior of the rotational lattice vibrations.[7] The Raman bands giving such high value of the isotopic factor could not be observed in our experiment.

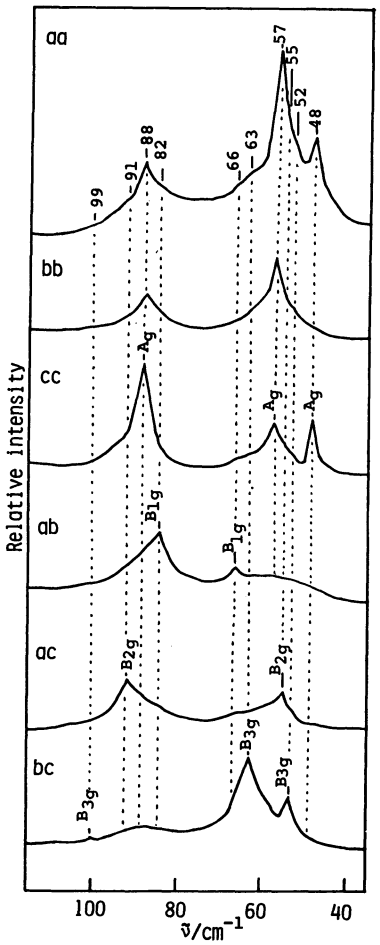

Fig. 4. The polarized Raman spectra of the tetramethylpyrazine crystal in the low-frequency region observed at 298 K.

The polarized Raman spectra of the TMP-d_0 and TMP-d_{12} crystals observed at 298 K are given in Figs. 4 and 5, respectively. Notations of the spectra such as aa and bb are exactly the same as those given in the previous paper reported on the intramolecular vibrations of TMP-d_0.[9] The observed polarization behavior of the Raman bands arising from the rotational lattice vibrations of the TMP-d_0 crystal is the same as that of the TMP-d_{12} crystal. The calculated squared values of the elements of the Raman (derived polarizability) tensor based on the oriented gas model for the TMP crystal are given in Table 2.[9] According to Table 2, the lattice vibrations belonging to the symmetry species A_g will be observed in the aa, bb, and cc spectra and those belonging to the B_{1g}, B_{2g}, and B_{3g} species in the ab, ac, and bc spectra, respectively. Figures 4 and 5 show that the Raman bands having frequencies of 52(47), 63(58), and 99(91) cm^{-1} are clearly observed in the bc spectrum, those of 55(50) and 91(83) cm^{-1} are in the ac spectrum, those of 66(60) and 82(74) cm^{-1} are in the ab spectrum, and those of 48(43), 57(52), and 88(80) cm^{-1} are in the aa, bb, and cc spectra, where the first numbers refer to

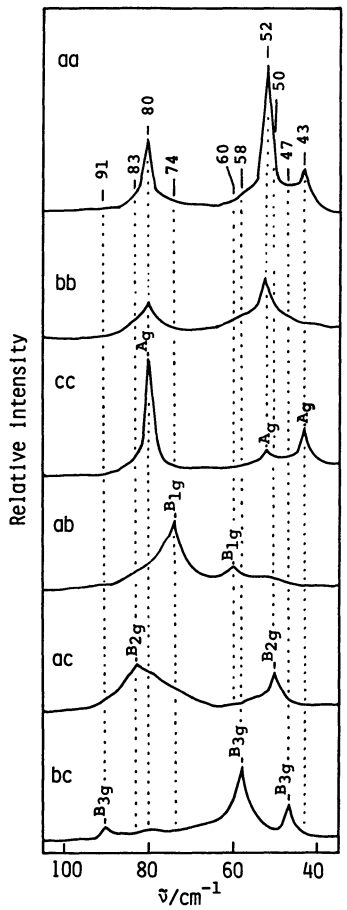

Fig. 5. The polarized Raman spectra of the tetramethyl-d_{12}-pyrazine crystal in the low-frequency region observed at 298 K.

Table 2. Squared Values of Elements of Raman Tensor for Tetramethylpyrazine

Crystal		Molecule		
		$b_{1g}(R_w)$	$b_{2g}(R_v)$	$b_{3g}(R_u)$
A_g	$(A_{aa})^2$	0.19	0.76	0.10
	$(A_{bb})^2$	0.08	0.06	0.91
	$(A_{cc})^2$	0.53	0.39	0.41
B_{1g}	$(A_{ab})^2$	0.40	0.15	0.05
B_{2g}	$(A_{ac})^2$	0.10	0.01	0.24
B_{3g}	$(A_{bc})^2$	0.10	0.23	0.00

the frequencies for the TMP-d_0 crystal and the numbers in parentheses to the TMP-d_{12} crystal. These observed facts indicate that the 52(47), 63(58), and 99(91) cm^{-1} bands are to be assigned to the B_{3g} lattice vibrations, the 55(50), 91(83) cm^{-1} bands to the B_{2g} vibrations, the 66(60) and 82(74) cm^{-1} bands to the B_{1g} vibrations, and the 48(43), 57(52), and 88(80) cm^{-1} bands to the A_g vibrations. These assignments are given in Table 1 and Figs. 4 and 5. Table 2 also indicates that for the A_g rotational lattice vibrations the relative intensities of the Raman bands arising from the rotational oscillations of the molecule about

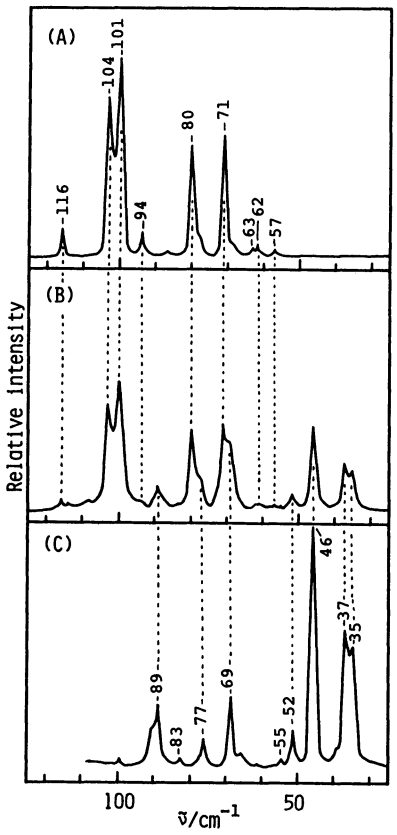

Fig. 6. The Raman spectra of the unhydrated(A), partially hydrated(B), and completely hydrated(C) tetramethylpyrazine crystals.

Table 3. Root Mean Square Amplitudes (degree) of Rotational Lattice Vibrations of Tetramethyl-d_0- and Tetramethyl-d_{12}-pyrazine Crystals about v Axis

	4.2 K	77 K	298 K
TMP-d_0	1.5	1.8	3.6
TMP-d_{12}	1.5	1.8	3.6

the u, v, and w axes are strongest in the bb, aa, and cc spectra, respectively. However, the observed relative intensities are not consistent with the expectation, although the observed intensities of the bands for the intramolecular vibrations are quantitatively consistent with the expected values.[9] This phenomenon may be caused by mode mixing among the rotational lattice vibrations about the u, v, and w axes and also by coupling of the rotational lattice vibrations with the torsional vibrations of the methyl groups. This means that the oriented gas model is rather a poor approximation for the determination of modes of the rotational lattice vibrations.

The moment of inertia of TMP about the v axis is smaller than those about the u and w axes, and linear combinations of the in-phase and out-of-phase rotational oscillations of four molecules about the v axis in the crystal give four rotational lattice

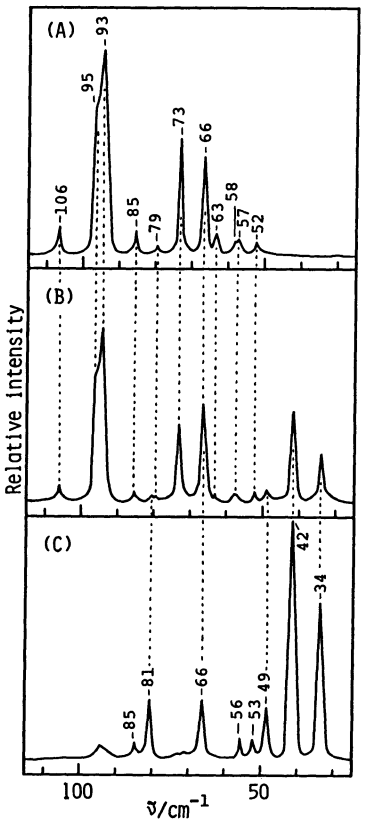

Fig. 7. The Raman spectra of the unhydrated(A), partially hydrated(B), and completely hydrated(C) tetramethyl-d_{12}-pyrazine crystals.

vibrations belonging to symmetry species A_g, B_{1g}, B_{2g}, and B_{3g}. Thus, the Raman bands observed at 82, 88, 91, and 99 cm^{-1} in the TMP crystal could be assigned to the lattice vibrations arising mainly from the oscillation about the v axis, because these bands are located in the higher wavenumber region than the other bands and showed the B_{1g}, A_g, B_{2g}, and B_{3g} polarization behavior, respectively, although these vibrations might couple with the rotational motions about the u and w axes as described above. The mean square amplitudes of the rotational motions about the v axis of the molecule in the crystal can be calculated. Calculation was made using the equation given by Cruickshank[11] and the results are given in Table 3. The values of the rotational mean square amplitude decrease with decreasing temperature.

It has been known that TMP crystallizes with three molecules of water of crystallization when the crystal is grown in aqueous solution.[10] The Raman spectra of the hydrated TMP-d_0 and TMP-d_{12} crystals in the low-frequency region are shown in Figs. 6 and 7, respectively. The spectra shown in (A), (B), and (C) of the figures are for the unhydrated, partially hydrated, and completely hydrated TMP crystals, respectively. The crystal structure of the trihydrated TMP crystal belongs to the monoclinic space group C_{2h}^5 with four molecules in the unit cell and thus, the rotational lattice vibrations are all Raman active. The Raman bands arising from the rotational lattice vibrations of the hydrated crystal were located in the lower wavenumber region of the bands of the unhydrated crystal. This may be due to differences of the mass and potential field of the hydrated TMP from those of the unhydrated TMP in crystals. The Raman bands arising from the lattice vibrations of the hydrated TMP crystal are observed when the unhydrated TMP crystal is exposed in the humid air. Thus, the preparation of the TMP crystal was made in the air free from moisture.

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