calculated structures themselves and between each and the experimental structure are comparable, and one is led to believe that all three have similar uncertainties, perhaps with a root-mean-square value of 0.01 or 0.02 of 1 Å. All three yield planar, unsymmetrical structures with markedly bent H bonds. The Karlstrom[9] structure disagrees somewhat seriously in the O···O distance and H bond local structure.

It should be noted that the analysis of the experimental data has yielded, not the structure averaged over the two equivalent oppositely unsymmetrical equilibrium configurations, but the unsymmetrical structures themselves.

The theoretical results can be viewed as a considerable success in the prediction of a rather complicated situation, even as one wishes that both theory and experiment were perhaps 5 times more accurate. On the other hand, there still remain two difficulties with the theory. The first is the present uncertainty in deciding which calculation to believe, even when one calculation uses a more flexible basis set. The second is the fact that an equally good prediction of structure can often be made by transferring bond lengths and angles from similar molecules.

A geometrical optimization by the CNDO/2 semiempirical method[28] gives an unsymmetrical structure with a bent H bond which is somewhat further from the experimental structure than are the a priori calculations referred to above.

A good deal of data on rates of tunneling will be discussed in paper 3.

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Supplementary Material Available: Part 1, the Cartesian coordinates and the valence force field, and part 2, microwave transitions (24 pages). Ordering information is given on any current masthead page.

Spectroscopy and Decay Dynamics of Several Methyl- and Fluorine-Substituted Benzene Radical Cations

V. E. Bondybey,[*,†] C. Vaughn,[†,𝒮] Terry A. Miller,[†] J. H. English,[†] and R. H. Shiley[‡]

Contribution from Bell Laboratories, Murray Hill, New Jersey 07974, and Illinois State Geological Survey, Urbana-Champaign, Illinois 61801. *Received March 9, 1981. Revised Manuscript Received June 4, 1981*

Abstract: Spectra of several fluorobenzene cation radicals containing 1–3 methyl substituents were observed in solid Ne matrix and analyzed. Comparisons between these compounds and other fluorobenzenes studied previously as well as comparisons between the $\tilde{B}$ state lifetimes in the gas phase and in the matrix are used to gain a deeper insight into the $\tilde{B}$ state decay dynamics.

Substantial progress has occurred in the last several years in the field of electronic spectroscopy of molecular cations. While several years ago the spectra of only a handful of diatomics were known, a variety of new techniques have been recently developed[1–15] which permitted observation and characterization of a large number of polyatomic cations. In these experiments the ions were produced by electron impact,[1,2] Penning ionization,[3–5] in electric discharge,[6–8] or by photoionization[9,10] in media as diverse as molecular beams,[11,12] ion traps,[13–15] and low temperature matrices.

While the information obtainable from gas-phase studies is frequently limited due to the complexity and congestion of the high temperature spectra and by the weakness of the available signals, these problems are often overcome in low temperature condensed phase studies. We have recently developed techniques for obtaining absorption,[16] fluorescence excitation,[10] and laser-induced resolved emission spectra[16–19] of molecular cations, usually in solid Ne matrix, and demonstrated that such spectra show in general insignificant perturbatin by the solid Ne medium.[18]

These techniques are particularly valuable for large, polyatomic ions whose ambient temperature spectra frequently appear like featureless continua with only hints of vibrational structure but whose matrix spectra provide a wealth of detailed vibrational information. Thus matrix spectra were instrumental in providing

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[†] Bell Laboratories.

[‡] Illinois State Geological Survey.

[𝒮] Summer student.

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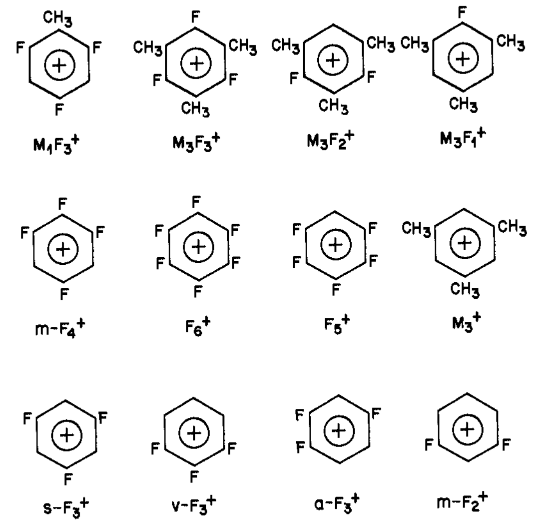

Figure 1. Structural formulas of some of the cations discussed and studied in this work. Below each formula we give an abbreviated symbol we use to refer to these species in the text.

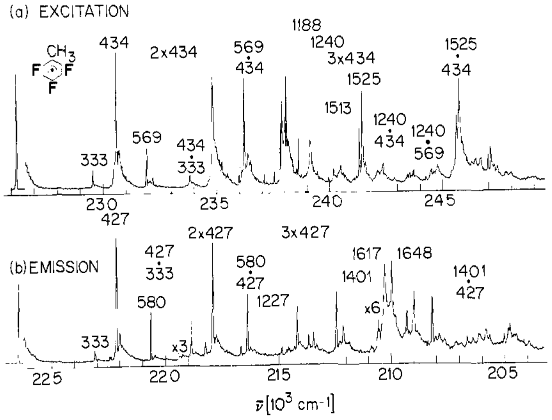

Figure 2. Ne Matrix spectra of 1,3,5-trifluorotoluene cation ($M_1F_3^+$). (a) Excitation spectrum. (b) Resolved emission spectrum. Note that the vibrational frequencies given above the bands (in cm^{-1}) are used as mode labels. Thus a label of 2 × 434 means a first overtone of the 434-cm^{-1} frequency, which may, however, be due to anharmonicity and other interactions slightly displaced from 868 cm^{-1}.

understanding of the Jahn–Teller distortion of the doubly degenerate ground states of $C_6F_6^+$ and several other related species.[16,17] Similarly extensive information was recently obtained also for the methyl substituted penta- and octafluoro toluene cation radicals.[19] Less detailed information is obtained for toluenes and benzenes with only one or two halogen substituents. The fluorescence quantum yields of these species are exceedingly low and only their absorption spectra were observed.[16,20]

In this manuscript we extend our work to several other methyl substituted species of this type. In particular, we have observed and analyzed the spectra of the cations of 2,4,6-trifluorotoluene ($M_1F_3^+$) and mono-, di-, and trifluoromesitylene ($M_3F_1^+$, $M_3F_2^+$, and $M_3F_3^+$). In Figure 1 we show the structural formulas of these species as well as of several other related cations of importance for this study. We show below the formulas abbreviated symbols which we will use in our discussion in referring to the above compounds.

One of the interesting aspects of the photophysics of substituted benzene cations is the diversity in the decay behavior of the fluorescing $\tilde{B}$ states.[21,22] In some molecules like $C_6F_6^+$ and a number of other highly halogenated cations intense fluorescence is observed, suggesting that their emission quantum yields are high. In others, like benzene cation itself and a variety of its substituted derivatives, fluorescence quantum yields are apparently $<10^{-5}$, suggesting an extremely efficient nonradiative transition into the ground electronic state.[23,16]

Large advances have occurred in the last decade in our understanding of nonradiative transitions, and the importance of the intramolecular density of states in the relaxation process is well-known. Introduction of polyatomic substituents into the molecule of interest is a convenient way of modifying this density of states. In addition to the purely spectroscopic interest, we will examine in the present manuscript to what extent can comparison of the relaxation behavior of compounds previously studied with that of their methyl substituted analogues, as well as comparisons between the gas phase and condensed medium, contribute to our understanding of the relaxation dynamics in the benzene cation derivatives.

Experimental Section

Our experimental techniques were described in our previous works and details can be found there.[16-18] We give here only a brief outline. Mixtures of the parent compounds and Ne (~1:5000) were deposited on a metal mirror at 4 K and subsequently ionized by 1216-Å Lyman α radiation. Absorption spectra of these photolyzed deposits are obtained by using a waveguide absorption technique with a tungsten-halogen lamp as a background source. Fluorescence of the samples is excited by a pulsed dye laser and the time and wavelength resolved emission is detected by a photomultiplier, amplified, digitized, and eventually processed by a minicomputer to provide the desired spectra or lifetimes.

The parent compounds were prepared as described by Finger et al.[24] Prior to use, they were degassed and purified by several freeze–pump–thaw cycles and a simple vacuum distillation.

Results and Discussion

Photolysis of each of the deposits resulted in the appearance of an intense absorption spectrum. Typically, only 5–10-s photolysis by the 1216-Å radiation was required to produce strong, structured spectra, with nearly 100% absorption in the strongest bands. This highly efficient product formation is characteristic of matrix photoionization processes.[18,19] One exception was the sample of unsubstituted mesitylene, for which only broad, unstructured absorption appeared. We interpret this in terms of an efficient nonradiative decay of the excited electronic state and strong lifetime broadening of the M_3^+ spectrum.

Excitation by a laser tuned to one of the absorption bands identified in the absorption studies produced an intense fluorescent spectrum exhibiting in most cases extensive vibrational structure. In the following paragraphs we will first discuss briefly the spectra of the individual compounds and, where appropriate, make comparisons with the related fluorobenzenes. In the last section we will then review the results of lifetime studies and present a more general discussion of the decay processes deactivating the excited $\tilde{B}$ states of the benzenoid cation radicals.

1,3,5-Trifluorotoluene Cation ($M_1F_3^+$). In our previous analysis of the spectra of pentafluoro toluene cation,[19] we have noted that the methyl group is similar in mass to fluorine and that also electronically it apparently mimics well the fluorine atom. Replacement of one fluorine atom in $C_6F_6^+$ by a methyl group does not split appreciably the degeneracy of the ground electronic state, as evidenced by the strongly perturbed vibrational structure in its emission spectrum. One might therefore expect a similarity between the spectrum of 1,2,3,5-tetrafluorobenzene cation[25] (m-F_4^+) and that of the $M_1F_3^+$ species. There is indeed a close similarity in the vibrational structure of the two spectra. Furthermore, just as for m-F_4^+, the components of the degenerate ground state are apparently split far apart, and the emission spectrum of $M_1F_3^+$ shows a regular vibrational structure un-

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Table I. Vibronic Bands of 1,3,5-Trifluorotoluene Cation ($M_1F_3^+$) in Solid Ne (cm^{-1})

emission		excitation	
$\bar{\nu}$	assignment[a]	$\bar{\nu}$	assignment
22 636	origin	22 636	origin
22 303	333 (ν_{11} = 303)	22 969	333 (ν_{11} = 305)
22 239	397	23 069	433 (ν_{10} = 428)
22 209	427 (ν_{10} = 426)	23 205	569 (ν_9 = 573)
22 056	580 (ν_9 = 581)	23 398	433 + 333
21 877	427 + 333	23 500	2 × 433
21 816	427 + 393	23 617	
21 783	2 × 427	23 637	569 + 422
21 659	580 + 397	23 725	
21 630	580 + 427	23 771	2 × 569
21 477	2 × 580	23 797	1161 (ν_6 = 1140)
21 409	1227	23 805	1169
21 358	3 × 427	23 816	1180
21 336	1300 (ν_5 = 1305)	23 824	1188
21 235	1401 (ν_3 = 1449)	23 876	1240 (ν_5 = 1259)
21 204	580 + 2 × 427	23 929	3 × 433
21 019	1617	24 065	569 + 2 × 433
20 988	1648 (ν_2 = 1647)	24 149	1513
20 809	1401 + 427	24 161	1525
20 656	1401 + 580		

[a] Corresponding vibrational modes in M-F_4^+ whose spectrum shows a remarkable similarity to that of $M_1F_3^+$, are given in parentheses.

Table II. Vibronic Bands of Difluoromesitylene Cation ($M_3F_2^+$) in Solid Ne (cm^{-1})

emission		excitation	
$\bar{\nu}$	assignment[a]	$\bar{\nu}$	assignment
22 086	origin	22 086	origin
21 801	285 (ν_{11} = 278)	22 361	275 (ν_{11} = 268)
21 739	347	22 422	336
21 615	471 (ν_9 = 460)	22 549	463 (ν_9 = 456)
21 519	567 (ν_8 = 575)	22 721	635
21 390	2 × 347	22 821	463 + 275
21 268	471 + 347	22 884	463 + 335
21 145	2 × 471	23 010	2 × 463
21 048	567 + 471	23 180	635 + 463
20 920	471 + 2 × 347	23 282	2 × 463 + 275
20 797	2 × 471 + 347	23 344	2 × 463 + 336
20 742	1344	23 365	1309
20 725	1361 (ν_5 = 1356)	23 373	1317 (ν_5 = 1335)
20 676	3 × 471	23 471	3 × 463
20 578	567 + 2 × 471	23 561	
20 546	1540	23 622	1536
20 496	1590	23 630	
20 257	1361 + 471	23 826	1309 + 463
20 030	1590 + 471	23 939	
19 791	1361 + 2 × 471	24 079	1536 + 463

[a] Corresponding modes in F_5^+ are given in parentheses.

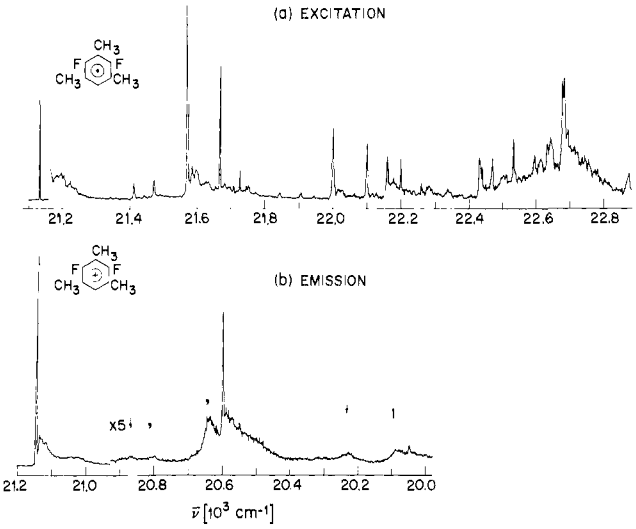

Figure 3. Spectra of trifluoromesitylene cation ($M_3F_3^+$). (a) Excitation spectrum uncorrected for variation in laser power. (b) Emission spectrum. The heavy arrows point out several broadened bands (see Discussion).

perturbed by the low-lying Ã state.

The emission and laser excitation spectra are compared in Figure 2, and they show clearly similarity in the vibrational structures of the $\tilde{B}$ and $\tilde{X}$ states. Most prominent in the spectrum is a progression in a frequency of 427 cm^{-1} (434 in the $\tilde{B}$ state) which is analogous to the ring distortion ν_{10} vibration of m-F_4^+ (426 and 428 cm^{-1} in the $\tilde{X}$ and $\tilde{B}$ states, respectively). Also moderately active in the spectrum are two other low frequency modes of 333 and 580 cm^{-1}, respectively. The latter corresponds to the ν_9 frequency of m-F_4^+ (581 cm^{-1}) and clearly derives from the totally symmetric "ring breathing" ν_2 of $C_6F_6^+$ or ν_4 of s-F_3^+. The lower frequency is analogous to ν_{11} of m-F_4^+. As in all other substituted benzene cations, a C–C stretching frequency appears strongly at 1648 cm^{-1} and decreases to 1525 cm^{-1} in the $\tilde{B}$ state. Both bands are doubled in $M_1F_3^+$, possibly due to Fermi resonance with some overtone bands. The observed $M_1F_3^+$ vibronic bands are listed in Table I, where we give assignments for some of them in terms of the m-F_4^+ mode numbering.

Trimethyldifluorobenzene Cation ($M_3F_2^+$). Very similar conclusions to those made above apply also to the $M_3F_2^+$ spectrum. Like in the $M_1F_3^+$ compound, the asymmetric substitution results in a large splitting of the ground-state degeneracy, and over the range studied (up to ~3000 cm^{-1} in energy), the $\tilde{X}$ state vibrational structure shows no hint of perturbations due to the Ã state interactions. The $M_3F_2^+$ compound with five substituents shows again some similarity to the spectra of pentafluorobenzene cation (F_5^+). The most active mode in the emission spectrum with a frequency of 471 cm^{-1} is rather close to the similarly prominent ν_9 mode in the F_5^+ spectrum,[25] 460 cm^{-1}, and also shows a small decrease in the excited $\tilde{B}$ state to 463 cm^{-1}. We again give a partial listing of the observed vibronic bands in Table II.

In our recent study of m-F_2^+ spectra,[26] we have observed that the excitation spectrum showed signs of perturbation, with numerous levels which did not fit the expected pattern and with unusual isotopic shifts. We suggested that this may be due to the presence of a nearby perturbing state or to a deviation from planarity in one of the electronic states involved. It is interesting to note that no such irregularities appear in the present spectra of $M_3F_2^+$.

1,3,5-Trifluoro-2,4,6-trimethylbenzene Cation ($M_3F_3^+$). This is perhaps the most interesting species of the compounds studied here. If one makes the assumption that the three methyl groups are free to rotate, the molecule would possess D_{3h} symmetry and the degenerate ground state would be subject to a Jahn–Teller distortion,[27] similar to the $C_6F_6^+$ or s-F_3^+ cations. A barrier to free rotation could, in principle, break this symmetry and result in splitting of the ground-state degeneracy.

The excitation spectrum of $M_3F_3^+$ is shown in Figure 3. It has an origin at 21 140 cm^{-1} and exhibits a striking similarity to that of $C_6F_6^+$, both in terms of the vibrational frequencies and, to some extent, in relative intensities. The most active frequencies in the spectrum at 434, 1551, and 534 cm^{-1} are clearly analogues of the equally intense e_{2g} ν_{17} and ν_{15} vibrations of $C_6F_6^+$ and the totally symmetric ring-breathing ν_2 (426, 1551, and 540 cm^{-1}, respectively).[10,28] A vibrational mode of 277 cm^{-1} is also present in the spectrum and is apparently the counterpart of ν_{18} of $C_6F_6^+$ (265 cm^{-1}), but appears with a considerably lower intensity, suggesting less Jahn–Teller activity for this mode. A vibrational frequency of 593 cm^{-1} which appears weakly in the spectrum may be due to the same level which was observed at 631 cm^{-1} in $C_6F_6^+$

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Table III. Spectra of Trifluoromesitylene Cation ($M_3F_3^+$) in Solid Neon (cm^{-1})

excitation				emission	
$\bar{\nu}$	assignment[a]	$\bar{\nu}$	assignment[a]	$\bar{\nu}$	$\Delta\bar{\nu}$
21 140	origin	22 208	2 × 534	21 140 (<2)	origin
21 417	277 (ν_{18} = 265)	22 440	3 × 434	20 863 (~30)	277
21 477	337	22 478	1338 (ν_{16} = 1190)	20 792 (~30)	348
21 574	434 (ν_{17} = 426)	22 541	534 + 2 × 434	20 629 (~30)	348
21 674	534 (ν_2 = 540)	22 640	2 × 534 + 434	20 590 (<2)	550
21 733	593 (ν_a = 631)	22 651		20 224 (~50)	916
21 851	434 + 277	22 686	1546	20 070 (~50)	1070
21 912	434 + 337	22 691	1551 (ν_{15} = 1552)	20 040 (~4)	1100
21 951	534 + 277	22 882		19 958 (~50)	1182
22 008	2 × 434	22 911	1338 + 434	19 589 (~120)	1551
22 108	534 + 434	23 120	1546 + 434		
22 169	593 + 434	23 125	1551 + 434		

[a] In parentheses we show the corresponding vibrational modes of $C_6F_6^+$.

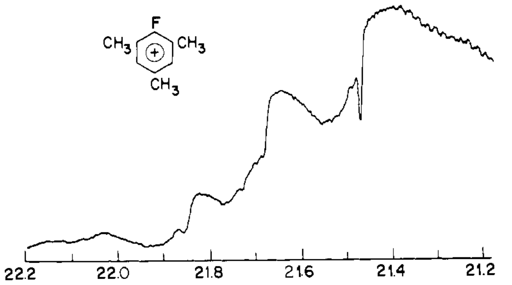

Figure 4. A section of the fluoromesitylene cation ($M_3F_1^+$) absorption spectrum near the origin band. The spectrum is shown with transmittance increasing from 0 at the bottom to 100% at the top of the figure.

and was not assigned to any specific mode. A similarly weak band at 337 cm^{-1} has no counterpart in the $C_6F_6^+$ spectrum and may be associated with some motion of the methyl groups. We list the observed bands in Table III and give their assignments in terms of the $C_6F_6^+$ mode numbering.

The emission spectrum of $M_3F_3^+$ is shown in Figure 4. Unlike the excitation spectrum and unlike the emission spectra of the asymmetrically substituted species, it shows very little vibrational detail. A harmonic progression of sharp bands with 550-cm^{-1} spacing is clearly due to the totally symmetric "ν_2" vibration. The remaining bands are all broad and do not fit any regular pattern, suggesting clearly a significant Jahn–Teller distortion of the ground electronic state. We include the observed emission bands in Table III and give in parenthesis also their approximate widths. In our previous studies we have shown that as long as more than one Jahn–Teller vibrational mode is active in the spectrum,[27,29] the structure is not adequately described by the simplest, single mode theory,[30,31] and mode mixing effects have to be considered[27,32,33] by treating simultaneously all of the active modes. In the present case, the relative intensity of the lowest frequency ν_{18} mode is considerably decreased, and one can get a crude idea of the magnitude of the distortion by treating only the most active "ν_{17}" mode. Thus if one assigns the two strongest broad bands at 511 and 916 cm^{-1} from the origin as the 17^0_1 and 17^0_2 ($j = {}^1/_2$) transitions, respectively, one obtains values of 406 cm^{-1} for the deperturbed frequency ω_{17} and 0.38 for the Jahn–Teller parameter D_{17}. This is roughly the same order of magnitude as in the other halobenzenes, when a single mode analysis is performed. However, a multimode analysis, which is also almost certainly appropriate here, clearly alters the quantitative result.

The cause of the broadening of the bands in the $M_3F_3^+$ spectrum is puzzling. The most interesting aspect of this broadening is that it affects selectively the Jahn–Teller active modes in the emission spectrum, but neither the totally symmetric emission bands nor the vibronic levels in the excitation spectrum are affected.

Table IV. Effect of Methyl Substitution upon the B State Energy of Several Fluorobenzene Cations

cation	T_e	cation	T_e	$\Delta\nu$
s-F_3^+	21 776	$M_3F_3^+$	21 440	−636
m-F_2^+	22 998	$M_3F_2^+$	22 092	−906
F_1^+		$M_3F_1^+$	21 468	

One could contemplate two different types of broadening mechanisms. In the first place, the shapes could be due to homogeneous lifetime broadening caused by a very efficient nonradiative relaxation of the Jahn–Teller active modes in the condensed medium. Alternatively, one might postulate an inhomogeneous broadening mechanism which operates selectively on the Jahn–Teller modes by assuming that these are more readily perturbed by small imperfections in the host lattice. We have indeed seen that in the more strongly interacting Ar and Kr matrices the Jahn–Teller modes of $C_6F_6^+$ were more strongly shifted than the totally symmetric levels.[28]

1-Fluoro-2,4,6-trimethylbenzene Cation ($M_3F_1^+$). When a matrix containing M_3F_1 is photolyzed under conditions where the other cations are generated, a strong absorption spectrum appears with origin at 21 468 cm^{-1}. This spectrum is presented in Figure 4 and shows only little vibrational structure. The quantum yield of $M_3F_1^+$ fluorescence is apparently extremely low and only the 0–0 emission band was detected. In this respect, $M_3F_1^+$ is apparently similar to the F_1^+ and $M_1F_1^+$ compounds for which no fluorescence at all was observed and only relatively uninformative and broad absorption spectra could be obtained.[16,20]

Table IV compares the experimental energies of the π–π^* transitions of the $M_3F_3^+$, $M_3F_2^+$, and $M_3F_1^+$ cations with the corresponding fluorobenzenes. It can be seen that in both $M_3F_3^+$ and $M_3F_2^+$, the $\tilde{B}$ state is stabilized by ~0.1 eV with respect to the corresponding fluorobenzene cation. If this correlation has a more general validity, one would expect the $\tilde{B}$ state in monofluorobenzene cation near 22 500 cm^{-1}. The photoelectron spectra[34,35] place the second photoelectron band just below 21 000 cm^{-1}. This would seem to support the idea that the second photoelectron band in this compound is due to σ ionization, and that the ordering of the states is reversed compared with the more highly fluorinated benzenes.

Radiative Lifetimes and Emission Quantum Yields. The question of fluorescence quantum yields of the fluorobenzene cations is of considerable interest. While we can perhaps state qualitatively from the very intense fluorescence that for several of the species the reemission quantum yields are probably high, our data unfortunately do not provide direct information about the fluorescence yields. Dujardin et al.[21] have recently attempted to measure the emission yields of several related fluorobenzenes using pho-

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Table V. Comparison of Ne Matrix and Gas-Phase Lifetimes of the B States of Several Substituted Benzene Cations

	lifetime (nsec)			T_e of B State	
cation[a]	Ne[b]	gas[c]	gas/Ne	Ne	gas
m-F_2^+	<0.1	<0.1		22 998	23 229
s-F_3^+	53	58	1.09	21 774	21 862
a-F_3^+	~10	10		24 177	24 274
v-F_3^+	51	58	1.14	22 288	22 460
o-F_4^+	44	50	1.14	239 192	23 298
m-F_4^+	43	50	1.16	23 232	23 331
p-F_4^+	30	35	1.17	24 358	24 440
F_5^+	40	47	1.17	23 014	23 097
F_6^+	42	48	1.14	21 557	21 606
s-Cl_3^+	19	22	1.15	15 265	15 398
ClF_5^+	37	43	1.16	19 914	19 990
$Cl_3F_3^+$	29	34	1.17	16 785	16 859
$M_1F_5^+$	40	43	1.08	21 750	
$M_1F_3^+$	41			22 636	
$M_3F_3^+$	33	37	1.12	21 140	
$M_3F_2^+$	27			22 086	
$M_3F_1^+$	<0.01			21 468	
F_5OH^+	31	33	1.06	22 407	22 410

[a] The definitions of the symbols not in Figure 1 are as follows: o-F_4^+ = 1,2,3,4-tetrafluorobenzene cation. p-F_4^+ = 1,2,4,5-tetrafluorobenzene cation, s-C_3^+ = 1,3,5-trichlorobenzene cation, ClF_5^+ = chloropentafluorobenzene cation, $Cl_3F_3^+$ = 1,3,5-trichloro-2,4,6-trifluorobenzene cation, $M_1F_5^+$ = methylpentafluorobenzene cation, and F_5OH^+ = pentafluorophenol cation. [b] Lifetimes in Ne are believed accurate to ±2 ns. [c] Gas-phase lifetimes from ref 20 and 21.

ton–photoion coincidence techniques. They concluded that only for the s-F_3^+ cation is the yield near 1 and that for many of the other fluorobenzenes the yields are close to 0.5, corresponding to nonradiative rates of the order of 10^7 s^{-1}. Well over 20 different benzenoid cations have now been studied, many of them both in the gas phase and in solid–rare gas matrices. While, as noted above, our data do not provide direct information about possible nonradiative contributions of the measured $\tilde{B}$ state decay rates, one can perhaps gain some insight by comparing the available data for the wide range of compounds studied.

It appears that the benzenoid cations fall clearly into two categories. A large number of these species seem to exhibit very strong fluorescence and have measured $\tilde{B}$ state lifetimes in the relatively narrow range of ~30–60 ns. Of the cations studied in this work, $M_3F_3^+$, $M_3F_2^+$, and $M_1F_3^+$ fall into this category, with lifetimes of 33, 27, and 41 ± 2 ns, respectively, in solid Ne. In the second group belong cations, e.g., $M_3F_1^+$ whose $\tilde{B}$ state lifetimes are clearly shortened and which exhibit either only weak or, in some cases, no detectable fluorescent decay.

The rates of statistical limit nonradiative transitions in large molecules of this type are a sensitive function of molecular symmetry, Franck–Condon factors, density of states, spin selection rules, and other factors, and the experimentally observed lifetimes span more than 15 orders of magnitude. Yet, in spite of the differing symmetries, densities of states, and molecular geometries, the lifetimes of the $\tilde{B}$ states of the first group of substituted benzene radical cations remain within the relatively narrow range of 30–60 ns, as can be seen clearly from the data collected in Table V. Nonradiative transitions are often also a sensitive function of the molecular environment. Again, however, we can see in Table IV that for most of the benzenoid cations the lifetimes in the Ne matrix are reduced to ~90% of their gas-phase value, an effect which is fully explicable in terms of a change in the radiative rate due to an increased index of refraction in the solid medium. Similarly, we can see that the lifetimes are not appreciably affected by deuterium substitution or introduction of one or more methyl groups into the molecule which surely change substantially the intramolecular density of states.

We therefore believe that for most of the cations whose $\tilde{B}$ states have lifetimes in this 30–60-ns range, the fluoresence quantum yields are essentially unity, with insignificant nonradiative contribution to the measured lifetimes. The observed small differences in radiative rates are probably due to minor variation in the transition dipoles, wavelengths, or Franck–Condon factors. An alternative explanation of these differences in terms of nonradiative decay channels would require the rates to vary in a manner not in concert with current theoretical models.

For numerous other benzenoid cations in the second category described above the situation is reversed with, in some cases, quite negligible fluorescence quantum yields and with $\tilde{B}$ state lifetimes dominated by nonradiative decay. Benzene, fluorobenzene, or, from the compounds investigated in the present work, mesitylene cations belong into this category. This reversal in behavior has been attributed to a change in ordering of the excited electronic states and by dropping of the state formed by σ ionization below the fluorescent state.

A few cations represent intermediate cases, with measurable contributions of both a radiative and a nonradiative path. For example, a-F_3^+ and m-F_2^+ apparently fall into this category. Of the compounds studied here, $M_3F_1^+$ tends toward this group. From its fluorescence intensity we can estimate a quantum yield of $<10^{-4}$ for $M_3F_1^+$, corresponding to a $\tilde{B}$ state lifetime of ~5 ps.

Finally it should be noted that our conclusions about lifetimes and quantum yields apply only to the vibrationless level of the excited $\tilde{B}$ state. Even for selective excitation to excited vibrational levels, the rapid vibrational relaxation in the matrix causes the preponderance of emission to occur from the vibrationless level. Comparison of the very similar intensity patterns recorded for excitation spectra in the Ne matrix and the gas phase would indicate little change in the quantum yields, within 1000–2000 cm^{-1} above the origin. Beyond this excitation energy, our data provide no insight into the decay processes.

Summary

Laser excitation, absorption, and resolved fluorescence spectra of several methyl- and fluorine-substituted benzene cations in solid Ne matrices are reported and analyzed. The $\tilde{B}$ state lifetimes of several of these species are measured and compared with those of other related halogenobenzenes and with their gas-phase values. On the basis of these comparisons, it is proposed that for most of the benzenoid cations with lifetimes in the 30–60-ns range the $\tilde{B}$ state emission quantum yields are very close to unity.