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MRCI study on potential energy curves, spectroscopic parameters and rovibrational energy levels of CS($X^1\Sigma^+$) molecule

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ABSTRACT

Using the highly accurate valence internally contracted multireference configuration interaction (MRCI) approach in combination with several groups of correlation-consistent basis sets, this paper investigates the potential energy curves (PECs), spectroscopic parameters and vibrational manifolds including rovibrational levels and transition lines of the CS($X^1\Sigma^+$) molecule. The PECs are fitted to the Murrell–Sorbie function form, which are used to accurately reproduce the spectroscopic parameters (D_0, $\omega_e\chi_e$, α_e and B_e). By comparison with the available experiments, the PEC obtained at the basis sets, aug-cc-pCV5Z for C and cc-pV5Z for S, is selected to investigate the spectroscopic parameters and rovibrational energy levels. The present D_0, D_e, R_e, ω_e, $\omega_e\chi_e$, α_e and B_e are of 7.2646 eV, 7.3436 eV, 0.15403 nm, 1278.00 cm^{-1}, 6.4924 cm^{-1}, 0.005837 cm^{-1} and 0.8144 cm^{-1}, respectively, which almost perfectly conform to the available measurements. With the interaction potential obtained at the basis sets, aug-cc-pCV5Z for C and cc-pV5Z for S, by numerically solving the radial Schrödinger equation of nuclear motion, a total of 82 vibrational states is predicted when the rotational quantum number J equals zero. The complete vibrational levels, classical turning points, inertial rotation and centrifugal distortion constants are determined when $J = 0$, which are in excellent agreement with the available experiments. The rovibrational energy levels of the CS($X^1\Sigma^+$) molecule are calculated until $J = 30$. According to the rovibrational levels, a number of transition lines for the CS($X^1\Sigma^+$) molecule are evaluated, which agree well with the available experimental observations.

1. Introduction

The CS molecule is an important species of astrophysical, atmospheric and environmental interest [1,2]. It is formed as intermediate in the photochemical and oxidative reactions of CS_2 [1,3]. On the one hand, it is one of the most abundant sulfur-containing species in interstellar clouds [4,5]. A variety of astronomical objects contain it, including carbon-rich stars, such as IRC + 10216 [6], star-forming regions [7] and comets [8,9]; on the other hand, environmental damage has becoming a serious problem in modern life. In this respect, the existence of sulfur derivatives in the stratosphere, which lead to the formation of sulfate aerosols, has been directly connected to the undesirable acid rain effect. A similarly harming effect has been produced by the reaction of chemical radicals with ozone in the stratosphere thus contributing to its depletion and making the planet more vulnerable to UV light [2]. From these standpoints, we can easily understand why the CS molecule has received considerable attention in the past several decades, both experimentally [1,10–29] and theoretically [2,30–37].

In experiment, the CS has been extensively investigating in various wavelength regions from IR to vacuum UV [1,10–29]. Of these experiments, the pioneering one on the electronic spectrum was done by Crawford and Shurcliff [10] in 1934. In their experiments, they reported limited spectroscopic parameters and molecular constants of its $X^1\Sigma^+$ and $A^1\Pi$ states with poor accuracy. More than 20 years later, Mockler and Bird [11] observed the microwave spectra, and determined the rotational constants of four isotopic species in their ground-states. Their measurements were extended later by several researchers such as Kewley et al. [12] in 1963. And the microwave results obtained to date were summarized by Lovas and Krupenie [13] in 1974. Especially in 1995, Coppens and Drowart [14] reported that the accurate dissociation energy D_0 of the CS($X^1\Sigma^+$) was 7.353 ± 0.025 eV; Ram et al. [1] observed a number of transition lines in the vibration–rotation bands and determined that the accurate spectroscopic parameters ω_e, B_e, α_e and $\omega_e\chi_e$ equals 1285.1546 cm^{-1}, 0.8200 cm^{-1}, 0.005918 cm^{-1} and 6.5026 cm^{-1}, respectively. And recently in 2003, Kim and Yamamoto [15] observed some transition lines of the CS molecule. They evaluated two important spectroscopic parameters, B_e and α_e, which were almost identical with the measurements obtained by Ram et al. [1]

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in 1995. In theory, the earlier spectroscopic calculations were carried out by Robbe and Schamps [30] in 1976, who used the self-consistent field configuration interaction (SCF-CI) approach and a double zeta basis set including set 18σ-type and 8π-type STO functions to investigate the perturbation parameters between valence states of the CS($X^1\Sigma^+$). Botschwina and Sebald [31] performed the *ab initio* calculations by the SCF, the singles and doubles CI (CI-SD) with respect to SCF determinant and the version 1 of the coupled electron pair appropriation (CEPA-1) approaches with the basis sets of Gaussian-type orbitals. For C, the basis set is 10*s*, 6*p*, 2*d* contracted to [7,4,2]. And for S, the basis set is 13*s*, 9*p*, 2*d* contracted to [10,7,2]. But both Robbe et al. [30] and Botschwina et al. [31] only determined limited spectroscopic parameters of the CS($X^1\Sigma^+$) molecule. In recent 20 years, a number of researchers, including Peterson and Woods [32–34], Martin et al. [35], Midda and Das [36] and Coriani et al. [37], also investigated the spectroscopic properties of the molecule. As a whole, these results have presented a set of theoretical spectroscopic data, which compare well with the available experiments. However, as summarized in Section 2, no experimental or theoretical investigations have been given the complete spectroscopic parameters (D_e, R_e, ω_e, $\omega_e\chi_e$, α_e, B_e and D_0), let alone the vibrational manifolds (vibrational levels, classical turning points, inertial rotation and centrifugal distortion constants, rovibrational levels and transition lines). All these motivate us to perform the present work.

In this paper, we will make the spectroscopic parameter and vibrational manifold calculations. The paper is organized as follows. First, the equilibrium internuclear separation, harmonic frequency and potential energy curve (PEC) are investigated by the highly accurate valence internally contracted multireference configuration interaction (MRCI) approach [38,39] in combination with several Dunning's correlation-consistent basis sets [40–42]. Then, the PECs are fitted to the Murrell–Sorbie (M–S) function form with the least-squares fitting method, which are used to accurately determine the spectroscopic parameters. And finally, with the potential obtained at present, by numerically solving the radial Schrödinger equation of nuclear motion, a total of 82 vibrational states has been predicted when the rotational quantum number *J* is equal to zero. The complete vibrational manifolds are reproduced when $J = 0$. The rovibrational levels of the CS($X^1\Sigma^+$) molecule are calculated until $J = 30$. According to the rovibrational levels, some transition lines for the CS($X^1\Sigma^+$) molecule are evaluated. As a whole, the present investigations provide more complete and accurate theoretical predictions on the spectroscopic parameters and molecular constants of the CS($X^1\Sigma^+$) molecule to this day.

2. Computational details

Here, we determine the equilibrium internuclear distance R_e and harmonic frequency ω_e of the CS molecule by the geometry optimization and frequency calculations using the full valence complete active space self-consistent field (CASSCF) approach, which is followed by the MRCI calculations. Therefore, the full valence CASSCF is used as the reference wavefunction for the MRCI calculations at this work. Several groups of Dunning's correlation-consistent basis sets [40–42] have been used at present. By comparison with the available experiments, the selected basis sets, aug-cc-pCV5Z for C and cc-pV5Z for S, are employed to compute the spectroscopic properties. All the calculations are performed with the MOLPRO 2008.1 program package [43] running on the Dawning computer. The R_e and ω_e results determined at the basis sets, aug-cc-pCV5Z for C and cc-pV5Z for S, are tabulated in Table 1.

The PEC is calculated at the basis sets, aug-cc-pCV5Z for C and cc-pV5Z for S, over the internuclear distance range from about 0.09 to 2.00 nm. In general, the PEC calculations are carried out at intervals of 0.04 nm. Only near the equilibrium position, will the interval be of 0.005 nm. On the one hand, the PEC is completely smooth over the present internuclear distance range; on the other hand, it is convergent. Thus, the dissociation energy D_e can be evaluated by the difference between the molecular energy in the equilibrium position and the energy sum of the atomic fragments in the dissociation limit. Here, the D_e value is also tabulated in Table 1 for convenient comparison.

For the CS($X^1\Sigma^+$) molecule, the recent experimental D_0 was given by Coppens and Drowart [14] in 1995, and it is equal to 7.353 ± 0.025 eV. The present D_0 calculated at the basis sets, aug-cc-pCV5Z for C and cc-pV5Z for S, is in good accord with this value, and the deviation of the present result from the experimental one is of 1.20%. If we take into considerations the experimental errors, there is possible that the deviation falls into 1.0%. Here, we should notice that the D_e value determined by Crawford and Shurcliff [10] in 1934 is of low accuracy. As to the R_e and ω_e results at present, we find that the excellent agreement also exists between the present ones and the recent experiments [1,10,11,18]. For example for the ω_e, the largest deviations from all these experiments [1,10,11,18] are within 0.0557%. And for the R_e, the largest deviation from all these experiments [11,12,18,28] is of only 0.352%. According to these, we can conclude that the spectroscopic parameters (D_0, R_e and ω_e) obtained here is of high accuracy.

By the way, we have ever evaluated the R_e, ω_e and D_e at several Dunning's correlation-consistent basis sets, and compared these results with the available experiments. By comparison, We find that the D_e obtained at the basis sets, aug-cc-pCV5Z for C and cc-pV5Z for S, is almost closest to the experiments among them, though the R_e and ω_e is not the most favorable ones when compared with the available measurements in these calculations. For example, when the basis set for both S and C is aug-cc-pCV5Z, although the R_e and ω_e results are closer to the experiments than the present ones, the PEC cannot be calculated properly. According to these, we are certain that the basis sets, aug-cc-pCV5Z for C and cc-pV5Z for S, are suitable to determine the spectroscopic parameters of the CS molecule at the present level of accuracy. Other spectroscopic parameter and molecular constant results obtained here further confirm that the present basis sets are one of the most suitable sets for such PEC and spectroscopic calculations, though only valence–electrons are correlated in the present investigations.

In order to obtain more accurate equilibrium internuclear distance R_e, harmonic frequency ω_e and dissociation energy D_e of the CS($X^1\Sigma^+$) molecule, we take into account the effects on these parameters by the relativistic corrections. By carefully calculations, we find that the R_e, ω_e and D_e are equal to 0.15365 nm, 1287.79 cm^{-1} and 7.3989 eV when using the second-order Douglas–Kroll Hamiltonian approximation (DKH = 2) for the relativistic corrections. That is to say, the R_e and ω_e are closer but the D_e becomes further to the available measurements when compared with the present ones. Because the relativistic correction calculations consume more CPU time, and because the relativistic corrections only improve the R_e and ω_e accuracy small, here we only use the PEC obtained at the non-relativistic corrections for further calculations when we considers various situations.

The PEC is fitted to the M–S function with the least-squares fitting method. Then, the analytic potential energy function (APEF) is determined. Based on the APEF fitted here, the force constants, quadratic f_2, cubic f_3 and quartic f_4, are deduced. Then the rest spectroscopic parameters, $\omega_e\chi_e$, α_e, B_e and D_0, are derived. Thirdly, with the APEF obtained at present, by numerically solving the radial Schrödinger equation of nuclear motion, the radial Schrödinger equation of nuclear motion is solved to get all the vibrational states. And the complete vibrational levels, the classical turning points, R_{min} and R_{max}, and the inertial rotation and centrifugal distortion constants are calculated when $J = 0$. And finally, The