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# A Spectroscopic Investigation of the Low-Lying Excited States of 9-Fluorenone

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**Abstract**—The low energy electronic states of 9-fluorenone have been investigated by absorption and emission spectroscopy at low temperatures. The two lowest $^1(\pi\pi^*)$ states have been found to be of $B_2$ symmetry. The $^1(n\pi^*)$ state is expected to be of $A_2$ symmetry and its origin is estimated to be at 4550 Å. Vibronic mixing of the lowest $^1(\pi\pi^*)$ and $^1(n\pi^*)$ states is responsible for the diffuseness of the lowest $^1(\pi\pi^*)$ state even at liquid helium temperatures.

## 1. Introduction

9-Fluorenone has been the subject of various investigations because of its unusual spectroscopic properties.(1,2) We were therefore interested in obtaining definite information about the low-lying excited states of 9-fluorenone. The study of 9-fluorenone, a nonalternate aromatic hydrocarbon, also provides an opportunity to investigate an interesting class of molecules.

Azulene, the most prominent of the nonalternate hydrocarbons, has been well characterized under conditions of moderate resolution ($\sim 1$ cm$^{-1}$) and known molecular orientation,(3,4) and the dipole moments of the two lowest excited states have been determined.(5) Acenaphthylene, another common nonalternate hydrocarbon, has been studied to a lesser extent.(6,7) 9-Fluorenone's low-lying, relatively weak transitions have not been characterized under conditions of moderate resolution and known molecular orientation; however, it has been shown fairly conclusively that the lowest singlet state is of $(\pi^* \leftarrow \pi)$ character.(1,2) The position of the expected $(\pi^* \leftarrow n)$ transition is unknown, as is the symmetry of the lowest $(\pi^* \leftarrow \pi)$ transitions. It is for these reasons that we have undertaken the spectroscopic investigation of 9-fluorenone.

## 2. Experimental

All 4.2 °K spectra were taken on a one-meter Jarrell Ash Czerny Turner spectrograph with a linear dispersion of 8.2 Å/mm in first order. Some low resolution spectra were taken at 77 °K on a medium quartz Hilger spectrograph. The spectra were recorded on Kodak spectroscopic plates, types Ia-O and 103-F. Wavelength calibration was obtained by overlapping an iron spectrum from a hollow cathode iron arc lamp. The crystals were immersed directly in liquid helium contained in a double Pyrex dewar with a quartz tail section. The visible spectra were obtained with a quartz–iodine lamp and for the ultraviolet region a 500-W high pressure xenon lamp was used as a source. As an excitation source for the emission spectra, a 200-W high pressure mercury arc lamp was used in conjunction with a Bausch and Lomb high intensity monochromator and appropriate band pass filters. The light was polarized with an ultraviolet transmitting polarizer (Polacoat Co.).

The samples used were of two types: pure crystals and mixed crystals. The pure crystal samples were grown between quartz disks by slow cooling of the melt. 9-Fluorenone normally grows with a prominent *ac* face, but the *bc* face is occasionally found. The two faces are readily distinguished by their color in transmitted light and their conoscopic figures. The mixed crystal samples were grown under vacuum in a modified Bridgman furnace. Crystal orientations were determined by conoscopic methods and confirmed in the case of 9-fluorenone by X-ray studies.

The following notation has been used throughout this paper: $M(z)$ is the direction along the molecular $C_2$ axis (along the C—O bond); $L(y)$ is perpendicular to $M$ and in the molecular plane, and $N(x)$ is out of the plane.

All materials used were Eastman reagent chemicals and were zone refined under vacuum (100 passes). 9-Fluorenone and fluorene were analyzed by vapor phase chromatography. The zone-refined 9-fluorenone was found to contain no impurities down to the level of detection ( $<100$ ppm). An upper middle section of the tube containing the zone-refined fluorene was found to contain several impurities, a methylbiphenyl, anthracene, benz[*f*]indan, and possibly phenanthrene; their concentrations were on the order of 100 ppm or less.(8) The region of investigation was from 4000 to 5000 Å, so that none of these impurities have interfering absorption in this region. Biphenyl was also used as a host. Zone-refined biphenyl was found to be free of absorbing impurities in the 3000 to 5000 Å range, indicating a spectroscopic impurity level of $< 1$ ppm.

## 3. Crystal Structure

9-Fluorenone crystallizes in the orthorhombic space group *Pcab* ($D_{2h}^{15} \equiv V_h^{15}$) with 16 molecules per unit cell.(9) There are two molecules in the asymmetric unit; that is, one half of the molecules exist in a crystal field different from that of the other half. A projection of the top layer of molecules on the *ac* plane is shown in Fig. 1. The bottom layer of molecules can be obtained by a two-fold screw operation about *b*. Carbon number two is labeled on each molecule and the two types of molecules in the asymmetric unit are

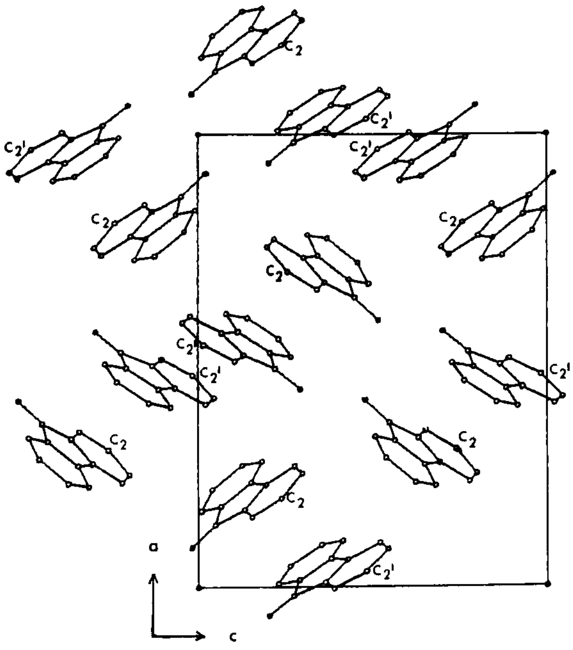

Figure 1. A projection of the top layer of 9-fluorenone molecules onto the *ac* crystal face. The corners of the *ac* face are 0 and $+a$, and $\mp c/2$. The oxygen atoms are denoted by the solid circles.

designated as primed and unprimed. The unit cell constants and relevant optical data are given in Table 1. The direction cosines for the two molecules in the asymmetric unit are given in Table 2. Finally, we should note from Fig. 1 and Table 2 that the two molecules in the asymmetric unit have similar orientations and occur in pairs. From structure data the average interplanar distance between asymmetric pairs is 3.58 Å.(9)

Table 1

Crystallographic and Optical Properties of 9-Fluorenone(9)

| | |
|---|---|
| $a = 16.068$ Å | $Z = 16$ |
| $b = 18.650$ | optic plane 001 |
| $c = 12.550$ | $+2V$ = large |

Table 2 Direction Cosines for 9-Fluorenone

| | *L* | | *M* | | *N* | |
|---|---|---|---|---|---|---|
| | Unprimed | Primed | Unprimed | Primed | Unprimed | Primed |
| *a* | 0.0491 | 0.0261 | 0.3511 | 0.3155 | 0.7440 | 0.8081 |
| *b* | -0.9313 | -0.9174 | 0.6145 | 0.5632 | 0.2751 | 0.2563 |
| *c* | -0.3608 | -0.3971 | 0.7065 | 0.7637 | -0.6089 | -0.5304 |

Fluorene, which was used as a host crystal, is also orthorhombic and belongs to the space group *Pnam* ($D_{2h}^{16}$) with four molecules per unit cell.(10) The lattice constants and the optical data are given in Ref. 11 and the direction cosines are given in Ref. 12. Biphenyl, the other host crystal, is monoclinic $P_{2_1}/a(C_{2h}^{5})$ with two molecules per unit cell. Its optical constants and direction cosines are also given in Refs. 11 and 12.

## 4. Results

The polarized absorption spectra of the lowest ($S_1 \leftarrow S_0$) transition in 9-fluorenone at 4.2 °K are shown in Fig. 2. The transition is predominantly *b*-axis polarized and broad (~150 cm$^{-1}$). The *a*-axis spectrum is the lamp spectrum except for the two peaks at 1680 cm$^{-1}$

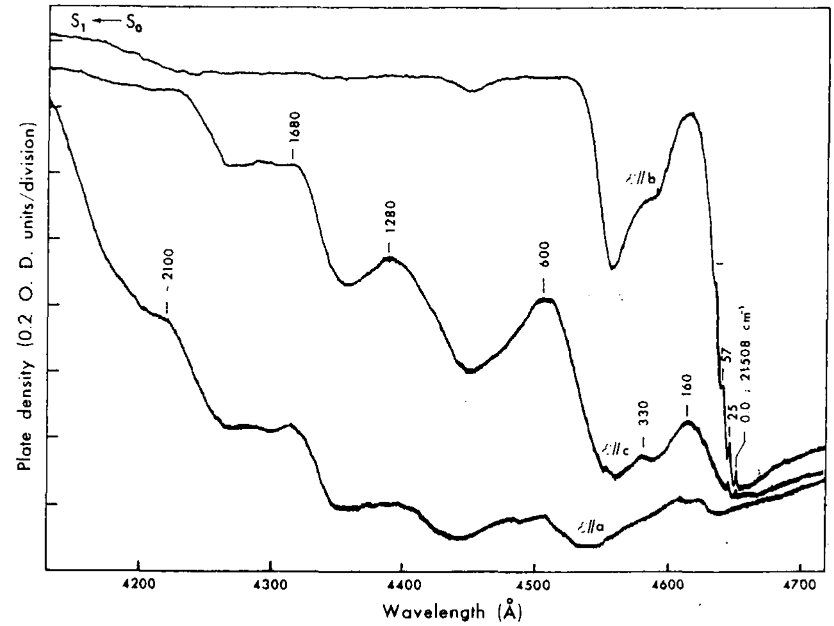

Figure 2. The polarized absorption of a pure crystal of 9-fluorenone at 4.2 °K. The prominent vibronic bands are marked with their energy separation from the origin in $cm^{-1}$.

and $\sim 2100$ $cm^{-1}$. There are several sharp bands about the origin and some additional sharp structure is discernible on the original plate up to 600 $cm^{-1}$ away from the origin. The energies of the prominent vibronic peaks are labeled in the spectrum and we have assigned the relatively weak peak at 21508 $cm^{-1}$ (vacuum wave numbers) as the 0—0 band. The observed polarization ratios of the broad bands and those calculated assuming oriented gas ratios of the three possible molecular transition moments are shown in Table 3. For the calculated polarization ratios the average of the

TABLE 3 Observed and Calculated Polarization Ratios for the $S_1 \leftarrow S_0$ Transition of 9-Fluorenone

| Ratio | Obs. | Calculated | | |
|---|---|---|---|---|
| | | *L* | *M* | *N* |
| *b/c* | $5.4 \pm 0.3$ | 5.9 | 0.64 | 0.22 |
| *c/a* | $\geqslant 30 \pm 5$ | 96 | 4.9 | 0.54 |

squares of the two-direction cosines has been used, as no substantial evidence for asymmetric site splitting was found.(13) Comparison of observed and calculated polarization ratios clearly indicates that the transition is long-axis polarized.

Confirmation of the assignment of the 0—0 band in absorption is given by the emission spectrum shown in Fig. 3. The 0—0 band of the absorption and of the emission coincide within experimental error ( ± 2 $cm^{-1}$). The emission spectrum shows little mirror image symmetry to the absorption spectrum except for the few weak, sharp bands about the origin.

The absorption of 9-fluorenone in fluorene has been observed and is shown in Fig. 4 for the region about the origin. The transition has not sharpened on going to a mixed crystal host. This is in contrast to what is observed for azulene and acenaphthylene,(4,6) in which the line widths in mixed crystals are found to be on the order of $\sim 1$ $cm^{-1}$ at 4.2 °K. The spectrum is *c*-axis polarized, as the *b* spectrum is essentially the lamp spectrum. The *c*-axis polarization confirms the long-axis character of this state obtained from pure crystal measurements, as 9-fluorenone is expected to substitute into fluorene with its long axis parallel to the crystal *c*-axis.

A higher energy absorption has been observed in 9-fluorenone-doped biphenyl crystals at 77 °K and 4.2 °K in the 3000 to 3400 Å region. This state has its origin at about 3280 Å and appears from preliminary polarization data to be long-axis polarized.

## 5. Discussion

In a molecule of rigorous $C_{2v}$ symmetry all the $\pi$ orbitals will be of $a_2$ and $b_1$ symmetry, giving rise to in-plane polarized states of $A_1$ and $B_2$ symmetry.(14) The addition of a nonbonding orbital of $b_2$ symmetry can give rise to ($n\pi^*$) states of $A_2$ symmetry with no dipole strength and $B_1$ symmetry which is out-of-plane polarized. The lowest energy state observed in 9-fluorenone appears to be allowed and from its long-axis character is assigned as a ${}^1B_2$ state. The higher energy state observed in a biphenyl host is also assigned as a ${}^1B_2$ state from its long-axis polarization. The assignment of the two lowest ($\pi\pi^*$) states as ${}^1B_2$ states confirms the theoretical predictions of Kuroda and Kunii.(15)

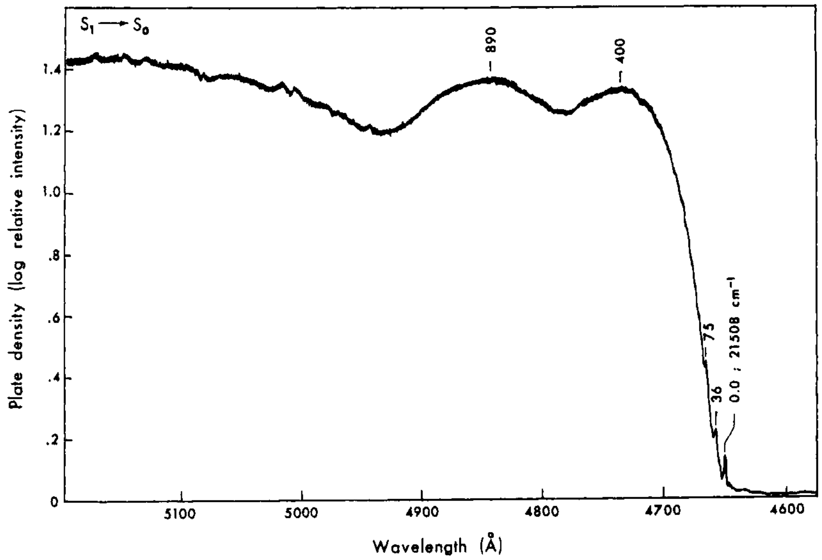

Figure 3. The emission spectrum of pure crystalline 9-fluorenone at 4.2°K.

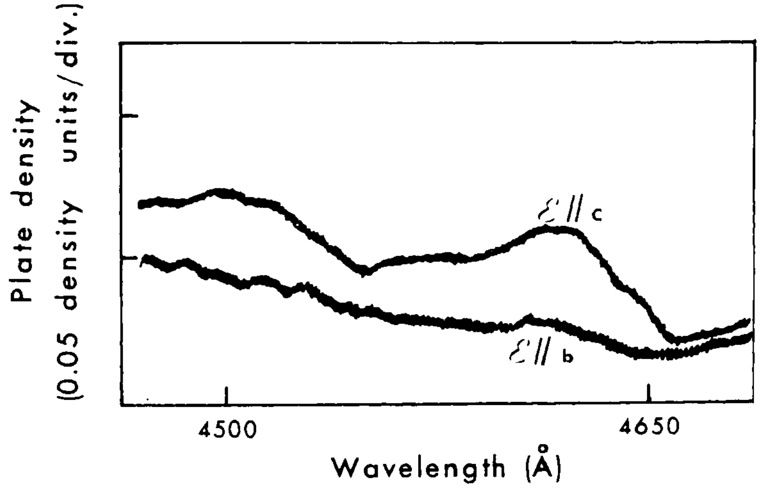

Figure 4. The absorption spectrum of 9-fluorenone in fluorene. The ε//b spectrum is essentially the lamp spectrum.

The *a*-axis intensity observed in Fig. 2 could be a vibronic origin of the lowest state, but the rather high energy (1680 $\mathrm{cm}^{-1}$) of this band would indicate that this is probably not the case. A more plausible explanation would be that this band is associated with an underlying $\pi^* \leftarrow n$ transition. The band could be the origin for a $B_1$ state or a vibronic origin for an $A_2$ state, the latter being more probable as the lowest unfilled $\pi^*$ orbital appears to be of $b_1$ symmetry ($b_2 \times b_1 = A_2$).(2,15) The origin of the ($\pi^* \leftarrow n$) transition is thus estimated to be at 4550 ± 100 Å, assuming that the 1680 $\mathrm{cm}^{-1}$ band is a vibronic origin. It should be noted that the origin of the singlet $\pi^* \leftarrow n$ transition of anthraquinone has about the same energy.(16)

The lowest energy transition of 9-fluorenone is broad in the pure and mixed crystal spectrum, indicating that the explanation of the broadness lies in the molecule itself and not in crystal effects such as possible asymmetric site interactions. Thus the broadening is most probably due to a very large vibronic interaction of the very close ($n\pi^*$) state with the lowest ($\pi\pi^*$) state.(17) Broadening of a second excited state because of vibronic perturbation is well known experimentally(18) and theoretically.(19) 9-Fluorenone appears to be an extreme case of this interaction where the two states lie very close together. This very large vibronic interaction for close-lying ($\pi\pi^*$) and ($n\pi^*$) states has been predicted by Hochstrasser.(18) This vibronic interaction is probably responsible for the lack of mirror symmetry between absorption and emission as it is expected to cause large changes in the normal coordinates of both the ($n\pi^*$) and ($\pi\pi^*$) states.

## Note Added in Proof:

The absorption spectrum of the lowest singlet state of 9-fluorenone has been examined in the gas phase and was found to be broad ($>100\ \mathrm{cm}^{-1}$). The gas phase spectrum resembles the solution spectrum in nonpolar solvents.

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