Polarized Absorption Spectra of the Hydroquinone and 1,4-Dimethoxybenzene Crystals in the Near and Vacuum Ultraviolet Regions

Koji KAYA,*,*1 Kiyokazu FUKE,** and Saburo NAGAKURA*,**

*The Institute of Physical and Chemical Research, Wako, Saitama 351

**The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato, Tokyo 106

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We measured the polarized absorption spectra of the γ-hydroquinone and 1,4-dimethoxybenzene crystals in the wave number region between 30000 cm^{-1} and 65000 cm^{-1}. The dichroic ratios determined for the spectra of both crystals show that the bands at ~290 nm and at ~220 nm are polarized parallel with the short and long molecular axes, respectively; these support the assignment that they correspond to the L_b and L_a bands of benzene, respectively. The dichroic ratios and intensities determined for the bands in the vacuum ultraviolet region show that they do not simply correspond to the $B_{a,b}$ bands of benzene and that mixing among appropriate excited states occurs in both crystals.

The measurements of polarized electronic absorption spectra have played an important role in the studies of the electronic structures of molecules and molecular crystals.[1-5] Most of the studies made hitherto have, however, been concerned with polarized spectra in the wavelength regions longer than 250 nm; polarized absorption measurements in the vacuum ultraviolet region are rather scanty because of their experimental difficulties.[6]

In the present study, we have extended the polarized absorption measurements of single crystals to the vacuum ultraviolet region and have studied the electronic structures of the γ-hydroquinone and 1,4-dimethoxybenzene crystals from both theoretical and experimental points of view.

Experimental

Commercially-available (G. R. Grade) hydroquinone and 1,4-dimethoxybenzene were purified by repeated recrystallizations from water and by repeated sublimations in a vacuum, respectively. Single crystals used for the polarized absorption measurements were prepared by sublimation.

Polarized absorption spectra in the wave number region from 30000 cm^{-1} to 65000 cm^{-1} were measured by a vacuum ultraviolet microspectrophotometer constructed in our laboratory, the details of which were described in a previous paper.[7] Sample crystals were sandwiched between two quartz plates (optically flat) and were then put on the stage of the microscope of the spectrophotometer. The polarized absorption measurements were made along the b and c axes on the (100) surface and along the a and b axes on the (001) surface for the γ-hydroquinone and the 1,4-dimethoxybenzene crystals, respectively. The crystal surfaces were determined by comparing the crystal habits observed with the help of an orthonoscope with the crystal structure data obtained by Maartmann-Moe[8] and by Goodwin *et al.*[9] We could not measure the absorption at wavelengths shorter than 180 nm for the 1,4-dimethoxybenzene crystal because of the quick sublimation of the sample due to temperature elevation by the irradiation of the vacuum ultraviolet light.

The absorption spectrum of hydroquinone in the gaseous state was measured by the spectrophotometer used for the polarized absorption measurement, a microscope attached to the instrument being replaced by a gas cell.

*1 Present address: Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai.

Results and Discussion

Absorption Spectrum of Gaseous Hydroquinone and the Band Assignment. An absorption spectrum measured with gaseous hydroquinone is shown in Fig. 1. It consists of three bands with maxima at 34600, 45200, and 53300 cm^{-1}. Judging from their positions and intensities, they correspond to the $^1B_{2u} \leftarrow {}^1A_{1g}$ (L_b), $^1B_{1u} \leftarrow {}^1A_{1g}$ (L_a), and $^1E_{1u} \leftarrow {}^1A_{1g}$ ($B_{a,b}$) transition bands of benzene, respectively. In order to certify these assignments, the π-electron structure of hydroquinone was calculated by the Pariser-Parr-Pople SCF MO method[10] including the configuration interaction. The calculated and observed transition energies and oscillator strengths are given in Table 1. The calculated wave functions and polarizations are also shown in this table. The wave functions of the respective excited states show that the above-mentioned assignments are correct.

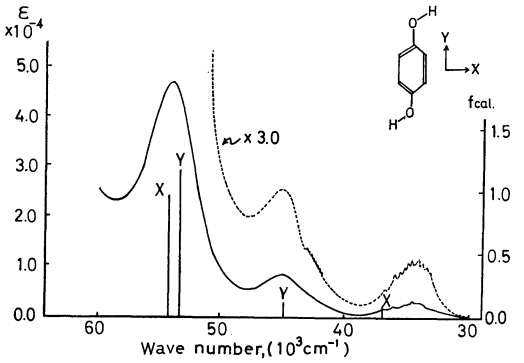

Fig. 1. The absorption spectrum of hydroquinone in the gaseous state. The vertical lines show the band positions and oscillator strengths calculated by the Pariser-Parr-Pople method: x and y indicate the polarization directions.

Polarized Absorption of the γ-Hydroquinone Crystal. The polarized absorption spectrum of the γ-hydroquinone crystal (monoclinic ($P2_1/c$)) is shown in Fig. 2. The projection of the four molecules within a unit cell of the crystal on the (100) face is shown in Fig. 3. Maartmann-Moe[8] reported that hydroquinone crystallizes in the γ-form upon sublimation.

Table 1. Observed and theoretical transition energies (ΔE) and oscillator strengths (f) of hydroquinone

Band	Experimental $\Delta E(\times 10^3\ cm^{-1})$	Experimental f[a)]	Theoretical $\Delta E(\times 10^3\ cm^{-1})$	Theoretical f	Polarization	Configurations mainly contributed to each state[b)]
	34.6	0.040	36.9	0.092	x	$0.879\phi(5\rightarrow6)$, $-0.476\phi(4\rightarrow7)$
	45.2	0.097	44.8	0.130	y	$0.863\phi(5\rightarrow7)$, $0.503\phi(4\rightarrow6)$
	53.3	1.330	53.3	1.222	y	$-0.503\phi(5\rightarrow7)$, $0.864\phi(4\rightarrow6)$
			54.2	0.970	x	$0.477\phi(5\rightarrow6)$, $0.879\phi(4\rightarrow7)$

a) The f values of the first and second bands were obtained from the absorption spectrum in cyclohexane. Concerning the third band, f was obtained from the absorption spectrum in gas phase, the molar extinction coefficient (ε) of which was normalized by the absorption spectrum in cyclohexane.

b) $\phi(i\rightarrow j)$ represents the electron configuration in which one electron is excited from the i-th MO to the j-th MO. The coefficient of each configuration is that in the state wave function. ϕ_4, ϕ_5, ϕ_6, and ϕ_7 are as follows:

	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
ϕ_4		0.500	0.500		−0.500	−0.500		
ϕ_5	−0.497	−0.301	0.301	0.497	0.301	−0.301	0.269	−0.269
ϕ_6		0.500	−0.500		0.500	−0.500		
ϕ_7	0.576	−0.265	−0.265	0.576	−0.265	−0.265	−0.167	−0.167

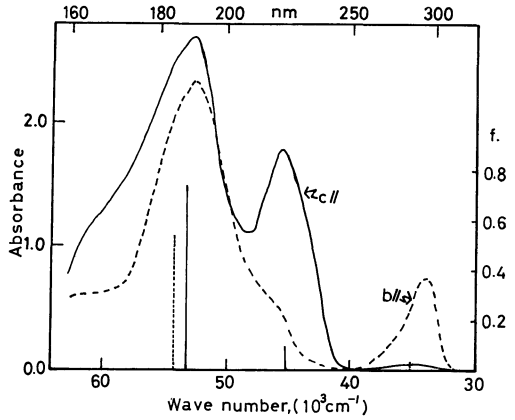

Fig. 2. The polarized absorption spectrum observed with the γ-hydroquinone crystal. The vertical full and broken lines show the absorption intensities estimated for the c- and b-polarized bands by the aid of the oriented gas model, respectively.

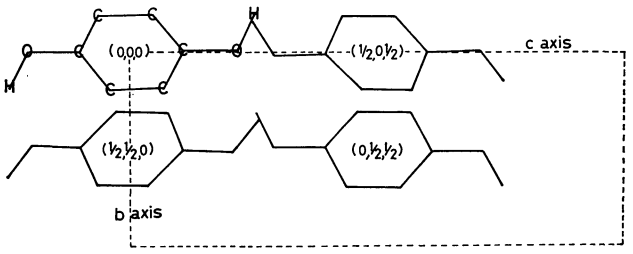

Fig. 3. Projection of the four site molecules on the bc plane of the γ-hydroquinone crystal.

As is clearly seen in Fig. 2, the polarized absorption spectrum of the γ-hydroquinone crystal has four peaks at 34500, 45500, 52000, and 60600 cm^{-1}. The dichroic ratios (D_b/D_c) are 20 : 1 and 1 : 4 for the first and the second bands, respectively, D_b and D_c being the absorbancies observed for each band along the b and c crystal axes, respectively. From the dichroic ratio observed with the crystal and from the orientations of the four site molecules in a unit cell, the molecular dichroic ratio, D_x/D_y, was obtained for the bands at 34500 and 45500 cm^{-1} as shown in Table 2. Here,

Table 2. The dichroic ratios observed for the first and second bands of γ-hydroquinone and 1,4-dimethoxybenzene

	γ-Hydroquinone $D_b : D_c$	γ-Hydroquinone $D_x : D_y$
290 nm band	20 : 1	1 : 0
220 nm band	1 : 4	1 : 2.6
	1,4-Dimethoxybenzene $D_b : D_a$	1,4-Dimethoxybenzene $D_x : D_y$
295 nm band	2 : 1	3 : 1
220 nm band	5 : 1	1 : 8

the x and the y axes are taken to be perpendicular and parallel to the molecular axis connecting the two oxygen atoms on the molecular plane.

Table 2 shows that the band of the crystal at 34500 cm^{-1} is polarized parallel with the x molecular axis and thus corresponds to the 34600 cm^{-1} band of the molecule in the gaseous state, which is expected from theoretical considerations to be polarized in the x-direction. The 45500 cm^{-1} band of the γ-hydroquinone crystal is polarized almost parallel with the y molecular axis; it corresponds to the 45200 cm^{-1} band of the molecule.

Let us turn to polarized absorption bands in the vacuum ultraviolet region. The spectra of the crystal polarized parallel with the b and c crystal axes show the intense absorption peaks at 52000 cm^{-1} and also have shoulders at around 60600 cm^{-1}.[11] As is seen in Fig. 3, the molecular x axis of each molecule in the crystal is almost parallel with the b crystal axis and the y molecular axis with the c crystal axis. Therefore, it is reasonable to assign the b-polarized band at 52000 cm^{-1} of the crystal to the x-polarized component of the intense absorption band of the molecule at 53300 cm^{-1}. The c-polarized absorption of the crystal with a peak at 52000 cm^{-1} can be assigned to the y-polarized absorption of the molecule, which is thought, from theoretical considerations, to overlap with the x-polarized component.

The intensities of the bands polarized parallel with the b and c crystal axes can be obtained on the as-

sumption of the oriented gas model from the experimental values of the oscillator strengths given in Table 1.[12] The results are shown by the vertical lines in Fig. 2. From this figure, it is seen that the polarized absorption spectra observed with the γ-hydroquinone crystal can be explained qualitatively by the oriented gas model. From the quantitative point of view, however, the observed intensity ratios of the 52000 cm^{-1} bands to the first and second bands are much smaller than those to be expected from the oriented gas model. For instance, the intensity ratio of the c axis polarized bands at 52000 cm^{-1} and at 45500 cm^{-1} is observed at 2 : 1 taking the integrated intensities; in case of the oriented gas model, the corresponding value is 7.5 : 1. This discrepancy is beyond the limitations of experimental error and may be due to the fact that the 53300 cm^{-1} band of the molecule in the gaseous state decreases its intensity in the crystalline state because of the intensity borrowing.

In the case of strong coupling, the intensity borrowing among the different excited states of the molecule may occur through the configuration interaction; consequently, the dichroic ratios of the crystal become different from those of the free molecule. Organic molecular crystals have many excited states including a continuous state (excitation from the valence band to the conduction band), so the intensity-borrowing effect may be significant for the exciton bands in this region. Tanaka and Tanaka[13] explained the spectrum of the anthracene crystal by considering the interaction among different exciton configurations. The observed decrease in the intensity of 52000 cm^{-1} bands polarized along the b and c axes of the γ-hydroquinone crystal may be due to the above-mentioned effect.

1,4-Dimethoxybenzene. The crystal of 1,4-dimethoxybenzene is orthorhombic (Pbca) and contains four molecules per unit cell. The polarized absorption spectrum was measured with the (001) plane of the single crystal prepared by sublimation; the results are shown in Fig. 4. The projection of the four molecules within a unit cell of the crystal on the (001) plane is shown in

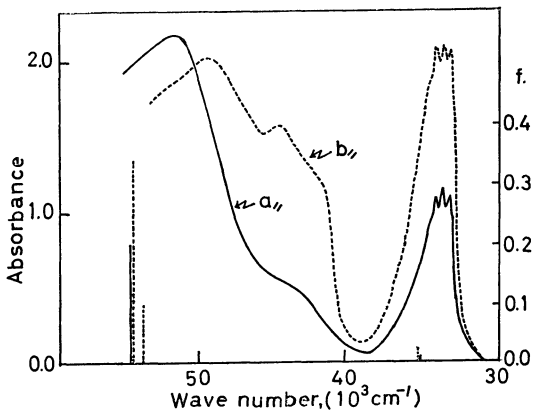

Fig. 4. The polarized absorption spectrum observed with the 1,4-dimethoxybenzene crystal. The vertical full and broken lines show the absorption intensities estimated for the a- and b-polarized bands by the aid of the oriented gas model, respectively.

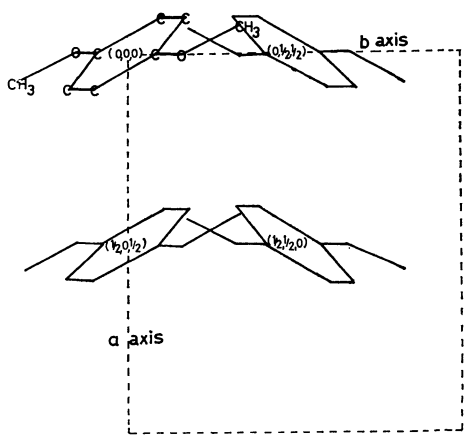

Fig. 5. Projection of the four site molecules on the ab plane of the 1,4-dimethoxybenzene crystal.

Fig. 5. The first and second bands at 295 nm and at 220 nm are polarized along the x and y axes, respectively, as is seen in Table 2. This result which is consistent with that by Albercht and Simpson[14] shows that the 295 nm and 220 nm bands correspond to the L_b and L_a bands of benzene.

In addition to the above-mentioned bands, we succeeded in observing the two absorption peaks at 49500 c n^{-1} and 51800 cm^{-1} polarized along the b and a axes, respectively. From the crystal structure data and the assumption of the oriented gas model, we can expect that the components polarized parallel with the a and b axes are 0.5 and 13.0 percent for the y-axis polarized band, respectively, and that they are 30.0 and 61.4 percent for the x-axis polarized one, respectively. Furthermore, the absorption intensities are almost equal for the bands polarized parallel with the x and y axes. Therefore, the two absorption peaks at 49500 cm^{-1} and 51800 cm^{-1} polarized along the b and a axes, respectively, are interpreted to correspond to the x-polarized band (B_b band for benzene), which is expected to show the Davydov splitting in the crystal. The splitting was calculated for the x-polarized transition by taking the dipole-dipole interaction between molecules within a sphere with a radius of 50 Å. The theoretical result that the a-axis spectrum shifts to higher frequencies than the b-axis one is consistent with the observation. The calculated value of the splitting, 480 cm^{-1} is, however, smaller than the observed value, 2300 cm^{-1}.

A small shoulder at 52200 cm^{-1} in the b axis spectrum may be assigned to the y-polarized transition band (the B_a band of benzene).

The relative intensities of the bands observed with the 1,4-dimethoxybenzene crystal are abnormal compared with those of the free molecule. This may be explained in terms of the interaction among various configurations in the crystals, as was done in the case of the γ-hydroquinone crystal.

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11) Shoulders at $\sim$170 nm in the b- and c-axis polarized spectra of the γ-hydroquinone crystal are reproducible for the repeated measurements and their existence is conclusive.
12) It is necessary for this estimation to divide the oscillator strength of the 53300 cm^{-1} band into two components polarized along the x- and y-molecular axes. In actuality, we divided the observed oscillator strengths, 1.330, into two parts proportional to the theoretical values, 1.222 and 0.970, calculated for the y- and x-polarized bands.
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