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Some new studies on intermolecular interaction of $C_3$-Ar complex

Abstract: Theoretical studies of the intermolecular potential energy surfaces (PESs), the intermolecular vibrational states and the wavefunctions for the $C_3$-Ar complex have been performed at the CCSD(T) level with four different basis sets. Each PES can be characterized by two symmetrical T-shaped global minimum at $\theta = 75^\circ$ and $\theta = 105^\circ$, a saddle point between them at $\theta = 90^\circ$, and two collinear saddle points at $\theta = 0^\circ$ and $\theta = 180^\circ$. Moreover, we also calculated the intermolecular vibrational frequencies and the average structural parameters of the ground vibrational states for the $C_3$-Ar complex. The vdW bending and stretching frequencies are calculated to be 8.682 and 34.511 cm$^{-1}$, which are in agreement with the experimental results and a more accurate result was determined for the bending mode. Studies show that the larger the basis set is used, the more accurately the results are calculated.

Keywords: $C_3$-Ar, potential energy surface, wavefunctions, vdW vibrational frequencies, the average structural parameters.

1 Introduction

Since 1987, J. M. Lehn, a Nobel laureate, proposed the concept of supramolecular chemistry, the study of intermolecular interaction, which plays an important role in many physical, chemical, and biological fields, and have been developed rapidly [1]. The Van der Waals complex is an ideal model in the research of intermolecular interaction, and such complexes have been extensively studied both with experiment and theory [2-5]. These studies have greatly enhanced our understanding on intermolecular interactions.

Due to isovalent electrons, linear molecules such as $CO_2$, $OCS$, $N_2O$, and $CS_2$, which belong to a class, have similar properties. Complexes with these linear molecules and rare gas atoms can be easily observed by an experimental technique called supersonic molecular beam and accurately described by a quantum chemistry calculation. Hence, many scientists have focused on both experimental [6-11] and theoretical studies [12-16] for their fundamental nature and practical importance. However, there are fewer studies of complexes consisting of a rare gas atom weakly bound to a non-steady linear molecule such as $Rg-C_3$. Until 2004, in order to better understand the nature of intermolecular interaction between $C_3$ and a rare gas atom, Zhang’s group performed a systemic study on $C_3$ with the rare gas atom ($Rg$) using laser-induced fluorescence and dispersed fluorescence techniques, and recorded many experimental spectra [17]. In [18], the authors not only studied fluorescence excitation spectra and wavelength-resolved emission spectra of the $C_3$-Kr and $C_3$-Xe van der Waals complexes near the $2^2\Sigma^-, 2^2\Pi$, and $1^2\Sigma^+$ bands of the $^1\Pi_g - ^3\Sigma_g$ system of the $C_3$ molecule, but also performed ab initio calculations of the Xe complex with CCSD(T)/aug-cc-pVTZ(C) and aug-cc-pVTZ-pp(Xe). Because $C_3$ itself has a wide bending motion amplitude of 80° [19], the coupling between intermolecular and intramolecular motions makes the spectra of $C_3$-Ar complex very complicated but interesting for both experimentalists and theorists. Theoretical results have been reported based on high resolution potential energy surfaces for this complex. This is a study of ab initio potential surfaces for $C_3$-Ar complex with fourth-order Moller-Plesset (MP4, cc-pVTZ basis set) perturbation and the single and double excitation coupled-cluster theory with a noniterative perturbation treatment of triple excitations (CCSD(T), aug-cc-pVTZ basis set) methods, respectively [20].

Since there is a large discrepancy between the experimental results and the calculated results of paper [20], it is necessary for us to construct new high-level
Some new studies on intermolecular interaction of C$_3$-Ar complex. The four PESs that were constructed at the CCSD(T) level with different basis sets are listed in detail in Table 1. Bound state calculations were also carried out to study the dynamics for T-shaped isomers. Based on the analysis of bound state wavefunctions, some intermolecular vibrational states were assigned unambiguously. Meanwhile, we still determined the intermolecular vibrational frequency and the average structural parameters of the ground vibrational states for C$_3$-Ar complex. The accuracy of the PESs is assessed by a comparison of the vibrational frequencies and the average structural parameters for the T-shaped isomers between the theoretical calculation and experimental measurement. There is no doubting that these results will be useful for the further observation and detailed analysis of experimental spectra.

This paper is organized as follows: the computational details for the ab initio PESs and bound state calculations are described in Sec. 2. The results, including the PESs, bound state energy levels, intermolecular vibrational frequencies, and the average structural parameters are presented in Sec. 3. Finally, we conclude in Sec. 4.

2 Computational Details

The intermolecular potential energy surface of the C$_3$-Ar complex can be described by two Jacobi coordinates (R, $\theta$). R is the distance between the rare gas Ar atom and the center of mass of C$_3$, $\theta$ denotes the enclosed angle between the R vector and the molecular axis of C$_3$. The C$_3$ monomer is assumed to be in its ground vibrational state and is approximated as linear rigid rotors with fixed C-C bond lengths in their ground state average values of 1.29497 Å [21].

The ab initio potential energy grids for C$_3$-Ar complexes were chosen as following: the radial grids includes 34 points for C$_3$-Ar along the R coordinates between 1.50 Å to 10.00 Å. $\theta$ varies from 0° to 180° in increments of 15°. The global two-dimensional intermolecular PES is constructed by executing two one-dimensional interpolations with the Lagrange polynomial formula [22]. The intermolecular potential energy was calculated using the supermolecular method at the level of single and double excitation coupled-cluster method with a noninteractive perturbation treatment of triple excitations (CCSD(T)) [23]. The calculations of ab initio potential energies are performed at the CCSD(T) level with four different large basis sets listed in Table 1.

3 Results and Discussion

3.1 Ab initio PES

The full counterpoise procedure of Boys and Bernardi is employed to correct the basis set superposition error (BSSE) [24]. All the calculations are carried out using the Molpro 2010 software package. Because of the symmetry of the C$_3$ molecule, the eigenfunctions of C$_3$-Ar complex could be labeled with indexes ($\varepsilon$, $j$) and are divided into 4 symmetry blocks: (+1, odd), (+1, even), (-1, odd), (-1, even). Each block can be solved separately. For the calculation of the bound state, the parameters of C$_3$-Ar complex that we adopt were as follows, $J_{\text{tot}} = 0$, $j_{\text{max}} = 90$, $N_{\text{Gauss-Legendre}} = 90$, $N_{\text{sine}} = 100$, $R_{\text{min}} = 4$, $R_{\text{max}} = 18$. The calculated energy levels are all converged within 0.001 cm$^{-1}$.

Table 1: Four different basis sets

|                | basis set I | basis set II | basis set III | basis set IV |
|----------------|-------------|--------------|---------------|--------------|
| Ar             | aug-cc-pVQZ | aug-cc-pVTZ  | aug-cc-pVQZ   | aug-cc-pVTZ  |
| C              | aug-cc-pVQZ | aug-cc-pVTZ  | aug-cc-pVTZ   | aug-cc-pVQZ  |

Figure 1: Jacobi coordinates for C$_3$-Ar complex

The contour plots for the potential energy surfaces with four different basis sets for the C$_3$-Ar complex are shown in Fig. 2. It is clear that these four PESs are almost equivalent and each PES can be characterized by two symmetrical T-shaped global minimum with a saddle point between them, and two collinear saddle points. For every different PES, the symmetrical global minimum all corresponds to the T-shaped isomer with angles of $\theta = 75^\circ$ and $\theta = 105^\circ$, a saddle point between at $\theta = 90^\circ$, and two collinear saddle points all with corresponding angles of $\theta = 0^\circ$ and $\theta = 180^\circ$. There is small difference between the intermolecular distance and well-depth in the four PESs. Clearly, with the near T-shaped and linear configurations,
the potential energy curves are very flat with respect to the angular coordinate. Instead, the intermolecular energy between the two configurations varies sharply along the angular coordinate. These features indicate that the C₃- Ar potential has a significant angular anisotropy. Furthermore, we can see that the C₃-Ar complex has a large amplitude vdw bending motion around the T-shaped geometry and radial-angular coupling from the contour plots of PESs.

The geometries and energies of the minima and saddle points on the ab initio PESs are listed in Table 2. For this study, only the results of the first basis set are analyzed.

**Table 2:** The calculated geometries and their corresponding energies on the PESs with different basis sets (R in angstrom, angle in degree, and energy in cm⁻¹).

|                | Basis Set I                  | Basis Set II                | Basis Set III                | Basis Set IV                |
|----------------|------------------------------|------------------------------|------------------------------|------------------------------|
| **Global Minimum** | (3.81, 75.0, -161.580)       | (3.82, 75.0, -160.486)       | (3.82, 75.0, -160.648)       | (3.82, 75.0, -161.126)       |
| **Saddle Point 1**  | (3.76, 90.0, -159.272)       | (3.77, 90.0, -158.487)       | (3.76, 90.0, -158.491)       | (3.76, 90.0, -158.930)       |
| **Saddle Point 2**  | (5.19, 0.0, -90.169)         | (5.20, 0.0, -89.513)         | (5.19, 0.0, -90.228)         | (5.20, 0.0, -89.233)         |

**Figure 2:** Contour plots of PES, R(Å) in angstrom and θ in degree. (a) basis set I, (b) basis set II, (c) basis set III, (d) basis set IV.
Two symmetrical global minima have an intermolecular distance of 3.81 Å and a depth well of 161.580 cm⁻¹ with θ = 75° or θ = 105°. The collinear saddle point is located at R = 5.19 Å with a barrier height of 71.411 cm⁻¹ and the T-shaped barrier is located at R = 3.76 Å, θ = 90° with a barrier height of 2.308 cm⁻¹ relative to that of well depth for global minima. From Table 2, we can see that the major features of our results are in good agreement with those presented in [20], such as equilibrium geometry and anisotropy. Some of the quantitative differences within these potentials still exit, such as well depths. Especially, the calculated results that are very close to that of the second method (CCSD(T), aug-cc-pVTZ). However, there have great differences between our method (71.411 cm⁻¹ and the first method (MP4, 95.596 cm⁻¹) with the barrier height of the collinear saddle point. This can be attributed to the greater angular anisotropy of the MP4 potential. It also shows that the calculated results are not much different at the CCSD(T) level compared with these different basis sets.

### 3.2 Intermolecular vibrational states

In order to further the understanding of the complicated spectra for C₇⁻Ar complex, the vibrational energy levels and their corresponding wavefunctions for six lower bound vibrational states has been obtained by performing bound state calculations. By analyzing the wavefunctions for the six lower bound vibrational states, the wavefunctions of the four different basis sets have similar characteristics. Accordingly, the contour plot of the wavefunctions with the basis set I is shown in Fig. 3. The vibrational states are labeled with two intermolecular vibrational modes (nstretch, nbend), where the nstretch is the van der Waals stretch vibration and nbend is bend vibration. These vibrational modes can be assigned by counting the number of nodal points or nodal surfaces on the wavefunction plots in DVR. Using this method, the vibrational bound states of the C₇⁻Ar complex have been assigned. The energy levels, vibrational frequencies, their corresponding indexes (ε, j) and the number of roots in block are summarized in Table 3.

From Table 3, the ground state of the T-shaped C₇⁻Ar complex are assigned unambiguously, with (0,0), (0,1), (0,2), (0,3), (1,0) and (0,4) states. The ground state (0,0) of the C₇⁻Ar complex which is in the 1st root in the (1,even) block is bound by the energy level -139.085 cm⁻¹, indicating that the corresponding zero point energy is 22.495 cm⁻¹. Moreover, the resulting the saddle energy level (-159.272 cm⁻¹) is lower than the first calculated energy level (-139.085 cm⁻¹) demonstrates that the corresponding rotational energy level does not exist and the rotational constants A, B and C can also not be obtained.

The intermolecular fundamental vibrational frequencies for the bend vibrational state and the stretch vibrational state are 8.682 cm⁻¹ and 34.511 cm⁻¹, respectively. As a comparison, the calculated results, together with the experimental observations and previous work on the C₇⁻Ar complex, are given in Table 4. The first basis set (aVQZ) is in better agreement with the experimental data (8 ± 5 cm⁻¹) for the vdw bending frequencies. This shows that the larger aVQZ basis set at the CCSD(T) level is more accurate than other basis set to analyze intermolecular interaction of C₇⁻Ar complex. However, the vdw stretching frequency is calculated to be 34.5 cm⁻¹ based on each potential, which is significant higher than the experimental data (23 ± 5 cm⁻¹). We infer that the vibrational frequencies of higher excited states are probably not calculated accurately because the wavefunctions of the bend vibrational state mix heavily with those of the stretching vibrational mode. On the

| Assign. | Energy | Freq. | (ε, j) | No. in block |
|---------|--------|-------|--------|-------------|
| (0,0)   | -139.085 | 0.000 | (1,even) | 1 |
| (0,1)   | -130.403 | 8.682 | (1,odd)  | 1 |
| (0,2)   | -119.625 | 19.460 | (1,even) | 2 |
| (0,3)   | -110.503 | 28.582 | (1,odd)  | 2 |
| (1,0)   | -104.574 | 34.511 | (1,even) | 3 |
| (0,4)   | -101.516 | 37.569 | (1,even) | 4 |

### Table 3: The intermolecular vibrational energy levels (in cm⁻¹) and assignments (nstretch, nbend) for T-shaped isomer of the C₇⁻Ar complex.

| basis set I | 34.511 | 8.682 |
|-------------|--------|-------|
| basis set II| 34.401 | 8.900 |
| basis set III| 34.418 | 8.759 |
| basis set IV| 34.497 | 8.795 |
| CCSD(T)(aug-cc-pVTZ) [20]| 34.061 | 9.127 |
| MP4(cc-pVTZ) [20]| 37.481 | 11.438 |
| MP2(aug-cc-pVTZ) [17]| 46.7 | 5.8 |
| CCSD(T)(cc-pVTZ) [17]| 34 | 19.9 |
| Exp [25]| 23(5) | 8(5) |

### Table 4: The intermolecular vibrational frequency (in cm⁻¹) of the C₇⁻Ar complex.
other hand, by imposing a rigid monomer approximation of the collinear molecule $C_3$, probably caused the deviation between the calculation and experimental results.

### 3.3 Average structure parameters

The average structural parameters $<R>$ and $<\theta>$ for a vibrational state can be determined from the related wave functions using the following formulas [26]:

$$<R> = \sqrt{\frac{1}{<R^2>}}$$

and

$$<\theta> = \left(\left<P_2(\cos\theta)\right>\right)$$

$P_2$ is the second order Legendre function and $<P_2(\cos\theta)>$ is the average value of the Legendre function for the state of interest. The calculated structural parameters of the ground states for the $C_3$-Ar complex are listed in Table 5.

From Table 5, the intermolecular distances deviate slightly from the global minima on PES $0.05$ Å, reflecting the effects of a small amplitude motion and zero point energy. The larger deviations of $\theta$ from their equilibrium values can be thought as an effect of large amplitude vdw bending motion of the $C_3$ atom in the complex. To the best of our knowledge, this is the only theoretical study and there are no relevant reports from experiment on the average structural parameter for the $C_3$-Ar complex. Therefore it will be useful to continue further theoretical and experimental study with this system.

| basis set | $<R>$   | $<\theta>$ |
|-----------|---------|-----------|
| basis set I | 3.856   | 77.093    |
| basis set II | 3.865   | 77.240    |
| basis set III | 3.861   | 77.148    |
| basis set IV | 3.860   | 77.170    |

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Figure 3: $R$-$\theta$ contour plots of the wavefunctions for the assigned vibrational states for $C_3$-Ar complex. The states are assigned by (nstretch, nbend): (a) (nstretch, nbend) = (0,0), (b) (nstretch, nbend) = (0,1), (c) (nstretch, nbend) = (0,2), (d) (nstretch, nbend) = (0,3), (e) (nstretch, nbend) = (1,0), (f) (nstretch, nbend) = (0,4).

Table 5: The average structural parameters for the ground vibrational states of the $C_3$-Ar complex ($R$ in angstrom and angles in degree).
4 Conclusions

In this paper, four two-dimensional intermolecular potential energy surfaces of the \( \text{C}_3\text{-Ar} \) complex are constructed at the CCSD(T) level with four different basis sets. We find that each PES can be characterized by two collinear saddle points and two global T-shaped minima with a saddle point between them. Bound states are performed for the \( \text{C}_3\text{-Ar} \) complex and intermolecular vibrational states are assigned from the analysis of their wavefunctions. Furthermore, the corresponding vibrational frequencies are also obtained from the bound state energies of these assigned states. Studies show that the larger the basis set is used, the more accurately the results are calculated. In the end, the calculated the results are calculated. In the end, the calculated the average structural parameters of the ground vibrational states for \( \text{C}_3\text{-Ar} \) complex have been determined. All these results will be useful for the further observation and detailed analysis of experimental spectra for the \( \text{C}_3\text{-Ar} \) complex.

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