203. Laser Induced Excitation Spectra of the Cations of Some Fluoro-substituted Phenols ($\tilde{B}^2 A'' \leftrightarrow \tilde{X}^2 A''$) in the Gaseous Phase

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Summary

Excitation spectra of the cations of pentafluorophenol, 2,3,4-trifluorophenol, 2,4,5-trifluorophenol, 2,5-difluorophenol and 3,5-difluorophenol have been obtained by pumping the $\tilde{B}^2 A'' \leftarrow \tilde{X}^2 A''$ transition with a dye laser. The cations were first produced in their ground states by *Penning* ionisation using argon metastables. Vibrational frequencies of some of the fundamentals have been inferred for these cations in the $\tilde{B}^2 A''$ state from the excitation spectra, and in the $\tilde{X}^2 A''$ state from the emission spectra. Possible applications of the reported results are suggested.

Introduction. - One of the newly developed techniques for spectroscopic studies of cations in the gaseous phase is by means of laser induced fluorescence [1] [2]. As yet, this approach has been used to investigate a few open-shell cations of organic molecules whose emission spectra were detected using an apparatus centered around a low energy electron beam [3]. The organic cations which have been probed by the laser technique in the gas phase comprise of the fluorinated benzenes [4], of 1,3,5-trichlorobenzene [5], of 2,4-hexadiyne [6] as well as of 1,3-pentadiynes [7]. The optical resolutions used in such experiments are typically 0.02 nm, which is better than that usually used for the recording of the emission spectra ($\approx$0.2 nm). It should be pointed out that in the latter case there is no difficulty to attain comparable resolutions; but based on experience, no significant new features usually appear for the larger cations on improving the resolution from 0.2 to 0.02 nm. What the laser excitation approach does offer is, however, an accessibility to the excited electronic state of the cation. Whereas the emission spectra ($^2\tilde{A} \rightarrow {}^2\tilde{X}$) yield the vibrational frequencies of mainly the totally symmetric fundamentals for the cations in their ground state ($\tilde{X}$), the corresponding data can now be obtained for the excited state ($\tilde{A}$ or $\tilde{B}$) from the laser induced excitation spectra. In the case of such studies on the halo-substituted benzene cations [4] [5] and alkyl substituted diacetylene cations [6] [7], the inferred frequencies could be assigned to specific vibrational fundamentals.

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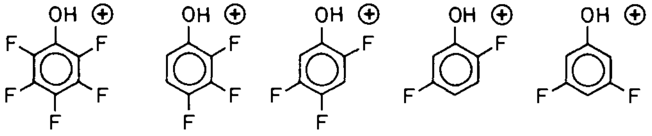
In contrast, for the studies reported in this article we chose a class of larger organic cations of low symmetry, in order to see the sort of spectra and information that could nevertheless be obtained. The laser induced excitation spectra of the following five fluoro-substituted phenol cations in the gas phase have been obtained:



These cations could be probed by this technique because their raditive relaxation $\tilde{B}^2A'' \rightarrow \tilde{X}^2A''$ was detected previously (as well as for 2,3,5,6-tetrafluorophenol cation which was presently not studied) but not for phenol or monofluoro phenol cations [8]. These observations enabled us to infer the symmetries of their four lowest doublet electronic states ($\tilde{X}$, $\tilde{A}$, $\tilde{B}$, $\tilde{C}$). The present data compliment these studies as vibrational frequencies for the excited state, $\tilde{B}^2A''$, are inferred from the laser excitation spectra, and those for the ground states, $\tilde{X}^2A''$, are obtained from the emission spectra, which were not given in the earlier article [8].

Experimental part. - A detailed description of the apparatus has been given recently [7]. The cations were produced by *Penning* ionisation using argon metastables (excited to energies of 11.5 and 11.7 eV) at argon pressures of ≈0.5 Torr. As the adiabatic ionisation energies leading to the $\tilde{B}^2A''$ states of the fluoro-phenol cations lie between 11.7 and 12.1 eV, these cations are initially formed in their ground states, or sometimes in the lowest levels of their $\tilde{B}^2A''$ states. Anyway, they are subsequently thermalyzed by collisions with the argon carrier, as is evident by comparison of the excitation and emission spectra (cf. *Fig. 1*).

The fluorescence was excited with a nitrogen pumped dye laser (*Lambda Physik* M 2000/FL 2000) at a frequency of 30 Hz (with typically 0.2 mJ per pulse). The undispersed fluorescence signals from a photomultiplier were repetitively accumulated by a *Tektronix* 7912AD programmable digitizer interfaced to a PDP 11-03 computer, which also advanced the laser wavelength.

The excitation spectra shown in *Figures 1-3* were recorded with a laser band-width of 0.02 nm using various dye solutions to cover the wavelength range. The segments covered by each dye were normalized by recording bands common to the successive dye ranges. The spectra were automatically corrected for the laser intensity variation as a reference signal from a photodiode was also digitized for each shot. The wavelengths were internally calibrated by means of the fluorescence lines of excited argon atoms generated during the laser pulse. Many of such lines are apparent in the *Figures 1-3*, and they are marked with a dot.

The samples of the fluoro-substituted phenols were synthesized and purified according to procedures which have been reviewed [9].

Results and discussion. - The laser induced excitation spectra of the fluoro-substituted phenol cations are shown in *Figures 1-3*. These band systems can be identified in all the cases to be the $\tilde{B}^2A'' \leftrightarrow \tilde{X}^2A''$ electronic transitions of these cations by comparison with the emission spectra reported earlier [8]. The latter were detected in the 400-600 nm wavelength region and were assigned to the $\tilde{B}(\pi^{-1}) \rightarrow \tilde{A}(\pi^{-1})$, $\tilde{X}(\pi^{-1})$ transitions. Since the symmetry of all the species is merely C_s, all the states formed by the π^{-1}-ionisation processes have the $^2A''$-symmetry.

In the emission spectra either the most intense, or at least one of the most intense, bands lying to high energy side of the emission spectra were attributed to

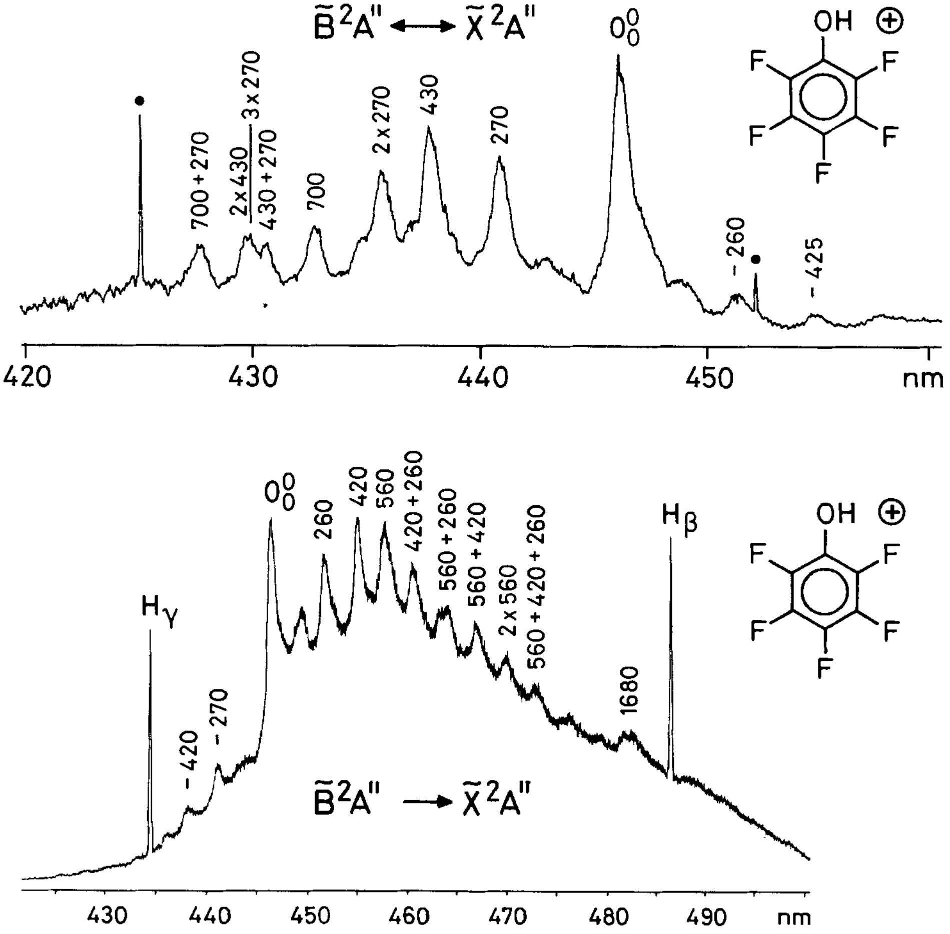


Fig. 1. *Laser excitation* (top) *and emission* (bottom) *spectra of 2,3,4,5,6-pentafluorophenol-cation:* $\tilde{B}^2A''\leftrightarrow\tilde{X}^2A''$ *transition,* recorded with 0.02 nm and 0.2 nm band-widths respectively. The stronger argon lines are marked with a dot.

the 0^0_0-transitions of the $\tilde{B}^2A\to\tilde{X}^2A''$ system. A complementary situation is apparent in the laser induced excitation spectra *(Fig. 1-3)* where the 0^0_0-bands are labelled and the band systems lying on the high energy side correspond to vibrational excitation in the $\tilde{B}^2A''$ state. In the *Table* are compared the energy positions of the maxima of the 0^0_0-bands in the emission (± 10 cm^{-1}) and excitation (± 5 cm^{-1}) spectra, which were recorded with optical resolutions of 0.2 nm and 0.02 nm respectively. The agreement is good.

As is the case with the emission spectra [8], the excitation spectra become less congested as the number of fluorine substituents is decreased; the bands are most well separated in the spectra of 3,5-difluorophenol cation. In addition, in the emission spectra the $\tilde{B}^2A''\to\tilde{X}^2A''$ bands are overlapped to some extent by the

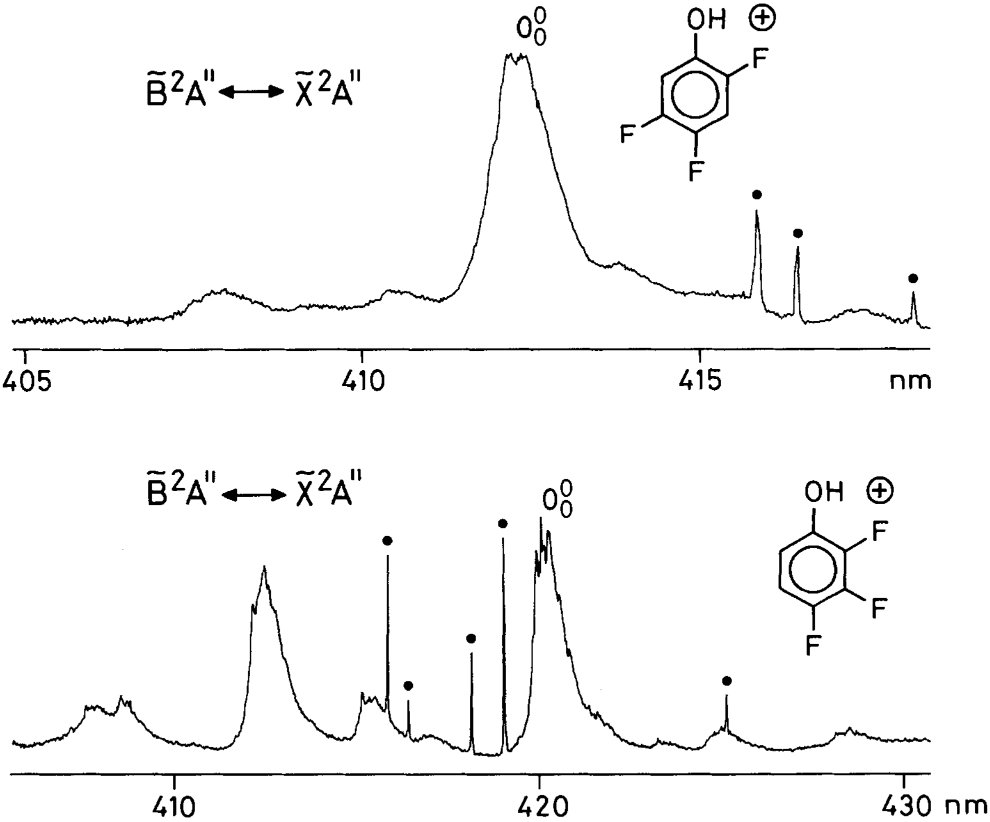


Fig. 2. *Laser excitation spectra of 2,4,5-trifluorophenol- and of 2,3,4-trifluorophenol-cations:* $\tilde{B}^2A'' \leftrightarrow \tilde{X}^2A''$ *band systems,* recorded with 0.02 nm band-width. The stronger argon lines are marked with a dot.

Table. *Vibrational frequencies* (cm^{-1}) *of the fluoro-substituted phenol cations in the* $\tilde{X}^2A''$ *and* $\tilde{B}^2A''$ *electronic states inferred from the emission and laser excitation spectra respectively.* All values ± 10 cm^{-1}. In the last column the maxima of the 0_0^0-bands in the excitation (ex) (± 6 cm^{-1}) and emission (em) (± 10 cm^{-1}) spectra are compared.

Cation	$\tilde{X}^2A''$	$\tilde{B}^2A''$	0_0^0
Pentafluorophenol	260, 420, 560, 1680	270, 435, 540, 700	22406 exc. 22410 em.
2,3,4-Trifluorophenol	260, 460, 1660	270, 450, 680	23795 exc. 23790 em.
2,4,5-Trifluorophenol	290, 480, 1620	250	24245 exc. 24240 em.
2,5-Difluorophenol	310, 360, 500, 940, 1530, 1560	290, 425, 485	23784 exc. 23785 em.
3,5-Difluorophenol	230, 340, 480, 600, 1620	325, 490, 580	21994 exc. 21990 em.

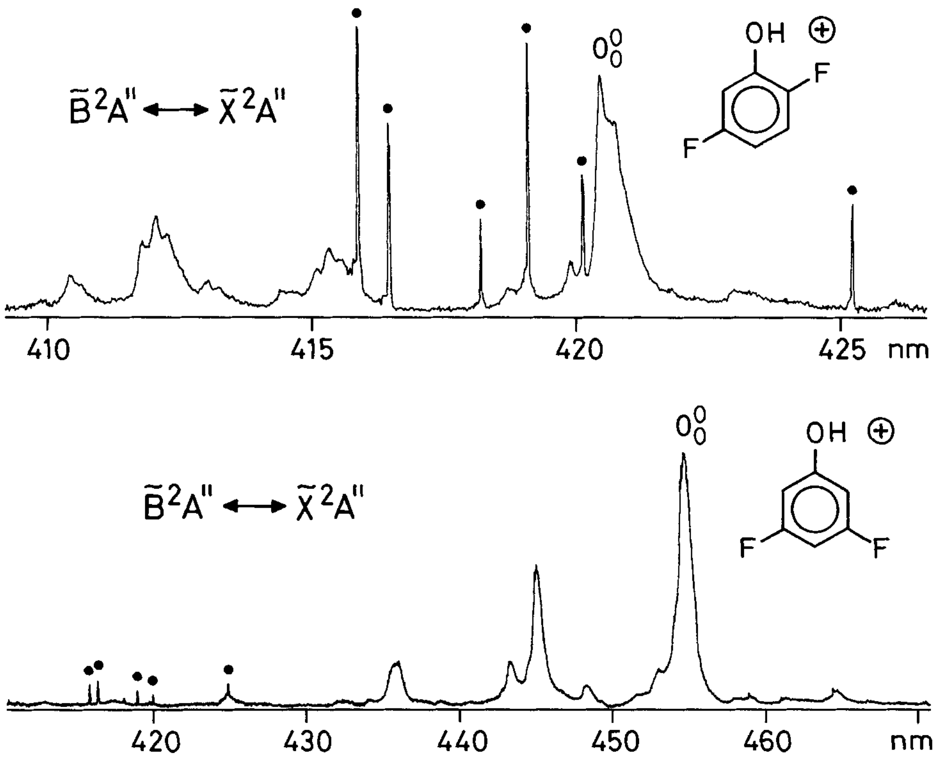


Fig. 3. *Laser excitation spectra of 2,5-difluorophenol- and of 3,5-difluorophenol-cations: $\tilde{B}^2A'' \leftrightarrow \tilde{X}^2A''$ band systems,* recorded with 0.02 nm band-width. The stronger argon lines are marked with a dot.

structureless $\tilde{B}^2A'' \rightarrow \tilde{A}^2A''$ system, whereas in the excitation spectra only the $\tilde{B}^2A'' \leftarrow \tilde{X}^2A''$ transition is laser pumped.

In the *Table* are collected the vibrational frequencies obtained for the six fluoro-substituted phenol cations in the $\tilde{B}^2A''$ and $\tilde{X}^2A''$ states by assignment of the laser induced excitation spectra and of the emission spectra respectively. As an illustration, the two spectra of pentafluorophenol-cation are reproduced in *Figure 1* and the vibrational analyses are indicated. In the case of the cations whose 0_0^0-bands lie near 400 nm, only a small wavelength region could be covered in the excitation spectra *(Fig. 2)*, because below 400 nm the intense N_2^+ $\tilde{B}^2\Sigma_u^+ \leftrightarrow \tilde{X}^2\Sigma_g^+$ O–O band system, always present as the lowest pressure in the ionisation region is only $\approx 10^{-2}$ Torr, obscures all other features. Furthermore, on the whole the excitation spectra were observed over a smaller wavelength region than the emission bands because of the more favourable signal to background ratios that could be attained in the latter measurements.

The vibrational frequencies of the modes excited both in the $\tilde{X}^2A''$ and $\tilde{B}^2A''$ states are similar. This implies that in the excitation and emission spectra the prominent bands are comprised of not only the fundamentals excited but also of the many possible sequence transitions. This is evident by the asymmetry and subsidiary peaks, for example, of the 0_0^0-bands, in *Figures 1-3*. Hot bands are apparent in the spectra as well and the vibrational frequencies corresponding to these agree with values deduced from the complementary spectra, emission or excitation, as listed in the *Table*.

Attribution of the vibrational frequencies to specific modes is however, not possible. Although only totally symmetric fundamentals are by and large excited, there are still 23 A′ fundamentals (under C_s classification) for the fluoro-substituted phenols to be chosen from. Furthermore, only in the case of pentafluorophenol have the molecular vibrational frequencies been given in the literature as well as tentative assignments [10]. Nevertheless, the frequencies given in the *Table* may be useful in other areas of radical cation investigations, for example in the growing field of IR. multiphoton dissociation of ions [11]. In such experiments at present fluoro-substituted cations are advantageous because of the frequency range of the IR. lasers. Thus, some of the fluorophenol-cations may be good candidates as a reasonable selection of vibrational frequencies is known for their ground and excited electronic states. Another potential application is to use such cations in the study of ion-molecule reactions [12] in conjunction with their laser induced fluorescence as a sensitive probe.

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