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Reinvestigation of the Nontotally Symmetric g-Type Normal Vibrations of [$^1H_4$]- and [$^2H_4$]Pyrazines

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Synopsis. The assignment of the nontotally symmetric g-type normal vibrations of [$^1H_4$]- and [$^2H_4$]pyrazines was reinvestigated through the analyses of the single vibronic level fluorescence spectrum. The assignment given in this work was consistent with the assignment made based on the polarization behavior of the phosphorescence spectrum.

In spite of a large number of works made on the assignment of the normal vibrations of pyrazine the assignment given for some of the nontotally symmetric vibrations has not been established yet.1–7) Many workers made the assignment through the analyses of the Raman and infrared spectra.1–4) Udagawa et al.5) and McDonald and Rice6) studied the assignment based on the analyses of the single vibronic level (SVL) fluorescence spectra and Azumi et al.7,8) studied the assignment based on the polarization behavior of the phosphorescence spectrum. Their results are summarized in Table 1. The assignment given for the totally symmetric and ν_{10a} vibrations is established based on the various experimental results, while the assignment given for the ν_4, ν_5, and ν_{6b} is not consistent with each other.

Since the reasonable and definite assignment of the normal vibrations is very important for the study of the nature of the electronic excited states, the assignment of the ν_4, ν_5, and ν_{6b} vibrations is reinvestigated through the analyses of the SVL fluorescence and polarized Raman spectra of [$^1H_4$]- and [$^2H_4$]pyrazines in this work.

Experimental

Material. [$^2H_4$]Pyrazine was synthesized by exchange reaction of [$^1H_4$]pyrazine with D_2O using palladium asbestos as a catalyst. The sample was purified by repeated vacuum distillation.

Optical Measurements. The SVL fluorescence spectra were observed in vapor and in supersonic free jets. The excitation light source was a frequency doubled dye laser pumped by the second harmonic of a YAG laser (Qunta-Ray PDL-II DCR-11). The fluorescence spectrum dispersed by a 1.26 m monochromator (Spex. 1269) was detected by a photomultiplier tube (EMI 9789QB) and the signal was processed by a gated integrator (Stanford Research Systems SR 250).

The polarized Raman spectrum was observed with a laser Raman spectrophotometer (Jeol 400T) and the 514.5 nm beam from an Ar^+ ion laser, whose power was adjusted low enough because of high sublimation property of the pyrazine crystal. A single crystal grown by the Bridgman method was cut along the cleavage (101) plane, which will be referred to as the bc′ plane, where the c′ axis is taken to be inclined counterclockwise by 57.6° from the c axis in the ac plane.9) The bb, c′c′, and bc′ polarized Raman spectra were observed by the back scattering method in the same way as described previously,10) where the first and second letters refer to the polarization directions of the excitation and scattering lights, respectively.

Results and Discussion

Fluorescence Spectrum. The fluorescence excitation spectra of [$^1H_4$]- and [$^2H_4$]pyrazines observed in supersonic free jets are given in Fig. 1. The

Table 1. Nontotally Symmetric g-Type Normal Vibrations of [$^1H_4$]- and [$^2H_4$]Pyrazines in the Ground State

	[$^1H_4$]Pyrazine						[$^2H_4$]Pyrazine					
	b_{1g}	b_{2g}		b_{3g}			b_{1g}	b_{2g}		b_{3g}		
	ν_{10a}	ν_4	ν_5	ν_{8b}	ν_3	ν_{6b}	ν_{10a}	ν_4	ν_5	ν_{8b}	ν_3	ν_{6b}
Simmons a)	757	703	918.6	1524	1118	516	580	678	721.1	1505		
Califano b)	925	703	753	1523	1350	641	724					
Sbrana c)	952	754	983	1520	1361	697	740	649	842	1501	1038	672
Zarembowitch d)	927	756	983	1525	1346	704						
Udagawa e)	919	660	756				721	590	651			
McDonald f)	918	705	757			662						
Azumi g,h)	929	756	971			692	726	645	844			679
This work												
Fluorescence	921	755	965			704	725	648	841			687
Raman	943	756	978	1523	1360	700 697	735	648	840	1503	1037	674 671

(in cm^{-1} units)

a, b, c, d, e, f, g, and h are taken from Refs. 1, 2, 3, 4, 5, 6, 7, and 8, respectively (see the text).

assignment made on the vibronic bands is the same as that given by Udagawa et al.[5] except for the band at $0^0+509\ \mathrm{cm}^{-1}$ in the [$^1H_4$]pyrazine spectrum and the weak band at $0^0+473\ \mathrm{cm}^{-1}$ in [$^2H_4$]pyrazine, which was newly detected in this work. The SVL fluorescence spectra generated by pumping to the 0^0 level at 30875 (31032) cm^{-1}, to the $10a^1$ level at $0^0+383\ \mathrm{cm}^{-1}$ ($0^0+293\ \mathrm{cm}^{-1}$), and to the level at $0^0+509\ \mathrm{cm}^{-1}$ ($0^0+473\ \mathrm{cm}^{-1}$) are given in Fig. 2, where the first number refers to the frequency for [$^1H_4$]pyrazine and the number in parentheses to that for [$^2H_4$]pyrazine. The assignment given for the vibronic bands in the 0^0 and $10a^1$ SVL fluorescence spectra is exactly the same as that given by Udagawa et al. and McDonald and Rice, except for the bands at $0^0-755\ \mathrm{cm}^{-1}$ and $10a^1-704\ \mathrm{cm}^{-1}$ ($0^0-648\ \mathrm{cm}^{-1}$, $0^0-886\ \mathrm{cm}^{-1}$, $0^0-1008\ \mathrm{cm}^{-1}$, and $10a^1-687\ \mathrm{cm}^{-1}$). In the 0^0 SVL spectrum of pyrazine the 0^0_0 and totally symmetric vibronic bands showed parallel band envelope in correspondence with the out-of-plane transition moments, while the vibronic bands at $0^0-755\ \mathrm{cm}^{-1}$ and $0^0-921\ \mathrm{cm}^{-1}$ ($0^0-648\ \mathrm{cm}^{-1}$ and $0^0-725\ \mathrm{cm}^{-1}$) showed perpendicular band envelope as observed by Udagawa et al. This indicates that these vibronic bands are induced by the vibronic coupling through certain out-of-plane vibrations. Since the frequencies of 921 (725) cm^{-1} was already assigned to the ν_{10a} vibration of b_{1g} species,[5,6] the frequency of 755 (648) cm^{-1} should be assigned to one of the normal vibrations of b_{2g} species in the ground state.

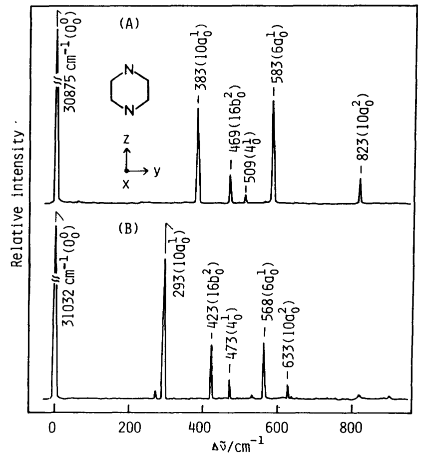

Fig. 1. Fluorescence excitation spectra of [$^1H_4$]- (A) and [$^2H_4$]- (B) pyrazines. The difference in wavenumber from the 0–0 band is expressed by $\Delta\tilde{\nu}$.

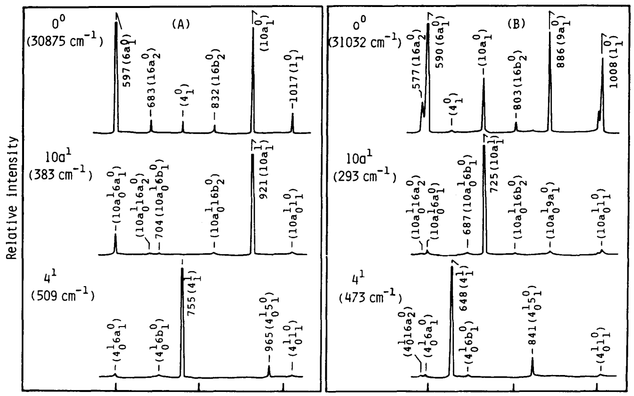

Fig. 2. SVL fluorescence spectra of [$^1H_4$]- (A) and [$^2H_4$]- (B) pyrazines. Excited level is indicated in the left hand side of the each spectrum. The difference in wavenumber from the exciting light is expressed by $\Delta\tilde{\nu}$.

In the $0^0+509\ \mathrm{cm}^{-1}$, which will be written as ν_{509}, SVL spectrum of [$^1H_4$]pyrazine several bands were newly detected at $\nu_{509}-597\ \mathrm{cm}^{-1}$, $\nu_{509}-704\ \mathrm{cm}^{-1}$, and $\nu_{509}-965\ \mathrm{cm}^{-1}$ in the fundamental vibrational region in addition to the band at $\nu_{509}-755\ \mathrm{cm}^{-1}$ which was assigned to the 5^1_1 band by Udagawa and McDonald. In the $0^0+473\ \mathrm{cm}^{-1}$ (ν_{473}) SVL spectrum of [$^2H_4$]pyrazine several bands were clearly observed at $\nu_{473}-577\ \mathrm{cm}^{-1}$, $\nu_{473}-590\ \mathrm{cm}^{-1}$, $\nu_{473}-648\ \mathrm{cm}^{-1}$, $\nu_{473}-687\ \mathrm{cm}^{-1}$, and $\nu_{473}-841\ \mathrm{cm}^{-1}$. The assignment for the vibronic bands involving a_g vibrations was made straightforwardly by comparing the bands with the 0^0 SVL spectra and is given in Fig. 2.

For the nontotally symmetric vibrations the potential minimum would not change upon excitation and therefore the overlap integral of the vibrational wave functions of the ground and excited states $\langle X_i|X_j'\rangle$, which governs the transition probability, is close to δ_{ij}. Thus, the fact that the intensity of the band at $\nu_{509}-755\ \mathrm{cm}^{-1}$ became strongest in the [$^1H_4$]pyrazine spectrum when the $0^0+509\ \mathrm{cm}^{-1}$ level was excited indicates that the $509\ \mathrm{cm}^{-1}$ band should be ascribed to the b_{2g} vibration in the $^3B_{3u}$ (n, π^*) state as indicated by Udagawa and McDonald. Similarly the fact that the intensity of the $\nu_{473}-648\ \mathrm{cm}^{-1}$ band became strongest in the [$^2H_4$]pyrazine spectrum when the $0^0+473\ \mathrm{cm}^{-1}$ level was excited indicates that the frequency of $473\ \mathrm{cm}^{-1}$ should be assigned to the upper state b_{2g} vibration.

It was shown that two normal modes that belong to the same symmetry species and are effective to the vibronic coupling concerning to a certain electronic transition can exhibit Duschinski effect. In pyrazine the vibronic coupling between the $^1B_{3u}$ (n, π^*) and $^1B_{1u}$ (π, π^*) states can be induced through the ν_4 and ν_5 vibrations of b_{2g} species. The observations that the $\nu_{509}-965\ \mathrm{cm}^{-1}$ ($\nu_{473}-841\ \mathrm{cm}^{-1}$) band is the second strongest band in the fundamental vibrational region of the $0^0+509\ \mathrm{cm}^{-1}$ ($0^0+473\ \mathrm{cm}^{-1}$) SVL spectrum while the vibronic band involving the frequency of 965 (841) cm^{-1} was hardly detected in the 0^0 SVL spectrum and could not be detected in the $10a^1$ SVL spectrum as shown in Fig. 2 suggest that (1) the 965 (841) cm^{-1} band can be classified into the same symmetry species as that of the 755 (648) cm^{-1} band, (2) the 755 and 965 (648 and 841) cm^{-1} bands can be assigned to the ν_4 and ν_5 vibrations in the ground state, respectively, and (3) the 509 (473) cm^{-1} band can be assigned to the ν_4 vibration in the $^1B_{3u}$ (n, π^*) state.

The vibronic band involving the frequency of 704 (687) cm^{-1} was not observed in the 0^0 SVL spectrum but observed clearly in the $10a^1$ and 4^1 SVL spectra. Symmetry consideration suggests that this frequency

Table 2. Squares of Relative Values of Elements of the Raman Tensor for Pyrazine Crystal

	b_{1g}	b_{2g}	b_{3g}
$(A_{bb})^2$	0.50	0.00	0.00
$(A_{c'c'})^2$	0.04	0.12	0.70
$(A_{bc'})^2$	0.14	0.61	0.10

can be ascribed to one of the b_{3g} vibrations. The study of the normal vibrations of pyridine[11)] and pyrimidine[12)] suggests that the frequencies of 886 and 1008 cm^{-1} observed in the fluorescence spectrum of [$^2H_4$]pyrazine should be assigned to the ν_{9a} and ν_1 vibrations, respectively, although Udagawa et al. assigned these to the ν_1 and ν_{9a} vibrations, respectively.

The assignment given in this work for the vibronic bands observed in the fluorescence excitation and SVL fluorescence spectra is given in Figs. 1 and 2 and Table 1.

Polarized Raman Spectrum. Pyrazine crystallizes in the orthorhombic space group P_{mnn} with two molecules in the unit cell.[9)] The matrix elements of the Raman tensor of the pyrazine crystal was calculated based on the simple oriented gas model approximation. The squares of relative values of the elements of the Raman tensor are given in Table 2. The bb, bc′, and c′c′ polarized Raman spectra of the [$^1H_4$]- and [$^2H_4$]pyrazine crystals are shown in Fig. 3. In the bb spectrum the Raman bands were observed at 1582 (1540), 1250 (899), 1017 (1003), 598 (591), and 943 (735) cm^{-1}. The first four bands can be assigned to the totally symmetric vibrations as already established by various workers. The band at 943 (735) cm^{-1} can be assigned to the ν_{10a} vibration based on the SVL fluorescence spectrum but the observed polarization behavior of this Raman band was not consistent with the expected behavior given in Table 2.

The Raman bands at 978 (840) and 756 (648) cm^{-1} observed in the c′c′ and bc′ spectra can be assigned to the ν_5 and ν_4 vibrations based on the SVL fluorescence spectrum, respectively, but the polarization behavior of these Raman bands did not entirely coincide with the expected behavior. The Raman bands at 1523 (1503), 1360 (1037), and 700 (674) cm^{-1} were observed in the c′c′ and bc′ spectra. The last band splits into doublets at 700 and 697 (674 and 671) cm^{-1} in the crystal, which may be caused by the factor group splitting. The first two Raman bands can be assigned to the ν_{8b} and ν_3 vibrations of the in-plane vibration of b_{3g} species, respectively, because of their higher frequencies than 1000 cm^{-1}. The last Raman band can be assigned to the ν_{6b} vibration of b_{3g} species because the corresponding frequency was not observed in the 0^0 SVL fluorescence spectrum but observed in the $10a^1$ and 4^1 SVL spectra. The observed polarization behavior of these b_{3g} vibrations did not entirely coincide with the expected one. The inconsistency of the observed and expected polarization behavior of the Raman bands may be ascribed to the characteristics in the pyrazine crystal which is invariably twinned on the (101) plane as indicated by Wheatley,[9)] and therefore this suggests that the simple oriented gas model approximation cannot be applied to the analysis of the polarized Raman spectrum of the pyrazine crystal. Polarization behavior of the Raman bands can only give a reasonable evidence for the Raman bands observed in the bb spectrum being assigned to the a_g or b_{1g} vibration but not to the b_{2g} and b_{3g} vibrations since the vanishing values of the matrix elements for the b_{2g} and b_{3g} vibrations in the bb spectrum given in Table 2 result from the fact that the molecular z axis is parallel to the crystal a axis. The assignment made in this work, which is given in Figs. 2 and 3 and Table 1, is completely coincided with that made by Azumi et al. based on the polarized phosphorescence spectra of [$^1H_4$]- and [$^2H_4$]pyrazines.[7,8)]

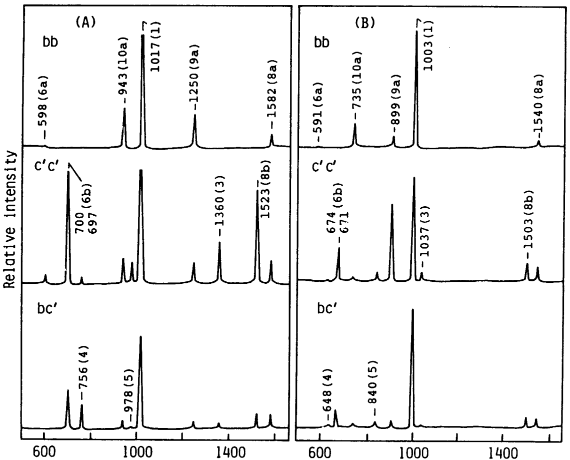

Fig. 3. Polarized Raman spectra of [$^1H_4$]- (A) and [$^2H_4$]- (B) pyrazine single crystals.

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