



Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

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

Theoretical study of the low-lying electronic states of magnesium sulfide cation including spin–orbit interaction



Peng Chen, Ning Wang, Song Li*, Shan-Jun Chen

School of Physics and Optoelectronic Engineering, Yangtze University, Jingzhou, China

ARTICLE INFO

Article history:

Received 6 February 2017

Revised 28 June 2017

Accepted 28 June 2017

Available online 6 July 2017

Keywords:

MgS⁺*ab initio* calculations

Electronic structure

Spin–orbit couplings

Spectroscopic constants

ABSTRACT

Highly correlated *ab initio* calculations have been performed for an accurate determination of electronic structures and spectroscopic features for the low-lying electronic states of the MgS⁺ cation. The potential energy curves for the four Λ -S states correlating to the lowest dissociation asymptote are studied for the first time. Four Λ -S states split into nine Ω states through the spin–orbit coupling effect. Accurate spectroscopic constants are deduced for all bound states. The spin–orbit couplings and the transition dipole moments, as well as the PECs, are utilized to calculate Franck–Condon factors and radiative lifetimes of the vibrational levels. To verify our computational accuracy, analogous calculations for the ground state of MgS are also carried out, and our derived results are in reasonable agreement with available experimental data. In addition, photoelectron spectrum of MgS has been simulated. The predictive results are anticipated to serve as guidelines for further researches such as assisting laboratorial detections and analyzing observed spectrum.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Alkaline earth chalcogenides have attracted a wide range of interests from scientific researches to technological applications based on their specific characteristics of wide band gap, high-pressure behaviors and low dielectric constants. Owing to their promising potential uses for various electrical and optical devices, researches on structural, electronic, spectroscopic and transport properties of the species have been subjects to both experimental and theoretical investigations.

Extensive research efforts have been made for the alkaline earth monoxides (MO, M=Be, Mg, Ca, Sr and Ba) [1–12]. Transitions originated from the $A^1\Sigma^+$ and $A^1\Pi$ states to the ground $X^1\Sigma^+$ state were recorded in different spectral regions. Isotopic species of MO with M=²⁴Mg, ²⁵Mg, ²⁶Mg, ⁸⁶Sr, ⁸⁷Sr, ⁸⁸Sr, ¹³⁵Ba and ¹³⁷Ba were studied experimentally. For CaO, the measurements cover only one isotopic species, ⁴⁰Ca¹⁶O. Perturbations were analyzed for the low-lying electronic states of the MO radicals involving the $a^3\Pi$, $b^3\Sigma^+$, $A^1\Sigma^+$ and $A^1\Pi$ states. According to the global least-squares procedures, which include infrared, microwave and millimeter-wave data, the vibrational and rotational constants describing interactions among these states were determined.

Studies on electronic structure, spectroscopy and stability of the lowest electronic states have been performed on the alkaline

earth monoxide ions (MO⁺, M=Be, Mg, Ca, Sr and Ba) [13–17]. The bonding nature in the ground states of MO⁺ are mostly due to M²⁺O⁻ ionic interactions. Besides, with the increment of the atomic number of the metal atom, bonding between the two atoms in MO⁺ becomes increasingly ionic, while the ionization energy decreases.

The alkaline earth sulfides (MS, M=Be, Mg, Ca, Sr and Ba) [18–31] have been widely investigated experimentally. Spectroscopic observations were mainly focused on the $A^1\Sigma^+-X^1\Sigma^+$ and $B^1\Sigma^+-X^1\Sigma^+$ bands by the high-resolution Fourier transform spectrophotometer, dye laser spectroscopy and optical Stark spectroscopy. Rotational analyses yielded molecular parameters of the ground, first and second excited vibrational states. Spectroscopic constants of individual vibrational levels and equilibrium molecular constants were determined. Besides, the $A^1\Sigma^+$ state was found to be extensively perturbed by two low-lying electronic states, $A^1\Pi$ and $a^3\Pi_i$.

As for the alkaline earth sulfide ions MS⁺, molecular geometries and spectroscopic information for these systems are lacking. To our knowledge, the only systematical research was carried out for BeS⁺ [18] from a theoretical perspective. No literature associating with experimental research of the MS⁺ family has been reported. The absence of essential information on the geometric structure prevents us from understanding relevant characteristics of the molecular ion. Therefore, we are motivated to carry out investigations for MS⁺. In this work, we have performed the first high-level *ab ini-*

* Corresponding author.

E-mail address: lsong@yangtzeu.edu.cn (S. Li).

tio computations to investigate molecular constants, spectroscopic parameters and transition properties for the MgS^+ species.

The aims of the present work are (1) to fill the knowledge gap on molecular structure, spectroscopy and metastability of this experimentally unknown species; (2) to model the system with accurate geometric and spectroscopic parameters; (3) to gain insight into the variation of the ionic character of the cation; (4) to motivate experimental studies on MgS^+ and its derivatives, and (5) to serve as a guideline for assisting spectroscopic detections and astronomical observations.

However, we believe it is possible to perform laboratorial observations for MgS^+ . Production of the cation sample is a prerequisite to perform spectroscopic detections. It can be achieved by generating MgS molecule and then ionizing the neutral species to MgS^+ . The MgS molecule can be formed by reacting Mg vapor with sulfur vapor [21] or with OCS [22], where the Mg vapor can be produced either from a laser ablation source [22] or by heating Mg metal to its melting point [2]. Following the reactions that formed MgS , a discharge [2] as well as a resonantly enhanced two-photon excitation [17] can be used for ionization.

This paper is organized as follows. In Section 2, it begins by describing theoretical methods and basis sets used in this study. In Section 3, we present a wealth of computation results together with corresponding discussions, including equilibrium geometric parameters, potential energy curves (PECs), spectroscopic constants, vibrational energy levels, permanent dipole moments (PDMs), transition dipole moments (TDMs), Franck–Condon factors (FCFs), Einstein coefficients and radiative lifetimes. Subsequently, our computational results for neutral MgS are presented and are compared with literature data. In addition, the single photo-ionization spectrum of MgS is simulated.

2. Computational details

The energy scans of all the PECs are calculated using the Hartree–Fock method [32,33] to generate an initial guess of the molecular orbitals (MOs). The MOs obtained are further optimized using the state-averaged complete active space self-consistent field (SA-CASSCF) method [34,35]. The final wave function is then generated with the multireference configuration interaction (MRCI) method [36,37] on a reference set from the CASSCF configurations. Size non-consistency errors are minimized by employing the Davidson correction (+Q). To take into account both the core-valence correlation and the relativistic effect, the all-electron Douglas–Kroll–Hess relativistic augmented correlation-consistent polarized core-valence quintuple-zeta basis set [38,39], aug-cc-pCV5Z-DK, coupled with the second-order Douglas–Kroll–Hess Hamiltonian [40,41] is used in our computations. The spin-orbit coupling (SOC) effect is included into the PEC calculations by the state interaction method with the Breit–Pauli Hamiltonian [42] on the MRCI level. The SOC effect is considered across the entire PEC of each state.

The PECs of all states of interest are calculated over the internuclear separation range from 0.14 nm to 5.0 nm. The scanning step used in the calculations varies from 0.0025 nm to 0.5 nm in different regions of the PECs. In the vicinity of the minima of all PECs, from 0.2 nm to 0.24 nm for the ground electronic state and from 0.26 nm to 0.32 nm for three excited states, the smallest interval of 0.0025 nm is applied. Over 300 energy points are computed for each PEC. All calculations have been performed in the C_{2v} subgroup of the $C_{\infty v}$ main group with the MOLPRO package [43]. Average atomic masses are used in these computations.

To obtain smooth PECs for both Λ -S and Ω states, we have tested several different combinations of the occupied, closed-shell and core orbitals. Testing calculations reveal the electron correlation effect should be taken into account sufficiently. In the final

CASSCF and MRCI+Q computations, five outermost MOs of $3a_1$, $1b_1$ and $1b_2$, correspond to valence electrons in the 3s atomic orbital of Mg and the 3s3p orbitals of S, are placed in the active space. Electrons in the 2s2p orbitals of both Mg and S atoms are distributed into the closed-shell MOs. Four electrons in the 1s closed-shell of both atoms are used as core electrons for the core-valence correlation calculations. The number of external orbitals is 418, including $148a_1$, $103b_1$, $103b_2$ and $64a_2$ symmetry MOs.

The Murrell–Sorbie (M–S) potential energy function [44], which has been used to deduce the PECs of several species by our group [45–47], is used in the present fitting process. The M–S potential energy function is given by the following expression,

$$V(\rho) = -D_e \left(1 + \sum_{i=1}^n a_i \rho^i \right) \exp(-a_1 \rho), \quad (1)$$

where $\rho = R - R_e$. R and R_e are internuclear distance and equilibrium internuclear distance respectively. D_e is the well depth. To obtain better fitting accuracy, it is necessary to perform testing fittings with adjustment of the order of the polynomials in this potential energy function [48]. In this work, all parameters are floated in our fittings by using the M–S function with $n = 12$.

According to our equilibrium parameters and PECs, vibrational energy levels, rotational and centrifugal distortion constants for the vibrational levels of the low-lying electronic states of MgS^+ are obtained by numerically solving the one-dimensional Schrödinger equation of nuclear motion with the LEVEL 8.0 program package [49]. The Franck–Condon factors, Einstein coefficients and radiative lifetimes have also been determined.

The present paper mainly focuses on the MgS^+ cation, however, no literature associating with structural or electronic properties of MgS^+ has been published to the best of our knowledge. The lack of data made it impossible for us to verify the accuracy of the present results as well as to perform detailed comparisons with other works. Nevertheless, as the neutral MgS radical has been examined both experimentally and theoretically, the available data provide us an opportunity to testify the accuracy of our computation results. Therefore, we have also carried out a series of calculations for neutral MgS . The computation methodology and basis sets that have been used in the energy estimations for MgS^+ are employed here for energy predictions of the ground electronic state of MgS .

3. Results and discussions

In this section, we report molecular structures and transitions properties of the low-lying electronic states of MgS^+ as well as the ground state of MgS . Firstly, we will focus on the PECs and structural constants of MgS^+ . Secondly, we present vibrational energy levels, spectroscopic parameters, dipole moments and transition properties for this cation. Subsequently, we report computation results on neutral MgS , and finally the simulated photoelectron spectrum of MgS is presented.

3.1. Equilibrium parameters and PECs of the Λ -S states of MgS^+

In the present paper, electronic states correlate with the first dissociation channel, $\text{Mg} + ({}^2S_g) + \text{S}({}^3P_g)$, of the MgS^+ molecular ion is characterized theoretically. According to our single point energy computations, the PECs of all the Λ -S states, $X^2\Pi$, $1^4\Sigma^-$, $1^2\Sigma^-$ and $1^4\Pi$, are obtained by our fitting procedures. To illustrate the figure more informative, detailed PECs of the internuclear distance ranging from 0.15 nm to 0.85 nm are presented in Fig. 1. Spectroscopic constants such as the excitation energy terms (T_e), equilibrium internuclear distances (R_e), rotational constants (B_e), vibrational frequencies (ω_e), dissociation energies (D_e), first

Download English Version:

<https://daneshyari.com/en/article/5427022>

Download Persian Version:

<https://daneshyari.com/article/5427022>

[Daneshyari.com](https://daneshyari.com)