



# Ab initio MRCI + Q calculations on the low-lying excited states of the MgBr radical including spin–orbit coupling



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## ABSTRACT

Accurate theoretical calculations on the MgBr radical have been carried out by using the high-level relativistic multireference configuration interaction method with Davidson correction (MRCI + Q) using correlation-consistent Quintuple- $\zeta$  quality basis set. The potential energy curves (PECs) of the 14  $\Lambda$ -S states of MgBr have been computed. In order to improve the PECs, the core–valence correlation, scalar relativistic effect, and spin–orbit coupling effect are taken into account in the computations. The spectroscopic constants of the bound states have been determined from the computed PECs. The results of the ground state  $X^2\Sigma^+$  and the first excited state  $A^2\Pi$  are in good agreement with those from the available experiments, while spectroscopic constants of the other electronic states are firstly reported. The low-lying ion-pair state  $B^2\Sigma^+$  correlated to ion-pair dissociation limit  $Mg^+ (^2S_g) + Br^- (^1S_g)$  is characterized. The permanent dipole moments (PDMs) of  $\Lambda$ -S states and the  $R$ -dependent spin–orbit (SO) matrix elements are computed. The results indicate that the abrupt changes of PDMs and the SO matrix elements are attributed to the changes of the electronic configurations near the avoided crossing point. After taking the SOC effect into account, the 14  $\Lambda$ -S states split into 30  $\Omega$  states, and the SOC splitting for the  $A^2\Pi$  is calculated to be  $102.58\text{ cm}^{-1}$ . The SOC effect, leading to the double-well potential of the  $\Omega = (3)1/2$  state, is found to be substantial for MgBr. In order to further illustrate the SOC effect and the avoided crossing phenomenon of the PECs, the  $\Lambda$ -S compositions in the  $\Omega$  state wavefunctions are analyzed in detail. Finally, the transition dipole moments (TDMs) of several transitions from upper  $\Omega$  states to the ground  $X^2\Sigma^+_{1/2}$  state and the corresponding radiative lifetimes have been studied. It is shown that the  $(1)3/2-X^2\Sigma^+_{1/2}$  and  $(2)3/2-X^2\Sigma^+_{1/2}$  are particularly important to the observed transitions  $A^2\Pi-X^2\Sigma^+$  and  $C^2\Pi-X^2\Sigma^+$ . The present study should shed more light on the electronic structures and transition properties of electronic states of the MgBr radical.

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## 1. Introduction

The first spectroscopic detection of the MgBr radical was reported by Olmsted at the beginning of the 20th century [1]. This work was extended in 1928 by Walters and Barratt, who made an absorption study of the same spectra region [2]. Morgan observed the first vibrational resolved spectra which were assigned to the  $A^2\Pi-X^2\Sigma^+$  transition [3]. Harrington observed the  $A^2\Pi-X^2\Sigma^+$  and  $C^2\Pi-X^2\Sigma^+$  absorption transitions and noted a predissociation in the  $A^2\Pi-X^2\Sigma^+$  system for the first time [4]. Hirao et al. [5] recorded the rotationally resolved (0, 0) and (0, 1) spectra of  $A^2\Pi-X^2\Sigma^+$  transition in MgBr with Fourier transform spectrometer. By considering Harrington's results [4], they determined improved vibrational constants and RKR potentials for the  $A^2\Pi$  and  $X^2\Sigma^+$  states. Walker and Gerry examined the Fourier transform microwave spectrum of MgBr and obtained rotational transitions for a few low-lying rotational levels of the ground state [6]. Patel made a partial

rotational analysis of the  $A^2\Pi-X^2\Sigma^+$  (0–0) band [7]. On the basis of the equilibrium bond distance value and the hyperfine structure, they concluded that the unpaired electron is located on the Mg atom and the Mg–Br bond is almost completely ionic in the ground state. As summarized above, early experiments mainly focused spectroscopic parameters of low-lying electronic states in MgBr, while the studies on couplings between electronic states and potential energy curves (PECs) for repulsive states and other low-lying bound states are not very extensive.

Recently, both theoretical and experimental studies of predissociation in the  $A^2\Pi$  state of MgBr [8,9] have been made. Sadygov et al. [8] carried out *ab initio* calculations by using second order configuration interaction (SOC) on MgBr and compared the results with a medium resolution laser induced fluorescence (LIF) spectrum of the  $A^2\Pi-X^2\Sigma^+$  band system. They investigated the resonances in predissociation mechanisms of  $\Omega$  components of  $A^2\Pi$  state by introducing the interstate coupling and spin–orbit coupling (SOC) interaction. Several other theoretical studies examined the  $A^2\Pi-X^2\Sigma^+$  transition [4,10] and the transitions from higher excited electronic states to the

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ground state [11,12]. The SOC splits of  $A^2\Pi$  state [13] and Franck-Condon (FC) factors of  $A^2\Pi-X^2\Sigma^+$  transition [14] in MgBr were theoretically examined. While in these computational studies, the core–valence (CV) correlation and scalar relativistic effect were not fully considered.

To date, the spectroscopic characters and transition properties of the low-lying excited states of MgBr are not very extensive. As far as we know, only part of spectroscopic constants are available for the ground state  $X^2\Sigma^+$  and the first excited state  $A^2\Pi$  [8,15]. As for other higher excited states, almost no *ab initio* calculations, which may provide extensive and accurate information for experimental investigation on the electronic states of MgBr radical, are available in the literatures.

In the present paper, we have performed comprehensive high-level *ab initio* calculations on the ground and low-lying excited states of MgBr radical by using internally contracted multi-reference configuration interaction with Davidson correction (ic-MRCI + Q) method. The correlations of core–core and core–valence electrons were partially included in computations. The PECs of the 14  $\Lambda$ -S states associated with the lowest two dissociation limits of MgBr, as well as those of 30  $\Omega$  states generated from the  $\Lambda$ -S states after considering the SOC effect, were computed. Based on the calculated PECs, the spectroscopic constants for the bound states were obtained, most of which have not been reported previously. The SOC effect of the  $\Lambda$ -S states was evaluated by spin–orbit (SO) matrix elements. The  $\Lambda$ -S compositions of the corresponding  $\Omega$  states were also discussed in detail for further illuminating the importance of SOC effect. The transition properties including the transition dipole moments (TDMs), FC factors, and the radiative lifetimes of the several lowest transitions were also predicted. The calculation presented here will provide more comprehensive results about the structure and behavior of the low-lying electronic states of MgBr.

## 2. Calculation method

All of electronic structure calculations of the MgBr molecule were performed with the MOLPRO 2012 quantum chemistry package [16,17]. The symmetry point group of MgBr radical belongs to the  $C_{\infty v}$ . However, because of the limit of the MOLPRO program, the  $C_{2v}$  point group, the Abelian subgroup of the  $C_{\infty v}$  point group, is adopted in the calculations, which holds A1/B1/B2/A2 irreducible representations. For MgBr,  $4a_1$ ,  $2b_1$ , and  $2b_2$  symmetry molecular orbitals are determined as the active space, corresponding to the atoms Mg  $3s3p$  and Br  $4s4p$  shells. The outermost  $3s^2$  electrons of the Mg atom and  $4s^24p^5$  electrons of the Br atom are placed in the active space.

The ten electrons in the  $3d$  shell of Br are put into the closed-shell orbitals in ic-MRCI computations. These orbitals are doubly occupied in all reference configuration state functions but are correlated through single and double excitations. The rest of the inner electrons are put into the core orbitals. That is to say, there are total 19 electrons in the correlation energy calculations.

In order to obtain the high-level PECs of MgBr, the potential energies at a set of bond lengths were calculated using the restricted Hartree–Fock (RHF) self-consistent field (SCF) method at first. Then the state-averaged complete active space self-consistent field (SA-CASSCF) calculations are carried out by using the previous RHF orbitals as starting guess for orbital optimization [18,19]. Finally, the ic-MRCI approach [20–23] is employed to launch the correlation energy calculation and achieve correlation energies. The Davidson correction (+Q) is taken into account to balance the size-consistency error of the MRCI method. Since Bromine is heavy element, the relativistic effect is expected to be very important. Therefore, the one-electron third-order Douglas–Kroll integrals have been utilized to consider scalar relativity [24]. The contracted Gaussian-type all-electron augmented correlation consistent basis sets aug-cc-pwCV5Z-DK [25] and aug-cc-pV5Z-DK [26] are selected for Mg and Br atoms, respectively.

In the SOC calculations, the state-interacting method is employed [27], the off-diagonal SO matrix elements are calculated with the

MRCI wavefunctions, while the diagonal SO matrix elements are substituted with the ic-MRCI + Q energies.

The PECs are plotted by connecting the calculated points with the aid of the avoided crossing rule between electronic states with same symmetry. The spectroscopic constants, including equilibrium internuclear distance  $R_e$ , excitation energy  $T_e$ , vibrational constants  $\omega_e$  and  $\omega_e\chi_e$ , rotation constant  $B_e$  and vibration–rotation coupling constant  $\alpha_e$  and dissociation energy  $D_e$  are derived by fitting the PECs. The TDMs and the FC factors are evaluated with the LEVEL8.0 program [28]. At last, the radiative lifetimes of the several lowest transitions are calculated.

## 3. Results and discussion

### 3.1. The PECs and spectroscopic constants of the $\Lambda$ -S states

The 14  $\Lambda$ -S states of MgBr, including 8 doublet states and 6 quartet states, were studied by using the MRCI + Q method with aug-cc-pwCV5Z-DK for Mg and aug-cc-pV5Z-DK for Br, respectively. The single-point energies of the set of internuclear distances from 1.6 to 5 Å were calculated and the corresponding PECs were obtained and depicted in Fig. 1. As clearly illustrated in Fig. 1, the 14  $\Lambda$ -S states are correlated with the three dissociation limits including neutral Mg ( $^1S_g$ ) + Br ( $^2P_u$ ), Mg ( $^3P_u$ ) + Br ( $^2P_u$ ), and ion-pair Mg<sup>+</sup> ( $^2S_g$ ) + Br<sup>−</sup> ( $^1S_g$ ). In contrast to the two neutral atomic limits, the ion-pair dissociation limit Mg<sup>+</sup> ( $^2S_g$ ) + Br<sup>−</sup> ( $^1S_g$ ) corresponds to the one-electron transfer from Mg to Br. And only the  $B^2\Sigma^+$  state is associated with the ion-pair limit.

For the calculated  $\Lambda$ -S states, five doublet states  $X^2\Sigma^+$ ,  $A^2\Pi$ ,  $B^2\Sigma^+$ ,  $C^2\Pi$  and  $3^2\Sigma^+$  are bound or quasi-bound states. The corresponding spectroscopic constants are determined from the PECs and listed in Table 1, along with their main electronic configurations and weights around the  $R_e$  in the MRCI wavefunction. For comparison, the available experimental and other theoretical results are also listed in Table 1.

The ground state  $X^2\Sigma^+$  of the MgBr molecule is correlated with the lowest dissociation limit Mg ( $^1S_g$ ) + Br ( $^2P_u$ ). The state is mainly characterized by the closed-shell electronic configuration  $10\sigma^211\sigma^212\sigma^{\alpha}13\sigma^05\pi^46\pi^0$ , which confirms previous experimental conclusion [7]. The molecular  $10\sigma$  and  $11\sigma$  orbitals mainly correspond to the  $3s$  (Mg) and  $4s$  (Br) atomic orbitals, while the  $12\sigma$  and  $13\sigma$  orbitals to the  $3p_z$  and  $4p_z$  orbitals. The molecular  $5\pi$  and  $6\pi$  orbitals correspond to the atomic  $3p_x + 3p_y$ (Mg) and  $4p_x + 4p_y$ (Br) orbitals. Due to the ionic character the ground state has a deep potential well and is calculated to be 3.157 eV. The calculated spectroscopic constants are of good accuracy when compared with the observed values [5]. The calculated  $\omega_e$ ,  $\omega_e\chi_e$ ,  $B_e$ ,  $R_e$ , and  $\alpha_e$  deviate from the experimental values [29] by 4.594  $\text{cm}^{-1}$  (1.23%), 0.071  $\text{cm}^{-1}$  (5.29%), 0.002  $\text{cm}^{-1}$  (1.16%), 0.011 Å (0.47%), and 0.006  $\text{cm}^{-1}$  (6.52%) [6], respectively.

The first excited state  $A^2\Pi$  has the same dissociation limit with the ground state, of which the wavefunction is mainly described by the electronic configuration  $10\sigma^211\sigma^212\sigma^013\sigma^05\pi^46\pi^{\alpha}$ . The electronic configuration also could indicate that the  $A^2\Pi$  state corresponds to the one-electron  $13\sigma \rightarrow 6\pi$  excitation as in the  $X^2\Sigma^+$  state. The excitation energy  $T_e$  for  $A^2\Pi$  state is 25,890.69  $\text{cm}^{-1}$ , which is very close to the recent experimental result 25,824.31  $\text{cm}^{-1}$  [5]. Due to the avoided crossing with the  $C^2\Pi$  state, an obvious barrier with the energy of 28,069.64  $\text{cm}^{-1}$  has been placed in the potential at  $R = 2.62$  Å ( $R_{ACP}$ ) of the  $A^2\Pi$ . The local minimum of  $A^2\Pi$  state lies only 0.346 eV below the first atomic limit. The values of  $T_e$  and  $\omega_e\chi_e$  are in good agreement with the recent experimental results [5], the relative errors are 0.28% and 11.55%, respectively. The  $B_e$  and  $R_e$  are consistent with the experimental results [29]. The value of  $\omega_e$  is close to the observed value and the recent theoretical result determined by the SOCI method [8]. For the  $C^2\Pi$  state, due to the avoided crossing with the  $A^2\Pi$  state, the minimum point of the energy (29,096.07  $\text{cm}^{-1}$ ) is located at the avoided crossing point ( $R_{ACP}$ ). The energy gap of the two states at  $R_{ACP}$  was calculated to be 1113.45  $\text{cm}^{-1}$ . However, different from the  $A^2\Pi$  state, the  $C^2\Pi$  state is

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