Electronic Spectrum of Fluorenone[*]

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Heretofore the electronic spectra of fluorenone and its derivatives have been reported on by many authors. Though fluorenone is a fundamental substance in organic chemistry, there have been few papers in which these spectra have been studied in detail either theoretically or experimentally. In this work, the electronic spectrum of fluorenone in various solvents will be measured, and from these results and from the results calculated with the simple MO[1] method for the π-electronic system of fluorenone the nature of each absorption band of fluorenone will be studied. It will be shown that the weak absorption band near 380 mμ, which has been heretofore regarded as an $n \rightarrow \pi^*$ band,[2-5] is really a $\pi \rightarrow \pi^*$ band.

Experimental and Results

Materials. — Commercially-available fluorenone was purified by means of vacuum sublimation (m. p. 83∼84°C). All the solvents used in the present study were of special grade. Ethanol (99.5 vol.%) was distilled. Chloroform was washed several times with water, dried with calcium chloride, and distilled. Carbon tetrachloride was dried with calcium chloride and distilled. Dioxane and

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[*] The major part of this paper was presented at the Symposium on the Electronic Structure of Molecules, Sendai, October, 1963.

[1] In this paper the term "molecular orbital" is abbreviated as "MO."

[2] E. D. Bergmann, G. Berthier, Y. Hirshberg, E. Loewenthal, B. Pullman and A. Pullman, *Bull. soc. chim. France*, **17**, 669 (1951).

[3] J. R. Platt, *J. Chem. Phys.*, **19**, 101 (1951).

[4] F. Dörr, *Z. Elektrochem.*, **61**, 950 (1957).

[5] E. Lippert and H. Walter, *Angew. Chem.*, **71**, 429 (1959).

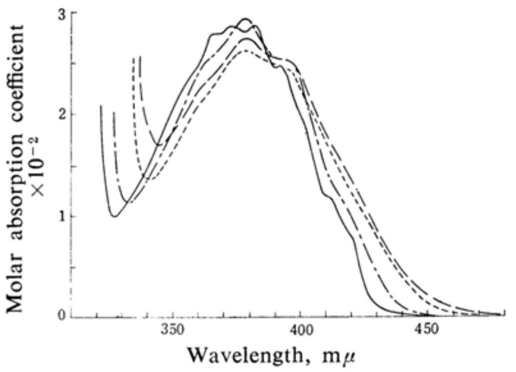


Fig. 1. Fluorenone. Solvent; —— *n*-heptane, —·— ethanol, ---- chloroform, —— carbon tetrachloride.

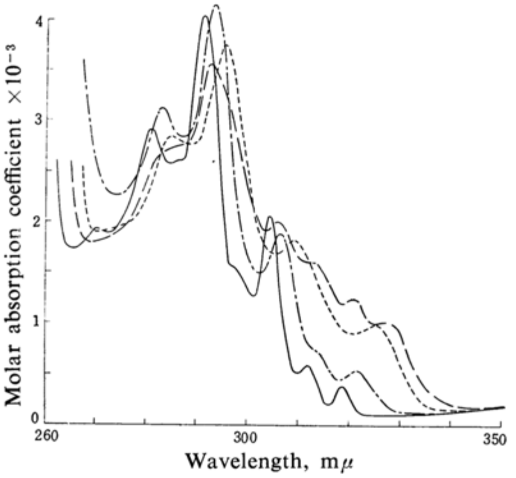


Fig. 2. Fluorenone. Solvent; —— *n*-heptane, —·— ethanol, ---- chloroform, —— carbon tetrachloride.

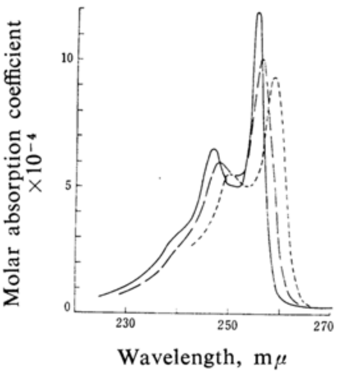


Fig. 3. Fluorenone. Solvent; —— *n*-heptane, —·— ethanol, ---- chloroform.

n-heptane were purified according to the methods described in a previous paper.⁶⁾

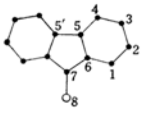
Measurements. — The absorption spectra were measured with a Cary 14M recording spectrophotometer with the fused quartz cells of 1 and 5 cm. path.

Results.—The absorption spectra obtained are given in Figs. 1—3.

Method of Calculation

It is thought that, in the calculations with the MO method for the π-electronic system of unsaturated carbonyl compounds such as fluorenone, the effect of the configuration interaction in explaining the low energy electronic spectra qualitatively is not indispensable as in quinones,⁷⁾⁸⁾ and so, that the results obtained with the simple MO method are useful to some extent in this case. Therefore, in this work we used results obtained with the simple MO method.

Though the molecular dimensions of fluorenone have never been established, considering the molecular dimensions of fluorene studied by X-ray analysis⁹⁾ it is thought that fluorenone is planar or almost so, and that in the calculations with the simple MO method the Coulomb and the exchange integrals used in quinones can reasonably be applied to fluorenone. In *o*- and *p*-benzoquinones,⁸⁾ in order to make the MO's in the simple MO method simulate those obtained with the SCF MO method, including electronic interaction, the Coulomb integral (α_i) of the oxygen atom should be far smaller (in β units) than those generally used; the exchange integral (β_{ij}) of the conventional single bond also should be smaller (in β units) than those generally used. These new integral values are thought to be better than those generally used. The integral values used with this in mind are shown in Chart 1(a). The dependence of the orbital energy levels upon the Coulomb integral of



(a)

$$\alpha_1=\alpha_2=\cdots=\alpha_6=\alpha_7=\alpha$$
$$\alpha_8=\alpha+0.3\beta$$
$$\beta_{12}=\beta_{23}=\cdots=\beta_{56}=0.9\beta$$
$$\beta_{55'}=\beta_{67}=0.5\beta$$
$$\beta_{78}=1.2\beta$$

(b)

$$\alpha_1=\alpha_2=\cdots=\alpha_6=\alpha$$
$$\alpha_7=\alpha+0.2\beta$$
$$\alpha_8=\alpha+1.3\beta$$
$$\beta_{12}=\beta_{23}=\cdots=\beta_{56}=\beta_{78}=\beta$$
$$\beta_{55'}=\beta_{67}=0.9\beta$$

Chart I. Values of Coulomb and exchange integrals

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6) A. Kuboyama, This Bulletin, **33**, 1027 (1960); *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 558 (1960).

7) J. W. Sidman, *J. Chem. Phys.*, **27**, 429 (1957).

8) A. Kuboyama and K. Wada, Published in the Annual Meeting of the Chemical Society of Japan (1964).

9) G. M. Brown and M. H. Bortner, *Acta Cryst.*, **7**, 139 (1954); D. M. Burns and J. I'ball, *Nature*, **173**, 635 (1954); *Proc. Roy. Soc.*, **A227**, 200 (1955).

the oxygen atom of fluorenone was also calculated. Furthermore, the calculations with the integral values used in our previous studies[10] of quinones were also carried out for the sake of comparison. These integral values are shown in Chart I(b).

Calculated Results and Discussion

As may be seen in Figs. 1—3, it appears that fluorenone has three absorption bands (near 380 mμ, 300 mμ, and 250 mμ, respectively) in the near-ultraviolet region. Unfortunately, the vibrational structure of the 380 mμ band is not clear. The 380 mμ band shifts considerably toward longer wavelengths from *n*-heptane to carbon tetrachloride, chloroform, and ethanol. In chloroform and ethanol the 380 mμ band is at almost the same position and seems to be at a little longer wavelengths than in carbon tetrachloride. The shift of the center of the 380 mμ band from *n*-heptane to chloroform and ethanol is estimated at ca. 8 mμ. As for the 300 mμ band, in *n*-heptane, the intervals (ca. 770 cm^{-1}) in the three peaks on the longer wavelength side (at 319 mμ, 311.5 mμ and 304 mμ, respectively) are far smaller than that (1470 cm^{-1}) between the two peaks on the shorter wavelength side (at 291 mμ and 281 mμ). The former peak group shifs ca. 10 mμ toward longer wavelengths from *n*-heptane to ethanol, while the latter one shifts only ca. 1.5 mμ toward longer wavelengths. The orders of the magnitude of the red-shift[11] of the former and the latter peak groups in various solvents are ethanol>chloroform>carbon tetrachloride and chloroform>carbon tetrachloride>ethanol respectively.

These differences in vibrational structure and solvent effect between the two peak groups show that the two peak groups originate in different eletronic transitions. The 250 mμ band shifts only ca. 1 mμ toward longer wavelengths from *n*-heptane to ethanol, and the order of the magnitude of the red-shift is chloroform>ethanol, as in the 290 mμ band. The interval (1235 cm^{-1}) between the two peaks (at 255 mμ and 247 mμ) of the 250 mμ band in *n*-heptane also almost agrees with that of the 290 mμ band in *n*-heptane. From the facts mentioned above it may be concluded that fluorenone has four absorption bands in the near-ultraviolet region (near 380 mμ, 310 mμ, 290 mμ, and 250 mμ respectively). The facts about the vibrational structure and solvent effect mentioned above may show that the excited electronic states of the 290 mμ and 250 mμ bands are substantially similar and different from that of the 310 mμ band.

Considering that, as a proton-donor in the hydrogen-bond formation, ethanol is stronger than chloroform and that *n*-heptane and carbon tetrachloride are not proton donors, the large red-shift of the 310 mμ band in ethanol and chloroform is thought to be mainly due to hydrogen-bond formation between the carbonyl oxygen atom of fluorenone and these solvents. On the other hand, the polarizability of solvents is generally thought to be almost equally effective for the red-shifts of all absorption bands of solutes. The order of the magnitudes of the polarizability of various solvents, as a bulk effect, agrees with that of the refractive indices of the solvents. The refractive indices[12] (for the sodium D line at 20°C) of chloroform and carbon tetrachloride (1.445 and 1.463 respectively) are considerably larger than those[12] of ethanol and *n*-heptane (1.361 and 1.388 respectively). Therefore, from the facts mentioned above, it may reasonably be concluded that, for the red-shift of the 310 mμ band, the hydrogen-bond formation mentioned above is far more effective than the polarizability of the solvents and that, for the red-shifts of the 290 mμ and 250 mμ bands, the hydrogen-bond formation mentioned above is less effective than the polarizability of the solvents. As for the 380 mμ band, for its red-shift the hydrogen-bond formation mentioned above is thought to be effective.

The 310 mμ, 290 mμ, and 250 mμ bands may be safely regarded as $\pi\rightarrow\pi^*$ bands. The 380 mμ band has, heretofore, been described as an $n\rightarrow\pi^*$ band. As has been pointed out by Blealey and Kasha,[13] however, $n\rightarrow\pi^*$ bands shift toward longer wavelengths with hydrogen-bond formation between hetero-atoms in solutes, participating in the $n\rightarrow\pi^*$ transition, and solvents. Therefore, the solvent effect for the 380 mμ band shows that this band should be a $\pi\rightarrow\pi^*$ band. The maximum molar absorption coefficient of the 380 mμ band (ca. 250) seems too large for $n\rightarrow\pi^*$ bands of planar unsaturated carbonyl compounds. It is well known that $n\rightarrow\pi^*$ bands shift toward shorter wavelengths with the substitution of electron-donating groups, such

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[10] A. Kuboyama, This Bulletin, **31**, 752 (1958); **32**, 1226 (1959).

[11] In this paper the terms "shifts of absorption bands toward longer wavelengths and toward shorter wavelengths" are abbreviated as a "red-shift" and "blue-shift", respectively.

[12] A. Weissberger et al., "Organic Solvent," Interscience Publishers, Inc., New York, N. Y. (1955), pp. 59, 91, 193 and 194.

[13] G. J. Blealey and M. Kasha, *J. Am. Chem. Soc.*, **77**, 4462 (1955).

TABLE I. POSITIONS OF THE CENTER OF THE 380 mμ BAND

	Solvent	λ(mμ)	Lit.
Fluorenone	*n*-Heptane	~377	
Fluorenone	Ethanol	~385	
2-Methylfluorenone	Isooctane	~395	Ref. 2
3-Methylfluorenone	Isooctane	~375	Ref. 2
2-Dimethylaminofluorenone	Heptane	~485	Ref. 18
2-Dimethylaminofluorenone	Ethanol	~520	Ref. 18
2-Hydroxyfluorenone	Dioxane	~425	Ref. 18
3-Methoxyfluorenone	Isooctane	~365	Ref. 19

as alkyl, hydroxyl, and amino groups.[14-17] In Table I, the center positions of the 380 mμ bands of several, electron-donating-group substituted fluorenones in various solvents are shown. The solvent effects by *n*-heptane and isooctane are thought to be nearly the same. From this table it may be seen that the 380 mμ band shifts toward longer wavelengths with "2"-substitution and more or less toward shorter wavelengths with "3"-substitution respectively. This "2"-substitution effect also shows that the 380 mμ band should be a $\pi\rightarrow\pi^*$ band. All the experimental facts mentioned above show that the 380 mμ band should be a $\pi\rightarrow\pi^*$ band. Therefore, the 380 mμ band will henceforth be so regarded. Since the position of the $n\rightarrow\pi^*$ band of fluorenone is thought to be not far from that of the 380 mμ band, the former band is probably hidden in the latter one because of its low intensity. The blue-shift of the 380 mμ band with the "3"-substitution of electron-donating groups will be explained later on the basis of the π-electronic structure of fluorenone.

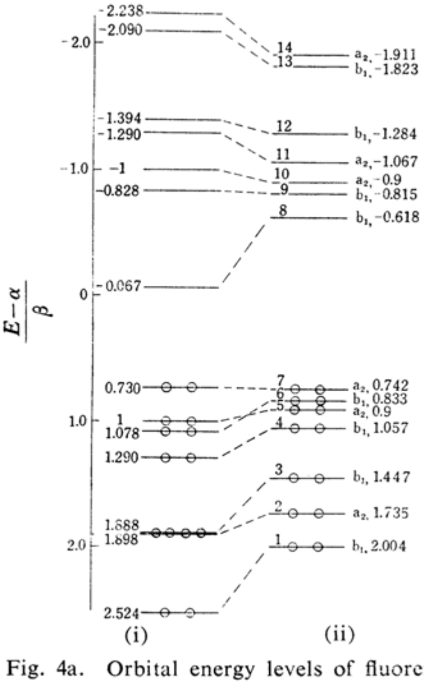

Fig. 4a. Orbital energy levels of fluorenone.

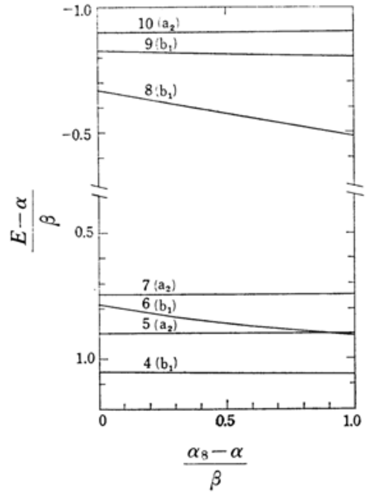

Fig. 4b. Dependence of orbital energies upon Coulomb integral of oxygen atom.

The calculated orbital energy levels of fluorenone and the dependence of energy upon the Coulomb integral of the oxygen atom of fluorenone are shown in Figs. 4a and 4b, respectively. The energy levels in Fig. 4a(i) were obtained with the integral values in Chart I(b). The MO's are classified according to their symmetry properties in the symmetry group C_{2v}. Considering Figs. 4a and 4b together, the transitions which may reasonably be assigned to the 380 mμ band are thought to be safely limited to the three transitions (7→8, 6→8, and 5→8) on the basis of the magnitude of transition energy. It is reasonable to expect that, with the hydrogen-bond formation between fluorenone and solvents, the Coulomb integral of the oxygen atom of fluorenone becomes larger (in β unit). In Fig. 4b it may be seen that, with the increase in the Coulomb integral of the oxygen

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14) H. Bada, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**, 341 (1951).
15) S. Nagakura, This Bulletin, **25**, 164 (1952).
16) L. E. Orgel, *J. Chem. Soc.*, **1955**, 121.
17) A. Kuboyama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 1062 (1956).

atom, the energies of the transitions (7→8 and 5→8) become smaller to a larger extent than that of the transition (6→8). Therefore, from the solvent effect the 380 mμ band may favorably be assigned to either of the two transitions (7→8 or 5→8), both ($A_1 \rightarrow B_2$). Similarly, from the solvent effect, the 310 mμ band also may be assigned to either of these two transitions.

The blue-shift of the 380 mμ band with the "3"-substitution of electron-donating groups is explained as follows. Generally, in a transition ($m \rightarrow n$) in a π-electronic system, where m and n denote orbital energy levels in the simple MO method, the change in the transition energy with the substitution of electron-donating groups in the j-th atom position of the π-electronic system depends upon C^2_{mj} and C^2_{nj} in the approximation of the perturbation method,[17] where C_{ij} denotes the coefficient of the j-th atomic orbital of the LCAO MO of the i-th orbital energy level. If $C^2_{mj} \gtrsim C^2_{nj}$, the transition energy decreases with the substitution, and if C^2_{mj} is considerably smaller than C^2_{nj}, we may expect that the transition energy will rather increase with the substitution. In Table II, the C^2_{ij} values of fluorenone ($i=5, 6, 7, 8$; $j=2, 3$) are shown. In Table II, in all the cases ((a), (b), and (c)), the relative magnitudes of C^2_{ij} are similar; on the basis of them, only the transition (7→8) ($A_1 \rightarrow B_2$) can reasonably be assigned to the 380 mμ band in consideration of the substitution effect mentioned before; therefore, the transition (5→8) ($A_1 \rightarrow B_2$) may be assigned to the 310 mμ band. According to this assignment, from Table II the blue-shift of the 310 mμ band with the "2"-substitution of electron-donating groups may be expected, but, unfortunately, we have no available data about this point. In fluorenone only two kinds of electronic transition ($A_1 \rightarrow B_2$ and $A_1 \rightarrow A_1$) are possible. Therefore, the assignment of the 290 mμ and 250 mμ bands to the transition ($A_1 \rightarrow A_1$) is thus favorable.[20] The directions of the polarization of the transitions ($A_1 \rightarrow B_2$ and $A_1 \rightarrow A_1$) are perpendicular to and along the C–O bond axis of fluorenone respectively.

TABLE II. VALUES OF C^2_{ij}

(1)

	C^2_{52}	C^2_{62}	C^2_{72}	C^2_{82}
(a)	0	0.001	0.160	0.066
(b)	0	0	0.160	0.031
(c)	0	0	0.159	0.017

(2)

	C^2_{53}	C^2_{63}	C^2_{73}	C^2_{83}
(a)	0.125	0.116	0.027	0.070
(b)	0.125	0.114	0.027	0.065
(c)	0.125	0.084	0.021	0.068

Note: In (a) and (c) integral values in Charts I(a) and I(b) respectively were used. In (b) the integral values in Chart I(a) were used except that $\alpha_8 = \alpha + \beta$.

Summary

The electronic spectrum of fluorenone in various solvents has been measured; from these results and from the results obtained with the simple MO method for the π-electronic system of fluorenone, the nature of each absorption band of fluorenone has been studied. It has been concluded that fluorenone has four $\pi \rightarrow \pi^*$ absorption bands (near 380 mμ, 310 mμ, 290 mμ, and 250 mμ respectively) in the near-ultraviolet region. The assignments of the 380 mμ and 310 mμ bands to the transition ($A_1 \rightarrow B_2$) and the 290 mμ and 250 mμ bands to the transition ($A_1 \rightarrow A_1$) are favorable in view of the obtained results.

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18) E. D. Bergmann et al., *Bull. soc. chim. France*, **18**, 70 (1952).

19) S. Cohen, *J. Am. Chem. Soc.*, **79**, 1500 (1957).

20) From the solvent effect the 290 mμ band seems to be reasonably assigned to the transition (6→8) in Fig. 4b.