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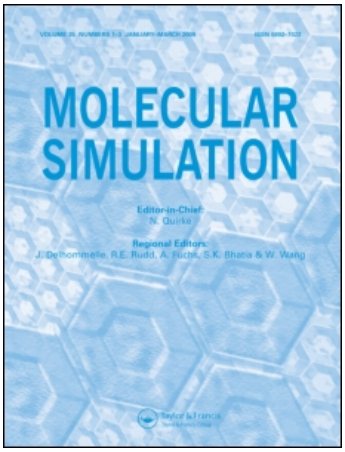

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Test Study on the Excitation Spectrum of the COAr van der Waals Molecule

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Test Study on the Excitation Spectrum of the CO···Ar van der Waals Molecule

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In the present contribution, we performed *ab initio* Møller-Plesset perturbation theory second-order (MP2) calculations in the framework of the supermolecule approach on the vertical excitation spectra of the weakly bound van der Waals CO–Ar molecule in its "near T-shaped" most stable ground state structure, as a guideline for future theoretical and experimental work. These test calculations indicate a ground CO($X^1\Sigma$)–Ar(^1S) interaction with $R_e = 3.72$ Å, $D_e = 109\,cm^{-1}$ and $D_o = 92\,cm^{-1}$. They also indicate an excited CO($A^1\Pi$)–Ar(^1S) interaction with $R_e = 3.55$ Å, $D_e = 141\,cm^{-1}$ and $D_o = 121\,cm^{-1}$. A red shift of $29\,cm^{-1}$ for the CO($X^1\Sigma$)–Ar(^1S) → CO($A^1\Pi$)–Ar(^1S) vertical excitation energy, with respect to the corresponding CO($X^1\Sigma$) → CO($A^1\Pi$) excitation in the absence of Ar, can be obtained by comparing the corresponding D_o values.

Keywords: van der Waals molecules; *Ab initio* calculations; Møller-Plesset perturbation theory; Excitation spectra

Pacs: 31.15.Ar; 31.25.Nj; 31.25.Qm; 31.15.Md; 31.50. + w

INTRODUCTION

Laser spectroscopy employing the combination of a narrow bandwidth tunable laser source and molecular beam techniques is ideal for spectroscopic investigation of molecules and molecular interactions. The implementation of high-resolution state selective spectroscopy and controllable sample conditions facilitate the study of van der Waals molecules [1–6]. Van der Waals molecules have attracted much attention in recent years since the study of these molecules gives insight into weak intermolecular forces. The CO-rare gas van der Waals molecules such as CO–Ar are prototype species. In contrast to extensive experimental and theoretical studies on their vibrational and rotational spectra [7,8] there is a complete lack of data on their electronic excitation spectrum lying in the vacuum ultraviolet region.

In this study, we present the first *ab initio* calculation of the vertical electronic excitation spectrum of the diatomic van der Waals CO–Ar molecule in its "near T shape" most-stable ground and excited state structure using standard perturbation methods of quantum chemistry. Despite many technical difficulties, *ab initio* methods offer a sound basis for the calculation of vdW potential energy surfaces valid over the whole range of molecular distances and orientations [9,10].

THEORETICAL METHOD

The interaction potential has been obtained in the framework of the supermolecule approach [9,10] at the Hartree-Fock Self-Consistent-Field (HF-SCF) and Møller-Plesset perturbation theory (MP) levels of approximation for the total energy

$$E = E^{\mathrm{HF-SCF}} + E^{\mathrm{MP}}, \tag{1}$$

where the correlation energy is split into contributions that are due to different orders of perturbation

$$E^{\mathrm{MP}} = E^{\mathrm{MP2}} + E^{\mathrm{MP3}} + \cdots \tag{2}$$

The interaction energy (IE) has been defined as:

$$\mathrm{IE}(\mathbf{R}) = E(\mathrm{CO}\cdots\mathrm{Ar};\mathbf{R}) - E(\mathrm{CO}\cdots X;\mathbf{R}) - \mathrm{E}(\mathrm{X}\cdots\mathrm{Ar};\mathbf{R}), \tag{3}$$

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where E(CO-X; **R**) and E(X-Ar; **R**) are used to indicate that the monomer energies are derived in the dimer centered basis set (DCBS). This amounts to applying the counterpoise procedure of Boys and Bernardi [11] to correct for the basis set superposition error (BSSE), at both, the HF-SCF and the correlation levels of approximation, at each molecular configuration **R**. The interaction energy in Eq. (3) can be expressed in perturbation [12] at any particular geometrical configuration **R** as:

$$\mathrm{IE} = \mathrm{IE}^{\mathrm{HF-SCF}} + \mathrm{IE}^{\mathrm{MP2}} + \mathrm{IE}^{\mathrm{MP3}} + \cdots \qquad (4)$$

In the present work, we have adopted the augmented correlation-consistent triple zeta (aug-cc-pVTZ) basis sets for Ar, C and O. They were complemented with a set of bond function taken from Tao and Pan [13,14], referred here as BF: 3s ($\alpha = 0.9, 0.3, 0.1$), 3p ($\alpha = 0.9, 0.3, 0.1$), 2d ($\alpha = 0.6, 0.2$). The bond functions were placed at the midpoint of the line which joins Ar with the center of mass of CO. A recent report on the use of bond functions and related problems is offered by Tao [15].

The necessary energies were calculated using GAUSSIAN 98 molecular package [16] for the Gaussian integrals, HF eigenvectors and energies, molecular properties, four-index molecular integral transformation and Møller-Plesset perturbation theory calculations, respectively.

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RESULTS AND DISCUSSION

Ground CO($X^1\Sigma$)–Ar(^1S) State

Ab initio calculations in the framework of the supermolecule approach [9,10] were performed to determine the interaction energy of the CO–Ar vdW dimer in its ground electronic state at the restricted HF-SCF and second-order MP levels of approximation [12,17] for the total energy. The final counterpoise-corrected interaction energies were computed according to Eq. (4) where CO was kept rigid at its experimental equilibrium bond length of 1.128 Å. The dimer geometry is specified by **R**, which represents the distance between the center of mass of CO and Ar, and by the polar angle of orientation β of the vector along the CO bond (directed from the C to the O atom) with respects to the vector along R. In the present contribution, the angle β was fixed at the optimal value of 93° reported by Toczylowski and Cybulski [8], which represents the best geometry estimate of this dimer to date. The equilibrium bond distance (R_e) and well depth (D_e) are obtained by fitting the calculated points to a eight-order polynomial in the stretching coordinate R, analytically continued with a seventh-order polynomial on $1/R$ (from $1/R^6$ to $1/R^{12}$) in the asymptotic $R \to \infty$ region.

The computed stretching interaction energy for the ground state of CO–Ar shows that this "near T-shaped" structure has a well depth D_e of 109 cm^{-1} at a minimum distance R_e of 3.72 Å, in close agreement with the values of $D_e = 105\,cm^{-1}$ and $R_e = 3.71$ Å suggested by Toczyłowski and Cybulski [8] for the same optimal β angle of 93°.

Excited CO($A^1\Pi$)–Ar(^1S) State

We have considered to study the **CO**($\mathbf{A}^1\Pi$)–**Ar**($^1\mathbf{S}$) → **CO**($\mathbf{X}^1\Sigma$)–**Ar**($^1\mathbf{S}$) transition as our first choice in the present study for the following reasons. (a) The $\mathbf{A}^1\Pi \to \mathbf{X}^1\Sigma$ transitions in CO is well known experimentally. (b) Although there are experimental and theoretical studies on the **CO**($\mathbf{X}^1\Sigma$)–**Ar**($^1\mathbf{S}$) ground state system [7,8], there is no evidence on the formation of the excited **CO**($\mathbf{A}^1\Pi$)–**Ar**($^1\mathbf{S}$) vdW dimmer.

High-level *ab initio* calculations in the framework of the supermolecule approach were performed to determine the interaction of **CO**($\mathbf{A}^1\Pi$) with **Ar**($^1\mathbf{S}$) at the unrestricted HF-SCF and the second-order unrestricted MP level of approximation (UMP) for the total energy. The interaction energy through second order in UMP is then obtained as:

$$\mathrm{IE} = \mathrm{IE}^{\mathrm{UHF-SCF}} + \mathrm{IE}^{\mathrm{UMP2}}. \qquad (5)$$

Ab initio calculations of open-shell vdW complexes have been traditionally accomplished using multi-determinant wave function methods, which in general impose severe demands on the computational resources (in time and storage). UMP represents an alternative size-consistent economical method available for a reliable calculation of interaction energies in open-shell molecules. The use and validity of the UMP procedure in conjunction with the counterpoise correction has been investigated by Chałasinski *et al.* [18–20]. The necessary UMP correlation energies are all calculated by means of the GAUSSIAN 98 molecular package [16] using the basis sets already described in the previous section. As for the ground state, stretching interaction energy calculations were carried out with respect to the intermolecular parameter R for a fixed value of $\beta = 93°$, where R_e and D_e are also obtained by fitting the calculated points to a eight-order polynomial in the stretching coordinate R, analytically continued with a seventh-order polynomial on $1/R$ (from $1/R^6$ to $1/R^{12}$) in the asymptotic $R \to \infty$ region.

In contrast to the closed-shell MP procedure, the counterpoise open-shell calculations in this section cause additional complications. The valence electron configuration of CO in its first singlet $^1\Pi$ state corresponds to $(1\pi_u)^4(3\sigma_g)^1(1\pi_g^*)^1$. The degeneracy of the $1\pi_g^*$ orbital is removed by the Ar atom for any

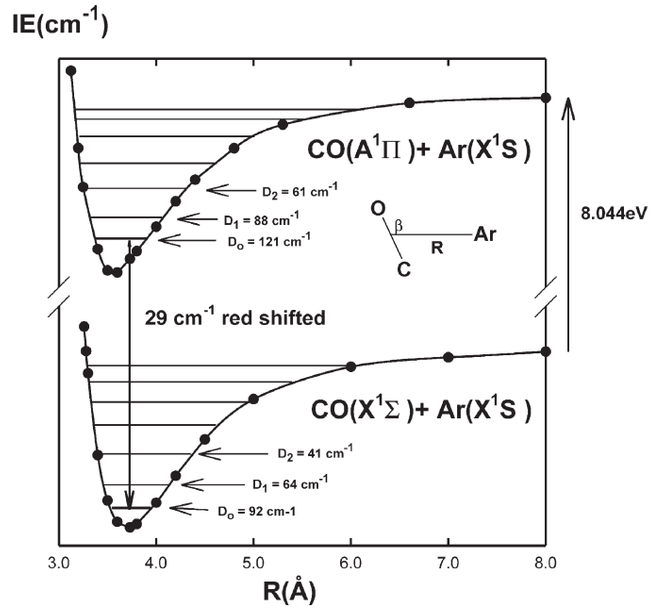

FIGURE 1 $\mathbf{CO}(\mathbf{A}^1\Pi)-\mathbf{Ar}(^1\mathbf{S}) \rightarrow \mathbf{CO}(\mathbf{X}^1\Sigma)-\mathbf{Ar}(^1\mathbf{S})$ vertical excitation energies for the near T structure of CO–Ar.

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nonlinear conformer of the molecular vdW complex, giving rise to the $\mathbf{A}'$ and $\mathbf{A}''$ (in C_s symmetry) states, respectively [21]. The $^1\mathbf{A}'$ state corresponds to a configuration where the electron is occupying a $1\pi_g^*$ orbital located "parallel" to the C–O–Ar plane. In the $^1\mathbf{A}''$ state, the electron is occupying a $1\pi_g^*$ orbital located "perpendicular" to the C–O–Ar plane. All the calculations reported in the present contribution are based on the Bohr–Oppenhaimer approximation and provide adiabatic interactions for the $\mathbf{A}'$ and $\mathbf{A}''$ states. Spectroscopy experiments do not probe such states because one has to additionally account for the spin-orbit coupling, which leads to interaction among the above adiabatic states. In this particular case, a proper formalism for bound states accessible in spectroscopy has been set forth by Dubernet *et al.* in the atom–diatom case [22], where the diabatic interaction can be represented as the average of the $\mathbf{A}'$ and $\mathbf{A}''$ interaction potentials. In the present work, we have represented the $\mathbf{CO}(\mathbf{A}^1\Pi)-\mathbf{Ar}(^1\mathbf{S})$ interaction potential on CO–Ar as the average among their corresponding $\mathbf{CO}(^1\mathbf{A}')-\mathbf{Ar}(^1\mathbf{S})$and $\mathbf{CO}(^1\mathbf{A}'')-\mathbf{Ar}(^1\mathbf{S})$ states.

Another problem related to applying the supermolecular UMP method to open-shell molecular systems is the spin contamination, which has to be small and of about the same magnitude for the CO–Ar dimer and for the CO monomer [18,23,24]. In all our calculations the spin contaminations were small, $\langle S^2 \rangle$ was always equal to about 0.19 for the singlet $\mathbf{A}'$ and $\mathbf{A}''$ states for both CO–Ar and CO in the DCBS.

Our final $\mathbf{CO}(\mathbf{A}^1\Pi)-\mathbf{Ar}(^1\mathbf{S}) \rightarrow \mathbf{CO}(\mathbf{X}^1\Sigma)-\mathbf{Ar}(^1\mathbf{S})$ vertical excitation spectrum for CO–Ar in its near T-shaped ground and excited state geometry is depicted in Fig. 1. Vibrational energies were calculated from the fitted potential curves using an implementation of the numerical Numerov-Cooley procedure [25] by treating CO–Ar as a diatomic system with only one degree of freedom R. This procedure shows that for the ground $\mathbf{CO}(\mathbf{X}^1\Sigma)-\mathbf{Ar}(^1\mathbf{S})$ interaction (lower curve in Fig. 1) the calculated dissociation energy corresponds to a D_o value of 92 cm^{-1}. It also show that the minimum of the excited $\mathbf{CO}(\mathbf{X}^1\Sigma)-\mathbf{Ar}(^1\mathbf{S})$ singlet interaction (upper curve in Fig. 1) occurs at R_e of 3.55 Å, $D_e =$ 141 cm^{-1}, and $D_o = 121\,cm^{-1}$. A red shift of 29 cm^{-1} for the $\mathbf{CO}(\mathbf{X}^1\Sigma)-\mathbf{Ar}(^1\mathbf{S}) \rightarrow \mathbf{CO}(\mathbf{A}^1\Pi)-\mathbf{Ar}(^1\mathbf{S})$ vertical excitation energy, with respect to the corresponding $\mathbf{CO}(\mathbf{X}^1\Sigma) \rightarrow \mathbf{CO}(\mathbf{A}^1\Pi)$ excitation in the absence of Ar, can be obtained by comparing the corresponding D_o values. Although D_1 and D_2 values are also indicated in Fig. 1, they are less accurate than D_o and no attempt was done to obtain any other shifting values from them.

FINAL REMARKS

The vertical excitation spectrum described in Fig. 1 is to be taken only as a qualitative guide for future experimental–theoretical work. The main purpose of the present study is to present an educated guess of the electronic excitation spectrum lying in the vacuum ultraviolet region for the CO–Ar vdW dimer, which can be used to set up initial experimental conditions in laser induced fluorescence spectroscopy experiments of Ar gas seeded with CO. Although the present ground-state CO–Ar

calculation seems to be reasonable well represented as compared to recent *ab initio* results available, this may not necessarily be the case for the excited state examined here. In order to increase the predictive value of Fig. 1, the capability of the present basis sets to represent the electric properties and the reliability of the UMP2 correlation energy of the excited state involved remain to be investigated using higher-level correlation calculations. A theoretical and experimental study for CO–Ar, done along these guidelines, is underway in our laboratory and will be presented elsewhere.

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