EMISSION SPECTRA OF THE RADICAL CATIONS OF HEXA-, PENTA-, TETRA-, AND TRI-FLUOROBENZENES

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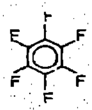
Emission spectra of the radical cations of the title fluorobenzenes were excited in the gaseous phase by electron impact. The spectra, vibrational fine structure discernible and the threshold energy of the emission are discussed in relation to the photoelectron spectra of the fluorobenzenes.

1. Introduction

The radiative channel for relaxation of excited radical cations of polyatomic molecules in the gas phase has been evident so far only by the emission spectrum of diacetylene cation [1] and the fluorescence postulated to be that of hexafluorobenzene cation [2]. The detailed analysis of the $C_4H_2^+$ spectrum by Callomon [1] confirmed the assignment as the $\tilde{A}\,^2\Pi_u \rightarrow \tilde{X}\,^2\Pi_g$ transition which was first detected in discharge tubes containing hydrocarbons [3]. Turner and co-workers observed a broad band (max. ≈475 nm) as fluorescence when hexafluorobenzene was irradiated by the HeI α (21.22 eV) resonance line. The wavelength region corresponded to the energy gap between the ground and the first excited state in the photoelectron spectrum of the cation.

In this communication we present the first emission spectra of the cations of the fluorobenzenes **1**–**7**, excited in the gas phase by controlled electron impact. However, no emission was observed which could be ascribed to the parent cations benzene, fluoro- and difluoro-benzenes.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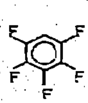
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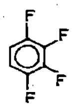
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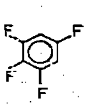
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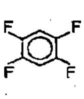
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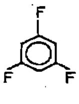
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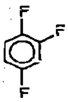
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2. Experimental

The electron gun comprised a directly heated tungsten filament, accelerating region and axial magnetic field (≈130 G) collimation. The samples were introduced into the interaction region by effusion from a 1 mm capillary perpendicular to the electron beam. A liquid nitrogen trap resided above the nozzle. The complete assembly was in a vacuum chamber. The background pressure of $\approx 5 \times 10^{-7}$ torr rose to $\approx 10^{-5}$ torr on introduction of sample. The rate of consumption indicated a typical pressure of 10^{-3} torr in the collision region. The photon emission was observed also at right angles to the electron beam and wavelength selection was accomplished by a Spex 0.5 m Czerny–Turner monochromator with a 1200 lines/mm grating blazed at 300 nm. A thermoelectrically cooled (–20°C) RCA C31034 PM tube was used with associated electronics in the single photon counting mode. The photon count rate versus the wavelength was displayed on a recorder and the spectra are shown in figs. 1–7, uncorrected for the instrument transmission function. An electron beam current of 100 μA, and acceleration potentials of ≈20 V for **3** to **7**, ≈100 V for **1** and ≈40 V for **2**, were employed. The profiles of the emission bands did not vary in the 20–100 V range of potential used, although the hydrogen Balmer ($H_{\alpha,\beta,\gamma...}$) lines and $CH(A\,^2\Delta \rightarrow X\,^2\Pi)$ bands were suppressed at ≈20 V accelerating potential. The optical resolution was 5 Å

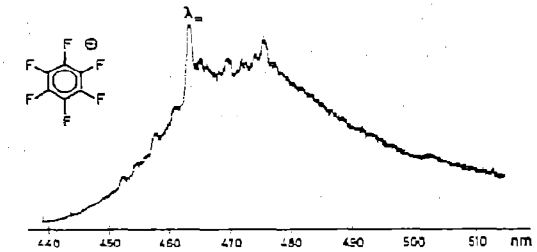

Fig. 1. Emission spectrum of hexafluorobenzene cation (1^+)

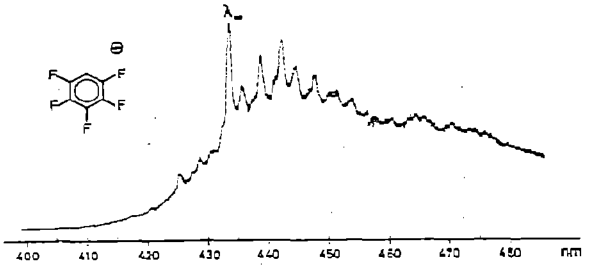

Fig. 2. Emission spectrum of pentafluorobenzene cation (2^+).

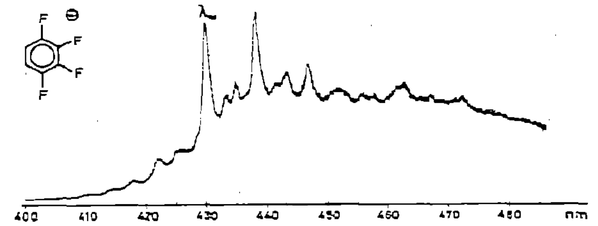

Fig. 3. Emission spectrum of 1,2,3,4-tetrafluorobenzene cation (3^+).

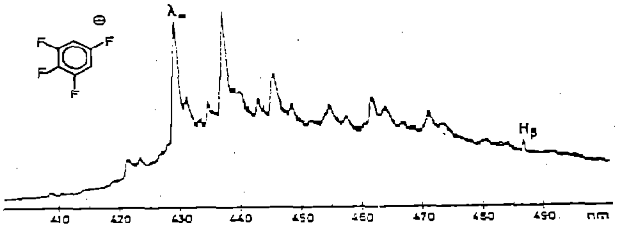

Fig. 4. Emission spectrum of 1,3,4,5-tetrafluorobenzene cation (4^+).

(fwhm) for 2 to 7, and 2 Å for 1. The optical system cut-off at ≈310 nm.

3. Discussion

The emission bands of interest obtained with the

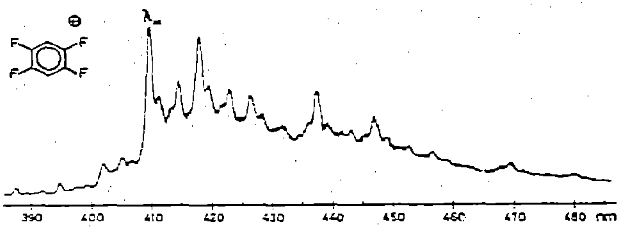

Fig. 5. Emission spectrum of 2,3,5,6-tetrafluorobenzene cation (5^+).

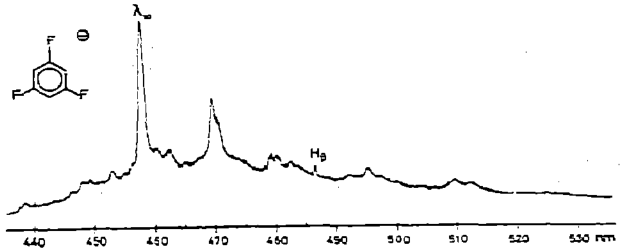

Fig. 6. Emission spectrum of 1,3,5-trifluorobenzene cation (6^+).

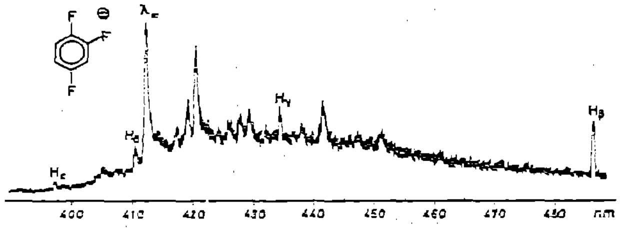

Fig. 7. Emission spectrum of 1,2,4-trifluorobenzene cation (7^+).

conditions described, lie in the 400–500 nm spectral region (figs. 1–7). The resolution attainable in these experiments enable vibrational fine structure to be resolved. The band of 1^+ [2] is also now structured. The wavelengths of the prominent peak discernible on the short wavelength part of the bands (marked as λ_{00} in figs. 1–7) are given in table 1, where the adiabatic ionisation energies (IE's) for the ground ($\tilde{X}$) and the first excited states ($\tilde{A},\tilde{B}$) of the cations obtained from photoelectron (PE) spectra are also collected [4]. The interpretation of the PE spectra shows that these ionisation processes lead to states of the ions 1–7, associated with ejection of electrons from the top three π-orbitals [5,6]. In the case of 1^+ and 6^+, the ground ionic state is degenerate (or almost degenerate due to Jahn–Teller distortion), whereas with the species of

Table 1
Adiabatic ionisation energies (eV) from photoelectron spectra a) and the wavelengths (nm) of the λ_{00} bands in the emission spectra of 1^+ to 7^+

	$IE_1(\tilde{X})$	$IE_3(\tilde{B})$	Δ(IE)	λ_{00} nm	(eV)	$IE_2(\tilde{A})$ b)
hexafluorobenzene 1	9.90	12.56	2.66	462.9	(2.678)	9.90
pentafluorobenzene 2	9.64	12.50	2.86	433.2	(2.862)	≈10.2
1,2,3,4-tetrafluorobenzene 3	9.56	12.42	2.86	429.6	(2.886)	9.88
1,3,4,5-tetrafluorobenzene 4	9.56	12.42	2.86	428.8	(2.891)	9.93
2,3,5,6-tetrafluorobenzene 5	9.36	12.35	2.99	409.2	(3.030)	10.04
1,3,5-trifluorobenzene 6	9.62	12.35	2.73	457.3	(2.711)	9.62
1,2,4-trifluorobenzene 7	9.30	12.31	3.01	411.9	(3.010)	≈9.9

a) The IE's given are taken from ref. [4] and those of 7 as determined with a π/2 PE spectrometer and calibrated with the first IE of benzene and xenon. The IE uncertainty is taken as ±0.03 eV whereas the λ_{00} as ±0.002 eV.
b) IE_2 adiabatic values are difficult to estimate due to overlap of the $\tilde{X}$ band.

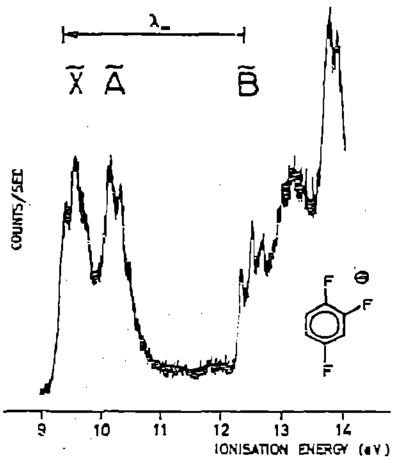

Fig. 8. Photoelectron spectrum of 1,2,4-trifluorobenzene.

the lower symmetry this degeneracy is removed. This is reflected in the separation of the bands in the PE spectra (table 1) and is illustrated by the PE spectrum of 7 (fig. 8).

The differences of the *adiabatic* IE's (ΔIE) of the ground ionic state ($\tilde{X}$) and the excited state ($\tilde{B}$) lying in the 12–13 eV IE region are given in table 1. These values should be accurate within ±0.03 eV. Comparison of the λ_{00} and the ΔIE values shows agreement in all cases (within the PE data uncertainty) over the range 2.68–3.03 eV. This is taken as a strong indication that the emission observed can be attributed to the radiative process of the parent radical cation from the excited to the ground ionic state. The transitions $\tilde{B} \rightarrow \tilde{X}$ are dipole allowed. The λ_{00} band in the emission spectra would correspond to the 0–0 transition. Fig. 8 exemplifies the correspondence of the PE spectra and the emission spectra.

The band in the PE spectra of 1–7 corresponding to the radiative state shows clear vibrational fine structure in all cases (cf. fig. 8). This feature has been taken to indicate that the ionic state may be of sufficient lifetime for radiative deactivation to be observable [2]. The lowest appearance potential of fragment ions in the mass spectrum of 1 was given as 15.8 ± 0.2 eV [7] and in benzene as 13.95 eV where the corresponding thermodynamic threshold lies at 12.94 eV [8]. Thus the radiative states of 1^+ to 7^+ are probably also stable with respect to fragmentation.

The emission spectra (figs. 1–7) also show bands to shorter wavelengths of the λ_{00} peak. These are associated with radiative transitions from the vibrationally excited ions. In the PE spectra of the fluorobenzenes two vibrational progressions are discernible on the 12–13 eV band as well as on the first band. On the latter the corresponding frequencies are resolved to be the same in the fluorobenzenes 2 to 7 [4], 65 meV (524 cm^{-1}) and 180 meV (1452 cm^{-1}), whereas 400 cm^{-1}, 1450 cm^{-1} in hexafluorobenzene [9]. In the excited state (B) of the cations of 2–7 the frequency of the main progression varies from 176 to 181 meV (1420–1450 cm^{-1}) and of the subsidiary, when resolved, 550–750 cm^{-1}. In 1^+ the vibrations (1550 cm^{-1} and 530 cm^{-1}) [9] correspond to the two totally symmetric modes; the C–F stretch and the ring breathing vibrations. The ion emission spectra show a good deal more vibrational excitation. A spectrum of $\mathbf{6}^+$ taken under higher resolution (1 Å fwhm) revealed substructure on the intense peaks (e.g., λ_{00}), and detailed vibrational analysis of the spectra is deferred. Nevertheless the frequency which would correspond to the most intense peaks in the spectra, taking λ_{00} as the origin, is again in the 430–560 cm^{-1} range. In some of the spectra (e.g., **4**–**7**) excitation of the 1550–1650 cm^{-1} frequency is also suggested.

The threshold for photon emission observed was determined by variation of the accelerating potential of the electron beam. In the instance of $\mathbf{5}^+$ the onset for the 409 nm band (λ_{00}) was obtained at 12.7 eV. The electron energy scale was calibrated by the 11.05 eV threshold for the N_2, $C\,^3\Pi_u \rightarrow B\,^3\Pi_g$, 0–0 band and the differential cross-section maximum at 14.0 eV [10]. The 12.7 eV value agrees with the adiabatic IE of the $\tilde{B}$ state of $\mathbf{5}^+$ of 12.35 eV, within the uncertainty of ±1 eV which is taken as the upper limit. It was also noted that the emission cross-section curve of the $\tilde{B} \rightarrow \tilde{X}$ band of $\mathbf{5}^+$ resembled that of the N_2^+ $\tilde{B}\,^2\Sigma_u \rightarrow \tilde{X}\,^2\Sigma_g$, whereas emissions from the neutral molecule usually show a different behaviour. The $S_1 \rightarrow S_0$ emission cross section of **5** was found to have two maxima within 10 eV above the threshold before falling off. This resembles the cross section of the corresponding transition in benzene [11].

In the emission spectra of $\mathbf{2}^+$, $\mathbf{3}^+$, $\mathbf{4}^+$, $\mathbf{5}^+$ and $\mathbf{7}^+$ an additional broad structureless band was observed to longer wavelengths. In $\mathbf{5}^+$ and $\mathbf{7}^+$ these bands are well separated from the $\tilde{B} \rightarrow \tilde{X}$ transitions with maxima ≈585 nm and 567 nm. In $\mathbf{2}^+$, $\mathbf{3}^+$, $\mathbf{4}^+$ these appear on the long wavelength side of the $\tilde{B} \rightarrow \tilde{X}$ bands; at ≈560 nm in $\mathbf{2}^+$ and $\mathbf{4}^+$ and at ≈540 nm in $\mathbf{3}^+$. However with $\mathbf{1}^+$ and $\mathbf{6}^+$ there is only one band system apparent. It is possible that these bands correspond to the dipole allowed $\tilde{B} \rightarrow \tilde{A}$ transitions of the cations. The PE spectra suggest that the separation of the ground and first excited state is largest in $\mathbf{5}^+$ and $\mathbf{7}^+$ (table 1) whereas in $\mathbf{1}^+$ and $\mathbf{6}^+$ they are degenerate. The changes in the energy of these bands parallel the differences in the separation of the bands in the PE spectra. The threshold of the emission (at $\lambda \approx 585$ nm) in $\mathbf{5}^+$ was observed at the same energy (within the calibration limits) as for the $\tilde{B} \rightarrow \tilde{X}$ emission.

No corresponding bands were detected with benzene, in the 450–550 nm region where the $^2A_{2u} \rightarrow {}^2E_{1g}$ emission of the cation would be anticipated, or in the mono- and di-fluoroderivatives. It is estimated that an attenuation of the emission flux by a factor of thousand relative to that observed from $\mathbf{1}^+$–$\mathbf{7}^+$ would be detectable. This apparent absence of the radiative emission of the cations of benzene, mono- and difluorobenzenes in their excited state (π^{-1}) may be a reflection of the changes observed in their PE spectra. These show two overlapping bands (σ^{-1}, π^{-1}), in the 11.5–13 eV region, in contrast to the PE spectra of **1**–**7**, where the band corresponding to the radiative state $\tilde{B}$ (π^{-1}) is separated (cf. fig. 8). The majority of workers favour the assignment of the $^2E_{2g}$ state (σe_{2g}^{-1}) as the first excited state of benzene at 11.5 eV just preceeding the $^2A_{2u}(\pi a_{2u}^{-1})$ state. In one study of the fluorobenzenes this order was also favoured for mono- and difluorobenzenes [5]. The presence of this intermediate state, in the case of the radical cations of benzene, mono- and difluorobenzenes, from which the radiative transition to the ground ionic state is dipole forbidden, may open up or enhance, a non-radiative pathway from the π^{-1} state, to isomer formation for example. On the other hand the radiative pathway of the radical cations of **1** to **7**, indicates that these excited ions with 2.5–3 eV internal energy retain their structure within the radiative lifetime.

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