(29) In processes where reactant and product species have similar structures entropy changes are negligible. Hence, the enthalpy difference associated with the HX exchange should reasonably reflect the free-energy change for such reactions. However, when cyclic and acyclic onium ions are compared, the entropy change associated with ring formation is generally in the neighborhood of 10 eu. This will cause $\Delta G°$ to favor the acyclic structure by 3 kcal/mol over $\Delta H°$ at 298 K.
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Matrix Laser Fluorescence Spectra of Several Fluorobenzene Radical Cations

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Received September 7, 1978

Abstract: Several fluorobenzene radical cations were generated by vacuum UV photolysis of the parent fluorobenzenes in solid Ar matrix, and their laser fluorescence excitation spectra were studied. Their spectra show a well-resolved vibronic structure, which appears to be essentially unperturbed by the solid. Vibrational analysis provides strong evidence for the occurrence of a Jahn–Teller distortion in the degenerate ${}^2E_{1g}$ ground state of $C_6F_6{}^+$

1. Introduction

Until fairly recently, the number of spectroscopic studies of polyatomic ions was rather restricted.[1-3] In the last few years there has been a surge of activity in this field.[4-8] Most of the reported ions were generated either in discharges or by electron impact and identified by analysis of their emission spectra. Although immensely useful, studies of this nature have several limitations. In the first place, the emission spectra provide mostly information about the ground electronic state, and only limited data are generally obtained about the vibrational structure of the excited electronic state. Furthermore, particularly in larger molecules, the dense rotational structure and the large number of levels populated at high or even ambient temperatures usually result in poorly resolved spectra with broad and overlapping bands and make the interpretation difficult.

The first limitation can be overcome by the study of laser fluorescence excitation spectra, which can provide extensive information about the excited electronic states. Very recently we have indeed reported such a study of the $C_6H_3F_3{}^+$ cation.[9] The difficulties inherent in the complexity of the spectra can be eliminated by reducing the sample temperature. A convenient means for the study of low temperature spectra is provided by the matrix isolation technique.

Numerous studies of the matrix spectra of a variety of polyatomic anions and cations have appeared in the last few years, most of them employing infrared spectroscopy. Jacox and Milligan[10] have observed the matrix spectrum of $CCl_3{}^+$. Since then a number of other halogenated methylene and methyl radical ions have been reported,[11-13] mainly by Jacox and by Andrews and co-workers. Also a variety of other small inorganic ions have been observed.[14-16]

In contrast to the large number of infrared studies, very little is known about the electronic spectra of matrix isolated ions, and only the diatomic $C_2{}^-$ was studied in some detail.[17,18] Studies of electronic spectra would clearly be desirable because of the inherent, much higher sensitivity. Furthermore, if vibrationally resolved electronic spectra can be obtained, they should provide mainly the symmetric vibrational modes and thus complement conveniently the infrared spectroscopy.

In the present manuscript we report the observation of vibrationally resolved emission and laser excitation spectra of several fluorobenzene radical cations. In a preliminary communication[19] we have already reported the matrix spectrum of $C_6F_6{}^+$. Such studies are desirable for two reasons. In the first place, the low-temperature spectra with their well-resolved vibrational structure should provide useful information about these interesting species or, when available, assist in the interpretation of the more congested gas-phase spectra.[20] In the second place, they provide the possibility of comparison of the molecular constants of these ionic species with their gas-phase values and give an indication of the extent to which the ions are perturbed by the solvent. This is of particular value, since, for most of the ions whose matrix IR spectra have been reported, such comparisons are not available.

2. Experimental Section

The parent fluorobenzenes (Aldrich) were purified by several freeze-pump-thaw cycles and mixed with Ar. Typically dilutions of 1:2000 to 1:5000 were employed. The samples were then deposited on a sapphire substrate at ≈5 K, mostly with simultaneous photolysis. In several experiments the samples were deposited without photolysis and subsequently photolyzed in situ. The photolysis was accomplished using an atomic resonance lamp excited by a microwave discharge. The hydrogen Lyman α 1216-Å line was usually employed, although the Xe 1470-Å radiation was used in several experiments.

The sample fluorescence was excited using a tunable dye laser pumped by an N_2 laser. To avoid saturating the individual vibronic transitions in the matrix isolated molecules, the laser power was typically attenuated by inserting an O.D. 2–3 neutral density filter into the laser beam. The sample emission was resolved in a SPEX 14018 monochromator. The PMT signal was time resolved and averaged in a Nicolet signal averager. The data acquisition as well as the scanning of the laser and the monochromator were controlled by a minicomputer.

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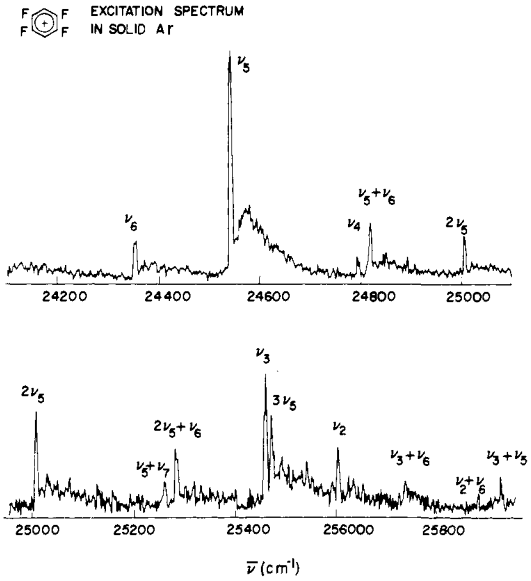

Figure 1. Two sections of the 1,2,4,5-$\overset{*}{C}_6H_2F_4^+$ excitation spectrum in solid Ar. Spectrum was not corrected for laser power variation. The signal in the 0-0 band at 24 072 cm^{-1} was monitored with ≈2-cm^{-1} band pass.

Table I. 1,2,4,5-$C_6H_2F_4^+$ Vibrational Frequencies[a] (D_{2h} Symmetry)

		B		
a_g species	X, solid Ar	solid Ar	gas	parent, $C_6H_2F_4$
ν_1				3097
ν_2		1536		1643
ν_3		1392		1374
ν_4		722		748
ν_5	480	470	460	487
ν_6	289	279	270	280

[a] In reciprocal centimeters. Parent data were taken from ref 21 and 22; gas-phase data were taken from ref 23. Note that in all of the fluorobenzenes studied we label the emitting, excited electronic state "B". The label "X" refers to the ground state which is, in the case of $C_6F_6^+$, doubly degenerate.

3. Results

1. 1,2,4,5-Tetrafluorobenzene. Two sections of the excitation spectrum of the photolyzed 1,2,4,5-tetrafluorobenzene sample are shown in Figure 1. This spectrum was obtained by tuning the laser and monitoring the intensity of the 0-0 emission band at 24 072 cm^{-1} as a function of the excitation wavelength. The monochromator band pass was ~2 cm^{-1}, and selected thus only a narrow range out of the inhomogeneously broadened line width. The origin band with a maximum at 24 072 cm^{-1} and an inhomogeneous linewidth of ≈25 cm^{-1} is slightly red shifted from its gas-phase position at 24 440 cm^{-1}. The spectrum consists of a large number of rather sharp bands, which clearly correspond to the upper state vibrational structure. The strongest bands in this spectrum form an array characterized by vibrational intervals of 470 and 279 cm^{-1}, which are readily assigned to the two lowest frequency a_g fundamentals, ν_5, the C-F bending, and ν_6, the C-C-C ring deformation. These frequencies agree extremely well with the parent 487- and 280-cm^{-1} values[21,22] and provide strong support for the reassignment[22] of the weak Raman band at 280 cm^{-1} as the lowest a_g fundamental. Vibrational frequencies of 1536 and 1392 cm^{-1} and their combinations with the ν_5 and ν_6 vibrations also appear moderately strongly in the spectrum. These are assigned to the ν_2 and ν_3 a_g modes—the C-F and C-C stretching frequencies, probably in that order. These occur in the parent fluorobenzenes at 1643 and 1514 cm^{-1}, respectively. Finally a weak band at 24 794 cm^{-1} does not fit the pattern of the other frequencies and must therefore involve an additional vibrational mode of 722 cm^{-1}. This is probably the ring "breathing" C-C stretching frequency, which was assigned at 748 cm^{-1} in the parent compound.

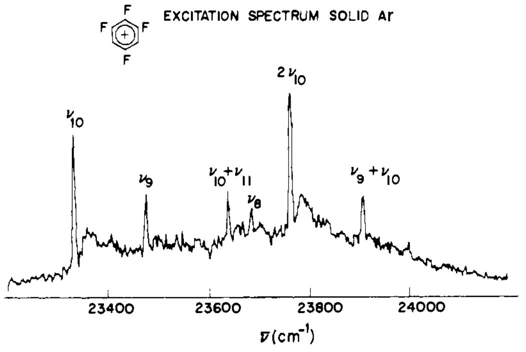

Figure 2. Part of the excitation spectrum of 1,2,3,5-$C_6H_2F_4^+$. The intensity of the 0-0 band at 22 903 cm^{-1} was monitored as a function of laser wavelength.

Emission spectra obtained by excitation in any of the sharp vibronic bands in Figure 1 are identical, indicating that vibrational relaxation is considerably faster than the radiation and that all the emission originates from the vibrationless level.

The vibrational frequencies derived from both the emission and excitation spectra are with their assignments summarized in Table I. For comparison, the corresponding ground-state frequencies of the parent compound are also given. Where data are available, we also give excited-state vibrational frequencies derived from the gas-phase laser excitation spectra.[23]

2. 1,2,3,5-Tetrafluorobenzene. The spectrum of this cation has an origin at 22 903 cm^{-1} in solid Ar. Its excitation spectrum is shown in Figure 2. While the 1,2,3,5-substituted benzene has a lower C_{2v} symmetry, and therefore all totally symmetric a_1 vibrations are allowed, its spectra are qualitatively very similar to those of the more symmetric isomer. Two low-frequency vibrations of 431 and 307 cm^{-1}, respectively, occur strongly in the spectrum, both as simple progressions and in combinations with other vibrations. These agree remarkably well with the lowest a_1 modes of the parent,[24] ν_{10} of 443 and ν_{11} of 305 cm^{-1}. Like the 279- and 470-cm^{-1} vibrations of 1,2,4,5-$C_6H_2F_4^+$, they are probably due to the C-F and C-C-C bending vibrations. Also frequencies of 576, 783, 1263, and 1536 cm^{-1} occur in the spectrum, both singly and in combinations and are readily assigned to ν_9, ν_8, ν_5, and ν_2 based on the close agreement with the parent a_1 vibrations at 580, 789, 1249, and 1531 cm^{-1}. Finally, a relatively strong band at 24 486 cm^{-1} implies a frequency of 1582 cm^{-1}; this may be due to ν_1 which occurs at 1642 cm^{-1} in the parent.

Vibrational frequencies of 586, 429, and 307 cm^{-1} appear in the emission spectrum. These are clearly due to the corresponding ν_3, ν_{10}, and ν_{11} ground-state frequencies. The vibrational data derived from our spectra are summarized in Table II.

3. Pentafluorobenzene. Part of the excitation spectrum of $C_6HF_5^+$ is presented in Figure 3. As in the other species, three low-frequency vibrations appear repeatedly in the spectra. Their 567-, 456-, and 273-cm^{-1} values are again remarkably close to the parent ν_8, ν_9, and ν_{11} vibrations (578, 470, and 272 cm^{-1})[22] and are therefore assigned accordingly. Two bands in the C-F stretching region occur at 1450 and 1545 cm^{-1} and are assigned to the ν_4 and ν_3 modes (1410 and 1514 cm^{-1} in the parent).

A 678-cm^{-1} frequency appearing weakly in the spectrum

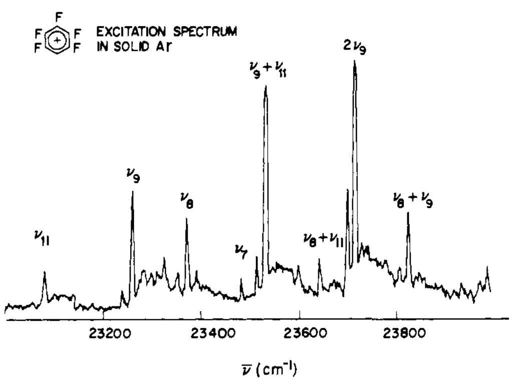

Figure 3. Partial excitation spectrum of $C_6HF_5^+$. Vibrational assignments for the stronger bands are shown. The 0-0 band at 22 810 cm^{-1} was monitored.

Table II. 1,2,3,5-$C_6H_2F_4^+$ Vibrational Frequencies[a] (C_{2v} Symmetry)

a_1 species	X, solid Ar	B, solid Ar	B, gas	parent, $C_6H_2F_4$
ν_1				3090
ν_2		1582		1642
ν_3		1536		1531
ν_4				1384
ν_5		1263	1264	1249
ν_6				1130
ν_7				1002
ν_8		783		789
ν_9	586	576	569	580
ν_{10}	429	431	426	443
ν_{11}	307	307	303	305

[a] In reciprocal centimeters. Parent frequencies were from ref 24; gas-phase data were from ref 23.

Table III. $C_6HF_5^+$ Vibrational Frequencies[a] (C_{2v} Symmetry)

a_1 species	X, solid Ar	B, solid Ar	B, gas	parent, C_6HF_5
ν_1				3105
ν_2				1648
ν_3		1545	1534	1514
ν_4		1450	1452	1410
ν_5				1286
ν_6				1075
ν_7		678		718
ν_8		567	572	578
ν_9	462	455	450	470
ν_{10}				325
ν_{11}	284	273	265	272

[a] In reciprocal centimeters. Parent data were from ref 22; gas-phase data were from ref 23.

Table IV. $C_6F_6^+$ Vibrational Frequencies[a]

species	X, solid Ar	B, solid Ar	B, gas	parent, C_6F_6
a_{1g}				
ν_1		1561		1494
ν_2	557	547	534	562
e_{2g}				
ν_{15}		1603		1659
ν_{16}		1196		1159
ν_{17}	444	428	426	445
ν_{18}	300	270	270	272
?		640	614	

[a] In reciprocal centimeters. Vibrational mode labeling was based on D_{6h} symmetry. Parent data were taken from ref 25 and 26. Gas-phase data were taken from ref 23.

can be assigned to ν_7 (690 cm^{-1} in the parent). Frequencies of 462 and 284 cm^{-1} derived from the emission spectrum are clearly the ground-state counterparts of ν_9 and ν_{11}. The results are compiled in Table III.

4. Hexafluorobenzene. The hexafluorobenzene vibrational structure has already been briefly discussed in a previous communication.[19] The two vibrations totally symmetric in the D_{6h} structure—ν_1, the C–F stretching, and ν_2, the ring "breathing" vibrations—are easily assigned to the relatively strongly occurring 1561- and 547-cm^{-1} intervals. Particularly prominent are progressions in 428- and 270-cm^{-1} vibrations, which are clearly the e_{2g} ν_{17} and ν_{18} vibrations, only weakly shifted from the parent hexafluorobenzene frequencies of 445 and 272 cm^{-1}, respectively.[25,26] The same two vibrations also appear in the emission spectrum at 444 and 299 cm^{-1}, respectively. The remaining two e_{2g} modes, ν_{15} and ν_{16}, also occur weakly in the excitation spectrum at 1603 and 1196 cm^{-1} (1659 and 1159 cm^{-1}, respectively, in the parent compound). The only remaining band not fitting into the above pattern is a weak feature at 22 012 cm^{-1}. This may be due either to some 640-cm^{-1} fundamental or to an overtone or combination band involving non-totally-symmetric vibrations.

4. Vibrational Structure and the Jahn–Teller Effect

The fluorobenzenes studied in this manuscript differ by their symmetry properties. Since the short lifetimes and high intensities associated with the observed spectra suggest a fully allowed electronic transition in all the species, one might expect the totally symmetric modes to be dominant. While in the C_{2v} symmetry $C_6HF_5^+$ and 1,2,3,5-$C_6H_2F_4^+$ species all the 11 a_1 modes are formally allowed, six a_g vibrations should be observed in the D_{2h} symmetry 1,2,4,5-$C_6H_2F_4^+$ and only two a_{1g} vibrations should appear in the D_{6h} symmetry $C_6F_6^+$. Actually, we observe that all of the spectra are of comparable complexity, with some four–five vibrations appearing with appreciable intensity in each spectrum.

Of particular interest is the spectrum of $C_6F_6^+$ where the low-frequency ν_{18} and ν_{17} e_{2g} modes actually occur with intensities considerably higher than the "totally symmetric" ν_1 and ν_2 (Table IV). The transition has a ≈30-ns lifetime in the gas phase[20] and is apparently fully allowed. The strong appearance of the e_{2g} modes suggests, specifically, that the "effective" symmetry governing the spectrum is D_{2h}. The lowest electronic state of $C_6H_6^+$ and that of its perfluorinated counterpart are believed[27] to arise from the parent by removal of an electron from the e_{1g} orbital. The Jahn–Teller effect in the resulting doubly degenerate $^2E_{1g}$ state is expected to result in just such an in-plane distortion, reducing the symmetry to D_{2h}. Some evidence to support this was found by the study of the C_6H_6 Rydberg states and photoelectron spectra.[28-30] The present experiments give clear evidence that similar distortions occur also in the perfluorinated benzene cation.

It is interesting to note that, in all of the fluorobenzenes studied, progressions in several low-frequency ring-deformation vibrations appear in the spectrum. The appearance of progressions in an electronic transition is controlled by the overlap integrals. In order to get favorable Franck–Condon factors for the appearance of a progression, there must either be a change in the shape of the appropriate potential surface with a resulting change in the vibrational frequency or a displacement in the equilibrium geometry along the associated normal coordinate. In the present case of the fluorobenzenes, there is very little change in the vibrational frequencies associated with the transition, and the excited-state frequencies are close to their ground-state values. We must therefore conclude, from the appearance of moderately long progressions (three–four members) in the deformation vibrations, that a distortion of the benzene ring occurs in the transition.

In addition to the small changes in the vibrational frequencies associated with the observed electronic transition in the fluorobenzene cations studied, there is also remarkably little change compared with the corresponding frequencies in the parent compounds. The ground and first excited state of the cation species are believed to be due to removal of an electron from the e_{1g} or a_1 orbital, respectively, of the neutral molecules. While both of these orbitals have a bonding character, the overall bonding energy and potential are apparently not strongly affected.

5. Spin Orbit Splitting

Relatively little is known about the spin orbit splitting in degenerate electronic states of polyatomic molecule systems. Several theoretical works,[31,32] while arriving at numerically differing results, reach a similar qualitative conclusion that even in states with nonquenched angular momentum the splitting is probably small. For splittings smaller than 10 cm^{-1} both of the fine structure components should be thermally populated even at the 4–7 K temperatures used in this study, and we should observe the appropriate transitions originating on the upper component in the excitation spectrum. Similarly, emission could occur into both ground-state sublevels and one could see the corresponding doublets in the emission spectrum. Yet, up to ≈ 300 cm^{-1} where the vibrational structure in the emission spectrum sets on, we observe no bands attributable to the higher fine structure component. While above 300 cm^{-1} the splitting could conceptually be masked by the vibrational structure, spin orbit splitting of this magnitude appears quite unlikely. It would thus appear that both of the fine structure components must be contained within the 2-cm^{-1} line width and the spin splitting is small.

6. Formation of the Cations

The photoelectron spectra of benzene and fluorobenzenes have been studied extensively, and their gas-phase adiabatic ionization energies are therefore well known. The first ionizing transition in all these compounds is located[33] between 9 and 10 eV; the 10.2-eV energy contained in the 1216-Å radiation is therefore quite adequate to accomplish the ionization. In several experiments an Xe lamp with MgF_2 window was used instead. This lamp emitting mainly the Xe resonance radiation at 1470 Å produced the ions with comparable efficiency. Since the 8.4-eV energy in this radiation is insufficient for ionization of the gas-phase molecules, this observation provides evidence for a strong shift accompanying ionizing transitions in solid matrices.

The energy of the radiation used is, of course, in each case also sufficient to accomplish fragmentation of the parent molecule. The cage effect in the solid matrix will in general tend to reduce the relative importance of the dissociative channel, in particular in the case of the hexafluorobenzene and other compounds not containing hydrogen. Hydrogen, on the other hand, is known to diffuse with relative ease through the solid rare gases and it is possible that phenyl radicals and other fragments are also formed in our samples. It is one of the advantages of the laser fluorescence techniques that one can selectively excite and study a specific component of a complex mixture.

We have also attempted to generate the 1,2,3,4-tetrafluoro and 1,3,5-trifluorobenzene radical cations, which are also known to relax in the gas phase via radiative channels. It is possible that an efficient dissociative process in these species competes successfully with the photoionization and is responsible for our failure to observe their spectra. We have actually searched briefly for the neutral fluorobenzene radicals and recorded the absorption spectra of the photolyzed samples. The visible absorption spectra of the phenyl and *o*-, *m*-, and *p*-fluorophenyl radicals were some time ago observed by Porter and Ward.[34] While the more highly substituted fluorophenyls were not reported, they should also absorb in the visible range. Yet our search gave in each case negative results. We should, however, note that, while the laser excitation spectra of the ions gave typically a S/N ratio of 10^3 or better, we have never observed these in absorption either, and even the strong 0-0 band must thus be in each case less than 2% absorbing in our matrix samples. This just demonstrates the high sensitivity of laser excitation spectra when compared with absorption studies. A search for the radicals using the laser fluorescence technique might be worthwhile.

Of interest would also be the fate of the electron ejected from the fluorocarbons. Unfortunately our spectra give no indication as to the identity of the counterion maintaining the overall electroneutrality of the sample. This is a difficulty common to most studies of matrix isolated ions. We can only speculate that the matrices may contain solvated free electrons, or more probably the electrons may attach either to another parent fluorobenzene, or to an impurity. Free electrons in solid Ar appear to lose their energy[35] over a length of 100–1000 Å, so that the electron from the ionized species can easily attach to another fluorobenzene even in highly dilute samples. The corresponding fluorinated benzene anions have actually been observed in adamantane matrix using EPR spectroscopy.[36] Similar EPR studies of photolyzed rare gas matrices containing fluorobenzene could provide useful information.

7. Effects of the Environment

The spectroscopy of the guest molecule in solid matrices is controlled by the guest–host interaction potential. The potential describing this interaction will be in general different for different electronic states of the guest molecule, and the difference will appear as a gas-matrix shift of the electronic transition energy. The overall interaction energy of a neutral molecule with the inert rare gas medium is usually small, and accordingly one observes that the gas-matrix shifts rarely exceed 1–2%.

In principle, the guest–host interaction may differ also for different vibrational states of the guest; i.e., the solid environment may modify the vibrational potential function of the guest. Such changes are usually found to be insignificant for the weakly interacting neutral molecules, and the vibrational frequencies of the matrix isolated molecules are very close to the free molecule values.

In contrast to the weakly interacting neutral species, the solvation energies of ions are even in the rare gas solids quite high. While direct measurements of this interaction energy for the compounds studied here are not available, the ionization potentials of several small organic molecules in rare gas solids were recently measured. These are lowered in the solid by an amount roughly equal to the sum of the solvation energies of the cation and of the ejected electron. For instance, for C_2H_4 in solid Ar, Kr, and Xe, these energies were found[35] to be in the range of 1.5–2.5 eV. In view of these strong interactions, the question of the extent to which our spectra of ionic species are perturbed by the solvent is of interest. This is particularly important since the infrared spectra of numerous matrix isolation cations were recently reported but comparisons with the gas phase could not be made because of the unavailability of any gas-phase data.

In the present case, the gas-phase transition energies are available both from photoelectron spectra and from recent optical studies. In Table V we compare the T_0 values derived

Table V. Comparison of the Gas-Matrix T_0 Shifts of Fluorobenzene Cations with Small Neutral Molecules

compd	transition	solid Ar	gas	$\Delta\nu$	%
$C_6F_6^+$	X → B	21 372	21 606	−234	−1.08
$C_6HF_5^+$	X → B	22 810	23 096	−286	−1.24
1,2,3,5-$C_6H_2F_4^+$	X → B	24 072	24 440	−368	−1.51
1,2,4,5-$C_6H_2F_4^+$	X → B	22 903	23 321	−418	−1.79
CF_2	X → A	37 054	37 220	−166	−0.45
Cl_2	X → A	17 585	17 801	−216	−1.21
ICl	X → B	17 177	17 363	−186	−1.08
Br_2	X → B	15 415	15 891	−476	−3.09

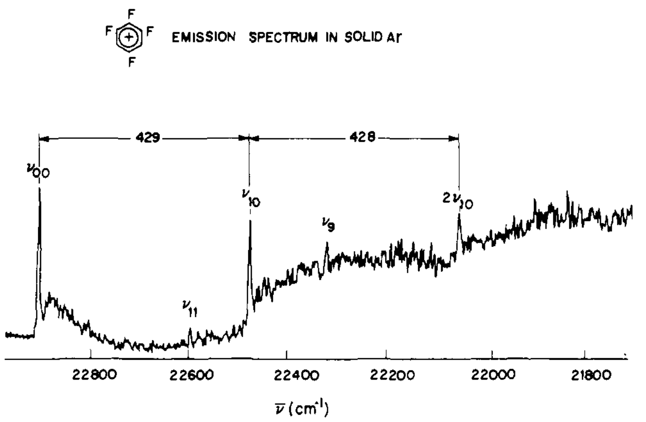

Figure 4. 1,2,3,5-$C_6H_2F_4^+$ emission spectrum in solid Ar at ≈5 K. The laser was in resonance with the 10_0^1 transition at 23 335 cm^{-1}.

from our matrix spectra with their gas-phase values. For comparison, analogous data for several small neutral molecules are also given in Table V. The shifts increase from 1% for $C_6F_6^+$ to 1.8% for $C_6H_2F_4^+$. These shifts are not significantly larger than those encountered for small neutral molecules, and in fact for numerous neutral molecules considerably larger shifts have been recorded. The relatively small shifts observed for the ionic species indicate that, while the ion-host interaction may be rather large, it is similar in both electronic states involved in the transition. This can perhaps be understood, since the transition simply interchanges electrons between the a_1 and e_{1g} orbitals. Both of these are of π bonding character, and the overall bonding energy is not strongly affected.

Examination of Tables I-IV indicates the magnitude of vibrational gas-matrix shifts. In most cases where the gas-phase data is available, it agrees with the matrix frequencies within the experimental uncertainty. While the matrix bands are sharp and the intervals are probably accurate to ±1 cm^{-1}, the gas-phase values are subject to uncertainties of up to ±10 cm^{-1} owing to the large widths and overlapping of some of the vibrational bands. The excellent agreement with the gas-phase values indicates that useful vibrational information can be obtained for strongly bound ionic species from matrix studies.

8. Phonon Line Shapes

The line shapes in the guest spectra are controlled by the guest-host interaction potential. If no change in this potential is associated with the guest transition and no change in the host atom geometry occurs, only a sharp zero-phonon line (ZPL) with no phonon wing will appear in the spectrum. Conversely, if a large change in the equilibrium positions of the lattice atoms is required, i.e., considerable resolvation accompanies the transition, the Franck-Condon factors will favor phonon mode excitation, and a weak zero phonon line with an intense phonon wing will be seen. Typically one finds that different vibrational bands of the same electronic transition exhibit the same line shapes. This reflects the fact that very little change in solvent geometry accompanies vibrational transitions in the guest.

In the excitation spectra of the fluorobenzene cations shown in Figures 1-4, the bands exhibit relatively strong ZPL's with only weak phonon wings. Furthermore, consistent with the above discussion, all the vibronic transitions appear to have similar band shapes. The spectra are indicative of little participation of the lattice, and clearly little rearrangement of the solvent takes place upon excitation.

Ordinarily, line shapes in the emission spectra closely match those observed in absorption. The appearance of the emission spectra of the fluorobenzene cations is unusual in this respect. While the 0-0 bands in emission have the expected line shape, this is not true for the excited vibrational levels. This is clearly visible in the emission spectrum of 1,2,3,5-$C_6H_2F_4^+$ in Figure 4. The first member of a progression in a 426-cm^{-1} frequency exhibits an extremely intense phonon wing extending more than 400 cm^{-1} red, while for the second member the wing is even more extensive. The presence of the strong phonon sidebands unfortunately obliterates the ground-state vibrational structure at higher energies. A similar situation prevails also for the other cations, and for this reason less vibrational information was obtained for their ground electronic states. The implication is that vibrational excitation in the ground electronic state requires extensive rearrangement of the argon matrix atoms. This should also result in the appearance of phonon wing in the purely vibrational spectrum of these cations. An infrared spectroscopic study of these ions in solid argon should therefore be very interesting. The underlying physical reasons for this effect are not well understood at this moment, but it is possible that the proximity of the second component of the degenerate ground state is involved. It should, however, be noted that this behavior is similar in the $C_6F_6^+$ $^2E_{1g}$ state and in the less symmetric fluorobenzenes where the degeneracy is split.

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Tests of the Pseudophase Model of Micellar Catalysis: Its Partial Failure[1]

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Abstract: Acid hydrolyses of *p*-nitrobenzaldehyde acetals are effectively catalyzed by micelles of tetradecanesulfonic acid (**1a**) and p-$ROC_6H_4SO_3H$, R = C_8H_{17} and $C_{12}H_{25}$ (**1b,c**, respectively). The kinetic forms are explained quantitatively in terms of reactions in the aqueous and micellar pseudophases, and the effects of added HCl can be explained qualitatively in these terms. Conductivity measurements show that ca. 75% of the hydrogen ions are bound to micelles of **1c**, and the second-order rate constants in the micellar pseudophase are in the range expected from earlier experiments using mixtures of HCl and sodium lauryl sulfate. The pseudophase model fails for reactions of 2,4-dinitrochlorobenzene and -naphthalene in p-$C_8H_{17}O_6H_4CH_2NMe_3OH$. The results can be explained by assuming that reaction occurs between reactants in the aqueous and micellar pseudophases, and also between OH^- in water and substrate in the micelle.

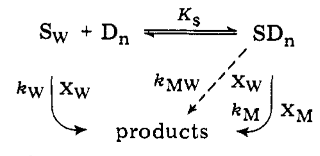
Micellar catalysis in water is generally rationalized in terms of reaction occurring either in the micellar or aqueous pseudophase.[3] The first quantitative application of this model was to the inhibition of ester saponification by anionic micelles,[8] and later to catalysis of the spontaneous hydrolyses of dinitrophenyl phosphates[9] and sulfates[10] by cationic micelles.

For micellar catalyzed bimolecular reactions it is necessary to consider the distribution of both reactants between the aqueous and micellar pseudophases (Scheme I).

In Scheme I and eq 1, S denotes organic substrate, D_n micellized surfactant (detergent), and K_s the binding of S to D_n. (The bracketed quantities are reactant concentrations in moles per liter of solution, the subscripts W and M denote water and micellar pseudophase respectively, m_X^s is the mole ratio of bound X to micellized surfactant, and k_M is the related second-order rate constant.[11])

Most models of micellar catalyzed reactions assume that the overall rate of reaction is the sum of the rates in each pseudophase, and that changes in rate with increasing surfactant concentration or added salt, for example, reflect changes in the distribution of reactants between the pseudophases. Other models also consider potential effects due to changes in the micellar surface charge on the initial and transition state free energies in the micellar pseudophase.[5a] A possible reaction path which has not been considered previously, and which we are now postulating, is reaction across the interfacial boundary, in this case, reaction between micellar bound organic substrate and an ionic reactant in the aqueous pseudophase, with a rate constant, k_{MW}, indicated by the broken line in Scheme I.

Scheme I



$$\text{rate} = k_W[S_W][X_W] + k_M[SD_n]m_X^s \qquad (1)$$

The pseudophase kinetic model has been applied successfully to a number of micellar catalyzed bimolecular reactions between nonionic reactants,[11] and with partial success to reactions between neutral organic substrates and hydrophobic anionic nucleophiles.[6,12] The model correctly predicts the rate maxima which are typically observed with micellar catalyzed bimolecular reactions. However, it has not been tested extensively for micellar catalyzed bimolecular reactions involving hydrophilic ions, except for reactions involving hydrogen ions[13] and nucleophilic addition to carbocations.[14]

Much of the kinetic work on micellar catalyzed reactions involving hydrogen or hydroxide ions has been done in buffer solutions, and often with added salts.[5] Ionic micelles perturb buffer equilibria,[15] and added salts may introduce further complications, for example, by lowering the critical micelle concentration (cmc), reducing the surface potential, increasing micelle size, and generally reducing reaction rates.[5-7] To test the simple kinetic model for reactions with hydrophilic reactants we needed a micellar system which avoided, or at least minimized, these complications.

The pseudophase model explicitly assumes that changes in micelle size and shape are not very important, so that only those factors which control the distribution of reactants will significantly affect the observed reaction rate. Buffer effects are particularly difficult to interpret, so we selected reactions which would not require use of buffers. Finally, the presence of both reactive and unreactive counterions results in uncontrolled variations in distribution of the counterions between the micellar and aqueous pseudophases with concomitant changes in micelle surface potential and the cmc further complicating the interpretation. However, even with all these problems, both the rate maxima in the rate-surfactant concentration profiles

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