The $T \leftarrow S_0$ Absorption of the Acetophenone Crystal

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The polarization and Zeeman splitting of the $T \leftarrow S_0$ absorption were measured with the acetophenone single crystal at 4.2 K. From the analyses of the polarization behavior and the Zeeman splitting pattern, it is concluded that the 26110 cm^{-1} band is in-plane polarized and has the character of the n,π^* type transition.

Aromatic carbonyls show interesting properties from both spectroscopic[1–14] and photochemical[15,16] points of view since their lowest π,π^* and n,π^* triplet states are close to each other. Acetophenone is one of the most typical aromatic carbonyls and the nature of its lowest triplet state has been studied by several authors.[2,7,8,10–14] Though there have been a number of studies for this molecule in rigid glass solutions and in mixed crystals, only a couple of papers have been published concerning the crystalline acetophenone.[13,14] From the consideration of absorption intensity, Dym and Hochstrasser[13] asserted that the longest wavelength $T \leftarrow S_0$ absorption band at 26108 cm^{-1} is due to the n,π^* type transition. On the other hand, Case and Kearns[14] obtained the $T \leftarrow S_0$ absorption spectra of the acetophenone single crystal at 4.2 K by the phosphorescence excitation (PE) method and concluded that its lowest triplet state is of π,π^* type. To clarify this discrepancy, we measured the polarization and Zeeman splitting of the $T \leftarrow S_0$ absorption band of the acetophenone single crystal. In our preliminary report[17] on this subject, we indicated that the 26108 cm^{-1} band was due to the π,π^* type transition. Thereafter, we have accurately determined the crystal structure of acetophenone by the X-ray crystal analysis technique.[18] In the present paper, we report the analysis of the polarization and Zeeman splitting data made on the basis of the newly determined crystal structure.

Experimental

Acetophenone single crystals were grown from ethanol solutions. The crystal axes were determined with the aid of the X-ray diffraction technique. Since only thin crystals were obtained, three or four pieces of the crystals were piled up for the measurement of the $T \leftarrow S_0$ absorption.

Polarization of the $T \leftarrow S_0$ absorption was measured in a usual way. Light from a 500 W xenon lamp was passed through a home-made polyvinyl alcohol-iodine polarizer[19] which was set in front of a sample in liquid helium, and focussed on the sample. Transmitted light was detected by a Spex 1700-II grating monochromator equipped with an EMI 6256S photomultiplier tube.

To obtain a strong magnetic field enough for the measurement of the Zeeman splitting in the $T \leftarrow S_0$ absorption bands, a solenoid type superconducting magnet was prepared. A superconducting wire (Supercon T48B, National Research Co.) was coiled on a brass bobbin ($20\phi \times 80$ mm) 15400 turns. Its main properties are as follows: the coil impedance is 90 Ω, the inductance is 7.4 mH at room temperature, the critical field is 50000 Oe, and the critical current is 24 A at 4.2 K.

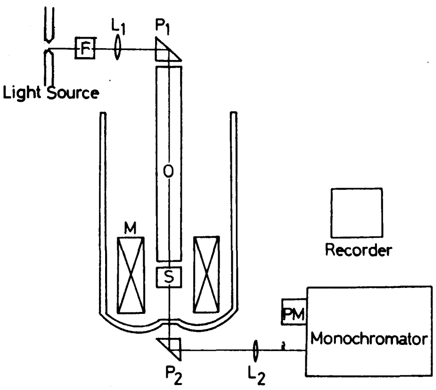

Fig. 1. Experimental setup for the Zeeman splitting measurement.
F, filter; L_1, L_2, lenses; P_1, P_2, prisms; O, optical pipe; S, sample holder; M, superconducting magnet; PM, photomultiplier tube.

Experimental arrangement for measuring the Zeeman splitting in the $T \leftarrow S_0$ absorption is schematically shown in Fig. 1. Light from a 1 kW xenon lamp was focussed on a prism and led into a sample surrounded by the superconducting magnet. Transmitted light passing through a window at the bottom of a cryostat was led into a Spex 1700-II monochromator. Magnetic field strength was monitored by a field plate (FP15V1, Siemens A. G.) inserted in the sample holder.

Results and Discussion

Polarization of the $T \leftarrow S_0$ Absorption. Figure 2 shows a polarized $T \leftarrow S_0$ absorption spectrum observed with the (110) plane of the acetophenone crystal. The

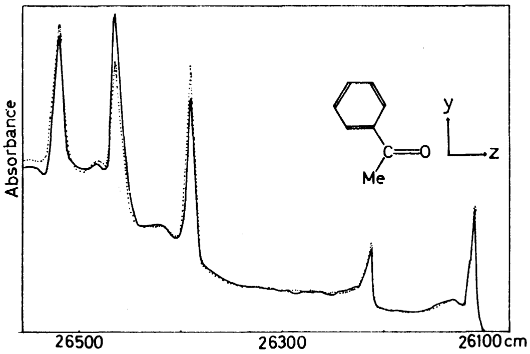

Fig. 2. Polarized $T \leftarrow S_0$ absorption spectrum.
Light propagation is perpendicular to (110). The solid and broken lines indicate the absorbances polarized parallel and perpendicular to $[1\bar{1}1]$, respectively.

solid and broken lines in the figure show the absorption spectra polarized, respectively, parallel and perpendicular to [1Ī1]. As has been reported earlier,[13,14] strong bands appear at 26110, 26389, 26455, and 26520 cm^{-1}.

The observed longest wavelength band at 26110 cm^{-1} has been assigned to the 0–0 band of the transition to the lowest triplet state,[13,14] and we will mainly focus our attention to this band. Polarization ratio ($P=D_{//}/D_{\perp}$) is 1.0±0.3 for this band. Here $D_{//}$ and $D_{\perp}$ are the absorbances for linearly polarized light whose electric vectors are, respectively, parallel and perpendicular to [1Ī1]. Molecular axes, x, y, and z are taken to be perpendicular to the molecular plane and perpendicular and parallel to C=O in the plane, respectively (see Fig. 2).

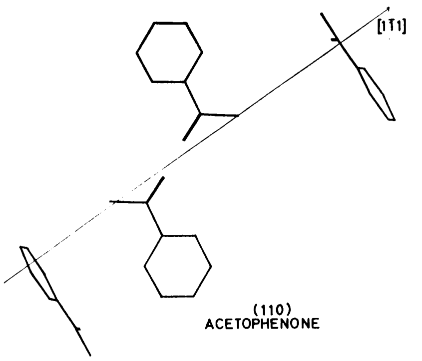

Fig. 3. (110) Projection of the structure of the acetophenone crystal.

The molecular orientation in the acetophenone crystal was determined by the X-ray crystal analysis technique.[18] The projection of the molecules in a unit cell on the (110) plane is shown in Fig. 3. From the crystal analysis data and the observed polarized spectrum shown in Fig. 2, it is concluded that the transition under consideration is polarized within the molecular plane. In order to determine the direction of the polarization within the plane, the polarization values (P) for various directions of the polarization in the plane are calculated and are shown in Fig. 4. From the figure the direction of the polarization under consideration is concluded to be inclined by ~40° or ~110° from y axis. The former and the latter directions of the polarization will be denoted by Polarizations I and II, respectively.

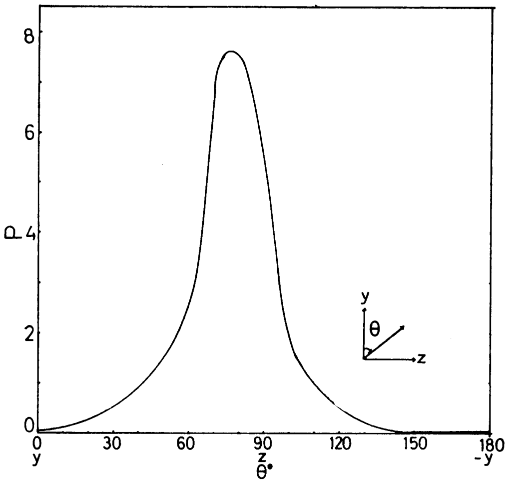

Fig. 4. Polarization ratio (P) calculated in the molecular plane.

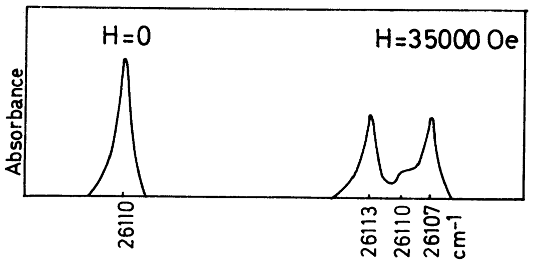

Fig. 5. Absorption profiles of the 26110 cm^{-1} band measured under the magnetic field of zero and of 35000 Oe. The field is perpendicular to (110).

The Zeeman Effect upon the T←S_0 Absorption. In Fig. 5, the Zeeman splitting pattern for the 26110 cm^{-1} band of the T←S_0 absorption at 4.2 K is shown. The directions of magnetic field and light propagation are perpendicular to the (110) plane. Magnetic field strength is 35000 Oe.

To obtain the relative intensities among the Zeeman levels quantitatively, we analyzed the spectrum by the computer simulation method. The band shape is assumed to be of the Gaussian type. Then, absorbance $D^\circ(a)$ at a cm^{-1} at zero field, is written as follows:

$$D^\circ(a) = D_{\max}\exp\left(-(a-m)^2/2\sigma^2\right)$$

At high field, the pattern of the splitting may reasonably be calculated by neglecting the contribution from the zero-field splitting parameters. Assuming that for each split component σ is invariant with magnetic field, absorbances of the split sublevels, $D_1(a)$, $D_0(a)$, and $D_{-1}(a)$, are expressed as follows:

$$D_0(a) = \alpha\beta\exp\left(-(a-m)^2/2\sigma^2\right)$$
$$D_{\pm1}(a) = \beta\exp\left(-(a-m\mp\Delta E)^2/2\sigma^2\right)$$

where, $\alpha=D_0(m)/D_{\pm1}(m\pm\Delta E)$, ΔE is Zeeman energy (cm^{-1}), and β is the normalization term which keeps the total integrated intensity invariant with magnetic field. By comparing the observed and calculated band shapes, the value of α was determined to be 0.22 for the 26110 cm^{-1} band.

Characteristics of the 26110 cm^{-1} Band. Let us consider the character of the 26110 cm^{-1} band in detail. First, we examine the polarization of the absorption. Assuming that the acetophenone molecule is planar, the expected polarizations of the T←S_0 absorptions are shown in Table 1. The experimental result that the observed absorption is polarized in-plane indicates that the relevant triplet state is one of either T_y and/or T_z of the n,π* state or T_x of the π,π* state. Usually, the former possibility is assumed on the basis of the estimated magnitude of the matrix elements. However, we shall try to give the assignments from the experimental view points.

To make the assignment more concrete, let us consider the α value of the Zeeman splitting of the transition obtained above. Let absorbances for the transitions

TABLE 1. POSSIBLE POLARIZATION OF THE $T \leftarrow S_0$ TRANSITION

Triplet state	Active sublevel	Polarization
n, π^*	T_x	out-of-plane
	T_y, T_z	in-plane
π, π^*	T_x	in-plane
	T_y, T_z	out-of-plane

Here we assumed only that the acetophenone molecule is planar. The contribution of the three-center integrals is considered in the spin-orbit coupling calculation.

of the Zeeman levels, T_1^i, T_0^i, and T_{-1}^i of the i'th molecule in the crystal be denoted by D_1^i, D_0^i, and D_{-1}^i.[20] (We hereafter use the superscript and subscript, i, to denote the position of the molecule in the crystal.) We obtain the following equation:

$$\begin{bmatrix} D_1^i \\ D_0^i \\ D_{-1}^i \end{bmatrix} = c \begin{bmatrix} \frac{1-l_i^2}{2} & \frac{1-m_i^2}{2} & \frac{1-n_i^2}{2} \\ l_i^2 & m_i^2 & n_i^2 \\ \frac{1-l_i^2}{2} & \frac{1-m_i^2}{2} & \frac{1-n_i^2}{2} \end{bmatrix} \begin{bmatrix} U_x^i \\ U_y^i \\ U_z^i \end{bmatrix} \qquad (1)$$

where, c is a proportionality constant, l_i, m_i, and n_i are direction cosines of the molecular axes, x, y, and z, respectively, with regard to the field direction, and U_x^i, U_y^i, and U_z^i represent the contribution to the transition intensity from the respective sublevels at zero field.

Since, in a crystal, α is represented by the equation,

$$\alpha = \sum_i D_0^i / \sum_i D_{\pm 1}^i \qquad (2)$$

α can be calculated with the aid of crystallographic and polarization data. Assuming that only one sublevel is the active one,[21] α's were calculated as shown in Table 2. From the table, it is clear that there are three cases in which the calculated α-values are reasonably close to the observed value for the 26110 cm^{-1} band (α=0.22), *i.e.*, the active sublevel, T_y, with Polarizations I and II (calculated α's are both 0.18), and the active sublevel, T_z, with Polarization II (calculated α is 0.16). Thus, we may conclude that the active sublevel is not T_x. Then, in conjunction with the polarization data discussed above, the possibility of π,π^* state is discarded. It is therefore concluded that the observed transition at 26110 cm^{-1} has the character of the n,π^* type, and the active sublevel is either T_y or T_z. Unfortunately, from the experiments discussed in this paper, we are unable to determine which of the sublevels T_y or T_z is the active state.

TABLE 2. THE VALUES OF α CALCULATED FOR THE ACETOPHENONE CRYSTAL

Active sublevel	Polarization I	Polarization II
T_x	2.17	10.7
T_y	0.18	0.18
T_z	1.47	0.16

Our conclusion on the 26110 cm^{-1} band agrees with the assertion made by Dym and Hochstrasser,[13] but disagrees with the conclusion of Case and Kearns.[14] The result of the latter authors seems to be ambiguous since they did not use the accurate crystal structure of acetophenone for the analysis of the polarized PE spectra.

We also analyzed the 26389 cm^{-1} band which was assigned to the n,π^* triplet state by Case and Kearns. From P=0.8±0.3 and α=0.27, this band has also the character of the n,π^* type transition.

In the preliminary paper,[17] we calculated α with the aid of Eq. (1) on an inadequate assumption,[22]

$$U_j^i = U_j \quad (j=x, y, z)$$

and were led to the misinterpretation that the 26110 cm^{-1} band had the character of the π,π^* type transition.

It may be emphasized that our result is concerned only with the transition character of the longest wavelength band at 26110 cm^{-1} and cannot give any conclusion about the nature of the upper state of this band itself. In this connection, it may be necessary to mention the result obtained by Cheng and Hirota[12e] who studied the dynamic properties of the lowest triplet state of the acetophenone trap in its crystal with the aid of the microwave phosphorescence double resonance technique. From the analysis of the results, they concluded that the lowest triplet state is the π,π^* state mixed with the nearby n,π^* triplet state and that the main emissive spin sublevel is T_z. As they discussed, however, the radiative character of the lowest triplet state is mainly controlled by the n,π^* component which contributes to the state only by a few per cent. Therefore, our result on the transition character of the 26110 cm^{-1} band is not inconsistent with their result.

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21) This assumption is reasonable, since, for most aromatic carbonyls, only one sublevel predominantly contributes to the T←S$_0$ transition. See Ref. 12.

22) This assumption is not adequate, because the U_J^t values depend on the positions of molecules in a crystal.