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Fluorescence Polarization Spectra along the Rotational Contour of the $10a_0^1$ Absorption Band of Pyrazine Vapor

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Synopsis. Fluorescence polarization spectra for the $10a_0^1$ perpendicular absorption band belonging to the $S_0 \rightarrow S_1$ transition of pyrazine vapor have been obtained at room temperature. The spectra are well reproduced theoretically by considering the resonance fluorescence from fully resolved rotational levels in S_1 and by employing a symmetric top approximation.

Fluorescence emission from free rotating molecules was demonstrated to be largely polarized even in such larger molecules as pyrazine, pyrimidine and 1,3,5-triazine.[1] The analysis of the degree of polarization of fluorescence along the rotational contour of the parallel vibronic absorption bands of these azaaromatic compounds was shown to give a clue to understand the mechanism of the intramolecular vibrational redistribution within the singlet manifold.[2] Similarly, the polarization of ensemble-averaged fluorescence was shown by Nathanson and McClelland to be important to determine the extent of intramolecular vibration-rotation energy transfer.[3]

Terazima and Lim[4] reported that excitation of the $10a_0^1$ band of S_1 pyrazine, which lies at 383 cm^{-1} above the $S_0 \rightarrow S_1$ origin and exhibits a rotational contour of typical perpendicular bands,[5] leads to the appearance of fluorescence which is nearly completely depolarized in a jet, in contrast with the 0-0 band. They suggested that these results come from a strong mixing between fluorescence emissions induced by the parallel and perpendicular transitions, respectively, since these two emissions are expected to show an opposite behavior on polarization. On the other hand, Pratt and co-workers[6] proposed a different interpretation of the fluorescence depolarization for the $10a_0^1$ band, based on the phosphorescence excitation spectrum in the $S_0 \rightarrow T_1$ absorption region. The S_1 surface is well known to be distorted along the coordinate of the ν_{10a} vibration because of strong vibronic coupling with higher lying singlet states,[7] whereas vibronic coupling is not important in T_1 according to the $S_0 \rightarrow T_1$ spectrum. Thus, the potential curve of the ν_{10a} vibration is different in S_1 and T_1. Because of enhanced Franck-Condon factor as well as differences in the admixed $\pi\pi^*$ character, therefore, the S_1-T_1 spin orbit matrix element might be significantly larger for the levels involving ν_{10a} vibration. Pratt and co-workers suggested that such a mode specificity in the S_1-T_1 spin orbit interaction may induce a mode specificity in the fluorescence polarization, i.e., fluorescence depolarization occurs following excitation into the S_1 vibronic levels effectively coupled to the triplet levels.

In the present study, excitation polarization (EP) spectra of pyrazine along the rotational contour of the $10a_0^1$ perpendicular absorption band were obtained in a bulk gas by monitoring the parallel and perpendicular fluorescence bands with out-of-plane and in-plane transition moments, respectively.

Experimental

All the optical measurements were carried out at room temperature. The experimental apparatus and procedures are the same as reported in previous papers.[2] Briefly, the output frequency of a pulsed dye laser (Molecron DL14), pumped by a nitrogen laser (Molectron UV22), was doubled by a KDP crystal. The generated UV light, which is linearly polarized and used for excitation, has a repetition rate of 20 pps, a linewidth of ca. 0.5 cm^{-1} and a duration of ca. 3 ns. The fluorescence emitted at right angles to the direction of propagation of the laser light for excitation was passed through a polarization analyzer and then through a scrambler. The emission was dispersed by a grating monochromator and detected by a photomultiplier. The intensities of the fluorescence polarized parallel and perpendicular to the polarization direction of the exciting light are denoted by $I_{/\!/}$ and $I_{\perp}$, respectively and the degree of polarization (P) is defined as $P=(I_{/\!/}-I_{\perp})/(I_{/\!/}+I_{\perp})$. The EP spectra along the rotational contour were obtained by combining two fluorescence excitation spectra obtained by monitoring $I_{/\!/}$ and $I_{\perp}$, separately.

Results and Discussion

Figure 1 shows the EP spectra of pyrazine along the rotational contour of the $10a_0^1$ band, together with the absorption spectrum. The sample pressure is 0.25 and 1.23 Torr (1 Torr=133.322 Pa) for the EP and absorption spectra, respectively. The EP spectra shown in Figs. 1(a) and 1(b) were obtained, respectively, by monitoring the fluorescence of parallel band of $10a_1^1 6a_0^1$ at 336 nm, and the perpendicular band of $10a_2^1$ at 339.8 nm with a spectral resolution of 0.2 nm.[7] The absorption band located at ca. 20 cm^{-1} higher than the $10a_0^1$ exhibits a parallel-type rotational contour and assigned as the $6a_0^1 16b_1^1$ bands.[8] The absorption spectrum of the $10a_0^1$ band exhibits a perpendicular-type rotational contour, and the rotational analysis was completed by Thakur and Innes.[5] The EP spectra shown in Figs. 1(a) and 1(b) are very different from each other, e.g., the P value near the origin is ca. -0.15 for the parallel fluorescence band, whereas P near the origin is ca. 0.1 for the perpendicular fluorescence band.

The EP spectra were simulated with a symmetric top approximation in the same manner as reported in the previous papers.[2] By assuming that wavefunction can be separated into a rotational part and a vibronic part, the intensity of the resonance fluorescence emitted from the optically prepared level is

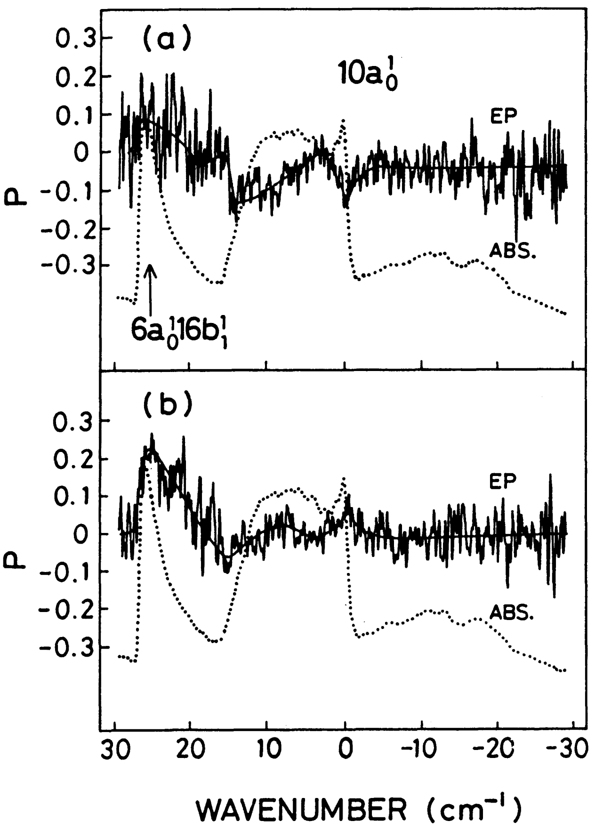

Fig. 1. Excitation polarization spectra of pyrazine vapor at 0.25 Torr along the rotational contour of the $10a_0^1$ band, obtained by monitoring the fluorescence at 336 nm (a) and at 339.8 nm (b). The dotted line represents the absorption spectrum. The band origin denoted by 0 is at 31258 cm^{-1}.[5] The absorption band lying at ~20 cm^{-1} above the $10a_0^1$ band is assigned as the $6a_0^1 16b_1^1$.[7]

given by

$$I \propto \nu_a \nu_c{}^4 \sum_{gg'} |M_g|^2 |M_{g'}|^2 f(\mathrm{JKJ'K'J''K''}) \tag{1}$$

where

$$f(\mathrm{JKJ'K'J''K''}) = (2J+1)^{-1} \times \sum_{\mathrm{MM'M''}} |\langle \mathrm{J'K'M'}|\Phi_{\mathrm{Fg}}|\mathrm{JKM}\rangle|^2 \, |\langle \mathrm{J''K''M''}|\Phi_{\mathrm{Fg'}}|\mathrm{J'K'M'}\rangle|^2 \tag{2}$$

Here, ν_a, ν_e are the frequencies of the absorbed and emitted lights, respectively; M_g, $M_{g'}$ are the vibronic part of the dipole moment along the g and g′ axes of the molecule-fixed Cartesian system, respectively; Φ_{Fg}, $\Phi_{\mathrm{F'g'}}$ are the direction cosines between the F and g axes and between the F′ and g′ axes, respectively; $|\mathrm{JKM}\rangle$, $|\mathrm{J'K'M'}\rangle$ and $|\mathrm{J''K''M''}\rangle$ represent the rotational wavefunctions of the initial, intermediate and final states, respectively. Note that F and F′ represent the axes of the space-fixed Cartesian system in terms of which the radiation field is described. It is also noted that the polarization direction of the exciting light and the figure axis are regarded as X and z, respectively. Then, the fluorescence intensity at ν is given by

$$I(\nu) = \sum_{\nu_1 \mathrm{JKJ'K'J''K''}} A(\mathrm{J'K'})\, I\, g_{\mathrm{JK}} P_{\mathrm{JK}}(T)\, L(\nu - \nu_1) \tag{3}$$

where g_{JK}, $P_{\mathrm{JK}}(T)$, $L(\nu-\nu_1)$ are the statistical weight, the Boltzman factor at a temperature of T, intensity of the exciting light at ν_a, respectively. ν_a is different from the excitation frequency ν of the maximum intensity by ν_1. A(J′K′) is the factor to which fluorescence quantum yield is proportional.

With the relations M=M′=M″ and M=M′=M″±1 for the parallel and perpendicularly polarized fluorescence emissions, respectively,[9] the intensities of $I_{/\!/}(\nu)$ and $I_{\perp}(\nu)$ can be obtained from the above equations.

In the present experiments, the optical excitation was made for the perpendicular absorption band, i.e., g=x(y). The f values of Eq. 2 for F=F′=X and for F=X, F′=Y were evaluated for the individual rotational transitions of a symmetric top with the direction cosine matrix elements reported by Cross et al.[10] The EP spectra simulated for the parallel-type transition of emission, i.e., g′=z and for the perpendicular-type transition of emission, i.e., g′=x(y) are shown in Fig. 2, together with the simulated absorption spectrum. These spectra were obtained with the rotational constants: B''=0.20531 and C''=0.10249 in S_0 and B'=0.20322, and C'=0.10166 cm^{-1} in S_1.[5] Fluorescence emissions of pyrazine consist of fast and slow components.[11] In fact, the slow component occupies about 15% of the total fluorescence in intensity at 0.25 Torr for excitation into the $10a^1$. The quantum yield of the fast component is independent of the rotational level excited, whereas that of the slow component is nearly proportional to $(2J'+1)^{-1}$.[12] The simulated spectra shown in Figs. 2(a) and 2(b) were obtained by assuming that A(J′K′) in Eq. 3 is constant, whereas the spectra in Figs. 2(c) and 2(d) were obtained by assuming that A(J′K′) is $(2J'+1)^{-1}$.

Actually, the absorption spectrum is not well reproduced theoretically, as far as symmetric top approximation is employed. However, the EP spectra both for the parallel- and perpendicular-type fluorescence bands are reproduced very well by assuming a symmetric top approximation, as is seen in Figs. 1 and 2. In fact, Ray's parameter defined by $(2B-A-C)/(A-C)$ is 0.985 at the $10a^1$ level of S_1,[5] indicating that pyrazine is well regarded as an oblate symmetric top at this level. Accordingly, it is known that the EP spectra are not influenced by an asymmetry so severely as the absorption spectrum.

At several excitation positions along the rotational contour, the P value of each of the fast and slow components was evaluated by combining the total integrated intensity with the decays, both of which were obtained for each of $I_{/\!/}$ and $I_{\perp}$. However, a difference of P was not confirmed between the fast and slow components. These results are well understood from Fig. 2, i.e., the EP spectra simulated with the assumption that A(J′K′) is constant are very similar to the spectra simulated with the assumption that A(J′K′) is $(2J'+1)^{-1}$. It should be also noted that the EP spectrum for the $6a_0^1 16b_1^1$ band are very similar to those for the 0-0 band and that the observed spectra are similarly reproduced theoretically very well.[2]

Polarization property of fluorescence indicates that the emission whose intensity is proportional to $I_{/\!/}+2I_{\perp}$ must be monitored to obtain the true yield spectrum.

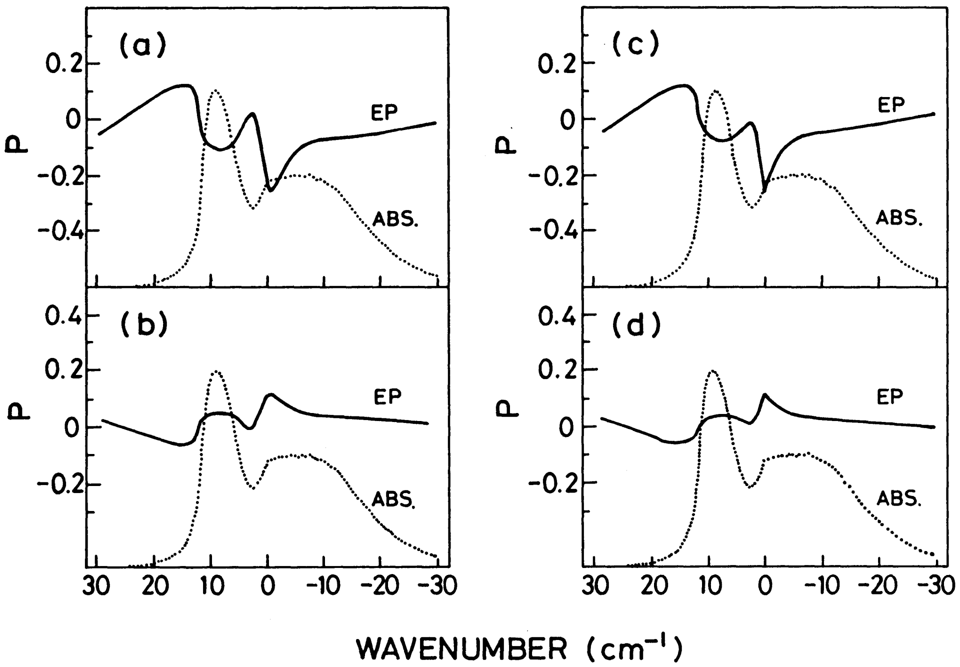

Fig. 2. Excitation polarization spectra at 298 K simulated for the $10a_0^1$ band of pyrazine according to Eqs. 1—3 with the following assumptions: (a) g=x(y), g′=z, and A(J′K′) is constant; (b) g=x(y), g′=x(y), and A(J′K′) is constant; (c) g=x(y), g′=z, and $A(J'K')=(2J'+1)^{-1}$; (d) g=x(y), g′=x(y), and $A(J'K')=(2J'+1)^{-1}$. The exciting light was assumed to have a triangle bandshape with a width (fwhm) of 0.5 cm^{-1}. Dotted line shows the simulated absorption spectra.

Previous conclusion for the $10a_0^1$ band that the fluorescence quantum yield of the fast component is nearly independent of the rotational level excited and that the yield of the slow fluorescence is proportional to $(2J'+1)^{-1}$ was derived from the yield spectra which were obtained without any polarization analyzer for emission.[12] The yield spectra obtained by setting the polarization analyzer for emission to the magic angle (54.7 °), i.e., the observed fluorescence intensity corresponds to $I_{//}+2I_{\perp}$, were confirmed to be very similar to the previous spectra. Fortunately, therefore, it is unnecessary to correct the previous conclusion concerning the excited rovibronic level dependence of the fluorescence quantum yield.

The EP spectra of pyrazine are well reproduced by considering the resonance fluorescence emitted from the individual rotational levels optically excited and by employing a symmetric top approximation, though the fluorescence consists of the fast and slow components which correspond to the dephasing decay and the population decay, respectively. Further, there is no evidence in the EP spectra that there is a mode specificity in the S_1-T_1 dynamics between the S_1 origin and the $10a^1$ level.

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