# Electronic States of Fluorene, Carbazole and Dibenzofuran

Masashi TANAKA

*Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464*

(Received March 8, 1976)

The polarized reflection spectra of the fluorene, carbazole, and dibenzofuran crystals have been measured from 30000 to 53000 $cm^{-1}$ and the absolute intensity of the absorption parallel to the a, b, and c axes of these crystals has been obtained by the Kramers-Kronig transformation; these data allowed an interpretation to be made for the solution spectra. Furthermore, the influence of the intermolecular interaction on each level has been examined. This analysis shows that the lowest excited state of the fluorene molecule is the $B_2$ state, while those of the carbazole and dibenzofuran are the $A_1$ states. In fluorene, the sum of the oscillator strengths of the transition to two lower excited states ($\alpha$ and $\alpha^*$ states) is 0.39 in the molecule and 0.61 in the crystal. Such hyperchromism is also observed in the $\alpha$, p, and $\beta$ states of carbazole and the $\beta$ state of dibenzofuran. On the other hand, the $\alpha^*$ state of dibenzofuran is hypochromic and the oscillator strengths in the molecule (0.87) decrease to 0.36 in the crystal. However, the factor group splitting and the crystal field shift are small and a one to one correspondence can easily be obtained between the solution and crystalline spectra.

The electronic spectra of fluorene, carbazole, and dibenzofuran are of interest because of the physical and chemical properties of five-membered heterocycles; many papers concerned with an experimental or theoretical analysis of their UV spectra have been reported.

These molecules have the symmetry of point group $C_{2v}$ and the $A_1$ (polarized to the short axis) and $B_2$ (polarized to the long axis) states can be observed in the UV measurement. According to the vapor spectra observed by Pinkham and Wait,[1] the lowest energy $\pi\rightarrow\pi^*$ transition of fluorene vapor has its origin at 33773 $cm^{-1}$ and was assigned to $A_1\rightarrow A_1$. Two $\pi\rightarrow\pi^*$ transitions were observed for dibenzofuran vapor. The one with the origin at 31488 $cm^{-1}$ was assigned to an $A_1\rightarrow A_1$ transition, while the one which originates at 33647 $cm^{-1}$ was assigned to $A_1\rightarrow B_2$. The strong $\pi\rightarrow\pi^*$ transition of carbazole which originates at 36346 $cm^{-1}$ was assigned to $A_1\rightarrow B_2$. The weaker $\pi\rightarrow\pi^*$ band system, originating at 30694 $cm^{-1}$, was assigned to $A_1\rightarrow A_1$.

Solution studies have been made of the absorption, fluorescence, and phosphorescence. Kanda *et al.*[2] measured the phosphorescence of fluorene and dibenzofuran in cyclohexane at 90 K. Mataga, Torihashi, and Ezumi[3] studied the solvent effects upon the fluorescence and absorption spectra of carbazole. As is cited in the paper by Dörr and Gropper,[4] Joop[5] appears to have obtained the polarization of the fluorescence excitation spectrum of fluorene and found that the *p*-values for fluorescence are positive when excitation is made to the first and second absorption bands. Schütt and Zimmerman[6] reported the fluorescence, phosphorescence, and absorption polarization ratio of carbazole and found that the *p*-values are positive for the first band at 29500 $cm^{-1}$ and negative for the second band at 34000 $cm^{-1}$, Lace *et al.*[7] measured the polarized absorption of dibenzofuran in 1,2,4,5-tetramethylbenzene host and decided that the 3000 Å transition should be assigned to $A_1\rightarrow B_2$. Siegel and Judeikis[8] determined the polarization by the method of magnetophotoselection and they also demonstrated that the lowest state of fluorene has a $B_2$ symmetry and those of carbazole and dibenzofuran have $A_1$ symmetries.

In the crystal of these compounds, there are four molecules in an orthorhombic unit cell;[9–11] the long axis of the molecule lies exactly parallel to one of the crystalline axes and the short axis is perpendicular to it. Accordingly, it is possible to assign the transitions to the $A_1$ and $B_2$ states distinctly by using the polarization technique. The polarized crystalline absorption spectra were measured by the group of Bree.[12–14] The a and b axes polarized spectra of a fluorene crystal showed that the 33000 $cm^{-1}$ system is the $B_2$ state, while the a and c axes spectra of a dibenzofuran crystal showed that the first band is the $A_1$ state. The polarized absorption spectra of carbazole in a fluorene matrix were measured by Bree and his coworkers; they made the assignment that the 30000 $cm^{-1}$ system is the $A_1$ state.

The author measured the polarized reflection spectra of titled crystals with several crystalline faces and attempted to give better assignments of absorption bands for a wide spectral range. Furthermore, the influence of the intermolecular interaction on the band position and intensity of each level was examined and compared with the results calculated by the SCF-RPA exciton method.[15] This method, which takes into account the double excitation configuration, is very usefull for studying the intermolecular interaction, because the double excitation has a large effect on the hypochromism, as was shown by Tinoco[16] and Rhodes.[17]

## Experimental

Single crystals of fluorene, carbazole, and dibenzofuran were grown by slow evaporation of the ethanol solution after purifying the material by column chromatography. The crystal showed well developed (001) or (010) faces.

Reflection spectra at the normal incidence have been measured over a range of 20000—53000 $cm^{-1}$ with a reflection spectrophotometer made in our laboratory and the absorption spectra have been obtained by the Kramers-Kronig transformation.[18] The oscillator strength along the $\alpha$ axis of the crystal may be evaluated by using the following equation:[19]

$$f^{\alpha} = 4.32\times10^{-9} \int n_{\alpha}(\sigma)\,\varepsilon_{\alpha}(\sigma)\,d\sigma$$

where the integration is calculated over the whole band, $\sigma$ is the wave number, and $n_{\alpha}$ and $\varepsilon_{\alpha}$ are the $\alpha$ component of the refractive index and the molar extinction coefficient.

Oscillator strengths for the three orthogonal axes in the orthorhombic crystal should be compared with that in solution:

$$f^{a} + f^{b} + f^{c} = 3f^{\text{solution}}$$

where the suffixes a, b, and c correspond to the crystal axes.

## Thoeretical

The electronic states of the molecules are calculated by the RPA method.[20] This method is formulated as an eigenvalue problem for the singlet energies $\Delta E$ of a many-electron system as follows:

$$\begin{pmatrix} A & B \\ B & A \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix} = \Delta E \begin{pmatrix} X \\ -Y \end{pmatrix}$$

where

$$A_{ij,kl} = (\varepsilon_j - \varepsilon_i)\delta_{ik}\delta_{jl} + 2(ij|kl) - (ik|jl)$$

and

$$B_{ij,kl} = 2(ij|kl) - (il|jk)$$

The indices $i$, $k$ refer to the HF orbitals occupied in the ground configuration $\Phi_0$ and the indices $j$, $l$ refer to the virtual orbitals of the HF eigenvalue problem

$$F\phi_i = \varepsilon_i\phi_i.$$

The two-electron integrals are defined by

$$(ij|kl) = \int \phi_i^*(1)\,\phi_j(1)\frac{1}{r_{12}}\phi_k^*(2)\,\phi_l(2)\,d\tau_1\,d\tau_2.$$

Then the above-mentioned equations can be evaluated with the approximations of the neglect of differential overlap[21] and of the use of two-center coulomb integrals $\gamma_{pq}$ estimated by Nishimoto-Mataga's method.[22] The one-center core coulomb integrals $\alpha_p$ and the two-center resonance integrals $\beta_{pq}$ are approximated in the following equations:

$$\alpha_p = -I_p - (n_p - 1)\gamma_{pp} - \sum_{r \neq p} n_r\gamma_{pr}$$

$$\beta_{pq} = -K(I_p + I_q)S_{pq}$$

where the constant $K$ is taken to be 0.29. The overlap integrals $S_{pq}$ are calculated between the nearest neighbor atoms by using the SCF-AO's[23] and neglected in other cases. The values of the ionization potentials $I_p$ are taken from Pilcher and Skinner's table[24] and the one-center integrals $\gamma_{pp}$ are estimated by the Pariser-Parr approximation.[25]

In theoretical studies of the ultraviolet spectra of five-membered rings, Momicchioli and Rasteli[26] showed that the lower excited states of these molecules have the $\alpha$, $\alpha^*$, p, $\beta$, $\beta^*$, and $\beta'$ characters in Clar's notation, where $\alpha$ and $\beta$ characters mean that the excited states derive mainly from the mixing of $\Phi$ (A→B′) and $\Phi$ (B→A′) configurations, and similarly $\alpha^*$ and $\beta^*$ characters from $\Phi$ (A→C′) and $\Phi$ (C→A′) and p and $\beta'$ from $\Phi$ (A→A′), $\Phi$ (B→B′), and $\Phi$ (C→C′). The letters ···C,B,A,A′,B′,C′··· are the molecular orbitals denoted according to increasing energy. In these compounds of point group $C_{2v}$, the molecular orbitals C, A, B′, and D′ span the $a_1$ representation and D, B, A′, and C′ the $b_2$, respectively. Therefore, the $\alpha$ and $\beta$ states belong to the $A_1$ symmetry and are the short axis polarized states, and the $\alpha^*$, p, $\beta^*$, and $\beta'$ states belonging to the $B_2$ symmetry are the long axis polarized states. In addition to the above-mentioned states, two other bands can be observed in the higher energy range and may be noted as the $\gamma$ and $\delta$ states of the $A_1$ symmetry. The $\gamma$ state has the large contribution from four configurations of $\Phi$ (B→C′), $\Phi$ (C→B′), $\Phi$ (A→B′), and $\Phi$ (B→A′), and the $\delta$ state from $\Phi$ (D→C′) and $\Phi$ (C→D′).

The exciton states of the crystal are calculated according to the RPA exciton method.[15] This method takes into account the effect of the doubly excited configurations in addition to the mixing between the singly excited configurations.

All of the above-mentioned computations were carried out on a FACOM 230—60 computer at the Nagoya University computation center.

## Results and Discussion

*Fluorene.* The solution spectrum is described in Fig. 1 and the theoretically calculated results of the molecule are given in Table 1, together with the assignment of the observed states. The first band in the region of 3000 Å has structure and consists of two electronic states. The lowest state at 33200 $cm^{-1}$ is the long axis polarized state of $B_2$ symmetry ($\alpha^*$ state) and the short axis state ($\alpha$ state) is covered by the $\alpha^*$ state, as shown below. The third state (p state) also has structure; its origin is at 35900 $cm^{-1}$ and other vibronic levels appear at 36900, 38100, 39200, and 40400 $cm^{-1}$. This state is assigned to the $B_2$ state. There are many other states in the higher energy region: two shoulders at 44300 $cm^{-1}$ ($\beta^*$ state) and 45500 $cm^{-1}$ ($\beta'$ state) and a stronger system ($\beta$ state) beginning near 48000 $cm^{-1}$.

Fluorene forms orthorhombic crystals of space group Pnam ($D_{2h}^{16}$) having four molecules in a unit cell.[9] Projections onto the (010) and (001) faces are shown in Fig. 2. Beacuse of site symmetry ($C_s$), the long axis of the molecule lies exactly parallel to the c crystalline axis and the short in-plane axis is in

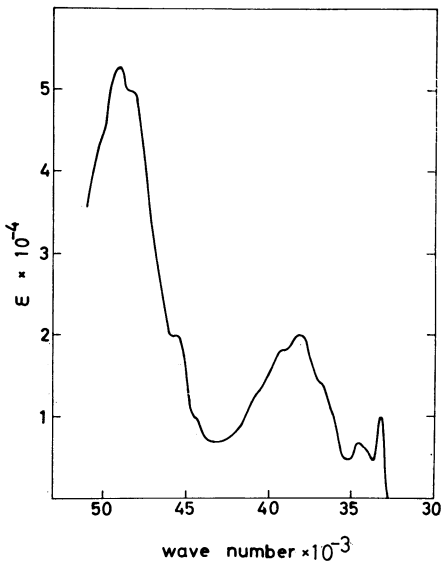


Fig. 1. The spectrum in isooctane of the fluorene molecule.

TABLE 1. THE LOWER EXCITED STATES OF THE FLUORENE MOLECULE, CALCULATED BY THE RPA METHOD
(All energy values are given in the units of $10^3\,cm^{-1}$.)

| State | | Obsd | | Calculated Values | | |
|---|---|---|---|---|---|---|
| | | $E$ | $(f)$ | $E$ | $(f)$ | Wavefunction |
| $A_1$ | $\alpha$ | >33.2 | (0.13) | 32.9 | (0.00) | $0.6482\,\Phi(6\to8)-0.6482\,\Phi(5\to7)+\cdots$ |
| $B_2$ | $\alpha^*$ | 33.2 | | 33.4 | (0.00) | $0.6424\,\Phi(6\to9)-0.6424\,\Phi(4\to7)+\cdots$ |
| $B_2$ | p | 35.9 | (0.43) | 36.2 | (0.55) | $0.9964\,\Phi(6\to7)+\cdots$ |
| $B_2$ | $\beta^*$ | 44.3 | (0.04) | 43.3 | (0.12) | $0.7008\,\Phi(6\to9)+0.7008\,\Phi(4\to7)+\cdots$ |
| $B_2$ | $\beta'$ | 45.5 | (0.13) | 45.1 | (0.77) | $0.7602\,\Phi(5\to8)+0.6511\,\Phi(4\to9)+\cdots$ |
| $A_1$ | $\beta$ | 48.2 | (1.08) | 45.5 | (0.70) | $0.6970\,\Phi(6\to8)+0.6970\,\Phi(5\to7)+\cdots$ |
| $A_1$ | $\delta$ | | | 55.5 | (0.59) | $0.7107\,\Phi(4\to10)+0.7107\,\Phi(3\to9)+\cdots$ |

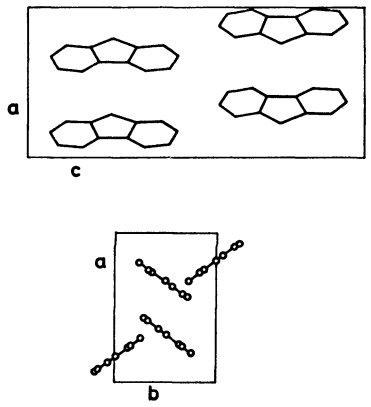


Fig. 2. Projection of fluorene onto the (010) and (001) planes.

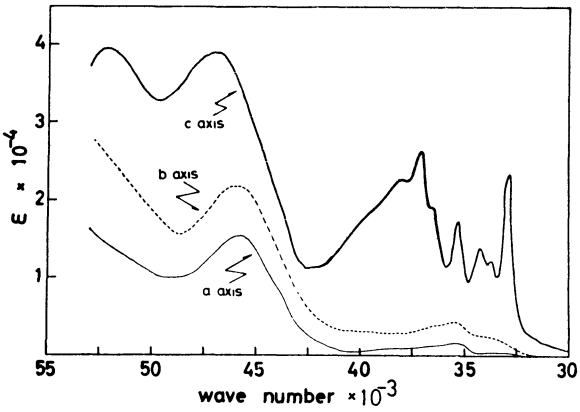


Fig. 3. The polarized absorption spectra of the fluorene crystal obtained by the K-K transformation of the reflection spectra.

the (001) plane. Thus, a long axis transition in the isolated molecule may not be observed in the (001) cleavage plane; only the short axis transition is allowed and is assigned to the $A_1\to A_1$ transition. The c axis spectrum is of the $B_2$ states allowed for the polarized light parallel to the long axis in the molecule. It will be expected that the $A_1$ and $B_2$ excited states can be separately measured and the absorption spectra for these crystalline axes can be obtained from the reflection spectra, as shown in Fig. 3.

In the crystalline c-axes spectrum, four transitions of $\alpha^*$, p, $\beta^*$, and $\beta'$ were observed at 32900, 35300, 47400, and 52600 $cm^{-1}$; these were assigned to the transition to the $B_2$ state. The a and b axes spectra have three bands ($\alpha$, $\beta$, and $\delta$) at 33500, 46000, and about 54000 $cm^{-1}$, which correspond to the short axis polarized bands of the molecule and are assigned to the $A_1$ state. The theoretical studies shown in Table 1 predict two transitions (one long and one short axis polarized) followed by a strong long axis transition. This experiment shows that the lowest excited state is the $\alpha^*$ state at 32900 $cm^{-1}$ and the second state is the $\alpha$ state at 33500 $cm^{-1}$, although the first and second states obtained theoretically are reversed in order. Bree and Zwarich[12] found that 32818 $cm^{-1}$ in fluorescence and 32910 $cm^{-1}$ in the c axis-polarized absorption may both connect the same lowest electronic levels ($B_2$ state) in the crystal. Our experimental result is in good agreement with their measurement. The successive levels of the lowest $\alpha^*$ state are located at 33700 and 34300 $cm^{-1}$ in the crystalline spectrum and at 34000 and 34700 $cm^{-1}$ in the solution spectrum. The origin of the p state is assigned to the peak at 35300 $cm^{-1}$ and higher vibronic levels appear at 36400, 37100, and 38100 $cm^{-1}$. The comparison of the vibronic levels between the solution and the crystalline spectra is shown in Table 2.

The excitation energies and oscillator strengths of the crystal were calculated by the RPA exciton me-

TABLE 2. VIBRONIC LEVELS FOR THE LOWER EXCITED STATES OF FLUORENE
(All energy values are given in the units of $cm^{-1}$.)

| State | Solution | | Crystal | |
|---|---|---|---|---|
| $\alpha^*$ | 33200 | | 32900 | |
| | | (800) | | (800) |
| | 34000 | | 33700 | |
| | | (700) | | (600) |
| | 34700 | | 34300 | |
| $\alpha$ | | | 33500 | |
| | | | | (1900) |
| | | | 35400 | |
| p | 35900 | | 35300 | |
| | | (1000) | | (1100) |
| | 36900 | | 36400 | |
| | | (1200) | | (700) |
| | 38100 | | 37100 | |
| | | (1100) | | (1000) |
| | 39200 | | 38100 | |
| | | (1200) | | |
| | 40400 | | | |

Table 3. The calculated and observed values of the transition energies ($E$ in $10^3\,cm^{-1}$) and oscillator strengths of the fluorene crystal

| State | | Obsd | | Calcd | |
|---|---|---|---|---|---|
| | | $E$ | $(f)$ | $E$ | $(f)$ |
| $B_{3u}$ | $\alpha$ | 33.5 | (0.05) | 33.0 | (0.00) |
| (a axis) | $\beta$ | 45.7 | (0.60) | 44.3 | (0.70) |
| | $\delta$ | ≈54 | (0.91) | 54.4 | (0.46) |
| $B_{2u}$ | $\alpha$ | 33.5 | (0.13) | 33.0 | (0.00) |
| (b axis) | $\beta$ | 46.2 | (0.86) | 47.0 | (1.04) |
| | $\delta$ | ≈54 | (1.12) | 56.5 | (1.65) |
| $B_{1u}$ | $\alpha^*$ | 32.9 | (0.43) | 33.5 | (0.00) |
| (c axis) | p | 35.3 | (1.18) | 33.7 | (2.35) |
| | $\beta^*$ | 47.4 | (1.50) | 42.5 | (0.55) |
| | $\beta'$ | 52.6 | (1.00) | 44.3 | (1.42) |

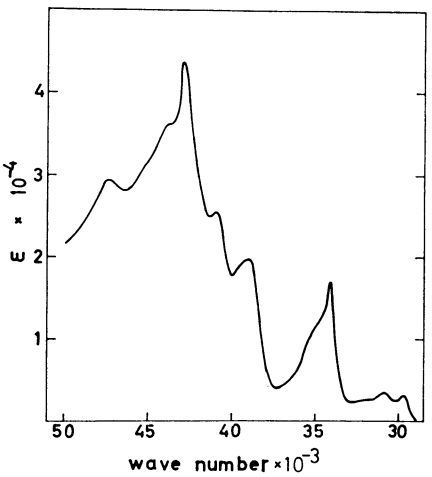


Fig. 4. The spectrum in ethanol of the carbazole molecule.

thod.[15] The results are shown in Table 3, in which the intermolecular interactions for the inner zone were calculated to 50 Å. As shown in Tables 1 and 3, the comparison between the oscillator strengths of the molecule and the crystal show that the sum of the oscillator strengths of two states ($\alpha$ and $\alpha^*$ states) is 0.39 ($3\,f^{\text{solution}}$) in the molecule and 0.61 ($f^a+f^b+f^c$) in the crystal. In the intense p band, the absorption intensity in the molecule ($3\,f^{\text{solution}}=1.29$) is comparable with 1.18 ($f^c$) in the crystal. The dichroic ratio($f^a/f^b=2.6$) of the $\alpha$ band is slightly larger than the oriented gas polarization ratio of 2.1. However, those of the higher states deviate from the values expected from the oriented gas model and can be explained by the intermolecular interaction.

*Carbazole.* The solution spectrum is described in Fig. 4 and the theoretically calculated results of the molecule are given in Table 4, together with the assignment of the observed states. The first band in the region of 30000 $cm^{-1}$ has structure; the origin is located at 29700 $cm^{-1}$ and other vibronic levels appear at 30900 and 32100 $cm^{-1}$. This state is assigned to the short axis polarized state of $A_1$ symmetry ($\alpha$ band). The second $\alpha^*$ band originating at 34100 $cm^{-1}$ is of $B_2$ symmetry and a successive vibronic level appears as the shoulder at 35300 $cm^{-1}$. Band positions of the $\alpha$ and $\alpha^*$ states are summarized in Table 5. There are many other states in the higher energy region, the p band at 39000 $cm^{-1}$ and a stronger and more complex system which probably contains four separate electronic transitions at 41000 $cm^{-1}$ ($\beta$ state), 43000 $cm^{-1}$ ($\beta'$ state), 45000 $cm^{-1}$ ($\beta^*$ state), and 47400 $cm^{-1}$ ($\gamma$ state).

Carbazole forms orthorhombic crystals of space group Pnma ($D_{2h}^{16}$) with four molecules, as shown in Fig. 5.[10] The crystal structure of carbazole resembles that of fluorene having the same space group (although the axes b and c have been interchanged) and has similar unit cell dimensions and molecular orientations. The polarized absorption spectra along three crystalline axes are obtained from the reflection spectra by the K-K transformation and are shown in Fig. 6. The excitation energies and oscillator strengths of the crystal were calculated by the SCF-RPA exciton method; the results are shown in Table 6 together with the observed values.

In the crystalline b axis spectrum, four transitions ($\alpha^*$, p, $\beta'$, and $\beta^*$) at 33900, 40300, 42000, and 45600 $cm^{-1}$ must be assigned to the $B_2$ state. The a and c axes spectra have four bands ($\alpha$, $\beta$, $\gamma$, and $\delta$) at 29400, ≈40000, ≈44000, and 53000 $cm^{-1}$ which should be assigned to the $A_1$ state. Band positions of the vibronic levels of the $\alpha$ and $\alpha^*$ states can be compared with those in the solution spectrum, as shown in Table 5. The factor group splitting and the crystal field shift are negligibly small in the a and c axes spectra,

Table 4. The lower excited states of the carbazole molecule, calculated by the RPA method
(All energy values are given in the units of $10^3\,cm^{-1}$.)

| State | | Obsd | | Calculated values | | |
|---|---|---|---|---|---|---|
| | | $E$ | $(f)$ | $E$ | $(f)$ | Wavefunction |
| $A_1$ | $\alpha$ | 29.7 | (0.04) | 31.9 | (0.01) | $0.7390\,\Phi(6\to8)-0.5828\,\Phi(7\to9)+\cdots$ |
| $B_2$ | $\alpha^*$ | 34.1 | (0.16) | 35.0 | (0.05) | $0.5905\,\Phi(5\to8)+0.5447\,\Phi(7\to10)+\cdots$ |
| $B_2$ | p | 39.0 | (0.17) | 37.7 | (0.33) | $0.9095\,\Phi(7\to8)+0.2640\,\Phi(6\to9)+\cdots$ |
| $B_2$ | $\beta'$ | 43.0 | (0.82) | 42.0 | (1.04) | $0.9351\,\Phi(6\to9)-0.2566\,\Phi(7\to8)+\cdots$ |
| $A_1$ | $\beta$ | 41.0 | (0.18) | 43.5 | (0.46) | $0.6291\,\Phi(7\to9)+0.5614\,\Phi(6\to8)+\cdots$ |
| $A_1$ | $\gamma$ | 47.4 | (0.25) | 44.6 | (0.26) | $0.6634\,\Phi(6\to10)+0.4311\,\Phi(7\to9)+\cdots$ |
| $B_2$ | $\beta^*$ | 45.0 | (0.1) | 45.6 | (0.00) | $0.7252\,\Phi(7\to10)-0.6645\,\Phi(5\to8)+\cdots$ |
| $A_1$ | $\delta$ | | | 57.0 | (0.60) | $0.8067\,\Phi(4\to10)-0.5936\,\Phi(5\to11)+\cdots$ |

TABLE 5. VIBRONIC LEVELS FOR THE LOWER EXCITED STATES OF CARBAZOLE

(All energy values are given in the units of $cm^{-1}$.)

| State | Solution | | Crystal | |
|---|---|---|---|---|
| $\alpha$ | 29700 | | 29400 | |
| | | (1200) | | (1300) |
| | 30900 | | 30700 | |
| | | (1200) | | (1300) |
| | 32100 | | 32000 | |
| $\alpha^*$ | 34100 | | 33900 | |
| | | (800) | | (800) |
| | 35300 | | 34700 | |

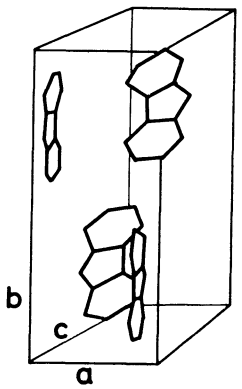


Fig. 5. The unit cell of the carbazole crystal.

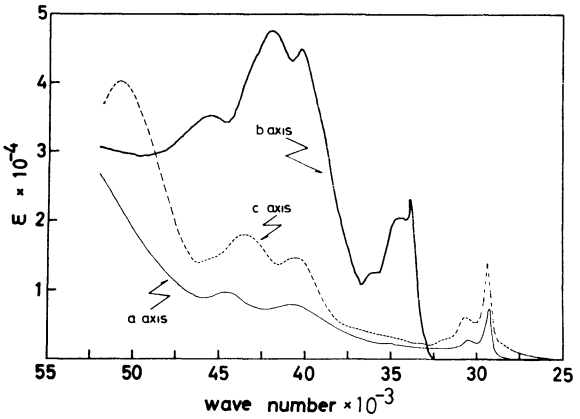


Fig. 6. The polarized absorption spectra of the carbazole crystal obtained by the K-K transformation of the reflection spectra.

although large shifts are observed in the b axis spectrum. Tables 4 and 6 show that the oscillator strength of the $\alpha$ state is 0.12 ($3\,f^{\text{solution}}$) in the molecule and 0.29 ($f^a+f^c$) in the crystal and the hyperchromism is observed. In the $\alpha^*$ state, the intensity of the molecule ($3\,f^{\text{solution}}=0.48$) is comparable with that of the crystal ($f^b=0.54$). The p and $\beta$ states are hyperchromic and the intensities of the molecule increase in the crystal. The observed dichroic ratios ($f^b/f^c$) of the $\alpha$ and $\gamma$ states are about 2.6, while the oriented gas polarization ratio is 3.2. Those of the other states ($\beta$ and $\delta$) deviate from the values expected from the oriented gas model and may be explained by the intermolecular interaction.

TABLE 6. THE CALCULATED AND OBSERVED VALUES OF THE TRANSITION ENERGIES ($E$ IN $10^3\,cm^{-1}$) AND OSCILLATOR STRENGTHS OF THE CARBAZOLE CRYSTAL

| State | | Obsd | | Calcd | |
|---|---|---|---|---|---|
| | | $E$ | ($f$) | $E$ | ($f$) |
| $B_{3u}$ | $\alpha$ | 29.3 | (0.08) | 32.0 | (0.01) |
| (a axis) | $\beta$ | 40.8 | (0.34) | 41.9 | (0.29) |
| | $\gamma$ | 44.5 | (0.21) | 44.4 | (0.27) |
| | $\delta$ | ≈53 | (1.04) | 56.6 | (0.38) |
| $B_{1u}$ | $\alpha$ | 29.4 | (0.21) | 32.1 | (0.02) |
| (c axis) | $\beta$ | 4.04 | (0.50) | 41.1 | (0.001) |
| | $\gamma$ | 43.5 | (0.52) | 44.8 | (1.16) |
| | $\delta$ | ≈50 | (1.43) | 58.1 | (1.79) |
| $B_{2u}$ | $\alpha^*$ | 33.9 | (0.54) | 34.1 | (1.39) |
| (b axis) | p | 40.3 | (0.90) | 36.0 | (0.90) |
| | $\beta'$ | 42.0 | (2.00) | 40.7 | (2.06) |
| | $\beta^*$ | 45.6 | (0.60) | 49.8 | (0.17) |

*Dibenzofuran.* The solution spectrum is depicted in Fig. 7 and the theoretically calculated results of the molecule are given in Table 7 together with the assignment of the observed states. The first band, extending from about 33000 to 40000 $cm^{-1}$, has structure and consists of both the short axis polarized state ($\alpha$ state) and the long axis polarized state ($\alpha^*$ state). The $\alpha$ state in the region of the lowest energy originates at 33100 $cm^{-1}$ and the successive vibronic levels occur as the shoulders at 34600 and 36100 $cm^{-1}$. The $\alpha^*$ state is observed as sharp peaks; the principal origin is at 33600 $cm^{-1}$ and the higher levels are located at 34800 and 35600 $cm^{-1}$. The assignment for these two bands is supported by comparison with the crystalline spectra, as shown below. The third state (p state) also has structure; the origin is observed at 40100 $cm^{-1}$ and other levels appear at 40900 and 41400 $cm^{-1}$. This band is assigned to the $B_2$ state. There are many other states in the higher energy region: two shoulders at 43900 $cm^{-1}$ ($\beta$ state) and 47200 $cm^{-1}$ ($\beta^*$ state) and two intense bands at 45800 $cm^{-1}$ ($\beta'$ state) and

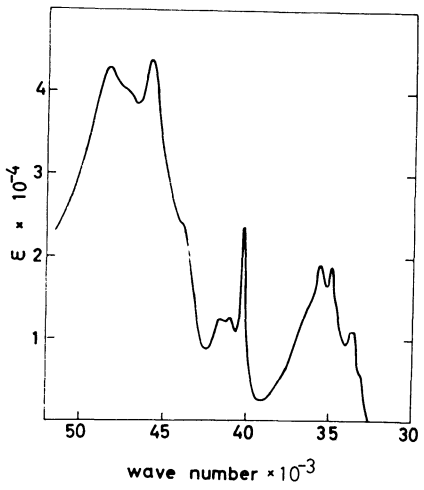


Fig. 7. The spectrum in light petroleum of the dibenzofuran molecule.

TABLE 7. THE LOWER EXCITED STATES OF THE DIBENZOFURAN MOLECULE, CALCULATED BY THE RPA METHOD
(All energy values are given in the units of $10^3\,cm^{-1}$.)

| State | | Obsd | | Calculated values | | |
|---|---|---|---|---|---|---|
| | | $E$ | $(f)$ | $E$ | $(f)$ | Wave function |
| $A_1$ | $\alpha$ | 33.1 | (0.04) | 33.7 | (0.003) | $0.6877\,\Phi(6\to8)-0.6186\,\Phi(7\to9)+\cdots$ |
| $B_2$ | $\alpha^*$ | 33.6 | (0.29) | 35.5 | (0.02) | $0.6252\,\Phi(5\to8)-0.5890\,\Phi(7\to10)+\cdots$ |
| $B_2$ | p | 40.1 | (0.15) | 38.0 | (0.55) | $0.9680\,\Phi(7\to8)+\cdots$ |
| $A_1$ | $\beta$ | 43.9 | (0.17) | 45.4 | (0.42) | $0.5437\,\Phi(7\to9)+0.5244\,\Phi(6\to8)+\cdots$ |
| $B_2$ | $\beta'$ | 45.8 | (0.54) | 45.7 | (0.86) | $0.8804\,\Phi(6\to9)+0.4016\,\Phi(5\to10)+\cdots$ |
| $B_2$ | $\beta^*$ | 47.2 | (0.25) | 45.9 | (0.01) | $0.6966\,\Phi(7\to10)+0.6671\,\Phi(5\to8)+\cdots$ |
| $A_1$ | $\gamma$ | 48.3 | (0.67) | 46.4 | (0.35) | $0.4943\,\Phi(7\to9)+0.4762\,\Phi(6\to10)$ $+0.4467\,\Phi(6\to8)+0.3957\,\Phi(5\to9)+\cdots$ |
| $A_1$ | $\delta$ | | | 57.5 | (0.59) | $0.7728\,\Phi(4\to10)+0.6390\,\Phi(5\to11)+\cdots$ |

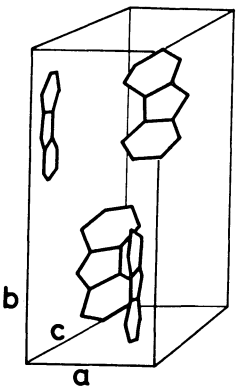


Fig. 8. The unit cell of dibenzofuran crystal.

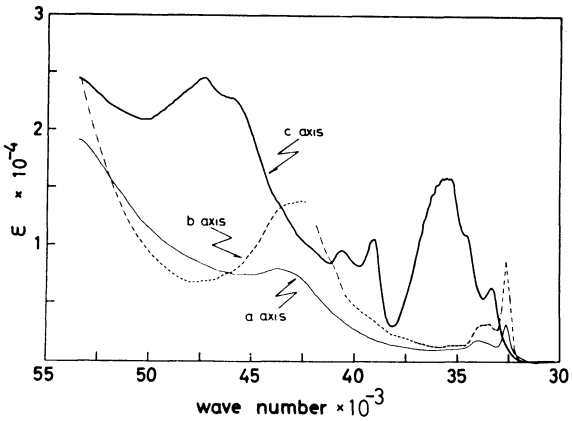


Fig. 9. The ploarized absorption spectra of the dibenzofuran crystal obtained by the K-K transformation of the reflection spectra.

48300 $cm^{-1}$ ($\gamma$ state).

Dibenzofuran crystallizes with four molecules in an orthorhombic unit cell having space group Pnam ($D_{2h}^{16}$).[14] Each molecule is held in the lattice with the long axis exactly parallel to the c crystal axis and with the short in-plane axis in the ab plane. The dispositions of the four molecules in the unit cell are shown clearly in Fig. 8. The polarized absorption spectra along these crystal axes are given from the reflection spectra by the K-K transformation, as shown in Fig. 9.

TABLE 8. VIBRONIC LEVELS FOR THE LOWER EXCITED STATES OF DIBENZOFURAN
(All enengy values are given in the units of $cm^{-1}$.)

| State | Solution | | Crystal | |
|---|---|---|---|---|
| $\alpha$ | 33100 | | 32600 | |
| | | (1500) | | (1400) |
| | 34600 | | 34000 | |
| | | (1500) | | (1400) |
| | 36100 | | 35400 | |
| $\alpha^*$ | 33600 | | 33300 | |
| | | (1200) | | (1200) |
| | 34800 | | 34500 | |
| | | (800) | | (800) |
| | 35600 | | 35300 | |
| p | 40100 | | 39100 | |
| | | (800) | | |
| | 40900 | | | (1500) |
| | | (500) | | |
| | 41400 | | 40600 | |

TABLE 9. THE CALCULATED AND OBSERVED VALUES OF THE TRANSITION ENERGIES ($E$ IN $10^3\,cm^{-1}$) AND OSCILLATOR STRENGTHS OF THE DIBENZOFURAN CRYSTAL

| State | | Obsd | | Calcd | |
|---|---|---|---|---|---|
| | | $E$ | $(f)$ | $E$ | $(f)$ |
| $B_{3u}$ | $\alpha$ | 32.6 | (0.02) | 33.8 | (0.003) |
| (a axis) | $\beta$ | 43.5 | (0.14) | 44.9 | (0.50) |
| | $\gamma$ | | | 49.6 | (0.02) |
| | $\delta$ | ≈55 | (0.65) | 56.9 | (0.37) |
| $B_{2u}$ | $\alpha$ | 32.6 | (0.06) | 33.8 | (0.004) |
| (b axis) | $\beta$ | 42.5 | (0.60) | 46.0 | (0.99) |
| | $\gamma$ | | | 49.0 | (0.04) |
| | $\delta$ | ≈53.5 | (0.76) | 50.5 | (0.39) |
| $B_{1u}$ | $\alpha^*$ | 33.3 | (0.36) | 34.8 | (1.55) |
| (c axis) | p | 39.1 | (0.20) | 36.0 | (0.92) |
| | $\beta'$ | ≈46 | (1.30) | 44.4 | (1.95) |
| | $\beta$ | ≈53.5 | (0.27) | 52.1 | (0.10) |

In the crystalline c axis spectrum, four transitions ($\alpha^*$, p, $\beta'$, and $\beta^*$) observed at 33300, 39100, 46000, and 53500 $cm^{-1}$ must be polarized along the long axis of the molecule and may be assigned to the $B_2$ state. The $\alpha^*$ state is located at 33300 $cm^{-1}$ and the following

levels are observed at 34500 and 35300 $cm^{-1}$. The p state originates at 39100 $cm^{-1}$ and the higher level appears at 40600 $cm^{-1}$, while the second level at 40900 $cm^{-1}$ in the solution spectrum can not be observed. The a and b axes spectra have three bands ($\alpha$, $\beta$, and $\delta$ states) at 32600, about 43000, and 55000 $cm^{-1}$, corresponding to the short axis polarized band of the molecule, and can be assigned to the $A_1$ state. The $\alpha$ state has its origin at 32600 $cm^{-1}$ and the higher successive levels are observed at 34000 and 35400 $cm^{-1}$.

The excitation energies and oscillator strengths of the crystal were calculated by the SCF-RPA exciton method; the results are shown in Table 9, in which the intermolecular interactions for the inner zone were calculated to be 50 Å. The factor group splitting is slightly observed for the $\beta$ and $\delta$ states. However, many transitions in the crystal are red-shifted by the crystal force compared with the transitions in solution. The comparison between the observed oscillator strengths of the molecule and crystal shows that the oscillator strength of the $\beta$ band is 0.51 ($3\,f^{\text{solution}}$) in the molecule and 0.74 ($f^{a}+f^{b}$) in the crystal and the hyperchromism is observed in the range of 44000 $cm^{-1}$. On the other hand, the $\alpha^*$ state is hypochromic and the intensity of the molecule ($3\,f^{\text{solution}}=0.87$) decreases to 0.36 ($f^{c}$) in the crystal. Such decreases of the intensity are also observed in all other state regions. The observed dichroic ratios ($f^{b}/f^{a}$) of the $\alpha$ and $\beta$ states are 3.0 and 3.6, respectively. These values are comparable with the oriented gas polarization ratio of 3.6. However, that of the $\beta$ state deviates from the values expected from the oriented gas model.

The author would like to express his deep gratitude to Professor Jiro Tanaka of this university for his kind encouragement and critical reading of the manuscript.

**References**

1) C. A. Pinkham and S. C. Wait, Jr., *J. Mol. Spectrosc.*, **27**, 326(1968).
2) Y. Kanda, R. Shimada, K. Hanada, and S. Kajigaeshi, *Spectrochim. Acta*, **17**, 1268 (1961).
3) N. Mataga, Y. Torihashi, and K. Ezumi, *Theor. Chem. Acta.* **2**, 158(1964).
4) F. Dörr and H. Gropper, *Ber. Bunsenges. Phys. Chem.*, **67**, 193 (1963).
5) N. Joop, *Diplom-Arbeit THMünchen*, 1960.
6) H. Schütt and H. Zimmerman, *Ber. Bunsenges. Phys. Chem.*, **67**, 55 (1963).
7) A. R. Lacey, A. E. W. Knight, and I. G. Ross, *J. Mol. Spectrosc.*, **47**, 307 (1973).
8) S. Siegel and H. S. Judeikis, *J. Phys. Chem.*, **70**, 2207 (1966).
9) D. M. Durns and J. Iball, *Proc. R. Soc. London, Ser. A*, **227**, 200 (1955).
10) M. Kurahashi, M. Fukuyo, and A. Shimada, *Bull. Chem. Soc. Jpn.*, **42**, 2174 (1969).
11) O. Dindenberg, L. Dupont, and J. M. Andrè, *Acta Crystallogr., Sect. B*, **28**, 1002 (1972).
12) A. Bree and R. Zwarich, *J. Chem. Phys.*, **51**, 903 (1969).
13) A. Bree and R. Zwarich, *J. Chem. Phys.*, **49**, 3355 (1968).
14) A. Bree, V. V. B. Vilkos, and R. Zwarich, *J. Mol. Spectrosc.*, **48**, 135 (1973).
15) M. Tanaka and J. Tanaka, *Theor. Chim. Acta*, **30**, 81 (1973).
16) I. Tinoco, Jr., *J. Chem. Phys.*, **33**, 1332 (1960), **34**, 1067 (1961).
17) W. Rhodes, *J. Am. Chem. Soc.*, **83**, 3609 (1961).
18) H. J. Bowlden and J. K. Wilmshurst, *J. Opt. Soc. Am.*, **53**, 1073 (1963).
19) A. Matsui and Y. Ishii, *J. Phys. Soc. Jpn.*, **23**, 581 (1967).
20) T. H. Dunning and V. McKoy, *J. Chem. Phys.*, **47**, 1735 (1967).
21) R. G. Parr, *J. Chem. Phys.*, **20**, 1499 (1952).
22) K. Nishimoto and N. Mataga, *Z. Phys. Chem.(NF).*, **12**, 335 (1957).
23) E. Clementi, C. C. J. Roothaan, and M. Yoshimine, *Phys. Rev.*, **127**, 1618 (1962).
24) G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **24**, 937 (1962).
25) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).
26) F. Momicchioli and A. Rastelli, *J. Mol. Spectrosc.*, **22**, 310 (1967); *J. Chem. Soc., B*, **1970**, 1354.