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# Observation of Spin Sublevel Excitation Spectra. An Application to Vibrational Analysis of T←S Absorption

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A new application of the $T_1 \leftarrow S_0$ excitation spectroscopy is presented by which absorptions to one or two of the three spin sublevels can be measured separately. This method has been applied to the $T_1 \leftarrow S_0$ excitation of crystalline 1,2,4,5-tetrachlorobenzene and 9*H*-xanthen-9-one at 1.4 K. The vibrational structures of the excitation spectra are analyzed in view of the spin selectivity observed.

The photoexcitation spectroscopy has achieved a considerable success in studying absorptions of aromatic compounds at low temperatures. In particular, the method using phosphorescence for detection has been applied successfully to observation of $T_1 \leftarrow S_0$ absorptions in crystalline aromatic compounds. In this case, triplet excitons in a crystal are formed by direct $T_1 \leftarrow S_0$ absorption and then the triplet excitation is transferred to guest or trap molecules having a lower $T_1$ energy, from which emission originates.

Since $T_1 \leftarrow S_0$ absorption requires anisotropic spin-orbit interactions, the absorption cross sections of the individual spin sublevels in a particular vibronic level are quite different from one another, resulting in formation of the state of spin alignment of triplet excitons in the crystal. It is well established that the triplet-triplet energy transfer occurs through the exchange mechanism[1] and that the spin angular momentum is conserved during energy transfer.[2] Consequently, at very low temperature, where the spin-lattice relaxation is negligible, the high degree of spin alignment in the excitons can be replicated on the guest or trap molecules in accordance with the relative orientation of the principal spin axes.

Then, if the spin alignment thus prepared in the guest or trap molecules is analyzed by applying the MIDP (microwave induced delayed phosphorescence) method to the trap emission, the spin selectivity in the $T_1 \leftarrow S_0$ excitation processes may be inferred. In fact, this technique has been developed previously[3] and applied successfully to the analyses of the spectra of *p*-chloroaniline,[4] pyrazine,[5] triphenylene,[6] and *p*-dichlorobenzene.[7]

In the present paper, a new method is described by which the $T_1 \leftarrow S_0$ spin sublevel excitation spectra can be obtained. This method is applied to neat crystals of 1,2,4,5-tetrachlorobenzene (TCB) and 9*H*-xanthen-9-one (xanthone) for the purpose of analyzing the vibrational structures of the $T_1 \leftarrow S_0$ absorptions. For successful application of this technique, some requirements have to be satisfied by the system selected. These conditions will be first described below.

## Description of the Method

Excitation spectroscopy provides information on excited states through the properties of the monitored emission. Therefore, when the emission which originates predominantly from one of the spin sublevels of the trap is monitored, the resulting spectrum would reflect the absorption cross section of the corresponding spin sublevel in the triplet state of the crystal to be examined, provided that the spin alignment produced in the triplet excitons by direct $T_1 \leftarrow S_0$ excitation is almost exactly replicated on the trap molecules. This is the essential point of the method presented in this paper. To populate the spin sublevels of the excitons in proportion to the absorption cross sections of the individual spin sublevels, it may be appropriate to use the pulse excitation method.

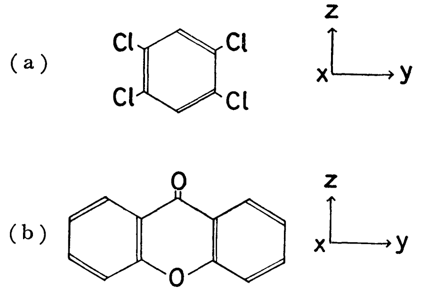

Fig. 1. Molecular structure and choice of the axis system; (a) 1,2,4,5-tetrachlorobenzene and (b) 9*H*-xanthen-9-one.

The spin alignment produced by T←S excitation plays a crucial role in this method; it should be maintained throughout the experiment which involves the processes of vibrational relaxation, energy transfer, trapping, and emission from the trap molecules. The first three processes are usually fast compared with the spin-lattice relaxation process at very low temperature. Therefore, molecules having a relatively short lifetime, such as halogenated aromatics and aromatic carbonyls, may be chosen as a trap to minimize the spin-lattice relaxation effect.

Another requirement to be satisfied by the trap molecules is that the individual spin sublevels should contribute quite differently to an emission band which is energetically resolvable for monitoring. Most of the compounds having a symmetry of $C_{2v}$ or higher are known to fulfill this requirement and may be used as a trap.

In addition, the trap molecules should enter into the crystal in such a way that the orientation of the principal spin axes of the trap relative to that of the triplet excitons can be inferred. The simplest case is an experiment on the system in which the directions

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of the spin axes of the trap triplet state are, at least approximately, coincident with those of the excitonic triplet state. In such a system, the populations of the spin sublevels in the emitting trap molecules are almost exactly proportional to the absorption cross sections of the spin sublevels in the excitons pumped by pulse excitation ($N_i \propto P_i$). Accordingly, the intensity of the phosphorescence to a selected vibrational band, $\nu$, is given by $I(\nu)=c\Sigma k_i^r(\nu)P_i$, where the sum is taken over the spin sublevels(i), $k_i^r(\nu)$ refers to the relative radiative decay rates to $\nu$, $P_i$ is the relative absorption cross sections of the individual spin sublevels, and $c$ is a proportional constant which also corrects for the sensitivity of the detection system. On the basis of the values of $k_i^r(\nu)$, the values of $P_i$ may be determined by observing the intensities of the emission to different vibrational bands. In an ideal case where the vibrational band having contribution only from one of the spin sublevels could be selected for monitoring, an absorption spectrum of that spin sublevel would be obtained. In a real system, however, contributions from the other two sublevels would not be eliminated completely, but the following examples demonstrate the usefulness of the method.

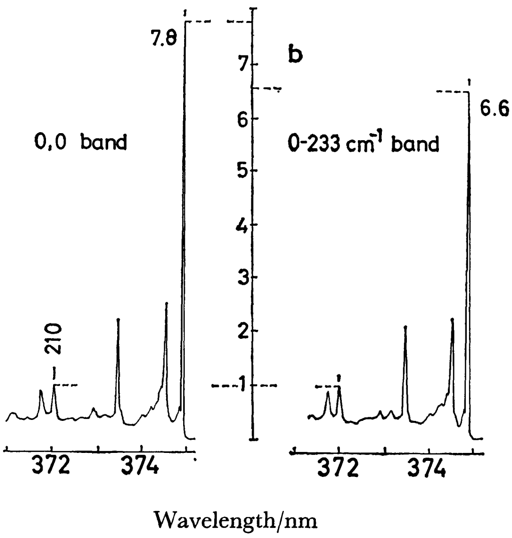

Fig. 2. The $T_1 \leftarrow S_0$ phosphorescence excitation spectra of the TCB neat crystal at 1.4 K, monitored (a) at the 0,0 band and (b) at the 0−233 cm$^{-1}$ band of the Y trap emission.

## Experimental

1,2,4,5-Tetrachlorobenzene (TCB) was purified by recrystallization and vacuum sublimation, followed by extensive zone-refining. 9*H*-Xanthen-9-one (xanthone) was recrystallized and then zone-refined. Single crystals were grown by the standard Bridgman technique.

Excitation of the crystals was performed with a Molectron DL-200 tunable dye laser equipped with a Molectron UV-1000 1 MW $N_2$ laser. Phosphorescence was monitored at right angle to excitation path through a Spex 1700 III 3/4 m monochromator. A PAR 162 boxcar integrator was used to acquire the average emission intensity for 2 ms. Other equipment for optical experiments was essentially the same as reported in the previous paper.[8]

## 1,2,4,5-Tetrachlorobenzene

A TCB crystal is triclinic below 188 K and belongs to the space group P$\bar{1}$ with two molecules in a unit cell.[9] The molecules in the translationally inequivalent lattice sites are interchanged by the action of inversion so that the molecular axes of these two are parallel. Therefore, the principal spin axes of the excitons are coincident with those of the molecule. The selection rules for the isolated molecule are expected to hold for the excitons.

The translationally equivalent molecules stack nearly plane-to-plane along the a axis with the out-of-plane molecular axis almost parallel to the a axis. Because of this card pack array of the molecules, together with the small value of the *a* lattice constant relative to the *b* and *c* lattice constants, the exchange interaction for the $\pi,\pi^*$ triplet state is largest along the a axis. In fact, the Davydov splitting, which is a measure of the interchain interaction, has been estimated to be about 1 MHz, that is orders of magnitude less than the intrachain matrix element of 0.35 cm$^{-1}$.[10] All these lead to the conclusion that the exciton migration in this system is essentially one-dimensional along the a axis and probably coherent at liquid helium temperatures. The manifestation of this nature has been discussed in great detail in the literature.[11]

In addition to the exciton, TCB crystals show phosphorescence from traps with the origin at 26626 cm$^{-1}$ (Y trap).[12] Francis and Harris[13] have reported that the electron spin transitions associated with the excitons are also observed by monitoring the Y trap emission. This evidently results from the spin selectivity of the exciton-trap interaction and, furthermore, indicates that the spin alignment in the excitons is transferred, for the most part, with electronic energy to the molecules in the Y trap site.

Figure 2 shows the excitation spectra of the TCB crystal at 1.4 K obtained by separately monitoring the 0,0 band and 0−233 cm$^{-1}$ band in the phosphorescence emission from the Y trap. There is a significant difference between the two spectra. The intensity of the 0+210 cm$^{-1}$ band relative to the intensity of the origin band is larger in the spectrum monitored at the 0−233 cm$^{-1}$ band than that at the 0,0 band. Since the emission of the Y trap originates mainly from the y sublevel at the 0,0 band and, on the other hand, predominantly from the z sublevel at the 0−233 cm$^{-1}$ band,[14] this difference can be attributed to the difference in the populations of the y and z sublevels. As mentioned above, the spin alignment in the excitons can be replicated on the Y trap without serious population rearrangement. Therefore, the observed results above indicate that the absorption to the 0+210 cm$^{-1}$ band occurs in the y sublevel in preference to the z sublevel, whereas the situation is opposite for the origin band.

A number of studies[14,15] on the phosphorescence of TCB have revealed that besides the vibronic bands due to the $a_g$ modes, only the band due to the C–Cl out-of-plane bending mode of $b_{2g}$ appears strongly in the phosphorescence spectrum and that the main mech-

Table 1. The important mechanisms for phosphorescence of TCB

| Band[a] | $k_z^r/k_y^r$ [a] | $k_x^r/k_y^r$ [a] | Mechanisms for the radiative decay[b] |
|---|---|---|---|
| 0, 0 | 0.2 | <0.02 | $T_y$ $^3B_{1u} \overset{\mathrm{so}}{\text{——}} {}^1B_{3u}$ |
| $0-233\ \mathrm{cm}^{-1}$ ($b_{2g}$) | 3.0 | <0.1 | $T_z$ $^3B_{1u} \overset{b_{2g}}{\text{——}} {}^3B_{3u} \overset{\mathrm{so}}{\text{——}} {}^1B_{2u}$<br>$T_y$ $^3B_{1u} \overset{b_{2g}}{\text{——}} {}^3B_{3u} \overset{\mathrm{so}}{\text{——}} {}^1B_{1u}$ |

a) Data for the Y trap of a TCB neat crystal; taken from Ref. 14. b) From Ref. 15.

Table 2. The important mechanisms for phosphorescence of xanthone[a]

| Band | $k_z^r/k_y^r$ | $k_x^r/k_y^r$ | Mechanisms for the radiative decay |
|---|---|---|---|
| 0, 0 | $\simeq 0.8$ | | $T_y$ $^3A_1 \overset{\mathrm{so}}{\text{——}} {}^1B_1(\sigma, \pi^*)$<br>$T_z$ $^3A_1 \overset{\mathrm{so}}{\text{——}} {}^1A_2(n, \pi^*)$ |
| $0-674\ \mathrm{cm}^{-1}$ ($b_1$) | 6.5 | 0.3 | $T_y$ $^3A_1 \overset{\mathrm{so}}{\text{——}} {}^1B_1(\sigma, \pi^*) \overset{b_1}{\text{——}} {}^1A_1(\pi, \pi^*)$<br>$T_z$ $^3A_1 \overset{\mathrm{so}}{\text{——}} {}^1A_2(n, \pi^*) \overset{b_1}{\text{——}} {}^1B_2(\pi, \pi^*)$ |

a) Taken from Ref. 18; data for the trap named site I in the neat crystal.

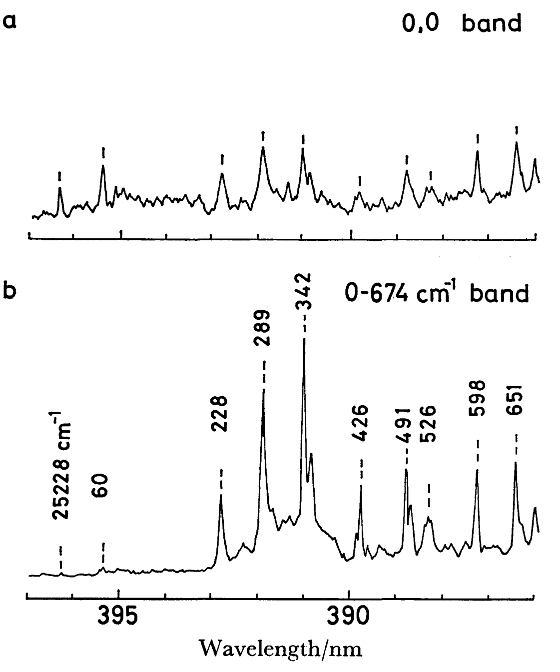

Fig. 3. The $T_1 \leftarrow S_0$ phosphorescence excitation spectra of the xanthone neat crystal at 1.4 K, monitored (a) at the 0,0 band and (b) at the $0-670\ \mathrm{cm}^{-1}$ band of the trap emission of site I.

anisms for the radiative decay are those listed in Table 1. A similar situation can be expected to hold for the absorption processes. Accordingly, the $0+210\ \mathrm{cm}^{-1}$ band can be assigned as being due to the C—Cl out-of-plane bending mode of $b_{2g}$, corresponding to that of $233\ \mathrm{cm}^{-1}$ in the ground state.

### 9*H*-Xanthen-9-one

A xanthone crystal is orthorhombic with four molecules in a unit cell.[16] The translationally equivalent molecules stack plane-to-plane along the a axis, with the out-of-plane molecular axis almost parallel to the a axis. The *a* lattice constant is small (4.894 Å) compared with the *b*(13.651 Å) and *c*(14.127 Å) lattice constants. The exciton motion in this system is therefore considered to be essentially one-dimensional along the a axis. No Davydov splitting has been resolved in the $T_1 \leftarrow S_0$ absorption, implying that the interaction between linear molecular chains is small. Therefore, the spin alignment of the excitons created by direct $T_1 \leftarrow S_0$ excitation is assumed to be appreciably preserved during the exciton migration. In addition, since the molecules in the trap sites have the orientations close to those in the host lattice, the populations of the spin sublevels of the trap molecules populated by the excitation trapping are considered to be just a replica of those of the excitons.

The $T_1 \leftarrow S_0$ absorption of the xanthone crystal was studied at 1.4 K by phosphorescence excitation method with short pulses. Some of the vibronic bands are found to behave in quite different ways from the 0,0 band as the wavelength for monitoring is changed. Figure 3 compares, as an example, the spectra obtained by monitoring the emission from the trap, named as site I, at the 0,0 band and $0-670\ \mathrm{cm}^{-1}$ band. These two bands have been reported to differ largely in the radiative activity of the z sublevel, whereas the x and y sublevels make similar contributions.[17,18] The remarkable difference between the two spectra can be attributed to the change in the relative population of the z sublevel of the site I trap as the wavelength of the excitation is changed. Furthermore, this indicates that both the spin-lattice relaxation and population rearrangement according to the relative orientation of the spin axes of donor and acceptor molecules have a little effect during the energy transfer process and is in good agreement with the expectation mentioned above that the excitation transfer may occur essentially in a one-dimensional manner.

Accordingly, the observed results imply that for excitation to the vibronic bands in the triplet manifold, such as $0+228$, $0+289$, and $0+342\ \mathrm{cm}^{-1}$, the z sublevel has preferable activity whereas the y sublevel is probably most active for the 0,0 band excitation. The y and z sublevels have been reported to gain the activity in the $T_1 \rightarrow S_0$ radiative decay through the mechanisms listed in Table 2, and similar mechanisms are expected to play a role in the $T_1 \leftarrow S_0$ absorption process. In fact, the experimental finding that the absorption cross section of the y sublevel is larger than that of the z sublevel in the case of the 0,0 band excitation is consistent with this expectation, and also the vibronic bands such as 0+228, 0+289, and 0+342 $cm^{-1}$ can be assigned as being due to the $b_1$ species in view of the intensity behavior. In addition, the vibronic bands probably due to the $a_2$ modes such as 0+670 $cm^{-1}$ are found to appear with considerable intensity at upward of 600 $cm^{-1}$ from the origin, although the bands involving $a_2$ species appear with little intensity in the phosphorescence spectrum. This is a consequence of the increased importance of the vibronic coupling with intermediate $^3A_2$ $(n,\pi^*)$ state resulting from the reduction of energy separation.

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