Observation of the set of the three sublevel phosphorescence spectra. III. External heavy atom effect on the phosphorescence spectra of quinoxaline and 2,3-dichloroquinoxaline

<table>
<thead>
<tr>
<th>報道</th>
<th>著者</th>
</tr>
</thead>
<tbody>
<tr>
<td>雑誌</td>
<td>理化学物理学会誌</td>
</tr>
<tr>
<td>年度</td>
<td>1981</td>
</tr>
<tr>
<td>号</td>
<td>10</td>
</tr>
<tr>
<td>巻</td>
<td>74</td>
</tr>
<tr>
<td>頁</td>
<td>5335-5340</td>
</tr>
</tbody>
</table>

URL: http://hdl.handle.net/10097/52427

doi: 10.1063/1.440960
Observation of the set of the three sublevel phosphorescence spectra. III. External heavy atom effect on the phosphorescence spectra of quinoxaline and 2,3-dichloroquinoxaline

Seigo Yamauchi,a) Hiroyuki Saigusa, and Tohru Azumi

Department of Chemistry, Faculty of Science, Tohoku University, Sendai, Japan
(Received 19 February 1980; accepted 27 March 1980)

The sublevel phosphorescence spectra of quinoxaline and 2,3-dichloroquinoxaline are obtained in a light atom host such as naphthalene-$d_4$ and 1,2,4,5-tetramethylbenzene and in a heavy atom host such as 1,2,4,5-tetramethylbenzene. Only the radiative decays, but not the nonradiative decays, are susceptible to external heavy atom effect. For the phosphorescence from the in-plane sublevels significant heavy atom effect is observed for the 0-0 and some vibronic bands involving nontotally symmetric vibrations. For the phosphorescence from the out-of-plane sublevel, external heavy atom effect exists but the enhancement is very slight. These features are interpreted satisfactorily in the framework of a theory. The external heavy atom effect observed in 1,4-dibromobenzene differs considerably, and the origin of the discrepancy is discussed.

I. INTRODUCTION

Even though external heavy atom effect has been investigated rather extensively by many workers,1-9 our understanding of the mechanism is still far from satisfactory. This is mainly due to the lack of experimental data which can be directly correlated with the theoretically derived quantities. The discussion has usually been limited to the bulk rate constants of the radiative and/or nonradiative decay from the triplet state in its entirety without focussing attention on the spin sublevels and on the vibronic structures of the spectrum. The effect of external heavy atom on the properties of these molecules in heavy atom containing host (heavy atom host) we have analyzed the effect of external heavy atom on the absolute values of (i) the radiative rate constants for the individual vibronic bands in the phosphorescence emission from the individual spin sublevels, and (ii) the nonradiative decay rate constants for the decay from individual spin sublevels.

As a heavy atom host 1, 2, 4, 5-tetramethylbenzene (TBB) has been chosen. The spectral properties observed in this host are compared with those observed in naphthalene-$d_4$(N-$d_4$) host (in the case of Q) or in 1, 2, 4, 5-tetramethylbenzene (TMB) host (in the case of DCQ). Hereafter the term light atom host will be used to denote N-$d_4$ and TMB.

As in previous papers, the $x$ axis is normal to the molecular plane, and the $z$ axis is along the long axis of the molecule. The lowest triplet state belongs to $B_2(z^2)$ in $C_{2v}$ point group for both Q and DCQ.

II. EXPERIMENTAL

Q and DCQ were recrystalized from ethanol followed by vacuum sublimation. TMB and TBB were purified by zone melting (+ 150 passes). All the mixed crystals ($\sim 10^{-2}$ mol/mol) were grown with the Bridgman method.

The apparatus was similar to that described in previous papers.15,16 The experiments were performed at 1.4 K; it was confirmed that at this temperature the spin–lattice relaxation rates were negligible compared with the triplet decay rates. Total decay rate constants and relative radiative rate constants were obtained by the MIDP method. The phosphorescence spectra from individual spin sublevels were obtained by utilizing the time resolved phosphorescence spectra with or without microwave in a manner described in pervious papers.15,16

III. RESULTS

The zero field transition energies are shown in Table I. The total decay rate constants and the ratios of the radiative rate constants at the 0-0 band are shown in Table II.

The sublevel spectra are shown in Figs. 1 and 2. The ordinate scale indicates the radiative rate constant. The sublevel spectra obtained directly from experiments are scaled in such a way that the ordinate is proportional to the radiative rate constant, but the proportionality constant was at the beginning unknown. The scaling of...
Yamauchi, Saigusa, and Azumi: Three sublevel phosphorescence spectra. III

the ordinate in terms of the radiative rate constant for Q and DCQ in the light atom host was achieved in a previous paper. 16 The scaling of the ordinate for the spectra in the heavy atom host was accomplished in the following manner.

We assume that none of the radiative and nonradiative rate constants decreases upon changing the host from light atom host to heavy atom host, i.e.,

\[ k_i'(0 - \nu, H) - k_i'(0 - \nu, L) \geq 0, \]  

\[ k_i''(H) - k_i''(L) \geq 0. \]  

The notations L and H in the parenthesis denote, respectively, the light and heavy atom hosts. This assumption further leads to

\[ k_i'(H) - k_i'(L) = \sum_\nu k_i'(0 - \nu, H) \]

\[ - \sum_\nu k_i'(0 - \nu, L) \geq 0. \]  

We first examine Q in detail. If we focus attention on the 0-877 cm⁻¹ vibronic band, we obtain, from the spectral distribution of the sublevel spectra,

\[ k_i'(0 - 877, L) = k_i'(L)/25, \]  

\[ k_i'(0 - 877, H) = k_i'(H)/190. \]  

We relate these two radiative rate constants for this vibronic band by introducing unknown parameter \( \alpha \) as follows

\[ k_i'(0 - 877, H) = \alpha k_i'(0 - 877, L). \]  

The parameter \( \alpha \) measures the extent of external heavy atom effect. The assumption expressed by Eq. (1) corresponds to

\[ \alpha \geq 1. \]  

TABLE II. Total decay rate constants and the ratios of the radiative rate constants at the 0-0 band.

<table>
<thead>
<tr>
<th>Guest Host</th>
<th>( k_a/s^{-1} )</th>
<th>( k_b/s^{-1} )</th>
<th>( k_c/s^{-1} )</th>
<th>( k_a/k_b )</th>
<th>( k_a/k_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q N-d_{12}</td>
<td>11.7</td>
<td>0.88</td>
<td>0.37</td>
<td>0.009</td>
<td>0.005</td>
</tr>
<tr>
<td>TBB</td>
<td>46.4</td>
<td>16.2</td>
<td>1.99</td>
<td>0.33</td>
<td>0.039</td>
</tr>
<tr>
<td>DCQ TMB</td>
<td>2.94</td>
<td>7.14</td>
<td>0.40</td>
<td>0.10</td>
<td>0.048</td>
</tr>
<tr>
<td>TBB</td>
<td>65.1</td>
<td>53.2</td>
<td>6.58</td>
<td>0.62</td>
<td>0.081</td>
</tr>
</tbody>
</table>

\( \alpha = 1.0 \),

By combining this result with the assumption expressed by Eq. (7) we obtain

FIG. 1. The sublevel phosphorescence spectra of quinoxaline in (a) naphthalene-\( d_{12} \) host and (b) 1,2,4,5-tetrabromobenzene host.

The differences of the total radiative rate constants observed in the heavy and light atom hosts are, from Eqs. (4)-(6),

\[ k_i'(H) - k_i'(L) = k_x(0 - 877, L) \times (190\alpha - 25). \]  

On the other hand, in view of Eq. (2),

\[ k_i''(H) - k_i''(L) = [k_x(H) - k_x(L)] \leq k_x(H) - k_x(L). \]  

Therefore, from Eqs. (8) and (9),

\[ k_i'(0 - 877, L)(190\alpha - 25) \leq k_x(H) - k_x(L). \]  

Experimentally we already obtained

\[ k_i'(0 - 877, L) = 0.21 \text{ s}^{-1}. \]  

Further, from Table II,

\[ k_x(H) - k_x(L) = 34.7 \text{ s}^{-1}. \]  

Eqs. (10)-(12) lead to

\[ \alpha = 1.0. \]  

I, 2, 4, 5-tetramethylbenzene host and (b) L, e (\varepsilon_0 u < !< f-)

found unaffected by the external heavy atom host.

changed by the effect of external heavy atom host. This

i.e., the radiative rate constant for the 0-877 cm\(^{-1}\)
vibronic band in the \(T_1\) phosphorescence remains un-
changed by the effect of external heavy atom host. This
statement was found true also for 0-641 cm\(^{-1}\) vibronic
band in the \(T_1\) phosphorescence.

Similar analysis was made for DCQ. In this case, the
0-490 cm\(^{-1}\) vibronic band in the \(T_1\) phosphorescence
was found unaffected by the external heavy atom host.

Once the absolute value of the radiative rate constant
is obtained for one, or more, of vibronic bands, we can
immediately scale the whole spectra in terms of the radia-
tive rate constant. By summing up the individual radia-
tive rate constant, we obtain the total radiative rate
constant and hence the nonradiative rate constants.
These rate constants are summarized in Table III.

IV. DISCUSSION

A. Theory of external heavy atom effect

In the first place, we try to examine theoretically how
the radiative transitions are influenced by external heavy
atom effect. We basically follow the treatment developed
by Robinson\(^5\) but we extend his treatment in such a way
that we can discuss the external heavy atom effect to the
vibronic bands as well.

The zeroth order Hamiltonian is chosen as the sum of
the pure spin crude adiabatic Hamiltonians for the guest
and the host molecules. That is

\[
H_0 = H_{so}(g) + H_{so}(h) .
\]

The zeroth order wave functions are therefore expressed
as the product of the wave functions of the parentages,
and are denoted, for example, as \(|T_1S_j\rangle\): the first and
the second designations for states refer, respectively,
to the guest and the host. As usual \(S_i\) and \(T_i\) represent
the ith singlet and triplet excited states of either parent-
age. The ground state is denoted by \(S_0\).

The perturbation we consider includes the intermolecu-
lar interaction \(H_{lat}\), spin-orbit coupling \(H_{so}\), and vibronic
coupling \(H_{vtb}\). The spin-orbit coupling is approximated
as the sum of the spin-orbit coupling within the guest
molecule and that within the host molecule. The inter-
molecular spin-orbit coupling is neglected. Thus

\[
H_{so} = H_{so}(g) + H_{so}(h) .
\]

Similarly, vibronic coupling due to intermolecular vibra-
tions is neglected. Further, vibronic coupling involving
vibrations in the host molecule needs not be considered
since no vibronic bands involving such vibrations are
observed in the spectra. Thus

\[
H_{vtb} = H_{vtb}(g) .
\]

The Hamiltonian for the perturbation is thus expressed as

\[
H' = H_{lat} + H_{so}(g) + H_{so}(h) + H_{vtb}(g) .
\]

In the perturbation expansion, the ground state of either
parentage is assumed unperturbed.

We then consider how the state corresponding to the
first excited state of the guest, \(|T_1S_0\rangle\), is influenced by
the perturbation. Among various terms only those which
involve either \(|S_0S_i\rangle\) or \(|S_iS_0\rangle\) are responsible for the
radiative transitions. Thus, in the perturbation treat-
ments carried to the third order we have

\[
|T_1S_0\rangle = \sum_i |S_iS_0\rangle \frac{\langle S_iS_0|H_{so}(g)|T_1S_0\rangle}{\Delta E(T_1S_0, S_0S_i)} + \sum_{i,j} |S_iS_0\rangle \frac{\langle S_iS_0|H_{vtb}(g)|T_1S_0\rangle}{\Delta E(T_1S_0, S_0S_i)} + \sum_{i,j} |S_0S_i\rangle \frac{\langle S_0S_i|H_{so}(g)|T_1S_0\rangle}{\Delta E(T_1S_0, S_0S_i)} + \sum_{i,j} |S_0S_i\rangle \frac{\langle S_0S_i|H_{so}(h)|T_1S_0\rangle}{\Delta E(T_1S_0, S_0S_i)}
\]

Among various terms in the above expression, those which involve $H_{so}(k)$ are responsible for the external heavy atom effect; the fourth and the seventh terms meet this requirement. The contribution from these terms to the enhancement of the radiative rate constant will henceforth be expressed schematically in the following manner:

$$|T_1 S_0 \rangle \langle H_{int} | S_0 T_1 \rangle \frac{H_{so}(k)}{\langle S_0 S_i \rangle \text{dipole}} |S_0 S_0 \rangle ,$$

(20)

$$|T_1 S_0 \rangle \langle H_{int} | S_0 S_i \rangle \text{dipole} |S_0 S_0 \rangle ,$$

(21)

The dipole transition between the perturbed singlet state and the ground state is denoted by "dipole." The first mechanism represents the external heavy atom effect on the 0-0 band and also on the vibronic bands involving totally symmetric vibrations. The second mechanism represents the external heavy atom effect to the vibronic bands involving nontotally symmetric vibrations. How the contributions from these terms differ for sublevels will be discussed in the following two sections.

We assume that the guest molecules are substitutionally replaced in the TBB host. In the crystal of TBB, the molecules of equivalent sites are exactly parallel and the molecules of nonequivalent sites are arranged in such a way that their molecular planes are nearly parallel. Thus, in the guest–host interaction through $H_{int}$, the out-of-plane sublevel of the guest molecule does not interact with the in-plane sublevels of the host molecule, and vice versa. Therefore, in the following, we classify the sublevels into the in-plane and out-of-plane sublevels.

### B. External heavy atom effect on radiative rate constant at the 0-0 band

Experimentally obtained results are summarized at the tops of Table IV and V. As is clearly observed, the increments of the radiative rate constants induced by the external heavy atom effect is large for the in-plane sublevels $T_*$ and $T_y$, and small for the out-of-plane sublevel, $T_x$. In the following, we try to interpret the observation in terms of the theory developed above.

We classify the excited states of either parentage into the types $(\pi^* \pi^*)$, $(\sigma^* \pi^*)$, and $(\sigma^* \sigma^*)$. We neglect the contribution from $(\sigma^* \sigma^*)$ states in view of the large energy denominators. Further, we neglect the two center and three center spin–orbit coupling terms. Then, mechanisms expressed in (20) are further classified in the following way.

1. Mechanisms responsible for the enhancement of the emission from the in-plane sublevels:

$$|T_1 \pi \sigma S_0 \rangle \langle H_{int} | S_0 T_y \pi \sigma \rangle \frac{H_{so}(k)}{\langle S_0 S_i \rangle \text{dipole}} |S_0 S_0 \rangle ,$$

(22)

$$|T_1 \pi \sigma S_0 \rangle \langle H_{int} | S_0 T_0 \pi \sigma \rangle \frac{H_{so}(k)}{\langle S_0 S_i \rangle \text{dipole}} |S_0 S_0 \rangle .$$

(23)

2. Mechanism responsible for the enhancement of the emission from the out-of-plane sublevel:

$$|T_1 \pi \sigma S_0 \rangle \langle H_{int} | S_0 T_y \sigma \pi \rangle \frac{H_{so}(k)}{\langle S_0 S_i \rangle \text{dipole}} |S_0 S_0 \rangle .$$

(24)

In view of the energy denominators, mechanism (24) is considered least important. Furthermore, in view of the large transition dipole moment involving $(\pi^* \pi^*)$ excited states, mechanism (23) is considered by far the most important. Consequently we expect that the heavy atom enhancement is significant for the $T_*$ and $T_y$ sublevels and is less significant for the $T_x$ phosphorescence. The experimental results shown in Tables IV and V are in accord with this prediction.

### C. External heavy atom effect on the radiative rate constant at vibronic bands involving nontotally symmetric vibrations

Experimentally obtained results are extracted for some vibronic bands also in Table IV and V. Even though the effect slightly differs for each vibronic band, there is a general tendency that the enhancement is more significant for the $T_*$ and $T_y$ phosphorescence and is less significant for the $T_x$ phosphorescence.

| TABLE III. Absolute values of radiative and nonradiative rate constants. |
|---|---|---|---|---|---|
| Guest Host | $k_\pi^\pi/s^1$ | $k_\sigma^\sigma/s^1$ | $k_\pi^\sigma/s^1$ | $k_\pi^\sigma/s^1$ |
| Q | 5.3 | 0.1 | 0.1 | 6.4 |
| TBB | 40.0 | 13.2 | 1.6 | 6.4 |
| DCQ | 2.0 | 3.2 | 0.2 | 0.9 |
| TMB | 64.2 | 40.7 | 5.2 | 0.9 |
| TBB | 125.5 | 15.4 | 1.4 | 0.9 |

We examine the mechanisms expressed in Eq. (21) in more detail. The mechanisms are classified in the following way:

(1) Mechanisms responsible for enhancement of the emission from the in-plane sublevels.

(a) Vibronic bands involving \( b_2 \) vibration:

\[
\begin{align*}
   |T_1(\pi\pi)S_0\rangle \ H_{bas}\langle g | \ T_4(\pi\pi)S_o\rangle \ H_{int}\langle |S_0 T_1(\pi\pi)\rangle \ H_{so}\langle |S_0 S_1(\pi\pi)\rangle \ \text{dipole} \ |S_0 S_0\rangle, \\
   |T_1(\pi\pi)S_0\rangle \ H_{bas}\langle g | \ T_4(\pi\pi)S_o\rangle \ H_{int}\langle |S_0 T_1(\pi\pi)\rangle \ H_{so}\langle |S_0 S_1(\pi\pi)\rangle \ \text{dipole} \ |S_0 S_0\rangle .
\end{align*}
\]

(27)

(b) Vibronic bands involving either \( b_1 \) or \( a_2 \) vibration:

\[
\begin{align*}
   |T_1(\pi\pi)S_0\rangle \ H_{bas}\langle g | \ T_4(\pi\pi)S_o\rangle \ H_{int}\langle |S_0 T_1(\pi\pi)\rangle \ H_{so}\langle |S_0 S_1(\pi\pi)\rangle \ \text{dipole} \ |S_0 S_0\rangle .
\end{align*}
\]

(28)

(2) Mechanism responsible for enhancement of the emission from the out-of-plane sublevel.

(a) Vibronic bands involving \( b_2 \) vibration:

\[
\begin{align*}
   |T_1(\pi\pi)S_0\rangle \ H_{bas}\langle g | \ T_4(\pi\pi)S_o\rangle \ H_{int}\langle |S_0 T_1(\pi\pi)\rangle \ H_{so}\langle |S_0 S_1(\pi\pi)\rangle \ \text{dipole} \ |S_0 S_0\rangle .
\end{align*}
\]

(29)

With the same arguments discussed above, we expect that the enhancement is more significant for the \( T_x \) and \( T_y \) phosphorescence and is less significant for the \( T_z \) phosphorescence. This feature is exactly what is observed in Tables IV and V.

As is revealed from (21), only the vibronic bands induced by the vibronic coupling among triplet manifold is enhanced by external heavy atom effect. Any vibronic band due to the vibronic coupling among singlet manifold is not enhanced. Therefore, the vibronic bands shown in Tables IV and V are all due to the vibronic coupling among triplet manifold. In this way, by examining the external heavy atom effect, one is able to make distinction between the vibronic coupling among singlet manifold and that among triplet manifold.

The fact that the external heavy atom effect is observed for vibronic bands involving nontotally symmetric vibration is of worth attention. This observation, which is supported by the theory outlined above, contradicts with the statement that only the 0-0 band and vibronic bands involving totally symmetric vibrations should be enhanced by external heavy atom effect.

<table>
<thead>
<tr>
<th>Band</th>
<th>Sublevel, ( i )</th>
<th>( k_1^{\dagger}(0-v,L)/s^{-1} )</th>
<th>( k_2^{\dagger}(0-v,L)/s^{-1} )</th>
<th>Increment/s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-0</td>
<td>( x )</td>
<td>1.71</td>
<td>9.70</td>
<td>7.99</td>
</tr>
<tr>
<td></td>
<td>( y )</td>
<td>0.92</td>
<td>2.20</td>
<td>3.18</td>
</tr>
<tr>
<td></td>
<td>( z )</td>
<td>0.01</td>
<td>0.38</td>
<td>0.37</td>
</tr>
<tr>
<td>0-208</td>
<td>( y )</td>
<td>0.001</td>
<td>0.10</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>( x )</td>
<td>0.002</td>
<td>0.008</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>( z )</td>
<td>0.02</td>
<td>0.10</td>
<td>0.08</td>
</tr>
<tr>
<td>0-405</td>
<td>( y )</td>
<td>0.0004</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>( x )</td>
<td>0.0008</td>
<td>0.004</td>
<td>0.003</td>
</tr>
</tbody>
</table>

D. External heavy atom effect on nonradiative decay rate constants

The experimental results shown in Table III demonstrate that the radiative transitions are much more susceptible to external heavy atom effect. For any sublevels, the heavy atom enhancement on the nonradiative decay rates are found vanishingly small. The unsusceptibility of nonradiative transitions to external heavy atom effect has been discussed previously by many investigators, and therefore there is little to add any more.

E. Comparison with the external heavy atom effect observed in 1,4-dibromobenzene host

The external heavy atom effect observed in 1,4-dibromobenzene (DBB) host by Cheng, Hirota, and Mao is quite different from the results discussed above for the TBB host. The total decay rate constants are \( k_x=27 \ s^{-1}, \ k_y=10 \ s^{-1}, \) and \( k_z=26 \ s^{-1}; \) and the ratio of the radiative rate constant is \( k_1^{\dagger}: k_2^{\dagger}: k_3^{\dagger}=4.4:1:1. \) We also confirmed the results. Thus, in the case of DBB host, external heavy atom enhancement is observed for all the three sublevels equally well,

<table>
<thead>
<tr>
<th>Band</th>
<th>Sublevel, ( i )</th>
<th>( k_1^{\dagger}(0-v,L)/s^{-1} )</th>
<th>( k_2^{\dagger}(0-v,L)/s^{-1} )</th>
<th>( k_3^{\dagger}(0-v,L)/s^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-0</td>
<td>( x )</td>
<td>0.68</td>
<td>20.0</td>
<td>19.3</td>
</tr>
<tr>
<td></td>
<td>( y )</td>
<td>0.07</td>
<td>12.4</td>
<td>12.3</td>
</tr>
<tr>
<td></td>
<td>( z )</td>
<td>0.03</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>0-104</td>
<td>( y )</td>
<td>0.12</td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>( x )</td>
<td>0.001</td>
<td>0.11</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>( z )</td>
<td>0.05</td>
<td>0.80</td>
<td>0.65</td>
</tr>
<tr>
<td>0-310</td>
<td>( y )</td>
<td>0.24</td>
<td>0.50</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>( x )</td>
<td>0.03</td>
<td>0.69</td>
<td>0.05</td>
</tr>
</tbody>
</table>
We believe that the discrepancy observed in the two different heavy atom hosts are due to the difference of crystal structures of the hosts. In the case of DBB, the molecules of nonequivalent sites are arranged in such a way that their molecular planes are close to perpendicular. Therefore, if the host–guest interaction between the molecules of nonequivalent sites is nonnegligible, the distinction between the in-plane and out-of-plane sublevels is lost. The results observed for the DBB host suggest the importance of this interaction.

ACKNOWLEDGMENTS

We wish to express our thanks to Professor Takeshi Nakajima and Miss Yuko Shimizu of this Department and to Professor Noboru Hirota of Kyoto University for stimulating discussion.

16The squares of the direction cosines between the out-of-plane axis of the guest and two in-plane axes of the host are 0.087 and 0.067. G. Gafner and F. H. Herbstein, Acta Crystallogr. 13, 706 (1960).
17Hereafter, (στ*) and (στ*) states are grouped together and are denoted simply as (στ*).
20The squares of the direction cosines between the out-of-plane axis of the guest and two in-plane axes of the host are 0.35 and 0.49. S. Bezzi and V. Croatto, Gazz. Chim. Ital. 72, 318 (1942).