

TIME-RESOLVED RESONANCE RAMAN SPECTROSCOPY OF PHOTOCHEMICAL REACTIVE INTERMEDIATES: RADICAL CATION OF FLUORENE AND TRIPLET STATE OF FLUORENE, DIBENZOFURAN AND DIBENZOTHIOPHEN

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(Received 15 October, 1989; in final form 5 January, 1990)

The time-resolved Raman spectra of the first triplet state—in resonance with the $T_n \leftarrow T_1$ absorption at 370 nm—and of the radical cation transient—in resonance with the $R^{+\cdot} \leftarrow R^+$ absorptions at 370 nm and in the 560–600 nm range—are reported for fluorene. The triplet state Raman spectra of dibenzofuran and dibenzothiophen are also given. The vibrational assignments, resonance Raman activity and intensity enhancement effects are studied. On this basis, the structures and electronic configurations of the triplet state and radical cation transients and the nature of the resonant $T_n \leftarrow T_1$ and $R^{+\cdot} \leftarrow R^+$ transitions are discussed. It turns out from this investigation that the title molecules present close analogies with biphenyl. The insertion of a methylene group or a heteroatom does not disturb markedly the electronic properties of the ground state, the first triplet state and the radical cation transient of biphenyl.

INTRODUCTION

Reactive intermediates such as excited singlet and triplet states, ions, and radicals, play a determinant role in most chemical and photochemical processes. In this regard, the spectroscopic investigation of these transient species is essential for understanding the molecular reactivity and a considerable work has been done by using time-resolved methods such as absorption and emission spectroscopies, photoconductivity and chemically induced dynamic nuclear polarization (CIDNP) or ESR spectroscopy. In particular, a great deal of chemical information can be obtained from transient absorption. Nonetheless, in condensed phases, absorption bands are generally broad and diffuse with limited inherent structural information. In contrast, resonance Raman spectroscopy is a particularly efficient technique to provide detailed structural information and excellent discrimination between species which present broad and overlapping absorption bands.

The Raman analysis of short-lived intermediate species has been made possible owing to the pioneering development by Bridoux and Delhaye¹ of the principle of multichannel analysis for Raman spectroscopy, and the considerable improvement in sensitivity and temporal resolution that has been realized in the last years by Bridoux *et al.*^{2,3} The first generation of multichannel Raman spectrometer used photographic plates as detective materials and had a comparatively low sensitivity. A second generation of instruments relied on image intensifiers and low light level television cameras.^{1a,1b} These detectors were characterized by high sensitivity but low stability, distortion of the image and limited resolution and dynamic range. Nevertheless, they were employed for obtaining the first vibrational spectra in the nanosecond, then the picosecond, time scales.² A third generation of multichannel spectrometers, using intensified photodiode arrays as detectors, has been recently developed.³ With the advantage of being gated in the 10 ns range, they present high stability, dynamic and sensitivity characteristics. Since the first observation of a species in an excited state—the lowest triplet state of paraterphenyl—by Wilbrandt *et al.*,⁴ the application of this technique to the vibrational detection of reactive intermediates has been largely adopted.⁵

Recently, we have developed an extensive resonance Raman investigation of photochemical transients of aromatic molecules by using a nanosecond pump/probe excitation system. By this method, the transient species is generated with a first laser excitation (pump pulse) and its Raman spectrum is induced by a second laser excitation (probe pulse) which is retarded from the former by an adjustable time delay. In previous works, we have investigated the lowest triplet state (T_1) and the radical cation state ($R^{\cdot+}$) of aromatic amines⁶⁻⁹ and of various derivatives of biphenyl.^{10,11} The present paper deals with the photoexcited triplet state of fluorene, dibenzofuran and dibenzothiophen (Figure 1) and the radical cation of fluorene.

Important analogies have been found between fluorene and biphenyl: both species are characterized in the triplet state by a strong $T_n \leftarrow T_1$ absorption peaking around 370 nm¹²⁻¹⁵ and in the radical cation state by two absorptions lying in the 360–390 and 530–700 nm regions, respectively.^{16,17} Molecular orbital calculations¹⁸ have suggested that the T_1 states of biphenyl (${}^3B_{1u}$) and of fluorene (3B_1) result mainly from the LUMO \leftarrow HOMO ($\pi\pi^*$) excitation configuration and have comparable

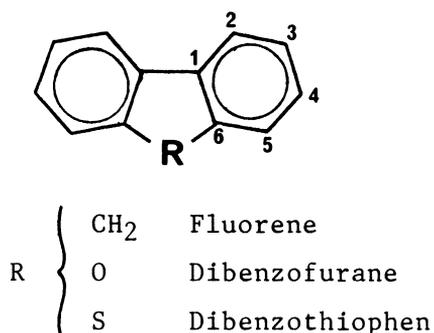


Figure 1 Representation of the molecules studied and numbering of the atoms.

orbital natures. Electron paramagnetic resonance results¹⁹ have indicated that the T_1 states of fluorene, dibenzofuran and dibenzothiophen are very similar to the T_1 state of biphenyl and that the methylene group and the heteroatoms have no significant contribution to the $T_1 \leftarrow S_0$ excitation. On the other hand, very detailed information on the triplet state and radical cation species has been obtained for biphenyl from time-resolved resonance Raman studies^{5c,10,11}. The analysis of the changes in wavenumber of the Raman bands with respect to the ground state values has clearly shown that both the T_1 and $R^{+\cdot}$ structures present a quinoidal distortion with a notable increase of the inter-ring bond order. In addition, the specific resonance enhancements of the band intensities have appeared very typical of the distortions of the T_1 and $R^{+\cdot}$ structures in the resonant upper electronic states, T_n and $(R^{+\cdot})^*$, respectively, and precise information concerning the orbital origins of the $T_n \leftarrow T_1$ absorption at 370 nm and of the $(R^{+\cdot})^* \leftarrow R^{+\cdot}$ absorptions at 370 and 690 nm could be established, in good agreement with predictions from simple molecular orbital considerations.

Here, the resonance Raman band wavenumbers and intensities of the triplet state and radical cation of fluorene are discussed in parallel with the analysis made for biphenyl.¹¹ The triplet state spectra of dibenzofuran and of dibenzothiophen are also studied. These results are compared to the time-resolved resonance CARS spectra and analysis reported recently for T_1 fluorene.²⁰

EXPERIMENTAL

Fluorene, dibenzofuran and dibenzothiophen were sublimated *in vacuo* prior to each measurement. In particular, the highly fluorescent species fluorenone, which is always present as a yellow impurity in fluorene, had to be carefully eliminated. Acetonitrile, methanol and cyclohexane (Prolabo) were used as received. Samples were contained in static 10×10 mm² quartz cells.

A single 10 Hz Q-switched Nd: Yag laser (Quantel YG581C) was used for the pump and the probe pulse excitations, which were temporally delayed by an optical delay line (~ 30 ns). The fourth harmonic (266 nm, 12 ns, 1.5 mJ) was employed as pump beam. Transient species were probed at 370 nm and at 625 nm. Excitation at 370 nm (8 ns, 1.5 mJ) was achieved by pumping rhodamine 610 in a dye laser (Quantel TDL50) with the second harmonic (532 nm) of the Yag laser, then mixing the output with the first harmonic (1064 nm). Probe excitation at 625 nm (8 ns, 5 mJ) was obtained directly by pumping DCM with the 532 nm output of the Yag laser.

Raman emission was collected at 90° to the incident excitation and focussed onto the entrance slit of a home-made single-monochromator multichannel spectrometer which has been already described.¹⁰ Two easily interchangeable gratings appropriate to the 370 and 625 nm probe wavelengths were used, and a gated intensified photodiode array (DILOR) was employed as detector (gate 20 ns FWHM, jitter less than 2 ns). Spectral resolutions of 8 and 4 cm⁻¹ and analyzed spectral fields of about 1600 and 800 cm⁻¹ were achieved at 370 and 625 nm, respectively. For each sample a

spectrum was recorded with both pump and probe beams and a second spectrum with probe only: the transient spectrum was thus obtained by subtracting these two spectra. Accumulations over 500 to 2000 laser pulses were performed in order to improve the signal-to-noise ratio.

RESULTS

The time-resolved resonance Raman spectra, excited at 370 and 625 nm, of 10^{-3} M solutions of fluorene, dibenzofuran and dibenzothiophen in cyclohexane, acetonitrile and methanol were recorded between 200 and 1900 cm^{-1} . A 266 nm pump wavelength was employed with a 30 ns time delay between pump and probe pulses. In the case of fluorene, the $T_n \leftarrow T_1$ extinction coefficient ϵ at 370 nm, estimated from the transient absorption spectra reported in ref. 12 and 15 is $\sim 10^4 \text{M}^{-1} \text{cm}^{-1}$ and the quantum fluorescence yield ϕ_F is 0.80.²¹ These values are much less favourable to the triplet state detection than those observed for biphenyl ($\epsilon_{T_n \leftarrow T_1} = 3.5 \times 10^4 \text{M}^{-1} \text{cm}^{-1}$ ²² and $\phi_F = 0.17$.²¹ As a matter of fact, the experimental signal-to-noise ratio of the Raman spectra were much lower for T_1 fluorene than for T_1 biphenyl.^{10,11} Considering the radical cation species, a $R^{+ \cdot} \leftarrow R^+$ absorption strength of $\sim 10^4 \text{M}^{-1} \text{cm}^{-1}$ at 625 nm is estimated from the transient absorption spectrum reported for fluorene⁺ in ref. 16.

Spectra recorded with probe pulses only show exclusively the solvent Raman peaks, indicating that the non-resonant ground state spectrum is not detectable. Spectra acquired with pump and probe pulses exhibit new Raman signals which depend on the solvent and on the probe wavelength and which are due to transient species. Figure 2 shows the ground state Raman spectra of the three title compounds, recorded from pure powder samples. Figure 3 displays the transient resonance Raman spectra obtained for fluorene in methanol and in acetonitrile solvents and Figure 4 shows the transient resonance Raman spectra observed for dibenzofuran and dibenzothiophen in methanol solvent.

Consider first the fluorene derivative. In methanol (Figure 3A) and in cyclohexane, comparable strongly enhanced spectra are excited at 370 nm whereas no transient spectrum is observed for probe excitation at 625 nm. This resonance effect is conform to that expected for the triplet state species which has only one absorption band in the 370 nm region. As shown in Figure 5, the resonance CARS spectrum reported by Matsunuma *et al.* for T_1 fluorene²⁰ and the resonance Raman spectrum have five components in common, indicated by dashed lines in the figure. However, the Raman spectrum is of much better quality and exhibits eight new peaks at 1868, 1778, 1374, 1222, 965, 813, 747 and 408 cm^{-1} which are ascribable to the triplet state. Two additional weak peaks at 1616 and 729 cm^{-1} (indicated with the symbol \times in Figures 3 and 5) are observed in methanol but not in cyclohexane. They correspond to strong bands of the transient spectrum obtained in acetonitrile (Figure 3B) and can be assigned to the radical cation species (see following paragraph).

In acetonitrile, new transient spectra with different resonance effects are observed at 370 and 625 nm (Figures 3B and 3C, respectively). These spectra are ascribed to

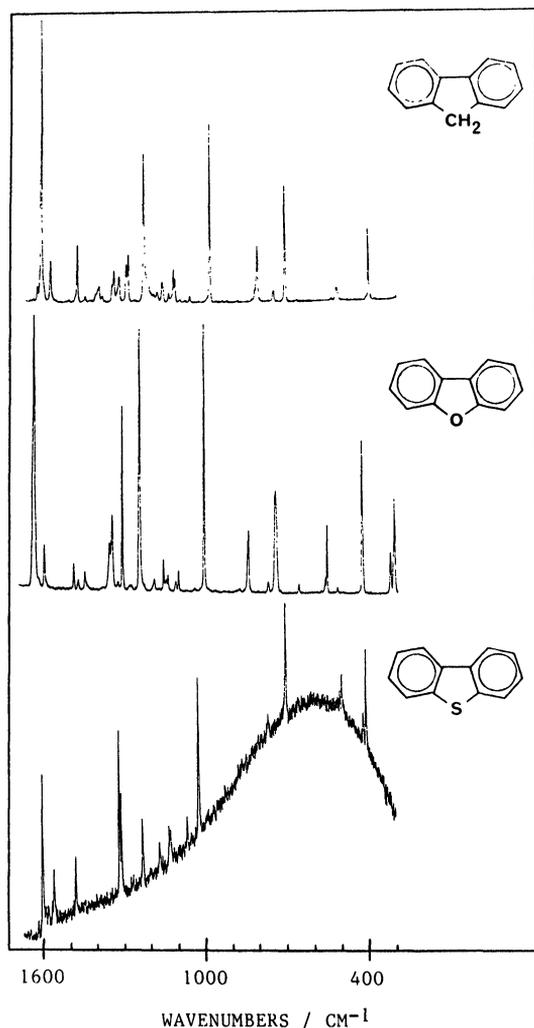


Figure 2 Raman spectra ($1700\text{--}300\text{ cm}^{-1}$) of fluorene, dibenzofuran and dibenzothiophen in the ground state S_0 (pure powder samples). CW excitation at 647.1 nm , 50 mW .

the fluorene radical cation by analogy with the biphenyl results.¹¹ This assignment is in agreement with the report by Delcourt and Rossi¹⁶ of rapid photoionization of fluorene in CH_3CN solution upon UV excitation. The double resonance Raman enhancement at 370 and 625 nm is conform to the existence of $R^{+\cdot*} \leftarrow R^{+\cdot}$ transitions in both regions. Several additional weak signals in the spectrum excited at 370 nm , noted with an asterisk in Figure 3B, are due to the triplet state. A biphotonic ionization process seems unlikely in reason of the quasi-linear dependence of the radical cation yield (as measured by the Raman intensity) upon pump pulse power. Electron ejection may occur either by direct photoionization and electron solvation,

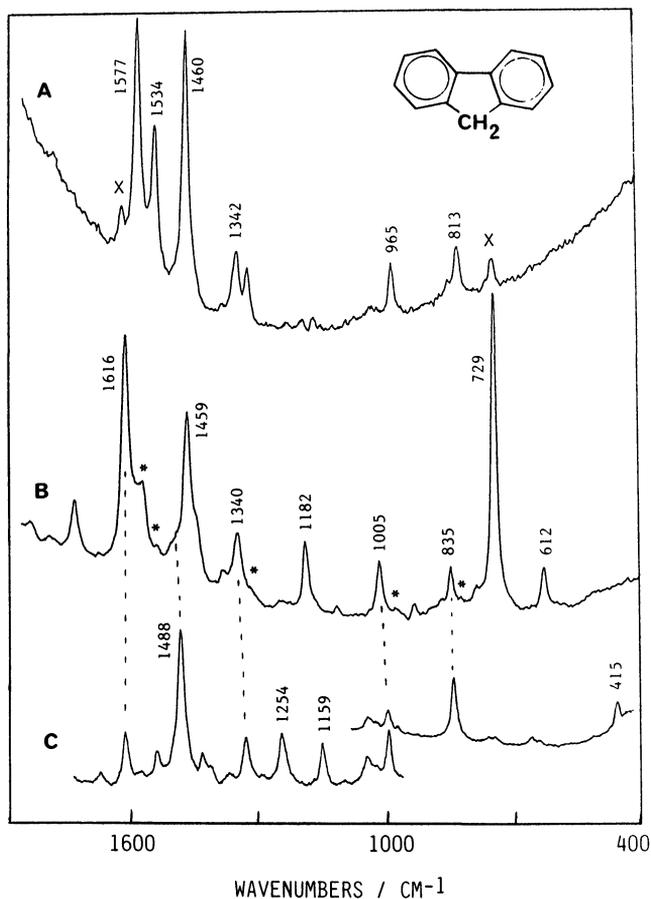


Figure 3 Original time-resolved resonance Raman spectra ($1800\text{--}400\text{ cm}^{-1}$) of $5 \times 10^{-3}\text{M}$ solutions of fluorene in (A) methanol, $\lambda_{\text{exc}} = 370.0\text{ nm}$, (b) acetonitrile, $\lambda_{\text{exc}} = 370.0\text{ nm}$, (C) acetonitrile, $\lambda_{\text{exc}} = 625.0\text{ nm}$. Pump excitation is at 266 nm and pump/probe delay is 30 ns in all cases. Solvent peaks have been subtracted. The principal band wavenumbers (cm^{-1}) are reported.

or by ionic photodissociation from a solvent-solute exciplex-type entity. The fact that photoionization is much more efficient in CH_3CN than in CH_3OH solutions can be accounted for by the higher solvent polarity in the first case. The absence of spectra from the ionized species in cyclohexane (only the triplet state spectrum is observed) is not surprising since this solvent is too inert to form an exciplex and to stabilize a radical cation or solvate an electron.

Finally, the transient spectra observed upon excitation at 370 nm for dibenzofuran and dibenzothiophen in methanol (Figure 4) and cyclohexane are comparable to those found for T_1 fluorene and, by analogy, are assigned to the triplet state species. Weak intensity spectra are excited in acetonitrile solutions which will not be discussed here in reason of their poor quality.

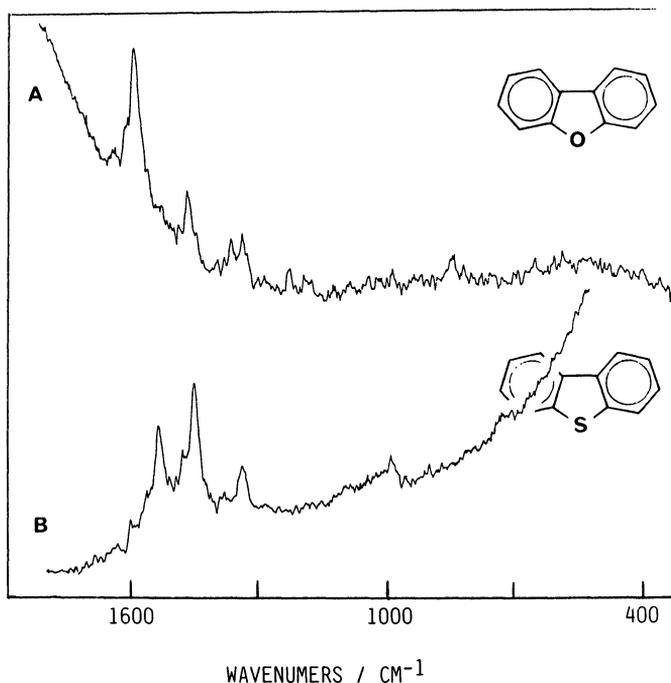


Figure 4 Original time-resolved resonance Raman spectra (1750–400 cm^{-1}) of (A) dibenzofuran and (B) dibenzothiophen in methanol ($5 \times 10^{-3}\text{M}$ solutions). Pump excitation at 266 nm, probe excitation at 370 nm, pump/probe delay 30 ns. Solvent peaks have been subtracted.

DISCUSSION

The experimental band wavenumber observed for the fluorene triplet state and radical cation and for the dibenzofuran and dibenzothiophen triplet state, and the proposed assignments are summarized in Tables 1 (fundamental) and 2 (overtones and combinations).

The high intensity of the $T_n \leftarrow T_1$ and $R^{+,*} \leftarrow R^{+}$ absorptions in the 370 and 625 nm ranges and the strong enhancement of the transient Raman spectra excited in resonance with these transitions suggest that the scattering process is dominated by Franck-Condon mechanisms (A-term of the Raman scattering cross section in the Albrecht's formalism).²³ Accordingly, only the totally symmetric vibrations which are disturbed in the resonant electronic transitions can be assumed to gain significant Raman intensity by resonance. Therefore, whereas the analysis of the changes in frequency in the transient states (T_1 , R^{+}) with respect to the ground state must inform on the distortion of the molecule in going from S_0 to T_1 or R^{+} , the analysis of the resonance Raman intensities is expected to provide information on the structural distortion of the transient species (T_1 , R^{+}) in the upper electronic states (T_n , $R^{+,*}$),

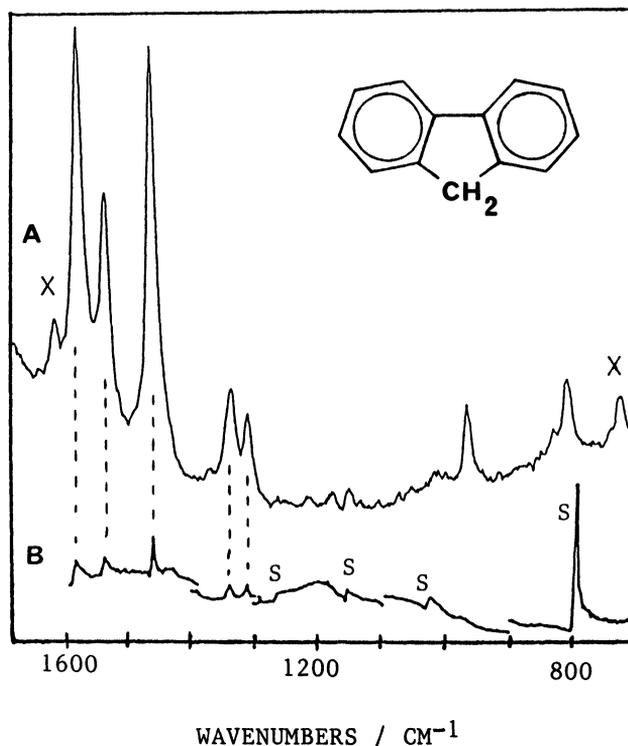


Figure 5 Comparison of the time-resolved resonance Raman (A) and CARS (from ref. 20) (B) spectra of fluorene in the T_1 state (1600–700 cm^{-1} region). The dashed lines indicate common peaks. Symbol \times designates bands due to the radical cation species. Solvent peaks have been subtracted in the Raman spectrum and are pointed out by symbol S in the CARS spectrum.

i.e., on the nature of the $T_n \leftarrow T_1$ and $R^{+,*} \leftarrow R^{\cdot+}$ absorptions. Both aspects are discussed below.

The similarity of the electronic excitation configurations (LUMO \leftarrow HOMO) in T_1 biphenyl and in T_1 fluorene, dibenzofuran and dibenzothiophen^{18,19} suggests that in all cases the triplet structure is characterized by an increase of the inter-ring bond order (the HOMO and LUMO are mainly antibonding and bonding with respect to the inter-ring bond, respectively). Similarly, one may expect that removing a HOMO electron will also lead to a strengthening of the inter-ring CC double-bond character in biphenyl and in fluorene. Therefore, nearly planar conformations with C_{2v} symmetry can be assumed for both the triplet state and radical cation transients. In this hypothesis, sixteen totally symmetric (a_g) vibrations are expected in the 300–1800 cm^{-1} region for the $C_{12}H_8R$ skeleton (Figure 1): thirteen ring modes and three inter-ring modes which include two stretches (ν inter-ring and ν^s ring-R-ring) and one in-plane bend (Δ inter-ring). An additional CH bending vibration of the methylene group ($\delta^s\text{CH}_2$) is of a_g type in the case of fluorene.

Table 1 Fundamental Raman wavenumbers (cm^{-1}) and assignments for the fluorene, dibenzofuran and dibenzothiophen triplet states (T_1) and for the fluorene radical cation ($R^{+\cdot}$), compared to the ground state (S_0), in the 200–1800 cm^{-1} region

a_g normal modes ^{a,b}	Fluorene			Dibenzofuran		Dibenzothiophen	
	S_0	$R^{+\cdot}$	T_1	S_0	T_1	S_0	T_1
8a	1,610	1,616	1,577	1,637	1,586	1,600	1,531
8b	1,574	1,572	1,534	1,596	1,470	1,558	—
19a	1,477	1,488	1,460	1,488	1,454	1,477	1,445
19b	1,448	1,436	—	1,447	1,440	—	—
δ^s CH ₂	1,397	1,415	—	—	—	—	—
14	1,342	—	—	1,356	—	1,332	—
3	1,328	—	1,310	1,347	1,320	1,319	—
ν inter-ring	1,295	1,340	1,342	1,310	1,345	1,310	1,330
ν^s ring-R-ring	1,231	1,182	—	1,247	—	419	—
9a	1,152	1,159	1,155	1,149	1,154 ^c	1,233	—
18a	1,092	1,109	—	1,102	—	1,133	—
18b	1,019	1,005	965	1,012	964	1,027	977
1	843	835	813	851	818	1,070	1,079 ^c
12	741	729	747	748	—	704	—
6b	633	612	—	662	—	—	—
6a	418	415	408	430	—	410	—
Δ inter-ring	218	—	—	222	—	217	—

^a ν = stretch, δ , Δ = in-plane distortions.^b in the hypothesis of a planar structure with C_{2v} symmetry.^c very weak signals.**Table 2** Assignment of the Raman overtone and combination bands (cm^{-1}) for the fluorene radical cation ($R^{+\cdot}$) and triplet state (T_1)^a

$R^{+\cdot}$		T_1	Assignment
Probe 370 nm	625 nm	370 nm	
1,910	—	—	12 + ν ring-R-ring
—	—	1,868	19a + 6a
1,839	1,840	1,778	18b + 1
1,794	—	—	6b + ν ring-R-ring
1,732	—	—	12 + 18b
(1,565)	—	—	12 + 1
1,675	—	—	2 × 1
1,459	—	—	2 × 12
—	1,419	1,374	18b + 6a
(1,340)	—	—	12 + 6b
—	1,254	1,222	1 + 6a
1,224	—	—	2 × 6b

^a Wavenumbers in parentheses correspond to observed shoulders.

Strong couplings certainly take place between these vibrational groups and serious difficulties for comparing the ground and transient state vibrations may be expected if important variations in these vibrational couplings appear where modifying the electronic configuration.

However, it turns out from our previous analyses of transient Raman spectra^{6–11}

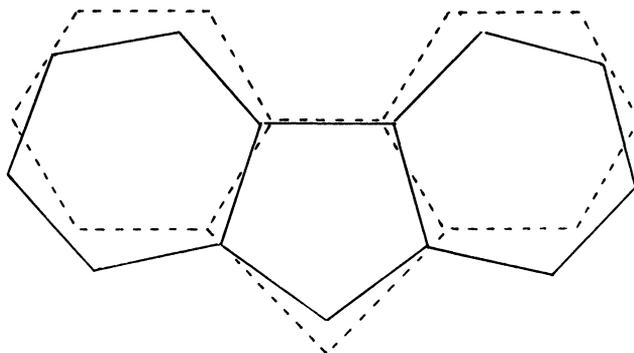
that, in the case of large aromatic molecules, a correlation can be established between the ground state and the excited transient state vibrations. In fact, in polyatomic molecules having high π -density and strong electronic conjugation resonance ability, structural distortions in the transient states with respect to the ground state are largely distributed on several bonds in such a way that each bond is only moderately disturbed. Accordingly, in the assumption that the anharmonic couplings between the different a_g vibrations (Dushinsky effect) are negligible, the same normal mode representation can be utilized in the different electronic states and we have adopted a unique notation for describing the vibrations in the S_0 , T_1 and R^+ states. A detailed vibrational analysis of the title molecules and of several isotopic derivatives of fluorene (rings and/or methylene group hydrogenated/deuterated) in the ground state S_0^{24} has indicated that, in these systems, the ring normal modes can be compared (frequency, isotopic effects) to the ring vibrations of ortho-disubstituted benzene molecules and thus can be described using the Wilson's notation for benzene, as adapted by Varsanyi for ortho-disubstituted benzenes.²⁵ In this formalism, the thirteen a_g ring vibrations of the fluorene-type molecules correspond to the symmetric combination (the two rings oscillate in phase) of the ortho-disubstituted benzene modes 8a, 8b, 19a, 19b, 14, 1, 12, 6a, 6b, 9a, 3, 18a and 18b.

The assignments proposed in Table 1 for the transient state spectra are based on comparisons with the related ground state spectra and also with the assignments made previously for the biphenyl triplet state and radical cation species.^{10,11} As expected, most of the observed Raman bands are ascribed to totally symmetric vibrations in the assumption of planar, C_{2v} conformations. Nevertheless, several very weak signals in the radical cation spectrum of fluorene recorded at 625 nm remain unassigned (e.g. 1543, 1059, 1032, 970, 634 and 625 cm^{-1}). They may be ascribed either to vibrations of another transient (photoproduct, dimer ion . . .), or to non-symmetric vibrations of the radical cation, the activity of which would reflect a slight distortion of the structure with respect to the C_{2v} symmetry.

Radical Cation of Fluorene

The shifts in frequency noted between the S_0 and R^+ spectra of fluorene are generally weak ($\Delta\nu < 20 \text{ cm}^{-1}$). The only significant variations are observed for the two bands located at 1295 and 1231 cm^{-1} in the S_0 spectrum, which are shifted upon ionization by +45 cm^{-1} and -49 cm^{-1} , respectively. According to our assignments, the first peak corresponds to a vibration involving a large contribution from the inter-ring stretching coordinate and the second one to a vibration predominantly characteristic of the ring- CH_2 -ring symmetric stretching coordinate. This suggests that the main structural distortion resulting from the $R^+ \leftarrow S_0$ transition is a strengthening of the inter-ring CC bond order and a simultaneous lengthening of the ring- CH_2 CC bonds, in accord with an increase of the quinoidal character of the structure (dashed trace in Scheme 1).

The increase of the inter-ring stretching frequency is similar to that found for the biphenyl radical cation ($\Delta\nu = +57 \text{ cm}^{-1}$),¹¹ indicating that fluorene and biphenyl



Scheme 1.

present comparable quinoidal distortions of the ring-ring skeleton upon ionization. This result confirms the resemblance of the electronic configurations of these two radical cations, in agreement with the predictions from simple MO considerations: in both compounds, ionization results from the ejection of an electron from the HOMO (ϕ_6) which has a marked anti-bonding character with respect to the inter-ring coordinate.

As can be seen in Figure 3, the spectrum obtained with excitation at 370 nm (trace B) is drastically different from that recorded upon 625 nm excitation (trace C). Striking variations in band intensity and enhancement effects are observed when changing the probe wavelength. As stated above, these variations in Raman intensity reflect the variations of vibronic activity (i.e., of Franck-Condon overlap) in the two electronic transitions $R^{+\cdot*} \leftarrow R^{+\cdot}$ which are in resonance, and are thus characteristic of the distortion of the molecular geometry in the related resonant states $R^{+\cdot*}$. The interpretation of these intensity enhancement effects in terms of structural distortions appears much more difficult in this compound than in biphenyl in reason of the lower symmetry of the molecule and of the larger number of observed Raman bands. However, a very typical behavior is remarked for the two peaks ascribed to the ring vibrations 8a (1616 cm^{-1}) and 19a (1488 cm^{-1}). The first one is by far the most enhanced upon excitation at 370 nm whereas the second one is prominent on excitation at 625 nm. Such a drastic inversion of intensity has been already encountered for biphenyl,¹¹ indicating that the origins of the two electronic transitions $R^{+\cdot*} \leftarrow R^{+\cdot}$ in the UV and visible regions are comparable in fluorene and in biphenyl. Another common point between the two molecules is the similar intensity of the ν inter-ring band (1340 cm^{-1} in fluorene⁺) in the spectra excited at 370 and 625 nm. In regard to these dominant resemblances, it seems reasonable to transpose to fluorene⁺ the schematic orbital diagram established for biphenyl⁺ (Figure 8 in ref. 11), which means that (i) the electron density distributions of the orbitals lying in the HOMO/LUMO region (ϕ_3 – ϕ_{10}) are not significantly altered in going from biphenyl to fluorene and (ii) the UV and visible absorptions of fluorene⁺ can be related to the $\phi_7 \leftarrow \phi_6$ and $\phi_6 \leftarrow \phi_3$ excitations of biphenyl⁺, respectively.

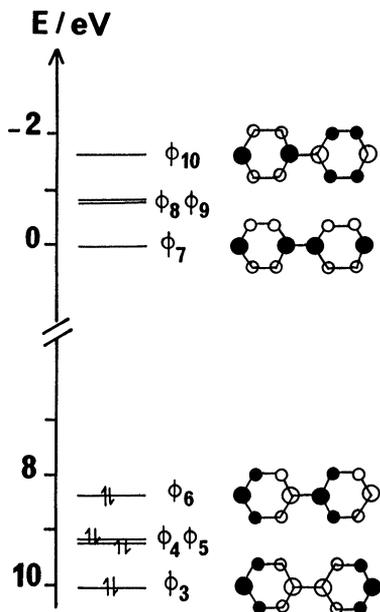


Figure 6 Molecular orbital diagram of biphenyl in the HOMO-LUMO region (from ref. 26) and schematic representation of some characteristic orbitals.

According to the schematic representation of the considered MOs (Figure 6), the $\phi_7 \leftarrow \phi_6$ transition leads mainly to a reinforcement of the π -density on the inter-ring bond and on the C_2C_3 and C_5C_6 ring bonds, which is consistent with the resonance activity of modes 8a (see Figure 7) and ν inter-ring; and the $\phi_6 \leftarrow \phi_3$ transition induces mainly a decrease in the inter-ring π -density and a distortion with respect to the inter-ring bond in the sense of the atomic displacements related to mode 19a (see Figure 7), in agreement with the resonance activity of these two vibrations.

In conclusion, the comparable resonance Raman behavior of modes 8a, 19a and ν inter-ring in the spectra of biphenyl⁺ and fluorene⁺ shows that the presence of the methylene group does not disturb markedly the electronic properties of the biphenyl system. The apparent confusion in the intensity enhancements noticed for the other vibrations can be accounted for by the lower symmetry and the larger mechanic constraints and couplings induced by this group in the fluorene framework.

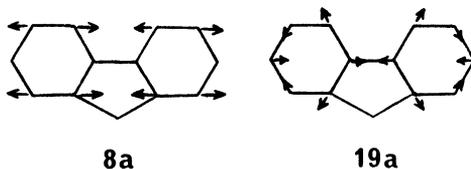
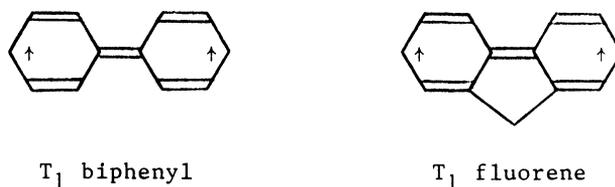


Figure 7 Schematic representation of the cartesian displacements of modes 8a and 19a.

Triplet State of Fluorene

The localization of modes 8a, 8b, 19a, 18b, 1, 12 and 6a (see Table 1) is fairly reliable but the assignment of the bands lying in the 1300–1350 cm^{-1} region is only tentative. In this respect, our assignment differs from that proposed in ref. 20 for the CARS spectrum of T_1 fluorene. In particular, the authors ascribe the 1310 cm^{-1} signal (1312 cm^{-1} in the CARS spectrum) to a mode containing a main contribution from the $\delta^s\text{CH}_2$ component, which is contradictory with the fact that this mode is still observed in the triplet Raman spectrum of dibenzofuran (see Table 1). On the other hand, they associate the T_1 signal at 1342 cm^{-1} (1337 cm^{-1} in the CARS spectrum) to a ground state band at 1397 cm^{-1} , which can be unambiguously ascribed to the $\delta^s\text{CH}_2$ vibration in view of its isotopic behaviour.²⁴ The observation of this T_1 signal in the Raman spectra of dibenzofuran (1345 cm^{-1}) and dibenzothiophen (1330 cm^{-1}) is also in contradiction with the assignment proposed in ref. 20.

As can be seen in Table 1, significant frequency decreases are noted for the ring modes 8a (-33 cm^{-1}), 8b (-40 cm^{-1}), 19a (-17 cm^{-1}), 3 (-18 cm^{-1}), 18b (-54 cm^{-1}), 1 (-30 cm^{-1}) and 6a (-10 cm^{-1}) in going from S_0 to T_1 state. These negative shifts reflect a noticeable lowering of the π -bonding density in the rings, in agreement with the presence of an electron in a π^* orbital. In contrast, according to the present assignment, the inter-ring stretching mode undergoes a 47 cm^{-1} positive shift which indicates that important strengthening of the inter-ring bond order takes place in the triplet state, as previously observed for T_1 biphenyl ($\Delta\nu = +79 \text{ cm}^{-1}$).^{10,11} Therefore, in both cases, a large contribution from a quinoidal-type conformation where the unpaired electrons are in para position may be assumed (Scheme 2).



Scheme 2.

This result confirms the prediction from MO calculations¹⁸ that T_1 fluorene and T_1 biphenyl have comparable orbital natures and results from a LUMO (ϕ_7) \leftarrow HOMO (ϕ_6) $\pi\pi^*$ excitation.

Consider now the resonance Raman activity and relative band intensities. As observed for biphenyl,¹¹ the triplet state spectrum of fluorene excited at 370 nm (Figure 3, trace A) is completely different from the radical cation spectrum recorded with the same wavelength (trace B) but it can be better compared to that excited at 625 nm (trace C). The main analogies are the high enhancement noted for mode 19a, the very weak intensity for mode 12, and a similar activity for the combination bands (see Table 2). This indicates that comparable distortions of the T_1 and R^+ structures

take place in the corresponding resonant states T_n and $R^{+\cdot}$, respectively. Therefore, in fluorene as in biphenyl the $T_n \leftarrow T_1$ transition at 370 nm is closely related to the $R^{+\cdot} \leftarrow R^{\cdot}$ transition in the 600–700 nm range and is ascribable mainly to a $\phi_6 \leftarrow \phi_3$ type excitation.

Triplet State of Dibenzofuran and Dibenzothiophen

The triplet state spectra of dibenzofuran and dibenzothiophen (Figure 4) have much lower signal-to-noise aspect than the spectrum of T_1 fluorene. In consequence, few Raman peaks can be detected for the heterocyclic molecules. However, the observed bands present similar frequency and intensity characteristics as the triplet bands of fluorene. One notes essentially a negative shift for the ring vibrations and a positive shift for the ν inter-ring mode on going from S_0 to T_1 states (see Table 1). Accordingly the distortion of the T_1 structures with respect to the ground state ones is comparable in dibenzofuran, dibenzothiophen and fluorene. This is in agreement with the conclusion from electron paramagnetic resonance measurements that replacing the methylene group by a heteroatom has no significant effect on the $T_1 \leftarrow S_0$ transition.¹⁹ In all cases, the triplet state configuration results mainly from a LUMO \leftarrow HOMO ($\pi\pi^*$) excitation as in biphenyl.

Anyhow, the decrease in frequency noted for modes 8a and 19a on going from S_0 to T_1 state is more pronounced in dibenzofuran (-51 and -34 cm^{-1} , respectively) and in dibenzothiophen (-69 and -32 cm^{-1} , respectively) than in fluorene (-33 and -17 cm^{-1} , respectively), whereas the increase in the ν inter-ring frequency is rather attenuated in dibenzofuran ($+35$ cm^{-1}) and dibenzothiophen ($+20$ cm^{-1}) compared to fluorene ($+47$ cm^{-1}). This suggests that the π^* charge is more localized on the rings and that the T_1 structures present a less quinoidal character in the heterocyclic derivatives than in fluorene.

In conclusion, this preliminary work on fluorene-type compounds demonstrates that it is possible to obtain good-quality Raman spectra of the first triplet state and of the radical cation photochemical transients of fluorene in solution. At first appearance, a notable analogy is found between these spectra and those reported for biphenyl,^{10,11} in accord with previous results from electron paramagnetic resonance¹⁹ and with predictions from MO calculations.¹⁸ However, more detailed and reliable Raman assignments are necessary to support the present analysis and to provide more complete information on the transient structures. Further studies, which involve a series of isotopically substituted derivatives of fluorene, are thus currently in progress.

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