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Polarized Absorption Spectrum of Acridone

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In previous papers, we reported the polarized absorption spectra of several aromatic compounds in stretched PVA sheets, and discussed the assignment of the electronic bands. Especially, as for a molecule of C_{2v} or D_{2h}, we could divide the absorption spectrum into two components, polarized parallel to and perpendicularly to the C_2-axis of the molecule.[1]

In the present paper, the divided spectra of acridone are determined, and the assignments of the electronic bands are established by a comparison of the observed results with theoretical ones.

Kokubun[2] measured the absorption and fluorescence spectra of acridone in various solvents, and discussed the assignment of the electronic bands. Zanker and Wittwer[3] compared the absorption and fluorescence polarization spectra of acridone with those of some hydroxyacridines.

Experimental

Materials. Commercially-available acridone was purified by repeated recrystallizations from ethanol.

Measurement of the Polarized Absorption Spectrum. The measurement and analysis of the polarized absorption spectrum were carried out following a method described elsewhere.[1,4]

Notations. The notations used in the figures of the polarized absorption spectrum and the divided spectra are as follows.

$D_{\parallel}$ and $D_{\perp}$: Absorbances measured for incident light polarized respectively parallel to and perpendicular to the stretched direction of the PVA sheet.

R_d: Ratio between $D_{\parallel}$ and $D_{\perp}$, $D_{\parallel}/D_{\perp}$.

R_s: Degree of stretching of the PVA sheet.

θ: Orientation angle, which means an angle between a transition moment for an electronic transition and an orientation axis of the molecule.

D: Absorbance in an unstretched PVA sheet.

D_x and D_y: Absorbances whose transition moments are along the X- and Y-axes of the molecule respectively. The D_x and D_y curves are called divided spectra.

Method of Calculation

The electronic transition energies and the oscillator strengths for acridone were calculated by means of the PPP approximation,[5] including the variable β method.[6] The valence-state ionization potentials and the electron affinities for carbon, oxygen, and nitrogen atoms were taken as $I_p(\mathrm{C})=11.42$ eV, $E_a(\mathrm{C})=0.58$ eV, $I_p(\mathrm{O})=33.0$ eV, $E_a(\mathrm{O})=11.47$ eV, $I_p(\mathrm{N})=14.16$ eV, and $E_a(\mathrm{N})=1.34$ eV. The two-center electron repulsion integrals were evaluated by using the Nishimoto-Mataga equation.[7] The resonance integrals, β_{rs}, were obtained by the equations:[6] $\beta_{\mathrm{CC}}=-1.84-0.51P_{\mathrm{CC}}$, $\beta_{\mathrm{CN}}=-2.02-0.53P_{\mathrm{CN}}$, and $\beta_{\mathrm{CO}}=-2.20-0.56P_{\mathrm{CO}}$, where P_{rs} is the bond order. All singly-excited configurations associated with the transitions between each of the five highest occupied levels and each of the five lowest vacant levels were included in the CI calculation. The geometry of the molecule used here is shown in Fig. 1. All the bond angles were assumed to be 120°.

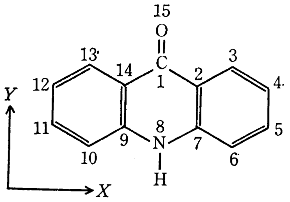

Fig. 1. The geometry of acridone.
$d_{1-15}=1.210$ Å $d_{1-2}=d_{2-3}=\cdots\cdots=d_{1-14}=1.395$ Å

Results and Discussion

Figure 2 shows the polarized absorption spectrum of

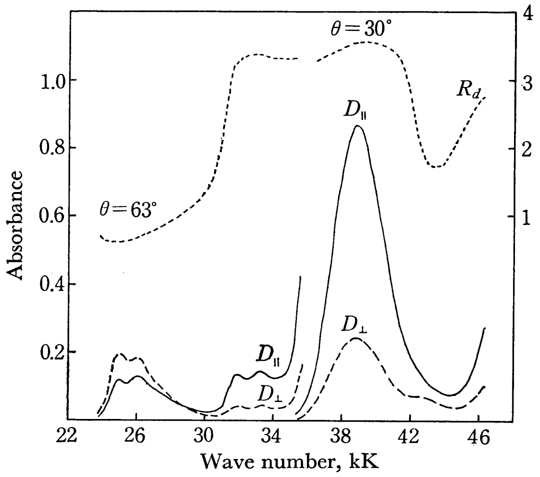

Fig. 2. The polarized absorption spectrum of acridone.

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acridone. The R_d values are the largest around 38.8 kK and the smallest around 24.9 kK in the observed wave number region. The orientation angles of the 38.8 kK and the 24.9 kK bands are, respectively, 30° and 63°. These bands seem to be polarized perpendicularly to each other, because the sum of the orientation angles mentioned above is nearly a right angle ($30°+63°=93°$). As in the cases of anthraquinones,[8] it is considered that the angle of the orientation axis against the X-axis is smaller than that against the Y-axis; therefore, the bands with large R_d values are considered to be polarized along the X-axis, and the bands with small R_d values, along the Y-axis. Since the 24.9 kK band is isolated from the other bands and since the R_d values of this band are almost constant, we can determine the divided spectra of this compound by using the polarization direction of the 24.9 kK band as the standard. As may be seen from the divided spectra in Fig. 3, the absorption spectrum of acridone below 50 kK consists of three X-polarized bands, at 31.8, 38.8, and 45.9 kK, and three Y-polarized bands, at 24.9, 38.2, and 42.6 kK.

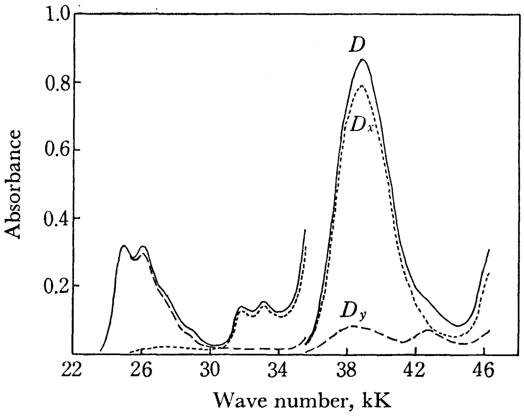

Fig. 3. The divided spectra of acridone.

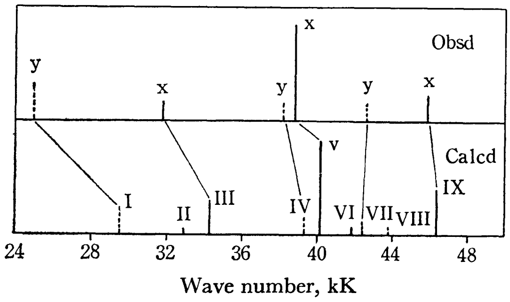

Fig. 4. Comparison of the observed and the calculated results.

According to Kokubun,[2] the two bands at 24.9 and 31.8 kK are to be assigned to the ^1L_a and the ^1L_b bands respectively; this assignment is not contradictory with the present results concerning the polarization directions. The observed results described above are compared with the theoretical ones in Fig. 4. The observed and the theoretical results are in good agreement, except for the position of the I transition. The two peaks of the D_y curve at 38.2 and 42.6 kK are due to different electronic transitions; they may correspond to two calculated transitions, IV and VII respectively. The 24.9 kK band is polarized along the Y-axis, and the >NH and >C=O groups have, respectively, electron-donating and electron-accepting characters, so the 24.9 kK band is expected to have a considerable intramolecular charge-transfer character. The calculated transition I is related to the electronic excitation from the ground state to the first excited state Ψ_I, $\Psi_I = -0.179\Psi_{5,11}+0.328\Psi_{6,10}+0.211\Psi_{7,12}+0.890\Psi_{8,9}-0.101\Psi_{8,12}$, where $\Psi_{i,j}$ is a configuration wave function associated with an one-electron excitation from the ith MO (ϕ_i) to the jth MO (ϕ_j). As is shown above, the coefficient of the $\Psi_{8,9}$ is relatively large; therefore, Ψ_I can be approximately represented by $\Psi_{8,9}$. The coefficients for the MO's, ϕ_8 and ϕ_9, are shown pictorially in Fig. 5. As may be seen from this figure, the electronic transition from ϕ_8 to ϕ_9 results in a considerable charge migration from the >NH group to the >C=O group. Hence, it can be deduced that the I transition is of the intramolecular charge-transfer type.

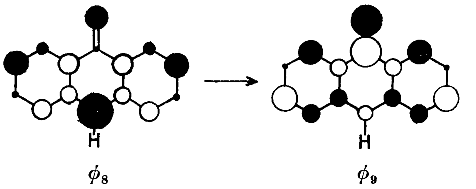

Fig. 5. The coefficients for the MO's ϕ_8 and ϕ_9.

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