J. At. Mol. Sci.
doi: 10.4208/jams.090213.112213a

Vol. 5 , No. 2, pp. 171-177
May 2014

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

Shu-Yuan Yu[a,*] and Cheng-Gen Zhang [a,b]

[a] *Department of Chemistry and Material Science, Langfang Normal College, Langfang 065000, China*
[b] *College of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, P.O. Box 4588, Beijing 100049, China*

Received 2 September 2013; Accepted (in revised version) 22 November 2013

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.

PACS: 31.10.+Z, 31.25.Eb, 31.25.Jf

Key words: CASPT2, electronic states, excitation energies, geometries

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,

---

[*] Corresponding author. *Email address:* `yushuyuan05@mails.ucas.ac.cn` (S. -Y. Yu)

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(σ,π). 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