# X, A, B, C, and D States of the $C_6H_5F^+$ Ion Studied Using Multiconfiguration Wave Functions

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Electronic states of the $C_6H_5F^+$ ion have been studied within $C_{2v}$ symmetry by using the complete active space self-consistent field (CASSCF) and multiconfiguration second-order perturbation theory (CASPT2) methods in conjunction with an atomic natural orbital basis. Vertical excitation energies ($T_v$) and relative energies ($T_{v'}$) at the ground-state geometry of the $C_6H_5F$ molecule were calculated for 12 states. For the five lowest-lying states, $1^2B_1$, $1^2A_2$, $2^2B_1$, $1^2B_2$, and $1^2A_1$, geometries and vibrational frequencies were calculated at the CASSCF level, and adiabatic excitation energies ($T_0$) and potential energy curves (PEC) for F-loss dissociations were calculated at the CASPT2//CASSCF level. On the basis of the CASPT2 $T_0$ calculations, we assign the X, A, B, C, and D states of the ion to $1^2B_1$, $1^2A_2$, $2^2B_1$, $1^2B_2$, and $1^2A_1$, respectively, which supports the suggested assignment of the B state to $(2)^2B_1$ by Anand et al. based on their experiments. Our CASPT2 $T_v$ and $T_{v'}$ calculations and our MRCI $T_0$, $T_v$, and $T_{v'}$ calculations all indicate that the $2^2B_1$ state of $C_6H_5F^+$ lies below $1^2B_2$. By checking the relative energies of the asymptote products and checking the fragmental geometries and the charge and spin density populations in the asymptote products along the CASPT2//CASSCF PECs, we conclude that the $1^2B_1$, $1^2B_2$, and $1^2A_1$ states of $C_6H_5F^+$ correlate with $C_6H_5^+$ $(1^1A_1)$ + F $(^2P)$ (the first dissociation limit). The energy increases monotonically along the $1^2B_1$ PEC, and there are barriers and minima along the $1^2B_2$ and $1^2A_1$ PECs. The predicted appearance potential value for $C_6H_5^+$ $(1^1A_1)$ is very close to the average of the experimental values. Our CASPT2//CASSCF PEC calculations have led to the conclusion that the $1^2A_2$ state of $C_6H_5F^+$ correlates with the third dissociation limit of $C_6H_5^+$ $(1^1A_2)$ + F $(^2P)$, and a preliminary discussion is presented.

## I. Introduction

The fluorobenzene ion, $C_6H_5F^+$, has been investigated by numerous experimental techniques,[1−12] such as photoelectron spectroscopy, multiphoton ionization photoelectron spectroscopy, penning ionization electron spectroscopy, mass analyzed threshold ionization spectroscopy, and photoinduced Rydberg ionization spectroscopy. Experimental vertical ionization potential (VIP) values for the $C_6H_5F^+$ ion were measured by several groups.[2,5,7,8] The experimental VIP values for the nine lowest-lying primary ionization states of the $C_6H_5F^+$ ion were reported to be 9.4, 9.8, 12.3, 12.3, 13.0, 13.9, 14.6, 15.2, and 16.4 eV by Bieri et al.[5] The difference between the VIP values for excited states and the VIP value for the ground state are the relative energy (denoted as $T_{v'}$ in the present paper) values of the excited states to the ground state of the ion at the ground-state geometry of the $C_6H_5F$ molecule, and therefore the (experimental) $T_{v'}$ values for the nine lowest-lying primary ionization states of $C_6H_5F^+$ are 0.0, 0.4, 2.9, 2.9, 3.6, 4.5, 5.2, 5.8, and 7.0 eV, respectively, evaluated using the VIP values of Bieri et al.[5] Experimental adiabatic ionization potential (AIP) values for the X and B states of the $C_6H_5F^+$ ion were reported to be 9.22 and 11.79 eV by Sell et al.[6] and Bieri et al.,[5] respectively. The adiabatic excitation energy ($T_0$) values for the $C_6H_5F^+$ ion are considered to be equal to the differences between the AIP values for excited states and the AIP value for the ground state, and therefore the (experimental) $T_0$ value for the B state of $C_6H_5F^+$ is 2.57 eV, evaluated using the AIP values of Sell et al.[6] and Bieri et al.[5] Experimental geometric data are not available for any state of the $C_6H_5F^+$ ion. Limited experimental frequency data are available for the X and B states.[1,3,8−10] On the basis of the experimental studies on F-loss dissociation of the $C_6H_5F^+$ ion, appearance potential (AP) for the $C_6H_5^+$ ion (AP for production of $C_6H_5^+$ from the ground-state $C_6H_5F$ molecule) was reported to be 14.50 eV by Majer and Patrick[11] and 13.10 eV by Nishimura et al.[12] The discrepancy between the two experimental AP values is not small.

Assignment of electronic states is fundamental to understanding of the experimental facts. On the basis of the energy ordering of the five highest-occupied molecular orbitals (HOMOs) (......$13a_1^2\ 2b_1^2\ 8b_2^2\ 1a_2^2\ 3b_1^2$) in the electronic structure of the ground-state $C_6H_5F$ molecule, the X, A, B, C, and D states of the $C_6H_5F^+$ ion could be presumably assigned to $1^2B_1$, $1^2A_2$, $1^2B_2$, $2^2B_1$, and $1^2A_1$, respectively, as in many of the previous experimental papers. In 1999 Anand et al.[1] suggested assignment of the B state of $C_6H_5F^+$ to $^2B_1$, since their vibrationally resolved PIRI spectra of the B state showed that the B ← X transition was an allowed $\pi$ to $\pi$ transition. For supporting their assignment Anand et al.[1] calculated excitation energies using CIS methods, but they were not able to perform geometry optimiza-

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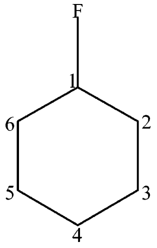

**Figure 1.** Atom labelings for the $C_6H_5F^+$ ion ($C_{2v}$ symmetry) used in this work.

tions on excited states and their calculated excitation energies were not accurate.

Theoretical studies on electronic states of the $C_6H_5F^+$ ion are quite few in the literature. The ground state of $C_6H_5F^+$ was previously calculated by using the UHF,[13] MP2,[1] and B3LYP[1] methods. As mentioned above, Anand et al.[1] calculated excited states of $C_6H_5F^+$ using CIS methods. Klippenstein[14] calculated potential energy curves (PECs) for F-loss dissociations from the $1^2B_1$, $1^2B_2$, and $1^2A_1$ states of $C_6H_5F^+$ at the MP2 level.

It is known that the CASSCF (complete active space self-consistent field)[15] and CASPT2 (multiconfiguration second-order perturbation theory)[16,17] methods are effective for theoretical studies of excited electronic states of molecules and molecular ions.[18,19] We have calculated vertical excitation energies ($T_v$) and relative energies ($T_{v'}$) at the ground-state geometry of the neutral molecule for twelve states ($1^2B_1$, $1^2A_2$, $2^2B_1$, $1^2B_2$, $1^2A_1$, $2^2B_2$, $3^2B_1$, $2^2A_2$, $3^2B_2$, $4^2B_1$, $2^2A_1$, and $3^2A_1$) of the $C_6H_5F^+$ ion using the CASSCF and CASPT2 methods. The primary focus of the present work is on the five lowest-lying states, $1^2B_1$, $1^2A_2$, $2^2B_1$, $1^2B_2$, and $1^2A_1$, of the $C_6H_5F^+$ ion. For these five states we have calculated geometries, vibrational frequencies, adiabatic excitation energies, and F-loss dissociation PECs using the CASSCF and CASPT2 methods. On the basis of our calculation results, we will assign the X, A, B, C, and D states of the $C_6H_5F^+$ ion and discuss the F-loss dissociation processes from these states.

## II. Calculation Details

The CASSCF and CASPT2 calculations were carried out using the MOLCAS 5.4 quantum-chemistry software.[20] With a CASSCF wave function constituting the reference function, the CASPT2 calculations were performed to compute the first-order wave function and the second-order energy in the full-CI space. A contracted atomic natural orbital (ANO) basis set,[21−23] F[5s3p1d]/C[5s3p1d]/H[3s2p1d], was used.

We assume that the 12 states of the $C_6H_5F^+$ ion studied in the present work have planar $C_{2v}$ structures. Geometry and atom labelings used for the $C_6H_5F^+$ ion are shown in Figure 1. We also assume that the $C_{2v}$ symmetry of the ionic systems remains in the processes of F-loss dissociation from the five lowest-lying states, and the $C_1-F$ distance ($R(C_1-F)$, see Figure 1) is taken as the reaction coordinate in the calculations of the dissociation PECs.

For the five lowest-lying states ($1^2B_1$, $1^2A_2$, $2^2B_1$, $1^2B_2$, and $1^2A_1$), the CASSCF geometry optimization and vibrational frequency calculations were performed. On the basis of the CASPT2 energies of the $1^2B_1$ ground state and the four excited states calculated at the respective CASSCF geometries, we obtained the CASPT2//CASSCF $T_0$ values for the excited states ("CASPT2//CASSCF $T_0$" will be abbreviated to "CASPT2 $T_0$"). For all the 12 states ($1^2B_1$, $1^2A_2$, $2^2B_1$, $1^2B_2$, $1^2A_1$, $2^2B_2$, $3^2B_1$, $2^2A_2$, $3^2B_2$, $4^2B_1$, $2^2A_1$, and $3^2A_1$), we calculated the CASPT2 relative energies at the ground-state geometries of the $C_6H_5F^+$ ion and the $C_6H_5F$ molecule. The CASPT2 relative energy values of the 11 excited states to the $1^2B_1$ ground state calculated at the CASSCF geometry of the $1^2B_1$ state are the CASPT2//CASSCF $T_v$ values ("CASPT2//CASSCF $T_v$" will be abbreviated to "CASPT2 $T_v$"). The CASPT2 relative energy values of the 11 excited states to the $1^2B_1$ ground state calculated at the experimental ground-state geometry[24] of the $C_6H_5F$ molecule are the CASPT2 $T_{v'}$ values.

**TABLE 1: CASPT2 $T_0$ Values for the $1^2B_1$, $1^2A_2$, $2^2B_1$, $1^2B_2$, and $1^2A_1$ States of the $C_6H_5F^+$ Ion and the CASPT2 $T_v$ and CASPT2 $T_{v'}$ (Calculated at the Experimental Ground-State Geometry of the $C_6H_5F$ Molecule[a]) for the 12 States of the Ion**

| | $T_0$ (eV) | | $T_v$ (eV) | $T_{v'}$ (eV) | |
|---|---|---|---|---|---|
| | CASPT2 | exptl | CASPT2 | CASPT2 | exptl[b] |
| $1^2B_1$ | 0.0 (0.0)[c] | 0.0[d] (0.0)[e] | 0.0 (0.0)[c] | 0.0 (0.0)[c] | 0.0 |
| $1^2A_2$ | 0.48 | | 1.03 | 0.54 | 0.4 |
| $2^2B_1$ | 2.77 (2.96)[c] | 2.57[d] (2.613)[e] | 3.00 (2.97)[c] | 2.85 (2.96)[c] | 2.9 |
| $1^2B_2$ | 2.84 (3.04)[c] | | 3.19 (3.26)[c] | 3.02 (3.22)[c] | 2.9 |
| $1^2A_1$ | 3.38 | | 4.13 | 3.61 | 3.6 |
| $3^2B_1$[f] | | | 4.68 | 4.75 | |
| $2^2B_2$ | | | 5.04 | 4.99 | 4.5 |
| $2^2A_2$[f] | | | 5.33 | 5.12 | |
| $4^2B_1$[f] | | | 5.70 | 5.65 | |
| $3^2B_2$ | | | 5.84 | 5.29 | 5.2 |
| $2^2A_1$ | | | 6.06 | 5.95 | 5.8 |
| $3^2A_1$ | | | 7.62 | 7.05 | 7.0 |

[a] Reference 24. [b] On the basis of the experimental VIP values for the primary ionization states reported in ref 5. [c] Values in parentheses are the MRCI calculation results (see text). [d] On the basis of the experimental AIP values for the X and B states of the ion reported in refs 6 and 5, respectively. [e] Reference 1. [f] Characterized as shake-up ionized states (at the CASSCF geometry of the $X^2B_1$ state and at the experimental ground-state geometry of the $C_6H_5F$ molecule).

The PECs for F-loss dissociations from the five lowest-lying states were calculated at the CASPT2//CASSCF level. At a set of fixed $R(C_1-F)$ values ranging from 1.3 to 4.5 Å, the CASSCF partial geometry optimization calculations were performed and then the CASPT2 energies were calculated at the CASSCF partially optimized geometries.

In the CASSCF calculations, 19 electrons were active and the active space included 14 orbitals (CASSCF (19,14)). The choice of the active space stemmed from the electron configuration of the ground-state $C_6H_5F$ molecule. On the basis of the HF/6-31+G(d,p) calculations, the ground-state molecule has the following electron configuration: $...(1b_1)^2$ $(11a_1)^2$ $(12a_1)^2$ $(6b_2)^2$ $(7b_2)^2$ $(13a_1)^2$ $(2b_1)^2$ $(8b_2)^2$ $(1a_2)^2$ $(3b_1)^2$ $(2a_2)^0$ $(4b_1)^0$ $(14a_1)^0$ $(9b_2)^0$....... The 14 (10 occupied plus 4 virtual) MOs listed in this sequence were included in our active space. Labeling these orbitals within the $C_{2v}$ point group in the order of $a_1$, $a_2$, $b_2$, and $b_1$, this active space is named (4244). In CASSCF calculations for electronic states of a molecular ion, we often take a " segment " of the electron configuration of the ground-state molecule constituting our active space. The " segment " includes many (sequential) occupied MOs for not missing primary ionization states in the CASSCF calculations and includes a few of virtual MOs for describing shake-up ionization character of some ionic states. In all the CASPT2 calculations, the same threshold and shift were used and the weight values of the CASSCF reference functions in the first-order wave functions were larger than 0.75.

## III. Results and Discussion

**A. Excitation Energies and Assignments of the Five Lowest-Lying States.** In Table 1 given are the CASPT2 $T_v$ and

**TABLE 2: CASSCF Optimized Geometries[a] for the $1^2B_1$, $1^2A_2$, $2^2B_1$, $1^2B_2$, and $1^2A_1$ States of the $C_6H_5F^+$ Ion (for Atom Labelings, See Figure 1)[b]**

| state | $R(C_1-F)$ | $R(C_1-C_2)$ | $R(C_2-C_3)$ | $R(C_3-C_4)$ | $\angle C_2C_1C_6$ | $\angle C_1C_2C_3$ | $\angle C_3C_4C_5$ |
|---|---|---|---|---|---|---|---|
| $1^2B_1$ | 1.269 | 1.417 | 1.364 | 1.424 | 123.8 | 117.6 | 120.8 |
| $1^2A_2$ | 1.300 | 1.373 | 1.442 | 1.408 | 120.7 | 120.1 | 119.7 |
| $2^2B_1$ | 1.281 | 1.407 | 1.425 | 1.431 | 122.7 | 118.7 | 119.5 |
| $1^2B_2$ | 1.291 | 1.384 | 1.359 | 1.448 | 119.9 | 118.3 | 105.9 |
| $1^2A_1$ | 1.302 | 1.377 | 1.416 | 1.382 | 123.8 | 120.5 | 134.3 |
| $1^1A_1$[c] | 1.356 | 1.387 | 1.399 | 1.401 | 123.4 | 118.0 | 120.2 |

[a] Only geometric parameters in the heavy-atom frameworks are given. [b] Bond lengths are given in angstroms, and bond angles are given in degrees. [c] The experimental ground-state geometry of the $C_6H_5F$ molecule, see ref 24.

$T_{v'}$ values for the $1^2B_1$, $1^2A_2$, $2^2B_1$, $1^2B_2$, $1^2A_1$, $3^2B_1$, $2^2B_2$, $2^2A_2$, $4^2B_1$, $3^2B_2$, $2^2A_1$, and $3^2A_1$ states of the $C_6H_5F^+$ ion and the CASPT2 $T_0$ values for the $1^2B_1$, $1^2A_2$, $2^2B_1$, $1^2B_2$, and $1^2A_1$ states. All these energetic calculations indicate that the $1^2B_1$ state is the ground state ($X^2B_1$) of the $C_6H_5F^+$ ion. Available experimental $T_0$ and $T_{v'}$ values (evaluated using the experimental AIP and VIP values) are listed in Table 1.

We will first briefly discuss the calculation results for the 12 states. By checking the CASSCF wave functions (at the ground-state geometries of the ion and the molecule), the $1^2B_1$, $1^2A_2$, $2^2B_1$, $1^2B_2$, $1^2A_1$, $2^2B_2$, $3^2B_2$, $2^2A_1$, and $3^2A_1$ states are characterized as primary ionized states, and the dominant configurations in their wave functions can be represented as $(3b_1)^{-1}$, $(1a_2)^{-1}$, $(2b_1)^{-1}$, $(8b_2)^{-1}$, $(13a_1)^{-1}$, $(7b_2)^{-1}$, $(6b_2)^{-1}$, $(12a_1)^{-1}$, and $(11a_1)^{-1}$, respectively, with respect to the electron configuration of the ground-state molecule (see section II). The $3^2B_1$, $2^2A_2$, and $4^2B_1$ states are characterized as shake-up ionized states, and the important configurations in their CASSCF wave functions involve the $2a_2$ and $4b_1$ virtual orbitals. The CASPT2 $T_v$ and $T_{v'}$ orderings for the 12 states are the same, except that the $4^2B_1$ and $3^2B_2$ states exchange their positions in the orderings (see Table 1). The experimental $T_{v'}$ values (evaluated using the experimental VIP values[5]) for the nine lowest-lying primary ionized states are 0.0, 0.4, 2.9, 2.9, 3.6, 4.5, 5.2, 5.8, and 7.0 eV. The CASPT2 $T_{v'}$ values for the nine primary ionized states, $1^2B_1$ ($X^2B_1$), $1^2A_2$, $2^2B_1$, $1^2B_2$, $1^2A_1$, $2^2B_2$, $3^2B_2$, $2^2A_1$, and $3^2A_1$, are 0.0, 0.54, 2.85, 3.02, 3.61, 4.99, 5.29, 5.95, and 7.05 eV, respectively, and they are quite close to the experimental $T_{v'}$ values for the nine lowest-lying primary ionized states, respectively, except that the discrepancy (0.49 eV) between the CASPT2 $T_{v'}$ value for $2^2B_2$ and the sixth experimental $T_{v'}$ value is quite large.

The main purpose of our $T_0$ calculations for the five lowest-lying states, $1^2B_1$, $1^2A_2$, $2^2B_1$, $1^2B_2$, and $1^2A_1$, is for assigning the X, A, B, C, and D states of the ion. The experimental $T_0$ value is available only for the B state, and the value of 2.57 eV may not be so accurate since the experimental AIP values for the X and B states were reported by two different groups.[5,6]

The CASPT2(//CASSCF) $T_0$ calculations predict the following ordering for the five states: $1^2B_1$ ($X^2B_1$), $1^2A_2$, $2^2B_1$, $1^2B_2$, and $1^2A_1$, and the CASPT2 $T_0$ values for the five states are 0.0, 0.48, 2.77, 2.84, and 3.38 eV, respectively. Preliminary CASPT2(//CASSCF) $T_0$ calculations were performed for the $2^2A_2$, $3^2B_1$, and $2^2B_2$ states and the calculated $T_0$ values for the three states are all larger than the CASPT2 $T_0$ value for the $1^2A_1$ state. This fact confirms that the $1^2B_1$, $1^2A_2$, $2^2B_1$, $1^2B_2$, and $1^2A_1$ states are the five lowest-lying states of the $C_6H_5F^+$ ion. On the basis of all these $T_0$ calculations, we assign the X, A, B, C, and D states of the $C_6H_5F^+$ ion to $1^2B_1$, $1^2A_2$, $2^2B_1$, $1^2B_2$, and $1^2A_1$, respectively. The CASPT2 $T_0$ value of 2.77 eV for $2^2B_1$ is quite close to the experimental $T_0$ value of 2.57 eV [5,6] for the B state of the $C_6H_5F^+$ ion and also quite close to an experimental $T_0$ value of 2.613 eV reported by Anand et al.[1] The CASPT2 $T_v$ and $T_{v'}$ orderings (see Table 1) also show that the $1^2B_1$, $1^2A_2$, $2^2B_1$, $1^2B_2$, and $1^2A_1$ states are the five lowest-lying states (at the ground-state geometries of the ion and the molecule) and support our assignments for the five states based on the $T_0$ calculations.

To the best of our knowledge, the B state of the $C_6H_5F^+$ ion was assigned to $^2B_2$ in all the published papers concerning excited states of the ion, except in the paper of Anand et al.[1] In 1999 Anand et al.[1] suggested assignment of the B state of $C_6H_5F^+$ to $^2B_1$ based on their analyses on the vibrationally resolved PIRI spectra. It is noted in Table 1 that, though the CASPT2 $T_0$, $T_v$, and $T_{v'}$ calculations all indicate that the $2^2B_1$ state lies below $1^2B_2$, the $T_0$, $T_v$, and $T_{v'}$ differences between $2^2B_1$ and $1^2B_2$ are all small. For confirmation of our assignments for the B and C states based on the CASPT2 calculations, we performed the $T_0$, $T_v$, and $T_{v'}$ calculations for the $1^2B_1$ ($X^2B_1$), $2^2B_1$, and $1^2B_2$ states using the MRCI method (using the MOLPRO quantum-chemistry software[25]). In the MRCI calculations, the same ANO basis was used, and the active space included 10 occupied and 2 virtual orbitals (it was formed by deleting the two highest virtual orbitals ($14a_1$ and $9b_2$) in the active space used in our CASPT2//CASSCF calculations (see section II)). As in the CASPT2 calculations, the CASSCF (19,14) geometries were used in the MRCI $T_0$ and $T_v$ calculations and the experimental ground-state geometry of the $C_6H_5F$ molecule was used in the MRCI $T_{v'}$ calculations. The MRCI $T_0$, $T_v$, and $T_{v'}$ values for the $2^2B_1$ and $1^2B_2$ states are given in Table 1, and the MRCI $T_0$, $T_v$, and $T_{v'}$ calculations all indicate that the $2^2B_1$ state lies below $1^2B_2$, supporting our assignments for the B and C states. The present theoretical work supports the suggested assignment of the B state to $^2B_1$ by Anand et al.[1] based on their experiments.

**B. Geometries and Frequencies.** In Table 2 given are the CASSCF geometries for the $1^2B_1$, $1^2A_2$, $2^2B_1$, $1^2B_2$, and $1^2A_1$ states of the $C_6H_5F^+$ ion, together with the experimental ground-state geometry[24] of the $C_6H_5F$ molecule. In the following, we will briefly describe the CASSCF geometries of the five ionic states in comparison with the geometry of the $C_6H_5F$ molecule. The C−F bond lengths in the CASSCF geometries of the five ionic states are all shorter than the bond length in the geometry of the molecule. The shortening of the C−F bond in the geometries of the $1^2B_1$, $2^2B_1$, and $1^2B_2$ states can be understood by realizing the antibonding character between the $C_1$ and F atoms in the $3b_1$, $2b_1$, and $8b_2$ MOs of the molecule, which are the “ SOMOs ” (“singly occupied MOs”) for the three ionic states, respectively. As compared with the C−C bond lengths in the geometry of the molecule, the $1^2B_1$ geometry has long $C_1-C_2$ ($C_1-C_6$) and $C_3-C_4$ ($C_4-C_5$) bonds and short $C_2-C_3$ ($C_5-C_6$) bonds; the $1^2A_2$ geometry has very long $C_2-C_3$ ($C_5-C_6$) bonds; all the C−C bonds in the $2^2B_1$ geometry are long; the $1^2B_2$ geometry has very long $C_3-C_4$ ($C_4-C_5$) bonds and very short $C_2-C_3$ ($C_5-C_6$) bonds; and the $1^2A_1$ geometry has long $C_2-C_3$ ($C_5-C_6$) bonds and short $C_3-C_4$ ($C_4-C_5$) bonds.

**TABLE 3: CASSCF Frequencies[a] (in $cm^{-1}$) for the $1^2B_1$, $2^2B_1$, and $1^2B_2$ States (X, B, and C, Respectively) of the $C_6H_5F^+$ Ion, Together with Available Experimental Frequencies for the X and B States**

| state | mode | CASSCF | exptl |
|---|---|---|---|
| $1^2B_1$ | $a_1$ | 542, 859, 1001, 1062, 1233, 1447 | X: [500, 795, 959, 999, 1164][b] [1619][c] |
| | $a_2$ | 383, 825, 1034 | [341][d] |
| | $b_2$ | 444, 549, 1099, 1184, 1396, 1420 | [400, 505][b] |
| | $b_1$ | 198, 440, 649, 843, 964, 1036 | [181, 345][b] |
| $2^2B_1$ | $a_1$ | 539, 866, 1004, 1075, 1188, 1412, | B: [458, 695, 1152][d] |
| | $a_2$ | 124, 592, 764 | [236][d] |
| | $b_2$ | 443, 629, 1116, 1195, 1399, 1488 | [430, 520][d] |
| | $b_1$ | 218, 470, 628, 652, 765, 929 | [207, 366][d] |
| $1^2B_2$ | $a_1$ | 519, 775, 985, 988, 1160, 1295 | |
| | $a_2$ | 377, 664, 968 | |
| | $b_2$ | 134, 450, 615, 1009, 1088, 1237 | |
| | $b_1$ | 241, 566, 652, 793, 935, 1243 | |

[a] Only the six smallest frequency values are listed here for the $a_1$ and $b_2$ modes. [b] Reference 3. [c] Reference 9. [d] Reference 1.

As compared with the CCC bond angles in the geometry of the molecule, the $C_2C_1C_6$ angles in the $1^2A_2$ and $1^2B_2$ geometries are small; the $C_1C_2C_3$ angles in the $1^2A_2$ and $1^2A_1$ geometries are large; the $C_3C_4C_5$ angle is too small in the $1^2B_2$ geometry and too large in the $1^2A_1$ geometry.

The CASSCF frequency calculations produced no imaginary frequencies for the $1^2B_1$, $1^2A_2$, $2^2B_1$, and $1^2B_2$ states, indicating that the CASSCF geometries of the four states correspond to energy minima in the respective potential energy surfaces (PESs). The CASSCF frequency calculations for the $1^2A_1$ state produced one imaginary frequency in the $b_2$ mode and one (very small) imaginary frequency in the $b_1$ mode, indicating that the CASSCF geometry of the $1^2A_1$ state corresponds to a second-order saddle point in the PES.

In Table 3 given are the CASSCF frequencies for the $1^2B_1$ (X), $2^2B_1$ (B), and $1^2B_2$ (C) states of the $C_6H_5F^+$ ion. Available experimental frequency values in the four modes of the X and B states are listed in Table 3 (the maximum being six in the $a_1$ mode of the X state). We would assume that these available experimental frequencies are the smallest frequencies in the respective modes, and hence we give only the six smallest CASSCF frequencies in the $a_1$ mode and in the $b_2$ mode in Table 3. By comparison of the CASSCF frequency values for the $1^2B_1$ and $2^2B_1$ states with the experimental frequency values for the X and B states, respectively, the largest discrepancy is found to be 170 $cm^{-1}$. By comparison of the CASSCF frequency values for the $1^2B_2$ state with the experimental frequency values for the B state, the largest discrepancy is found to be 300 $cm^{-1}$, which is too large to be acceptable. These facts support the assignment of the B state to $2^2B_1$ (rather than $1^2B_2$).

**C. PECs for F-loss Dissociations.** In Figure 2 are given the CASPT2//CASSCF PECs for F-loss dissociations from the $1^2B_1$, $1^2A_2$, $1^2B_2$, and $1^2A_1$ states (abbreviated to "$1^2B_1$ PEC, ......") of the $C_6H_5F^+$ ion (the CASPT2//CASSCF PEC calculations for the $2^2B_1$ state were not successful, see below). The CASPT2//CASSCF calculations were performed at selected $R(C_1-F)$ values ranging from 1.3 to 4.5 Å, and the $C_6H_5F^+$ systems in the $1^2B_1$, $1^2A_2$, $1^2B_2$, and $1^2A_1$ states at the $R(C_1-F)$ value of 4.5 Å will be called as asymptote dissociation products of the respective states (abbreviated to "$1^2B_1$ asymptote product, ......"). The charge values on the F-atom in the asymptote products of the four states are all very small (the absolute charge values being all smaller than 0.002 e) and the sums of the Mulliken spin population values on all the carbon and hydrogen atoms in the asymptote products of the four states are all very small (the absolute values of the sums being all smaller than 0.0002 e). These facts indicate that the products of F-loss dissociations from the $1^2B_1$, $1^2A_2$, $1^2B_2$, and $1^2A_1$ states are the neutral F atom plus the $C_6H_5^+$ ion in its singlet states.

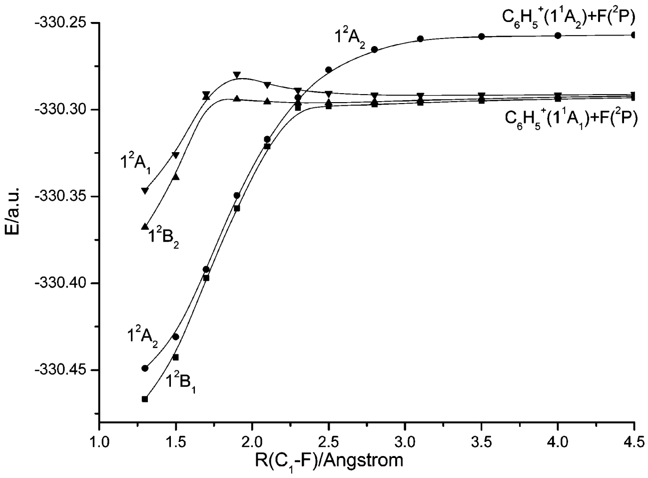

**Figure 2.** CASPT2//CASSCF PECs for F-loss dissociations from the $1^2B_1$, $1^2A_2$, $1^2B_2$, and $1^2A_1$ states of the $C_6H_5F^+$ ion.

In Table 4 are given the CASPT2//CASSCF energies of the four states at selected $R(C_1-F)$ values, together with the values of principal geometric parameters in the CASSCF partially optimized geometries.

In Table 5 are given the CASSCF geometries and CASPT2//CASSCF $T_0$ values for the $1^1A_1$, $1^3B_1$, $1^1A_2$, and $1^3A_2$ states (the four lowest-lying states) of the $C_6H_5^+$ ion. In the calculations for $C_6H_5^+$, the same ANO basis (C[5s3p1d]/H[3s2p1d]) was used. In the CASSCF calculations for $C_6H_5^+$, 10 electrons were active and an active space named (3213) was used. In the CASPT2 calculations for $C_6H_5^+$, we used the same threshold and shift as those in the CASPT2 calculations for $C_6H_5F^+$. The CASPT2(//CASSCF) $T_0$ calculations for the four states of $C_6H_5^+$ predict the following ordering: $1^1A_1$ (the ground state), $1^3B_1$, $1^1A_2$, and $1^3A_2$. As shown in Table 5, the $1^1A_2$ and $1^3A_2$ states of $C_6H_5^+$ have close CASPT2 $T_0$ values and similar CASSCF geometries.

The asymptote products of the $1^2B_1$, $1^2B_2$, and $1^2A_1$ states have similar CASPT2//CASSCF energies (see Table 5), and the geometries of the $C_6H_5$ fragment in the asymptote products of the three states are almost identical to the CASSCF geometry of the $1^1A_1$ state of the $C_6H_5^+$ ion (see Tables 4 and 5). We conclude that the $1^2B_1$, $1^2B_2$, and $1^2A_1$ states of the $C_6H_5F^+$ ion all correlate with the $1^1A_1$ ground state of the $C_6H_5^+$ ion (with the first dissociation limit of $C_6H_5^+$ ($1^1A_1$) + F ($^2P$)). Klippenstein[14] studied F-loss dissociation processes for the $1^2B_1$, $1^2B_2$, and $1^2A_1$ states of $C_6H_5F^+$ based on his MP2 calculations, and the three states were also considered to correlate with the first dissociation limit.

**TABLE 4: CASPT2//CASSCF Energies (*E*) at the Selected $R(C_1-F)$ Values along the PECs (Shown in Figure 2) for F-loss Dissociations from the $1^2B_1$, $1^2A_2$, $1^2B_2$, and $1^2A_1$ States of the $C_6H_5F^+$ Ion, Together with the Values of Principal Parameters in the CASSCF Partially Optimized Geometries (See Figure 1)[a]**

| $R(C_1-F)$ | *E* (a.u.) | $R(C_1-C_2)$ | $R(C_2-C_3)$ | $R(C_3-C_4)$ | $\angle C_2C_1C_6$ | $\angle C_1C_2C_3$ | $\angle C_3C_4C_5$ |
|---|---|---|---|---|---|---|---|
| $1^2B_1$ | | | | | | | |
| 1.3 | −330.46675 | 1.414 | 1.364 | 1.425 | 124.4 | 117.3 | 120.9 |
| 1.5 | −330.44276 | 1.400 | 1.366 | 1.428 | 128.0 | 115.5 | 121.5 |
| 1.9 | −330.35668 | 1.387 | 1.369 | 1.425 | 131.2 | 113.8 | 122.5 |
| 2.3 | −330.29897 | 1.353 | 1.416 | 1.384 | 144.0 | 105.2 | 121.8 |
| 2.5 | −330.29800 | 1.349 | 1.418 | 1.384 | 144.1 | 104.9 | 122.0 |
| 2.8 | −330.29708 | 1.348 | 1.420 | 1.384 | 144.6 | 104.7 | 122.0 |
| 3.1 | −330.29603 | 1.347 | 1.421 | 1.383 | 144.9 | 104.5 | 122.0 |
| 3.5 | −330.29483 | 1.346 | 1.421 | 1.383 | 145.1 | 104.4 | 122.0 |
| 4.5 | −330.29313 | 1.346 | 1.421 | 1.383 | 145.1 | 104.4 | 121.9 |
| $1^2A_2$ | | | | | | | |
| 1.3 | −330.44897 | 1.403 | 1.442 | 1.377 | 119.9 | 118.9 | 118.8 |
| 1.5 | −330.43078 | 1.392 | 1.445 | 1.379 | 124.0 | 117.0 | 118.8 |
| 1.9 | −330.34941 | 1.365 | 1.449 | 1.380 | 126.6 | 115.6 | 119.6 |
| 2.3 | −330.29308 | 1.368 | 1.449 | 1.380 | 125.6 | 116.2 | 119.6 |
| 2.8 | −330.26439 | 1.378 | 1.448 | 1.379 | 122.8 | 117.2 | 119.2 |
| 3.1 | −330.25784 | 1.384 | 1.448 | 1.378 | 122.4 | 117.6 | 119.1 |
| 3.5 | −330.25687 | 1.384 | 1.448 | 1.378 | 122.1 | 117.9 | 119.1 |
| 4.5 | −330.25669 | 1.384 | 1.448 | 1.378 | 122.1 | 117.9 | 119.1 |
| $1^2B_2$ | | | | | | | |
| 1.3 | −330.36766 | 1.416 | 1.356 | 1.411 | 118.6 | 117.3 | 107.5 |
| 1.5 | −330.33913 | 1.373 | 1.361 | 1.433 | 122.7 | 116.2 | 106.1 |
| 1.7 | −330.29300 | 1.370 | 1.402 | 1.385 | 135.8 | 109.6 | 122.2 |
| 1.9 | −330.29405 | 1.364 | 1.408 | 1.385 | 139.6 | 107.4 | 122.2 |
| 2.3 | −330.29606 | 1.353 | 1.416 | 1.384 | 143.3 | 105.3 | 122.1 |
| 2.8 | −330.29542 | 1.349 | 1.419 | 1.384 | 144.7 | 104.6 | 122.0 |
| 3.1 | −330.29459 | 1.348 | 1.420 | 1.384 | 144.9 | 104.5 | 122.0 |
| 3.5 | −330.29365 | 1.348 | 1.420 | 1.384 | 145.1 | 104.4 | 122.0 |
| 4.5 | −330.29214 | 1.348 | 1.420 | 1.384 | 145.2 | 104.4 | 122.0 |
| $1^2A_1$ | | | | | | | |
| 1.3 | −330.34620 | 1.377 | 1.416 | 1.382 | 123.8 | 120.5 | 134.3 |
| 1.5 | −330.32587 | 1.365 | 1.444 | 1.361 | 127.5 | 117.7 | 135.8 |
| 1.7 | −330.29089 | 1.344 | 1.436 | 1.371 | 139.0 | 108.2 | 122.5 |
| 1.9 | −330.27951 | 1.353 | 1.417 | 1.382 | 142.5 | 105.8 | 121.8 |
| 2.3 | −330.28879 | 1.348 | 1.420 | 1.383 | 144.7 | 104.6 | 121.9 |
| 2.8 | −330.29157 | 1.347 | 1.421 | 1.383 | 145.2 | 104.3 | 121.9 |
| 3.1 | −330.29174 | 1.347 | 1.421 | 1.383 | 145.2 | 104.3 | 122.0 |
| 3.5 | −330.29165 | 1.347 | 1.421 | 1.383 | 145.2 | 104.3 | 122.0 |
| 4.5 | −330.29126 | 1.347 | 1.421 | 1.383 | 145.2 | 104.3 | 122.0 |

[a] Bond lengths are in angstroms, and bond angles are in degrees.

**TABLE 5: CASSCF Gometries and CASPT2//CASSCF Relative Energies ($T_0$) for the $1^1A_1$, $1^3B_1$, $1^1A_2$, and $1^3A_2$ States (the Four Lowest-Lying States) of the $C_6H_5^+$ Ion (for Atom Labelings, See Figure 1)[a]**

| state | $R(C_1-C_2)$ | $R(C_2-C_3)$ | $R(C_3-C_4)$ | $\angle C_2C_1C_6$ | $\angle C_1C_2C_3$ | $\angle C_3C_4C_5$ | $T_0$ (eV) |
|---|---|---|---|---|---|---|---|
| $1^1A_1$ | 1.347 | 1.419 | 1.386 | 146.9 | 103.8 | 122.2 | 0.00 |
| $1^3B_1$ | 1.421 | 1.368 | 1.422 | 125.7 | 116.5 | 123.0 | 0.68 |
| $1^1A_2$ | 1.384 | 1.448 | 1.378 | 122.1 | 118.0 | 119.3 | 0.86 |
| $1^3A_2$ | 1.385 | 1.448 | 1.374 | 122.6 | 117.3 | 119.6 | 0.88 |

[a] Bond lengths are in angstroms, and bond angles are in degrees.

Along the $1^2B_1$ PEC, the energy increases monotonically with the $R(C_1-F)$ value. The relative energy of the $1^2B_1$ asymptote product to the $1^2B_1$ reactant (the $1^2B_1$ CASSCF optimized geometry) is considered to be the dissociation energy ($D_e$) for $C_6H_5F^+$ ($1^2B_1$) → $C_6H_5^+$ ($1^1A_1$) + F ($^2P$), and the CASPT2//CASSCF $D_e$ value is evaluated to be 4.70 eV. We assume that the AP value for the $C_6H_5^+$ ($1^1A_1$) ion be equal to the sum of the experimental AIP value of 9.22 eV [6] for the X state of $C_6H_5F^+$ and the CASPT2//CASSCF $D_e$ value for the $1^2B_1$ state of $C_6H_5F^+$. The predicted AP value of 13.92 eV for $C_6H_5^+$ ($1^1A_1$) is quite close to the experimental AP values of 14.50 eV[11] and 13.10 eV,[12] and it is very close to the average of the two experimental values. Along the $1^2B_2$ PEC, there is a barrier at $R(C_1-F) \approx 1.70$ Å and a shallow minimum at $R(C_1-F) \approx 2.50$ Å. The CASPT2//CASSCF relative energies of the barrier, minimum, and $1^2B_2$ asymptote product to the $1^2B_2$ reactant are 2.03, 1.95, and 2.06 eV, respectively. Along the $1^2A_1$ PEC, there is a barrier at $R(C_1-F) \approx 1.90$ Å and a minimum at $R(C_1-F) \approx 3.10$ Å. The CASPT2//CASSCF relative energies of the barrier, minimum, and $1^2A_1$ asymptote product to the $1^2A_1$ reactant are 1.81, 1.48, and 1.50 eV, respectively.

The $1^2A_2$ asymptote product is higher in (CASPT2//CASSCF) energy than the $1^2B_1$ asymptote product by 0.98 eV, which is close to the CASPT2(//CASSCF) $T_0$ value of 0.86 eV for the $1^1A_2$ state of the $C_6H_5^+$ ion (see Table 5). The geometry of the $C_6H_5$ fragment in the $1^2A_2$ asymptote product is almost identical to the CASSCF geometry of the $1^1A_2$ state of the $C_6H_5^+$ ion (see Tables 4 and 5). We would conclude that the $1^2A_2$ state of the $C_6H_5F^+$ ion correlates with the $1^1A_2$ state of the $C_6H_5^+$ ion (with the third dissociation limit of $C_6H_5^+$ ($1^1A_2$) + F ($^2P$)). We will discuss this conclusion in the rest part of the present section. As noted in Table 5, the $1^1A_2$ and $1^3A_2$ states of $C_6H_5^+$

have close CASPT2(//CASSCF) $T_0$ values and similar CASSCF geometries. However, the $1^2A_2$ state of $C_6H_5F^+$ does not correlate with the $1^3A_2$ state of $C_6H_5^+$ (the fourth dissociation limit) since the spin population analyses indicate that the $1^2A_2$ state of $C_6H_5F^+$ correlates with a singlet state of $C_6H_5^+$ (see above). Urbain et al.[26] suggested that the $1^2A_2$ state of the $C_6H_5Cl^+$ ion correlated with $C_6H_5^+$ ($1^3B_1$) + Cl ($^2P$) (the second dissociation limit). On the basis of the symmetry considerations, the $1^2A_2$ state (also the $2^2B_1$ state) of $C_6H_5X^+$ can correlate with $C_6H_5^+$ ($1^3B_1$) + X ($^2P$) (the second dissociation limit) or $C_6H_5^+$ ($1^1A_2$) + X ($^2P$) (the third dissociation limit). The present CASPT2//CASSCF PEC calculations have led to the conclusion that the $1^2A_2$ state of the $C_6H_5F^+$ ion correlates with the third dissociation limit. Our $1^2A_2$ PEC of $C_6H_5F^+$ was plotted based on the CASPT2//CASSCF calculation results at the 12 fixed $R(C_1{-}F)$ values of 1.3, 1.5, ......, and 4.5 Å, corresponding to the 12 points along the $1^2A_2$ PEC (see Figure 2), and the calculations were performed at one point by one point from the first point at $R(C_1{-}F) = 1.3$ Å. In the CASSCF (partial geometry optimization) calculations at point $n$ ($2 \leq n \leq 12$), we always used the converged CASSCF orbitals at point ($n - 1$) as input orbitals. The same technique was used in the $2^2B_1$ PEC calculations, but we still had CASSCF convergence problems at some of the selected $R(C_1{-}F)$ values. On the basis of our preliminary calculation results, we presume that the $2^2B_1$ state of $C_6H_5F^+$ correlates with $C_6H_5^+$ ($1^3B_1$). The character of the wave function varies along the $1^2A_2$ PEC, and at large $R(C_1{-}F)$ values, the wave function has the character of $(13a_1)^{-1}$ $(1a_2)^{-1}$ $(14a_1)^1$. The B3LYP and MP2 calculations for the $1^2A_2$ and $2^2B_1$ PECs will not be successful.

## IV. Conclusions

Electronic states of the $C_6H_5F^+$ ion have been studied within $C_{2v}$ symmetry by using CASSCF and CASPT2 methods in conjunction with an ANO basis. Vertical excitation energies ($T_v$) and relative energies ($T_{v'}$) at the ground-state geometry of the $C_6H_5F$ molecule were calculated for the $1^2B_1$ ($X^2B_1$), $1^2A_2$, $2^2B_1$, $1^2B_2$, $1^2A_1$, $2^2B_2$, $3^2B_1$, $2^2A_2$, $3^2B_2$, $4^2B_1$, $2^2A_1$, and $3^2A_1$ states of the ion, and the CASPT2 $T_{v'}$ values for the nine primary ionized states are in reasonable agreement with the relative energy values evaluated using the experimental VIP values. The focus of the present work is on the $1^2B_1$, $1^2A_2$, $2^2B_1$, $1^2B_2$, and $1^2A_1$ states. For these states, geometries and vibrational frequencies were calculated at the CASSCF level, adiabatic excitation energies ($T_0$) were calculated at the CASPT2//CASSCF level, and PECs for F-loss dissociations were calculated at the CASPT2//CASSCF level.

The CASPT2(//CASSCF) $T_0$ calculations indicate that the $1^2B_1$, $1^2A_2$, $2^2B_1$, $1^2B_2$, and $1^2A_1$ states are the five lowest-lying states of $C_6H_5F^+$ and that they are in the following CASPT2 $T_0$ ordering: $1^2B_1$, $1^2A_2$, $2^2B_1$, $1^2B_2$, and $1^2A_1$. Therefore we assign the X, A, B, C, and D states of $C_6H_5F^+$ to $1^2B_1$, $1^2A_2$, $2^2B_1$, $1^2B_2$, and $1^2A_1$, respectively. The CASPT2 $T_0$ value of 2.77 eV for $2^2B_1$ is in reasonable agreement with the experimental $T_0$ values for the B state. Our CASPT2 $T_v$ and $T_{v'}$ calculations and our MRCI $T_0$, $T_v$, and $T_{v'}$ calculations all indicate that the $2^2B_1$ state of $C_6H_5F^+$ lies below $1^2B_2$. The B state of $C_6H_5F^+$ was assigned to $^2B_2$ in the previous papers concerning excited states of the ion, except in the paper of Anand et al.[1] The present theoretical work supports the suggested assignment of the B state to $(2)^2B_1$ by Anand et al.[1] based on their experiments.

By checking the relative energies of the asymptote products and checking the fragmental geometries and the charge and spin density populations in the asymptote products along the CASPT2//CASSCF PECs, we conclude that the $1^2B_1$, $1^2B_2$, and $1^2A_1$ states of $C_6H_5F^+$ correlate with the first dissociation limit of $C_6H_5^+$ ($1^1A_1$) + F ($^2P$). Along the $1^2B_1$ PEC the energy increases monotonically with the $R(C_1{-}F)$ value, and the $D_e$ value for the $1^2B_1$ state of the $C_6H_5F^+$ ion and the AP value for $C_6H_5^+$ ($1^1A_1$) were predicted. The predicted AP value of 13.92 eV for $C_6H_5^+$ ($1^1A_1$) is very close to the average of the two experimental values of 14.50 and 13.10 eV. Along the $1^2B_2$ and $1^2A_1$ PECs there are barriers and minima. Our CASPT2//CASSCF PEC calculations have led to the conclusion that the $1^2A_2$ state of $C_6H_5F^+$ correlates with the third dissociation limit of $C_6H_5^+$ ($1^1A_2$) + F ($^2P$), and preliminary discussion on F-loss dissociations from the $1^2A_2$ and $2^2B_1$ states is presented.

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