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A three-dimensional potential energy surface and infrared spectra for the Ar–OCS van der Waals complex

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ABSTRACT

The first three-dimensional potential energy surface (PES) of the Ar–OCS complex is developed at the coupled cluster single and double with noniterative treatment of triple excitations [CCSD(T)] level with a large basis set plus midpoint bond functions. Two vibrationally adiabatic potentials at both the ground and the first vibrational v_3 excited states are generated by averaging the three-dimensional potential over the Q_3 coordinate. The predicted infrared spectra are in excellent agreement with the available experimental data, which again testifies the accuracy of the new potentials.

1. Introduction

The van der Waals (vdW) interaction between a rare-gas(Rg) atom and a linear OCS molecule has been actively studied both experimentally and theoretically. In experiments, the Ar–OCS complex [1] was at first studied in 1975 by the radio frequency and microwave spectrum. In this Letter, Harris et al. measured rotational constants and dipole moment components of the ground vibrational state, and found Ar–OCS has a T-shaped structure, in which Ar atom is closer to the O atom of the OCS molecule. Subsequently, further experimental studies of infrared and microwave spectra for Rg–OCS were reported. For example, Hayman et al. [2,3] investigated the infrared-absorption spectra for these complexes in the antisymmetric stretching v_3 region of the OCS monomer. Grebenev et al. measured the rotationally resolved infrared spectrum of the OCS embedded in large helium droplets [4,5]. In the same experiment, a red-shift of $-0.557\ \mathrm{cm}^{-1}$ was observed for the vibrational frequency corresponding to antisymmetric stretching v_3 of the OCS molecule.

On the theoretical side, much attention was devoted to the He–OCS, Ne–OCS and Ar–OCS complexes, and the Kr–OCS complex. The first He–OCS potential energy surface (PES) was obtained by Danielson et al. [6] in 1987 by fitting total differential cross section measurements. A more extensive *ab initio* study was carried out by Sadlej and Edwards [7] in 1993 using MP4 perturbation theory. The first attempt to explicitly include the dependence on the antisymmetric stretching vibration of the OCS molecule in the He–OCS interaction potential was made by Gianturco and Paesani [8] in 2000. In 1997, Yan et al. [9] reported the potential energy surface for Ne–OCS at the MP2 level. In 2005, Zhu et al. [10] recalculated an *ab initio* potential energy surface for the Ne–OCS complex using the coupled-cluster singles and doubles with noniterative inclusion of connected triples [CCSD(T)] with a large basis set containing midbond functions. For Ar–OCS complex [11], the first *ab initio* calculation was limited to Hartree–Fock (HF) level in providing short-range repulsive interactions. Recently, Zhu et al. [12] carried out a more extensive calculation of the PES at CCSD(T) level. They found two minima on the PES corresponding to the T-shaped and the collinear Ar–S–C–O structures. The calculated pure rotational transition frequencies for the vibrational ground state are in good agreement with the observed values. In 2012, we present three-dimensional potential energy surface for the Kr–OCS complex [13] explicitly including the dependence on the antisymmetric stretching vibration of the OCS molecule. The predicted infrared spectra are in excellent agreement with the available experimental data.

The asymmetric linear OCS monomer has polarity. Its permanent electric dipole moment is not zero. Because of the change of the electric dipole moment in the vibration process, it can produce the corresponding infrared absorption spectrum. Up to date, all of the theoretical studies on Ar–OCS have been focused on the PES of the complex by taking the OCS monomer as a rigid rotor. However, it might not be sufficient for predicting the infrared spectra as the transition in the intramolecular vibrational mode is usually involved. An improved approach is to take into account the dependence of the intramolecular vibrational coordinate in the potential and dynamical calculations. According to this method, the vibrational mode of OCS molecular must be used to calculate corresponding vibrational coordinate. The asymmetric linear OCS monomer has three kinds of vibrational modes. v_1 is the symmetric stretching vibration, v_2 is the bending vibration and v_3 is the antisymmetric stretching vibration.

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In this Letter, we present the ab inito determination of the PES for the Ar–OCS complex explicitly including the dependence on the antisymmetric stretching vibration of the OCS molecule for the first time. The PES is then used in the succeeding rovibrational energy levels calculations. The comparisons of predicted transition frequencies and spectroscopic constants with the experimental infrared spectra are given.

2. Computational details

2.1. Ab initio calculations

By convention, the geometry of the Ar–OCS complex is defined with the three Jacobi coordinates (R,θ,Q_3). The radial coordinate R denotes the distance from the Ar atom to the OCS center of mass, the angle θ is the angle between R and the OCS molecule with $\theta = 180°$ referring to the linear Ar-O-C-S configuration, and Q_3 is the normal coordinate for the υ_3 antisymmetric stretch vibration of the monomer OCS molecule.

The geometry optimization provided the expression for the OCS Q_3 normal mode coordinate,

$$Q_3 = -0.511z_o + 0.857z_c - 0.066z_s, \tag{1}$$

Where z_o, z_c, z_s refer to unit vector displacements from equilibrium of O, C, and S, respectively (see Figure 1). In the calculation of the full Ar–OCS PES $V(R,\theta,Q_3)$,we considered seven different values of Q_3: −0.5, −0.3, −0.1, 0, 0.1, 0.3, 0.5 relevant to extensions of the OCS molecule, with $Q_3 = 0$ corresponding to the equilibrium geometry. From Eq. (1), one can relate the Q_3 with corresponding actual values of r_1, r_2 and r ($r = r_1 + r_2$) as listed in Table 1, here r is the OCS bond length.

The *ab initio* potential energies for Ar–OCS were computed for a total of about 1729 points with R ranging from 6.0 a_0 to 20.0 a_0 at 19 values, 13 equidistant angles from $\theta = 0°$ to $\theta = 180°$ in a step of 15° and each of the seven Q_3 values.

The PES of Ar–OCS was constructed at the CCSD(T) level. The aug-cc-PVQZ basis set of Dunning [14] for all atoms were used, plus an additional set of functions (3*s*3*p*2*d*1*f*) of Tao and Pan [15] (for 3*s* and 3*p*, $\alpha = 0.9$, 0.3 and 0.1; for 2*d*, $\alpha = 0.6$, 0.2; for 1*f*, $\alpha = 0.3$) located at the center of the vdW bond. The supermolecular approach is employed and the full counterpoise procedure of Boys and Bernardi is used to correct for basis set superposition error. The calculations are carried out using the MOLPRO-2006 package [16].

2.2. Analytical representation of the potential energy surface

In this Letter, the complete three-dimensional PES $V(R, \theta, Q_3)$ of Ar–OCS is constructed by two steps. First, we construct seven two-dimensional PESs $V(Q_3^i, R, \theta)$ for each fixed Q_3^i ($i = 1$–7) respectively (another two values of −0.2 and 0.2 are used for test), using the potential model proposed by Bukowski et al. [17] and used by other researchers [13,18–19].

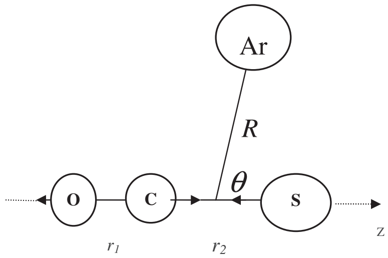

Figure 1. Jacobi coordinates for the Ar–OCS complex employed in the *ab initio* calculations.

Table 1
Range of the antisymmetric stretching coordinate Q_3, corresponding sets of (r_1, r_2, r) values of the internal coordinates (in a_0).

Q_3	r_1	r_2	r
−0.5	2.86855	2.48703	5.35558
−0.3	2.59494	2.67164	5.26658
−0.1	2.32133	2.85626	5.17758
0.0	2.18452	2.94856	5.13308
0.1	2.04772	3.04087	5.08858
0.3	1.77410	3.22548	4.99958
0.5	1.50049	3.41009	4.91058

The two-dimensional potential model contains short range V_{sh} and asymptotic V_{as} contributions,

$$V(R,\theta) = V_{sh}(R,\theta) + V_{as}(R,\theta). \tag{2}$$

Here,

$$V_{sh} = G(R,\theta)e^{B(\theta)-D(\theta)R}, \tag{3}$$

$$V_{as}(R,\theta) = \sum_{n=6}^{10} \sum_{\substack{l=0,2\ldots \\ l=1,3\ldots}}^{n-4} f_n(D(\theta)R) \times \frac{C_{nl}}{R^n} P_l^0(\cos\theta), \tag{4}$$

Where $D(\theta)$, $B(\theta)$ and $G(R,\theta)$ are all expansions in Legendre polynomials $P_l^0(\cos\theta)$,

$$B(\theta) = \sum_{l=0}^{5} b_l P_l^0(\cos\theta), \tag{5}$$

$$D(\theta) = \sum_{l=0}^{5} d_l P_l^0(\cos\theta), \tag{6}$$

$$G(R,\theta) = \sum_{l=0}^{5} (g_{0l} + g_{1l}R + g_{2l}R^2 + g_{3l}R^3) P_l^0(\cos\theta). \tag{7}$$

Here, b_l, d_l, g_{kl}, and C_{nl} are all adjustable parameters. The $f_n(x)$ is the Tang-Toennies damping function [20]:

$$f_n(x) = 1 - e^{-x} \sum_{k=0}^{n} \frac{x^k}{k!}. \tag{8}$$

In order to obtain the most reliable fit, in particular for the long-range part of the potential, we follow a two-step nonlinear least squares procedure [13,18–19]. Those grid points with energy more than 500 cm^{-1} are excluded from the fit.

Next, we use the seven two-dimensional PESs to construct the three-dimensional PES by interpolating along Q_3 using a fourth-order polynomial six-order polynomial:

$$V(Q_3^i, R_j, \theta_k) = \sum_{n=0}^{6} (Q_3^i)^n a_n(R_j, \theta_k), \tag{9}$$

For given values of (R_j, θ_k), the a_n ($n = 0, \ldots 6$) is thus determined from seven two-dimensional PESs $V(Q_3^i, R, \theta)$ by solving a seven-variables linear equations,

$$a_n(R_j, \theta_k) = \sum_{i=0}^{6} [A_{i,n}]^{-1} V(Q_3^i, R_j, \theta_k), \tag{10}$$

where $Q_3^i = (-0.5, -0.3, -0.1, 0.0, 0.1, 0.3, 0.5)$ respectively. The a_n are then used to calculate the $V(Q_3^i, R_j, \theta_k)$ according to Eq. (9).

Because of their much higher frequencies, the intramolecular vibrations in the weakly bound vdW complexes could be separated