The Triplet State of Acenaphthenequinone Crystals Studied by Means of Zeeman Spectroscopy

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The origin peak for the lowest singlet-triplet absorption transition of acenaphthenequinone crystals has been observed at 17981.7 cm^{-1} at 4.2 K. From the direction of the polarization and the Zeeman intensity pattern at 50 kOe, the lowest triplet-state configuration is identified as $^3B_1(n\pi^*)$. The transition to the state from the ground state gains its intensity from the z-polarized $^1A_1(\pi\pi^*)$—$^1A_1$ transition through the y-component in the spin-orbit interaction.

The phosphorescent emission of acenaphthenequinone has been reported to occur in various kinds of solvents[1,2] and in the vapor phase.[3] The spectral features, solvent effect, and lifetime are indicative of a triplet $n\pi^*$ emitting state. They, however, do not present information on the mechanism of spin-orbit coupling, through which the emission gains its intensity. If the emitting state were a pure triplet state, a radiative transition back to the ground singlet state would be forbidden by the spin-multiplicity rule. The phosphorescent emission indicates that the triplet state contains some singlet character through a spin-orbit interaction between the state and perturbing singlet states, and that the ground state contains a small admixture of a triplet character.

The transition from a ground state to a triplet state assumes a polarization of the transition to a perturbing singlet in the first-order approximation. Measurements of the polarized absorption spectra for single crystals will determine the polarization of the transition, and Zeeman spectroscopy will elucidate the mechanism of the spin-orbit interaction. In the presence of a sufficiently high, steady magnetic field, a triplet state splits into Zeeman levels which can be denoted by their magnetic quantum numbers. The relative probability for radiative transitions between the individual Zeeman levels and the ground state depends on a route effective in the spin-orbit coupling.

In this paper we will present sufficient experimental proof for the assignment of the lowest triplet-state configuration for acenaphthenequinone by determining both the polarization in absorption and an effective route in the interaction.

Experimental

Acenaphthenequinone (Tokyo Kasei Organic Chemicals) was purified by recrystallization three times from *o*-dichlorobenzene and then by repeated sublimation at 160 °C *in vacuo*. It could not be zone-refined, because it decomposed thermally upon prolonged heating at elevated temperatures. Single crystal platelets, *ca.* 30 μ thick with an area of *ca.* 6×3 mm^2, were obtained by sublimation. The platelets were found to be elongated along the c-axis, with the ac plane well developed, by X-ray diffractometry.

A crystal was mounted in an Oxford optical cryostat containing a 55 kOe superconducting magnet, and the absorption spectra were observed at 4.2 K. The spectra were analyzed with the aid of an NLM-E2M spectrometer with an Echelles grating in a 2-meter Czerny-Turner mount. The reciprocal dispersion at 550 nm was 0.068 nm mm^{-1} in the 10th order. They were photographed with Fuji spectroscopic plates and recorded with the aid of an HTV R189 photomultiplier tube and electrometer amplification. An Ushio 2 kW xenon arc was used as the light source, while a Polaroid HN-32 film placed between the crystal and the spectrometer acted as the polarizer.

The phosphorescence of a crystal immersed in liquid helium was excited by 365 nm radiation filtered from an ORC 1 kW superhigh pressure mercury arc through a $CuSO_4$ aqueous solution and Toshiba UV-DlC and UV-D25 filters.

Results and Discussion

The first peak was observed at 555.97 nm (17981.7 cm^{-1}) in the a-polarized absorption spectrum for a 30 μ thick crystal. The second peak, about 120 times stronger than the first one, was observed at 499.87 nm (19999.5 cm^{-1}). Under a magnetic field, the former was found to split into three lines, but the latter did not split, so the former could be assigned to the transition to a state of a triplet character, while the latter was assigned to a state of a singlet character. We could not find any prominent peak of a triplet character in the spectral region between these two peaks. Most of the intensity for the singlet-triplet transition lies in the first peak, which seems to show the feature of being orbitally allowed.

The phosphorescence spectrum observed at 2 K showed its first peak at 557.77 nm (17924 cm^{-1}). It is taken as the electronic origin of the phosphorescence. The spectral feature is also indicative of an orbitally allowed transition, the first peak being strongest in intensity in the spectrum. Another strong peak was found to be located at 1719 cm^{-1} from the origin. It is identified as the transition from the origin level to the ground-state vibrational level of the carbonyl stretching mode. The corresponding frequency in the Raman spectrum is 1724 cm^{-1}.[4] The good agreement between the values indicates that the phosphorescence originates not from an impurity but from crystalline acenaphthenequinone, probably from an X-trap level.

From these considerations, the first peak observed in the absorption spectrum is assigned to the origin for the lowest singlet-triplet transition. The second peak is assigned tentatively to the origin for the singlet-singlet transition.

The molecule is planar in a crystal, belonging to the C_{2v} point group. The z-axis is taken as the molecular twofold axis, and the z, y-plane, as the plane of the molecule. The z-axis is approximately parallel with the crystallographic a-axis.[5] The polarization ratio for the triplet origin peak was found to be $I_a/I_c=7.4+1.1$. The I_a/I_c ratios can be expected from the orientational data of the molecule to be 0.14, 0.24, and 6.4 for the x, y, and z polarizations respectively. The observed ratio indicates that the origin peak is predominantly z-polarized.

On the other hand, the singlet origin peak showed a polarization ratio of less than unity. This fact indicates that the peak is not z-polarized. More intense bands of a singlet character were observed around 22000 and 23000 cm^{-1} in the absorption spectrum for a crystal.

Figure 1 shows the Zeeman-absorption-intensity pattern for the triplet origin peak. The pattern was observed for a 30 μ thick crystal with the magnetic field directed along the b-axis, which is approximately perpendicular to the molecular z-axis. The single peak split into three sublines, the central line being found to be the most prominent in the magnetic-field direction mentioned above. The intensity ratio of the central line, I_0, to the wing lines, $I_{\pm1}$, was found to be 13 at the field of 50 kOe.

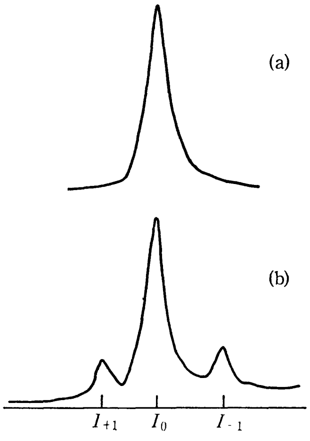

Fig. 1. Zeeman absorption pattern observed with the aid of a photomultiplier tube.
(a) $H=0$, (b) $H=50$ kOe, I_{+1}: 17985.8, I_0: 17981.7, I_{-1}: 17976.4 cm^{-1} (H//b, E//a).

If only one of the spin-orbit coupling routes is active in a spin-orbit interaction mechanism, the intensity ratio is expressed by:

$$\frac{I_0}{I_{\pm1}}=\frac{2\rho}{1-\rho}, \tag{1}$$

where ρ is the squared direction cosine of the molecular axis with respect to the crystal axis along which a magnetic field is directed.[6] The calculated ratios are 0.29, 14.0, and 0 for the x, y, and z routes respectively, with the magnetic field directed along the b-axis of the crystal. Only when the y route is active, the central line is expected to be stronger than the wing lines. The experimental finding is consistent only with the route involved in the spin-orbit coupling being y (a B_1 representation in the C_{2v} point group).

A simple molecular orbital description of acenaphthenequinone leads to the prediction that the lowest triplet states are those corresponding to the lowest singlet $n\pi^*$ states, A_2 and B_1. Here we may conclude from the experimental results that the lowest triplet state belongs to $^3B_1(n\pi^*)$, and that the transition to this state gains its intensity mainly from the z-polarized $^1A_1(\pi\pi^*)-^1A_1$ transition through the y-route in the spin-orbit coupling mechanism. An intensity stealing from an allowed triplet-triplet transition is possible, but a large energy separation between a perturbing triplet and the ground state would reduce its contribution.

References

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