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Vibronic Bands of Phosphorescence Spectra of Quinoxaline in Host Crystals

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The polarized phosphorescence spectra of quinoxaline in durene and *p*-dimethoxybenzene host crystals were observed at 4.2°K, and the vibronic bands of the phosphorescence spectrum were assigned. It was found that the intensity of vibronic bands polarized along long molecular axis arises from the vibronic spin-orbit coupling routes

$$^1A_2(\pi, \pi^*) \overset{b_1}{<} {}^1B_1 \overset{R_z}{>} {}^3B_2(\pi, \pi^*)$$
$$\qquad\qquad\quad \underset{R_z}{<} {}^3A_2 \underset{b_1}{>}$$

and the intensity of vibronic bands polarized along short molecular axis from the routes

$$^1B_2(\pi, \pi^*) \overset{R_z}{<} {}^3B_1 \overset{a_2}{>} {}^3B_2(\pi, \pi^*)$$
$$\qquad\qquad\quad \underset{a_2}{<} {}^1B_1 \underset{R_z}{>}$$

It was concluded that all the vibronic phosphorescence bands of quinoxaline originate from the Tz zero-field sublevel. This is in line with the results of El-Sayed and Brewer deduced from the magnetic field effect on the phosphorescence spectrum.

Effects of vibronic coupling or vibronic spin-orbit coupling on the phosphorescence spectrum of quinoxaline have been studied by several investigators using the method of photoselection[1,2] or with mixed crystal.[3,4] However, discussion is limited because of the ambiguity in the assignment of the fundamental vibrational frequencies. In this work the ploarized phosphorescence spectra of quinoxaline in several host crystals have been observed at liquid helium temperature, the orgin in vibronic bands being discussed.

1) M. A. El-Sayed and R. G. Brewer, *J. Chem. Phys.*, **39**, 1623 (1963).
2) E. C. Lim and J. M. H. Yu, *ibid.*, **49**, 3878 (1968).
3) N. K. Chaudhuri and M. A. El-Sayed, *ibid.*, **44**, 3728 (1966).
4) S. M. Ziegler and M. A. El-Sayed, *ibid.*, **52**, 3257 (1970).

Experimental

The polarized phosphorescence spectra were measured photographically with a Shimadzu GE-100 grating spectrograph (of reciprocal linear dispersion of 8.4 A/mm in the first order) equipped with a Wollaston prism behind entrance slit. A 500 W Hg lamp was used as an exciting source. A quarter-wave plate was placed behind the slit of the spectrograph for correction of the polarization characteristic of the spectrograph. Photoelectric recording of the spectra was also carried out with a Narumi 750Z—1200 grating double monochromator having a reciprocal linear dispersion of 11 A/mm in the first order.

Quinoxaline (Tokyo Kasei Co.) was purified by repeated recrystallization and distillation under several times reduced pressure. Durene and *p*-dimethoxybenzene used as host

crystals were purified by recrystallization and zone refining.

The single crystals were obtained by cutting large crystals grown by the Bridgeman method. The crystallographic axes were determined by observation of isogyric pattern under a polarizing microscope and by X-ray diffraction. The crystal was fixed on the copper plate of a helium cryostat and immersed directly into liquid helium.

Results and Discussion

The *p*-dimethoxybenzene crystal belong to a space group $V_h^{15}(P_{bca})$ with four molecules in a unit cell.[5] Projection of the molecule on plane *ab* of the crystal is shown in Fig. 1. The durene crystal belongs to a space group $C_{2h}^5(P_{21/a})$ with two molecules in a unit cell.[6,7] Rrojection of the molecules on plane *bc** of the crystal is shown in Fig. 2. In the mixed crystals of quinoxaline, we assumed that quinoxaline molecule occupies substitutional positions in the host crystals with the molecular orientation in which the *L,M,N* axes of quinoxaline molecule coincide with the *L,M,N* axes of the host molecules, respectively.

We see from Fig. 1 that when the polarized spectra of the guest molecule are observed on plane *ab* of *p*-dimethoxybenzene crystal, it is possible to distinguish the in-plane and out-of-plane polarized transitions of the guest molecule. The polarized phosphorescence spectra of quinoxaline on plane *ab* of *p*-dimethoxybenzene crystal at 4.2°K is shown in Fig. 3. It is clear that the bands 0-0, 0-527, and 0-603 cm^{-1} are out-of-plane polarized ones and the 0-466, 0-490, 0-635, and 0-872 cm^{-1} in-plane polarized ones. The vibrational frequency 527 cm^{-1} forms a long progression starting from band 0-0 and corresponds to the strong Raman line of 535 cm^{-1}.[8] Band 0-603 cm^{-1} is also the origin of a short progression of 527 cm^{-1}. Since bands 0-527 and 0-603 cm^{-1} behave in a similar way to band 0-0, the frequencies of 527 and 603 cm^{-1} are assigned to vibrational mode a_1.

On the other hand, when the polarized spectra are measured on plane *bc** of durene crystal, the short axis polarized transition can be distinguished from the long axis and out-of-plane plarized transitions (Fig. 2). The polarized phosphorescence spectra on plane *bc** of durene crystal is shown in Fig. 4. We see that bands

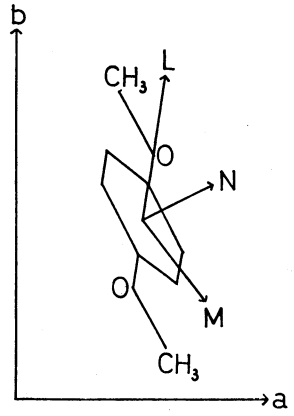

Fig. 1. Molecular projection on *ab* plane of *p*-dimethoxybenzene crystal.

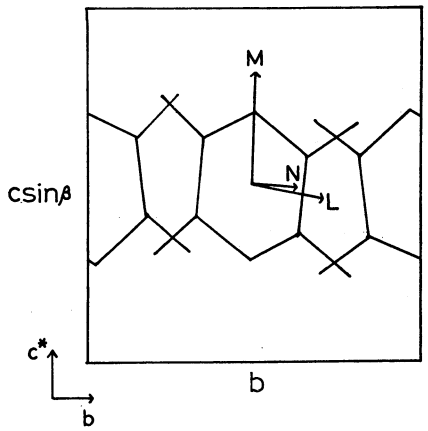

Fig. 2. Molecular projection on *bc** plane of durene crystal.

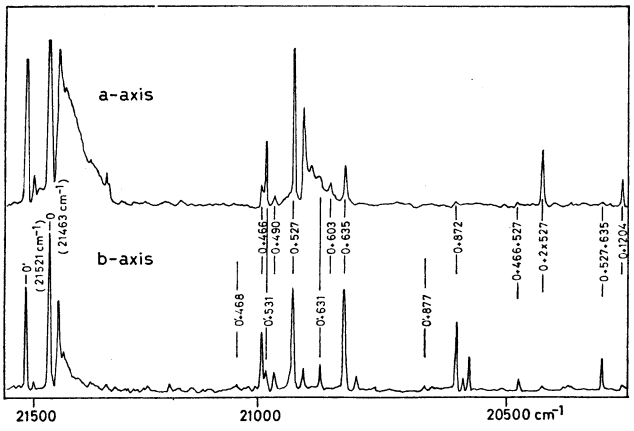

Fig. 3. The microphotometer tracing of the polarized phosphorescence spectra of quinoxaline in *p*-dimethoxybenzene host crystal at 4.2°K.

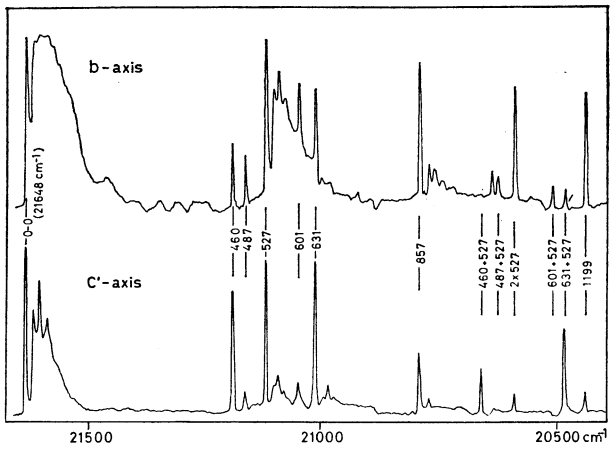

Fig. 4. The microphotometer tracing of the polarized phosphorescence spectra of quinoxaline in durene host crystal at 4.2°K.

5) T. H. Goodwin, M. Przybylska, and J. M. Robertson, *Acta Crystallogr.*, **3**, 279 (1950).
6) J. M. Robertson, *Proc. Roy. Soc. Ser. A*, **141**, 594 (1933).
7) J. M. Robertson, *ibid.*, **142**, 659 (1933).
8) R. W. Mitchell, R. W. Glass, and J. A. Meritt, *J. Mol. Spectrosc.*, **36**, 310 (1970).

TABLE 1. THE MAIN VIBRONIC BANDS OF QUINOXALINE PHOSPHORESCENCE IN *p*-DIMETHOXYBENZENE HOST CRYSTAL AT 4.2°K AND THEIR POLARIZATIONS

Vibronic bands of quinoxaline in *p*-dimethoxybenzene host crystal (cm^{-1})	Polarization direction of the vibronic band	Assignment of fundamental vibration involved
0-466	*Y*	a_2
0-490	*Z*	b_1
0-527	*X*	a_1
0-603	*X*	a_1
0-635	*Y*	a_2
0-872	*Z*	b_1
0-1204	*X*	a_1

0-466 and 0-635 cm^{-1} are the short polarized along axis. The remaining bands of 0-490 and 0-872 cm^{-1} are necessarily assigned to be polarized along the long axis. The polarization direction of the individual vibronic bands are given in Table 1.

Let us consider the symmetry species of the vibrations involved in the vibronic bands. In their study of the vapor absorption spectrum of quinoxaline, Glass *et al.* reported a hot band involving the vibration of 454 cm^{-1} which assigned to mode a_2 from the rotational contour of the band.[9] On the other hand, the 0-635 cm^{-1} band behaves in a similar way to the 0-466 cm^{-1} bands in the various polarization spectra, and thus the frequencies of 466 and 635 cm^{-1} are assigned to mode a_2. The vibrational frequencies of 490 and 872 cm^{-1} are assigned to mode b_1 based on the assignment by Mitchel *et al.*[8] The assignments are given in Table 1. It was found that the vibronic bands involving fundamental vibrations a_1, a_2, and b_1 are out-of-plane (*X*), short-axis (*Y*) and long-axis (*Z*) polarized, respectively.

The low-lying electronic states of quinoxaline are shown schematically in Fig. 5. The lowest singlet excited state of quinoxaline molecule is $^1B_1(n,\pi^*)$. The two higher states are $^1A_1(\pi,\pi^*)$ and $^1B_2(\pi,\pi^*)$ which correspond to $^1B_{1u}$ and $^1B_{2u}$ of naphthalene, respectively. For the triplet states, the lowest is established to be $^3B_2(\pi,\pi^*)$. $^3B_1(n,\pi^*)$ seems to lie at a slightly higher energy than $^3B_2(\pi,\pi^*)$ although its existence is not yet confirmed experimentally. Since the spin-orbit coupling between n,π^* and π,π^* is generally much greater than that between π,π^*,$^1B_1(n,\pi^*)$ is expected to be the intensity source of band 0-0 and the vibronic bands involving fundamental vibration a_1.

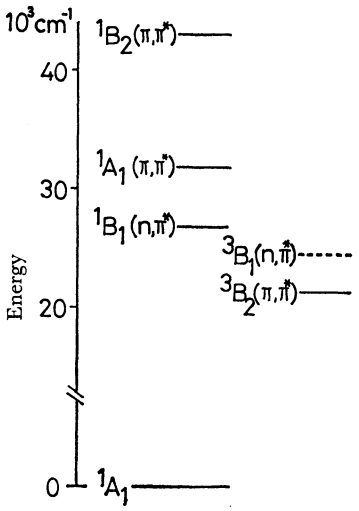

Fig. 5. The low-lying electronic states of quinoxaline.

The expectation is confirmed by our observation that they are out-of-plane polarized bands. Thus for band 0-0 and the vibronic bands involving fundamental vibration a_1, the route $^1B_1(n,\pi^*) \xrightarrow{R_z} {}^3B_2(\pi,\pi^*)$ is given,[10] where R_z is rotation operator of the spin-orbit coupling. For occurrence of the vibronic bands involving nontotally symmetric vibrations, we must consider the spin-orbit interaction as well as the vibronic interaction. For the long-axis polarized vibronic bands involving vibration b_1(0-490, 0-872) the following vibronic spin-orbit coupling routes are most probable.

$$^1A_1(\pi,\pi^*) \begin{cases} \xrightarrow{b_1} {}^1B_1(n,\pi^*) \xrightarrow{R_z} \\ \xrightarrow{R_z} {}^3A_2(n,\pi^*) \xrightarrow{b_1} \end{cases} {}^3B_2(\pi,\pi^*)$$

For the short-axis polarized bands involving vibtation a_2(0-466, 0-635), the following routes are given.

$$^1B_2(\pi,\pi^*) \begin{cases} \xrightarrow{R_z} {}^3B_1(n,\pi^*) \xrightarrow{a_2} \\ \xrightarrow{a_2} {}^1B_1(n,\pi^*) \xrightarrow{R_z} \end{cases} {}^3B_2(\pi,\pi^*)$$

It is seen that all the routes commonly involve the spin-orbit coupling through R_z. This means that the phosphorescence of all the vibronic bands originates from Tz sublevel of state $^3B_2$. This supports the results given by Zigler and El-Sayed that band 0-0 and all the vibronic bands occur from Tz sublevel in study of the magnetic field effect.[11]

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9) R. W. Glass, L. C. Robertson, and J. A. Meritt, *J. Chem. Phys.* **53**, 3877 (1970).

10) M. A. El-Sayed and R. G. Brewer, *ibid.*, **39**, 1623 (1963).

11) S. M. Ziegler and M. A. El-Sayed, *ibid.*, **52**, 3257 (1970).