Ab initio CI calculations on potential energy curves of low-lying states of BrF and its cation including spin–orbit coupling

Rui Li [a,b], Xiaomei Zhang [a], Wei Feng [a], Yuanfei Jiang [a], Dehou Fei [a], Mingxing Jin [a], Bing Yan [a,*], Haifeng Xu [a,*]

[a] Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, China
[b] Department of Physics, College of Science, Qiqihar University, Qiqihar 161006, China

ABSTRACT

Bromine monofluoride (BrF) and its cation (BrF$^+$) have attracted much scientific attention because of their potential significance in the stratospheric ozone depletion and the development of chemical laser. Despite that the structure and spectroscopic properties of the $1^3\Pi_{0+}$ ($B^3\Pi_{0+}$) and $1^3\Pi_1$ states of BrF have been experimentally investigated in the literature, theoretical investigations of BrF and its cation are relatively sparse. In this paper, the low-lying electronic states for BrF/BrF$^+$ were studied by means of relativistic multireference configuration interaction method (including Davidson correction). The spin–orbit coupling effect was considered by the state-interacting method with the full Breit-Pauli Hamiltonian. For BrF, the potential energy curves (PECs) of 12 Λ–S states and 23 Ω states generated from the Λ–S states were calculated. The avoided crossing mechanism of $\Omega = 0^+$ states were analyzed by the variations of dominant Λ–S composition for Ω states at several different internuclear distances. For BrF$^+$, the PECs of the ground states ($X^2\Pi_{3/2}$ and $X^2\Pi_{1/2}$) were computed. The spectroscopic constants of the bound states of BrF/BrF$^+$ were determined, which are in good agreement with previously available experimental results. Finally, the ionization energies from the neutral ground state ($X^1\Sigma^+$) to different ionic states ($X^2\Pi_{3/2}$, and $X^2\Pi_{1/2}$) were obtained.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The diatomic interhalogen BrF molecule and its cation have attracted much scientific interest in experiment and theory [1–5] because of their important role in the process of the destruction of ozone in the troposphere. Interhalogen molecules are also viewed as model systems for studying non-adiabatic interactions of the excited electronic states [6–9]. In addition, it has been demonstrated that the excitation for BrF ($B^3\Pi_{0+}$) by energy transfer [10] plays a significant role in development of chemical lasers. It is therefore of great importance to retrieve accurate electronic structure and transition properties of BrF and it cation.

Experimentally, the pioneering work of the microwave spectrum of BrF was recorded by Smith et al. in 1950, and the spectroscopic constants for $X^1\Sigma^+$ state were determined [11]. Brodersen and Sicre [12] observed the $A^3\Pi_1$–$X^1\Sigma^+$ and $B^3\Pi_{0+}$–$X^1\Sigma^+$ transitions of BrF and obtained spectroscopic constants of the two low-lying excited states ($A^3\Pi_1$ and $B^3\Pi_{0+}$) through vibrational-resolved absorption spectra. Later, the photoelectron spectra of BrF($X^1\Sigma^+$) was photographed by Colbourn et al. [13], from which the vertical

and adiabatic ionization energies from the neutral ground state ($X^1\Sigma^+$) to ionic states ($X^2\Pi_{3/2}$ and $X^2\Pi_{1/2}$) were obtained. Clyne et al. carried out a series of experimental studies to investigate the fluorescence lifetimes, dissociation energies, predissociation mechanisms of excited state $B^3\Pi_{0+}$ of BrF and IF [14–18]. Coxon et al. photographed the $B^3\Pi(0^+)$–$X^1\Sigma^+$ emission spectrum of BrF [19,20] and obtained the Rydberg–Klein–Rees (RKR) potential curves of both $B^3\Pi(0^+)$ and $X^1\Sigma^+$ states. The most recent experimental work by Müller and Gerry [1] observed the rotational resolved spectrum of BrF utilizing microwave Fourier transform spectroscopy. The accurate spectroscopic constants of the ground state $X^1\Sigma^+$ were determined from their high resolution spectroscopic study.

Along with the above-mentioned experimental studies, there are a few theoretical investigations on the spectroscopic properties of the ground state of BrF/BrF$^+$ using a number of ab initio methods. Early studies included calculations on spectroscopic constants of the ground state for BrF [21] by self-consistent field molecular orbital calculations. Subsequently, Colbourn et al. [13] computed valence ionization energies of BrF using the multiple scattering-$X\alpha$-self-consistent field (MS-$X\alpha$-SCF) method. Later, De Jong et al. investigated the relativistic and correlation effects on spectroscopic constants of the ground state of BrF [3] by using a set of

* Corresponding authors. Tel.: +86 431 85168817; fax: +86 431 85168816.
 E-mail addresses: yanbing@jlu.edu.cn (B. Yan), xuhf@jlu.edu.cn (H. Xu).

method including second-order Møller–Plesset perturbation theory (MP2), configuration interaction with single and double excitations (CISD), coupled cluster theory with single and double excitations (CCSD), and coupled cluster theory with single and double excitations and including a perturbative triples correction (CCSD(T)). They also discussed in detail the influence of relativistic effect on the electric dipole moment. However, the previous theoretical investigations have only focused on the ground state of BrF. In addition, the spin–orbit coupling (SOC) effect was not considered in the previous work, which may play a key role in spectroscopic and dynamic characters of the electronic states. It is well known that the SOC could lead to avoided crossing phenomenon of two different Λ–S electronic states with same Ω components, and the potential energy curves (PECs) near the avoided crossing region could become more complicated. The observed splitting energy for the ground ^2P_u state of Br atom is 3685.24 cm^{-1} [22], thus the SOC effect is expected to have great influence on the PECs and dissociation energy of BrF.

In the present work, we performed high level *ab initio* calculations on the low-lying electronic states of BrF/BrF$^+$. The PECs of 12 Λ–S states as well as those of 23 Ω states generated from the Λ–S states for BrF were computed. The PECs of X$^2\Pi_{3/2}$ and X$^2\Pi_{1/2}$ for BrF$^+$ were also calculated. The spectroscopic constants of the bound states were obtained from the computed PECs. With the aid of the variations of Λ–S composition for Ω = 0$^+$ states at a set of internuclear distances, the avoided crossing mechanism between B$^3\Pi_{0+}$/(3)0$^+$ states were analyzed in detail. Finally, the vertical and adiabatic ionization energies of BrF were evaluated.

2. Methods and computational details

The present *ab initio* calculations were performed by Molpro2010 [23] suite of quantum chemical package designed by Werner et al. The symmetry point group of BrF molecule is C$_{\infty v}$. However, because of the limitation of Molpro program, all the calculations were carried out in the C$_{2v}$ subgroup of C$_{\infty v}$ point group. The corresponding relationships between the irreducible representations of C$_{2v}$ and C$_{\infty v}$ point groups are Σ^+ = A$_1$, Π = B$_1$ + B$_2$, Δ = A$_1$ + A$_2$ and Σ^- = A$_2$. In order to minimize the errors originated from basis set truncation, large correlation consistent atomic basis set (aug-cc-pwCV5Z-DK [24–27]) was utilized in subsequent calculations. The method of state-average complete active space self-consistent field (SA-CASSCF) [28,29] was used to explore the PECs. 12 Λ–S states, including two $^1\Sigma^+$ states, two $^1\Pi$ states, one $^1\Sigma^-$ state, one $^1\Delta$ state, two $^3\Sigma^+$ states, two $^3\Pi$ states, one $^3\Sigma^-$ state, and one $^3\Delta$ state, were treated simultaneously in SA-CASSCF calculations. In the CASSCF calculations, active space was composed of 9 molecular orbitals (MOs) corresponding to F 2s2p and Br 4s4p5s orbitals. Further, by utilizing all configurations in the configuration-interaction (CI) expansion of the CASSCF wave functions as reference, the energies of 12 Λ–S states were computed with the internally contracted multireference configuration interaction method with the Davidson correction (MRCI + Q) [30–32]. The inner shell 1s^2 electrons of F and 1s^{2}2s^{2}2p^{6}3s^{2}3p^6 of Br atom were put into the core orbitals, while the 3d^{10} electrons of Br atom were correlated to account for the core–valence (CV) correlations. That is, a total of 24 electrons in BrF (3d^{10}4s^{2}4p^5 of Br and 2s^{2}2p^5 of F) were correlated in MRCI + Q calculations.

The scalar relativistic effect was treated by the second-order Douglas–Kroll [33] and Hess [34] one-electron integrals. The SOC effect was taken into account by employing the state-interacting method with the full Breit-Pauli (BP) [35] operator, which means that the spin–orbit eigenstates are determined by diagonalizing $\hat{H}^{el}$ + $\hat{H}^{SO}$ in the basis eigenfunctions of $\hat{H}^{el}$. The PECs were plotted by linking the energy points of electronic states considering the avoided-crossing rule between the electronic states with same Ω symmetry.

On the basis of the calculated bound Λ–S and Ω electronic states, the spectroscopic parameters were evaluated through numerical integration LEVEL program designed by Le Roy [36].

3. Results and discussion

3.1. PECs of the low-lying Λ–S electronic states of BrF

The 12 Λ–S states correlated to the lowest dissociation limit (Br(^{2}P) + F(^{2}P)) of BrF were computed at the MRCI + Q/aug-cc-pwCV5Z-DK level of theory. The PECs are displayed in Fig. 1, which are depicted in relative to minimum energy point of the ground state X$^1\Sigma^+$ of BrF. As shown in Fig. 1, the X$^1\Sigma^+$ and 1$^3\Pi$ states are bound states, while the other ten states are typical repulsive states. Table 1 gives the spectroscopic constants of the two bound states derived from the PECs, including adiabatic transition energies T_e, harmonic vibrational frequencies ω_e, anharmonic terms $\omega_e x_e$, rotational constants B_e, equilibrium distances R_e, and dissociation energies D_e. The D_e is obtained by the difference between the energy of the ground state at equilibrium bond length and the energy sum of separated atoms at 8.0 Å. For comparison, we also list the results of previously available experimental and theoretical studies. The leading electronic configurations of the 9 low-lying Λ–S states around equilibrium distance and the corresponding vertical excitation energies are shown in Table 2.

The ground state X$^1\Sigma^+$ of BrF is mainly described by the closed-shell electronic configuration $\sigma^2\pi^4\pi^{*4}\sigma^{*0}$. In comparison with experiment results [1,20], the calculated ω_e, $\omega_e x_e$, and R_e are only 5.35, 0.2193 cm^{-1} and 0.0041 Å underestimated, respectively, while the calculated B_e differs by no more than 0.0010 cm^{-1}. In addition, our computed D_e value of 2.40 eV is in accord with the experimental value of 2.60 eV [17,37], the deviation between the measured value and our computed value could be decreased when the SOC effect is taken into account (see the spectroscopic constants of Ω states in next section). The leading electronic configuration of the first excited state 1$^3\Pi$ ($\sigma^2\pi^4\pi^{*3}\sigma^{*1}$) is formed by one electron transition of $\pi^* \rightarrow \sigma^*$. The calculated equilibrium distance of 1$^3\Pi$ (2.1582 Å) is obviously larger than that of X$^1\Sigma^+$ (1.7549 Å), indicating that the σ^* molecular orbital is somewhat more antibonding than the π^* orbital. As shown in Table 2, the vertical excited energies of 1$^3\Pi$ and 1$^1\Pi$ are in the energy range of 23,000–31,000 cm^{-1}, while that of 2$^3\Pi$, 2$^1\Pi$, 1$^3\Sigma^+$, 1$^3\Sigma^-$, 1$^1\Delta$, and 2$^1\Sigma^+$ excited states are located in 55,000–65,000 cm^{-1}. Due to the high
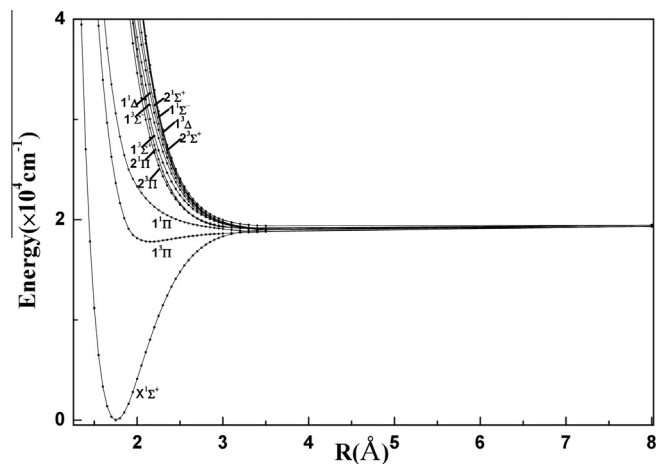

Fig. 1. MRCI + Q potential energy curves of the low-lying Λ–S states of BrF.