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INTERMOLECULAR POTENTIAL AND *AB INITIO* SPECTROSCOPY OF THE AR-CO COMPLEX

The intermolecular potential energy surfaces of the Ar-CO complex have been calculated using MP2, CCSD(T) and SIMPER-P methods. The comparative analysis of the intermolecular potential energy surfaces calculated using MP2 and CCSD(T) methods is carried out based on the comparison of the components of the total interaction energy using perturbation theory and monomer dipole-dipole polarizabilities obtained from experiment and estimated at different levels of theory. The intermolecular potential energy surfaces are used to calculate the vibrational bound states of the complex. SIMPER-P method is shown to produce results competitive to high-level CCSD(T) method and to be in excellent agreement with the results of the experiment.

Introduction

The aim of the present work is to check of efficiency of the SIMPER-P method applied to the description of the intermolecular interaction in Ar-CO complex. In present work we calculate the MP2

and CCSD(T) intermolecular potential energy surfaces of the Ar-CO complex. We then apply the SIMPER-P procedure to the MP2 intermolecular potential energy surface to obtain the SIMPER-P intermolecular potential. The comparison of the

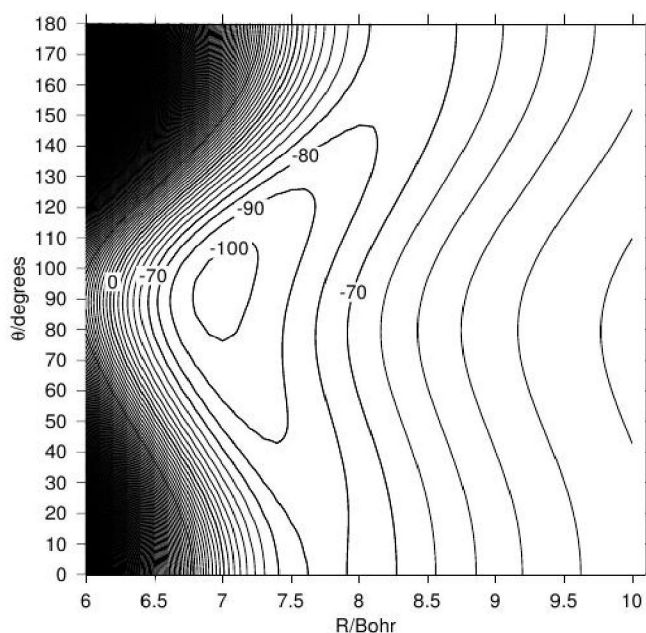


Figure 1: Contour plot in Jacobi coordinates of the SIMPER-P intermolecular potential energy surface of the Ar-CO complex. The successive contours are spaced by 10 cm^{-1}

intermolecular potentials calculated using different methods is carried out by the analysis in terms of components of the total interaction energies in the vicinity of the global minimum using intermolecular perturbation theory and monomer properties. SIMPER-P, CCSD(T) and MP2 intermolecular potentials are then used in the calculation of the rovibrational bound states of the Ar-CO complex. The energies of the calculated rovibrational bound states are compared against existing theoretical predictions and experimental measurements.

Calculations and results

The bond distance of the CO molecule is fixed at its equilibrium length of $2.132 a_0$ [1]. The intermolecular potential energy surfaces are calculated using MP2 and CCSD(T) supermolecule methods with the SP-aug-cc-pV5Z basis set [2]. A polar coordinate system is used to construct and represent the intermolecular potential energy surfaces. The intermolecular geometries are described by the R and θ coordinates of the Ar position vector \mathbf{R} with the origin coinciding with the center of the C-O bond and C-O bond directed along the positive z axis with C atom located on the negative z axis. The SIMPER-P intermolecular potential energy surface is obtained by applying the SIMPER-P method to the MP2 intermolecular potential energy surface [2].

The contour plot describing the intermolecular potential energy surface of the Ar-CO complex is shown in Figure 1. As in previous works [1,3] we found only one minimum corresponding to a T-shaped structure of the Ar-CO complex. The comparison of MP2, SIMPER-P and CCSD(T) interaction energies in the vicinity of the minimum is shown in Table 1.

As can be seen from the Table 1, MP2 method overestimates the interaction energy in the vicinity of the equilibrium geometry of the complex by 9 % compared to CCSD(T) method. In order to investigate the possible sources of the deviation of MP2 results and the effect of applying the SIMPER-P method we carried out the comparative analysis in terms of components of the total interaction energies using intermolecular perturbation theory. Components of the MP2 and SIMPER-P interaction energies are shown in Table 2.

We observed from Table 2 that the dispersion energy is the dominant component responsible for binding in the Ar-CO complex and the MP2 method, equivalent to UCHF method [2], considerably overestimates the dispersion energy, which is proved by comparing the static isotropic polarizabilities of the Ar and CO molecules estimated at different levels of theory shown in Table 3.

We used the RPA method to calculate the SIMPER-P non-expanded dispersion energies in

Table 1. Interaction energies of the Ar-CO complex in the region of equilibrium configuration estimated at three levels of theory

Orientation	Interaction energies (cm ⁻¹)		
R (a.u.) / Θ (degrees)	MP2	SIMPER-P	CCSD(T)
7.00 / 90.0	-110.952	-102.986	-101.918

Table 2. Components of the MP2 and SIMPER-P total interaction energies (cm⁻¹) in the vicinity of the minimum of the Ar-CO intermolecular potential energy surface, obtained with the sp-av5z basis set. Θ is given in degrees, R – in atomic units

Geometry/Energy	E _{electrostatic}		E _{induction}		E _{dispersion}		E _{exchange-repulsion}	
R/ Θ	MP2	SIMPER	MP2	SIMPER	MP2	SIMPER	MP2	SIMPER
7.0/90.0	-42.53	-38.99	-21.54	-22.01	-222.55	-204.97	175.67	162.98

Table 3. Calculated and experimental values of Ar and CO spherically averaged polarizabilities in atomic units

CO		Ar	
Property	Value (a.u.)	Property	Value (a.u.)
α_{UCHF}	11.281	α_{UCHF}	10.076
α_{RPA}	12.337	α_{RPA}	10.713
$\alpha_{\text{Exp}}[4]$	13.1	$\alpha_{\text{Exp}}[5]$	11.1

Table 4. Comparison of frequencies (in cm⁻¹) of intermolecular bending (1,0) and stretching(0,1) modes

Method	(1,0)	(0,1)	Reference
MP2	11.981	20.963	This work
CCSD(T)/avqz+(33211)	11.729	18.004	[3]
CCSD(T)/sp-av5z	11.795	17.861	This work
SIMPER-P	11.94	17.63	This work
Experiment	12.014	18.110	[1]

present work and the comparison of polarizabilities shows that RPA method reproduces the experimental values more accurately compared to UCHF method which underestimates the polarizabilities by 14 %. We used the SIMPER-P intermolecular potential energy surface to calculate the rovibrational spectra of the Ar-CO complex. Bound states for the SIMPER-P potential are calculated using the program BOUND [6]. The calculated transition wavenumbers are compared in Table 4 with experimental values and existing theoretical predictions.

As can be seen from Table 4, the SIMPER-P surface gives the bending and stretching transitions which are in excellent agreement with the experimental and existing CCSD(T) values, while MP2 surface overestimates the value of the experimental stretching mode frequency by 14 %.

Conclusions

The intermolecular potential energy surfaces of the Ar-CO complex have been calculated at three

levels of theory - MP2, SIMPER-P and CCSD(T). The MP2 method is shown to overestimate the dispersion energy component resulting to the overestimation of binding energy, SIMPER-P is shown to produce the potential energy surface that is close to the CCSD(T) potential. The effect of applying the SIMPER-P procedure to the MP2 intermolecular potential is analyzed by comparing the monomer properties and using intermolecular perturbation theory. Comparison of spectroscopic properties calculated from SIMPER-P potential and existing theoretical and experimental predictions shows that SIMPER-P is competitive to CCSD(T) method, while MP2 predicting qualitatively correct results considerably overestimates the binding.

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Резюме

MP2, CCSD(T) және SIMPER-P әдістері арқылы Ag-CO комплексінің бет қабат потенциалдық энергиясы есептелген. Осы үш әдістің эффектілігі қатынастың толық энергиясын және потенциалдың әртүрлі бөлшектері мәндерін салыстыру арқылы анықталған. Комплексінің спектралды параметрлері есептелген. SIMPER-P әдісінің дәлдігі жағынан жоғары деңгейлі болып келетін CCSD(T) әдісінен қалыспайтындығы көрсетілген.

Резюме

Методами MP2, CCSD(T) и SIMPER-P были рассчитаны поверхности межмолекулярной потенциальной энергии

комплекса Ag-CO. Был проведён сравнительный анализ поверхностей межмолекулярной потенциальной энергии рассчитанных методами MP2 и CCSD(T) сравнением компонент полной энергии с использованием теории возмущений и поляризуемостей мономеров, полученных из эксперимента и нескольких уровней теоретических оценок. Межмолекулярные поверхности потенциальной энергии были использованы для расчёта колебательных уровней комплекса. В работе показано, что метод SIMPER-P производит результаты, не уступающие по точности результатам метода CCSD(T) и находящиеся в отличном согласии с экспериментальными данными.

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