CHEMISTRY LETTERS, pp. 1289-1292, 1975. Published by the Chemical Society of Japan

THE LOWEST TRIPLET STATE OF 9,10-ANTHRAQUINONE

Takatoshi NARISAWA, Mizuka SANO, and Yasumasa J. I'HAYA
Department of Materials Science, The University of Electro-Communications, Chofu, Tokyo 182

The lowest energy absorption peak was found at 22154.0 cm^{-1} for a thick single crystal of 9,10-anthraquinone at 4.2 K. From the analysis of Zeeman absorption patterns for the intense, sharp peaks observed at 22319.3 and 22357.9 cm^{-1}, the lowest triplet state was assigned to $^3B_{1g}$.

9,10-Anthraquinone (abbreviated to AQ hereafter) is a simple type of para-quinone, with two carbonyl chromophores across a benzene ring. The lower excited electronic states involve $n\pi^*$ promotions which in a first approximation can be located on the two carbonyl groups. Molecular orbitals* $n_+(b_{2u})$ and $n_-(b_{3g})$ are formed by symmetry adapted linear combinations of the two carbonyl non-bonding orbitals, and the $n_+\pi^*$ excited states belong to $^{1,3}A_u$ and the $n_-\pi^*$ excited states belong to $^{1,3}B_{1g}$. Dearman, et al. measured the polarized $T \leftarrow S_o$ absorption spectra for single crystals of AQ at 77 K and assigned the lowest triplet state to $^3A_u(n\pi^*)$.[1] Singh and Singh observed the phosphorescence spectrum of AQ in the vapor phase using a transformer discharge technique, and assigned it to a $^3A_u \rightarrow {}^1A_g$ transition.[2]

In this paper we present an experimental proof for the assignment of the triplet state configuration for AQ. We measured polarized $T \leftarrow S_o$ absorption spectra for thicker single crystals at lower temperatures with the aid of a spectrometer with higher resolution, and moreover, we determined directly the effective route in a spin-orbit coupling by means of Zeeman spectroscopy.

AQ (Tokyo Kasei Organic Chemicals) was purified by the following procedures. Precipitates obtained by cooling a hot sulfuric acid solution of AQ were recrystallized several times from glacial acetic acid and from toluene, and then sublimed in vacuo. Fine crystalline powder thus obtained was zone-refined for 50 passes under a pressure of 400 mmHg of helium. The central fraction was zone-refined for additional 100 passes and then a crystal was melt grown in a Bridgman furnace. AQ crystallizes in the monoclinic system, with two planar molecules in the unit cell.[3] The principal cleavage was verified to be (001) by x-ray diffraction. Samples could also be cleaved along the secondary cleavage plane (100).

Absorption spectra were analyzed with the aid of an NLM-E2M spectrometer, the reciprocal dispersion of which was 0.045 nm mm^{-1} at 450 nm in the 13th order of an Echelles grating. They were photographed with Fuji spectroscopic plates and recorded with the aid of an HTV R189 photomultiplier tube and electrometer amplification.

Figure 1 shows the polarized $T \leftarrow S_0$ absorption spectra of AQ crystals at 4.2 K. Intense peaks were found at 447.92 nm (22319.3 cm^{-1}), 447.14 nm (22357.9 cm^{-1}), 443.76 nm (22528.2 cm^{-1}) and 443.39 nm (22547.1 cm^{-1}) in the longer wavelength region than 440 nm. The former two peaks were named B and A, respectively. The longest wavelength peak in the absorption spectrum was found at 451.26 nm (22154.0 cm^{-1}) for a 29.4 mm thick crystal with light incident on the (010) plane. The weakness of the peak demonstrates the forbidden character of the transition, and the peak is taken tentatively as the origin for the $^3B_{1g}(n\pi^*) \leftarrow\!\!- {}^1A_g$ transition. The b-polarized peaks were found to be located within 0.1 cm^{-1} from the corresponding c-polarized peaks. Hence the absorption spectra as well as Zeeman patterns were analyzed on a molecular basis.

A comparison between the absorption coefficients for polarized light and the orientational data of the molecule shows that most of the peaks are predominantly z-polarized. The B peak, however, possesses not only a z but also an x component in polarization. The peaks split threefold upon application of a magnetic field, indicating that they could be ascribed to $T \leftarrow S_0$ transition.

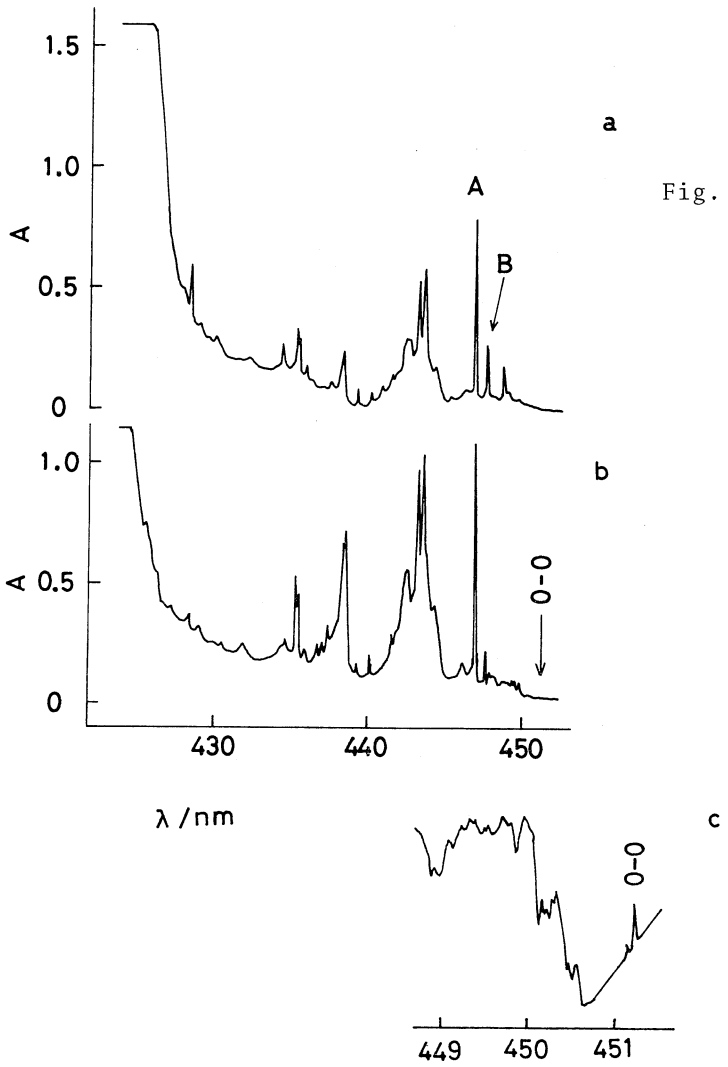

Fig. 1. Absorption spectra for 9,10-anthraquinone single crystals at 4.2 K.
(a) E//b, light incident on the (001) plane of a 10 mm thick crystal.
(b) E//c, light incident on the (100) plane of a 1 mm thick crystal.
(c) Light incident on the (010) plane of a 29.4 mm thick crystal.

Phosphorescence of an AQ crystal at 1.7 K, excited by 365 nm radiation, showed a weak first peak at 452.32 nm (22102.1 cm^{-1}), which was found to be 52 cm^{-1} lower in energy than the absorption origin (Fig. 2). It probably originates from an X-trap level. The weak peak being assigned as the electronic origin, the phosphorescence spectrum was analyzed. The strongest peak was found to be located at 1680 cm^{-1} from the origin. It corresponds to the b_{1u} C=O stretching mode observed at 1676 cm^{-1} in the infrared spectrum.[4)]

The Zeeman absorption patterns were analyzed for the sharp peaks (less than 1 cm^{-1} in width), A and B. The origin peak was too weak to be analyzed. The B peak split into three lines with the magnetic fields either parallel or perpendicular to the z-axis. These facts indicate that not only the z-route but also another route is active in the spin-orbit coupling. The central line was found to be stronger with the magnetic field directed along the b-axis, and the wing lines were stronger with the field along the a*-axis.

If either x-, y-, or z-route is active in the spin-orbit coupling of an AQ crystal, the intensity ratios of the central line to the wing lines for the direction of a magnetic field along the b-axis are expected to be 7.5, 0.53 and 0.002, respectively, and those for the direction of a field along the a*-axis are 0.32, 1.68 and 1.34, respectively.[5)] The experimental findings are explained by the mechanism that the x-route rather than the y-route is also active. From these results we conclude that the B peak is either a b_{1u} or a b_{3u} mode of 165.3 cm^{-1}

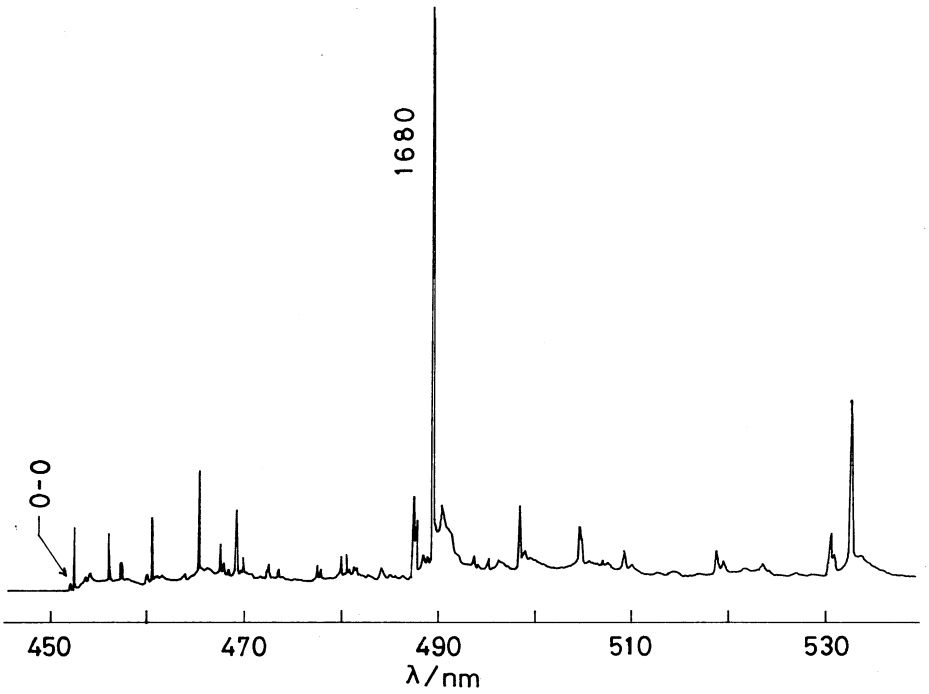

Fig. 2. Phosphorescence spectrum for a 9,10-anthraquinone single crystal at 1.7 K.

built on the $^3B_{1g}$ state.

In the Zeeman patterns for the A peak, only a central line appeared with the magnetic field directed along the z-axis, and two intense wing lines appeared with the field perpendicular to the axis in the (010) plane. These findings are consistent only with the route involved in the spin-orbit coupling being z. Taking into account the spin-orbit coupling route and the polarization of the transition, it is concluded that the A peak is due to the transition from the ground state to the level which possesses A_u total symmetry. It can not be decided from this experiment whether the A peak may be assigned to a b_{1u} mode of 203.9 cm^{-1} built on the $^3B_{1g}$ state or to the origin peak for the transition to the other triplet state, which belongs to ^3A_u.[6] The transition to the ^3A_u state is expected to be stronger than the symmetry forbidden transition to the $^3B_{1g}$ state.

All the experimental results can be explained in terms of the lowest triplet state configuration of $B_{1g}(n\pi^*)$.

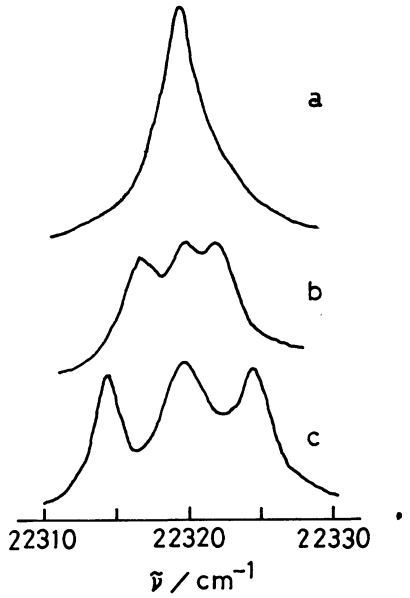

Fig. 3. Zeeman absorption patterns for the B peak at 4.2 K, H//z.

(a) H = 0, (b) 29.4, (c) 54.8 kOe.

REFERENCES AND NOTES

* The z-axis is taken as the molecular twofold axis in the oxygen-oxygen direction, and the y,z-plane as the plane of the molecule.

1) H. H. Dearman, N. Sunderachari, and D. Ülkü, J. Chem. Phys., 45, 4363 (1966).
2) S. N. Singh and R. S. Singh, Indian J. Pure Appl. Phys., 5, 342 (1967).
3) K. Lonsdale, H. J. Milledge, and K. El-Sayed, Acta Crystallogr., 20, 1 (1966).
4) C. Pecile and B. Lunelli, J. Chem. Phys., 46, 2109 (1967).
5) G. Castro and R. M. Hochstrasser, Solid State Commun., 3, 425 (1965).
6) D. A. Wiersma assigned the A peak to a b_{1u} mode built on the $^3B_{1g}$ state from the deuteration effect on its absorption coefficient (private communication).

(Received October 13, 1975)