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# KrF-Laser–Induced Fluorescence of Benzene and its Fluorinated Derivatives in the Gas Phase (*).

W. HACK and W. LANGEL

*Max-Planck-Institut für Strömungsforschung - Böttingerstr. 4-8, D-3400 Göttingen*

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**Summary.** — The fluorescence of $C_6H_6$, $C_6H_5F$, 1, 4-$C_6H_4F_2$ and $C_6F_6$ excited by a KrF laser has been observed in the gas phase. The collisionless lifetime of $C_6H_6$ ($\tilde{A}\,{}^1B_{2u}$) with 2000 to 3000 cm$^{-1}$ of vibrational energy is 28 ns, which is a factor of two less than earlier results. Self-quenching of benzene leads to redistribution of vibrational energy in the $S_1$ state. $C_6F_6$ yields $CF_2$ when irradiated by the laser.

## 1. – Introduction.

Benzene has been an object of pioneering research in photophysics for many years. Its well-resolved and easily detected absorption and fluorescence spectra were first assigned in 1939 ($^1$). Since then it has proven to be more advantageous to extend the knowledge on the « prototype » benzene molecule and then transfer to other molecules, rather than starting with these molecules *ab initio*.

One important feature of benzene photophysics is the increase of decay rate and decrease of fluorescence quantum yield with the vibrational energy in the first excited singlet state ($^2$). A so-called « third channel », the nature

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(*) Paper presented at the « European Conference on the Dynamics of Excited States », held in Pisa, April 14-16, 1980.

($^1$) H. SPONER, G. NORDHEIM, A. L. SKLAR and E. TELLER: *J. Chem. Phys.*, **7**, 207 (1939).

($^2$) K. G. SPEARS and S. A. RICE: *J. Chem. Phys.*, **55**, 5561 (1971).

of which is not definitely known (³), is thought to be responsible for this effect.

Radiationless transitions make the absorption spectrum diffuse and suppress fluorescence (⁴) at vibrational energies in $S_1$ above 3000 $cm^{-1}$. The KrF laser used in this work with its photon energy of 40200 $cm^{-1}$ excites some vibrational states of benzene near this threshold with high intensity. It was the aim of this study to observe the spectral and time-resolved fluorescence from these highly excited molecules to gain further information on the collisionless and collision-induced energy flow.

## 2. – Experimental.

Figure 1 shows the experimental set-up, used in this work. A home-made excimer laser was employed for excitation of laser-induced fluorescence. The preionized TEA laser was operated with a mixture of krypton and fluorine

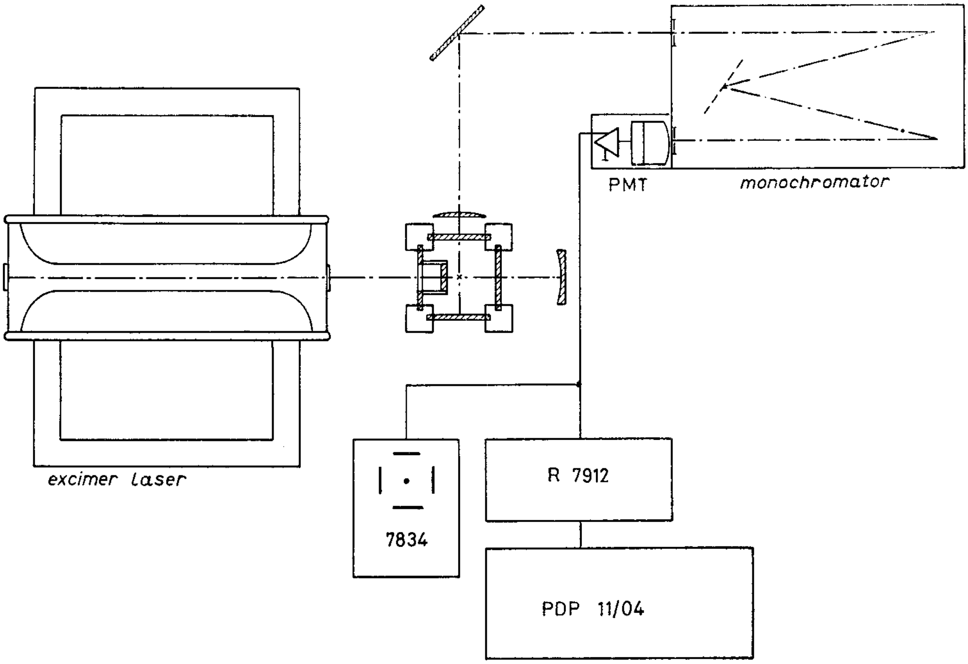

Fig. 1. – Experimental set-up.

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(³) M. JACON, C. LARDEUX, R. LOPEZ-DELGADO and A. TRAMER: *Chem. Phys.*, **24**, 145 (1977).

(⁴) *a*) J. H. CALLOMON, J. E. PARKIN and R. LOPEZ-DELGADO: *Chem. Phys. Lett.*, **13**, 125 (1972); *b*) C. S. PARMENTER and M. W. SCHUYLER: *J. Chem. Phys.*, **70**, 92 (1966).

in helium. The tube was fabricated from PVDF material (kynar) and was resistent to fluorine. The main discharge burns between two aluminium electrodes of Rogowski type and is driven by a thyratron-switched Blümlein circuit. The laser pulse has a FWHM of 17 ns and an energy of 100 mJ. Its spectrum is centred at 248.4 nm and has a FWHM of 0.36 nm.

The laser beam illuminates a teflon cell 48 mm in diameter, through one of the four suprasil windows. The cell is part of a vacuum line, which works at pressures of 0.050 to 100 mbar. The pressure is read out by a MKS-Baratron-220 Torrmeter below 20 mbar and by a mechanical gauge at higher pressures. The gas fill in the cell could be changed from shot to shot or, flowing very slowly, conserved for several shots. Before reaching the cell, the gas passed through a glass tube which allowed operation of a microwave discharge (2.45 GHz, 200 W). Chemicals of the highest commercially available purity from Merck, EGA-Aldrichs and Messer Griesheim were used without further purification. The purity of all reactants was tested by gas chromatography and the reactants were outgassed before use.

The fluorescence is dispersed by a Jobin-Yvon-THR monochromator ($f = 1.5$ m), equipped with a holographic grating (2400 l/mm), with a resolution of 0.1 to 0.2 nm. The fluorescence was detected by a RCA 4831 photomultiplier. A premplifier (Pacific Photometric Instruments 62/2A32) was integrated into the PMT-Socket and the signal fed to the 7A19 amplifier of a transient digitizer R 7912 or oscilloscope 7834 (Tektronix). The transient digitizer enabled measurements of fluorescence time dependence and pulse height to be made.

Signals were averaged in a minicomputer DEC PDP 11/04, normally from 50 to 150 times, to provide a signal-to-noise ratio better than 30:1, and then evaluated by using the Tek-SPS-BASIC software. Decay constants were found by comparing the averaged decay signal with the laser pulse convoluted with single exponential decay functions.

The spectra were measured stepwise with 1 to 10 shots per point. Some of them, especially those from fluorinated benzenes, had only weak structure on an intensive background. This structure could be evaluated after subtracting a low-resolution spectrum. This was computed by replacing each point of the original spectrum by the average of 40 points next to it.

## 3. - Results.

The KrF line at 248.4 nm is strongly absorbed by benzene and its fluorinated derivatives. The absorption from the electronic ground state ($S_0$) populates excited vibrational states in the first singlet ($S_1$). Fluorescence from $C_6H_6$, $C_6H_5F$, 1,4-$C_6H_4F_2$ and $C_6F_6$ was monitored spectrally and time resolved at pressures from 0.07 to 1.4 mbar.

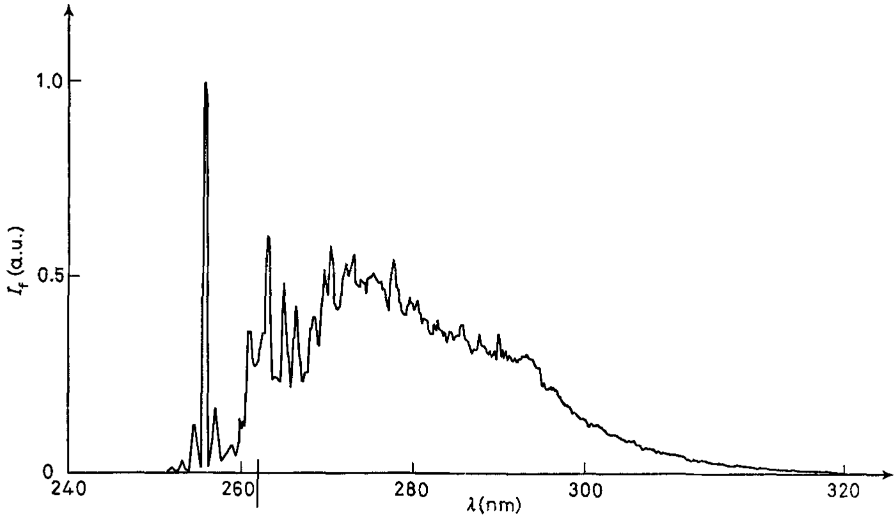

Fig. 2. – Fluorescence spectrum of benzene (1.05 mbar).

TABLE I. – *Population of vibrational states in the first excited singlet state after excitation with the* KrF *laser pulse.*

| Vibrational state | Vibrational energy ($cm^{-1}$) | Share (%) | Expected fluorescence |
|---|---|---|---|
| $11^1\,17^1\,1^1$ | 2157 | 25.9 | $6^0_1\,11^1_0\,17^1_0\,1^1_n$ |
| | | | $6^0_1\,11^1_1\,17^1_1\,1^1_n$ |
| $1^3$ | 2769 | 22.3 | $6^0_1\,1^3_n$ |
| $6^1\,10^1\,1^2$ | 2948 | 4.6 | $6^1_0\,10^1_1\,1^2_n$ |
| | | | $6^1_2\,10^1_1\,1^n_n$ |
| $6^2\,16^1\,1^2$ | 3126 | 29.8 | $6^2_1\,16^1_1\,1^2_n$ |
| | | | $6^2_3\,16^1_1\,1^2_n$ |
| $9^1\,1^1$ | 2071 | 0.1 | |
| $10^2\,1^1$ | 2084 | 1.2 | |
| $6^1\,16^5\,1^1$ | 2632 | 1.2 | |
| $6^1\,16^2\,17^1\,1^1$ | 2638 | 0.1 | |
| no assignment given in ref. (5) | | 14.8 | |

3'1. $C_6H_6$. – The absorption spectrum of benzene at room temperature was recently reviewed by ATKINSON and PARMENTER (5). Knowing the spectral distribution of the laser line, one can calculate the relative distribution

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(5) G. H. ATKINSON and C. S. PARMENTER: *J. Mol. Spectrosc.*, **73**, 20 (1978).

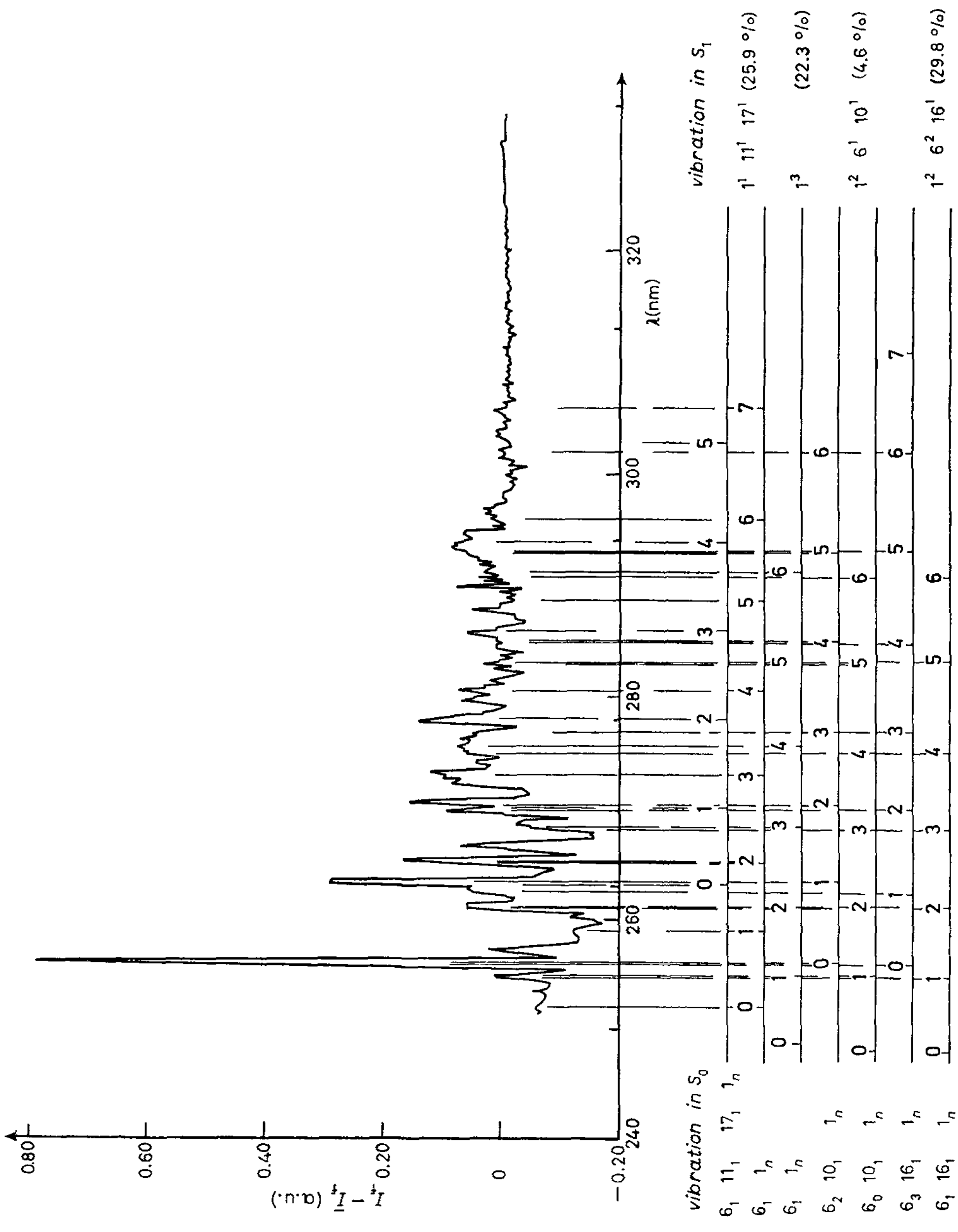

Fig. 3. – Benzene fluorescence with assignments (see the text), background subtracted.

of upper states, pumped by the laser pulse, using assignments and relative intensities from ref. (5) (table I). Hot bands contribute markedly to the absorption and populate levels with a vibrational energy around 3000 $cm^{-1}$.

The fluorescence spectrum at 1.05 mbar is plotted in fig. 2. It starts at 250 nm with strong bands on a low background. Further to the red, it has a maximum and a tail with poorly resolved structure. Subtraction of the background evaluated in the way described above results in the line spectrum shown in fig. 3. By following the selection rules, worked out by PARMENTER *et al.* (6), the structure is assigned to resonance fluorescence from the four most populated states, containing 82 % of all $S_1$-benzene. Most intensity is expected to occur in progressions in $v_1''$ with $\Delta v_6 = \pm 1$ (6). As shown in fig. 3, 19 of the 33 maxima can be assigned to them.

Fluorescence lifetimes of benzene were measured at various pressure from 0.07 to 13.5 mbar and wave-lengths from 254.78 to 315 nm. In fig. 4 the overall

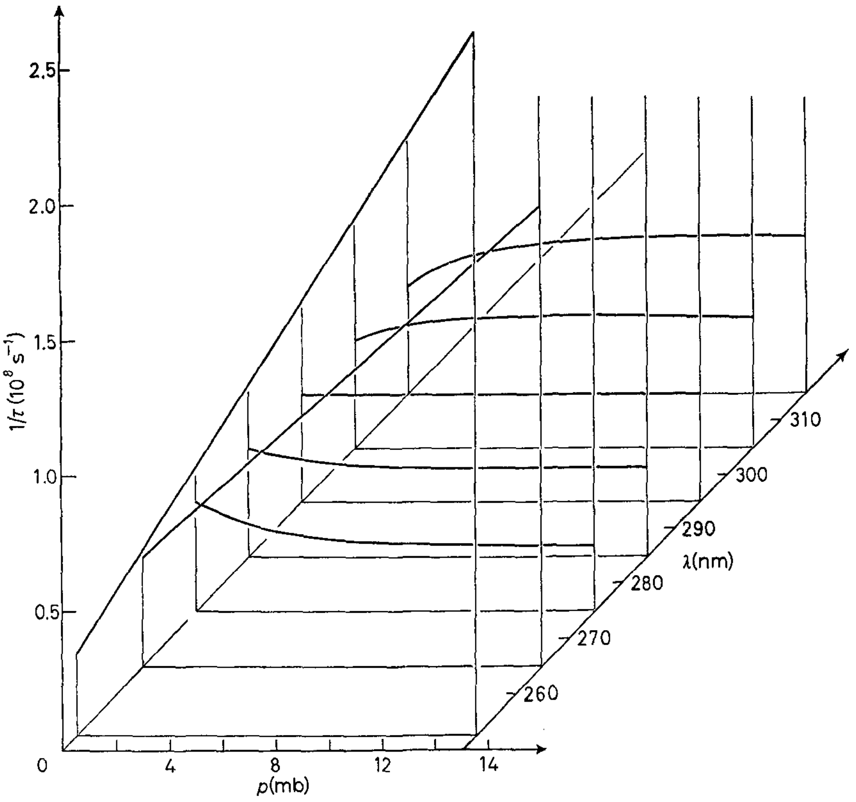

Fig. 4. – Decay rates of benzene fluorescence *vs.* pressure and wave-length.

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(6) A. E. W. KNIGHT, C. S. PARMENTER and M. W. SCHUYLER: *J. Am. Chem. Soc.*, **97**, 1993 (1975).

lifetimes *vs.* pressure and fluorescence wave-length are plotted in a three-dimensional form. At short wave-lengths, lifetimes describe the decay of single vibronic levels (254.78 and 255.98 nm: $1^2 6^1 10^1$ and $1^2 6^2 16^1$; 265.15 nm: $1^1 11^1 17^1$, see fig. 3), at longer wave-lengths the background does not allow any assignment of the fluorescence to individual states.

At low pressures the fluorescence decay time is almost independent of wave-length. It is the collisionless lifetime of the initially excited upper states. Extrapolation to zero pressure yields $\tau = (28 \pm 2)$ ns.

Only at short wave-lengths do the lifetimes show Stern-Vollmer behaviour (*i.e.* $1/\tau$ *vs.* $p$ is a straight line). Lifetimes increase with pressure around 270 nm, are independent of it at 280 nm and slightly decrease in a bent line at the red tail of the spectrum. Therefore, at higher pressure lifetimes vary dramatically with the wave-length, *e.g.* at 13.3 mbar, changing from 265.15 to 275 nm, the decay time increases from 8.5 to 42 ns.

**3·2.** $C_6H_5F$ *and* 1,4-$C_6H_4F_2$. – In contrast to benzene itself, the transitions

$$C_6H_5F \quad {}^1B_1 \leftrightarrow {}^1A_1 \quad C_{2v}\,, \qquad T_{0,0} = 37\,819 \text{ cm}^{-1}\,,$$

$$1,4\text{-}C_6H_4F_2 \quad {}^1B_{2u} \leftrightarrow {}^1A_g \quad D_{2h}\,, \qquad T_{0,0} = 36\,840 \text{ cm}^{-1}\,,$$

are allowed, since the sixfold symmetry is reduced by the fluorine atoms. The absorption spectra of these benzenes in the region of the KrF line are given in ref. ([7,8]).

The fluorescence spectra show a large amount of background, which was subtracted for assigning the structure. In the case of $C_6H_5F$ this can be done by using the totally symmetric modes $\nu_1$ and $\nu_{12}$.

The fluorescence spectrum of 1,4-$C_6H_4F_2$ is divided into two parts by a minimum in intensity near the 0-0 transition. In the blue part, four local maxima are observed which are assigned to

| | | |
|---|---|---|
| $(7a)^2_2 1^1_1$ | 36 814 cm$^{-1}$ | 272 nm, |
| $(7a)^2_1 1^1_2$ | 37 200 cm$^{-1}$ | 269 nm, |
| $(7a)^2_2 1^1_0$ | 37 672 cm$^{-1}$ | 265 nm, |
| $(7a)^2_1 1^1_1$ | 38 058 cm$^{-1}$ | 263 nm, |
| $((7a)^2_0 1^1_0$ | 40 159 cm$^{-1}$ | 249 nm). |

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(7) S. M. WOLLMANN: *J. Chem. Phys.*, **14**, 123 (1946).

(8) C. D. COOPER: *J. Chem. Phys.*, **22**, 503 (1954).

The modes are probably excited by coupling laser energy into the near-resonant strong mode, given in brackets.

Lifetimes of the excited states of $C_6H_5F$ and 1,4-$C_6H_4F_2$ have been measured at 280 and 290 nm, where the continuous background is strong, they increase with increasing pressure, similar to benzene at 270 nm.

3'3. $C_6F_6$. – Hexafluorobenzene belongs to the same symmetry class $D_{6h}$ as benzene itself. The location of $T_{0,0}$ is not known exactly, because the absorption spectrum is diffuse; $T_{0,0}$ probably lies near 290 nm (⁹). The symmetry class of the lowest excited singlet should be $B_{2u}$ as $S_1$ in benzene or $B_{1u}$ as $T_1$ in benzene, because the electron configuration is equal in both molecules. For $B_{1u}$ and $B_{2u}$ the transition is electronically forbidden and becomes vibronically allowed by $e_{2g}$-modes.

Figure 5 shows the gas phase fluorescence spectrum of $C_6F_6$, together with a spectrum of liquid $C_6F_6$. The relaxed spectrum observed in the liquid starts at the 0-0 transition and continues to the red, the gas phase spectrum has its maximum at 290 nm. The slight structure of the gas phase spectrum can be explained by two progressions, $1_0^n$ and $1_n^0$, both starting at the strongest peak at 33 998 cm$^{-1}$ with $v_1' = 507$ cm$^{-1}$ and $v_1'' = 540$ cm$^{-1}$. By assigning the strongest peak to $6_1^0$ as in benzene, the 0-0 transition lies at 34 441 cm$^{-1}$ ($v_6'' = 443$ cm$^{-1}$) or 290.4 nm.

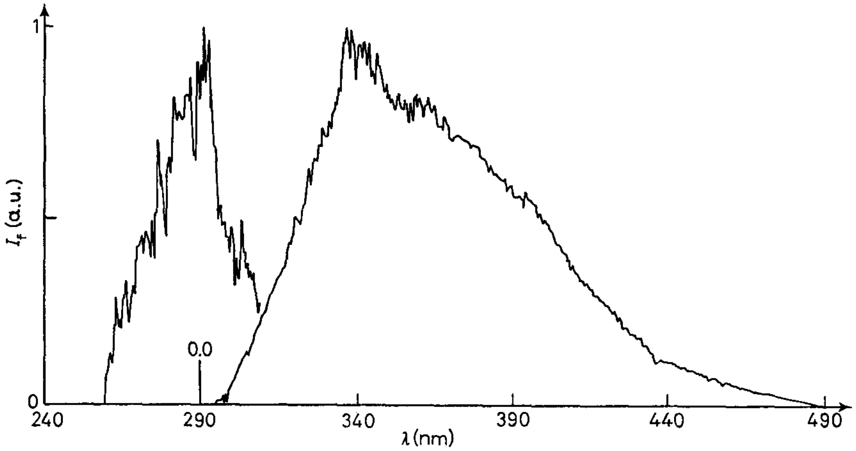

Fig. 5. – Fluorescence spectra of hexafluorobenzene vapour (left) and liquid (right).

Under quasi-static conditions (extremely low flow, 17 mbar pressure), after 5 ÷ 10 shots a much stronger fluorescence can be seen in the gas phase than that of $C_6F_6$ itself. Its spectrum and temporal behaviour are that of SVL fluorescence of $CF_2$ ($\tilde{A}\,^1B_1$, $v_2 = 6$) (fig. 6).

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(⁹) D. Phillips: *J. Chem. Phys.*, **46**, 4679 (1967).

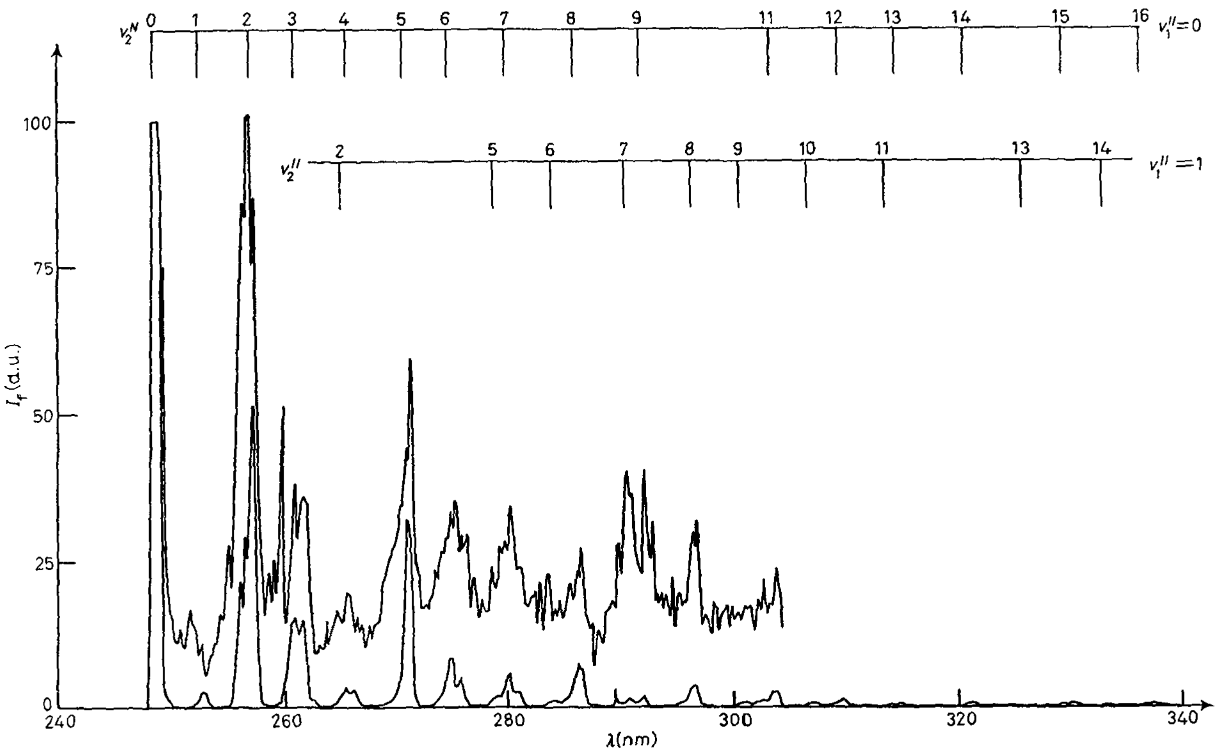

Fig. 6. – $CF_2$ fluorescence from photolysis of $C_6F_6$ at 17 mbar (upper line) and SVL excitation of $CF_2$ from $CF_2Cl_2$ discharge, $CF_2(\tilde{A}\,^1B_1(0,6,0) \rightarrow \tilde{X}\,^1A_1(v_1'', v_2'', 0))$ (lower line).

The decay time of the $CF_2$ emission was measured at various pressures of $C_6F_6$. A Stern-Vollmer plot gave a collisionless lifetime of 55 ns and a quenching rate of $2.5 \cdot 10^{14}$ cm$^3$/mol s. In contrast to $C_6F_6$, irradiation of $C_6HF_5$ leads to hardly any $CF_2$ fluorescence.

## 4. – Discussion.

4·1. *Resonance fluorescence and collisionless lifetime of benzene.* – Benzene was one of the first molecules, to which single-vibronic-level excitation (SVL) was applied ($^2$). By means of this technique, quantitative data on the decrease of lifetime and fluorescence quantum yield at higher vibrational energies were obtained. Above about 2000 cm$^{-1}$ of vibrational energy in $S_1$, low quantum yield of fluorescence, stray light and small separation between bands make it difficult to obtain reliable results, as the large scatter in the radiative lifetimes shows. On the other hand, above 3000 cm$^{-1}$ most bands are diffuse in absorption and yield no fluorescence.

The excimer laser yields pulses of about 55 cm$^{-1}$ band width. Because of the high density of the absorption spectrum, the laser excites four levels. Three of them are due to hot bands and have a vibrational energy of 2770 to 3130 cm$^{-1}$, the fourth has 2160 cm$^{-1}$ (table I). The assignments of the spectrum show that $11^1 17^1 1^1$ and the hot bands yield resonance fluorescence with similar intensity. From ref. ($^{4b}$) it is known, however, that the fluorescence of the hottest band, $6^2 16^1 1^2$, is very weak. Since it was not compared with one of the other bands excited here and our excitation/detection might be more sensitive, we cannot rule out the assignment $6^2 16^1 1^2$.

By examining the shape and the position of the peaks belonging to the overlapping progressions $6^0_1 1^3_n$, $6^1_0 10^1_1 1^2_n$, $6^2_1 16^1_1 1^2_n$, it seems that fluorescence from $1^3$ contributes to it. Spears and Rice ($^2$) found some fluorescence at 248.44 nm as well, which they assign to $1^3$. Since they could not spectrally resolve it, contributions of the neighbouring bands cannot be excluded in their work.

The question whether the $1^3$ fluoresces or not is of theoretical importance. The results of Callomon *et al.* ($^{4a}$) have shown that especially bands with $v'_1 > 3$ tend to show no fluorescence. Thus $6^1_0 1^3_0$ shows no fluorescence at 3288 cm$^{-1}$ of vibrational energy, but the $7^1_0$ state does at 3077 cm$^{-1}$. Based on this, mechanisms were developed which explain the opening of channel three by an enhanced internal conversion with $v_1$ as accepting mode ($^{11}$).

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($^{10}$) B. K. Selinger and W. Ware: *J. Chem.*, **53**, 3160 (1970).

($^{11}$) *a*) M. G. Prais, D. F. Heller and K. F. Freed: *Chem. Phys.*, **6**, 331 (1974); *b*) M. Jacon: *Chem. Phys. Lett.*, **47**, 466 (1977).

The collisionless lifetime of 28 ns, measured here, is considerably smaller than the 48 ns average measured in this spectral region by SPEARS and RICE. These authors had to correct for stray light, since they did not spectrally resolve fluorescence and admit that these lifetimes are too long. Moreover, together with the quantum yield of 0.07, measured at high vibrational energies, the radiative lifetime increases—with large scatter—from 300 ns at low vibrational energies to 700 ns at $1^3$. If we use our total lifetime of 28 ns, it increases only moderately to 400 ns, much more in accordance with results for $C_6D_6$ (12).

4'2. *Continuous spectra and collision-induced effects.* – Two different kinds of fluorescence can be seen in large molecules. Single vibronic levels show a selection-rule-determined line spectrum, especially in highly symmetric molecules. On the other hand, a statistical distribution of molecules over the levels in a given energy band shows a smooth fluorescence intensity distribution, which, since the number of transitions per wave-length is higher than the reciprocal Doppler width, cannot be resolved into lines. The intensity function varies steadily with the vibrational energy in the lower state, in contrast to resonance fluorescence spectra. Since all modes (except of the high C-H radial vibrations) are populated, selection rules have little influence on the shape of the spectrum, *i.e.* can only cause slight local maxima in strong transitions.

The relative wave-length dependence of the smooth fluorescence from a small energy band is described by the product of the density of final states and the mean Franck-Condon factor. In a molecule like benzene, the energy density in the ground state increases with increasing vibrational energy (13). The mean Franck-Condon factor is known from the Franck-Condon envelopes of the important progressions and has a maximum when the transition energy is approximately equal to the 0-0 transition. As a result, we get a continuous spectrum, which, at small vibrational energies in the upper state, starts at the 0-0 transition wavelength, has a maximum somewhat shifted to the red and a long tail further to the red end. If we increase the vibrational energy in the upper state, the spectrum shifts steadily to the blue.

Statistical distributions which show continuous spectra are prepared in different ways: by irradiation of background absorption, by isoenergetic energy flow in the molecule and by collisions.

Hexafluorobenzene shows an unresolved absorption spectrum. Its continuous gas phase spectrum is, therefore, caused by excitation of a statistical distribution of modes. They have a vibrational energy of about 5800 $cm^{-1}$. The fluorescence is considerably shifted to the blue, compared with a relaxed liquid-phase spectrum. Since the gas phase spectrum has its maximum near

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(12) A. S. ABRAMSON, K. G. SPEARS and S. A. RICE: *J. Chem. Phys.*, **56**, 2291 (1972).

(13) M. BIXON and J. JORTNER: *J. Chem. Phys.*, **48**, 715 (1968).

the 0-0 transition, and is not shifted to the red, its shape is obviously determined by the Franck-Condon envelope rather than by the increase of energy density (see fig. 5).

$C_6H_5F$ and 1,4-$C_6H_4F_2$ are also excited in a background absorption region. The maxima assigned above in 1,4-$C_6H_4F_2$ show that the intramolecular energy flow is efficient, even during the short lifetime of the difluorobenzene. Thus the state $(7a)^2 1^1$, which is not excited directly, fluoresces strongly.

The benzene spectrum exhibits a large amount of resonance fluorescence, which shows that in benzene the collisionless energy flow is not fast enough to depopulate the discrete vibronic levels completely, in spite of the longer lifetime of benzene and the high energy density at the vibrational levels excited in the experiment. The background emission is still much stronger compared to resonance fluorescence than in benzene excited at a longer wavelength (253.7 nm ([14])). This can be caused by the higher energy density at the vibrational energies of $S_1$ pumped by the excimer laser. The background is shifted to the blue compared with excitation at lower photon energies.

The temporal behaviour of benzene fluorescence depends in a complicated way on the pressure. The vibrational energy of the electronically excited molecules decreases by collisions and thus they reach levels which have longer collisionless lifetimes than the initially excited state. Thus it may happen that, monitoring a given emission wave-length, one sees at low pressure fluorescence from high vibronic levels with short lifetime, at high pressure fluorescence from levels near the vibrational ground state in $S_1$, which have much longer lifetimes. The effective lifetime then increases with pressure or, at least, does not decrease as fast as the initial vibronic states are quenched. In this way it is possible to interpret fig. 4.

At a wave-length of 255 nm only discrete vibronic levels fluoresce. They are quenched by benzene to a statistical distribution, which does not emit at this wave-length. The rate constant is $5 \cdot 10^{14}$ cm³/mol·s.

It is well known from the literature that this high rate in benzene self-quenching is not due to *v-v* transfer but to Coulomb interactions. The process

$$C_6H_6(S_1, v_i') + C_6H_6(S_0, v_i'') \to C_6H_6(S_0, v_f'' \geqslant v_i'') + C_6H_6(S_1, v_f' \leqslant v_i')$$

has the same effect as a vibrational deactivation unless the molecules are distinguished by isotopic substitution ([15]).

At all longer wave-lengths, the decay rate increases more slowly with pressure, since statistical distributions of lower vibrational energy interfere. As fig. 4 shows, the effect is very drastic near 270 nm at the false origin $6^0_1$ of the benzene fluorescence.

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([14]) J. M. BLONDEAU and M. STOCKBURGER: *Ber. Bunsenges. Phys. Chem.*, **75**, 450 (1971).

([15]) C. S. PARMENTER and K. Y. TANG: *Chem. Phys.*, **27**, 127 (1978).

The irregular behaviour of lifetime in benzenes can be approximated by the « step ladder model » ([16]). This model reduces the vibrational manifold in the excited state to a ladder formed by a single harmonic mode. The decay constant of the « steps » increases linearly with the vibrational quantum number.

The model qualitatively shows that the strong pressure dependence of the measured lifetimes can be explained by variation of decay rate with the vibrational level ([17]). The mathematical evaluation, however, makes essential use of a solution of stochastic equations for the population of the vibrational states. Since we need to introduce not only population factors, but also spectral distribution of emission, we cannot quantitatively apply this model to our results.

4·3. *Photodissociation.* – The appearance of $CF_2$ in the photolysis of $C_6F_6$ at 248 nm is surprising, since the molecule contains strong chemical bonds and is photochemically stable at wave-lengths longer than 230 nm ([18]). It can only be explained by multiphoton absorption. We propose a mechanism (eq. (4.1) to (4.6)), which explains our results:

$$\begin{array}{lll}
(4.1a) & C_6F_6(S_0) + h\nu_1 & \rightarrow C_6F_6(S_2)\,, \\
(4.2a) & C_6F_6(S_1) & \rightarrow C_6F_6(S_0) + h\nu_{f1}\,, \\
(4.2b) & C_6F_6(S_2) & \rightarrow C_5F_4 = CF_2\,, \\
(4.3) & C_2F_4 = CF_2 + h\nu & \rightarrow CF_2(\tilde{X}\,{}^1A_1, v_1, v_2, v_3) + C_5F_4\,, \\
(4.4) & CF_2(\tilde{X}\,{}^1A_1, v_1, v_2, v_3) & \xrightarrow{\pm M} CF_2(\tilde{X}\,{}^1A_1, 0, 0, 0)\,, \\
(4.5) & CF_2(\tilde{X}\,{}^1A_1, 0, 0, 0) + h\nu_1 & \rightarrow CF_2(A\,{}^1B_1, 0, 6, 0)\,, \\
(4.6) & CF_2(\tilde{A}\,{}^1B_1, 0, 6, 0) & \rightarrow CF_2(\tilde{X}\,{}^1A_1, v_1, v_2, 0) + h\nu_{f1}\,.
\end{array}$$

By absorption of one photon (4.1*a*), the fluorescence of $C_6F_6$ (4.2*a*) is excited. The states reached thereby can also serve as intermediates for the two-photon absorption (4.1*b*). $C_6F_6$ then has about 15 eV of energy and undergoes isomerization (4.2*b*).

The precursor of $CF_2$ is probably $C_5F_4 = CF_2$ (4.3).

The fluorescence spectrum of $CF_2$ from $C_6F_6$ photolysis (4.6) is the same as from SVL excitation of the state $\tilde{A}\,{}^1B_1(0, 6, 0)$ ([19]) (fig. 6). This shows that no electronically excited $CF_2$ is formed (4.3). Therefore, the $CF_2$ can be detected only from its laser-induced fluorescence spectrum ((4.5) and (4.6)).

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([16]) K. F. FREED and D. F. HELLER: *J. Chem. Phys.*, **61**, 3942 (1974).

([17]) R. P. STEER, M. D. SWORDS and D. PHILLIPS: *Chem. Phys.*, **34**, 95 (1978).

([18]) A. K. BASAK, G. P. SEMELUK and J. UNGER: *J. Phys. Chem.*, **70**, 1337 (1966).

$CF_2(\tilde{X}\,^1A_1)$ only absorbs the KrF laser radiation in its vibronic ground state (19). We suppose that the induction period of $CF_2$ fluorescence is seen, because $CF_2$ comes vibrationally excited from (4.3) and has to be quenched, before it can be detected. During the 17 ns of pulse duration, no significant vibrational quenching can take place at the pressures used in this experiment.

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The authors wish to thank Prof. H. GG. WAGNER for his interest in this work.

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(19) D. S. KING, P. K. SCHENCK and J. C. STEPHENSON: *J. Mol. Spectrox.*, **78**, 1 (1979).

## ● RIASSUNTO (*)

Si è osservata nella fase di gas la fluorescenza di $C_6H_6$, $C_6H_5F$, 1, 4-$C_6H_4F_2$ e $C_6F_6$ eccitati da un laser a KrF. La vita media senza collisione di $C_6H_6$ $(\tilde{A}\,^1B_{2u})$ con un'energia vibrazionale da 2000 a 3000 $cm^{-1}$ è 28 ns, cioè due volte più piccola che nei precedenti risultati. L'autospegnimento del benzene porta alla ridistribuzione dell'energia vibrazionale nello stato $S_1$. $C_6F_6$ dà $CF_2$ quando è irradiato col laser.

(*) *Traduzione a cura della Redazione.*

## Флуоресценция бензола и его фторных производных в газовой фазе, индуцированная KrF-лазером.

**Резюме** (*). — В газовой фазе наблюдается флуоресценция $C_6H_6$, $C_6H_5F$, 1, 4-$C_6H_4F_2$ и $C_6F_6$, возбужденных KrF-лазером. Бесстолкновительное время жизни $C_6H_6(\tilde{A}\,^1B_{2u})$ при значениях вибрационной энергии от 2000 до 3000 $см^{-1}$ составляет 28 нс, что в два раза меньше предыдущих результатов. Самогашение бензола приводит к перераспределению вибрационной энергии в $S_1$ состоянии. $C_6F_6$ превращается в $CF_2$ при облучении лазером.

(*) *Переведено редакцией.*