Theoretical study on spectroscopy and molecular constants of the ground and low-lying excited states of GeO molecule

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Abstract. The potential energy curves (PECs) of $X^1\Sigma^+, a'^3\Sigma^+, a^3\Pi, A^1\Pi$ states for GeO molecule are calculated by the multireference configuration interaction method (MRCI) and MRCI with the Davidson's corrections (MRCI+Q) with aug-cc-pVTZ basis set. All these states involved dissociate into the same dissociation channel Ge(^{3}P)+O(^{3}P). For the four states, the spectroscopic parameters (R_e, D_e, ω_e, B_e, $\omega_e\chi_e$ and T_e) have been obtained, which shows that our results are in very good agreement with the experimental value and other theoretical data at MRCI+Q level. The dipole moments of these states are also obtained. In addition, based on the accurate results of spectroscopic constants at MRCI+Q level, the first 30 vibrational states are determined for the four low-lying electronic states when J=0. The vibrational levels $G(v)$ and inertial rotation constants B_v at MRCI+Q level are calculated when J=0, the results of $X^1\Sigma^+$ and $A^1\Pi$ states are in concordance with the available other theoretical values and experimental work. The dissociation limits, dissociation energies, electronic configurations at equilibrium internuclear distance for $a'^3\Sigma^+$, $a^3\Pi$ states also are predicted for the first time.

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Key words: GeO molecule, spectroscopic constants, vibrational levels, molecular constants

1 Introduction

Germanium monoxide (GeO) as one of the important oxides of group IVa elements, has been studied very extensively. A variety of experiments have been reported including chemiluminescence studies of low-lying electronic states [1, 2], microwave spectroscopy

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[3, 4], photoelectron spectroscopy [5], emission spectroscopy and gas phase infrared spectroscopy [6]. The geometry and energy structures for the molecule attracted much more research interests.

In recent years, there have been numerous theoretical studies of GeO. Raymonda *et al.* [7] calculated the electric dipole moments of GeO in the lower vibrational states. The chemiluminescent reaction $Ge(^3P)+N_2O \rightarrow GeO+N_2$ have been studied, since such reaction has been shown to warrant investigation as potential chemical laser systems [8, 9]. Mummigatti *et al.* [10] applied the RKRV (Rydberg−Klein−Rees−Vanderslice) method to calculate potential energy curves (PECs) for $A^1\Pi$ and $X^1\Sigma^+$ states and Franck-Condon factors for $A^1\Pi \rightarrow X^1\Sigma^+$ band system of GeO molecule in 1977. Later, in 1993, molecular structures and vibrational IR spectra of GeX (X = O, S, Se) were studied by *ab initio* Hartree-Fock and Post-Hartree-Fock methods [11], respectively. Then Barandiarán and Seijo [12] presented the results of a systematic comparison between the values of the bond lengths and vibrational frequencies of group IV monoxides (XO, X = Ge, Sn, Pb), calculated with the spin-free quasi-relativistic *ab initio* core model potential method (AIMP) and the all-electron Dirac-Hartree-Fock method. In 1995, absolute oscillator strengths and related radiative properties of the $A^1\Pi - X^1\Sigma^+$ transition of the GeO molecule have been determined from accurate multireference configuration interaction (MRCI) calculations [13].An accurate analytical potential energy function is determined for the ground $X^1\Sigma^+$ state of GeO molecule by Lee *et al.* [14] in 1999. Later, analytical potential energy functions and theoretical spectroscopic constants for MX/MX^- (M = Ge, Sn, Pb; X = O, S, Se, Te, Po) and LuA (A = H, F) systems were presented by Jalbout *et al.* [15] with the LSDA/SDD, BLYP/SDD and B3LYP/SDD methods. Shi *et al.* [16] calculated the spectroscopic constants and molecular constants for $X^1\Sigma^+$, $A^1\Pi$, $C\Sigma^-$ and $b^3\Pi$ states with the aid of module VIBROT presented in the MOLCAS 7.4 program package.

However, to our knowledge, the dissociation limits, electronic configurations at equilibrium internuclear distance for $X^1\Sigma^+$, $a'^3\Sigma^+$, $a^3\Pi$, $A^1\Pi$ states and the PECs, vibrational levels for $a'^3\Sigma^+$, $a^3\Pi$ states have not been reported. The main goal of this paper is to investigate the PECs for $X^1\Sigma^+$, $a'^3\Sigma^+$, $a^3\Pi$, $A^1\Pi$ states of GeO. According to the accurately results, we also predict the well depths, electronic configurations at the equilibrium internuclear distance, spectroscopic constants, vibrational levels of these states.

2   Computational details

The calculations of electronic structure and PECs are performed with the MOLPRO 2010.1 program package [17]. The spectroscopic constants and molecular constants are investigated by solving the nuclear Schröodinger equations with Le Roy's LEVEL8.0 program [18]. The molecular orbitals of the ground state for GeO molecule are first calculated through the spin-restricted Hartree-Fock (RHF) method. Then, the state-averaged complete active space self-consistent-field (CASSCF) calculations are performed by using the preceding RHF orbitals as a starting point. Moreover, by utilizing the CASSCF wave