CASPT2 study on the low-lying electronic states of m-$C_6H_4F_2^+$ ion

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Abstract. Electronic states of the m-$C_6H_4F_2^+$ ion were studied by using the CASPT2 and CASSCF methods in conjunction with a contracted atomic natural orbital (ANO-L) basis set. For the five lowest-lying states, geometries and adiabatic excitation energies (T_0) were calculated at the CASPT2 level. The CASPT2 T_0 values and CASPT2 T_v' values are in reasonable agreement with the available experimental data. The assignments of the B, C, and D states of the m-$C_6H_4F_2^+$ ion were difficult since the three states are closely lying. Based on the CASPT2 T_0 calculations, the X, A, B, C, and D states of the m-$C_6H_4F_2^+$ ion were assigned to 1^2A_2, 1^2B_1, 2^2B_1, 1^2A_1, and 1^2B_2, respectively, which supports the suggested assignment of the lowest excited state to $^2B_1$ by Tsuchiya *et al.* based on their experiments.

1 Introduction

Halogen-benzene ions have long attracted a great deal of interest for its great significance for environmental protection. Fluorobenzene ions have attracted a great interest with respect to their emissive properties, and have been the subject of a great many spectroscopic studies [1-10]. Assignments of electronic states are fundamental to understanding of the experimental facts. Based on the energy orderings of the occupied molecular orbitals (MOs) in the electronic configurations of the ground-state m-$C_6H_4F_2$ molecule, the X, A, B, C, and D states of the m-$C_6H_4F_2^+$ ion could be presumably assigned to 1^2A_2, 1^2B_1, 2^2B_1,

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1^2A_1, and 1^2B_2, respectively. The assignments of the B, C, and D states are diffcult since the B, C, and D states were observed to be closely lying.[1] Tsuchiya *et al.*[2] suggested assignment of the lowest excited state of m-$C_6H_4F_2^+$ to $^2B_1$ based on their analyses by dissociation spectroscopy. But this was contrary to the generally accepted criterion that the lowest excited state of the nonemissive fluorobenzene cation is $D(\sigma,\pi)$. The accurate assignment on the electronic excited states of an ion should be based on the high-level theoretical calculations.

The experimental adiabatic ionization potential (AIP) values for the X, A, and B states of the m-$C_6H_4F_2^+$ ion were reported by Bieri *et al.*[1] to be 9.32, 9.68, and 12.19 eV, respectively. The adiabatic excitation energy (T_0) values for the m-$C_6H_4F_2^+$ 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 values for the A and B states of m-$C_6H_4F_2^+$ are 0.36 and 2.87 eV, respectively, evaluated using the AIP values of Bieri *et al.*.[1] The experimental vertical ionization potential (VIP) values for the X, A, B, C, D, and E states of the m-$C_6H_4F_2^+$ ion were reported by Bieri *et al.*[1] to be 9.5, 10.0, 12.4, 12.9, 13.6, and 13.6 eV, respectively. The differences between the VIP values for excited states and the VIP value for the ground state of a molecular ion are the relative energy (denoted as T_v') values of the excited states to the ground state of the ion at the ground-state geometry of the neutral molecule. Therefore, the experimental T_v' values for the A, B, C, D, and E states of the m-$C_6H_4F_2^+$ ion are 0.5, 2.9, 3.4, 4.1, and 4.1 eV, respectively, evaluated using the VIP values of Bieri *et al.* [1].

Theoretical studies on excited electronic states of the m-$C_6H_4F_2^+$ ion are few in the literature. The ground state of m-$C_6H_4F_2^+$ was previously calculated by using the HF,[6,7] MP2,[7] and B3LYP[7] methods. Vysotsky *et al.*[8] calculated the geometries and relative energies of the X, A, and B states of m-$C_6H_4F_2^+$ at the HF and CASSCF levels. These theoretical studies, while helpful, fell short of clarifying the excited electronic states of the m-$C_6H_4F_2^+$ ion.

In the present work we mainly studied the five lowest-lying states of the m-$C_6H_4F_2^+$ ion using the CASSCF (complete active space self-consistent field)[11] and CASPT2 (multiconfiguration second-order perturbation theory)[12,13] methods, which are effective for theoretical studies of excited electronic states of molecules and molecular ions.[14-18] We will report the equilibrium geometries and excitation energies of these states and present our assignments for the X, A, B, C, and D states of m-$C_6H_4F_2^+$ based on our CASPT2 calculation results. We hope the results would be helpful for further experimental and theoretical studies on electronic states of the m-$C_6H_4F_2^+$ ion.

2   Theoretical method and computational details

The CASPT2 and CASSCF calculations were carried out using the MOLCAS 7.8 quantum-chemistry software.[19] With a CASSCF wavefunction constituting the reference function, the CASPT2 calculations were performed to compute the first-order wavefunction

and the second-order energy in the full-CI space. A contracted atomic natural orbital (ANO-L) basis set,[20-22] F[4s3p2d]/C[4s3p2d]/H[3s2p1d], was used. Geometries and atom labelings used for the m-$C_6H_4F_2^+$ ion (C_{2v} symmetry) are shown in Fig. 1.
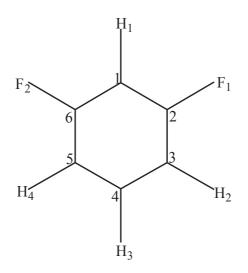

Figure 1: Atom labelings for the m-$C_6H_4F_2^+$ ion (C_{2v} symmetry) used in the present work.

For the five lowest-lying states, the CASPT2 and CASSCF geometry optimization calculations were performed. On the basis of the CASPT2 energies of the ground state and the excited states calculated at the respective CASPT2 and CASSCF geometries, we obtained the CASPT2//CASPT2 and CASPT2//CASSCF adiabatic excitation energy (denoted as " CASPT2 T_0 " and " CASPT2//CASSCF T_0 ", respectively) values for the excited states of the ion. For all the eight states, we calculated the CASPT2 relative energies at the ground-state geometries of the m-$C_6H_4F_2^+$ ion and the m-$C_6H_4F_2$ molecule. On the basis of the CASPT2 energy calculations at the CASPT2 geometry of the ground state of the ion, we obtained the CASPT2 vertical excitation energy (denoted as " CASPT2 T_v ") values for the excited states of the ion. On the basis of the CASPT2 energy calculations at the experimental ground-state geometry of the m-$C_6H_4F_2$ molecule, we obtained the CASPT2 relative energy (denoted as " CASPT2 T_v' ") values for the electronic states of the ion.

In the CAS calculations, 13 electrons were active and the active space included 12 orbitals [CASSCF(13,12)]. Based on the HF/6-31+G(d,p) calculations, the ground-state m-$C_6H_4F_2$ molecule has the following electron configuration (explicitly speaking, a sequence of the occupied and virtual MOs with the occupancies in increasing energy order): $\cdots(12a_1)^2\ (13a_1)^2\ (9b_2)^2\ (10b_2)^2\ (14a_1)^2\ (2b_1)^2\ (3b_1)^2\ (2a_2)^2\ (15a_1)^0\ (16a_1)^0\ (11b_2)^0$ $(4b_1)^0\ (17a_1)^0\ (12b_2)^0\ (3a_2)^0\ (5b_1)^0\ \cdots$. Our active space corresponded to a segment of this sequence from $13a_1$ to $15a_1$, augmented with $11b_2$, $3a_2$, $4b_1$, and $5b_1$ (for including all the π and π^* MOs). Labeling these orbitals (seven occupied plus five virtual) within the C_{2v} point-group in the order of a_1, a_2, b_2, and b_1, this active space is named (3234).

Table 1: Calculated energetic results (in eV) for the m-$C_6H_4F_2^+$ ion: CASPT2 and CASPT2//CASSCF T_0 values for the 1^2A_2, 1^2B_1, 2^2B_1, 1^2A_1, and 1^2B_2 states, CASPT2 T_v and T_v' (calculated at the experimental ground-state geometry of the m-$C_6H_4F_2$ molecule[a]) values for the 1^2A_2, 1^2B_1, 2^2B_1, 1^2A_1, 1^2B_2, 2^2B_2, 2^2A_2, and 3^2B_1 states, and B3LYP T_0, T_v, and T_v' values (for four states).

| State | T_0 | | | State | T_v | T_v' | |
	CASPT2	CASPT2 //CASSCF	expt.[b]		CASPT2	CASPT2	expt.[b]
1^2A_2	0.0	0.0	0.0(X)	1^2A_2	0.0	0.0	0.0(X)
1^2B_1	0.37	0.39	0.36(A)	1^2B_1	0.83	0.37	0.5(A)
2^2B_1	2.80	2.80	2.87(B)	2^2B_1	2.92	2.82	2.9(B)
1^2A_1	3.41	3.46		1^2A_1	3.71	3.60	3.4(C)
1^2B_2	3.54	3.61		1^2B_2	3.64	3.98	4.1(D)
				2^2B_2	4.55	4.17	4.1(E)
				2^2A_2	4.83	4.83	
				3^2B_1	4.98	5.10	

    [a] The experimental geometry of the ground-state m-$C_6H_4F_2$ molecule, see Ref. [23].
    [b] Ref. [1].

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.

3   Results and discussion

3.1   Excitation energies and assignments of the five lowest-lying sates

In Table 1 given are the CASPT2 and CASPT2//CASSCF T_0 values for the 1^2A_2, 1^2B_1, 2^2B_1, 1^2A_1, and 1^2B_2 states of the m-$C_6H_4F_2^+$ ion. The CASPT2 T_v and T_v' values for the 1^2A_2, 1^2B_1, 2^2B_1, 1^2A_1, 1^2B_2, 2^2B_2, 2^2A_2, and 3^2B_1 states are also given in Table 1. All the CASPT2 T_0, T_v, and T_v' values show that 1^2A_2 is the ground state of m-$C_6H_4F_2^+$. Available experimental T_0 and T_v' values (evaluated using the experimental AIP and VIP values) are listed in Table 1.

By checking the CASSCF wave functions, the 1^2A_2, 1^2B_1, 2^2B_1, 1^2A_1, 1^2B_2 and 2^2B_2 states are characterized as primary ionized states. The 2^2A_2 and 3^2B_1 states are characterized as shake-up ionized states. The CASPT2 T_v and T_v' orderings for the eight states are the same, except that the 1^2A_1 and 1^2B_2 states exchange their positions in the orderings. The CASPT2 T_v' values for the six primary ionized states, 1^2A_2, 1^2B_1, 2^2B_1, 1^2A_1, 1^2B_2 and 2^2B_2, are in reasonable agreement with the experimental T_v' values[1] of 0.0, 0.5, 2.9, 3.4, 4.1, and 4.1 eV for the six lowest-lying primary ionized states, respectively (the deviations being smaller than 0.20 eV).

The T_0 calculations for the 1^2A_2, 1^2B_1, 2^2B_1, 1^2A_1, and 1^2B_2 states is for assigning the X, A, B, C, and D states of the m-$C_6H_4F_2^+$ ion. Preliminary CASPT2//CASSCF T_0 calcula-

tions were performed for the 2^2A_2, 2^2A_1, 2^2B_2, and 3^2B_1 states, and the calculated T_0 values for these states are all larger than the CASPT2//CASSCF T_0 value for the 1^2B_2 state, which indicates that the 1^2A_2, 1^2B_1, 2^2B_1, 1^2A_1, and 1^2B_2 states are the five lowest-lying states of the m-$C_6H_4F_2^+$ ion. On the basis of our CASPT2 T_0 calculations the X, A, B, C, and D states of the m-$C_6H_4F_2^+$ ion are assigned to 1^2A_2, 1^2B_1, 2^2B_1, 1^2A_1, and 1^2B_2, respectively. The CASPT2 T_0 orderings for the five lowest-lying states are the same as the energy ordering of the five highest-occupied molecular orbitals of the m-$C_6H_4F_2$ molecule. The CASPT2 and CASPT2//CASSCF T_0 calculations all indicate that the 1^2B_1 state lies below 1^2A_1, supporting the asignment of the lowest excited state to $^2B_1$ by Tsuchiya *et al.* based on their experiments [2].

The experimental T_0 values[1] are available only for the A and B states (0.36 and 2.87 eV, respectively). The CASPT2 T_0 values of 0.37 and 2.80 eV for the 1^2B_1 and 2^2B_1 states are very close to the experimental values for the A and B states, respectively.

3.2 Optimized geometries

In Table 2 given are the CASPT2 and CASSCF optimized geometries for the 1^2A_2, 1^2B_1, 2^2B_1, 1^2A_1, and 1^2B_2 states of the m-$C_6H_4F_2^+$ ion. In Table 2 we also give the CASPT2 and CASSCF optimized geometries and experimental geometry [23] for the 1^1A_1 ground state of the m-$C_6H_4F_2$ molecule. Experimental geometric data are not available for any state of the m-$C_6H_4F_2^+$ ion.

The CASPT2 optimized geometries for the 1^1A_1 ground state of the m-$C_6H_4F_2$ molecule are almost identical to the experimental geometry[23]. For the ionic states (1^2A_2, 1^2B_1, 2^2B_1, 1^2A_1, and 1^2B_2) of the m-$C_6H_4F_2^+$ ion, the CASSCF calculations predict shorter C-F bond lengths than the CASPT2 calculations, and several parameter values in the CASSCF geometries of the 1^2A_2, 2^2B_1, 1^2A_1, and 1^2B_2 states are significantly different from those in the CASPT2 geometries. The CASPT2 calculations predict more accurate geometries for the ground-state halogen-benzene molecules than the CASSCF calculations based on our previous studies [15,16]. We expect that the CASPT2 calculations would predict accurate geometries for the ground and excited states of the m-$C_6H_4F_2^+$ ion.

In the following, we will briefly compare the CASPT2 geometries of the five ionic states with the CASPT2 geometry of the ground-state molecule, and all the geometric parameter values mentioned in the present paragraph are the CASPT2 values. The C-F bond lengths in all the five ionic states are shorter than the bond length in the neutral molecule. The C_1-C_2 bond lengths in the 1^2B_1, 2^2B_1, and 1^2B_2 states are significantly longer than the bond length in the neutral molecule. The C_2-C_3 bond lengths in the 1^2A_2, 2^2B_1, and 1^2A_1 states are significantly longer than the bond length in the neutral molecule while the C_2-C_3 bond length in the 1^2B_1 state is shorter than that in the neutral molecule. The C_3-C_4 bond lengths in the 1^2B_1 and 2^2B_1 states are significantly longer than the bond length in the neutral molecule while the C_3-C_4 bond length in the 1^2A_1 state is significantly shorter than that in the neutral molecule. The $C_2C_1C_6$ and $C_3C_4C_5$ bond angles in the 1^2A_1 state are larger than that in the neutral molecule. When the dominant configuration can be

Table 2: CASPT2 and CASSCF optimized geometries[a] for the 1^1A_1 (X^1A_1) state of the m-$C_6H_4F_2$ molecule and for the 1^2A_2, 1^2B_1, 2^2B_1, 1^2A_1, and 1^2B_2 states of the m-$C_6H_4F_2^+$ ion (bond lengths are given in Å and angles in degrees; for atom labelings, see Fig. 1).

State	Method	$R(C_2$-$F_1)$	$R(C_1$-$C_2)$	$R(C_2$-$C_3)$	$R(C_3$-$C_4)$	$\angle C_2C_1C_6$	$\angle C_1C_2C_3$	$\angle C_3C_4C_5$
1^1A_1	CASPT2	1.354	1.385	1.381	1.392	116.5	123.1	120.9
	CASSCF	1.328	1.385	1.384	1.393	117.0	122.7	120.9
	expt.[b]	1.356	1.389	1.375	1.396	115.7	123.7	120.9
1^2A_2	CASPT2	1.300	1.378	1.439	1.388	115.3	123.5	118.8
	CASSCF	1.282	1.379	1.436	1.407	115.9	123.1	118.3
1^2B_1	CASPT2	1.310	1.430	1.361	1.420	118.7	121.3	123.0
	CASSCF	1.293	1.429	1.362	1.417	118.2	121.5	123.1
2^2B_1	CASPT2	1.304	1.411	1.419	1.432	117.2	122.9	120.3
	CASSCF	1.286	1.417	1.417	1.452	117.7	122.2	119.9
1^2A_1	CASPT2	1.308	1.381	1.432	1.360	121.3	120.7	129.7
	CASSCF	1.297	1.382	1.444	1.356	112.0	122.7	136.3
1^2B_2	CASPT2	1.320	1.419	1.377	1.396	114.0	123.0	116.0
	CASSCF	1.299	1. 384	1.376	1.445	116.2	121.1	106.2

[a] Only geometric parameters in the heavy-atom frame-works are given.
[b] The experimental geometry of the ground-state m-$C_6H_4F_2$ molecule, see Ref. [23].

found in the CASSCF wavefunction for an ionic state and it could be represented as a "hole" with respect to the electronic configuration of the neutral molecule, the geometric changes in the ionized states could be rationalized by analyzing the (bonding and anti-bonding) features in the respective singly occupied molecular orbitals (SOMOs). For example, the shortening of the C-F bond in the geometries of the 1^2A_2, 1^2B_1, and 2^2B_1 states can be understood by realizing the antibonding character between the C and F atoms in the $2a_2$, $3b_1$, and $2b_1$ MOs of the molecule. The lengthening of the C_2-C_3 bond in the geometry of the 1^2A_2 state, the C_1-C_2 and C_3-C_4 bond in the geometry of the 1^2B_1 state can be understood by realizing the bonding character between the C_2 and C_3 atoms in the $2a_2$ MO, the C_1 and C_2 atoms, and C_3 and C_4 atoms in the $3b_1$ MO of the molecule. The lengthening of the C_1-C_2, C_2-C_3, and C_3-C_4 bond in the geometry of the 2^2B_1 state can be understood by realizing the bonding character among the six C atoms in the $2b_1$ MO of the molecule.

4 Conclusions

Electronic states of the m-$C_6H_4F_2^+$ ion have been studied within C_{2v} symmetry by using the CASPT2 and CASSCF methods in conjunction with the ANO-L basis set. The cal-

culations predict that the 1^2A_2 state is the ground state and indicate that the five states are the low-lying doublet states of the ion. The CASPT2 adiabatic (T_0) and vertical (T_v) excitation energies and the CASPT2 relative energies (T'_v) at the experimental geometry of the molecule were reported. Among the five lowest-lying states, the assignments of the B, C, and D states of the m-$C_6H_4F_2^+$ ion were difficult since the three states are closely lying. Based on our CASPT2 T_0 calculations, we assign the X, A, B, C, and D states of m-$C_6H_4F_2^+$ to 1^2A_2, 1^2B_1, 2^2B_1, 1^2A_1, and 1^2B_2, respectively, which supports the suggested assignment of the lowest excited state to $^2B_1$ by Tsuchiya *et al.* based on their experiments. We encourage other people to confirm our calculated results using experiments or other high-level calculations.

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