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Ab initio calculations on potential energy curves and radiative lifetimes for the band systems A²Π–X²Σ⁺ of magnesium monohalides MgX (X = F, Cl, Br, I)

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HIGHLIGHTS

- The first excited state of MgX (F, Cl, Br, and I) has been studied by high-level MRCI wavefunctions.
- The calculations include Davidson modification and scalar relativistic correction.
- The transition properties are evaluated and in good agreement with measurement.

GRAPHICAL ABSTRACT

The PECs of the X²Σ⁺ and A²Π states of MgX (X = F, Cl, Br, I) molecules.
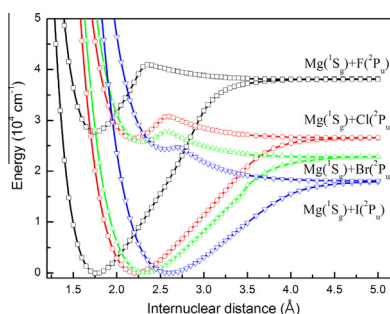
ARTICLE INFO

ABSTRACT

Ab initio calculations on potential energy curves (PECs), spectroscopic constants, transition dipole moments, radiative transition probabilities and lifetimes for the ground state (X²Σ⁺) and the first excited state (A²Π) of MgX (X = F, Cl, Br, I) molecules are determined by high-level internally contracted multi-reference configuration interaction (ic-MRCI) method. In order to improve the calculation, the Davidson modification (+Q) and scalar relativistic correction are included. The present results show that most of spectroscopic constants are in accordance with the measurements, the equilibrium internuclear distance R_e increases while the other spectroscopic constants reduce along with the increasing of the atomic number of the halogen from F to I. Diagonal vibrational transitions are found to be dominant for the A²Π→X²Σ⁺ system of MgX molecules. The corresponding radiative lifetimes of v' = 0 are computed to be 7.24, 9.98, 18.94 and 22.72 ns for MgF, MgCl, MgBr, and MgI, respectively. The calculated result of MgF molecule is in good agreement with the recent theoretical result of 7.16 ns, with a small relative error percent of 1.11%.

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Introduction

Alkaline-earth monohalides MX (M = Mg and X = F, Cl, Br, and I) have attracted theoretical and experimental interests of spectroscptists for a long time. These molecules are ionic compounds

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and have nine valence electrons outside closed atomic shells. The electronic structures of the ground state ($X^2\Sigma^+$) and the first excited state ($A^2\Pi$) can be described as an unpaired electron around a molecular ion core consisting of two closed-shell ions, M^{2+} and X^-. Several ionic bonding models have been developed to represent the electronic structures of the low-lying states [1–3], and alkaline-earth monohalides MX are appropriate candidates for testing these simply semiclassical ionic bond models. Therefore, the characterization of the $X^2\Sigma^+$ and $A^2\Pi$ of the magnesium monohalides MgX (X = F, Cl, Br, I) have been well studied both experimentally and theoretically. The simplest ionic molecule MgF, which has a greater degree of covalent bonding, was used to test some ionic bonding models at first. Anderson et al. recorded the pure rotational spectrum, and analyzed the structure and bonding for $X^2\Sigma^+$ [4]. Barber et al. recorded the bands of $v = 1 \rightarrow 0$, $7 \rightarrow 6$ and gained Dunham coefficients of $X^2\Sigma^+$ [5]. But, there were few *ab initio* calculations of the electronic structure and spectrum constants [6,7]. As for MgCl molecule, there were many experimental spectroscopic studies [8–12]. Rao et al. reported the $B^2\Sigma^+ \rightarrow A^2\Pi$ band system at first, while Morgan et al. studied the rotational structure of (0, 0) and (0, 1) bands for the $A^2\Pi \rightarrow X^2\Sigma^+$ system and assumed the $A^2\Pi$ state was inverted. Later, Patel et al. analyzed the same bands and obtained a series of molecular constants. The first spectroscopic detection of the MgBr radical was reported by Olmsted at the beginning of the 20th century [13–16], and Walters et al. obtained the absorption spectra in the same wavenumber region. Morgan made the first vibrational assignment for the $A \rightarrow X$ transition and attributed it to the $A^2\Pi \rightarrow X^2\Sigma^+$ transition. Recently, Sadygov et al. carried out *ab initio* calculations of spectroscopic characteristics at the SA-MCSCF/SOCI level, which agree with the experimental results of the $A \rightarrow X$ band system.

Despite of the existence of many experimental and theoretical investigations on these molecules, according to what we have learnt, there are few detailed studies on spectroscopic parameters and transition properties of the MgCl, MgBr and MgI except for MgF [17]. Recently, there are similar studies for the diatomic molecules formed by the alkaline-earth atoms (Be, Mg and Ca) with the second period atoms (F, B, C, and N) [17–22]. To provide detail results for future spectral analysis of these molecules, the present study aims to provide a unique comparative study of the spectroscopic properties with the theoretical approach for these magnesium monohalides. In this paper, the high-level internally contracted multi-reference configuration interaction (ic-MRCI) method is adopted for the calculations of potential energy curves and transition dipole moments. The Davidson modification and scalar relativistic correction are taken into account in the calculations, which will impact on the spectroscopic constants, radiative transition probabilities and lifetimes. Most of characterization of their emission processes via the calculations of radiative transition probabilities and radiative lifetimes of the band systems $A^2\Pi-X^2\Sigma^+$ is presented. It is expected that these results are helpful for further experimental work on relevant systems.

Methods and computational details

This paper focuses on the ground state ($X^2\Sigma^+$) and the first excited state ($A^2\Pi$) of the MgX (X = F, Cl, Br, I) molecules. Both states are correlated with the first lowest dissociation channel ($Mg(^1S_g) + X(^2P_u)$). We performed *ab initio* calculations with the MOLPRO2010 software package designed by Werner et al. [23]. The symmetry point group of MgX radical is $C_{\infty v}$. However, due to the limitation of the Molpro program, all the calculations are carried out in the C_{2v} subgroup of the $C_{\infty v}$ point group. The corresponding relationships between irreducible representations of the C_{2v} and $C_{\infty v}$ point groups are $\Sigma^+ = A_1$, $\Pi = B_1 + B_2$, $\Delta = A_1 + A_2$, and

$\Sigma^- = A_2$. The aug-cc-pVQZ-dk [24] basis set is selected for the Mg, F, Cl, Br atoms and effective core potential (ECP) in combination with aug-cc-pVQZ-PP for I [25] in the calculations.

In order to obtain the high-level PECs of $X^2\Sigma^+$ and $A^2\Pi$ states for MgX (X = F, Cl, Br, I), the potential energies at a set of bond lengths are calculated by adopting the state-averaged complete active space self-consistent field (SA-CASSCF) approach [26,27], followed by the internally contracted multireference configuration interaction method with the Davidson correction (icMRCI + Q) [28–32]. In the SA-CASSCF calculation all possible distributions of nine electrons into 8 valence orbitals comprising the active space ($4a_1$, $2b_1$, $2b_2$, 0) are allowed. At the same time, the scalar relativistic effect is taken into consideration via the third-order Douglas-Kroll [33] and Hess [34] one-electron integrals. The computed wavefunctions of $X^2\Sigma^+$ and $A^2\Pi$ states are saved and used for further computations of dipole moments and transition dipole moments functions. Based on the computed PECs of the $X^2\Sigma^+$ and $A^2\Pi$ states, we solve the one-dimension nuclear Schrödinger equations using the LEVEL8.0 program [35] and obtain the corresponding vibrational energy levels, spectroscopic parameters, and Franck–Condon factors (FCFs). Finally, the radiative lifetimes of the selected transitions are also calculated.

The total emission transition probability is given by the total Einstein $A_{v'}$ coefficient, which has been obtained by the expression [36].

$$A_{v'} = \frac{64\pi^4 |a_0 \cdot e \cdot \overline{TDM}|^2 \Sigma_{v''} q_{v',v''} (\Delta E_{v',v''})^3}{3h}$$
$$= \frac{(\overline{TDM})^2 \Sigma_{v''} q_{v',v''} (\Delta E_{v',v''})^3}{4.936 \times 10^5}$$

$$\tau_{v'} = (A_{v'})^{-1}$$

where v' and v'' symbolize the upper and lower vibrational states, $\Delta E_{v',v''}$ is the transition energy in units of cm^{-1}, *TDM* is the averaged electronic transition dipole moment in atomic units, $q_{v',v''}$ is the Franck–Condon Factors (FCFs) between the vibrational levels v' and v'', and $\tau_{v'}$ is the radiative lifetime (in seconds), which is evaluated as the inverse of the total Einstein $A_{v'}$ coefficient.

Results and discussions

The PECs for the two lowest-lying states

The PECs for the $X^2\Sigma^+$ and $A^2\Pi$ states of the isovalent molecules MgX (X = F, Cl, Br, I) are depicted in Fig. 1. The step lengths selected
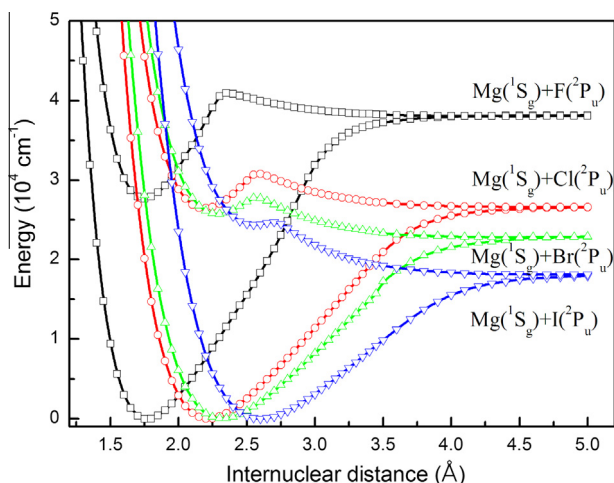

Fig. 1. Potential energy curves for the $X^2\Sigma^+$ and $A^2\Pi$ states of MgX (X = F, Cl, Br, I) molecules.