Theoretical calculation of a full-dimensional ab initio potential energy surface and prediction of infrared spectra for Xe–CS2

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An effective four-dimensional (4D) ab initio potential energy surface (PES) for Xe–CS2 which explicitly involves the intramolecular Q1 symmetric stretching and Q3 antisymmetric stretching vibrational coordinates of CS2 is constructed. The computations are carried out employing single- and double-excitation coupled-cluster theory with a non-iterative perturbation treatment of triple excitations [CCSD(T)] method with a large basis set. Two vibrationally averaged potentials at the ground and \( v_1 + v_3 \) (\( v_1 = 1, v_3 = 1 \)) excited states are obtained by integrating the 4D potentials over the \( Q_1 \) and \( Q_3 \) coordinates. The potentials have a T-shaped global minimum and two equivalent linear local minima. The radial discrete variable representation/angular finite basis representation and the Lanczos algorithm are employed to calculate the rovibrational energy levels for Xe–CS2. The infrared band origin shift associated with the fundamental band of CS2 is predicted, which is red-shifted by \(-1.996 \text{ cm}^{-1}\) in the \( v_1 + v_3 \) region. In addition, we further predict the spectroscopic parameters for the ground and the \( v_1 + v_3 \) excited states of Xe–CS2. Compared with the previous Rg–CS2 (Rg = He, Ne, Ar, Kr) complexes, we found that the complexes of the rare gas atoms with CS2 display obvious regularities.

I. Introduction

The linear CX2 (X = O, S) molecules play an important role in the investigation of atmosphere. While complexes consisting of small linear molecules (CO2, OCS, CS2) bound to a rare gas (Rg) have had a remarkable growth in interest in spectroscopic studies. Such studies are aimed at advancing our understanding of the weak intermolecular forces and dynamics of these bound molecules. As we know, CO2 exists extensively in nature and absorbs infrared radiation in the ground. Accordingly, complexes containing CO2 have been widely investigated both experimentally and theoretically. As an analog of CO2, CS2 is one of the sulfur compounds in the Earth’s atmosphere and has also been widely studied because sulfur is a key element in the spectroscopy of giant planets. In addition, some interesting differences were explored for Rg–CS2 compared to Rg–CO2.

Experimentally, the first infrared spectra for the Rg–CS2 complexes with Rg = He, Ne, Ar were studied in the CS2 \( v_3 \) region. Meanwhile, Mivehvar et al. also reported the high resolution spectra of the He–CS2 complex in the \( v_1 + v_3 \) region (2185 cm\(^{-1}\)). In their work, the structures were T-shaped and the spectroscopic parameters were presented. Theoretically, a number of ab initio potential energy surfaces (PESs) for Rg–CS2 were constructed at different levels of theory. For instance, Farrokhpour and co-workers first determined the PESs for the Rg–CS2 complexes using CCSD(T) theory with the aug-cc-pVDZ basis set. Soon after, Zang et al. reported the two-dimensional PES for the Rg–CS2 (Rg = He, Ne, Ar) complexes by using the aug-cc-pVTZ basis set at the CCSD(T) level. However, these theoretical studies have obtained the PESs that encompass only two intermolecular vibration coordinates and a fixed CS2 geometry. The results showed that the spectral pattern in the infrared region cannot be properly identified. Thus, construction of the PESs that involve the intramolecular vibration modes of CS2 is needed. Recently, we calculated a 3D PES of the Rg–CS2 complex including the antisymmetric stretching \( Q_3 \) coordinate of the CS2 monomer, and showed a good agreement with the experimental infrared data. In order to explore more detailed spectral information for Rg–CS2, we further carried out the calculation of a four-dimensional PES of the Rg–CS2 (ref. 31–33) complexes, which incorporates the \( Q_1 \) symmetric and \( Q_3 \) anti-symmetric stretching coordinates of CS2. We have successfully reported the 4D PESs for the complexes of the lighter rare gas atoms with CS2 by this method. To our knowledge, the experimental and theoretical information in the \( v_1 + v_3 \) region are absent for Xe–CS2.

In order to discover the trends and diversities among the Rg–CS2 complexes, we present a reliable 4D PES for Xe–CS2 with CS2 in the \( v_1 + v_3 \) region by applying the CCSD(T) method with the
aug-cc-pVQZ basis set. This paper is arranged as follows: in Section II, we show the computational details that include ab initio and rovibrational energy levels. The discussion of the PES, the calculated rovibrational bound states, and the predicted infrared spectra are presented in Sections III–IV. Finally, a brief conclusion is given in Section V.

II. Computational details

A. Ab initio calculations

For the Xe–CS$_2$ dimer, the Jacobi coordinates (R, $\theta$, Q$_1$, Q$_3$) are employed to describe the geometry. In the geometric variables, R denotes the intermolecular distance between the center of mass of CS$_2$ to the Xe atom, the angle of the vector R with respect to the CS$_2$ molecule is defined as $\theta$, Q$_1$ and Q$_3$ are the normal mode coordinates, which describe the r$_1$ symmetric stretching vibration and r$_3$ antisymmetric stretching vibration of CS$_2$, respectively. Here, the intramolecular vibrational coordinates ($Q_1$, $Q_3$) can be simply defined as

$$Q_1 = (r_{CS_1} + r_{CS_2} - 2r_c)/\sqrt{2}$$  

$$Q_3 = (r_{CS_1} - r_{CS_2})/\sqrt{2}$$

where $r_{CS_1}$ and $r_{CS_2}$ mean the two C–S bond lengths of CS$_2$, $r_c$ is the average bond length derived from experimental spectra data.$^{34}$ The two-dimensional $Q_1$ and $Q_3$ potential curves were computed at the CCSD(T) level to determine the energy levels and wave functions for the $Q_1$ and $Q_3$ modes. The coordinate scaling method$^{45}$ was employed to adjust the two-dimensional potential in order to reproduce the experimental frequencies for the fundamental band.$^{44,45}$ We generated 25 potential optimized discrete variable representation (PODVR)$^{36,37}$ grid points corresponding to $Q_1 = -0.122411$, $-0.044046$, $-0.027968$, $-0.101203$, $-183772a_0$, $Q_3 = -0.245743$, $-0.116813$, 0.0, 0.116813, 0.245743a$_0$ for the ground state, and $Q_1 = -0.139155$, $-0.060791$, 0.011220, 0.084454, 0.167022a$_0$, $Q_3 = -0.247934$, $-0.117859$, 0.0, 0.117859, 0.247934a$_0$ for the $r_1 + r_3$ ($r_1 = 1$, $r_3 = 1$) excited state.

The ab initio potential energies were computed for a total of about 9000 discrete points. A relatively dense grid was calculated with 27 values of R ranging from 5.50a$_0$ to 24.00a$_0$ and 13 points of $\theta$ from 0° to 180° at intervals of 15°. The four dimensional PES for Xe–CS$_2$ was performed using the CCSD(T)$^{38}$ method. The aug-cc-pVQZ basis set of Woon and Dunning$^{39}$ was used for carbon and sulfur atoms, and the quasirelativistic pseudopotential aug-cc-pVQZ-PP$^{40}$ basis set was used for the Xe atom, supplemented with an additional set of bond functions (3s3p2d1f1g).$^{41}$ The full counterpoise procedure (FCP)$^{42}$ was selected to correct the basis set superposition error (BSSE). The vibrationally averaged 2D potentials $V_{r_1+r_3}(R,\theta)$ were obtained by averaging the 4D potential over the $Q_1$ and $Q_3$ vibrational coordinates, which can be written as

$$V_{r_1+r_3}(R,\theta) = \int_{-\infty}^{\infty} \psi_{n_1+n_3}(Q_1, Q_3) V(R, \theta, Q_1, Q_3) \psi_{n_1+n_3}(Q_1, Q_3) dQ_1 dQ_3$$

The cubic spline interpolation was employed to generate the averaged PESs for R and $\theta$ coordinates. The root-mean-square (rms) deviation is about 0.08 cm$^{-1}$ in the final fit. All calculations were carried out using the MOLPRO package.$^{43}$

B. Calculations of rovibrational energy levels

With the Born–Oppenheimer approximation, the vibrational averaged 2D intermolecular Hamiltonian of the Xe–CS$_2$ complex can be written as$^{44,45}$

$$\hat{H} = \frac{1}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{j^2}{2I_{r_1+r_3}} + (j^2) \frac{(j^2)}{2\mu R^2} + V_{r_1+r_3}(R,\theta)$$  

where $\mu$ is the reduced mass of the Xe–CS$_2$ complex, $\hat{j}$ and $\hat{\jmath}$ are the angular momentum operators for the total and monomer rotations. $I_{r_1+r_3}$ represents the vibrationally averaged rotational moment of the inertia of CS$_2$, which can be defined by the following equation,

$$I_{r_1+r_3} = \int_{-\infty}^{\infty} \psi_{n_1+n_3}(Q_1, Q_3) I_{Q_1+Q_3} \psi_{n_1+n_3}(Q_1, Q_3) dQ_1 dQ_3$$

Based on the PES, the rovibrational Hamiltonian and wave functions were calculated with the radial DVR/angular FBR method.$^{46,47}$ In our work, 120 sine-DVR$^{48}$ grid points were used for the radial coordinate R. For the angular coordinate, we selected 90 DVR grids and 89 basis functions of associated Legendre polynomials. The Lanczos algorithm method$^{49,50}$ was used to diagonalize the Hamiltonian matrix, and we selected 10 000 Lanczos iterations to obtain the eigenvalues and eigenvectors. For the angular part, the parity-adapted rotational basis for the three Euler angles ($\alpha, \beta, \gamma$) can be written as

$$C_{KM}^{p}(\alpha, \beta, \gamma) = [2(1 + \delta_{K\beta})]^{1/2} [D_{MK}^{p} (\alpha, \beta, \gamma) + (-1)^{J+K+p} D_{MK}^{p} (\alpha, \beta, \gamma)], \quad p = 0, 1$$

where $D_{MK}^{p}(\alpha, \beta, \gamma)$ were the normalized rotational functions for Xe–CS$_2$, the space-inversion parity $p = 0$ or 1 illustrates that the basis is even or odd under inversion. The total parity was given by $(-1)^{J+K}$.

III. Potential energy surface

The contour plot of the vibrationally averaged 2D $r_1 + r_3$ excited state PES is showed in Fig. 1, which clearly displays that the global minimum is a T-shaped configuration at $R = 3.97$ Å and $\theta = 90.0°$ with a well depth of 413.875 cm$^{-1}$. In addition, there are two equivalent linear local minima at $R = 5.56$ Å and $\theta = 0°$ or 180° with a depth of 248.045 cm$^{-1}$. In our PES, between the two minima, there are two saddle points with an energy barrier of 187.997 cm$^{-1}$ relative to the global minimum, located at $R = 5.08$ Å and $\theta = 45°$ or 135°. In order to compare the Xe–CS$_2$ complex with the other Rg–CS$_2$ complexes, the differences in the geometries and well depths between the Rg–CS$_2$ complexes$^{31–33,31,32}$ are listed in Table 1. One can see that the Rg–CS$_2$ complexes have similar shapes, such as the T-shaped global minimum, two linear local minima, and two saddle points.
Table 2 The calculated energy levels (in cm\(^{-1}\)) for the first twenty vibrational bound states of Xe–CS\(_2\) with CS\(_2\) at the ground and the \(v_1 + v_3\) excited states

| \(N\) | \(v_5\) state | \(N\) | \(v_5\) state |
|-----|----------------|-----|----------------|
| 0   | –372.243 10   | 0   | –374.239 10   |
| 1   | –340.903 11   | 1   | –342.887 11   |
| 2   | –330.927 12   | 2   | –335.391 12   |
| 3   | –312.666 13   | 3   | –314.627 13   |
| 4   | –308.886 14   | 4   | –310.894 14   |
| 5   | –308.313 15   | 5   | –310.755 15   |
| 6   | –298.008 16   | 6   | –299.059 16   |
| 7   | –295.275 17   | 7   | –296.373 17   |
| 8   | –284.470 18   | 8   | –285.564 18   |
| 9   | –283.164 19   | 9   | –284.769 19   |

Table 1 The stationary geometries (Å and deg) and well depths (cm\(^{-1}\)) of Rg–CS\(_2\) (Rg = He, Ne, Ar, Kr, Xe)

| Rg–CS\(_2\) | Global minimum | Local minimum | Saddle point |
|------------|----------------|---------------|-------------|
| He–CS\(_2\) (ref. 31) | (3.36, 90, –52.68) | (5.00, 0/180, –32.11) | (4.56, 59/121, –21.39) |
| Ne–CS\(_2\) (ref. 33) | (3.44, 90, –104.35) | (5.03, 0/180, –67.15) | (4.56, 44/136, –51.12) |
| Ar–CS\(_2\) (ref. 32) | (3.68, 90, –279.77) | (5.26, 0/180, –173.47) | (4.92, 39/141, –146.75) |
| Kr–CS\(_2\) (ref. 52) | (3.76, 90, –367.06) | (5.39, 0/180, –226.16) | (4.92, 45/135, –203.49) |
| Xe–CS\(_2\) (ref. 51) | (3.97, 90, –414.77) | (5.56, 0/180, –243.66) | (5.08, 46/134, –224.37) |
| Xe–CS\(_2\) | (3.97, 90, –413.88) | (5.56, 0/180, –248.04) | (5.08, 45/135, –225.88) |

However, there are some deviations among the Rg–CS\(_2\) complexes. For example, the depth of the global and local minima become deeper from He–CS\(_2\) to Xe–CS\(_2\), which indicates the intermolecular interactions become stronger with the increasing mass of the rare gas atom. For another, the well depth of Xe–CS\(_2\) is much larger than the other Rg–CS\(_2\) complexes, which means the Xe atom is strongly hindered from free motion around the CS\(_2\) molecule. In addition, the minimum energy distance gradually become larger from He–CS\(_2\) to Xe–CS\(_2\). Compared with the previous theoretical study of the potential, the contour plots look almost the same as those for our work, and the positions and energies of the stationary points are shifted only slightly.

IV. Bound states of rovibrational energy levels and infrared spectra

Based on the potential, the energy levels of the bound states were calculated. In order to simplify our writing, we label the \(v_1 + v_3\) of CS\(_2\) as the \(v_5\) vibrational state for Xe–CS\(_2\). In Table 2, we display the first twenty pure vibrational bound states of the Xe–CS\(_2\) complex for the ground and \(v_5\) states of CS\(_2\). As seen in Table 2, the first bound state for the \(v_5\) state is –374.239 cm\(^{-1}\), which reveals the zero-point energy is 39.636 cm\(^{-1}\) relative to global minimum, only about one-tenth of the global well depths. Due to the deep well and high barrier for Xe–CS\(_2\), the bound states are much deeper than the other Rg–CS\(_2\) complexes.\(^{31–33}\) The \(v_1 + v_3\) band origin shift is determined by \(\Delta v = E_0^v – E_0^0\), where \(E_0^v\) are the ground state energies of Xe–CS\(_2\) with the CS\(_2\) monomer in the corresponding \(v\) vibrational state. Meanwhile, we further predicted the infrared band origin shift of Xe–CS\(_2\), which is –1.996 cm\(^{-1}\) indicating that is negative (red-shift) in sign and large in magnitude. In addition, the band origin shifts of the other Rg–CS\(_2\) complexes\(^{30,39–31,52}\) are listed in Table 3, together with the Rg–CO\(_2\) complexes.\(^{2,6}\) One can see that the tendency of the CS\(_2\) shifts are similar to CO\(_2\). Besides, the results indicate the lighter complexes (He, Ne) tend to positive (blue shifts), while the larger complexes (Ar, Kr, Xe) tend to negative (red-shifts). The predicted \(v_1 + v_3\) band shift for Xe–CS\(_2\) (–1.996 cm\(^{-1}\)) is larger than that for Xe–CO\(_2\) (–1.447 cm\(^{-1}\)), revealing that Xe–CS\(_2\) has a larger weakening of the vdW bond upon vibrational excitation in the \(v_1 + v_3\) region.

In Fig. 2, we present the contour plots of the wave functions of Xe–CS\(_2\) with CS\(_2\) at the ground state. It is clear from Fig. 2 that the vibrational ground state is localized around the T-shaped global minimum. The first two vibrational excited states are \(1^+\) of the averaged intermolecular potential and stretching vibration modes for the higher vibrational

Fig. 1 Contour plot (in cm\(^{-1}\)) of the averaged intermolecular potential energy surface for Xe–CS\(_2\) with CS\(_2\) at the \(v_1 + v_3\) excited state.
excited states. The calculated average distance $\langle R \rangle$ and the average angle $\langle \theta \rangle$ for the ground state are 3.99 Å and 87.85°, respectively, which is very close to the global minimum ($R = 3.97$ Å and $\theta = 90$°). The radial dispersion $\sqrt{\langle R^2 \rangle - \langle R \rangle^2}$ and angular dispersion $\sqrt{\langle \theta^2 \rangle - \langle \theta \rangle^2}$ are 0.14 Å and 2.15°, respectively. Therefore, the ground state is rigid.

The rovibrational energies of Xe–CS$_2$ are labeled by the asymmetric rotor quantum numbers $J_{K_a,K_c}$, where $J$ denotes the total angular momentum, $K_a$ and $K_c$ represent the projections of $J$ onto the $a$ and $c$ principal axes of inertia. The rovibrational energy levels consist of four blocks, (even/even), (even/odd), (odd/even), and (odd/odd) for different combination parity of ($j/p$). The rovibrational energies of Xe–CS$_2$ for the vibrational ground and $v_1 + v_3$ excited states are shown in Table 4, and the total angular momentum $J$ ranges from 0 to 5.

The rovibrational energy levels within $J \leq 3$ are used to fit to a Watson asymmetric top Hamiltonian$^{24}$ employing the $a$-type reduction in the $\tilde{I}$ representation,

$$H = \frac{1}{2} (B + C) J^2 + \left[A - \frac{1}{2} (B + C)\right] J_a^2 + \frac{1}{2} (B - C) (J_b^2 - J_c^2)
- \Delta_J J_a^4 - \Delta_K J_a^2 J_c^2 - \Delta_K J_a^4 - 2 \delta_J J_c^2 (J_b^2 - J_c^2)
- \Delta_K [J_a^2 (J_b^2 - J_c^2) + (J_b^2 - J_c^2) J_a^2]$$

(7)

The fitted molecular spectroscopic constants for the Xe–CS$_2$ complex are given in Table 5. Because the energy levels for Xe–CS$_2$ at the ground state are almost equal to the $v_1 + v_3$ excited state, the molecular parameters of the two states are very similar. The calculated inertial defects $\delta_0$ of this complex with CS$_2$ at the ground state and the $v_1 + v_3$ excited state are around 1.07 amu Å$^2$ and 1.13 amu Å$^2$, respectively. For Rg–CS$_2$ (Rg = He,$^{14}$ Ne,$^{14}$ Ar,$^{12}$ Kr$^{22}$), the inertial defects $\delta_0$ in the ground state

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**Fig. 2** Contour plots of the wave functions for the lowest six vibrational states of Xe–CS$_2$ with CS$_2$ at the $v_1 + v_3$ excited state.
The asymmetry parameter are more rigid with the increase in the mass of the rare gas.

\[
\begin{array}{c|c|c|c|c}
\text{Level} & J & E (J_{\text{Kuk})} & \text{Even/Even} & \text{Even/Odd} & \text{Odd/Even} & \text{Odd/Odd} \\
\hline
\text{Ground state} & 0 & -372.243 (0_{00}) & -372.021 (1_{01}) & -372.113 (1_{10}) & -372.116 (1_{10}) \\
 & 1 & -371.770 (1_{21}) & -372.040 (2_{12}) & -372.028 (2_{12}) \\
 & 2 & -371.769 (2_{20}) & -372.002 (3_{03}) & -371.902 (3_{12}) & -371.925 (3_{12}) \\
 & 3 & -371.629 (3_{22}) & -371.648 (3_{31}) & -371.207 (3_{31}) & -371.208 (3_{31}) \\
 & 4 & -371.487 (4_{04}) & -371.488 (4_{23}) & -371.772 (4_{14}) & -371.734 (4_{14}) \\
 & 5 & -370.430 (4_{04}) & -370.430 (4_{14}) & -371.047 (4_{22}) & -371.046 (4_{22}) \\
\hline
\nu_5 state & 0 & -374.239 (0_{00}) & -374.199 (1_{01}) & -374.110 (1_{10}) & -374.114 (1_{10}) \\
 & 1 & -373.770 (1_{21}) & -373.037 (2_{12}) & -373.026 (2_{12}) \\
 & 2 & -373.550 (2_{20}) & -373.999 (3_{03}) & -373.923 (3_{12}) \\
 & 3 & -373.550 (3_{22}) & -373.569 (3_{31}) & -373.213 (3_{31}) & -373.214 (3_{31}) \\
 & 4 & -373.487 (4_{04}) & -373.489 (4_{23}) & -373.770 (4_{14}) & -373.732 (4_{14}) \\
 & 5 & -372.442 (4_{04}) & -372.442 (4_{14}) & -373.053 (4_{22}) & -373.052 (4_{22}) \\
\end{array}
\]

The calculated spectroscopic constants (in cm\(^{-1}\)) and the inertial defects \(\Delta R\) (in amu \(\AA^2\)) for the Xe–CS\(_2\) complex with CS\(_2\) at the ground and the \(\nu_1 + \nu_3\) excited states

\[
\begin{array}{l|l|l}
\text{Ground state} & \nu_5 & \\
\hline
A & 0.108321 & 0.107674 \\
B & 0.022038 & 0.022023 \\
C & 0.018291 & 0.018261 \\
\Delta r & -2.443 \times 10^{-7} & -3.110 \times 10^{-7} \\
\delta r & 3.748 \times 10^{-7} & 3.258 \times 10^{-7} \\
\delta r & 4.563 \times 10^{-6} & 8.778 \times 10^{-6} \\
\delta r & 2.505 \times 10^{-6} & 2.225 \times 10^{-6} \\
\delta r & 9.176 \times 10^{-9} & 2.993 \times 10^{-9} \\
\Delta \eta & 1.07 & 1.13 \\
\end{array}
\]

were found to be 6.14, 3.09, 2.93, 2.32 amu \(\AA^2\), respectively. The decrease in the inertial defects reveals that the vdW complexes are more rigid with the increase in the mass of the rare gas atom. The asymmetry parameter \(\kappa = (2B - A - C)/(A - C)\) (equal to \(-1\) for the symmetric prolate top) is \(-0.917\) and \(-0.916\) for this complex with CS\(_2\) at the ground and the \(\nu_1 + \nu_3\) excited states, respectively.

V. Conclusions

In this paper, a new four-dimensional potential energy surface for the Xe–CS\(_2\) complex including the \(Q_1\) and \(Q_3\) normal modes was constructed. We calculated the intermolecular potential with five PODVR grid points for the \(Q_1\) and \(Q_3\) normal modes, respectively, using the CCSD(T) method with the aug-cc-pVQZ basis set plus bond functions. Based on the \textit{ab initio} potential points, two vibrationally averaged PESs of the Xe–CS\(_2\) complex were generated. We found that each potential energy surface has a T-shaped global minimum and two equivalent local linear minima. The bound rovibrational energy levels of Xe–CS\(_2\) were obtained by employing the radial DVR/angular FBR method and the Lanczos algorithm. The predicted band origin shift is \(-1.996\) cm\(^{-1}\). Meanwhile, we found that the Rg–CS\(_2\) complexes have very similar features. For example, each PES is characterized by a T-shaped global minimum. For another, the regularities were represented among the complexes from He–CS\(_2\) to Xe–CS\(_2\). It is expected that the work on the Rg–CS\(_2\) complexes in the \(\nu_1 + \nu_3\) region of CS\(_2\) should be useful for further theoretical and experimental studies.

Conflicts of interest

There are no conflicts to declare.

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