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MRCI study on spectroscopic parameters and molecular constants of ground and three low-lying excited electronic states of the GeO molecule

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ABSTRACT

The ground and three low-lying excited electronic states of the GeO molecule, including Σ^+, Σ^- and Π symmetry with singlet and triplet spin multiplicities, have been investigated employing the full valence complete active space self-consistent field (CASSCF) method followed by the highly accurate valence internally contracted multireference configuration interaction (MRCI) approach. The potential energy curves (PECs) of these states have been calculated with the cc-pV5Z basis set. And the effect on the PECs by the relativistic corrections has been taken into considerations. The way to consider the relativistic corrections is to use the second-order Douglas–Kroll Hamiltonian approximation. For the four electronic states, the spectroscopic parameters (T_e, D_0, D_e, R_e, ω_e, $\omega_e x_e$, α_e and B_e) of 10 isotopes (^{70}Ge^{16}O, ^{72}Ge^{16}O, ^{73}Ge^{16}O, ^{74}Ge^{16}O, ^{76}Ge^{16}O, ^{70}Ge^{18}O, ^{72}Ge^{18}O, ^{73}Ge^{18}O, ^{74}Ge^{18}O, ^{76}Ge^{18}O) have been determined. The spectroscopic parameters have been compared with those of previous investigations reported in the literature, and excellent agreement has been found between the present results and the available data. With the PECs determined here, the first 30 vibrational states for each species are computed for the four electronic states when the rotational quantum number J equals zero ($J = 0$). The vibrational level $G(\upsilon)$, inertial rotation constant B_υ and centrifugal distortion constant D_υ are determined when $J = 0$, which are in excellent agreement with the available experimental data. The ro-vibrational levels have been calculated for these low-lying electronic states of 10 isotopes when $J \leqslant 29$. And the transition lines are evaluated according to the transition rule. Comparison with the available experimental observations shows that the present ro-vibrational levels are reliable.

1. Introduction

As one of the important oxides of group IVA elements, germanium monoxide (GeO) has been important applications in fabricating integrated optics [1] and SiGe alloy-based devices [2,3]. Because the spectroscopic parameters and molecular constants of the GeO would facilitate its use in providing diagnostics [3], it is not surprising that it has become the subject of extensive investigations in the past years of several tens, both experimentally [3–16] and theoretically [17–24].

As we know, natural germanium is composed of ^{70}Ge (20.5%), ^{72}Ge (27.4%), ^{73}Ge (7.8%), ^{74}Ge (36.5%) and ^{76}Ge (7.8%). And natural oxygen consists of ^{16}O (99.762%), ^{17}O (0.038%) and ^{18}O (0.20%). Accordingly, 15 isotopes of the GeO can be formed. Their natural abundances are ^{70}Ge^{16}O (20.451%), ^{72}Ge^{16}O (27.334%), ^{73}Ge^{16}O (7.781%), ^{74}Ge^{16}O (36.413%), ^{76}Ge^{16}O (7.781%), ^{70}Ge^{17}O (0.0078%), ^{72}Ge^{17}O (0.0104%), ^{73}Ge^{17}O (0.0030%), ^{74}Ge^{17}O (0.0138%), ^{76}Ge^{17}O (0.0030%), ^{70}Ge^{18}O (0.041%), ^{72}Ge^{18}O (0.0548%), ^{73}Ge^{18}O (0.0156%), ^{74}Ge^{18}O (0.075%) and ^{76}Ge^{18}O (0.0156%), respectively.

In experiment, the first significant observations on the electronic spectra of the GeO were carried out by Jevons et al. [25] early in 1937. Sixteen years later, Rowlinson and Barrow [8] in 1953 conducted a comparative study of the absorption spectra of SiO and GeO in the Schumann region. Since then, the spectroscopic parameters and molecular constants of these isotopes have been extensively investigated by various absorption and emission spectroscopy, and a number of results have been presented in the past several decades. However in theory, on the one hand, very few investigations [17] can be found in the literature, which studied the spectroscopic parameters and molecular constants of the GeO isotopes; on the other hand, although several groups of spectroscopic results [18–24] have been reported, to our knowledge, only one of them [20] is involved with the excited states. Therefore, to more completely understand the spectroscopic and molecular properties of various GeO isotopes, more detailed high-level calculations are still needed at present, especially for the excited states.

For this reason, in the present paper, we will in detail investigate the spectroscopic parameters and molecular constants of 10

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species, $Ge^{16}O$ (including five isotopes $^{70}Ge^{16}O$, $^{72}Ge^{16}O$, $^{73}Ge^{16}O$, $^{74}Ge^{16}O$ and $^{76}Ge^{16}O$) and $Ge^{18}O$ (including five isotopes $^{70}Ge^{18}O$, $^{72}Ge^{18}O$, $^{73}Ge^{18}O$, $^{74}Ge^{18}O$ and $^{76}Ge^{18}O$). This paper is organized as follows. First, the potential energy curves (PECs) of the ground and three excited states ($A^1\Pi$, $C^1\Sigma^-$ and $b^3\Pi$) of GeO are calculated using the full valence complete active space self-consistent field (CASSCF) method, which is followed by the highly accurate valence internally contracted multireference configuration interaction (MRCI) approach [26,27] in combination with the cc-pV5Z correlation-consistent basis set for Ge and O [28–30]. With the PECs corrected by the second-order Douglas–Kroll Hamiltonian (DKH2) approximation, the spectroscopic parameters and molecular constants of these species are obtained. Then, the first 30 vibrational states are evaluated when the rotational quantum number J equals zero ($J = 0$). Finally, for these species, the ro-vibrational levels are determined for the four electronic states when $J \leqslant 29$. The transition lines are evaluated according to the transition rule.

2. Computational methods

Here we compute the PECs of $X^1\Sigma^+$, $A^1\Pi$, $C^1\Sigma^-$ and $b^3\Pi$ states by the CASSCF approach, which is followed by the MRCI calculations. Therefore, the full valence CASSCF is used as the reference wavefunction for the MRCI calculations in the present work. The present PEC calculations for the BO molecule are carried out in the MOLPRO 2008.1 program package [31] at the *spdfgh* cc-pV5Z correlation-consistent basis set in the valence range.

MOLPRO only uses the Abelian point group symmetry. For molecules with degenerate symmetry, an Abelian subgroup must be employed. That is to say, for a diatomic molecule such as GeO with $C_{\infty v}$ symmetry, it will be substituted by C_{2v} symmetry with the order of the irreducible representations being $a_1/b_1/b_2/a_2$. In the CASSCF and subsequent MRCI calculations, these four kinds of states would be evaluated. In detail, for the electronic states $X^1\Sigma^+$, $A^1\Pi$, $C^1\Sigma^-$ and $b^3\Pi$ of the GeO, eight molecular orbitals (MOs) are put into the active space, including four a_1, two b_1 and two b_2 symmetry MOs which correspond to the $4s4p$ shell of Ge and the $2s2p$ shell of O atom. The rest of the electrons in the GeO molecule are put into the closed-shell orbitals, including eight a_1, three b_1, three b_2 and one a_2 symmetry MOs. However, when we employ these MOs (twelve a_1, five b_1, five b_2 and one a_2) to investigate the PECs of the ground and three low-lying excited electronic states, we can find that all these PECs are not smooth. It is very obvious that a bump exists in each PEC. Analysis shows that this situation is caused by skipping from the PEC of one state to another. To improve the smoothness of these PECs, we put more MOs into the active space, here including one additional a_1 MO. Having these MOs (thirteen a_1, five b_1, five b_2 and one a_2) employed, the PECs of these four electronic states calculated at the present level of theory are smooth and convergent over the present internuclear separation range. We should notice that the basis set used here is valence electron correlation, which does not include the $3d$ electrons of Ge atom. As pointed in Ref. [23], the $2s$ orbital of O tends to strongly mix with the $3d_\sigma$ orbital of Ge because they have very similar orbital energies. Therefore, to get more accurate PECs of these low-lying electronic states, one additional a_1 MO is included in the active space in the present calculations.

To accurately determine the dissociation energies of these four electronic states, we calculate the PECs over a large internuclear separation range from about 0.05 to 2.00 nm. In so large internuclear separation range, the PECs of these four states are convergent. The intervals employed in the present PEC calculations are 0.01 nm for each electronic state. Only near the equilibrium position will the interval be 0.002 nm. The smaller step is adopted around the equilibrium position of each state so that the properties of these PECs can be displayed more clearly.

To reduce the effect on the spectroscopic parameters and molecular constants by the relativistic effects, we have taken into considerations the effect on the PECs by the relativistic corrections. In the present calculations, we consider the relativistic correction employing the second-order Douglas–Kroll Hamiltonian (DKH2) approximation [32,33]. Comparison with the results obtained at the correlation-consistent basis set *spdfgh* cc-pV5Z for Ge and O atom without the relativistic corrections, accuracy improvements can be obviously achieved about the spectroscopic parameters after taking into account the relativistic corrections. Therefore, we use the PECs corrected by the DKH2 approximation to make all the calculations in the present paper.

With the PECs determined at the MRCI/cc-pV5Z level of theory and corrected by the DKH2 approximation, the spectroscopic parameters and molecular constants for these four electronic states are evaluated with the aid of module VIBROT presented in the MOLCAS 7.4 program package [34]. The module VIBROT can be used to compute a vibration–rotation spectrum for a diatomic molecule. In the VIBROT, the potential is fitted to an analytical form using cubic splines. The ro-vibrational Schrödinger equation is then solved numerically by Numerov's method [35] for one vibrational state at a time and for a number of rotational quantum numbers as specified by the input. And the spectroscopic parameters are determined by fitting the vibrational levels. The present spectroscopic results (T_e, D_e, R_e, ω_e, $\omega_e x_e$, B_e, α_e and D_0) for the $X^1\Sigma^+$, $A^1\Pi$, $C^1\Sigma^-$ and $b^3\Pi$ states are tabulated in Tables 1–4, respectively.

3. Results and discussion

3.1. Spectroscopic parameters

In order to conveniently compare the present results with those from the experimental and other theoretical studies, we collect the spectroscopic parameters available in the experimental [3,12–14] and other theoretical [17–24] literature in Tables 1–4, respectively. In addition, we also include the experimental D_e and R_e collected in Ref. [36] and the experimental spectroscopic parameters tabulated in Ref. [37] in these Tables.

A number of theoretical investigations [17–24] have been made on the spectroscopic parameters of the GeO molecule. Of these investigations, only one [17] took into considerations the isotope effect. In the investigations [17], however, the R_e and ω_e were evaluated only for two species, $^{74}Ge^{16}O(X^1\Sigma^+)$ and $^{74}Ge^{18}O(X^1\Sigma^+)$, by using the B3LYP density functional theory (DFT) and the basis sets, 6-311+G (2*df*, 2*pd*) for O and 6-311G(*d*) for Ge. Obviously, the two spectroscopic parameters are in excellent agreement with the available measurements in previous studies [3,12–14,37], as stated in Ref. [17].

All the theoretical spectroscopic parameters reported in Ref. [18–24] are not involved the isotope effect. Among these GeO isotope molecules, the natural abundances of $^{74}Ge^{16}O$, $^{72}Ge^{16}O$ and $^{70}Ge^{16}O$ are of 36.413%, 27.334% and 20.451%, respectively, whereas the natural abundances of the rest 12 species are of only 15.802%. Therefore, the comparison with the present results in this section is made only for three species, $^{74}Ge^{16}O$, $^{72}Ge^{16}O$ and $^{70}Ge^{16}O$.

About the spectroscopic parameters of the GeO molecule, early theoretical work was done by Dyall [18] in 1993, who made the Dirac–Hartree–Fock (DHF) investigations on the R_e and ω_e of the ground-state group IVA monoxides. As shown in Table 1, his R_e and ω_e are far from agreeing with the experimental data when compared with the present ones. Barandiarán and Seijo [19] in 1994 performed the quasi-relativistic *ab initio* model potential calculations on the IVA hydrides and oxides. And two important parameters, R_e and ω_e, were determined in their calculations. By