Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 159 (2016) 60–67

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

# Extensive theoretical studies on the low-lying electronic states of $BBr^+$

Xianghong Niu [a,1], Huabing Shu [a,1], Zunlue Zhu [b], Qian Chen [a,*]

[a] Department of Physics, Southeast University, Nanjing 211189, China
[b] College of Physics and Electronic Engineering, Henan Normal University, Xinxiang 453007, China

A R T I C L E I N F O

*Article history:*
Received 11 October 2015
Received in revised form 9 January 2016
Accepted 19 January 2016
Available online 22 January 2016

*Keywords:*
Spectroscopic parameters
Potential energy curves
Relativistic correction
Transition properties

A B S T R A C T

The potential energy curves (PECs) of two lowest dissociation channels of $BBr^+$ have been thoroughly investigated using the internally contracted multireference configuration interaction method with Davidson correction and relativistic correction. All PECs are extrapolated to complete basis set limit. Several quasibound excited states caused by avoided crossings are found. Based on the PECs, the spectroscopic parameters of bound and quasibound states are obtained. The transition dipole moments and radiative lifetimes are predicted for all possible transitions. Finally, the spin–orbit coupling matrix elements are computed using the states interaction approach with the full Breit–Pauli Hamiltonian to analyze the interactions in PECs crossing regions. We propose that the $2^2\Sigma^+$–$X^2\Sigma^+$ and $2^2\Pi$–$X^2\Sigma^+$ transitions which cannot be observed in experiments are attributed to the intricate couplings among $1^2\Pi$, $2^2\Pi$, $2^2\Sigma^+$, $1^4\Sigma^+$, $1^4\Delta$, $1^4\Sigma^-$, $1^2\Delta$ and $1^2\Sigma^-$ states.

## 1. Introduction

The group IIIA monohalides cations are isoelectronic to the neutral monohalides of alkaline earth atoms. Both these species are ionically bound and significant prototypical systems to research the fundamental electrostatic interactions [1–5]. More interesting, these compounds also play important roles in their semi-conducting properties and development of microelectronic and optoelectronic devices applications [6–9]. Therefore, the detailed elucidation of their electronic and molecular structures deserves great attention.

Glenewinkel-Meyer [10] made a comprehensive research for $AX^+$, with A = B, Al, Ga, In and X = F, Cl, Br via chemiluminescent ion–molecule reactions. The chemiluminescence spectra were observed at the range of 2000–6000 Å. Unlike the lowest $^2\Sigma^+$–$^2\Sigma^+$ transition of isoelectronic MX (M, alkaline earth atom) species with rather narrow spectral regions, the $B^2\Sigma^+$–$X^2\Sigma^+$ transition of $AX^+$ showed broad quasi continuum spectra with undulatory structure. The feature was attributed to the larger equilibrium inter-nuclear distance of $B^2\Sigma^+$ state, with respect to the ground state of $X^2\Sigma^+$ [10]. This hypothesis was confirmed by subsequent theoretical calculations of $AlF^+$ [5], $AlCl^+$ [5], $GaF^+$ [11], $GaCl^+$ [11], $InF^+$ [4] and $InCl^+$ [8,9]. These ab initio calculations presented avoided crossings between the $B^2\Sigma^+$ and $X^2\Sigma^+$ states correlating with two different dissociation channels, $A^+(^1S) + X(^2P)$ and $A^+(^3P) + X(^2P)$, respectively. However, for the $BCl^+$ and $BBr^+$ [10], the $B^2\Sigma^+$–$X^2\Sigma^+$ transition was lacking. Glenewinkel-Meyer [10] considered that the $BBr^+$ had an exceptional ordering of dissociation channels. The second lowest lying channel was not $B^+(^3P) + Br(^2P)$, but $B(^2P) + Br^+(^3P)$. Unfortunately, they did not observe any $BBr^+$ spectra in experiment. Yamaguchi [12] observed the emission spectra of $BBr^+$ and obtained $A^2\Pi$–$X^2\Sigma^+$ system from flowing afterglow reactions of $BBr_3$ in the region of 470–515 nm. The excitation energy, harmonic and anharmonic vibrational constants were estimated. However, Glenewinkel-Meyer [10] held that the $^2\Pi$–$X^2\Sigma^+$ transition should lie at 300 nm or less due to the progressive blue shift of the $BF^+$, $BCl^+$, $BBr^+$ systems, rather than the region of 470–515 nm observed by Yamaguchi [12], with a excitation energy of 2.50 eV. In addition, Glenewinkel-Meyer [10] demonstrated that the result of excitation energy by Yamaguchi [12] was hardly compatible with the predicted *Te* value coming from the dissociation energies according to linear Birge–Sponer plot using the results of Yamaguchi [12].

Theoretically, in 1997, only Kim [13] evaluated the mainly bound states spectroscopic parameters of $BBr^+$ with two lowest dissociation asymptotes. But they did not take into account all the possible transitions of excited states to ground state and excited states to excited states. As for the objectionable experimental observations [10,12], the intricate couplings between the $2^2\Sigma^+$, $2^2\Pi$ and others states were lack to analysis. Besides, they only calculated a narrow range (1–4 Å) to all potential energy curves (PECs). The important spectroscopic parameters, dissociation energy, cannot be estimated, and several quasibound excited states caused by avoided crossings cannot be found. In view of the lack of crucial information for $BBr^+$, a comprehensive research of the low-lying electronic states is necessary.

The aim of this work is to extend the spectroscopic knowledge of $BBr^+$. We perform high-quality internally contracted multireference configuration interaction (icMRCI) with Davidson modification and relativistic correction all-electron calculations for the ground and low-

---

[*] Corresponding author.
*E-mail address:* cqseu@sina.com (Q. Chen).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.saa.2016.01.028
1386-1425/

lying excited states. All PECs are extrapolated to complete basis set limit. We predict some quasibound states coming from the avoided crossings of PECs. All possible transitions are taken into account, and radiative lifetimes are reported for the first time. More importantly, the intricate couplings among $1^2\Pi$, $2^2\Pi$, $2^2\Sigma^+$, $1^4\Sigma^+$, $1^4\Delta$, $1^4\Sigma^-$, $1^2\Delta$ and $1^2\Sigma^-$ states are analyzed which results in the unobserved transitions of $2^2\Sigma^+$–$X^2\Sigma^+$ and $2^2\Pi$–$X^2\Sigma^+$ in experiments.

## 2. Computational details

In present work, the first two dissociation channels of $BBr^+$ will be studied. All PECs are calculated with the MOLPRO 2010.1 program package [13]. The $BBr^+$ belongs to the $C_{\infty v}$ symmetry. To make the calculations in this package, we must substitute the $C_{\infty v}$ symmetry with the $C_{2v}$ point group which has four irreducible representations, $A_1$, $A_2$, $B_1$ and $B_2$.

Because a number of electronic states with different characteristics in wave-functions will be taken into account simultaneously, it is significant to generate balanced orbitals for subsequent multi-reference correlation calculations. Thus, the state-averaged complete active space self-consistent field (CASSCF) method is performed to assure the required degeneracy of relevant electronic states. Then, the icMRCI approach is performed to treat dynamical electron correlation. The selection of active space is important to the CASSCF and icMRCI calculations. We employ eight molecular orbitals (MOs) are in the active space, including four $a_1$, two $b_1$ and two $b_2$ symmetry MOs which correspond to the 2s2p shell of B and 4s4p shell of Br atoms or cations. This consists of nine electrons and eight molecular orbitals (referred to CAS (9, 8)). The rest of electrons are put into fifteen closed-shell core orbitals (eight $a_1$, three $b_1$, three $b_2$ and one $a_2$ symmetry). When we use the MOs (twelve $a_1$, five $b_1$, five $b_2$ and one $a_2$) to carry out calculations, the PECs are not smooth. The electronic excitation may involve more outer-shell orbitals. In Fig. S1, we illustrate molecular orbital energies obtained from CASSCF calculations. The longer the bond length, the lower the energies of $11\sigma$ and $12\sigma$ (outer-shell orbital) is (due to strong antibonding character). The energies of $11\sigma$ and $12\sigma$ are high and should have some interaction around 2 Å where the potential wells of most states lie in this region. In view of the above, we add the $12\sigma$ orbital into active space and acquire a new active space labeled as CAS (9, 9). When we use the MOs (thirteen $a_1$, five $b_1$, five $b_2$ and one $a_2$) to carry out the PECs calculations, we find that the PECs are smooth over the internuclear separation range from 1.0 to 10.0 Å, and each PEC is convergent. So, CAS (9, 9) is used in the present calculations.

As for B and Br, the aug-cc-pVQZ-DK (AVQZ) and aug-cc-pV5Z-DK (AV5Z) basis sets [14–16] are employed. Both basis sets are uncontracted in the calculations. To improve the quality of PECs, Scalar relativistic effects are taken into account using third-order Douglas–Kroll Hamiltonian approximation (DKH3) [17–19]. The icMRCI method only considers all single and double excitations. So, the Davidson correction (icMRCI + Q) [20,21] is employed to estimate the triple and quadruple excitations. The coefficients squared of configuration state function ($c^2$) associated with the electronic configuration are found within the range of 0.894–0.925, which demonstrate that Davidson correction work properly. Besides, to detail analyze the interactions in PECs crossing regions, the spin–orbit couplings are calculated through the states interaction approach with the Breit–Pauli Hamiltonian ($H_{BP}$) [22].

Basis set extrapolation to the CBS limit has become a widely employed technique. Two correlation-consistent basis sets, AVQZ and AV5Z, are used for the extrapolation scheme. The total energy is consisted of reference (HF) and correlation parts [23,24].

$$E^{tot} = E^{HF} + E^{cor}. \tag{1}$$

The extrapolation formula of energy components is written as:

$$E_X^{HF} = E_\infty^{HF} + A^{HF}X^{-\alpha}, \text{ and} \tag{2}$$

$$E_X^{cor} = E_\infty^{cor} + A^{cor}X^{-\beta}. \tag{3}$$

Here, X is the cardinal number of basis set. The parameters $\alpha$ and $\beta$ are different which have been obtained by Truhlar [23] ($\alpha$, 3.4 and $\beta$, 2.4). The total energies obtained by two successive basis sets, aug-cc-pV(X)Z-DK and aug-cc-pV(X + 1)Z-DK, respectively.

The spectroscopic constants for all quasibound and bound electronic states are evaluated, and transition properties of all possible electronic states are also obtained by solving the nuclear Schrödinger equation using LE ROY'S LEVEL program [25].

## 3. Results and discussions

Foremost, we have to find out the electronic states of first two dissociation channel of $BBr^+$. As for B and Br atoms, the ground states are $^2P_u$. The ground states of $B^+$ and $Br^+$ cations are $^1S_g$ and $^3P_g$, respectively. The first dissociation limit is $B^+(^1S_g) + Br(^2P_u)$, and subsequently, is $B(^2P_u) + Br^+(^3P_g)$. Unlike other IIIA group monohalides cations, the second dissociation limit is $A^+(^3P) + X(^2P)$. The atomic group representation $S_g$, $P_u$ and $P_g$ are resolved into molecule group $C_{\infty v}$,

$\Sigma_g^+$,$\Sigma_u^+\oplus\Pi_u$and $\Sigma_g^-\oplus\Pi_g$respectively.

For $B^+(^1S_g) + Br(^2P_u)$ and $B(^2P_u) + Br^+(^3P_g)$, their direct product is

$${}^1\Sigma_g^+\otimes\left({}^2\Sigma_u^+\oplus{}^2\Pi_u\right) = {}^2\Sigma^+\oplus{}^2\Pi \text{ and} \tag{4}$$

$$\left({}^2\Sigma_u^+\oplus{}^2\Pi_u\right)\otimes\left({}^2\Sigma_g^-\oplus{}^2\Pi_g\right) = {}^{2,4}\Sigma^+\oplus{}^{2,4}\Sigma^-(2)\oplus{}^{2,4}\Pi(2)\oplus{}^{2,4}\Delta. \tag{5}$$

The direct product generates 14 electronic states. The $X^2\Sigma^+$ and $1^2\Pi$ states correlate to the first dissociation limit $B^+(^1S_g) + Br(^2P_u)$, and the $2^2\Sigma^+$, $1^2\Sigma^-$, $2^2\Sigma^-$, $2^2\Pi$, $3^2\Pi$, $1^2\Delta$, $1^4\Sigma^+$, $1^4\Sigma^-$,$2^4\Sigma^-$, $1^4\Pi$, $2^4\Pi$ and $1^4\Delta$ states attach to the second dissociation limit $B(^2P_u) + Br^+(^3P_g)$. To display clearly of these states, the PECs of all $\Sigma$ states are plotted in Fig. 1a, and all $\Pi$ and $\Delta$ states in Fig. 1b. The energy difference of the first two dissociation limits is 28,470 $cm^{-1}$ which agrees well with the measurement of 28,356 $cm^{-1}$ [26]. To present clearly of PECs with double potential well due to avoided crossing, we show an amplified view of these PECs in Fig. S2.

The dipole moments of electronic states in the first dissociation channel are presented in Fig. 2a, and the second dissociation channel in Fig. 2b and c, which are calculated with the aug-cc-pV5Z-DK basis set. At large internuclear distance, a linear dependence is expected for all electronic states (a specific character of ionic states). The dipole moments of $X^2\Sigma^+$ and $1^2\Pi$ states linearly decreasing with a negative sign indicates that the positive charge is located at the B atom, which is on the negative side of the z axis. This is agree with the first dissociation limit $B^+(^1S_g) + Br(^2P_u)$. In contrast to the first dissociation limit, the dipole moments of electronic states in the second dissociation channel increases linearly with a positive sign in large internuclear distance associated with the $B(^2P_u) + Br^+(^3P_g)$.

Now, we discuss the effect of the basis set and CBS extrapolation to the computational results. For the sake of length limitation and convenient discussion, we only collect the $D_e$, $R_e$ and $\omega_e$ results of $1^4\Sigma^+$ and $1^4\Delta$ states obtained by the icMRCI + Q approaches in association with the correlation consistent basis sets from the AVTZ to AV5Z and the extrapolation to the CBS limit using the AVQZ and AV5Z basis. The $D_e$ and $\omega_e$ values increase as systematically increasing the quality of basis sets. For $1^4\Sigma^+$ state, the $D_e$ values are 2.113, 2.208, 2.239 and 2.311 eV, and the $\omega_e$ values are 588.1, 594.3, 596.3, 597.5 $cm^{-1}$, for AVTZ, AVQZ, AV5Z and CBS extrapolation, respectively. For $1^4\Delta$ state, the $D_e$ values are 1.852, 1.953, 1.985 and 2.055 eV, and the $\omega_e$ values are 541.7, 551.8, 554.6, 554.9 $cm^{-1}$ for AVTZ, AVQZ, AV5Z and CBS extrapolation, respectively. The $R_e$ value decrease with increasing the quality of basis sets. For $1^4\Sigma^+$ and $1^4\Delta$ states, the $R_e$ values are 1.997, 1.992, 1.990,