Factor Group Splitting and the Lowest Triplet State of Tetrachlorophthalic Anhydride Crystals

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(Received April 22, 1977)

The electronic configuration of the lowest triplet state for tetrachlorophthalic anhydride (TCPA) was determined to be $B_2(\pi\pi^*)$ by means of Zeeman spectroscopy. The electronic origin for the singlet-triplet absorption of a TCPA single crystal was found in the region of 421.3 nm at 1.7 K. The first peak in the absorption spectrum was found to possess two components; the one observed at 23726.1 cm^{-1} corresponds to the transition to the B_u, and the other observed at 23728.5 cm^{-1} to that to the A_u triplet factor group state. The splitting between the two states is 2.4 cm^{-1}.

The lower excited triplet $n\pi^*$ and $\pi\pi^*$ states of aromatic carbonyls are closely spaced and change their energies differently under the influence of environments (solvents and/or host molecules) or substituent effects. The properties of these nearby triplet states have been the subject of numerous spectroscopic and related studies in recent years.[1] In previous papers we attempted to explain the excited triplet states of aromatic quinones.[2] As an extension of these studies, we take up tetrachlorophthalic anhydride (abbreviated to TCPA hereafter). TCPA is a typical electron acceptor and forms stable charge-transfer complexes with a number of aromatic compounds. Although much effort has been made in understanding spectroscopic properties of TCPA charge-transfer complexes, the excited triplet states of TCPA in a single crystal appear to be less understood.

The present study was undertaken in order to clarify the electronic configuration of the lowest triplet state of TCPA by means of Zeeman spectroscopy. In principle, the electronic configuration of a triplet state can be assigned by determining both the polarization in absorption and an effective route in the spin-orbit interaction. This is because the transition from the ground state to the triplet state in question is assumed to gain its intensity from the transition from the ground state to a perturbing singlet state through the spin-orbit coupling between the triplet state and the perturbing singlet state in the first-order spin-orbit interaction mechanism. In case that a perturbing triplet state is located closely to the triplet state in question, the intensity stealing from the transition between these triplet states must also be taken into consideration. In this work both the direction of polarization in the singlet-triplet absorption transition and the Zeeman intensity pattern were observed for thick TCPA single crystals.

Experimental

The experimental procedures were the same as described in the previous papers.[2] TCPA (Tokyo Kasei Organic Chemicals) was purified by zone-refining for 40 passes with additional 40 passes, and then grown into a single crystal from the melt. Crystal samples with suitable size, about 5×5 mm^2 in area and 3—18.4 mm in thickness, were taken from the crystal, and their faces were identified by the X-ray diffraction method. The reciprocal dispersion of an NLM-E2M spectrometer used for absorption measurements was 0.053 nm mm^{-1} at 420 nm in the 13th order of an Echelles grating. Phosphorescence of a crystal immersed in liquid helium was excited by 365 nm radiation from an ORC 1 kW superhigh-pressure mercury arc.

Results and Discussion

Figures 1 and 2 show the singlet-triplet absorption and the phosphorescence spectra of a TCPA single crystal at 1.7 K, respectively. The first peak in the absorption spectrum was found in the region of 421.3 nm and that in the phosphorescence spectrum at 422.2 nm (23677 cm^{-1}). The intensity of the first absorption peak was measured for the light polarized along each crystallographic axis. The polarization ratio I_a^*/I_c was found

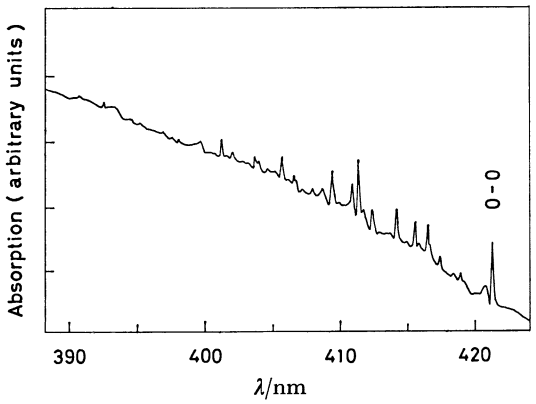

Fig. 1. The c-polarized singlet-triplet absorption spectrum of a TCPA crystal at 1.7 K; broad background due to a xenon arc light source.

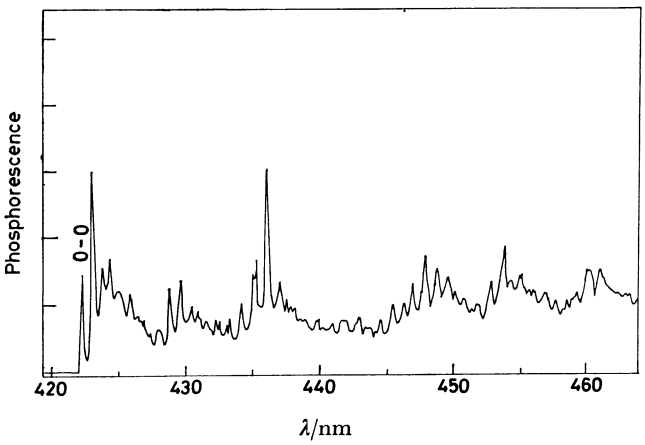

Fig. 2. The phosphorescence spectrum of a TCAP crystal at 1.7 K.

to be 0.53 and the ratio I_c/I_b to be 1.6. This peak was found to split into sublines upon the application of a magnetic field. From these results, the first peak is assigned to the origin of the lowest singlet-triplet transition for crystalline TCPA. Other intense, sharp absorption peaks were found at 24010.3, 24061.5, 24139.1, 24246.7, 24308.3, 24333.8, 24425.9, and 24641.5 cm^{-1} in the spectral region to 400 nm. No absorption peak was observed in the region between 400 and 380 nm, but a broad absorption band with polarization different from the first peak was found at 370 nm (27000 cm^{-1}).

Figure 3a shows the high-resolution absorption spectrum of the first peak for a 18.4 nm oriented crystal with the light propagating along the b axis and polarized along the c axis. The peak was found to possess two components, O_1 at 23726.1 cm^{-1} and O_2 at 23728.5 cm^{-1}. The intensity ratio of the O_1 to the O_2 components, $(I_1/I_2)_c$, was found to be 0.14. The intensity ratio obtained through the light propagating along the c axis, however, depended on the direction of polarization of light. The ratios were found to be 0.07 for the light polarized along the a* axis and 1/0.13 for the light polarized along the b axis.

Upon the application of a magnetic field of 50 kOe along the b axis, the O_2 component observed through the c-polarized light was found to split into two sublines with a separation of about 9.5 cm^{-1}, and the O_1 component remained unchanged, as shown in Fig. 3b. Upon the application of a magnetic field along the a* axis, there appeared five sublines in total, originating from both components, and their intensities were dependent on the polarization of light used for the observation (Fig. 4a).

All the experimental results mentioned above can be reasonably explained in terms of the scheme that the spatial symmetry of the lowest triplet state for TCPA belongs to $B_2(\pi\pi^*)$, and the O_1 and O_2 components in the absorption spectrum correspond to the transitions to

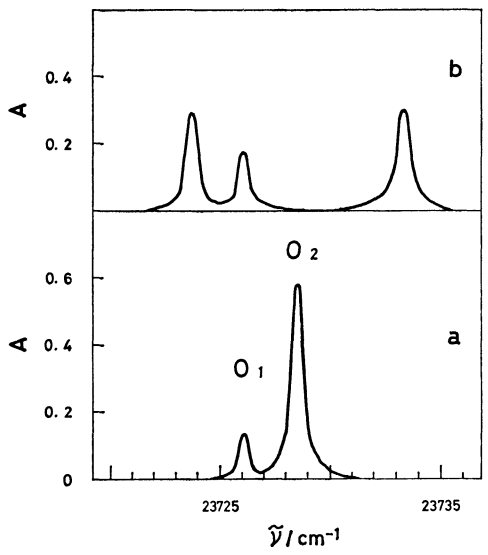

Fig. 3. The electronic origin of the c-polarized singlet-triplet absorption spectrum of a TCAP crystal at 4.2 K. (a) $H=0$, (b) $H=50$ kOe, H//b.

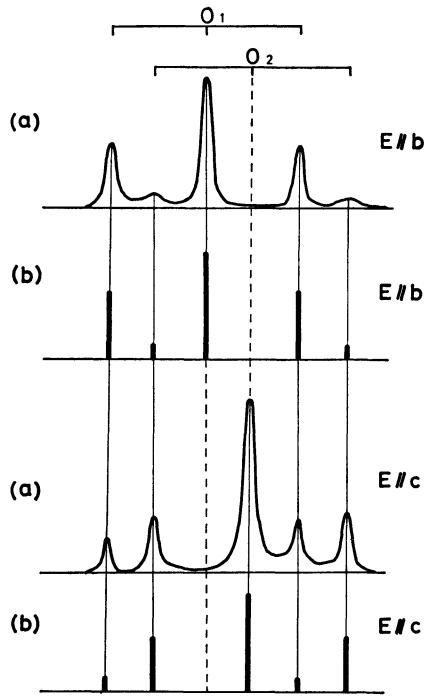

Fig. 4. Zeeman absorption patterns of a TCAP crystal. A magnetic field of 50 kOe was applied along the a* axis.
(a) The observed spectra, (b) the calculated intensities for the scheme of the x-polarized transition with the z-route in the spin-orbit coupling.

the B_u and A_u triplet factor group states, respectively.

The crystal structure of TCPA gives the space group symmetry C_{2h}^5 with four molecules per unit cell. The molecule in a crystal can be regarded as planar, belonging to the C_{2v} point group.[3] The molecular framework z-axis is taken as the molecular twofold axis, and the z,y-plane as the plane of the molecule. If we assume that only one route is active in mixing molecular singlet and triplet states through the spin-orbit coupling, the transition to the A_u state is expected to split into two wing sublines $I_{\pm 1}$, while that to the B_u state to remain unchanged, showing only the central subline I_0, when a magnetic field is applied along the b axis and the absorption is observed through the c-polarized light. The intensity ratio of I_0 to $I_{\pm 1}$ is expressed by

$$\left(\frac{I_0}{I_{\pm 1}}\right)_c = \frac{2m_u^2}{1-m_u^2}, \tag{1}$$

where m_u consists of the direction cosines of the molecular axes x, y, and z with respect to the b axis.[4] This ratio is just twice the absorption intensity ratio between the two factor group splitting components observed through the c-polarized light $(I_1/I_2)_c$. The absorption intensity ratios between the components obtained through the light polarized along each crystallographic axis are related to one another by the equation,

$$\left(\frac{I_1}{I_2}\right)_c = \left(\frac{I_1}{I_2}\right)_{a^*} = 1\Big/\left(\frac{I_1}{I_2}\right)_b. \tag{2}$$

This is just what we have observed for the TCPA crystals. The values of the ratio in Eq. 1 were calculated from the direction consines to be 1.1, 2.8, and

0.13 for x, y, and z routes in the spin-orbit coupling, respectively. The experimental finding is consistent only with the z route involved in the spin-orbit coupling (an A_2 representation in the C_{2v} point group).

The polarization ratio for the first peak, that is, the sum of the O_1 and O_2 components, can be explained in terms of the transition which is primarily out-of-plane polarized (a B_1 representation in the C_{2v} point group). Furthermore, the Zeeman absorption pattern obtained for the light polarized along the c axis or the b axis under the magnetic field directed along the a* axis can be most satisfactorily represented by the scheme that the absorption intensity is taken from the x-polarized transition and the effective route in the spin-orbit coupling is z, as shown in Fig. 4b. Therefore, it is concluded that the lowest triplet state for TCPA belongs to $B_2(\pi\pi^*)$.

The lowest singlet-singlet absorption band of TCPA in the region from 30000 to 32500 cm^{-1} has been assigned theoretically to the transition of $\pi\pi^*$ character. The next band in the region from 35000 to 38000 cm^{-1}, however, has not been explained in terms of a $\pi\pi^*$ transition.[5] The broad absorption band observed at 27000 cm^{-1} in the present study was found to be stronger than the lowest singlet-triplet absorption, but weaker than the singlet-singlet absoption in oscillator strength. Considering the intensity, the broadness, the direction of polarization (mainly z-polarized), and the location of the band in the spectrum, the absorption is tentatively ascribed to the transition to a triplet state of $n\pi^*$ character.

The triplet factor group splitting was observed only for the first absorption peak, which was the strongest in intensity among the peaks in the transition to the lowest triplet state. This result shows that the coupling between molecules in the TCPA crystals is interpreted on the basis of a weak coupling model, where the magnitude of each splitting is roughly proportional to the intensity of a peak.[6]

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