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REGULAR ARTICLE

Mary C. Salazar · Indira Lugo
Antonio J. Hernández · Carlos Manzanares I

Ab initio interaction and spectral properties of CO^+–He

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Abstract In this contribution, ab initio methods have been used to study the open-shell CO^+–He van der Waals (vdW) complex in both the ground and the first Π excited electronic state. Calculations were performed at the UCCSD(T) level of theory in the framework of the supermolecule approach using the cc-pVTZ basis set complemented with a set of standard bond functions in the middle of the vdW bond. Calculations predict a most-stable equilibrium conformation with $\beta e = 45^\circ$, $R_e = 2.85\,\text{Å}$ and $D_e = 275\,\text{cm}^{-1}$ for the ground $CO^+(X^2\Sigma)$–He(^{1}S) state and $\beta e = 90^\circ$, $R_e = 2.70\,\text{Å}$ and $D_e = 218\,\text{cm}^{-1}$ for the excited $CO^+(A^2\Pi)$–He(^{1}S) state. The dipole moment μ and independent components of the field polarizability α of the CO^+-He vdW complex have been studied at the calculated equilibrium geometry of these states. The vertical excitation energies from the ground $CO^+(X^2\Sigma)$–He(^{1}S) to the excited $CO^+(A^2\Pi)$–He (^{1}S) electronic state and corresponding shifts in the fluorescent spectrum with respect to the isolated CO^+ molecule are also presented.

Keywords van der Waals molecules · Ab initio calculations · Coupled cluster theory · Excitation spectra · Dipole moments · Dipole polarizabilities

1 Introduction

Theoretical and experimental research on neutral closed-shell weakly molecular complexes has always been a very active research field. Its knowledge is essential for the understanding of a variety of biological, chemical and physical phenomena in molecules and clusters [4,5]. There has been recent work on charged complexes where at least one of the interacting species contains one or more open shells [6–10]. It is expected in general, that the attractive ion-induced interaction leads to larger dissociation energies and cross sections. Furthermore, many of these van der Waals (vdW) complexes have unusual spectra due to the influence of their large-amplitude vibrational modes. Concurrently, experiments have provided crucial reference for theoretical chemists, and spectral data have played an important part in the development of potential energy surfaces for these complexes. In some cases, however, for which no or insufficient experimental data exist, ab initio calculations remains the method of choice. For this reason, we have tested the quality of the UCCSD(T) method on predicting the spectral and bonding properties of CO^+ ion weakly interacting with He.

In the present study, we are able to describe the two-dimensional interaction potential and the vertical excitation electronic spectra of the vdW CO^+–He complex in its "tilted" most-stable ground-state structure using high-quality basis set functions and taking the basis set superposition error (BSSE) into account [5]. Since all the highly effective ab initio methods developed for single-molecule calculations are in principle applicable without change, we have used the supermolecule approach at present [5]. The equilibrium dipole moment and polarizability of the ground and first Π excited electronic state of the complex also have been studied using carefully designed basis set functions.

2 Theoretical method

The interaction potential has been obtained in the framework of the supermolecule approach at the spin-unrestricted Hartree-Fock self-consistent-field (UHF-SCF) and at the single and double coupled cluster theory with perturbative triplets UCCSD(T) levels of approximation for the total energy

$$E = E^{UHF-SCF} + E^{UCCSD(T)}, \tag{1}$$

were we have used the cc-pVTZ basis set functions, as implemented in the GAUSSIAN98 [11] molecular package, complemented with a set of bond function taken from Tao and Pan [12,13]: 3s (α=0.9, 0.3, 0.1), 3p (α=0.9, 0.3, 0.1), 2d

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M. C. Salazar (✉) · I. Lugo · A. J. Hernández
Departamento de Química, Universidad Simón Bolívar,
Apdo 89000, Caracas 1080A, Venezuela
E-mail: msalazar@usb.ve

C. Manzanares I
Department of Chemistry and Biochemistry, Baylor University,
Waco, TX 76798, USA

(α=0.6, 0.2), 1f (α=0.3). The bond functions were placed at the midpoint of the vector R, which joins He with the center of mass of CO^+.

The interaction energy (IE) has been defined as:

$$\mathrm{IE(R)} = \mathrm{E(CO^+ \cdots He; R)} \\ -\mathrm{E(CO^+ \cdots X; R)} - \mathrm{E(X \cdots \cdot He; R)}, \quad (2)$$

where E(CO^+–X; R) and E(X–He; R) are used to indicate that the monomer energies (He and CO^+) are derived in the dimer-centered basis set (DCBS). This amounts to applying the counterpoise procedure of Boys and Bernardi [14] to correct for the BSSE at each molecular configuration R. Although 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), we have used the unrestricted UHF-SCF as the starting point for the open-shell $CO^+(X^2\Sigma)$–He(^{1}S) ground and $CO^+(A^2\Pi)$–He(^{1}S) excited state calculations. Unrestricted UCCSD(T) represents an alternative size-consistent economical method available for a reliable calculation of interaction energies [15].

In contrast to the closed-shell procedures, the counterpoise open-shell calculations cause additional complications for Π states. The valence electron configuration of CO^+in its electronic excited $A^2\Pi$ state corresponds to $(1\pi u)^3$ $(3\sigma g)^2$. The degeneracy of the $(1\pi u)^3$ orbital is removed by the He atom for any nonlinear conformation of the molecular vdW complex, giving rise to the A' and A" (in Cs symmetry) states, respectively [16]. The A' state corresponds to a configuration where the electron occupying a 1πu orbital is located "parallel" to the C-O-He plane. In the A" state, the electron is occupying a 1πu orbital is located "perpendicular" to the C–O–He plane. All the calculations reported in the present contribution are based on the Bohr–Oppenheimer approximation and provide adiabatic interactions for the A' and 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 [17], where the diabatic interaction can be represented as the average of the A' and A" interaction potentials. In the present contribution we have represented the $CO^+(A^2\Pi)$–He(^{1}S) interaction potential on CO^+–He as the average among their corresponding $CO^+(^2A')$–He(^{1}S) and CO^+(2A")–He(^{1}S) states.

Another problem related to applying the supermolecular unrestricted UHF–SCF method to open shell molecular systems is the spin contamination, which has to be small and of about the same magnitude within the CO^+–He complex and the CO^+ monomer [18]. In all our calculations the spin contaminations were small, $<S^2>$ was equal to about 0.78–0.79 (very close to the expected 0.75 value for a doublet state) for both the CO^+–He complex and the CO^+ monomer in the DCBS.

3 Results and discussion

3.1 Ground $CO^+(X^2\Sigma)$–He(^{1}S) State

The bond length for $CO^+(X^2\Sigma)$, calculated by point wise optimization at the UCCSD(T) level of theory, was found to be r[CO^+ $(X^2\Sigma)$]=1.116 Å, which agrees closely with the experimental value of 1.115 Å [19]. In the supermolecule calculations, CO^+ was kept rigid at this calculated equilibrium bond length of 1.116 Å and the complex geometry was specified by R, which represents the distance between the center of mass of CO^+ and He, and by the polar angle of orientation β of the vector along the CO^+ (directed from the O to the C atom) with respect to the vector along R. The equilibrium bond distance (R_e) and well depth (D_e) were obtained, at each polar angle of orientation β examined in this contribution, by fitting the calculated fully ab initio UCCSD(T) IE points to an 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 main result for the ground $CO^+(X^2\Sigma)$–He(^{1}S) complex is depicted in Fig. 1, which shows a contour plot of IE with respect to R and β. This figure shows a "tilted" structure to be the most stable configuration with βe=46°, a well depth D_e=275 cm^{-1} at a equilibrium distance R_e=2.85 Å for the present calculation, in relatively close agreement with βe=43.6°, D_e of 298 cm^{-1} at a R_e value of 2.852 Å, as found by Maclagan et al. [20] at the UMP4/6-311++G(3df, 3pd) [6] level of theory using a slightly smaller CO^+ bond length of 1.089 Å. A closer comparison can be seen in Fig. 1, which shows how the well depth changes with β. We can notice that although the well depth obtained in the present contribution differs by 23 cm^{-1}, as compared to the calculation of Maclagan et al. [20], the optimized polar angle of orientation β of both calculations differs only by 2°. This is not surprising since, already at the SCF level of theory, the present calculation predicts the correct anisotropy of the interaction potential (as shown in Fig. 1) giving a most stable "tilted" structure with βe=40°. This in turn, shows that the IE anisotropy is basically due to induction effects, determined mainly by the polarizability of He and the charge and multipole moments of CO^+.

A much less demanding ab initio method to study ionic systems, using the IE and the vertical ionization potential of the neutral species, was introduced very recently by Lotrich and van der Avoird [21]. This ionization potential method was successfully tested for $CO^+(X^2\Sigma)$–He(^{1}S) by comparison against partially spin restricted RCCSD(T) results therein. Although these authors considered β= 0°, 90° and 180° only, which is not sufficient for a complete comparison, we should point out that our UCCSD(T) calculations agree within 1 cm^{-1} to their RCCSD(T) results (for all values of R presented in Table 1 of reference [20]), which shows that the present UCCSD(T) calculations are not appreciably contaminated

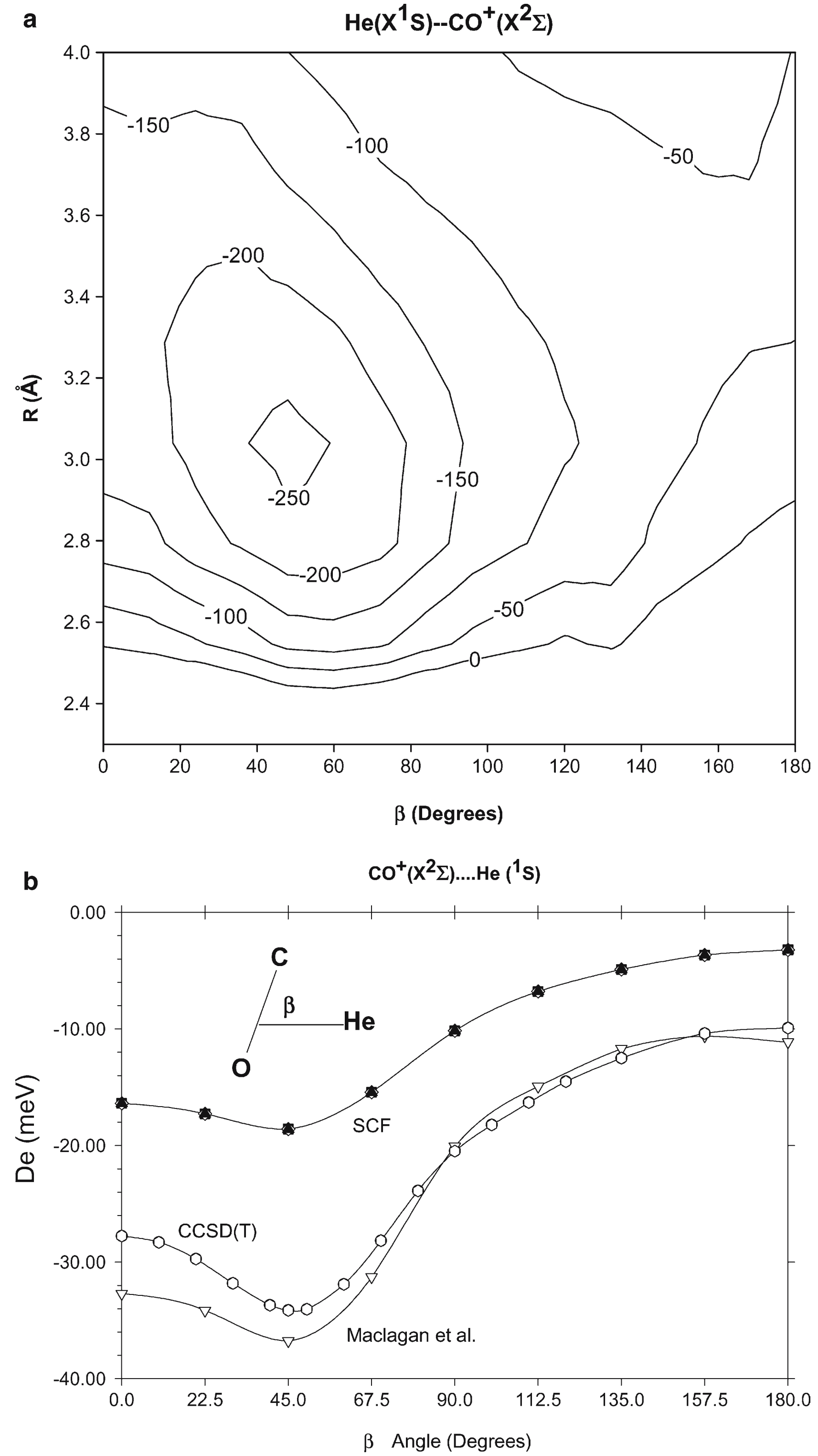

Fig. 1 **a** Contour plot of IE (cm^{-1}) with respect to R and β for the ground CO$^+$(X$^2\Sigma$)–He(^{1}S) electronic state **b** Angular dependence of D_e for the ground CO$^+$(X$^2\Sigma$)–He(^{1}S) electronic state

with higher multiplicity spin states, as pointed out before in connection with the small deviation from $<S^2> = 0.75$ for the doublet states of CO$^+$–He and CO$^+$ examined in this study.

3.2 Excited CO$^+$(A$^2\Pi$)–He(^{1}S) State

Although the CO$^+$(X$^2\Sigma$)→CO$^+$(A$^2\Pi$) transition is well known experimentally [18], there is no direct experimental

Table 1 Dipole moments and dipole polarizabilities of CO^+, He and CO^+–He (in a.u.)

CO^+ ($X^2\Sigma$)–He(^1S)	μ_z	1.0837
	μ_x	0.0737
	α_{xx}	9.17
	α_{zz}	12.85
CO^+ ($X^2\Sigma$)	μ_z	1.0271[a]
	α_{xx}	7.40
	α_{zz}	11.31
CO^+ ($A^2\Pi$)–He(^1S)	μ_z	0.2881
	μ_x	0.0683
	α_{xx}	9.61
	α_{zz}	13.34
CO^+ ($A^2\Pi$)	μ_z	0.2924
	α_{xx}	9.09
	α_{zz}	13.62
He(^1S)	α	1.4012[b]

[a] 1.027a.u.: Theoretical value from RCCSD(T)/cc-pVTZ calculations [26]

[b] 1.386a.u.: Experimental value from [27]

evidence of the formation of the excited $CO^+(A^2\Pi)$–He(^1S) complex. The bond length for $CO^+(A^2\Pi)$, calculated by point wise optimization at the UCCSD(T) level of theory, was found to be r[$CO^+(A^2\Pi)$]=1.248 Å, which agrees well with the experimental value of 1.244 Å [18]. In the supermolecule calculations, $CO^+(A^2\Pi)$ was kept rigid at this calculated equilibrium bond length of 1.248 Å and the complex geometry as specified by R and by the polar angle of orientation β. The bond length R_e and the well depth D_e were obtained at each polar angle of orientation β examined in this contribution by fitting the calculated fully ab initio UCCSD(T) IE points, as explained already for the ground state.

The main result for the ground $CO^+(A^2\Pi)$–He(^1S) complex is depicted in Fig. 2, which shows a contour plot of how the **IE** changes with R and β. This figure shows a “perpendicular” structure to be the most stable configuration with βe=90°, a well depth D_e=218 cm^{-1} at a minimum distance R_e=2.70 Å. This result is to be compared to the value of βe=90°, D_e of 138 cm^{-1} at a R_e value of 2.85 Å, as found by Hamilton et al. [21] at the projected UMP2/6-311++G** level of theory [6], using the slightly smaller CO^+ bond length of 1.241 Å . A closer comparison is depicted in Fig. 2b, which shows how the well depth changes with β. Although both potentials show a “perpendicular“ most-stable geometry, the well depth obtained in the present contribution is significantly deeper than the minimum obtained by Hamilton et al. [22].

In more detail, the interaction minimum for $CO^+(A^2\Pi)$–He(^1S) occurs at R_e of 2.40 Å and D_e=373 cm^{-1} for the “parallel” $CO^+(^2A')$–He(^1S) state and at R_e of 2.90 Å and D_e=156 cm^{-1} for the “perpendicular” $CO^+(^2A'')$–He(^1S) state, the A’ level being considerably more stable. The large A”–A’ splitting for the most stable T-shaped structure examined in this study implies that there is indeed a significant variation in the interaction between a CO^+ molecule in its electronic $^2\Pi$ excited state and a Helium atom when the unfilled π^* orbital is parallel or perpendicular to the O–C–He plane. The deeper minimum found in connection with ^{2}A’ (as compared to the ^{2}A” state) in the T-shaped geometry examined in this study reveals that the attractive interaction between CO^+ and He is indeed stronger when the singly-filled $1\pi_g^*$ electron of CO^+ lies in the O–C–He plane.

3.3 Vertical excitation energy

Our final $CO^+(X^2\Sigma)$–He(^1S) $\rightarrow CO^+(A2\Pi)$–He(^1S) vertical excitation spectrum for CO^+–He, frozen at its “tilted” most-stable ground-state geometry (r(CO^+) = 1.116 Å and β=46°) is depicted in Fig. 3. Vibrational energies were calculated from the fitted potential curves using the numerical Numerov-Cooley procedure [23] by treating CO^+–He as a diatomic system with only one degree of freedom R. This procedure shows that for the ground $CO^+(X^2\Sigma)$–He(^1S) electronic state (lower curve in Fig. 3) the calculated dissociation energy corresponds to a D_o=215 cm^{-1} with five vibrational states supported by this ground IE curve. Present calculations also show that the minimum of the excited $CO^+(A^2\Pi)$–He(^1S) interactions (upper curve in Fig. 3), frozen at the ground state geometry (r($CO^{+)}$ =1.116 Å and β = 46°), occurs at R_e of 3.35 Å, D_e=106 cm^{-1}, and D_o=69 cm^{-1}, with three vibrational states supported by this IE excited curve. Figure 3 depicts the three most intense excitation lines (with larger overlap among their vibrational functions). They show significant blue shifts (146 and 50 cm^{-1}) and a moderate red shift (13 cm^{-1}) for the transition from the lowest three vibrational states of $CO^+(X^2\Sigma)$–He(^1S) to the lowest vibrational state of $CO^+(A^2\Pi)$–He(^1S) with respect to the corresponding $CO^+(X^2\Sigma) \rightarrow CO^+(A^2\Pi)$ excitation in absence of He.

3.4 Electric properties

The dipole moment μ and independent components of the field polarizability α of the CO^+–He vdW complex has been studied at the calculated equilibrium geometry for the $CO^+(X^2\Sigma)$–He(^1S) ground and the $CO^+(A^2\Pi)$–He(^1S) excited electronic states, respectively. Calculations are performed at the CCSD(T) level of theory using the second-order polarized HyPol basis sets described by Pluta and Sadlej [24], which has been used successfully in the prediction of the dipole moment of the vdW CO_2–CO complex [25]. All calculations of μ and α have been carried out using the finite-field numerical approximation to the energy derivatives [26]

$$\mu_i = -[E(+F_i) - E(-F_i)]/2F_I$$
$$\alpha_{ii} = -[E(+F_i) + E(-F_i) - 2E(0)]/F_i^2,$$

where $E(F_i)$ represents the CCSD(T) energy calculated in the presence of the electric field strength F_i equal to ±0.001 a.u.. We have chosen z as the symmetry axis and zx as the molecular plane, i.e. the above indices are to be taken as defining the only no vanishing moments and polarizabilities μ_z, μ_x, α_{xx} and α_{zz}, respectively.

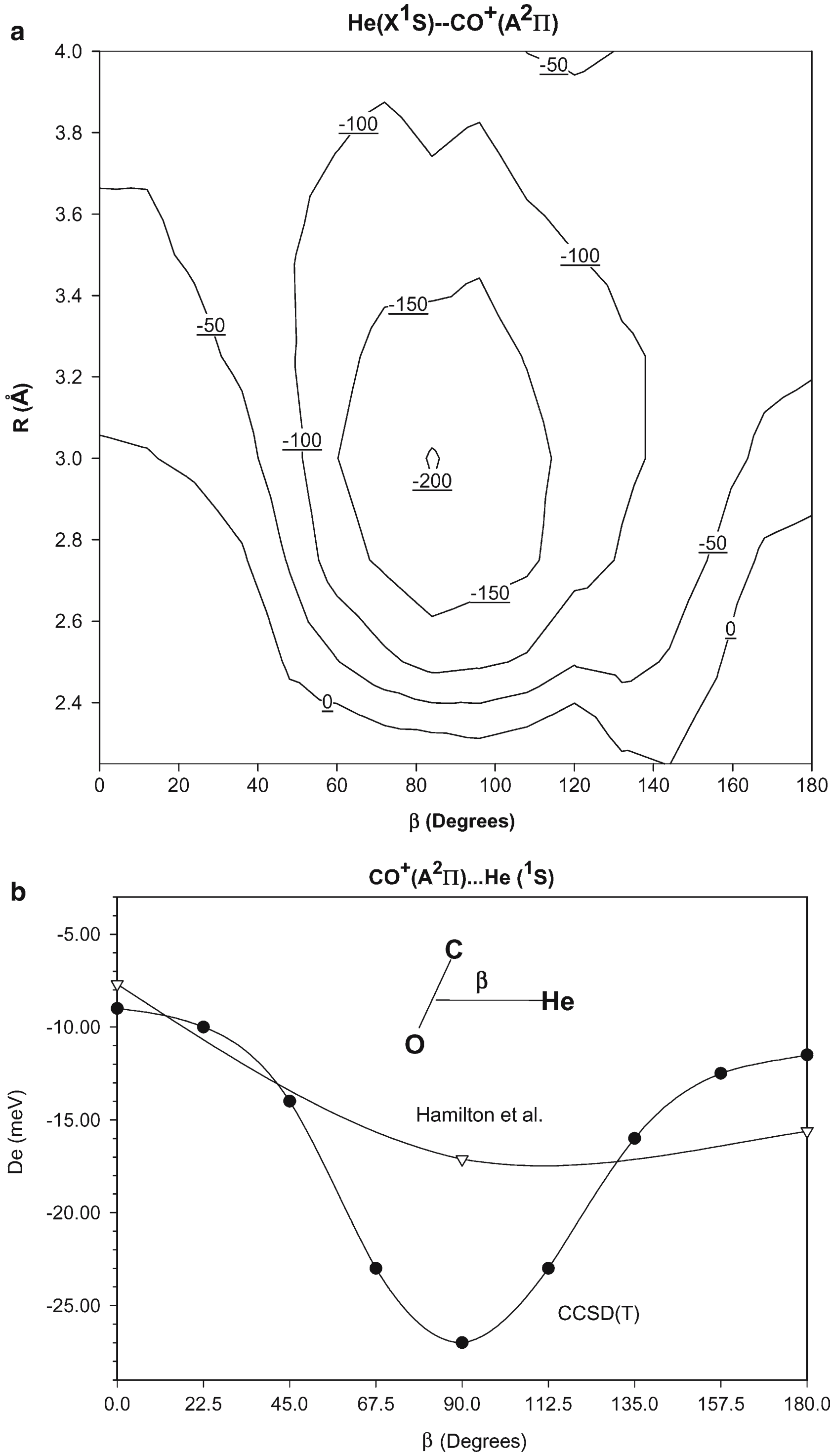

Fig. 2 **a** Contour plot of IE (cm^{-1}) with respect to R and β for the excited CO$^+$(**A**$^2\Pi$)–He(^{1}S) electronic state **b** Angular dependence of D_e for the excited CO$^+$(**A**$^2\Pi$)–He(^{1}S) electronic state

The calculated CCSD(T) dipole moments and dipole polarizabilities for the most stable geometry of the CO$^+$(X$^2\Sigma$)–He(^{1}S) ground and the CO$^+$(A$^2\Pi$)–He(^{1}S) excited electronic state, respectively, are displayed in Table 1, where we have also included the corresponding isolated systems for comparison. All properties were calculated relative to the center of mass of CO$^+$ with the z axis coinciding with the molecular axis of CO+ (with the light atom at the top) and He lying on the zx plane. The properties included in Table 1 for CO$^+$(A$^2\Pi$)–He(^{1}S)are taken as the average value between the parallel CO$^+$(^{2} A')–He(^{1}S) and perpendicular CO$^+$(^{2}A")–He(^{1}S) electronic states.

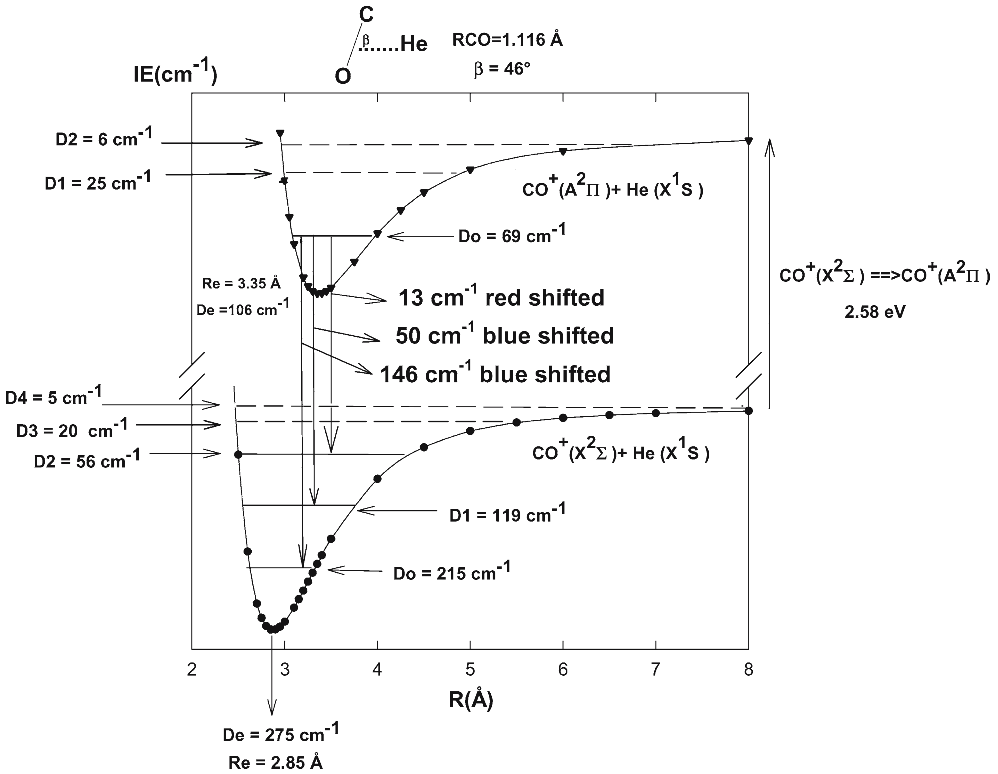

Fig. 3 CO$^+$ (X$^2\Sigma$)–He(^{1}S) → CO$^+$(A$^2\Pi$)–He(^{1}S) vertical excitation spectrum for CO$^+$–He, frozen at its "tilted" most-stable ground-state geometry

First, it is noticed that μ and α are more affected along the x axis than along the z axis during the changes accompanying the CO$^+$ association to He for all electronic state examined in the present work. For the ground state, μ_z increases 6% and $\mu_x$increases from 0 to 0.0737 a.u. in going from CO$^+$(X$^2\Sigma$) to CO$^+$(X$^2\Sigma$)–He(^{1}S). Similarly, α_{zz} increases 14% and α_{xx} increases 20%, in going from CO$^+$(X$^2\Sigma$) to CO$^+$(X$^2\Sigma$)–He(^{1}S) when He approaches CO$^+$ along the zx plane (β=46°). For the excited state, μ_z decreases 2% and μ_x increases from 0 to 0.0683 a.u., in going from CO$^+$(A$^2\Pi$) to CO$^+$(A$^2\Pi$)–He(^{1}S). Similarly, α_{zz} decreases 2% and α_{xx} increases 6% in going from CO$^+$(A$^2\Pi$) to CO$^+$(A$^2\Pi$)–He(^{1}S) when He approaches CO$^+$ along the x axis (β=90°). These results show that changes in electronic polarization for the ground state is larger as compared to the excited state when He approaches the CO$^+$ molecule, which in turn is due to the already large electronic polarization presented in the isolated CO$^+$(A$^2\Pi$) molecule as compared to CO$^+$(**X**$^2\Sigma$).

4 Final remarks

In the present study, ab initio calculations at the CCSD(T) level of theory in the framework of the supermolecule approach were used to study the CO$^+$–He vdW dimer. The interaction energy of the ground CO$^+$(X$^2\Sigma$)–He(^{1}S) and excited CO$^+$(A$^2\Pi$)–He(^{1}S) electronic states, as a function of the distance R between the He atom and the center of mass of CO$^+$ and the angle β among the monomers, were determined in order to calculate their corresponding equilibrium values: βe, R_e, D_e and D_o. These calculations indicated a ground CO$^+$(X$^2\Sigma$)–He(^{1}S) most-stable interaction with βe=46°, R_e=2.85 Å, D_e=275 cm^{-1} and D_o=215 cm^{-1}, and an excited most-stable CO$^+$(A$^2\Pi$)–He(^{1}S) interaction with βe=90°, R_e=2.70 Å, D_e=218 cm^{-1} and D_o=165 cm^{-1} . Significant blue shifts (146 cm^{-1} and 50 cm^{-1}) and a moderate red shift (13 cm^{-1}) were obtained for the CO$^+$(X$^2\Sigma$)–He(^{1}S) →CO$^+$(A$^2\Pi$)–He(^{1}S) vertical excitation energy with respect to the corresponding CO$^+$(X$^2\Sigma$)→CO$^+$(A$^2\Pi$) excitation in the absence of He. The vertical excitation spectrum described here is to be taken only as a qualitative guide because we have included only the most stable ground-state conformer into account. A most realistic approach must involve the complete interaction between the energy surfaces of both the ground and excited states. Finally, CCSD(T) dipole moments and dipole polarizabilities of the most stable geometry of the CO$^+$(X$^2\Sigma$)–He(^{1}S) ground and the CO$^+$(A$^2\Pi$)–He(^{1}S) excited electronic state were investigated, showing only moderate changes of their electric properties when He approaches the CO$^+$ molecule.

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