2618 *J. Phys. Chem. A* **1999,** *103,* 2618−2623

Photoinduced Rydberg Ionization (PIRI) Spectroscopy of the $\tilde{B}$ State of the Fluorobenzene Cation

Richa Anand, Jeffrey E. LeClaire,[†] and Philip M. Johnson*,[‡]

Department of Chemistry, The State University of New York at Stony Brook,
Stony Brook, New York 11794-3400

Received: December 10, 1998; In Final Form: February 1, 1999

Vibrationally resolved PIRI spectra of the $\tilde{B}$ state of the fluorobenzene cation via the origin, 16a, 6b, and 11 vibrational modes in the ground ionic state require a reassignment of the accepted state symmetry. On the basis of lower resolution studies, the $\tilde{B} \leftarrow \tilde{X}$ transition has been previously assigned as an electronically forbidden $^2B_2 \leftarrow {}^2B_1$ transition. Vibrational analyses of the spectra observed via various ground-state nonsymmetric vibrations, particularly from the 16a vibrational mode, unambiguously locate the origin of the transition at 21 075 cm^{-1}, resulting in the reassignment of the ionic state as $^2B_1$. Ab initio calculations, while not conclusive, also suggest that the $\tilde{B} \leftarrow \tilde{X}$ transition is an allowed π to π transition.

Introduction

Excited states of polyatomic molecular ions have been of great interest because their study provides information about occupied molecular orbitals, among other reasons. Assignment of these states is essential to confirm the accuracy of electronic structure calculations and is fundamental to our understanding of molecular bonding. In many cases in the past, spectroscopic studies have been hampered by either poor resolution or lack of selectivity which prevented unambiguous analysis of the excited ionic states. Here we address the issue of the symmetry assignment of the second excited state (the $\tilde{B}$ state) of fluorobenzene cation, a molecule which provides insight into the perturbative effects of substitution of a strongly electronegative fluorine atom onto the benzene ring.[1]

Numerous photoelectron spectroscopy (PES)[2] studies have attempted to assign the state symmetries of the excited states of the fluorobenzene cation but were hampered by a lack of vibrational resolution in most bands. Various other low-resolution studies have also been performed in an effort to elucidate the state ordering of these ionic states, for instance, Penning ionization electron spectroscopy (PIES)[3] and emission spectroscopy.[4] It has been inferred that symmetry of the $\tilde{B}$ state is $^2B_2$, which leads to an electronically forbidden transition from the $\tilde{X}$ state ($^2B_1$). However, due to the proximity of the $\tilde{B}$ and $\tilde{C}$ states, the assignment of the $\tilde{B}$ state is difficult. The most convincing arguments are based on fluorescence emission studies,[4] which have indicated that the $\tilde{B}$ state of fluorobenzene cation is a half-filled $^2B_2$ σ-state corresponding to the conclusively assigned σ-state appearing approximately at the same energy in the benzene cation. This conclusion stems from the observation that the fluorescence quantum yield of the ion is very small ($<10^{-5}$), similar to that of benzene, in which the $\tilde{B}$ state does not fluoresce. Fujii et al.[5] have also assigned the second excited ionic state to be a σ-state, based on mass-selected ion dip spectroscopy. An alternate assignment, indicated to be possible from ab initio calculations, is that of a $^2B_1$ π state since the two states (π and σ) are very close in energy.

The ground state of fluorobenzene cation (IP$_0$ = 74 229 cm^{-1}) has been studied by Brustchy et al.[6] using mass analyzed threshold ionization (MATI) spectroscopy, and a few vibrational modes of the ground ionic state have been well-defined. A few vibrational modes in the ground ionic state have also been characterized by resonance-enhanced two-photon ionization spectroscopy.[7] Interestingly, dimers and larger clusters of fluorobenzene with other molecules have been well studied by other workers in the ground ionic state,[8] but those studies do not report the vibrational spectrum of the ground ionic state of uncomplexed fluorobenzene.

A vibrationally resolved spectrum of the $\tilde{B} \leftarrow \tilde{X}$ transition has been obtained by Walter et al.,[9] using the technique called resonance enhanced multiphoton dissociation spectroscopy (REMPDS). The REMPDS technique was initially developed by Boesl et al.[10] to study the excited ionic state of the benzene cation and has also been applied to various other molecular ions. In REMPDS, ions are created in the ground ionic state by two-photon excitation from the neutral ground state, while a second tunable photon causes a resonant multiphoton excitation of ions leading to dissociation. The presence of fragment ions thus produced indicates cationic resonances as the second photon is scanned through appropriate wavelengths, creating an electronic spectrum. A REMPD spectrum can attain much greater resolution than PES but is complicated by hot band structure due to nonselectivity in the ion creation.

Another technique to obtain vibrationally resolved spectra of the cations in the excited electronic states has been developed in our laboratory, photoinduced Rydberg ionization (PIRI) spectroscopy. The PIRI technique has been successfully applied to the $\tilde{B}$ state of the benzene cation[11] as well as the phenol cation[12] and has been discussed in detail in the previous papers. In short the PIRI technique utilizes the long-lived Rydberg states converging to various ionization thresholds as the intermediate states to access the higher electronic states of the ion. PIRI relies on the fact that the Rydberg electron interacts very little with the optical radiation; hence, the absorption cross sections for a Rydberg molecule correspond almost exactly to those of the bare ion.

[†] Present address: Sandia National Laboratory, Livermore, CA 94551.
[‡] Electronic mail: Philip.Johnson@sunysb.edu.

10.1021/jp984697a CCC: $18.00

In the PIRI technique used here, after Rydberg molecules are created by a two color laser excitation, and any prompt ions have been spatially separated from the neutral molecules (as in MATI,[13] which is a precursor to the PIRI method), a third tunable laser beam (PIRI laser) is sent coaxially down the molecular beam to irradiate the Rydberg molecules. This results in core-excited Rydberg molecules and then rapid autoionization when the laser is tuned to a cation transition. The group of ions formed from autoionization (parent PIRI ions) are spatially separated from the remaining Rydbergs with a small electric field and then detected separately in a mass spectrometer. The high-resolution spectrum of the electronically excited state is obtained by scanning the PIRI laser while monitoring the production of PIRI ions.

An alternative to separating the PIRI cations from the remaining Rydbergs is to create a resonant multiphoton transition of the core, dissociating the cation and simultaneously causing autoionization. Fragment ions are then detected in mass channels free from any background interference cause by spontaneous autoionization (called fragment PIRI).[12]

The PIRI technique has a distinct advantage over REMPDS since it utilizes the neutral Rydberg molecules as intermediate states to access the excited electronic state of the ion. Therefore, the vibrational spectrum of the excited ionic state can be acquired cleanly via different vibrational levels of the ground ionic state. Moreover, utilization of Rydbergs in the ground ionic state negates the possibility of most hot band structure and PIRI spectra from single lower vibrational quantum states can be obtained.

The only vibrationally resolved spectrum of the $\tilde{B}$ state of the fluorobenzene cation has been the REMPD spectrum acquired by Walter et al.[9] Their vibrational assignment was based on the previous characterization of the state as having a vacancy in a σ orbital (because no fluorescence is observed) and the transition is therefore a forbidden $^2B_2 \leftarrow {}^2B_1$ excitation. On the basis of this electronic assignment of the $\tilde{B}$ state, the 16a and 17a vibrational modes of a_2 symmetry were used as the inducing modes for the $\tilde{B} \leftarrow \tilde{X}$ transition with symmetric (mainly 6a) vibrational modes built on them. Almost equally well, however, the spectrum acquired by Walter et al. can be assigned as an allowed transition by eliminating the 16a or 17a vibrational modes from each assignment. This vibrational analysis therefore does not uniquely establish the symmetry of the $\tilde{B}$ state.

Theoretical calculations to back the assignment of the $\tilde{B}$ state of the fluorobenzene cation have been nonexistent. The vibrational modes of the first excited neutral state (S_1) have been assigned,[14] and on the basis of that, a few vibrational modes of the ground ionic state have been characterized.[6]

The assignment of the $\tilde{B}$ state in the REMPD spectrum[9] is made quite difficult by the presence of the hot band structure. Due to ambiguity of previous assignments it was desirable to measure the vibrationally resolved cold PIRI spectrum of the $\tilde{B}$ state of the fluorobenzene cation via different vibrational levels of the ground ionic state. The acquired PIRI spectra clearly indicate that absence of fluorescence emission is not an adequate criterion to establish the symmetries of excited ionic states. From the vibrationally resolved cold PIRI spectra of the $\tilde{B}$ state and higher level ab initio calculations, we present here a possible state ordering of the lower excited ionic states of the fluorobenzene cation. Results and the analysis of the data indicate that the $\tilde{B} \leftarrow \tilde{X}$ transition is an allowed π to π transition.

Experimental Section

The apparatus used to obtain the PIRI spectrum of the fluorobenzene cation is similar to that used for a previous experiment on phenol and has been described in detail.[12] It consisted of two differentially pumped vacuum chambers. The source chamber contained two 2400 L/s (air) diffusion pumps, a 3 mm diameter skimmer, and a variable-temperature pulsed nozzle (300 μm orifice diameter). The sample chamber contained a Wiley−McLaren type, time-of-flight (TOF) mass detection system and a single 1500 L/s (air) diffusion pump. The molecular beam of fluorobenzene was created by heating a sample cell containing fluorobenzene, seeded into He gas with a backing pressure of about 3.5 atm. Both the sample container and the pulsed nozzle were heated to temperatures between 50 and 65 °C. Typical source chamber pressure was $(1-2) \times 10^{-5}$ Torr, and that in the ionization region was between 7×10^{-7} and 2×10^{-6} Torr.

Coumarin 522B dye was used in a Quanta-Ray PDL1 dye laser to resonantly excite the molecule to its respective S_1 state. Fluorescein 548 dye in a Lambda-Physik FL2002 dye laser was then used to create Rydbergs converging to the origin and different excited vibrational states in the ground ionic state of the cation. Both dye lasers were pumped with a single Nd:YAG laser. To record the PIRI spectra of the $\tilde{B}$ state of the cation, various dye outputs in the wavelength range covering approximately 425−513 nm were used in a Lumonics HyperDYE-300 laser pumped by a Lumonics XeCl excimer HyperEX-400 laser. Typically, the frequency doubled output power for both Rydberg preparation lasers was 0.5−1.5 mJ/laser shot. The visible output power obtained from the third PIRI laser was typically 8−10 mJ/laser shot. The PIRI laser light was gently focused down the molecular beam to avoid any fragmentation of the prepared Rydbergs in the ground ionic state of the cation, facilitating the acquisition of the parent PIRI spectrum. A reflection of the third laser beam was sent to a hollow cathode discharge lamp containing neon, and the optogalvanic effect used for wavelength calibration. Each of the dyes used to obtain the PIRI spectra were calibrated against the neon absorption lines to within an error of about 1 cm^{-1}.[12]

The voltage separation scheme used in the PIRI technique to separate and detect the three packets of ions in the ionization region has been described in detail previously.[11,12] However, to acquire better separation of the prompt ions from Rydbergs before the third PIRI laser was focused in the ionization region, a slightly different voltage separation scheme was used. This also facilitated minimizing the background signal that was observed in the same mass channel as the PIRI ions formed by autoionization. An initial separation voltage of −20 V for 1 μs and then −10 V for another 1 μs was applied to separate prompt ions from the Rydbergs. After a third (PIRI) laser created autoionization, the resulting PIRI ions were then separated from the rest of the ion packets by applying +10 V for 2 μs before the extraction of all three into the TOF tube.

Electronic structure calculations, including geometry optimization, population analysis, and normal mode calculations, were all done using GAUSSIAN 94[15] and Q-Chem 1.1.[16] Using Gaussian, density functional theory (B3LYP) calculations using a 6-31G** basis set and second-order Møller−Plesset theory (MP2) using a 6-31G basis set were done both on the ground ionic state ($^2B_1$) and the first excited σ state ($^2B_2$), keeping the ion in C_{2v} symmetry. As usual for this type of calculation, it was not possible to examine any excited state of the same symmetry as the ground ionic state using simple Hartree−Fock methods. To determine state ordering, configuration interaction-

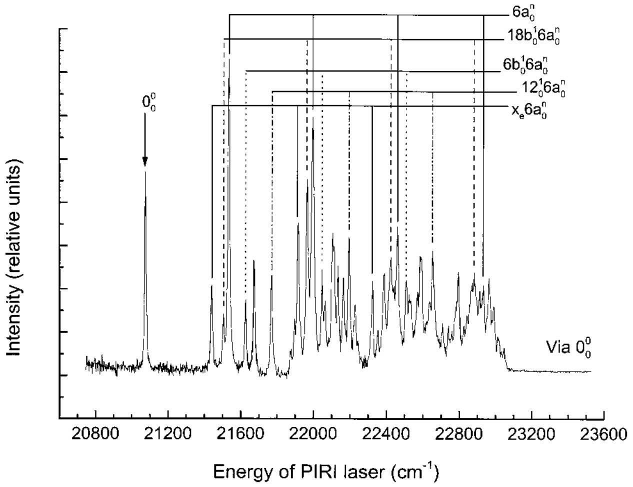

Figure 1. PIRI spectrum of the $\tilde{B}$ state of fluorobenzene cation via the origin of the ground ionic state. The *x*-axis is the excess energy of the PIRI laser above the ground ionic state in cm^{-1}.

singles (CIS) method was employed, using a 6-31G basis set. Using Q-Chem, extended CIS on a restricted open-shell system (XCIS) was also performed.

A note should be made about the vibrational numbering used here. We are using the Wilson notation for the numbering, in which the modes are supposedly correlated with those of benzene to establish the labeling. Unfortunately, for most substituted benzenes the calculated normal modes are significantly different from benzene modes, and thus it is impossible to make a unique correlation. Without the benefit of modern calculations, the ground-state neutral vibrations of most molecules have been numbered, apparently mostly by comparing the symmetry and frequencies of the vibrations to those of benzene. In many cases, the choices probably would not have been made the same way if the eigenvectors of the modes had been available. An example is the mixture of the 6a and 1 vibrations. In C_{2v} these are both totally symmetric, and in fluorobenzene the lower frequency of the two looks more like benzene's 1 mode. However, this is labeled 6a historically because in benzene 6a has lower frequency than 1. Rather than try to correct the situation, which could lead to confusion, we have adopted the historic numbering derived from the neutral ground-state assignments, even if the modes are quite different motions than in benzene.

Despite these problems we still feel that the Wilson notation is more useful than the Herzberg notation because one is able to do at least some valid correlation between substituted benzenes of different symmetry, and the entire numbering scheme does not change with changes in a single symmetry assignment.

Results and Discussion

The PIRI spectrum of the $\tilde{B}$ state was recorded via the origin of the ground ionic state ($\tilde{X}$ state) of the cation, as shown in Figure 1. The PIRI spectra of the $\tilde{B}$ state of the fluorobenzene cation was also recorded via the 16a, 6b, and 11 vibrational modes of the ground ionic state, as shown in Figure 2. In the PIRI spectrum of the fluorobenzene cation, the observed progression is not long and anharmonic, as was observed in case of phenol cation,[12] and thus does not indicate a major geometry change in the $\tilde{B}$ state of the cation. However, with an increase in the energy, the vibrational structure observed becomes much more dense as compared to that at lower energy. The width of the vibrational peaks is in the approximate range of 10−12 cm^{-1}.

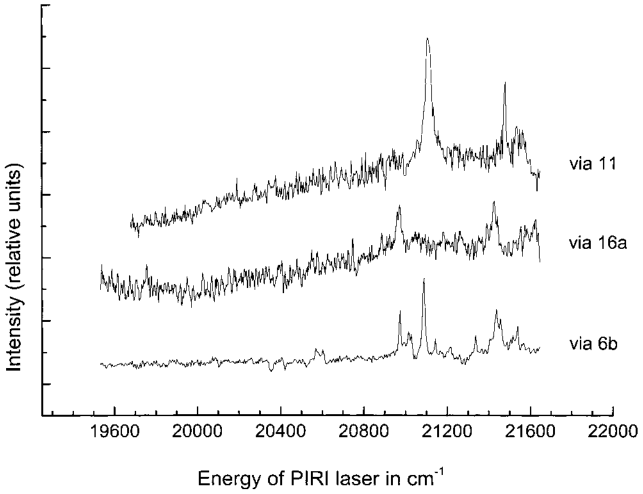

Figure 2. PIRI spectra obtained for the $\tilde{B} \leftarrow \tilde{X}$ transition in the fluorobenzene cation via the 6b, 16a, and 11 vibrations in the ground ionic state.

An interesting aspect of the PIRI spectra via the16a and 6b ground-state vibrations is that it was possible to use the parent PIRI technique, as opposed to the phenol case where only fragment PIRI was successful. It was previously thought that the parent PIRI technique may be impossible in substituted benzenes via these excited vibrational levels because of rapid vibrational autoionization.[11] These parent spectra indicate the ample stability of the Rydberg levels of fluorobenzene, which gives the best PIRI signals of any molecule studied to date.

The vibrationally resolved selective PIRI spectra provide a means of reassessment of the symmetry of the $\tilde{B}$ state. If the assignment is assumed to be of $^2B_2$ symmetry,[9] as was assigned previously, then the first vibrational peak observed in the origin-resonant spectrum at 21 075 cm^{-1} would have to be a 16a inducing mode. This has a symmetric vibrational progression built upon it. The origin of the $\tilde{B}$ state should not be observed when making a transition via the origin of the ground ionic state ($\tilde{X}$ state of $^2B_1$ symmetry) to the excited state of $^2B_2$ symmetry. PES studies[2] predicted the origin of the $\tilde{B}$ state at 20 800 cm^{-1}, which gives the value of the 16a vibrational mode in the excited state to be 195 cm^{-1}. This is fairly low as compared to the value in the ground state of the cation and also compared to the value obtained for the excited state of the benzene cation (226 cm^{-1}).[9] From a MATI spectrum acquired in our laboratory during this study, the value of the 16a vibrational mode in the ground ionic state was found to be 341 cm^{-1}, agreeing very well with the calculated value (Table 1).

Using PIRI, the $\tilde{B}$ state assignment could easily be checked. The vibrationless level in an electronically forbidden transition from the $\tilde{X}$ state should be observed at about 20 800 cm^{-1} above the vibrationless ground electronic state (from PES)[2] while making transitions from the 16a (a_2 symmetry), 6b (b_2), and 11 (b_1) vibrations of the ground state of the cation, particularly from the 16a vibrational mode. However, no peaks at or near the appropriate positions were observed via any of these excited vibrational states of the ground state. This strongly indicates that the $\tilde{B}$ state of the fluorobenzene cation cannot have $^2B_2$ symmetry (see Figure 2).

The PIRI spectrum via the 6b vibration of the ground ionic state shows similar features to the PIRI spectrum obtained via the origin of the ground ionic state, as can be compared from Figures 1 and 2. As in all the spectra, the 6b scan shows a predominant 6a progression and the vibrational features can be assigned by assuming that $\tilde{B} \leftarrow \tilde{X}$ is an allowed transition. The

TABLE 1: Frequency Values Experimentally Observed for the S_1 State,[14] the Ground Ionic State ($^2B_1$ Symmetry),[6,7] and the $\tilde{B}$ State ($^2B_1$ Symmetry) Attained from the PIRI Spectrum and the Values Obtained from Calculations using B3LYP/6-31G and MP2/6-31G for the Ground ($^2B_1$) State of the Cation[a]**

	experimentally obsd vibrational freqs			theoretically obtained freq values for ground ionic state ($^2B_1$)	
	S_1 state ($^1B_2$)	$\tilde{X}$ state ($^2B_1$)[b]	$\tilde{B}$ state ($^2B_1$)	DFT/ 6-31G**	MP2/ 6-31G
1 (a_1)	961.0	983		1147.19	1187.47
6a (a_1)	459.5	500	458	493.12	500.54
6b (b_2)	519.4	505	520	504.12	616.15
8a (a_1)		1619			
9a (a_1)	922.5	1164	1152	959.03	1015.85
10a (a_2)				754.39	723.87
10b (b_1)				583.87	678.53
11 (b_1)	181.9	181	207	181.73	
12 (a_1)	765	795	695	779.92	784.06
16a (a_2)		341[c]	236	345.06	287.77
17a (a_2)				968.17	905.83
17b (b_1)				915.05	840.89
18a (a_1)	916.2	959		938.22	928.64
18b (b_2)	387.2	400	430	388.22	331.90
x_e (b_1)		345	366	394.52	403.48

[a] The calculated frequency values have been corrected for the optimal scaling factor (0.9613 for B3LYP and 0.9427 for MP2). [b] Obtained from Brutschy et al.[6] and Yoshida et al.[7] [c] From the MATI experiment reported here.

peaks observed at 20 568 cm^{-1} and at 21 088 cm^{-1} can therefore be assigned as $6b^0_1$ and $6b^1_1$, respectively. The vibrational feature observed to the right of 20 568 cm^{-1} by 34 cm^{-1} (at 20 602 cm^{-1}) is most likely a band arising from a vibration that gets populated because its absorption overlaps that of 6b in S_1 and D_0. The 6b vibration would be susceptible to that kind of contamination because its frequency hardly changes between S_1 and D_0.[6,14] This vibrational feature has a steady progression in 425 cm^{-1} which could not be assigned.

The PIRI spectra procured via the 16a and 11 vibrational modes show very similar vibrational structure (see Figure 2). The PIRI spectrum via the 16a vibrational mode in the ground ionic state shows a progression in the 6a vibrational mode built on the $16a^1_1$ vibrational feature. The vibrational feature observed at 21 101 cm^{-1} in the PIRI spectrum via the 11 excited vibration can be similarly assigned as an 11^1_1 vibrational transition in an allowed π to π transition. The frequency value obtained for the 11 vibration for the $\tilde{B}$ state is 207 cm^{-1}, close to the values in S_1 and D_0 states.[6] The vibrational structure observed via the 11 vibration at 376 cm^{-1} offset from the 11^1_1 vibration is similar to a vibrational feature observed via the origin at 21 075 cm^{-1}. This can be correlated with a vibrational feature (x_e) observed by Brutschy et al.,[6] in the ground state at 345 cm^{-1} using MATI, but was not assigned. From vibrational calculations, we find that this can be attributed to a C−F stretching mode which does not have an analogous benzene vibration to provide a number for it. This vibrational feature has been termed as x_e in this paper as well and shows a 6a vibrational progression built upon it.

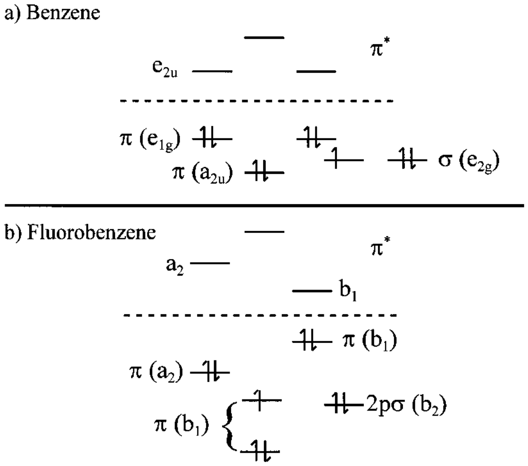

Figure 3. Schematic of molecular orbital diagrams for (a) benzene and (b) fluorobenzene states, including the π, π*, and the highest occupied σ orbitals along with their symmetries. The energy levels in benzene are not drawn to scale.

TABLE 2: Excited-State Energies of the Fluorobenzene Cation Obtained from CIS/6-31G Using Gaussian 94 and XCIS/6-31G Using Q-Chem, along with the Symmetries of States[a]

symm of states	energy values obtained from CIS (eV)	energy values obtained from XCIS (eV)
A_2	1.33	0.22
B_1	3.15	2.78
B_2	4.85	3.24
B_1	4.94	4.68

[a] The theoretically obtained values for the second excited ionic state are high, as compared to the experimental value of 2.62 eV.

To corroborate the results of the vibrational analyses, electronic structure calculations were performed to ascertain the symmetry ordering of the excited states of the cation and determine vibrational information. From the molecular orbital picture of the fluorobenzene cation as shown in Figure 3, it is clear that the $\tilde{B} \leftarrow \tilde{X}$ transition of the cation can be either a π to π transition or a σ to π transition. Configuration interaction of singles (CIS) with a 6-31G basis set was performed with Gaussian to obtain the energy values of the excited ionic states and their respective symmetries. The same state ordering was given by extended CIS (XCIS) using Q-Chem. XCIS includes some doubles excitation and is designed to give better results for open-shell systems. Both of these calculations indicate that there is at least one state of $^2B_1$ symmetry below the first state of $^2B_2$ symmetry in the cation. As usual for CIS methods, the excitation energies obtained for the ionic states are considerably higher than experimental values and are provided in Table 2. Density functional theory (B3LYP/6-31G**) and second-order Møller−Plesset (MP2/6-31G) calculations were also performed to obtain the geometry and frequency values for the ground ionic state of the cation ($^2B_1$ symmetry). The frequency values agree very well with those obtained experimentally by Brutschy et al. using MATI.[6] The calculated frequency values using DFT and MP2 are given in Table 1 along with the values obtained by Brutschy et al.

We were not able to perform geometry optimizations on excited states using CIS methods, apparently because the energy potentials of these ionic states are so intermixed and geometry dependent that geometry optimizations would not converge. More complete CI treatments (for which optimization methods are not available) on the $^2B_1$ excited ionic states were deemed unreliable for state ordering since it was found that the molecular geometry was an important determining factor for this property.

DFT (B3LYP/6-31G**) was also used to optimize and calculate the frequency values for the excited state with $^2B_2$ symmetry. Remarkably, this method produced a double-well potential for this state, with an out-of-plane deformation along the 16a vibration. MP2 calculations did not give such a deformation, and therefore, it could not be determined whether this was anomalous.

TABLE 3: Proposed Assignments of the Vibrational Features Observed in the PIRI Spectrum of the Fluorobenzene Cation

freq value (cm^{-1})	proposed assgnt	dist from the origin (cm^{-1})
Via the Origin of the Ground Ionic State for the $\tilde{B}(^2B_1) \leftarrow \tilde{X}(^2B_1)$ Transition		
21 075	0^0_0	0
21 441	x_e	366
21 505	$18b^1_0$	430
21 533	$6a^1_0$	458
21 626	$6b^1_0$	551
21 673	$10b^1_0$	598
21 770	12^1_0	695
21 915	$x_e6a^1_0$	840
21 966	$18b^1_06a^1_0$	891
21 995	$6a^2_0$	920
22 046	$6b^1_06a^1_0$	971
22 104		1029
22 134		1059
22 163		1088
22 193	$12^1_06a^1_0$	1118
22 227	$9a^1_0$	1152
22 324	$x_e6a^2_0$	1249
22 389		1314
22 424	$18b^1_06a^2_0$	1349
22 459	$6a^3_0$	1384
22 507	$6b^1_06a^2_0$	1432
22 589	$x_e11^1_06a^2_0$	1514
22 653	$12^1_06a^2_0$	1578
22 792		1717
22 881	$18b^1_06a^3_0$	1806
22 930	$6a^4_0$	1855
22 962		1887
Via the 6b Vibration of the Ground Ionic State for the $\tilde{B}(^2B_1) \leftarrow \tilde{X}(^2B_1)$ Transition		
20 568	$6b^0_1$	
20 602		
20 973	$6b^0_118^1_0$	
21 013		
21 026		
21 088	$6b^1_1$	
21 142		
21 336	$6b^0_118^1_0x_e$	
21 436	$6b^0_118b^1_06a^1_0$	
21 455		
21 538	$6b^1_16a^1_0$	
Via the 16a Vibration of the Ground Ionic State for the $\tilde{B}(^2B_1) \leftarrow \tilde{X}(^2B_1)$ Transition		
20 971	$16a^1_1$	
21 425	$16a^1_16a^1_0$	
Via the 11 Vibration of the Ground Ionic State for the $\tilde{B}(^2B_1) \leftarrow \tilde{X}(^2B_1)$ Transition		
21 102	11^1_1	
21 478	$11^1_1x_e$	

All evidence obtained from the electronic structure calculations supports the argument that the $\tilde{B}$ state has $^2B_1$ symmetry and the $\tilde{B} \leftarrow \tilde{X}$ transition can therefore be considered to be allowed with the origin at 21 075 cm^{-1}. Most of the vibrations observed are symmetric in nature (a_1 vibrations which are z-polarized), with the remainder having b_2 symmetry (y-polarized) and b_1 symmetry (x-polarized). A convincing set of vibrational assignments can be made on the basis of the selection rules of spectra from different ground-state vibronic symmetries and the proposition that state vibrational frequencies do not differ greatly from those of the ground ionic state. These are presented in Table 3.

Given a knowledge of benzene's molecular orbitals, those of fluorobenzene can be understood by simply considering the interaction of the fluorine 2p orbitals with the benzene ring orbitals that are similar in energy. By symmetry, the out of plane $2p_x$ orbital interacts only with the ring π system. Energetically, this fluorine orbital is considerably below the lowest ring π-orbital (a_{2u} in benzene) and interacts mainly with it, resulting in bonding and antibonding combinations as shown in Figure 3. Hartree−Fock calculations show that the lower energy bonding combination is comprised mainly of the fluorine orbital, while the antibonding orbital primarily has ring contribution, as shown in Figure 4. The interaction in the antibonding combination is enough to drive the energy of that π orbital above the $2p\sigma$ orbital in that vicinity, which is higher in benzene. However, these orbitals are very close in energy and a Hartree−Fock picture cannot be relied upon to give the proper orbital ordering. The observance of origin of the $\tilde{B}$ state at 21 075 cm^{-1} in the PIRI spectrum clearly indicates that $\tilde{B} \leftarrow \tilde{X}$ is an allowed transition and therefore the antibonding combination of the fluorine $2p_x$ and the ring π orbitals is above the $2p\sigma$ orbitals in that region.

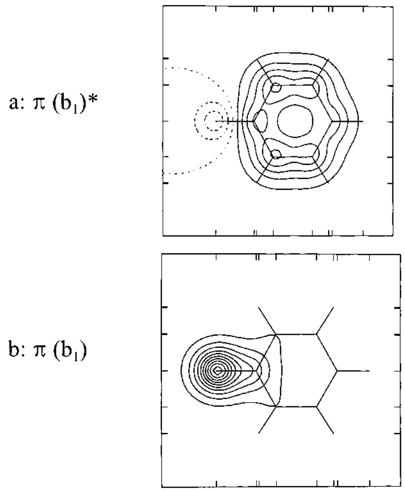

Figure 4. Electron density distributions (0.75 D above the ring) of the orbitals of b_1 symmetry resulting from the interaction of the $2p_x$ fluorine orbital with the lowest π ring orbital, obtained from the Hartree−Fock method. The electron density distributions are not evenly distributed between the fluorine and the benzene ring but are concentrated on opposite individual components for the bonding and antibonding interactions.

Conclusion

Vibrationally resolved PIRI spectra of the $\tilde{B}$ state of the fluorobenzene cation have been acquired via the origin and 16a, 6b, and 11 excited vibrational modes of the ground ionic state ($\tilde{X}$ state). The spectra via nonsymmetric ground-state vibrational modes, particularly 16a, indicate that the $\tilde{B} \leftarrow \tilde{X}$ transition is an allowed transition since line positions do not support a forbidden assignment. This has allowed a reasonably complete vibrational assignment of the spectra.

Electronic structure calculations using CIS/6-31G by Gaussian and XCIS/6-31G by Q-Chem gave a state ordering consistent with the spectral analysis. DFT and MP2 calculations were useful in calculating ionic ground-state frequencies but for excited states gave inconsistent results.

Together, the selectively produced PIRI spectra of the fluorobenzene cation and ab initio calculations clearly propound that $\tilde{B} \leftarrow \tilde{X}$ is an allowed transition, providing a better understanding of the orbital ordering of fluorobenzene, as well as providing assigned vibrational frequencies.

Acknowledgment. This work was supported by a grant from the Department of Energy, Division of Chemical Sciences. We also thank Dr. Claudina Cossart for valuable discussions concerning monohalogenated benzenes.

References and Notes

(1) Wollman, S. H. *J. Chem. Phys*. **1945**, *14*, 123.

(2) (a) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of He (I) Photoelectron Spectra of Fundamental Organic Molecules*; Halsted: New York, 1981. (b) Palmer, M. H.; Moyes, W.; Spiers, M.; Ridyard, J. Neil A. *J. Mol. Struc*. **1978**, *49*, 105.

(3) Fujiswaka, S.; Ohno, K.; Masuda, S.; Harada, Y. *J. Am. Chem. Soc*. **1986**, *108*, 6505.

(4) (a) Allan, M.; Maier, J. P.; Marthaler, O. *Chem. Phys*. **1977**, *26*, 131. (b) Bondybey, V. E.; Miller, T. A. *J. Chem. Phys*. **1979**, *70*, 138.

(5) Fujii, M.; Tscuchiya, Y.; Ito, M. *J. Mol. Struc*. **1991**, *249*, 55.

(6) Lembach, G.; Brutschy, B. *J. Phys. Chem*. **1996**, *100*, 19758.

(7) Yoshida, M.; Lee, S.; Mihara, H.;. Aoyagi, H.; Kato, T. *Mem. Fac. Sci., Kyushu Univ., Ser. C* **1992**, *18*, 161.

(8) (a) Lembach, G.; Brutschy, B. *J. Chem. Phys*. **1997**, *107*, 6156. (b) Djafari, S.; Barth, H.-D.; Buchhold, K.; Brutschy, B. *J. Chem. Phys*. **1997**, *107*, 10573. (c) Shinohara, H.; Sato, S.; Yoshihara, K.; Kimura, K. *J. Elec. Spectrosc. Relat. Phenom*. **1998**, *88*−*91*, 131.

(9) Walter, K.; Boesl, U.; Schlag, E. W. *Chem. Phys. Lett*. **1989**, *162*, 261.

(10) Boesl, U. *J. Phys. Chem*. **1991**, *95*, 2949.

(11) (a) Taylor, D. P.; Goode, J. G.; LeClaire, J. E.; Johnson, P. M. *J. Chem. Phys*. **1995**, *103*, 6293. (b) Goode, J. G.; LeClaire, J. E.; Johnson, P. M. *Int. J. Mass Spectrom. Ion Processes* **1996**, *159*, 49. (c) Goode, J. G.; Hofstein, J. D.; Johnson, P. M. *J. Chem. Phys*. **1997**, *107*, 1703.

(12) LeClaire, J. E.; Anand, R.; Johnson, P. M. *J. Chem. Phys*. **1997**, *106*, 6785.

(13) (a) Zhu, L.; Johnson, P. M. *J. Chem. Phys*. **1991**, *94*, 5769. (b) Johnson, P. M.; Zhu, L. *Int. J. Mass Spectrom. Ion Processes* **1991**, *131*, 193.

(14) (a) Lipp, E. D.; Seliskar, C. J. *J. Mol. Spectrosc*. **1981**, *87*, 242. (b) Lipp, E. D.; Seliskar, C. J. *J. Mol. Spectrosc*. **1981**, *87*, 255.

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Relpogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94 (Revision A.1)*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(16) Johnson, B. G.; Gill, P. M. W.; Head-Gordon, M.; White, C. A.; Baker, J.; Maurice, D. R.; Adams, T. R.; Kong, J.; Challacombe, M.; Schwegler, E.; Oumi, M.; Ochsenfeld, C.; Ishikawa, N.; Florián, J.; Adamson, R. D.; Dombroski, J. P.;. Graham, R. L.; Warshel, A. *Q-Chem 1.1*; Q-Chem, Inc.: Export, PA, 1997.