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Origin of the Fine Structure of the Electronic Spectra of Pyrazine in Benzene Crystals

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The absorption, fluorescence, and phosphorescence spectra of pyrazine doped in benzene crystal have been observed at 4.2°K. It was found that the 0-0 band and the main vibronic bands are accompanied by the fine structures consisting of several very sharp bands and few broad bands. A detailed examination of the fine structures has suggested that the sharp bands arise from the differently oriented guest molecules in the host crystal, and the broad bands come from coupling of the host crystal phonon with the guest molecule.

Low temperature electronic spectra of aromatic compounds doped in host crystal often exhibit fine structure in $0\sim200\ \mathrm{cm}^{-1}$ region near main vibronic band. As the fine structure is in most cases very different for the same guest spectra on different host crystals, a coupling of the host crystal phonons with the electronic state of the guest molecule has been suggested to be the cause of the fine structure. Many workers have attempted to explain the fine structure with the $k=0$ phonons. However, the attempt seems unsuccessful because of lack of definite correspondence with the Raman and IR active phonon frequencies. Recently, Zahlan[1] and Ostertag[2] *et al.* have suggested that the $k\neq0$ phonons also play an important role and the fine structure represents more or less the frequency distribution of phonon density of the host crystal. Hochstrasser and Small[3] have pointed out, on the other hand, that the fine structure is partly explained by existence of several differently oriented guest molecules in the host lattice.

In the present investigation, the absorption, fluorescence and phosphorescence spectra of pyrazine in benzene crystal have been observed at 4.2°K. It was found that the main vibronic bands of these spectra are accompanied by the fine structures consisting of several very sharp bands and a few broad bands. Comparison among the fine structures of the absorption, fluorescence and phosphorescence spectra and effects of changing the host crystal from benzene to benzene-d_6 on their features revealed possible causes of the fine structure.

Experimental

The absorption, fluorescence and phosphorescence spectra were measured photographically with a Shimadzu GE-100 grating spectrograph in the second and third orders, the linear reciprocal dispersions being 4.1 and 2.7Å/mm, respectively. Exposure time ranged from 1 min to 4 hours with slit width of 50 μ.

Wave numbers of the sharp and broad bands were determined within accuracies of 0.5 and $1.0\ \mathrm{cm}^{-1}$, respectively. Photoelectric spectral measurements were also carried out by using a Narumi grating double monochromator having a linear reciprocal dispersion in the first order of 11 Å/mm and an EMI 9558 BQ photomultiplier. The optical arrangement for taking the spectra at low temperatures is essentially the same as that described by Mikami.[4] The emission spectra were excited by Hg line of 3130Å from a Ushio high pressure mercury lamp, which was isolated by a Shimadzu Baush & Lomb high intensity monochromator as well as a Corning CS-75 filter.

Pyrazine (Tokyo Kasei, GR grade) was sublimated several times in vacuum. Benzene (Wako, GR grade) was purified by the procedure recommended by Kanda *et al.*[5] Benzene-d_6 (E. Merck, spectro-grade) was vacuum distilled. Concentration of the sample solutions were 10^{-2}—10^{-4} mol/*l*. The solution was degassed several times and transferred to a quartz cell of 1 mm path length in vacuum. The sample inserted in a cryostat was slowly cooled until 77 °K by cooled nitrogen gas, then, immersed in liquid He.

Results and Discussion

The absorption, fluorescence, and phosphorescence spectra of pyrazine in benzene crystal at 4.2°K are shown in Fig.1. These spectra are all due to an n-π^* transition of pyrazine. The spectra were sharp in benzene crystal compared with those in other host

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[1] A. B. Zahlan, in "Excitons, Magnons and Phonons in Molecular Crystals", ed. A. B. Zahlan, Cambridge Univ. Press (1968), p. 153.

[2] R. Ostertag and H. C. Wolf, *Phys. Stat., Sol.* **31**, 139 (1969).

[3] R. M. Hochstrasser and G. J. Small, *Chem. Commun.*, **5**, 87 (1965).
R. M. Hochstrasser and G. J. Small, *ibid.*, **45**, 2270 (1966).
R. M. Hochstrasser and G. J. Small, *ibid.*, **48**, 3612 (1968).

[4] N. Mikami, *J. Mol. Spectry.*, **37**, 147 (1971).

[5] Y. Kanda and R. Shimada, *Spectrochim. Acta*, **17**, 7 (1961).

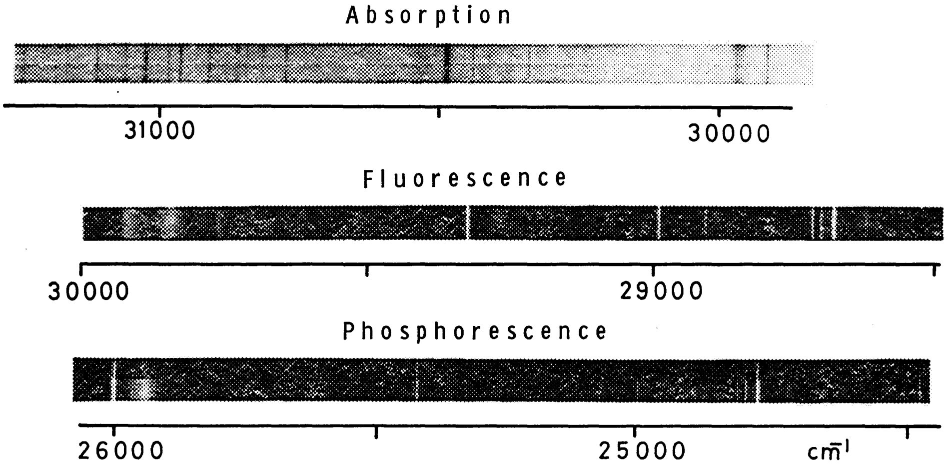

Fig. 1. The n-π^* absorption, fluorescence, and phosphorescence spectra of pyrazine crystal at 4.2°K.

TABLE 1. FREQUENCY DIFFERENCES OF THE MAIN BANDS NEAR THE 0-0 BANDS MEASURED FROM THE STRONGEST REFERENCE

Host	Absorption		Fluorescence		Phosphorescence	
	C_6H_6	C_6D_6	C_6H_6	C_6D_6	C_6H_6	C_6D_6
Sharp band					−22.8	−22.2
	−9.2	−11.4	−8.1	−8.1	−5.7	−5.6
	0	0	0	0	0	0
	7.6	5.9	11.4	11.0	36.0	36.5
Broad band	77.0	44.0	49.0	48.0	48.0	45.5
	56.0	53.0	57.0	54.5	57.0	55.0
	62.0	58.5	64.0	60.0	63.5	60.0

crystal such as cyclohexane.[6] The essential feature of the spectra did not change when temperatrue and concentration of the sample were varied in the ranges of 4.2°K—77°K and 10^{-2}—10^{-4} mol/l, respectively.

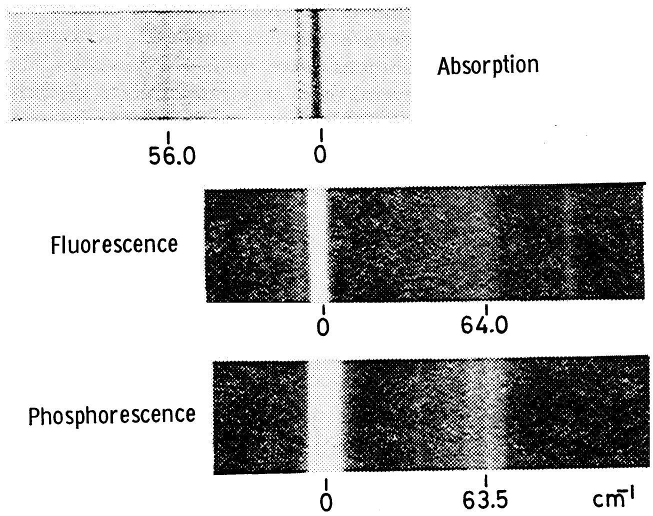

Fig. 2. Fine structures near the 0-0 bands of the absorption, fluorescence, and phosphorescence spectra of pyrazine in benzene crystal at 4.2°K.

The fine structures of the 0-0 bands of the absorption, fluorescence and phosphorescence spectra in benzene are reproduecd in Fig.2.[7] It is seen that the 0-0 bands are composed of very sharp bands and broad bands. A good mirror image relationship is seen between the absorption and fluorescence. Table 1 gives the frequency differences of the individual main bands measured from the strongest band in each spectrum selected as reference. It is seen that a good correspondence exists among the three spectra, especially the broad bands. Such broad bands are often observed in the electronic spectra of aromatic molecules doped in host crystal as side bands of the main vibronic bands. They are usually interpreted as "lattice or phonon bands" of the host crystal without evidence. If this interpretation would be correct, the broad bands should shift as a whole relative to the reference band when the host crystal is changed from C_6H_6 to C_6D_6. It is seen from Table 1 that the frequency differences between the broad bands and the reference band decrease in changing the host crystal from C_6H_6 to C_6D_6. The ratio of the frequency differences between C_6H_6 and C_6D_6 hosts is in average 1.05. This is close to the ratio of the lattice vibrational frequencies of C_6H_6 and C_6D_6 crystals, which is about 1.11 and 1.04 for optical active rotational and translational phonon modes, respectively.[8] It is

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[6] I. Suzuka and M. Ito, unpublished data.

[7] The 0-0 band of the fluorescence spectrum was not observed because of reabsorption. The fine structure shown in the figures and the tables of this paper is for 0-596 cm^{-1} band which was assumed to have same structure as that of the 0-0 band.

[8] M. Ito and T. Shigeoka, *Spectrochim. Acta*, **22**, 1029 (1966).

suggested therefore that the broad bands arise from coupling with the host crystal phonons. Broadness of the bands is reasonable because all the phonons of various wave vectors *k* having quasi-continuous frequencies are able to contribute to intensity of the phonon bands.

Now, we shall consider the origin of the sharp bands. In Table 2 the frequencies of the sharp bands near the 0-0 bands of the absorption spectra of pyrazine in C_6H_6 and C_6D_6 are compared with the corresponding frequencies of the fluorescence spectra, the latter being estimated from the observed frequencies of the sharp bands near the 0—596 cm^{-1} vibronic bands of the fluoresence by adding a constant frequency of 596 cm^{-1} to them.

Table 2. THE FREQUENCIES OF THE SHARP BANDS NEAR THE 0-0 BANDS

	Absorption		Fluorescence[a)]	
	cm^{-1}	Int.	cm^{-1}	Int.
	29918	w	29917	w
Pyrazine	29912	s	29919	s
in C_6H_6	29904	v. s	29904	v. s
	29895	m	29894	m
	29916	w	29916	w
	29913	w		
Pyrazine	29908	s	29911	s
in C_6D_6	29902	v. s	29902	v. s
	29890	m	29891	w
	29871	w	29873	w

a) see the footnote in text.

Assuming the same structure for the 0-0 and 0-596 cm^{-1} bands, the fluorescence frequencies listed in Table 2 may be regarded as representing the sharp bands near the 0-0 bands of the fluorescence spectrum which would be observed in absence of reabsorption. It is seen from the table that the sharp bands of the absorption and fluorescence agree very well within 2 cm^{-1}. Furthermore, the relative intensities are parallel between the two spectra. Similar results were found also for the absorption and fluorescence spectra of pyrazine in cyclohexane crystal.[6)] We may conclude therefore that the individual sharp bands represent common origins of the absorption and fluorescence spectra. Recently, Small[9)] reported the mixed crystal spectrum of anthracene in terphenyl, in which he found three fluorescence bands coinciding in frequency with the absorption bands. He interpreted them as due to the guest molecules differently oriented in the host lattice. This interpretation seems to be applied to our present case. In Fig.3, the fine structures associated with several main vibronic bands of the phosphorescence spectrum of pyrazine in benzene crystal are compared. The spectral pattern of the sharp bands which occur mainly on higher frequency side of the most intense band in each vibronic band is considerably different for different vibronic bands. This may also be taken as an evidence supporting the above interpretation that the sharp bands arise from different guest molecules situated in different circumstances in the host crystal. The molecules situated at different sites will have different frequencies of the molecular vibrations depending on degree of distortion of the guest molecules induced by crystal field of the host lattice. Since these guest molecules give rise to their own spectra having different 0-0 bands and different vibrational structures, different patterns of the fine structures are expected for different vibronic bands. The sharp bands associated with the main vibronic bands of the fluorescence spectrum also showed different spectral patterns similar to that of the phosphorescence spectrum.

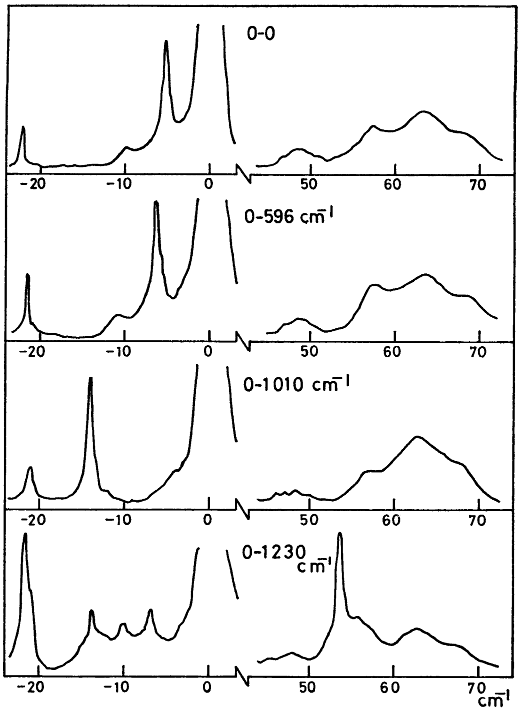

Fig. 3. Fine structures accompanied by several main vibronic bands of the phosphorescence spectrum of pyrazine in benzene crystal at 4.2°K.

In contrast to the sharp bands, the broad bands associated with the main vibronic bands of the phosphorescence spectrum, which occur mainly on lower frequency side of the strongest band in each vibronic band, are very similar in spectral feature to each other (Fig.3). As described before, when the host is replaced from benzene to benzene-d_6, these broad bands shift as a whole toward the strongest bands (hereafter, referred to as "reference band"), and this was taken as evidence supporting that the broad bands are host phonon bands. In this interpretation, we implicitly assumed that the broad bands are resulting from coupling of the host crystal phonons with the vibronic states of the guest molecule which gives the reference bands. The host crystal phonons will be able to couple also with other guest molecules which give the sharp bands other than the reference bands.

However, intensities of the phonon bands resulting from the sharp bands other than the reference bands will be much smaller than intensities of the phonon bands associated with the reference bands, because the

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9) G. J. Small, *J. Chem. Phys.*, **52**, 656 (1970).

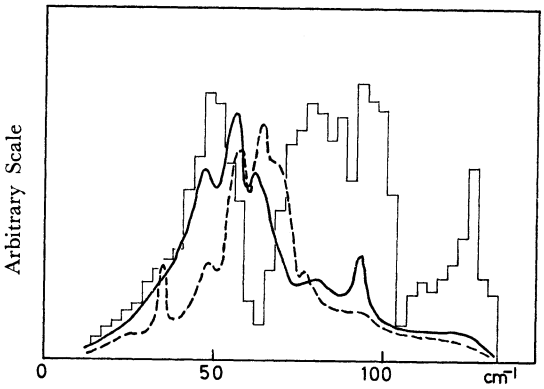

Fig. 4. Typical phonon bands of the absorption (—) and phosphorescence (----) of pyrazine in benzene at 4.2°K compared with the calculated D(ν) (—) of benzene at 135°K (taken from ref. (9)).

former are much weaker in intensity than the latter. Thus, the observed broad bands may be regarded as the phonon bands belonging mainly to the reference bands.

It may be worthwhile to mention here that the spectral pattern of the phonon bands seems not to depend on symmetry species of the molecular vibrations involved in the vibronic bands. For example, in the fluorescence spectrum we found two kinds of vibronic bands involving totally symmertric and nontotally symmetric molecular vibrations which give the same pattern of the phonon bands. This suggests that no specific selection rule is operative in coupling between the vibronic states of guest molecule and the phonons of host crystal. If it would be the case, the phonon bands should represent the density of states of the phonon, $D(\nu)$. Recently, Nakamura and Miyazawa[10] calculated $G(\nu)$ ($D(\nu)$ weighted with squared amplitude) of benzene crystal, which agrees well with that obtained from the neutron inelastic scattering experiment[11]. In Fig. 5, the $D(\nu)$ calculated by Nakamura and Miyazawa is compared with typical phonon structures of the phosphorescence and absorption spectra. According to Nakamura and Miyazawa, the peak near 50 cm^{-1} and the long tail in the region less than 50 cm^{-1} is mainly contributed from the acoustic phonons. The fact that greater part of intensity of the phonon bands is concentrated in the above frequency range suggests that the acoustic phonons of the host lattice play an important role in coupling of the electronic state of the guest molecule with the lattice vibrations of the host crystal.

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[10] M. Nakamura and T. Miyazawa, *J. Chem. Phys.*, **51**, 3146 (1969). T. Miyazawa and M. Nakamura, *ibid.*, **52**, 5972 (1970).

[11] K. W. Logan, S. F. Trevino, H. J. Prask, and J. D. Gault, *ibid.*, **53**, 3417 (1970).