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Rotational Lattice Vibrations of [$^1H_4$]- and [$^2H_4$]Pyrazine Crystals

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Synopsis. Low-frequency Raman bands of the [$^1H_4$]- and [$^2H_4$]pyrazine crystals were studied at various temperatures between 4.2 and 300 K. All six rotational lattice vibrations were identified based on the isotopic factor (the ratio of the vibrational frequency of the [$^1H_4$]- and [$^2H_4$]pyrazine crystals) of the individual vibrations. Classification of the rotational lattice vibrations into symmetry species was made through the polarization measurement of the Raman bands in single crystals.

The rotational lattice vibrations of pyrazine crystal were first studied by Ito and Shigeoka.[1] They observed five low-frequency Raman bands due to the rotational lattice vibrations and gave assignments for these bands on the basis of the normal coordinate calculation assuming intermolecular force constants of the pyrazine crystal. Their calculation indicated that the lowest vibrational frequency of the rotational lattice vibration would be about 20 cm^{-1} and they considered that the Raman band due to this lattice vibration could not be observed under their experimental conditions. Pasquier et al. also observed the low-frequency Raman bands of pyrazine crystal and determined the six rotational lattice vibrations based on the normal coordinate calculation,[2] although their assignments given for some bands are different from those given by Ito et al.

In this work the low-frequency Raman bands of the [$^1H_4$]- and [$^2H_4$]pyrazine crystals are reinvestigated and the assignments of the six rotational lattice vibrations are discussed based on the isotopic factor and the polarization behavior of the bands.

Experimental

Material. [$^2H_4$]Pyrazine was synthesized by exchange reaction of [$^1H_4$]pyrazine with D_2O using palladium asbestos as a catalyst.[3] The isotopic purity of the product was confirmed by nuclear magnetic resonance measurement. The samples were purified by repeated vacuum distillations.

Optical Measurements. Low-frequency Raman bands of the pyrazine crystals were observed with a SPEX 1402 doublemonochromator at 4.2 K and with a JEOL 400T laser Raman spectrophotometer at various temperatures between 77 and 300 K. The polarization behavior of the Raman bands was observed in the following way. It is known that the pyrazine crystal grows along the b axis and the crystal is twinned on the cleavage (101) plane.[4] A well-grown single crystal obtained by the Bridgman method was cut along the cleavage plane, which will be referred to as bc′ plane, where the c′ axis is inclined counterclockwise by 57.6° from the c axis in the ac plane, and was sealed in a small rectangular glass cell with the bc′ plane attaching to the cell face. The crystal in the cell was excited with the 514.5 nm beam from an Ar^+ ion laser. The power of the laser beam was adjusted low enough because of high sublimation property of the pyrazine crystal. The propagation direction of the excitation light beam was set to be parallel to the c′ axis or perpendicular to the bc′ plane. In this alignment the a′a′, bb, c′c′, a′b, and bc′ polarized Raman spectra were obtained by the back scattering method, where the a′ axis is taken to be perpendicular to the c′ axis in the ac plane and the first and second letters refer to the polarization directions of the excitation and scattering lights, respectively.

Results and Discussion

Pyrazine crystallizes in the orthorhombic space group P_{mnn} (D_{2h}^{12}) with two molecules in the unit cell.[4] The six rotational lattice vibrations are distributed among the four symmetry species: $1A_g+1B_{3g}+2B_{1g}+2B_{2g}$. The rotational modes of the molecule around the z axis give rise to the A_g and B_{3g} lattice vibrations and the rotational modes around the x and y axes give rise to the B_{1g} and B_{2g} lattice vibrations as shown in Table 1.[1] The x axis is taken to be perpendicular to the molecular plane and the y and z axes in the plane with the z axis passing through the nitrogen atoms.

The Raman spectra of the [$^1H_4$]- and [$^2H_4$]pyrazine crystals in the low-frequency region observed at 4.2 K are shown in Fig. 1. Seven Raman bands were clearly observed and their frequencies are given in Fig. 1 and Table 2. In this table the frequencies and assignments of the rotational lattice vibrations of the [$^1H_4$]pyrazine crystal determined by Ito et al.[1] and Pasquier et al.[2] are also given. The Raman band at 56 cm^{-1} observed by Ito et al. at 4.2 K resolved into two bands at 57 and 58 cm^{-1} and a weak additional Raman band was clearly observed at 116 cm^{-1}. No bands could be observed in the low frequency region around 20 cm^{-1} contrary to the prediction given by Ito et al. The observed Raman bands can be ascribed to the rotational lattice vibrations, if the isotopic factor of the bands ($\tilde{\nu}[^1H_4]/\tilde{\nu}[^2H_4]$) is equal to the value of $\{I_r[^2H_4]/I_r[^1H_4]\}^{1/2}$, where $\tilde{\nu}$ is the Raman frequency and I_r is the moment of inertia of the molecule about the axis r(=x, y, z). Using the values of the moments of inertia of the

Table 1. Raman Active Rotational Lattice Vibrations of Pyrazine Single Crystal

Symmetry species	Raman active polarization	Rotational modes about molecular axes
A_g	aa, bb, cc	R_z
B_{1g}	ab	R_x, R_y
B_{2g}	ac	R_x, R_y
B_{3g}	bc	R_z

Table 2. Rotational Lattice Vibrations of [$^1H_4$]- and [$^2H_4$]Pyrazine Crystals

[$^1H_4$]Pyrazine						[$^2H_4$]Pyrazine			Isotopic factors		Assignments
Ito[a]		Pasquier[b]	This work			This work			$\tilde{\nu}[^1H_4]/\tilde{\nu}[^2H_4]$		
$\tilde{\nu}$/cm^{-1}		$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}		Pol	$\tilde{\nu}$/cm^{-1}		Pol			
4.2 K	293 K	298 K	4.2 K	300 K		4.2 K	300 K		4.2 K	300 K	
		43	57	46	a′b, bc′	54	44	a′b, bc′	1.06	1.05	B_{1g} R_x, R_y
56	42	44	58	47	a′a′, c′c′	55	45	a′a′, c′c′	1.05	1.04	B_{2g} R_x, R_y
97	80	92	88	72	a′b, bc′	84	69	a′b, bc′	1.05	1.04	B_{1g} R_x, R_y
86	68	70	98	78	a′a′, c′c′	93	74	a′a′, c′c′	1.05	1.05	B_{2g} R_x, R_y
			116	93	a′a′, bb, c′c′	105	85	a′a′, bb, c′c′	1.11	1.09	A_g overtone
126	97	103	128	104	a′a′, bb, c′c′	116	94	a′a′, bb, c′c′	1.10	1.11	A_g R_z
134	109	109	136	115	a′b, bc′	125	104	a′b, bc′	1.09	1.11	B_{3g} R_z

a) See Ref. 1. b) See Ref. 2.

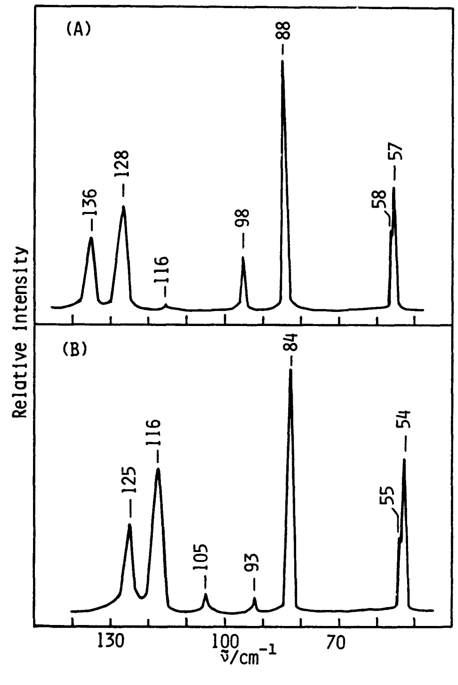

Fig. 1. The Raman spectra of the [$^1H_4$]- (A) and [$^2H_4$]pyrazine (B) crystals in the low-frequency region observed at 4.2 K.

[$^1H_4$]- and [$^2H_4$]pyrazine molecules calculated based on the molecular structure determined by Wheatley,[4] the isotopic factors were calculated to be 1.069, 1.036, and 1.105 for the rotational lattice vibrations about the x, y, and z axes, respectively.

The structures of the Raman spectra observed at various temperatures between 300 and 77 K are the same as that observed at 4.2 K except for the band width, which increases with increasing temperature. This indicates that no apparent phase transition takes place between 300 and 4.2 K. The polarized Raman spectra of the [$^1H_4$]pyrazine single crystal observed at 300 K are given in Fig. 2. According to Table 1, 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. The a′a′ and c′c′ spectra include the aa, cc, and ac spectra, while the a′b and bc′ spectra include the ab and bc spectra because the a′ and c′ axes are in the ac plane. Therefore, the Raman bands observed in the bb spectrum should be assigned to the A_g species, those in the a′a′ and c′c′ spectra to the A_g or B_{2g} species, and those in the a′b and bc′ spectra to the B_{1g} or B_{3g} species. The band at 115 cm^{-1}, whose isotopic factor is 1.11, was observed in the a′b and bc′ spectra and the band at 104 cm^{-1} giving the isotopic factor of 1.11 was observed in the a′a′, bb, and c′c′ spectra. Therefore, these bands were assigned to the rotational lattice vibrations of the B_{3g} and A_g species about the molecular z axis, respectively. The

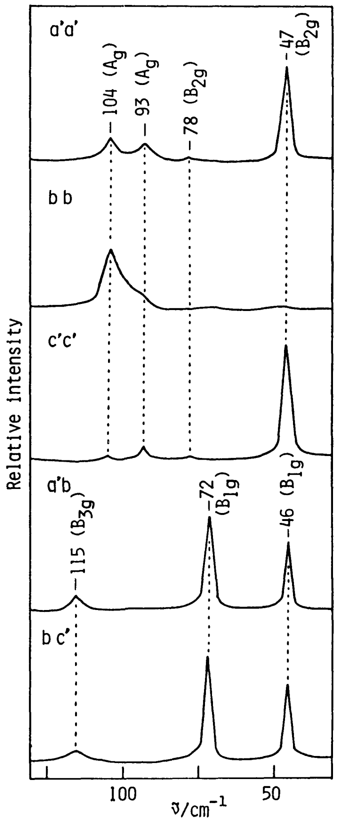

Fig. 2. The polarized Raman spectra of the [$^1H_4$]-pyrazine single crystal in the low-frequency region observed at 300 K.

lowest wavenumber band could not resolve into doublet at 300 K. However, careful observation showed that the frequency of the bands observed in the a′a′ and c′c′ spectra was 47 cm^{-1} and that observed in the a′b and bc′ spectra was 46 cm^{-1}. This observation indicates that the 47 and 46 cm^{-1} bands should be assigned to the vibrations belonging to the different symmetry species. The 46 and 47 cm^{-1} bands correspond to the 57 and 58 cm^{-1} bands observed at 4.2 K, respectively. The observed isotopic factors of the bands at 46, 47, 72, and 78 cm^{-1} ranges between 1.06 and 1.04 and thus these bands are to be assigned to the rotational modes about the molecular x and y axes. The 72 cm^{-1} band showed the a′b and bc′ polarization and the 78 cm^{-1} band the a′a′ and c′c′ polarization behavior. Therefore, the 46 and 72 cm^{-1} bands were assigned to the B_{1g} species and the 47 and 78 cm^{-1} bands to the B_{2g} species although Ito et al. and Pasquier et al. gave different assignments for the 72 and 78 cm^{-1} bands as shown in Table 2. The band at 93 cm^{-1} showing the a′a′, bb, and c′c′ polarization behavior and giving the isotopic factor of 1.09 was assigned to the overtone vibration of the 46 and/or 47 cm^{-1} bands although Pasquier et al. assigned this band to the B_{1g} vibration. These assignments are given in Table 2.

The polarization behavior of the Raman bands of the [$^2H_4$]pyrazine crystal is exactly the same as that of the [$^1H_4$]pyrazine crystal. The assignments for the low-frequency Raman bands of the [$^2H_4$]pyrazine crystal are also given in Table 2. We believe that the polarization behavior of the Raman bands in single crystals gives clear and definite experimental justification for the vibrational assignments and the six rotational lattice vibrations of the [$^1H_4$]- and [$^2H_4$]-pyrazine crystals determined in this work are quite reasonable. The isotopic factors measured for the individual bands also confirm the reliability of the assignments.

The tetramethylpyrazine crystal hydrates quite easily with moisture in the air and the Raman bands due to the hydrated crystal were observed in the intramolecular and lattice vibrations.$^{5)}$ In order to study the effect of hydration on the intramolecular and lattice vibrations of the pyrazine crystal, the Raman spectra of wet pyrazine crystal prepared by adding water to the pyrazine crystal were observed, but no distinct change of the spectral structure and vibrational frequencies were observed untill the pyrazine crystal deliquesces by water.

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