

AN INVESTIGATION OF TRANSIENT ABSORPTIONS AND A STREAK CAMERA STUDY OF THE FLUORESCENCE GENERATED BY UV EXCITATION OF HEXAFLUOROBENZENE

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Summary

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. The fluorescence is emitted by short living (S_0) and long living (S_1) species which are formed from the primary excited state S_p . The previous results from a streak-camera study are not reproduced. Transient absorptions at 600 nm reveal that a precursor of the Dewar isomer and an as yet unidentified species are also formed directly from S_p .

1. Introduction

An important question in the understanding of photoinduced chemical reactions is how the redistribution of internal energy after the primary electronic excitation of the molecule determines the ultimate product distribution. We try to answer this question for the particular case of the photo-reactions of hexafluorobenzene (C_6F_6) occurring when the excitation wavelength is within its first electronic absorption band. We have already studied several aspects of the mechanisms involved in the deactivation of the primary excited state of C_6F_6 [1 - 4]. One of our conclusions is that there are intramolecular mechanisms which cause the lack of vibrational structure in the broad first electronic absorption band of C_6F_6 [1]. These mechanisms involve at least the formation of a "biradicaloid" (BR) intermediate in the isomerization to the Dewar form of C_6F_6 , as well as the first electronically excited state BR^* of the species BR [2, 3]. Note that previously we have [2, 3] incorrectly attributed the suggestion of a biradical as an intermediate in the photoisomerization to the Dewar form to I. Haller [5], who considered a biradical with a C(1)—C(3) bond of normal length, but rejected it as an intermediate leading to the Dewar form. We have introduced an intermediate resembling the biradical but with a C(1)—C(3) bond length equal to

the C(1)—C(3) distance in the original phenyl ring and we refer to it as biradicaloid, since it lacks biradical character [2]. In ref. 2, we have also mentioned incorrectly that the Dewar isomer of C_6F_6 may be isolated from a continuously irradiated solution of hexafluorobenzene in cyclohexane. The solution in cyclohexane does not yield the Dewar isomer [6]. In the gaseous state, the quantum yield of the fluorescence and of the Dewar form depend on the pressure and on the excitation wavelengths within the first absorption band. In the case of the fluorescence, these dependences have been related to collision-induced relaxation of the primary excited state to lower excited singlet states whose radiationless decay is insensitive to collisions [4].

The decay of the fluorescence from C_6F_6 in the gaseous state is reported to be bi-exponential [7]. The two decay rate constants obtained for the fluorescence show an oscillatory behaviour as a function of pressure [7]. This has not previously been noticed and it needs an explanation.

C_6F_6 is photochemically unstable in solvents such as cyclohexane, diethyl ether and methanol, which contain hydrogen atoms that can be abstracted in reactions with radicals. These photoreactions involve the addition of a solvent molecule to C_6F_6 and the formation of polymers derived from C_6F_6 . There is then no formation of the Dewar isomer of C_6F_6 [5]. In the gaseous state and in solvents without hydrogen atoms (e.g. $Cl_2FC-CClF_2$) the photoproducts of C_6F_6 are its Dewar isomer and polymers. In trifluoroethanol (TFE) as the solvent there are no irreversible photoinduced modifications of C_6F_6 .

In the present article we discuss new experimental results for the secondary transient species, arising after excitation of C_6F_6 in its first electronic absorption band, in relation to the photophysical and photochemical behaviour just mentioned. The new results have been obtained by means of streak-camera investigations of the fluorescence, the study of scavenging reactions using picosecond kinetic absorption spectroscopy, and gas chromatographic analysis of the photoproducts.

2. Experimental details

2.1. Streak camera operation

The UV fluorescence of C_6F_6 was excited with a 266 nm laser pulse with a duration of 25 ps full width at half-maximum (FWHM). The decay of the fluorescence at various wavelengths within the emission band was observed with a Hadland Imacon 500 streak camera. The wavelengths were selected with interference filters (bandwidth, 10 nm) between the sample cell and the streak camera. The sample cell had a path length of 1 mm and was placed at an angle of 45° with the laser beam to prevent reflected laser light from entering the streak camera, which viewed in a direction perpendicular to the laser beam, *i.e.* fluorescence was collected from the direction opposite to the reflected beam.

The phosphor screen of the streak camera tube is coupled by fibre optics to a Philips image intensifier model XX1385 with low (2%) distortion. The intensifier output image is then transferred by a lens system to a silicon intensified target (SIT) type vidicon television camera (EG and G model 1254) whose output is digitized and transmitted through a direct memory access interface to a computer system based on an LSI 11/02 processor from Digital Equipment. The digitally stored image is acquired by accumulating 20 frame scans of the vidicon target after each laser shot to assure a linear intensity response for the whole streak camera detection system [8]. Between successive laser shots the vidicon target is blanked. The image intensifier is normally blocked and operates only for a period of about 200 μs after a trigger signal has been applied. This reduces the chance of accumulating spurious signals. Just before the laser is fired the background signal is measured with the intensifier off. This signal is subtracted from the fluorescence signal.

The image of the entrance slit of the camera appears as a curved line when the sweep rate is faster than 50 ps mm^{-1} and is a straight line at slower rates. In the former case the central portion is practically a straight line. Only the central strip of the image is taken into account in the evaluation of the data when the sweep rate is 50 ps mm^{-1} or faster.

When a streak camera is used in time-resolved spectroscopy the calibration of the time axes and the correction of image distortions are of prime importance. Although streak cameras have previously been used in time-resolved spectroscopy, image correction procedures have been mentioned but have not been fully described. It has not been noted previously that the calibration of the time axes is intimately connected with the image correction. The required procedures are non-trivial and the adequacy of the procedures cannot be derived from the previous brief reports [7, 9, 10]. Since we obtain results after the corrections which are different from previous results obtained with a streak camera we present our calibration and correction procedures in detail.

The time axis of the whole detection system is calibrated with a sequence of equidistant optical pulses as input. The sequence of pulses emerges from an optical resonator when a 530 nm pulse from a picosecond laser is injected into it. The resonator consists of two 90% reflecting plane mirrors which are parallel to each other and which are separated by an adjustable accurately known distance.

Three imperfections in the detection system have to be corrected by calibrations, namely (i) the non-linearity in the time dependence of the sweep voltage of the streak camera, (ii) the image distortion caused by electro-optical and glass lenses and (iii) the non-uniform intensity response over the image. The first two imperfections are corrected simultaneously. The procedure is as follows. The final image is divided along the time axis in 500 equal segments whose intensities are stored as elements of an array $I_j(k)$ of dimension 500. A single laser pulse generates a sequence of secondary pulses spaced equally in time. These are observed as non-equidistant intensity peaks in the image plane and the intensity distribution is stored as the

array $I_j(k)$. This is repeated a number of times and the intensity distribution arising from the j th sequence of pulses is stored as the array $I_j(k)$. The intensity peaks arising from different sequences of pulses are generally not coincident owing to jitter or deliberate shifts in the start of the sweep. The total number N of images needed for the correction is selected in such a way that superposition of peaks from all the N different images fills the whole image field.

The array index $k = 0$ refers to the location of the peak closest to the centre of the image displaying the first sequence of pulses. The peak sequence arising from the j th pulse sequence has an offset Δ with respect to $k = 0$. Let L_{jm} denote the array index corresponding to the m th peak in the j th image. Without the imperfections (i) and (ii) this peak would have corresponded to array index A_{jm} . We determine A_{jm} from the expansion

$$A_{jm} = L_{jm} + \sum_{n=2}^7 a_n L_{jm}^n \quad (1)$$

Note that for a given value of j both L_{jm} and A_{jm} are one-dimensional arrays of dimension α_j equal to the number of peaks in the j th image. The expansion coefficients are determined from the condition that the peaks in the perfect image should be equidistant with a separation τ , *i.e.*

$$A_{jm} = m\tau + \Delta_j \quad (2)$$

Equations (1) and (2) together yield

$$L_{jm} + \left(\sum_{n=2}^7 a_n L_{jm}^n \right) - m\tau - \Delta_j = 0 \quad (3)$$

The number of algebraic equations represented by eqn. (3) is equal to $\sum_{j=1}^N \alpha_j$ and these contain the unknowns $\alpha_2, \dots, \alpha_7; \Delta_2, \dots, \Delta_N$ and τ . We denote the left-hand side of eqn. (3) F_{jm} . The unknowns are determined by finding the minimum of $\sum_{jm} F_{jm}^2$ as a function of the unknowns. The separation τ obtained in the solution of eqn. (3) corresponds to the known time interval t_c between two pulses in a sequence from the resonator. This yields a calibration factor γ (s^{-1}) for the time axis, *i.e.*

$$\tau = \gamma t_c \quad (4)$$

Correction of imperfection (iii) is achieved by calibrating the overall intensity gain as a function of the position coordinates in the image. The input light used for the calibration of the gain is the fluorescence from a sample whose fluorescence lifetime is at least five times longer than the sweep time. The fluorescence is excited with a single laser pulse of about 25 ps. The change in input intensity during the sweep is taken into account in the calibration. The fluorescence decay of the calibration sample is determined with a fast photodiode and a 500 MHz transient digitizer with an overall rise time of 700 ps. As before, the image obtained after a single laser

shot is transformed into an array $I(k)$, *i.e.* the magnitude of the element $I(k)$ corresponds to the intensity of the k th segment of the image. The required correction involves two steps. First we map the k th element $I(k)$ onto the p th element of another array B , *i.e.* on $B(p)$ with eqn. (1) determining the relation between the indices p and k . Identifying p with A_{jm} and k with L_{jm} the relation takes the more transparent form

$$p = k + \sum_{n=2}^7 a_n k^n \quad (5)$$

Note that the coefficients a_n in eqn. (5) have been determined already. Let $D(p)$ denote the array corresponding to the image that would have been observed if the intensity gain were uniform over the image plane. We express $D(p)$ as

$$D(p) = B(p) \sum_{n=0}^{14} b_n G_n(p) \quad (6)$$

where b_n are coefficients and $G_n(p)$ is the n th-order Chebyshev polynomial in p [10]. The exponential decay of the input intensity is taken into account by writing

$$D(p) = D(0) \exp(-p/\gamma\tau_F) \quad (7)$$

where τ_F is the lifetime of the fluorescence from the calibration sample. Equations (6) and (7) together yield the relation

$$H(p) = 0 \quad (8)$$

where $H(p)$ is defined as

$$H(p) = \left[B(p) \sum_{n=0}^{14} b_n G_n(p) \right] - D(0) \exp(-p/\gamma\tau_F) \quad (9)$$

The value of $D(0)$ is set equal to the mean value of $B(p)$, *i.e.*

$$D(0) = \frac{1}{500} \sum_{p=1}^{500} B(p) \quad (10)$$

The expansion coefficients are found by minimizing the quantity $\sum_p H(p)^2$ as a function of the values of b_n .

The advantages of using Chebyshev polynomials $G_n(p)$ in eqn. (6) are that they form a complete set of orthonormal functions defined in a finite domain of p , that there are recurrence relations facilitating their evaluation and that their values are between -1 and 1 .

2.2. Determination of fluorescence lifetimes

Observed fluorescence decay curves are analysed either as a sum of a single exponential function of time and a constant baseline [12] or as a sum

of two exponential functions and a baseline [13]. The decay curves are determined over a time interval equal to about four times the fluorescence lifetime.

The decays of fluorescences with lifetimes longer than 1 ns have been measured using a vacuum photodiode having a rise time of 100 ps and our 500 MHz transient digitizer. The response function of the whole detection system has been taken as its recorded response to a laser pulse of 25 ps FWHM as input. The response function of the detection system is taken into account in deriving the lifetime. The lifetime is derived by means of a numerical simulation of the observed signal. The simulation involves an iterative procedure which convolutes the detection response function with a single exponential function [14].

2.3. Picosecond kinetic absorption spectroscopy

Transient absorptions induced by UV laser pulse excitation have been measured by probing the excited region of the solution at various time delays with a wavelength continuum of duration about 25 ps. The method has already been described in detail [15]. The total energy in the pulse at 266 nm of 25 ps FWHM used for the primary excitation is roughly estimated to be 0.5 mJ. The excitation beam was focused on the sample cell of path-length 1 mm in such a way that it could burn a spot of area 0.15 mm^2 on black Polaroid photo prints. Note that only the central part of the beam is able to burn the paper and that the real spot size cannot be derived from the spot on the paper. Since it is conceivable that multiphoton processes can take place under our conditions of inducing transient absorptions, we have studied the initial height of the transient absorbances as a function of the integrated energy I_{ex} of the laser pulse. The initial height of the transient absorbances is found to vary linearly with I_{ex} as we have also previously noted [2]. Because the fluorescent state is accessible by single-photon excitation with the laser pulse, the previously reported [3] linear variation of the fluorescence intensity with I_{ex} up to the level used in inducing transient absorptions means that the absorption by ground state molecules does not become saturated. An accuracy in the transient optical densities of 2×10^{-3} could be achieved after averaging over seven determinations. The maximum transient optical density observed in our experiments with C_6F_6 was 3×10^{-2} . The concentration C_6F_6 was then 0.1 M.

2.4. Photochemistry under continuous illumination

Light from a 125 W high pressure mercury lamp was filtered through a quartz cell of path length 1 cm containing the solvent $\text{Cl}_2\text{FC}-\text{CClF}_2$ and was then used to irradiate the samples. After filtering, the light had no intensity at wavelengths below 240 nm. The photochemically formed Dewar isomer of C_6F_6 was detected using gas chromatography by passage through a diisodecylphthalate column kept at 50°C [6]. The retention times of C_6F_6 and its Dewar isomer were 45 min and 8 min respectively, nearly equal to what has been reported previously [6].

3. Results and discussion

The fluorescence band at 360 nm of C_6F_6 vapour at a pressure of 17 Torr has been studied with the streak camera in the wavelength region between 360 and 400 nm. This region is limited by the transmission of the lens system which images the entrance slit on the streak tube. The decay of the fluorescence does not depend on wavelengths selected between 360 and 400 nm. The observed decay of the fluorescence in this region is shown in Fig. 1. The vapour phase fluorescence intensity $I_F(t)$ decays in a non-exponential fashion, which can be described by

$$I_f(t) = c_s \exp(-t/\tau_s) + c_l \exp(-t/\tau_l) \quad (11)$$

with $\tau_s = 520 \pm 50$ ps, $\tau_l = 1820 \pm 60$ ps and $c_s/c_l = 0.75 \pm 0.05$. The value c_s/c_l did not change when the energy of the excitation pulse was varied by a factor of 5. Therefore, the fluorescence may be considered as a monophotonically excited spontaneous emission.

When 740 Torr nitrogen is added to 17 Torr C_6F_6 vapour the value of τ_s is reduced to $\tau_s = 280 \pm 50$ ps, while τ_l and c_s/c_l remain unchanged, namely $\tau_l = 1800 \pm 50$ ps and $c_s/c_l = 0.80 \pm 0.05$.

If 20 Torr TFE is added to 17 Torr C_6F_6 we find $\tau_s = 250 \pm 50$ ps, $\tau_l = 1690 \pm 60$ ps and $c_s/c_l = 1.0 \pm 0.05$.

In the 0.1 M C_6F_6 - $Cl_2FC-CClF_2$ liquid solution the fluorescence decay has become single exponential with a lifetime $\tau_l = 2060 \pm 90$ ps which is practically equal to that of the long-lived component of the fluorescence of C_6F_6 in the gaseous state. The decay curve for the liquid solution obtained

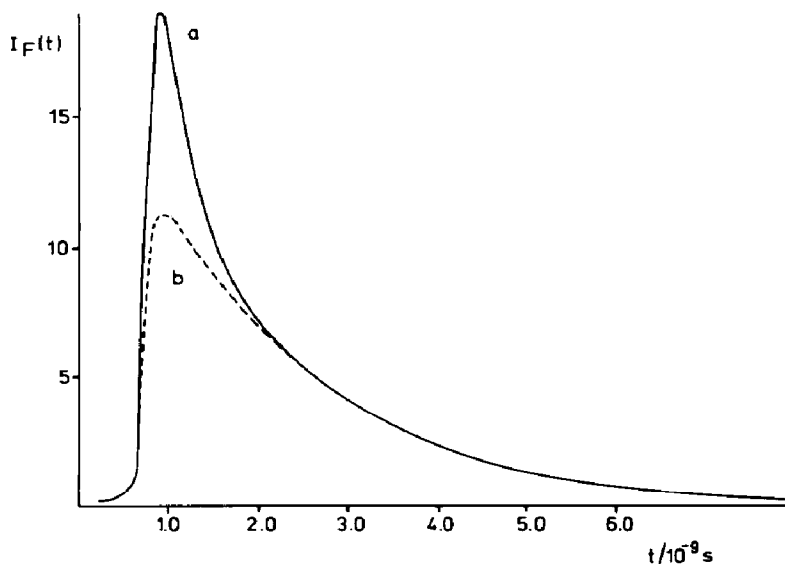


Fig. 1. Decay of the fluorescence of C_6F_6 transmitted through an interference filter with peak transmittance at 360 nm and a bandwidth of 10 nm. The fluorescence is excited with a 266 nm laser pulse of 25 ps FWHM: curve a, pure C_6F_6 in the vapour phase ($p = 17$ Torr) at 296 K; curve b, a 0.1 M liquid solution of C_6F_6 in $Cl_2FC-CClF_2$.

with the streak camera is shown in Fig. 1. This curve is reproduced with our photodiode detection system which gave $\tau_1 = 2000 \pm 200$ ps.

A single exponential decay of the fluorescence is also observed with the streak camera and with the photodiode in the case of a 0.1 M solution of C_6F_6 in liquid TFE. With the streak camera we determine $\tau_1 = 1060 \pm 60$ ps and with the photodiode we find $\tau_1 = 1100 \pm 200$ ps.

The growth of the fluorescence band of C_6F_6 at 360 nm upon excitation with the 25 ps UV laser pulse has been studied with the streak camera. The growth curve is the same for C_6F_6 in the gaseous state or in liquid solutions. The growth is shown in Fig. 2. It is completely determined by the temporal profile of the laser pulse and does not reveal any retardation in the appearance of the fluorescence.

The values which we have determined for τ_s and τ_1 in the cases of the pure vapour of C_6F_6 and of the gas mixture with nitrogen are larger by more than a factor of 2 than those reported previously [7] (Table 1). The discrepancy is probably due to inappropriate corrections and calibrations of the streak camera in the previous work, which only mentions a calibration of the time axis. The irregular pressure dependence of τ_s , τ_1 and c_s/c_1 noted in ref. 7 cannot be real, because collisional deactivation of the emitting species is negligible under the given conditions. The effect of collisions on the lifetime may be estimated in a manner which we have described previously [4]. If there is a 100% chance that an excited molecule becomes deactivated by radiationless processes when it suffers a collision, we calculate that a lifetime of 1 ns under collision-free conditions is reduced by less than 5% when the pressure increases to 10 Torr.

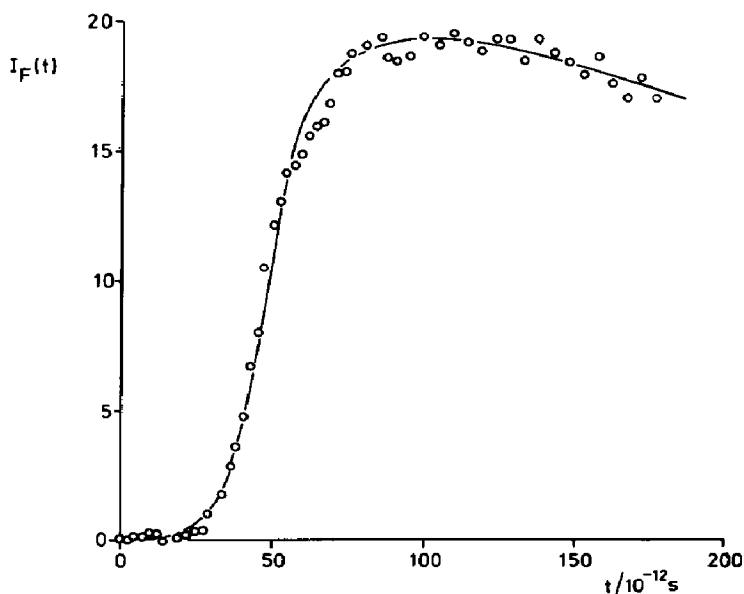


Fig. 2. Growth of the total intensity in the fluorescence band of C_6F_6 at 360 nm following excitation of the pure vapour ($p = 1.7$ Torr) with a 266 nm laser pulse of 25 ps FWHM.

Our observed value of τ_s for C_6F_6 in the gas mixture with 740 Torr nitrogen is reduced by a factor of 1.9 relative to its value for the pure vapour at 17 Torr. The latter, *i.e.* $\tau_s = 520$ ps, may be considered as the value under collision-free conditions. We attribute the bi-exponential decay in the case of the gaseous state to populations in two different emissive states of C_6F_6 , because τ_s is collision dependent and τ_1 is independent of collisions. This confirms our previous suggestion that a collision-induced transition from a high to a low lying emissive state is essential for the explanation of the pressure dependence of the fluorescence quantum yield [4]. The value of the parameter α representing the efficiency of a collision to induce a transition from a state $|s\rangle$ to a state $|l\rangle$ changes from the previously determined value of 0.05 based on the low pressure limit ($\tau_s^{(0)} = 2.2$ ns) to the value 0.21 when $\tau_s^{(0)} = 520$ ps is taken into account.

The decay behaviour of the fluorescence in liquid $Cl_2FC-CCl_2F$ is to be expected in the limit of high pressures of added non-reactive buffer gas. The value of τ_1 remains practically constant under collisions with non-reactive molecules up to the liquid state. However, it is affected by collisions with reactive molecules such as TFE (Table 1). Nevertheless, no stable reaction products are found using gas chromatography 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 h.

We denote the two emitting states $|l\rangle$ and $|s\rangle$ and assume that they are both populated at a time $t = 0$ as the result of excitation with the laser pulse. The concentrations $C_l(t)$ and $C_s(t)$ of molecules in states $|l\rangle$ and $|s\rangle$ respectively are governed by the differential equations

$$dC_l(t)/dt = -\tau_1^{-1}C_l(t) + k_c(p)C_s(t) \quad (12)$$

$$dC_s(t)/dt = -\{\tau_s^{-1} + k_c(p)\}C_s(t) \quad (13)$$

TABLE 1

Contribution of the short (τ_s) and long-lived (τ_1) components in the 360 nm fluorescence band of hexafluorobenzene under different conditions

$P(C_6F_6)$ (Torr)	$P(\text{buffer gas})$ (Torr)	τ_s (ps)	τ_1 (ps)	c_s/c_l
17		520 ± 50	1820 ± 60	0.75 ± 0.05
17	750 (N_2)	280 ± 50	1800 ± 50	0.80 ± 0.05
17	20 (TFE)	250 ± 50	1690 ± 60	1.00 ± 0.05
0.22 ^a		87 ± 7	1236 ± 271	4.0
0.6 ^a		47 ± 11	564 ± 92	1.0
1.0 ^a		164 ± 21	762 ± 148	1.5
10 ^a		120 ± 11	814 ± 59	1.0
20 ^a		94 ± 8	705 ± 42	1.0

Solution data: 0.1 M C_6F_6 in $Cl_2FC-CCl_2F$, $\tau_1 = 2060 \pm 90$ ps; 0.1 M C_6F_6 in TFE, $\tau_1 = 1060 \pm 60$ ps.

^aResults from ref. 7.

in which τ_1 and τ_s are the low pressure lifetimes of states $|1\rangle$ and $|s\rangle$ respectively and $k_c(p)$ represents the pressure-dependent rate constant for the collision-induced conversion of a molecule from state $|s\rangle$ to state $|1\rangle$. Integration of these equations yields

$$C_1(t) = C_1^0 \exp(-t/\tau_1) + C_s^0 Z (\exp(-t/\tau_1) - \exp[-\{\tau_s^{-1} + k_c(p)\}t]) \quad (14)$$

$$C_s(t) = C_s^0 \exp[-\{\tau_s^{-1} + k_c(p)\}t] \quad (15)$$

where Z is defined by

$$Z = k_c(p) \{k_c(p) + \tau_s^{-1} - \tau_1^{-1}\}^{-1} \quad (16)$$

The total fluorescence intensity $\phi(t)$ is given as a function of time by

$$\phi(t) = (\Phi_{11}C_1^0 + \Phi_{11}C_s^0Z) \exp(-t/\tau_1) + (\Phi_{fs}C_s^0 - \Phi_{11}C_s^0Z) \exp[-\{\tau_s^{-1} + k_c(p)\}t] \quad (17)$$

in which Φ_{11} and Φ_{fs} denote the fluorescence quantum yields of states $|1\rangle$ and $|s\rangle$ in the absence of collisions. When $k_c(p) = \infty$, as in the case of high gas pressures and in liquid solutions, the fluorescence intensity is described by eqn. (18).

$$\phi(t) = (C_s^0 + C_1^0) \Phi_{11} \exp(-t/\tau_1) \quad (18)$$

It follows from eqn. (18) that the total fluorescence decays mono-exponentially in the high pressure limit.

From eqns. (11) and (16) we find that the ratio of the coefficients C_s and C_1 is given by

$$\frac{C_s}{C_1} = \frac{\Phi_{fs}C_s^0 - \Phi_{11}C_s^0Z}{\Phi_{11}C_1^0 + \Phi_{11}C_s^0Z} \quad (19)$$

Although one may expect from eqn. (17) that C_s/C_1 is pressure dependent, we find experimentally that it is practically independent of pressure below 757 Torr. This may arise when the conditions $\Phi_{11} \leq \Phi_{fs}$ and $C_s^0 \leq C_1^0$ are satisfied simultaneously.

The action of TFE in the relaxation of electronically excited C_6F_6 will be now considered in relation to the photoinduced isomerization to the Dewar form. Continuous UV irradiation of C_6F_6 vapour (17 Torr) in equilibrium with a drop in the liquid phase and with 740 Torr nitrogen resulted in a 6.7% yield in the Dewar isomer after a period of 90 min. About 50% of C_6F_6 at an initial concentration of 0.01 M in $Cl_2FC-CClF_2$ disappears after 90 min 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 C_6F_6 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, because quenching of the emissive states would lead to a complete

absence of fluorescence from C_6F_6 in liquid TFE. We identify the scavenged intermediate as BR (mentioned in Section 1).

After excitation of a 0.1 M solution of C_6F_6 in $Cl_2FC-CClF_2$ with our picosecond UV laser pulse, we are able to immediately observe a transient absorption in the solution at 600 nm which has a lifetime τ_a of 6.0 ns. This absorption has been assigned to BR [2]. We have now studied the attenuation of the transient optical density $D(\lambda, \Delta t)$ at 600 nm, owing to the presence of TFE in the solution, by keeping the concentration of C_6F_6 constant and by varying the amount of TFE and then measuring the optical density at $\Delta t = 0, 1$ 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. 3 for $\lambda = 600$ nm and $\Delta t = 2$ ns. Figure 3 reveals an asymptotic approach of $D(\lambda, \Delta t)$ to a non-zero value when C_Q tends to infinity. We may explain this behaviour by assuming that two species contribute to the transient absorption at 600 nm, namely BR and an unknown species Z which is formed simultaneously with BR from the primary excited state. This

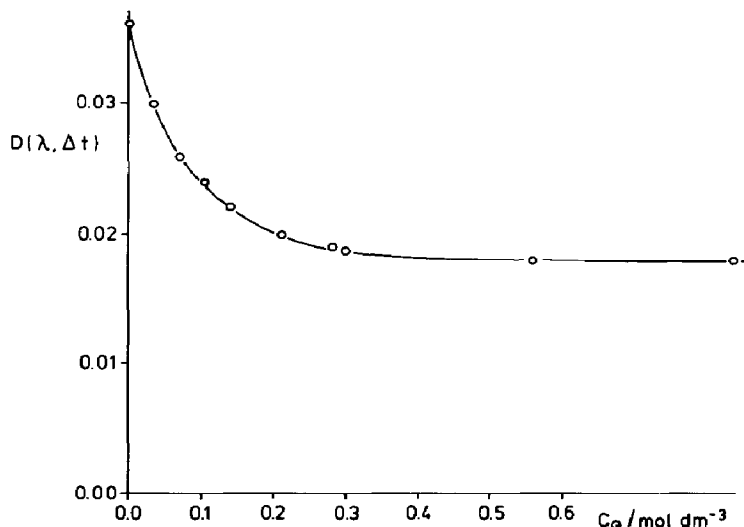


Fig. 3. Quenching of the transient absorption at 600 nm induced by excitation of a 0.1 M liquid solution of C_6F_6 in $Cl_2FC-CClF_2$ with a 266 nm laser pulse of 25 ps FWHM. The quencher Q is TFE ($\Delta t = 2.0$ ns).

explanation implies that the transient absorption at 600 nm of the solution of C_6F_6 in TFE is entirely due to Z. This implication is evident from eqn. (24) below. The species Z cannot be transformed into the Dewar isomer of C_6F_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 C_6F_6 [2]. These arrangements also exclude the identification of Z with S_1 or with T_0 .

We assume that Z disappears only in a first-order reaction with a rate constant k_Z . We denote the second-order rate constant for the reaction of

TFE with BR by k_q , the concentration of BR and of Z by C_{BR} and C_Z respectively and we write t' instead of Δt .

The time dependence of $C_{BR}(t)$ and of $C_Z(t)$ is governed by eqns. (20) - (22) if $C_Q(0) \gg C_{BR}(0)$.

$$dC_{BR}/dt = -k_0 C_{BR} - k_q C_Q C_{BR} \quad (20)$$

$$dC_Z/dt = -k_Z C_Z \quad (21)$$

$$dC_Q/dt = 0 \quad (22)$$

The total optical density may be expressed in terms of the molar extinctions $\epsilon_{BR}(\lambda)$ and $\epsilon_Z(\lambda)$ of BR and Z respectively. The solution of the differential equations leads to

$$D(\lambda, t') = \epsilon_{BR}(\lambda) C_{BR}(0) \exp\{-(k_0 + k_q C_Q)t'\} + \epsilon_Z(\lambda) C_Z(0) \exp(-k_Z t') \quad (23)$$

which yields

$$\lim_{C_Q \rightarrow \infty} D(\lambda, t') = \epsilon_Z(\lambda) C_Z(0) \exp(-k_Z t') \quad (24)$$

We define the function $P(C_Q, \lambda, t')$ by

$$P(C_Q, \lambda, t') = D(C_Q, \lambda, t') - \lim_{C_Q \rightarrow \infty} D(C_Q, \lambda, t') \quad (25)$$

By using eqns. (23) and (24) we obtain the simple expression

$$P(C_Q, \lambda, t') = \epsilon_{BR}(\lambda) C_{BR}(0) \exp\{-(k_0 + k_q C_Q)t'\} \quad (26)$$

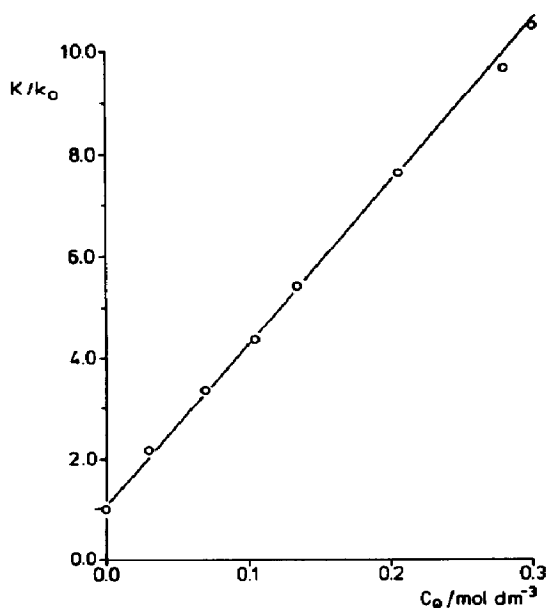


Fig. 4. Verification of the linear relation $K/k_0 = 1 + (k_q/k_0)C_Q$ for the quenching of the transient absorption at 600 nm by TFE.

In order to verify our explanation of the behaviour shown in Fig. 3, we determine experimental values of $P(C_Q, \lambda, t')$ according to eqn. (25) and then we determine the value of $K = (k_0 + k_q C_Q)$ from the time dependence of P . In Fig. 4 we have plotted the experimental values of the quantity K/k_0 as a function of C_Q and we observe that they satisfy a relation of the form $K/k_0 = 1 + \alpha C_Q$. The already-known value $k_0 = 1.7 \times 10^8 \text{ s}^{-1}$ has been used in constructing the graph. The slope α in Fig. 4 may be identified with k_q/k_0 . This yields a value $k_q = 5.3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Equation (24) enables us to determine the value of k_z from the decay of the transient absorption at 600 nm of the solution of C_6F_6 in TFE. We obtain $k_z = 1.7 \times 10^8 \text{ s}^{-1}$, which means that $k_z = k_0$. The equality of k_z and k_0 explains why a single exponential decay of $D(\lambda, \Delta t)$ at 600 nm is observed for the solution of C_6F_6 in $Cl_2FC-CClF_2$ which contains both BR and Z [2].

In the present work we arrive at the conclusion that at least four distinct species emerge along parallel routes from the primary excited state S_p of C_6F_6 , prepared by excitation with light of wavelength 266 nm. These are BR, Z and the species S_1 and S_s emitting the long-living and short-living components respectively of the fluorescence at 360 nm. They are all formed from S_p during the period of excitation with our UV laser pulse of 25 ps FWHM, which means that each of them has a formation rate constant k_f which is at least $5 \times 10^{10} \text{ s}^{-1}$. These reactions contribute a total of k_f to the rate constant k_d for the radiationless decay of S_p . We may state with certainty that $k_f \geq 2 \times 10^{11} \text{ s}^{-1}$. Previously we have estimated $k_d \geq 4 \times 10^{13} \text{ s}^{-1}$ based on the width of the homogeneous first electronic absorption band of hexafluorobenzene [1].

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