NOTES

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (8), 2315—2316 (1976)

Reflection Spectra of Acenaphthene Crystals

Masashi Tanaka
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464

(Received February 10, 1976)

Synopsis. The reflection spectra have been measured for acenaphthene crystals. The excited states of the acenaphthene molecule are similar to those of the naphthalene molecule; the lower $\pi \rightarrow \pi^*$ excited states are observed at 31100 (α), 32600 (p), 43700 (β), and 47400 (β') cm^{-1}. In the reflection spectra of the crystal, the α and β states polarized along the b axis are observed at 30900 and 41800 cm^{-1}, respectively. The p and β' states are found at 32100 and 44000 cm^{-1} in the a axis spectrum and at 31400 and 45000 cm^{-1} in the c axis spectrum.

Four lower $\pi \rightarrow \pi^*$ excited state (α, p, β, and β' bands) of the naphthalene molecule were found to be located at 32000, 34500, 45500, and 60000 cm^{-1} respectively by the study of UV spectra in solution. The α and β bands are reported to be polarized along the long molecular axis (B_{2u} symmetry) and the p and β' along the short axis (B_{1u} symmetry).

McClure[1] succeeded in obtaining the polarization direction of the first $\pi \rightarrow \pi^*$ state (α band) with the mixed crystal of naphthalene in durene. Bree[2] observed the α, p, and β' bands of acenaphthene crystal by the polarized absorption method. However, he could not find the intense β band, although the dipole-dipole approximation predicted this band would lie at 58730 and 48230 cm^{-1}, with all the intensity effectively concentrated in the higher energy component.

We have determined the band position of the β state by measuring the reflection spectra of acenaphthene crystal and have theoretically explained the difference between the observed and predicted values.

Experimental

Single crystals of acenaphthene were grown by slow evaporation from ethyl acetate solution. The crystals showed well-developed (010), (100), (101), and (111) faces. These faces were identified by a morphological examination.

Reflection spectra at normal incidence were measured over a wavelength range 650—192 nm with a reflection spectrophotometer made in our laboratory. Reflection spectra for the (010) and (100) faces are shown in Fig. 1 and the corresponding absorption spectra obtained by the Kramers-Kronig transformation[3] are shown in Fig. 2.

Results and Discussion

The acenaphthene crystal has four molecules in an orthorhombic unit cell of space group Pcm2_1 (C_{2v}^2)[4] in which a molecular and a crystallographic mirror plane coincide. Therefore, the B_{1u} states (p and β' bands) are polarized in the ac plane, while the B_{2u} states (α and β bands) appear only in the b polarization.

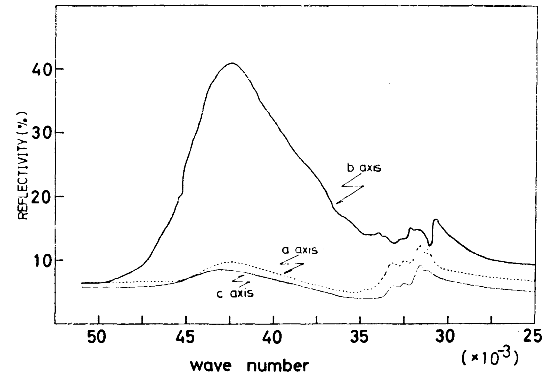

Fig. 1. The reflection spectra of the acenaphthene crystal on the ac and bc planes.

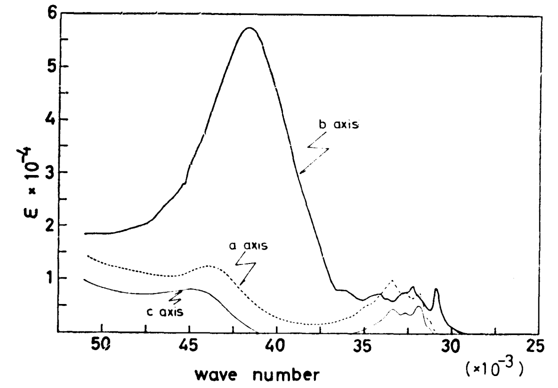

Fig. 2. The absorption spectra obtained by the Kramers-Kronig transformation of the reflection spectra of the acenaphthene crystal.

Two bands in the b axis spectrum are observed, at 30900 and 41800 cm^{-1}. The weak band at 30900 cm^{-1} corresponds to the α band at 31100 cm^{-1} in solution and is assigned to the α state of B_{2u} symmetry in the free molecule. Bree[2] observed this band at 31020 cm^{-1}. However, the intense band at 41800 cm^{-1} was not observed by Bree and can be obtained only by the reflection method. This band corresponds to the β band at 43700 cm^{-1} in solution and is assigned to the B_{2u} state of the molecule. The spectra for the ac plane has two bands. The one band in the region of 3200 cm^{-1} has a vibronic structure and the other, at about 45000 cm^{-1}, is broad; these bands correspond to the p and β' states in the free molecule, respectively. The band positions of these bands are consistent with those obtained by Bree.

In Table 1 are given the calculated exciton state energies and oscillator strengths, obtained by the CI[5]

Table 1. Calculated and observed transition energies (E in 1000 cm^{-1}) and oscillator strengths (f) of exciton states of the acenaphthene crystal

State			CI method[b]		RPA method I[c]		RPA method II[c]		Obsd	
			E	(f)	E	(f)	E	(f)	E	(f)
A_1	c axis	p	34.8	(0.39)	34.4	(0.31)	34.4	(0.31)	31.4	(0.10)
		p	35.9	(0)	35.2	(0)	35.2	(0)		
		β'	50.2	(0.80)	49.1	(0.52)	49.1	(0.53)	45.0	(0.4)
		β'	52.5	(0.18)	51.1	(0.10)	51.1	(0.10)		
B_1	a axis	p	34.1	(0.69)	33.6	(0.24)	33.7	(0.21)	31.2	(0.15)
		p	35.4	(0.05)	34.7	(0.25)	34.7	(0.26)		
		β'	49.4	(0.68)	48.8	(0.46)	48.9	(0.40)	44.0	(0.4)
		β'	50.6	(0.54)	49.8	(0.56)	49.9	(0.63)		
B_2	b axis	α[a]	34.1	(0)	34.0	(0)	34.0	(0)	30.9	(0.18)
		β	49.0	(6.34)	46.6	(4.39)	46.4	(4.39)	41.8	(2.0)
		β	65.2	(0)	57.0	(0)	57.0	(0)		

a) The α band in the B_2 exciton state is doublet. b) Calculation by the exciton CI method[4] when the inner zone radius is 50 Å. c) Calculations by the exciton RPA method[5] where the inner zone radii are 50 and 100 Å, respectively.

and RPA[6] methods; where the intermolecular interactions were estimated for two inner zone radii, 50 and 100 Å. The calculated values for the two inner zone radii are nearly equal; hence, convergence of the summation of intermolecular interactions has been achieved. Table 1 shows that the exciton state energies and oscillator strengths decrease more and are closer to the observed values in the RPA method than in the CI method.

The intense β band was predicted to lie at 58700 cm^{-1} by Bree, while the observed value is 41800 cm^{-1}. Using the CI and RPA methods, this band was calculated to be located at 49000 and 46600 cm^{-1}, respectively. The difference between these three calculated values can be explained by the fact that the RPA method includes the polarization effect by taking account of the double excitation, by comparison with the CI and dipole-dipole approximations. That is, the polarization effect has a strong influence on the Davydov splitting and band shift of the intense band.

The other band system (α state) at 30900 cm^{-1} is theoretically forbidden, but seems to be allowed by the mixing of higher excited states than the states taken into account in this calculation. The p band at 32000 cm^{-1} is expected to arise from a short axis transition. The calculated exciton state energies are 34400 and 35200 cm^{-1} for the A_1 exciton state and 33700 and 34700 cm^{-1} for the B_1 exciton state; these are supported by the observed values. The measured polarization ratio (f^a/f^c) is 1.5, comparable to the calculated value of 1.7. The oscillator strengths of two p states in the B_1 exciton state show different values: (0.69/0.05) in the CI method and (0.21/0.26) in the RPA method. This can be explained by the difference in the CI and RPA methods of the mixing of the nearly degenerate exciton configurations belonging to crystallographically nonequivelent sites.

References

1) D. S. McClure, *J. Chem. Phys.*, **22**, 1668 (1954); **24**, 1 (1956).

2) A. Bree, *Mol. Phys.*, **6**, 563 (1963).

3) H. J. Bowlden and J. K. Wilmskurst, *J. Opt. Soc. Am.*, **53**, 1073 (1963); D. M. Roesler, *Brit. J. Appl. Phys.*, **16**, 1119 (1965).

4) H. W. Ehrlich, *Acta Crystallogr.*, **10**, 699 (1957).

5) M. Tanaka and J. Tanaka, *Mol. Phys.*, **16**, 1 (1969).

6) M. Tanaka and J. Tanaka, *Theoret. Chim. Acta*, **30**, 81 (1973).