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Phosphorescence of Quinoxaline-Durene Mixed Crystal — Analysis of Fine Structures and Decay Characteristics

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The phosphorescence spectrum of quinoxaline doped in durene crystal is observed at 4.2°K. The spectrum is composed of a number of sharp bands, many of which being interpreted as arising from the coupling with the ground state molecular vibrations of quinoxaline. Associated with the 0,0 and vibronic bands three weak bands were observed which are separated from the vibronic band by 19, 30 and 52 cm^{-1}. The nature of these three bands is not well understood, but it is certain that they are not due to the lattice vibrations of the durene host. The decay of the phosphorescence is investigated at fifteen different temperatures between 4.21 and 1.59°K. Above 2.41°K the decay is single exponential with a lifetime of 0.246 sec. Below 2.19°K, however, the decay is expressed as a sum of two exponential decays whose lifetimes are 0.757 and 0.093 sec. The shorter one is approximately one third of the lifetime at 4.21°K. The change of the decay characteristics at a temperature between 2.19 and 2.41°K is interpreted to be associated with the spin alignment. In terms of these data, together with the polarization ratio observed by Chaudhuri and El-Sayed, radiative and radiationless rate constants are estimated for each of the three magnetic subcomponents of the triplet state. The experimental results and their interpretation are partly in disagreement with the work by de Groot, Hesselmann and van der Waals, and the source of the discrepancy is analyzed.

Quinoxaline exhibits relatively intense phosphorescence of π,π^* nature. As is revealed from the polarization measurements carried out for rigid glass solution by El-Sayed and Brewer,[1] the phosphorescence is polarized normal to the molecular plane. This out-of-plane polarization of the phosphorescence is in line with the π,π^* nature of the phosphorescence.[2] Namely, if the contribution from the two-electron operators for spin-orbit coupling is neglected, the π,π^* triplet state of a planar aza-aromatic molecule mixes only with π,σ^* or σ,π^* singlet states, from which the transition to the ground state is polarized normal to the molecular plane.

The situation is more complicated when quinoxaline is doped in durene host. As Chaudhuri and El-Sayed[3] showed, a significant part of the phosphorescence is polarized in-plane along the long axis of the molecule. This abnormal in-plane polarization was interpreted by Chaudhuri and El-Sayed to be due to the host-guest interaction. The exact nature of the host-guest interaction is, however, not well understood.

Vibrational analysis of the phosphorescence might give us more information on the host-guest interaction. The phosphorescence spectrum at 77°K or above is, however, broad and detailed fine structure analysis is not feasible. In the present paper, effort was made to accomplish the detailed fine structure analysis for the phosphorescence spectrum observed at 4.2°K.

The path of excitation and deexcitation of the triplet state were analyzed with emphasis on the three individual magnetic subcomponents of the triplet state. For this purpose analysis of the phosphorescence decays at very low temperatures was carried out in some detail.

At temperatures not very low, the decay constant of the phosphorescence is a population weighted average of the three individual rate constants for the three magnetic subcomponents. Specifically, the rate constant k for the triplet state as a whole is expressed as

$$k = \sum_i^3 n_i k_i \qquad (1)$$

where n_i and k_i are the fraction of the population and the decay constant for the ith subcomponents, respectively. This averaging results from the fact that, in ordinary condition, spin-lattice relaxation

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1) M. A. El-Sayed and R. G. Brewer, *J. Chem. Phys.*, **39**, 1623 (1963).

2) S. P. McGlynn, T. Azumi and M. Kinoshita, "Molecular Spectroscopy of the Triplet States," Prentice Hall, New Jersey (1969).

3) N. K. Chaudhuri and M. A. El-Sayed, *J. Chem. Phys.*, **44**, 3728 (1966).

time is much shorter than the phosphorescence lifetime and that the population of any one sublevel is strayed over all the three levels. However, at very low temperatures, the spin-lattice relaxation time is expected to become longer than the phosphorescence lifetime. If this condition is realized, the phosphorescence emission would now start from each sublevel independently. The decays observed under this condition directly reflect the rate constants for the individual subcomponents. One may also obtain information regarding the population of the sublevels too.

The notations for states, rate constants and axes to be used in the following discussion are schematically shown in Fig. 1. Three magnetic subcomponents are denoted by T_x, T_y and T_z, which transform like rotations around x, y and z axis, respectively. The energy separations among three sublevels are obtained from the results of the ESR studies of Vincent and Maki.[4] The ordering of energies is consistent with the assumption of positive D and negative E. The radiative and radiationless decay constants for T_x are denoted by k_{px} and k_{qx}, respectively, and the sum of these two simply by k_x. Similar notations are adopted for decay constants for T_y and T_z. In C_{2v} point group, if the lowest triplet state is assumed to be of π,π^* $^3B_2$, the emission from T_x, T_y and T_z should be z-polarized, forbidden and x-polarized, respectively.

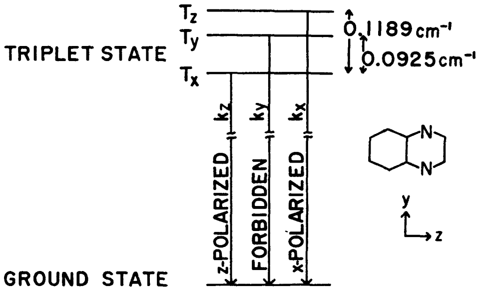

Fig. 1. Notation for states, rate constants and axes concerned with quinoxaline phosphorescence.

Experimental

Quinoxaline was purified by sublimation in a vacuum. Durene was purified by recrystallization from ethanol and by zone refining. Emission was observed for mixed crystals of 10^{-3} mol/mol in a polycrystalline form.

Emission spectra were obtained by a Spex 1700-II grating monochromator (reciprocal dispersion of 11 Å/mm) either photographically with a Kodak 103a-F plate or photoelectrically with an EMI 6256S photomultiplier tube. The locations of phosphorescence bands are determined from the photographic plates by reference to the iron arc spectrum.

The decays of the phosphorescence were measured at 462 nm using a JASCO CT-50 grating monochromator with an EMI 9529 A photomultiplier tube connected to an oscilloscope. In measurements of both spectra and decays, the exciting radiation was obtained from a 500 W high pressure mercury lamp. A Becquerel type phosphoroscope was used to separate the phosphorescence from the exciting light.

Temperature below 4.2°K was obtained by reducing the pressure above boiling helium, and the temperature was estimated from the known temperature-pressure curve.[5]

Infrared spectra of quinoxaline crystal were measured[6] at room temperature by a JASCO 402G spectrometer for the range from 4000 to 650 cm^{-1}, a Hitachi EPI-L spectrometer for the range from 700 to 250 cm^{-1}, and a Hitachi FIS-I spectrometer for the range from 300 to 50 cm^{-1}. Raman spectra of quinoxaline crystal were measured at 77°K in these laboratories by a three prism spectrograph by Yoko Kaizu, a low pressure mercury lamp being used as an exciting source.

Fine Structure Analysis

The phosphorescence spectrum of quinoxaline in durene host observed at 4.2°K is shown in Fig. 2a. The highest energy band at 21639 cm^{-1} is quite sharp and intense, and, in view of the vibrational analyses discussed below, is considered as the 0,0 band. Following this band, three relatively broad and weak bands were observed which are 19, 30 and 52 cm^{-1} apart from the 0,0 band (see Fig. 2b). As seen in Fig. 2, these four bands appear repeatedly in the whole spectral region. The fine structure analysis of the spectrum is attempted in Table 1, in which the wavenumber differences from the 21639 cm^{-1} band are compared with the molecular vibrations observed in infrared and Raman spectra. As shown in Table 1, the wavenumber separations among groups of the above mentioned four bands are in good agreement with the intramolecular vibrations of quinoxaline. Thus, as far as progressions of intramolecular vibrations are concerned, no immediate influence of the host-guest interaction is revealed.

The nature of the three weak bands always accompanied by the intense and sharp bands, however, remains unsolved. The energy separations of 19, 30 and 52 cm^{-1} are, of course, too small to be ascribed to intramolecular vibrations. One might then suppose that these fine structures are due to lattice vibration of the durene host. In fact, Hochstrasser and Small[7] interpreted some

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[4] J. S. Vincent and A. H. Maki, *ibid.*, **39**, 3088 (1963).

[5] G. K. White, "Experimental Techniques in Low Temperature Physics," Oxford Univ. Press, London (1959).

[6] We acknowledge Professor Takehiko Shimanouchi, Department of Chemistry, The University of Tokyo for the use of these spectrometers. We also thank Dr. Masako Suzuki for the experimental assistance.

[7] R. M. Hochstrasser and G. J. Small, *J. Chem. Phys.*, **45**, 2270 (1966).

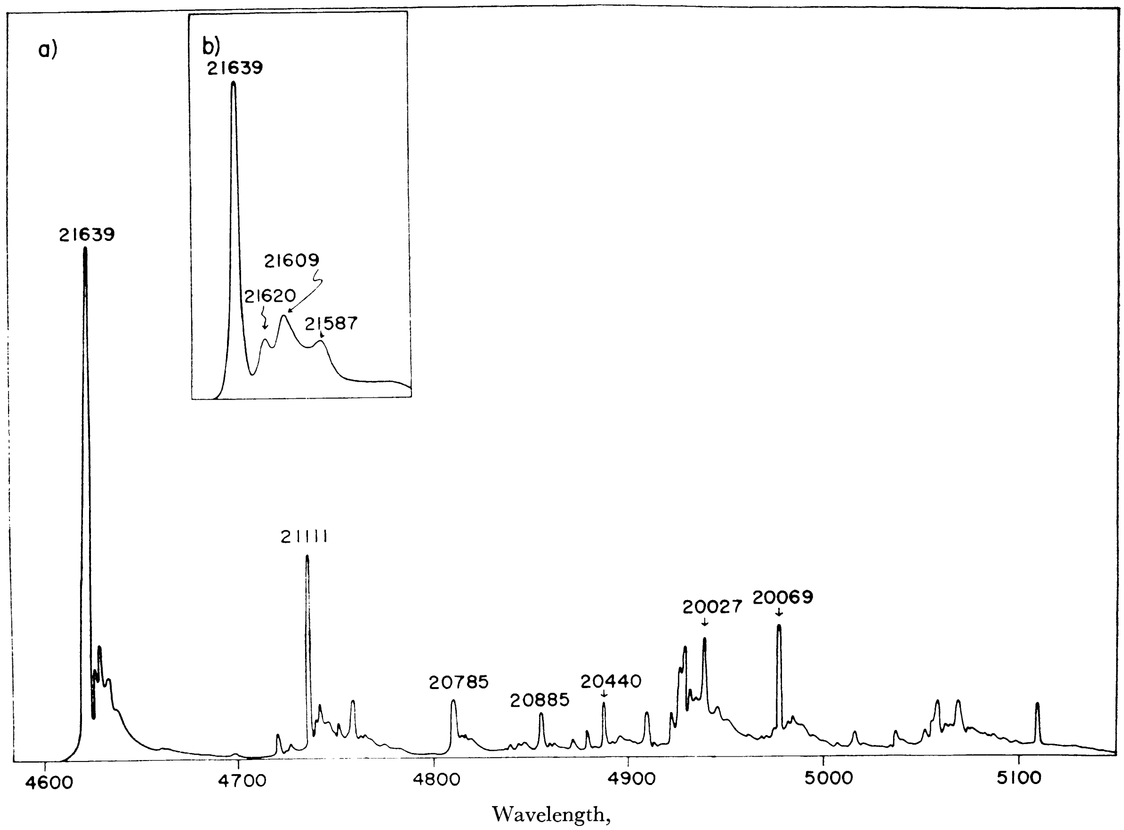

Fig. 2. a) Phosphorescence spectrum of quinoxaline-durene mixed crystal at 4.2°K. The numbers shown in the figure represent the frequencies of the main peaks in wavenumber unit.
b) Enlarged spectrum in the neighborhood of 0,0 band.

of the fine structures observed in phenanthrene fluorescence in biphenyl host to be due to the lattice vibrations of the biphenyl. Similar interpretations have also been given by Shigeoka, Koyanagi and Kanda[8] for fine structures observed in the phosphorescence of pyrazine in various hosts. In order to see if such supposition is also applied in this case, we compare the above mentioned energy intervals with the observed lattice vibrations. Raman spectra of durene crystal observed by Ito, Suzuki and Yokoyama[9] are at 50, 84 and 116 cm^{-1}; in each of these bands two rotational lattice vibrations are considered to be overlapped. As is evident, the intervals of 19 and 30 cm^{-1} are too small even compared with the rotational lattice vibrations. The translational lattice vibrations have not been observed. These frequencies may be a little smaller than the rotational lattice vibrations, but never as low as 19 cm^{-1}. If a lattice vibration of such low frequency existed, because of too large amplitude, it would manifest some unexpected specific heat properties, but such is not the case. All of these considerations lead us to conclude that the fine structures with small frequency intervals observed in the phosphorescence spectrum are not due to the lattice vibrations of the durene host.

A question still remains as to what the fine structures are due to, but cannot be answered at the moment. However, from our efforts in the defect phosphorescence observed in the crystalline states of azaaromatics[10] we regard it not meaningless to surmise that, in this case too, the phosphorescence originates from various perturbed quinoxaline molecules. It might be the guest-host interaction which causes this perturbation. Researches focussing on this point are under way and will be discussed in later publications.

Whatever the origins of the three weak bands associated with the 0,0 and other vibronic bands, the fine structure analysis presented in Table 1 clearly demonstrates that the phosphorescence

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[8] T. Shigeoka, M. Koyanagi and K. Kanda, Conference on Molecular Spectroscopy, Oct. 7, 1967, Sapporo.

[9] M. Ito, M. Suzuki and T. Yokoyama, "Excitons, Magnons and Phonons in Molecular Crystals," ed. by A. B. Zahlan, Cambridge Univ. Press (1968).

[10] T. Azumi and Y. Nakano, *J. Chem. Phys.*, **51**, 2515 (1969).

Table 1. Vibrational analysis of the phosphorescence spectrum of quinoxaline-durene mixed crystal
(All figures are wavenumbers *in vacuo*.)

Phosphorescence	Intensity	Difference from the 21639 cm^{-1} band	Assignment	IR and Raman frequencies	Phosphorescence	Intensity	Difference from the 21639cm^{-1} band	Assignment	IRamd Raman frequencies
21639	vs	0	0		20350	m	1289	1289	1289(R)
21620	m	19	19		20296	m	1343	1343	
21609	m	30	30		20280	m	1359	1359	1361(R)
21587	m	52	52		20268	s	1371	1371	1378(R)
21179	m	462	462	467(IR)	20246	m	1393	528+858	
21149	w	490	490	487(IR)	20227	s	1412	1412	1412(IR,R)
21111	s	528	528	525(IR)	20069	s	1570	1570	1570(R)
21092	w	547	528+19		20051	w	1588	1570+18	
21080	m	559	528+31		20038	w	1601	1570+31	
21061	w	578	528+50		20018	w	1621	1570+51	
21037	w	603	603	603(IR,R)	19911	vw	1729	528+1199	
21006	m	633	633	637(R)	19821	vw	1818	1818	1825(IR)
20988	w	651	633+18		19767	w	1872	528+1343	
20975	w	664	633+30		19752	w	1887	528+1359	
20781	m	858	858	862(IR)	19738	w	1901	528+1371	
20764	w	875	858+17		19698	w	1941	528+1412	
20751	w	888	858+30		19541	w	2098	528+1570	
20729	w	910	858+52		19419	w	2220	858+1359	
20585	m	1054	528+528		19412	w	2227	858+1371	
20567	w	1072	528+528+18		19368	w	2271	858+1412	
20555	w	1084	528+528+30		19215	w	2424	858+1570	
20532	w	1107	528+528+53		18910	w	2729	1359+1359	
20511	vw	1128	1128	1125(IR)	18883	vw	2750	528+528+1359	
20479	w	1160	633+528		18866	w	2773	1359+1412	
20440	m	1199	1199	1202(IR,R)	18860	vw	2779	1371+1412	
20421	w	1218	1199+18		18712	vw	2912	1359+1570	
20409	w	1230	1199+31		18658	vw	2981	1412+1570	

comes from the quinoxaline molecules and not from any impurities. This conclusion is important in interpreting the decay results discussed in the following section, especially in analyzing the discrepancies of experimental results from the work by other workers; any possible complication due to impurity emissions is eliminated.

Spin Alignment as Revealed from Decay Characteristics

The decay of the phosphorescence was measured at fifteen different temperatures between 4.21 and 1.59°K. At any temperature above 2.41°K (and below 4.21°K) decay is found to be identical; it is single exponential decay with lifetime of 0.246 sec. These lifetime data indicate that the phosphorescence is of π,π^* nature, and validate the sublevel specifications shown in Fig. 1. The shortening of lifetime, by a factor of about 10, as compared with the lifetime of π,π^* phosphorescence of aromatic hydrocarbons, say, naphthalene, is due to the presence of n,π^* singlet states, which enhance the spin-orbit coupling.[11]

Below 2.19°K, however, a drastic change in decay characteristics is observed. First, the significant part of intensity is decayed with a rate approximately three times as fast as the decay rate at 4.21°K. In addition to this decay, there exists some component of longer lifetime. At all the temperatures observed below 2.19°K, the decay is expressed as a sum of two exponential decays with lifetimes of 0.757 and 0.093 sec, the component of shorter lifetime emitting more intensely. The manner in which decay is separated into two exponential decays is shown in Fig. 3b.

Such decay behavior at lower temperatures is due to spin alignment as has already been discussed by de Groot, Hesselmann and van der Waals[12] and by Hall, Armstrong, Moomaw and El-Sayed.[13] At very low temperatures, the spin-lattice relaxation time becomes much longer than the phosphorescence lifetime, and consequently "straying" among the spin states is frozen. For quinox-

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[11] H. Baba and T. Takemura, This Bulletin, **40**, 2215 (1967).

[12] M. S. de Groot, I. A. M. Hesselmann and J. H. van der Waals, *Mol. Phys.*, **12**, 259 (1968).

[13] L. Hall, A. Armstrong, W. Moomaw and M. A. El-Sayed, *J. Chem. Phys.*, **48**, 1395 (1968).

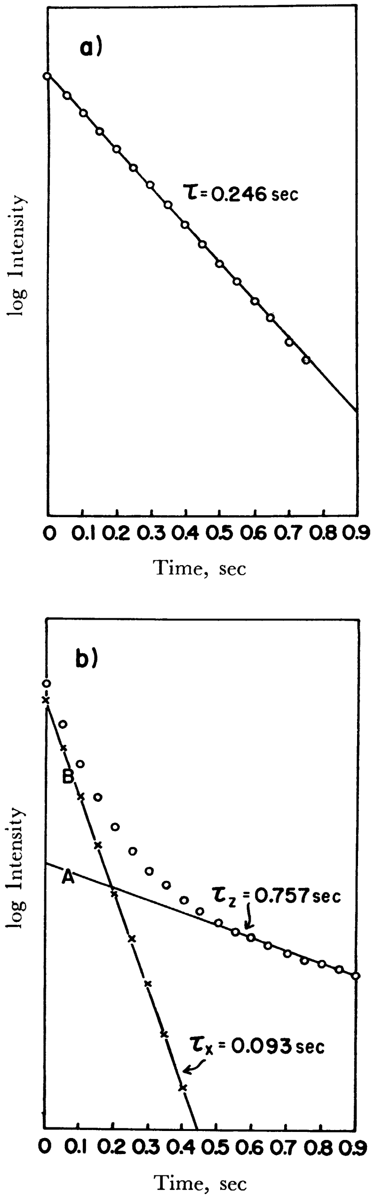

Fig. 3. Decay of phosphorescence in semilogarithmic plot. The points are experimental.
a) Observation at 77, 4.21, 4.00, 3.80, 3.45, 2.74, 2.58 and 2.41°K. The decay is single exponential, and the lifetime is 0.246 sec.
b) Observation at 2.19, 2.02, 1.97, 1.94, 1.84, 1.81, 1.74 and 1.59°K. The decay is expressed as a sum of two exponential decays whose lifetimes are 0.093 and 0.757 sec. Line A is as extrapolation from the long-time decay region. The × marks on the lower curve are differences between the experimental points and the corresponding points on Line A. Line B is drawn through these latter difference intensities.

aline-durene mixed crystal, de Groot *et al.* found that the inversion in magnitude between the spin-lattice relaxation time and the phosphorescence lifetime takes place at a temperature between 4.21 and 1.56°K. Our data indicate that this takes place somewhere between 2.19 and 2.41°K. The fact that the complete inversion of the order of the lifetimes at some temperatures in the narrow range of 0.2° may indicate that the spin-lattice relaxation time is very strongly dependent on temperature.

We shall next see if the above data could be used to estimate the decay constants for each of the magnetic subcomponents. First we note that the decay characteristics are identical at any temperatures between 1.59 and 2.19°K and also between 2.41 and 4.21°K. The identity of the decays indicates that decay constants are unchanged in the two temperature ranges. Thus we could assume that they keep constant all through 1.59 to 4.21°K.

The lifetime observed at temperatures above 2.41°K should be expressed by Eq. (1), thus

$$(k_x+k_y+k_z)/3 = 1/0.246 \tag{2}$$

Since the emission from T_y is forbidden, the two phosphorescence components observed at lower temperatures should be associated with the emission from T_x and T_z. The correspondence between the two components and the two emitting states is not determined uniquely. However, in view of the observation by Chaudhuri and El-Sayed[3] that the significant part of intensity comes from T_x, we shall assign the component of shorter lifetime as the emission from T_x.
Thus

$$k_x = 1/0.093 \tag{3}$$

$$k_z = 1/0.757 \tag{4}$$

From Eqs. 2—4, we obtain

$$\begin{aligned} k_x &= k_{px} + k_{qx} = 10.72\ \text{sec}^{-1} \\ k_y &= k_{qy} = 0.15\ \text{sec}^{-1} \\ k_z &= k_{pz} + k_{qz} = 1.32\ \text{sec}^{-1} \end{aligned} \tag{5}$$

Note that even though the emission from T_y is forbidden, the radiationless decay from this state takes place with a rate of $k_y = 0.15\ \text{sec}^{-1}$.

We shall next separate the above rate constants into the radiative and radiationless parts. The polarization ratio observed by Chaudhuri and El-Sayed[3] indicates that

$$k_{px}/k_{pz} = 9 \tag{6}$$

We assume that the rates of radiationless decays are indentical for the three subcomponents. This assumption is only based upon the observation that the rates of radiationless transitions are mostly governed by energy difference.[14] No further justification exists and we admit that the assumption might not represent reality. However, we shall examine what information we could get.

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[14] R. E. Kellogg and N. C. Wyeth, *J. Chem. Phys.*, **45**, 3156 (1966); W. Siebrand, *ibid.*, **47**, 2411 (1962).

We obtain

$$k_{qx} = k_{qz} = 0.15 \text{ sec}^{-1} \tag{7}$$

which coincides with the k_{qy} value obtained independently. The coincidence is consistent with the above assumption that all of the three radiationless decay rates are the same. The radiative rate constants are then obtained as

$$\begin{aligned} k_{px} &= 10.75 \text{ sec}^{-1} \\ k_{pz} &= 1.17 \text{ sec}^{-1} \end{aligned} \tag{8}$$

From the above estimation, we view the path of excitation and deactivation in the following way: The T_y component is non-emissive, but radiationless deactivation from this state is not nonexisting. Both of the other two states, T_x and T_z, are emissive. Observation of emission from the two states in lower temperatures reveals that at least two subcomponents are populated by intersystem crossing from singlet excited states. Contrary to our view, however, de Groot *et al.*[15] concluded, for the same system, that only the T_z component is populated by intersystem crossing and phosphorescence comes exclusively from the same states. This discrepancy is puzzling, and we try to analyze the source of the discrepancy in the following.

Comparison with, and Comment on, the Work by de Groot, Hesselmann and van der Waals. The most significant source of discrepancy between the two groups of authors is apparently the difference in experimental results. Specifically, we found, at the temperatures where spins are aligned, decays consisted of *two* different exponential decays, whereas de Groot *et al.*[12,15] reported that the decay is always *single* exponential. A question immediately arises why the two sets of experiments, both concerned with apparently the same quinoxaline-durene mixed crystals, give different results. In the experiment of de Groot *et al.*, excitation is effected for a period of 1 msec by a xenon flash lamp, whereas in our case excitation is continued for about 10 sec until further irradiation does not increase the phosphorescence signals. Apparently, excitation is more efficient in our case. We believe that this difference in excitation efficiency is the primary cause of the differences in the observed decay behaviors.

In general, the rise time of the phosphorescence is shorter than or equal to the decay time; lower efficiency in the excitation leads to longer rise time.[16] Now, suppose we have two emitting states characterized by two different decay constants. When excitation is carried out for a sufficiently long time, the population of the two states are increased to their maximum (saturated) values, and consequently the decays from the two states may be separated without much difficulty. On the other hand, if excitation is interrupted after a very short time, as in the case of flash excitation, the state of the longer lifetime is not populated as much as in that of the shorter lifetime. Consequently the emission from the state of longer lifetime may be hidden under the emission from the state of shorter lifetime. It is probably due to this latter effect that de Groot *et al.* did not find the phosphorescence component of longer lifetime. From this viewpoint we emphasize that the phosphorescence decay measurement for a system of more than one emitting states must be carried out with high efficiency of excitation.

In view of what is discussed above, let us for a moment disregard the results of the decay measurements by de Groot *et al.* and see what information concerning the decay rates is available from other data. The most meaningful experiment in this regard is the optical detection of magnetic resonance (hereafter abbreviated as ODMR) carried out by Schmidt, Hesselmann, de Groot and van der Walls[15] for perdeuterated quinoxaline and also by Forman and Kwiram[17] for perhydrated quinoxaline. In this experiment one sees how application of microwave corresponding to magnetic resonance varies the phosphorescence intensity. Both of the above two groups of authors obtained identical results. Analysis of their experimental results leads to the following three inequalities:

$$\begin{aligned} 2k_{pz} &> k_{px} + k_{py} \\ k_{py} + k_{pz} &> 2k_{px} \\ k_{px} + k_{pz} &> 2k_{py} \end{aligned} \tag{9}$$

where no assumptions or preliminary knowledge regarding the values of the rate constants are introduced. If now, in view of our experimental results, k_{py} is set equal to zero, then inequality (9) is reduced to

$$k_{pz} > 2k_{px} \tag{10}$$

This indicates that k_{pz} is larger than twice of k_{px}; it does not indicate that k_{px} is zero. It is therefore not correct to conclude that emission comes exclusively from the T_z component. If, and only if, it becomes certain that only one of the three states is emissive, then conclusion that only k_{pz} is non-zero is justified. From this viewpoint, we suggest that when one tries to see the path of de-excitation from experiments on ODMR, other data such as polarization measurements or decay measurements followed by high efficiency of excitation should be consulted.

One more comment should be added with regard to inequality (10). The inequality, which was derived from the analysis of experimental results

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[15] M. S. de Groot, I. A. M. Hesselmann, J. Schmidt and J. H. van der Waals, *Mol. Phys.*, **15**, 17 (1968).

[16] M. Nakamizo and T. Matsueda, *J. Mol. Spectrosc.*, **27**, 450 (1968).

[17] A. Forman and A. L. Kwiram, *J. Chem. Phys.*, **49**, 4714 (1968).

on ODMR, clearly contradicts the polarization results, Eq. 6, reported by Chaudhuri and El-Sayed. At this moment we have no way of judging which of the results are correct; however, if the polarization data be erroneous, the rate constant estimate given in this paper would be meaningless.

The unambiguous determination of the x and z axes of quinoxaline molecule is not an easy task since in durene host x axis of a molecule is nearly parallel to the z axis of another molecule in the same cell.[18] Nonetheless attempts to decide which of the conflicting results are correct are under way and will be treated in the future.

We wish to express our appreciation to Professor Saburo Nagakura, Professor Mitsuo Ito and Mr. Yasuo Udagawa for fruitful discussions.

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[18] J. M. Robertson, *Proc. Roy. Soc.*, **141A**, 594 (1933); *ibid.*, **142A**, 659 (1933).