

PICOSECOND SPECTROSCOPY IN STUDY OF THE  
PHOTOINDUCED ISOMERIZATION OF HEXAFLUOROBENZENE

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There is a continuing interest in the chemical and physical consequences of substitution of the hydrogen atoms of benzene ( $C_6H_6$ ) by fluorine<sup>1-9</sup>, because no systematic explanation exists as yet for the large effects caused by such substitution. When all hydrogen atoms are replaced by fluorine the molecular behaviour does not resemble that of benzene. In the present context, for instance the near absence of fluorescence and the total absence of phosphorescence upon excitation of hexafluorobenzene ( $C_6F_6$ ) within its first electronic absorption band, are of interest. From the chemical point of view the formation of the relatively stable Dewar isomer, shown in Fig. 1, formed after UV excitation of  $C_6F_6$ , is relevant. The investigations reported here were aimed at an elucidation of the factors responsible for the photophysical and photochemical behaviour of hexafluorobenzene.

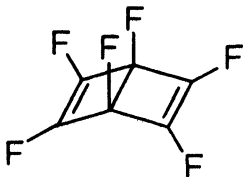


FIGURE 1 Dewar-hexafluorobenzene

In 1967 D. Phillips reported a study on the pressure dependence of the fluorescence quantum yield  $\Phi_f$  of  $C_6F_6$ <sup>10</sup>. The pressure dependence of  $\Phi_f$  in the case of  $C_6F_6$  could not be explained by the kinetic model introduced by E.M. Anderson and G.B. Kistiakowsky<sup>11</sup>, as used in their interpretation of the pressure dependence of  $\Phi_f$  for gaseous  $C_6H_6$ . In order to compare the collisional deactivation processes for  $C_6F_6$  and  $C_6H_6$  we reinvestigated both sets of data by means of a simple two level relaxation model in which we have taken the statistics of the collisions in the gas into account<sup>12</sup>. In our model, illustrated in Fig. 2, the observed pressure dependence for both  $C_6F_6$  and  $C_6H_6$  can be simulated by a single parameter  $\alpha$ , which represents the probability to induce a transition from the upper to the lower level in a single collision. Whereas for benzene  $\alpha$  is close to unity it is very small for hexafluorobenzene, from which we conclude that the collisional deactivation efficiency is decreased enormously by fluorine substitution. The scheme shown in Fig. 2 applies to the case of excitation within the first UV absorption band. It considers two emissive states  $|a\rangle$  and  $|b\rangle$  and collision induced relaxation from  $|a\rangle$  to  $|b\rangle$ .

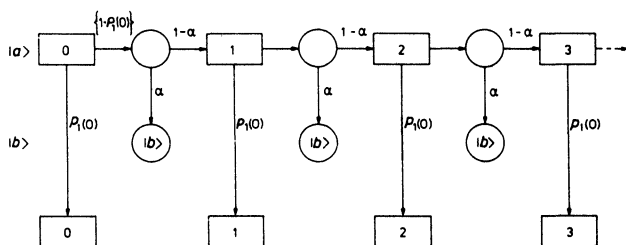


FIGURE 2 Scheme indicating competition between unperturbed decay of initial state  $|a\rangle$  and collision-induced transition from state  $|a\rangle$  to state  $|b\rangle$ . The  $i$ th numbered rectangle in the upper part indicates that a selected molecule  $A$  is still in state  $|a\rangle$  after its  $i$ th collision. The  $i$ th  $s$  rectangle in the lower part indicates that  $A$  disappears from  $|a\rangle$  between its  $n$ th and  $(n + 1)$ th collision.

Circles represent binary collisions involving  $A_S$ . Probabilities for spontaneous and induced transitions are  $P_1(0)$  and  $\alpha$ , respectively.

In Figures 3 and 4 it is shown that the pressure dependence of the fluorescence quantum yield of benzene and hexafluorobenzene may be simulated accurately by choosing the value of  $\alpha$  appropriately.

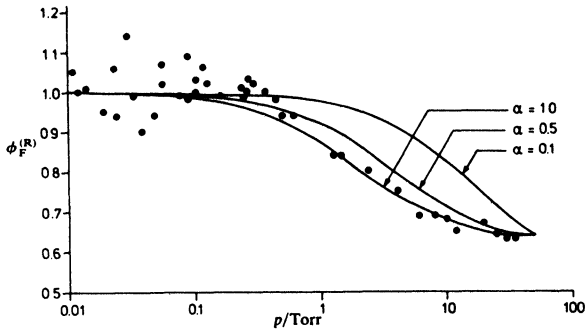


FIGURE 3 Experimental points from ref. (11), representing the relative fluorescence quantum yield  $\phi_F^{(R)}$  of  $C_6H_6$  as a function of pressure. The curves are single-parameter fits according to the scheme in Fig.2 ( $\lambda_{ex} = 254$  nm).

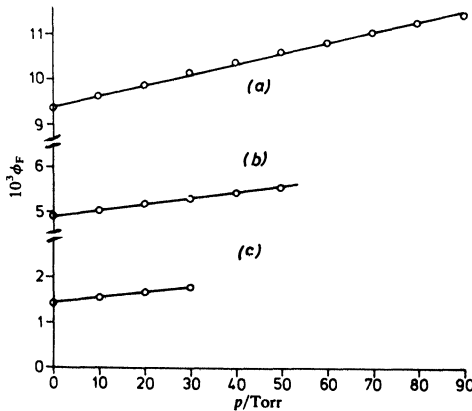


FIGURE 4 Lines according to ref. (10), representing experimental

behaviour of total fluorescence quantum yield  $F$  of  $C_6F_6$ , excited at different wavelengths. The points are obtained by adjusting  $\alpha$  according to the scheme in Fig. 2.

(a)  $\alpha = 0.13$ ,  $\lambda_{ex} = 270$  nm; (b)  $\alpha = 0.05$ ,  $\lambda_{ex} = 265$  nm;  
 (c)  $\alpha = 0.05$ ,  $\lambda_{ex} = 254$  nm.

In his article Phillips also reported the first, indirect, observation of the lowest triplet state of hexafluorobenzene. He studied the quenching of the biacetyl phosphorescence by  $C_6F_6$  molecule, causing a transition of the latter to its lowest triplet state. From sensitization experiments of the isomerization of cis-buten-2 by electronically excited  $C_6F_6$ , he concluded that both the observed triplet quantum yield and the triplet lifetime are more than an order of magnitude smaller than the corresponding values in the case of  $C_6H_6$ . This brought us to look more directly for the triplet state of  $C_6F_6$ , but we did not succeed in observing any phosphorescence nor any triplet ESR signal from our pure samples of  $C_6F_6$  at low temperature after UV excitation.

In 1967 I. Haller<sup>13</sup> reported a study on the kinetics and mechanism of the photochemical valence isomerization of  $C_6F_6$  to its Dewar isomer. The experiments were conducted in the gas phase and the sample was excited with UV light of several wavelengths. He determined the quantum yields of isomerization as a function of gas pressure for all the excitation wavelengths involved. From triplet quenching and triplet sensitization experiments he concluded that the triplet of hexafluorobenzene was not involved in the isomerization to the Dewar valence isomer, and he was the first to suggest that the isomer is formed from the first excited singlet state, via the unstable biradical BR shown in Fig. 5.

In an attempt to shed more light on the mechanism of the isomerization to the Dewar form we initiated a study of the metastable species arising from excitation of  $C_6F_6$  in its first electronic absorption band by means of picosecond time-resolved absorption

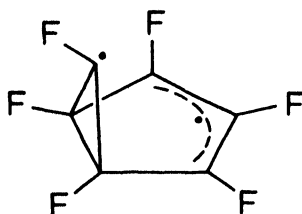


FIGURE 5 The biradical BR

and emission spectroscopy. In these experiments a gaseous or liquid sample is excited with a 265 nm laser pulse of about 10 or 25 ps duration. In the absorption experiments the excited region is then probed by a second pulse after a well defined time delay<sup>14</sup>. In the fluorescence experiments the induced emission from the sample is studied in real time by means of a fast photodetector coupled to a 500 MHz transient digitizer<sup>15</sup> or by means of a streak camera system. A number of metastable species were detected through the transient optical absorptions shown in Fig. 6<sup>17</sup>.

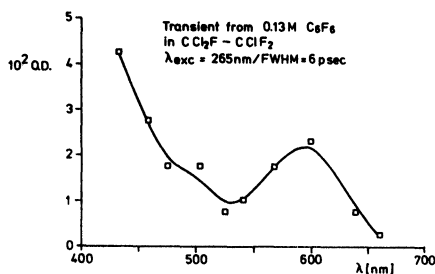


FIGURE 6 Transient absorptions observed at time delay of 50 ps.

The difference in the growth of the absorption at 430 and at 600nm shown in Fig. 7 indicates the formation of several species. The transient absorption around 430 nm is attributed to the cation and anion of hexafluorobenzene, based on the known spectra of these ions. They are formed monophotonically via electron transfer with-

in a pair hexafluorobenzene molecules. The absorption band around 600 nm is attributed to the intermediate BR, based on a semi-empirical quantum mechanical calculation (CNDO/S) of its spectrum.

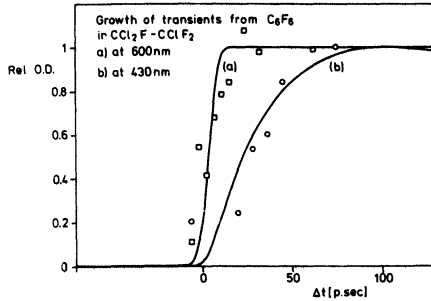


FIGURE 7 Growth of the transient absorption at different wavelengths.

We have discovered UV laser induced fluorescence from hexafluorobenzene in the visible to near infrared wavelength region. A similar red fluorescence could also be observed in the case of other monocyclic aromatic molecules such as benzene and pyridine<sup>15</sup>. These fluorescence bands are shown in Fig. 8.

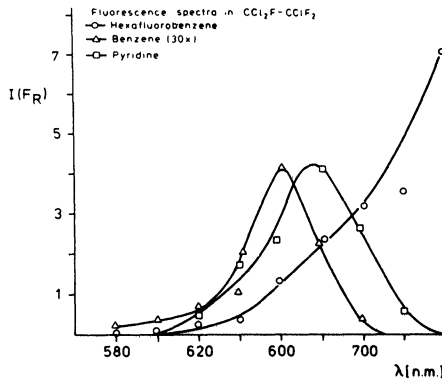


FIGURE 8 Fluorescence in the visible and near-infrared regions observed when solutions of benzene, pyridine and

hexafluorobenzene in  $\text{Cl}_2\text{FC}-\text{CClF}_2$  are excited with a 266 nm laser pulse, having a width of 25 ps.

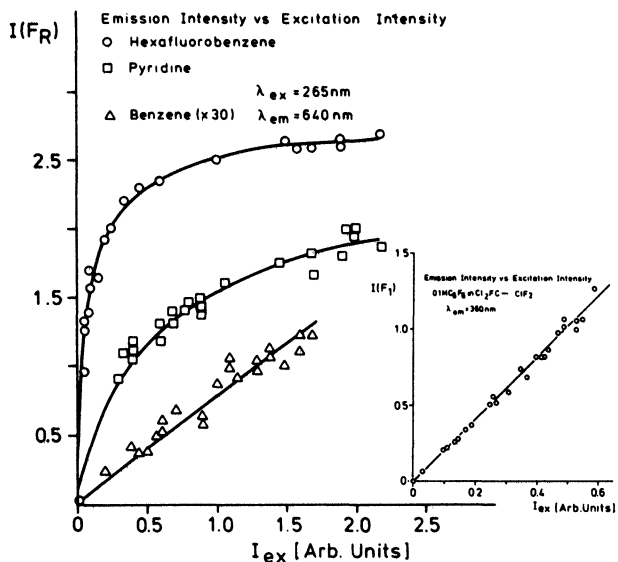


FIGURE 9 Variation of the intensity  $I(F_R)$  of the fluorescence of benzene, pyridine and hexafluorobenzene in  $\text{Cl}_2\text{FC}-\text{CClF}_2$  at 640 nm as a function of the integrated energy  $I_{\text{ex}}$  in the excitation pulse. The insert in the figure shows the variation of the intensity of the ordinary fluorescence of hexafluorobenzene in  $\text{Cl}_2\text{FC}-\text{CClF}_2$  at 360 nm as a function of the integrated energy in the excitation pulse. The largest absolute value of the integrated excitation energy is the same as in the main part of the figure.

Fig. 9 shows that the intensity of the red fluorescence varies linearly with the integrated energy  $I_{\text{ex}}$  of the excitation pulse in the case of benzene, but in the case of hexafluorobenzene and pyridine there is saturation at high values of  $I_{\text{ex}}$ . Since the normal fluorescence of hexafluorobenzene varies linearly with  $I_{\text{ex}}$  under identical excitation conditions, the saturation does not arise from depletion of the ground state population. The satura-

tion is probably a consequence of absorption of laser photons by the emitting species. From the linear behaviour in the case of benzene we infer that the red fluorescence is induced monophotonically in all the three cases. We have taken advantage of the fact, that the lifetime of the species emitting the red fluorescence of hexafluorobenzene is shorter than that of the metastable species BR, to prove that the red emission arises from an electronically excited state BR\* of BR. The evidence is provided in Fig. 10.

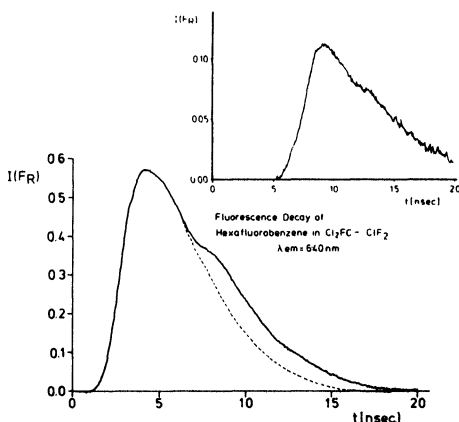
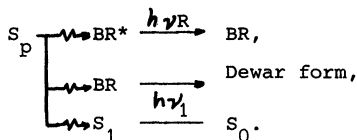


FIGURE 10 Decay of the red fluorescence of hexafluorobenzene in Cl<sub>2</sub>FC-CClF<sub>2</sub> at 640 nm when a second delayed pulse is absorbed in the transient absorption band at 600 nm (solid curve) and when the latter is absent (dashed curve). The insert in the figure represents the difference between the solid and dashed curves.

It follows from Fig. 7 that the growth in the population of BR comes to an end within less than 10 ps after preparation of the primary excited state S<sub>p</sub> of hexafluorobenzene. From this and from the lifetime of BR\*, namely  $\tau_R = 3.2$  ns, it follows that BR is not formed from BR\*, at least not predominantly. The deactivation of



the primary prepared state of hexafluorobenzene may be summarized as in the following scheme:



When hexafluorobenzene in the gaseous state is excited with the UV laser pulse, the red fluorescence may also be detected. In a gas mixture of 740 Torr nitrogen and 17 Torr hexafluorobenzene at 296 K the lifetime  $\tau_R = 3.2$  ns. By comparing this with the value  $\tau_R = 3.2$  ns for the liquid solution, we conclude that the lifetime of the state  $BR^*$  of  $C_6F_6$  is not strongly affected by collisions. It is unlikely that  $BR$  and  $BR^*$  may have to be identified with molecular aggregates like dimers, excimers or solute-solvent exciplexes of hexafluorobenzene, because we find that the ratio of the quantum yields of the red fluorescence in the vapour phase and in the liquid solution is as high as 0.75 whereas the ratio of the concentrations  $C_6F_6$  is 0.14.

The decay of the fluorescence at 360 nm of hexafluorobenzene in the vapour phase and in liquid solutions has been studied with a carefully corrected and calibrated streak camera<sup>16</sup>. This fluorescence band is emitted by a short living species  $S_s$  and a long living species  $S_1$ , which are formed from the primary excited state  $S_p$ . The decay of the fluorescence at 360 nm shown in Fig. 11 is different from what has been reported previously<sup>18</sup>. The decay profile is independent of wavelength. We have not observed a time delay in the growth of the fluorescence at 360 nm. In the case of pure gaseous hexafluorobenzene at 17 Torr and 296 K the lifetimes  $\tau_s$  and  $\tau_1$  of the states  $S_s$  and  $S_1$  respectively are  $\tau_s = 520 \pm 50$  ps and  $\tau_1 = 1820 \pm 50$  ps. Based on gas kinetics the former value may be considered as unperturbed by collisions. When 740 Torr nitrogen is

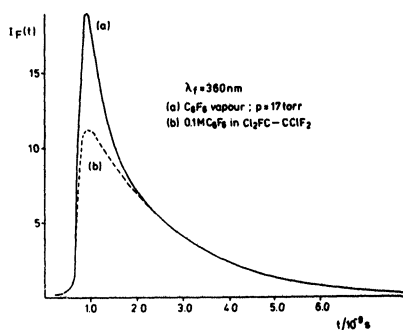


FIGURE 11 Decay of the fluorescence of hexafluorobenzene transmitted through an interference filter with peak transmittance at 360 nm and a bandwidth of 10 nm. The fluorescence is excited with a 266 nm laser pulse of 25 ps FWHM. Curve (a): pure  $C_6F_6$  in the vapour phase at 296 K. Curve (b): 0.1 molar liquid solution of  $C_6F_6$  in  $Cl_2FC-CClF_2$ . Time scale in ns.

added to the 17 Torr of hexafluorobenzene vapour, the value of  $\tau_s$  is reduced to  $\tau_s = 280 \pm 50$  ps, while  $\tau_1$  remains unchanged, namely =  $1800 \pm 50$  ps. This behaviour justifies the relaxation model given in Fig. 2.

If 20 Torr trifluoroethanol (TFE) is added to 17 Torr of hexafluorobenzene we find  $\tau_s = 260 \pm 50$  ps and  $\tau_1 = 1690 \pm 60$  ps. In the liquid solution of 0.1 M of hexafluorobenzene in  $Cl_2FC-CClF_2$  the fluorescence decay has become single exponential with a lifetime  $\tau_1 = 2060 \pm 90$  ps which is practically equal to that of the long lived component of the fluorescence of  $C_6F_6$  in the pure gas. In the case of a liquid solution of 0.1 M hexafluorobenzene in TFE the fluorescence decays mono-exponentially with a lifetime  $\tau_1 = 1060 \pm 60$  ps. These observations indicate that TFE quenches the long lived component of the UV fluorescence. Nevertheless, no stable reaction products are found gaschromato-graphically and the UV absorption spectrum of gaseous or liquid samples with  $C_6F_6$  and TFE

remain unchanged upon continuous UV irradiation even after a period of 24 hours. By comparing the lifetime of state  $S_1$  in the solvents  $Cl_2FC-CClF_2$  and TFE, we conclude that this state does not lead to the Dewar isomer, because otherwise the quantum yield of the isomer would only be reduced by 50% in changing from the first to the second solvent.

The action of TFE in the relaxation of electronically excited  $C_6F_6$  will be considered now in relation with the photoinduced isomerization to the Dewar form. Continuous UV irradiation of hexafluorobenzene vapour (17 Torr) in equilibrium with a drop in the liquid phase and with 740 Torr of nitrogen resulted in a 6.7% yield in the Dewar isomer after a period of 90 minutes. About 50% of hexafluorobenzene at an initial concentration of 0.01 M in  $Cl_2FC-CClF_2$  disappears after 90 minutes of continuous UV irradiation and 4.9% of it is then converted to the Dewar form and the other part which is lost is transformed into polymeric material. The quenching of the photoinduced conversion of hexafluorobenzene to its Dewar form and to polymers by TFE must involve the scavenging of an intermediate in these reactions arising as a secondary product of the excitation. We identify the scavenged intermediate with the species BR, causing the transient absorption at 600 nm. We have studied the attenuation of the transient optical density  $D(\lambda, \Delta t)$  at 600nm, by TFE in the solution, by keeping the concentration of  $C_6F_6$  constant and by varying the amount of TFE and measuring then the optical density at  $\Delta t = 0, 1, \text{ and } 2$  ns after the primary excitation. The transient absorption at 600 nm is still observable if TFE is used as the solvent for  $C_6F_6$ . The behaviour of  $D(\lambda, \Delta t)$  as a function of the concentration  $C_Q$  of TFE is shown in Fig. 12 for  $\lambda = 600$  nm and  $\Delta t = 2$  ns.

The figure reveals an asymptotic approach of  $D(\lambda, \Delta t)$  to a non-zero value when  $C_Q$  tends to infinity. We may explain this behav-

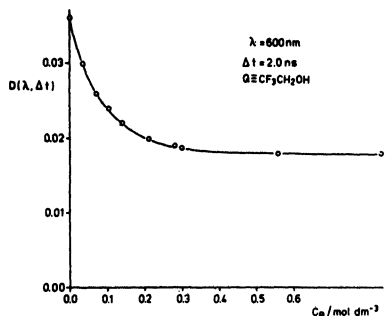


FIGURE 12 Quenching of the transient absorption at 600 nm induced by excitation of a 0.1 molar liquid solution of hexafluorobenzene in  $\text{Cl}_2\text{FC}-\text{CClF}_2$  with a 266 nm laser pulse of 25 ps FWHM. The quencher  $Q$  is 2,2,2-trifluoroethanol.

our by assuming that two species contribute to the transient absorption at 600 nm, namely BR and an unknown Z, which is formed simultaneously with BR from the primary excited state. The explanation implies that the transient absorption at 600 nm of the solution of  $\text{C}_6\text{F}_6$  in TFE is entirely due to Z. The species Z can not be transformed into the Dewar isomer of  $\text{C}_6\text{F}_6$ , because this is not formed when TFE is used as the solvent. Previously we have excluded the possibilities that the absorption at 600 nm involves a transition from the lowest excited singlet state  $S_1$  to a higher singlet state or from the lowest triplet state  $T_0$  to a higher triplet state of hexafluorobenzene<sup>17</sup>. The same reasoning excludes therefore the identification of Z with  $S_1$  or with  $T_0$ . The nature of Z remains unknown.

In 1976 R. Pottier and G.P. Semeluk reported a near and far UV spectroscopic study of the fluorinated benzenes<sup>19</sup>. They observed a loss of vibronic structure in the first electronic absorption band which increases with the number of fluorine atoms. The Stokes-shift of the fluorescence increases also with the number of fluorine atoms. We have tried to find vibrational structure in

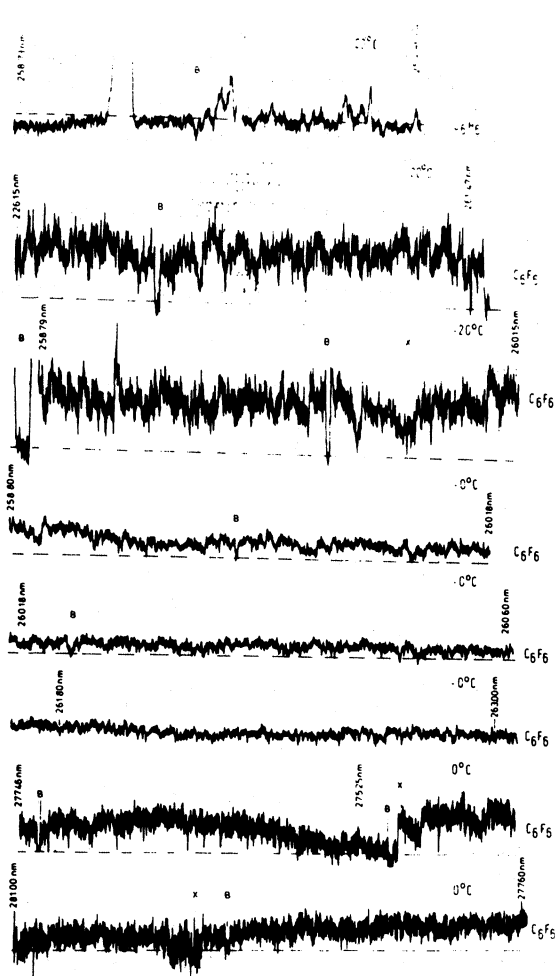


FIGURE 13 Excitation spectrum of the fluorescence of C<sub>6</sub>F<sub>6</sub> in a supersonic beam observed at 320 nm. The vapour of a solidified sample was equilibrated with helium at a pressure of 1900 Torr before expansion. The temperature of the solid sample, either -20°C or 0°C, is indicated. The (X) marks the wavelength where the crystal for doubling the frequency of the dye laser was readjusted

or interchanged. The (B) marks where the excitation was interrupted to check the height of the baseline. The upper track illustrates that the signal to noise ratio for the excitation of the fluorescence of  $C_6H_6$  is much larger than in the case of  $C_6F_6$  under identical conditions.

in the first UV absorption band and in the UV fluorescence band of hexafluorobenzene by determining the spectra of the molecule in a supersonic molecular beam (Fig. 13) or in low temperature solid matrices (Fig. 14).

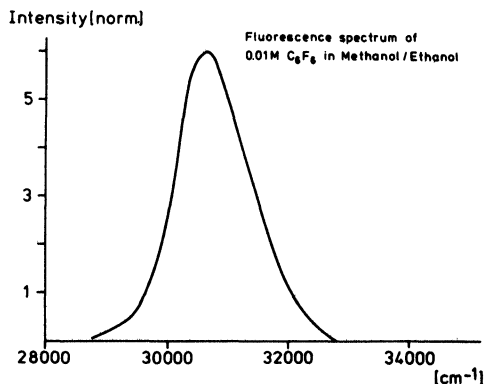


FIGURE 14 UV fluorescence band of hexafluorobenzene in a solid matrix at 4.2 K. The band is three times wider when the molecule is dissolved in a 1:1000 ratio in an argon matrix at 12.4 K.

Neither of the two bands reveal vibrational structure. Based on our observations that the primary excited state  $S_p$  decays completely, radiationless and yields in less than 10 ps at least the five products  $S_s$ ,  $S_1$ ,  $BR^*$ ,  $BR$  and  $Z$ , we conclude that the absence of vibrational structure in the absorption band is a consequence of the lifetime of state  $S_p$ . The lifetime of  $S_p$  is probably less than  $10^{-13}$  s<sup>20</sup>. The lifetime of 2 ns for the fluorescence indicates that the absence of structure in the fluorescence band is

not due to lifetime broadening. The absence of structure in this band may be explained by a large difference in equilibrium molecular geometries in initial and final electronic states involved in the emission and by an additional inhomogeneous broadening arising from a conformational equilibrium of emitting molecules.

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