On Atomic Delocalization in van der Waals Bonding: Evidence from a Stochastic Picture

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Abstract: The distributions of nuclear positions in the lowest bound states of a single rare gas atom in a van der Waals complex with a CO molecule are examined by means of diffusion Monte Carlo (DMC) calculations performed on ab initio potential energy surfaces. The He atom is found to be nearly uniformly distributed around the molecule, whereas the Ar atom is more highly localised in a broadside position. This analysis highlights the problems associated with assigning conventional specific structures to such floppy systems, while the DMC calculations are found to provide a fairly direct representation of the quantum nature of these weakly bound molecular systems.

Keywords: ab initio calculations · bond theory · delocalization · Monte Carlo methods · van der Waals

Introduction

Because of their importance in several areas of chemical, physical and astrophysical research, van der Waals complexes of simple molecules and rare gases (Rg) have for some time received a great deal of experimental and theoretical attention.[1–6] Recently additional impetus has come from the possible role of such systems in materials sciences and the observation of new phenomena in large clusters of rare gases with molecular impurities, either neutral or ionic.[7–13]

The aim of the present study is to demonstrate, by using the specific example of carbon monoxide, how a more global description of rare gas atoms weakly bound as van der Waals (vdW) complexes to the CO molecule can be obtained from quantum Monte Carlo calculations of the distribution of their nuclear positions within the final molecule. State-of-the-art quantum chemical treatments[13–15] start, in fact, with a fixed-nuclei (FN), Born–Oppenheimer (BO) approach and therefore search for the most stable structure of the three atomic partners without any initial reference to the nuclear dynamics. Thus, although this aspect is correctly accounted for by later constructing the bound state levels of the triatomic complex, this approach implies a cluster structure in which the atoms have specified geometrical positions determined by the minima in the potential energy surface (PES). This latter description presents problems in the extraction of the structural properties of such weakly bound complexes from fully resolved infrared spectra,[16] since the progression of the transitions can be assigned either in terms of a set of approximate rigid body quantum numbers or in terms of the nearly free internal rotor dynamics of the component diatom.[17] In both limits a full set of measured and assigned spectral transitions or of estimated spectroscopic constants is used to determine the intermolecular potential. In either case, the diatom component rovibrational states are often used as a zeroth-order starting basis, and the overall rotations, plus a radial basis related to the vdW vibrations, are employed in further expansions with the appropriate angular momentum recoupling.[13, 16, 18, 19] This spectroscopic analysis thus recognizes the floppy nature and the wide-amplitude motions which nuclei or groups of nuclei can undergo in these species and underlines the difficulty of obtaining meaningful structural parameters from traditional spectroscopic analyses. By considering the motion of the component diatom as the primary dynamical reference[15, 16] it also acknowledges the fact that the very notion of an equilibrium structure may become irrelevant in such systems. On the other hand, an inspection of bound and metastable final eigenfunctions that could help to visualize the 3D behavior of such complexes is not commonly used in studies of the energy levels and the predissociation dynamics for vdW systems, since they tend to focus instead on the calculation of the matrix elements for transitions and for state lifetimes.[20, 21]

In the following we intend to show that a stochastic approach can lead, with only a moderate computational effort, to an overall representation of floppy, bound species in their ground states that can provide additional insight into

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their true structural features. This alternative approach complements the information already gathered from either structural or dynamic representations of rovibrational and metastable levels, as in the more conventional analysis,[3] and can easily be extended to larger clusters with several Rg as adatoms to the molecule; we are currently studying such extensions of the title systems.[22]

The Stochastic Approach

One of the most general methods currently available for the accurate treatment of quantum systems with more than a few degrees of freedom is based on stochastic approaches which are collectively referred to as quantum Monte Carlo (QMC) methods.[23–25] Some of their main advantages are the absence of size-dependent errors and by the favorable scaling of the computational and storage requirements with the number of degrees of freedom. The absence of a reference geometry around which a basis expansion would be centered makes them suitable for the treatment of floppy bound species where the quantum mixing of several possible classical structures frequently occurs. A further practical advantage, which will be employed in the present study, is its ability to use a full Hamiltonian generated in Cartesian coordinates and to provide very accurate information on the ground state of the bound system. The present calculations use the diffusion Monte Carlo (DMC) algorithm, which is briefly described below and more extensively in several recent publications.[26–29]

The Schrödinger equation for N bodies is given in Equation (1), in atomic units and imaginary time $\tau = it$, where ψ is the required wavefunction, $\hat{V}$ the potential energy term, x collectively describes all the position coordinates and m_k are the particle masses. E_ref is a reference energy, which shifts the origin of the energy scale to a convenient value. The above

$$\frac{\partial\psi(x,\tau)}{\partial\tau} = \sum_{k=1}^{N} \frac{1}{2m_\mathrm{k}} D_\mathrm{j} \nabla_\mathrm{k}^2 \psi(x,\tau) - [\hat{V}(x) - E_\mathrm{ref}]\,\psi(x,\tau) \tag{1}$$

$$\frac{\partial C(x,t)}{\partial t} = \sum_{j=1}^{N} D_\mathrm{j} \nabla^2 C(x,\tau) - k(x) C(x,\tau) \tag{2}$$

equation is isomorphic to a multidimensional anisotropic diffusion equation with additional position-dependent rate processes [Eq. (2)]. This implies that the original Schrödinger equation may now be treated as a reaction–diffusion process and solved by a random walk. The linearity of the equation allows many noninteracting random walkers (replicas) to be used in each simulation and they are defined in terms of Cartesian coordinates which are randomly changed and have varying weight $w(\tau)$ to simulate the kinetic and potential energy terms in Equation (1). The population is propagated along τ by finite time steps. By considering the formal solution of the time-dependent wavefunction in Equation (3), one sees

$$\psi(x,\tau) = \sum_{n} C_\mathrm{n} \phi_\mathrm{n}(x) \exp[-(E_\mathrm{n} - E_\mathrm{ref})]\tau \tag{3}$$

that, as τ increases, the dominant term of the sum on the r.h.s. of Equation (3) will become the lowest eigenstate of the N-particle system, since the higher states will have decayed to zero. It is interesting to note at this point, to make a further contact with the calculations described below, that the primary product of DMC calculations is the total wavefunction, while the more conventional diagonalization processes[3] produce primarily energy levels, often disregarding the information provided by the eigenvectors. The asymptotic evolution of the amplitude of the wave function over imaginary time as measured by the total weight of the random walker ensemble $W(\tau) = \Sigma_\mathrm{walks} w(\tau)$ provides one mechanism to compute the quantum energy within the DMC formalism. $W(\tau)$ decays exponentially according to the mismatch between the reference energy E_ref and the ground state energy E_0.[25, 29]

Although the study of excited bound states using QMC has recently been undertaken,[30] the chief interest of the above approach in the present analysis is its ability to generate the nodeless ground states of weakly interacting molecular systems.

Present Computations

The electronic degrees of freedom are first separated out by solving the conventional fixed nuclei (FN) problem for all the electrons as discussed below. Since the interaction between C and O in the CO target corresponds to a strong chemical bond, the high-frequency motion of the CO stretch vibration can also be adiabatically decoupled from the soft vibrational modes of the clusters. This implies that the full three-dimensional He- and Ar–CO potentials may be parametrized in terms of the vibrational state i of the molecule with quantum numbers v_i [Eq. (4)].[31] A convenient way of generating such adiabatic potentials is to average the full interaction over target vibrational states, as in Equation (5); the residual two Jacobi coordinates now represent the He

$$V(R,\theta,r) \Rightarrow V_\mathrm{i}(R,\theta;v_\mathrm{i}) \tag{4}$$

$$V_\mathrm{i}(R,\theta;v_\mathrm{i}) = \langle v_\mathrm{i} \,|\, V(R,\theta r) \,|\, v_\mathrm{i} \rangle \tag{5}$$

distance from the CO center of mass (c.o.m.) and its angle with the molecular bond axis, starting on the carbon side with $\theta = 0°$. An even simpler representation is obtained by replac-

Abstract in Italian: *Le distribuzioni spaziali degli stati legati di atomi di Elio e Argon con la molecola di CO vengono esaminate partendo dalla superficie di potenziale elettronica per lo stato fondamentale del rotatore rigido. Il problema dello stato elettronico quantico viene risolto passando alla forma diffusionale dell'eq. di Schrödinger ed ottenendo tali stati per via numerica con metodi Montecarlo. Si può chiaramente vedere dai risultati presentati che le deboli interazioni di van der Waals implicano una forte componente di energia di punto zero per gli stati fondamentali e quindi generano una marcata delocalizzazione strutturale dei complessi in esame.*

ing the vibrational functions in Equation (5) with delta functions at the CO equilibrium distance ($r_{CO} = 2.13a_0$), thereby recovering the rigid rotor (RR) potential energy surface $V_{RR}(R,\theta) = V(R,\theta;r_{CO})$. The latter scheme has been used in the present study, while the adiabatic approximation will be employed in a subsequent analysis of larger clusters,[22] with several He and Ar adducts, where frequency-shift calculations similar to previous work will be carried out.[22, 28, 32]

The He–CO rigid rotor potential V_{RR} was determined by means of a density functional treatment (DFT) of the electronic part at short and intermediate distances and switched to dispersion interactions at larger distances beyond the well region. This PES[32] compares well with the previous calculated and empirical PES and therefore provides an accurate description of the $V_{RR}(R,\theta)$ interaction. It is interesting to note that it gives the position of the potential minimum at a nonlinear structure ($\theta \approx 140°$) as suggested by the earlier studies.[13–16]

Similar DFT calculations were carried out for Ar–CO, and the PES compares well with the most recent ab initio results[14] (which were, however, limited to the shape of the well region), as well as with other recent studies[34–35] and with the earlier empirical surfaces.[36, 37] This suggests that the DFT method, with long-range forces added, can provide realistic descriptions of vdW interactions, as will become clear in the following discussion. A full comparison of our DFT calculations with the earlier data will be presented elsewhere,[38] where a broader range of the molecular properties of the complex will be discussed.

The general shapes of the present PES's are shown in the lower diagrams of Figure 1 (for He–CO) and of Figure 2 (for Ar–CO). For the argon complex the potential minimum (≈ -98 cm^{-1}) is located at about $R = 3.8$ Å and around $\theta = 85°$, as suggested by earlier calculations.[34, 35] The much shallower He–CO minimum (≈ -22 cm^{-1}) is located at $R = 3.5$ Å at an angle of $\theta \approx 140°$ as found in earlier studies.[13–16]

We therefore used the above potential functions to carry out the DMC calculations. They were done with an ensemble of fixed size of 1000 random walkers using an ensemble control scheme which splits the walker with highest weight whenever a walker with small weight has not survived the stochastic termination attempt.[29] Initial ensembles were propagated for several thousand steps in order to reach equilibrium. Time steps as short as 10 au were employed to check for time-step errors. For both systems, time steps below 100 au caused no systematic effects exceeding our statistical error bars. The quoted statistical accuracy amounts to one σ for a Gaussian error distribution, which is a good model for the distribution of block energies in the present cases.

As expected, ^{4}He–CO is only a very weakly bound complex: the present calculations yield the lowest bound state at -6.65 ± 0.007 cm^{-1}, which compares reasonably well with the result of -6.96 cm^{-1} of Moszynski et al.,[13] who found twelve bound states for their PES by a variational method. We have also obtained a value of -73.93 ± 0.01 cm^{-1} for the lowest bound state of Ar–CO within the V_{RR} approximation. The results from the best ab initio calculations[35] suggest a binding energy of -74.50 cm^{-1}, with a zero-point energy (ZPE) value of 21.786 cm^{-1}, in good accord with the present findings in spite of the use of a different PES. One should also point out that the discrete variable representation (DVR) method[35] is a very accurate way of obtaining bound states for one-adduct complexes but rapidly becomes intractable for large complexes with many Rg adducts. On the other

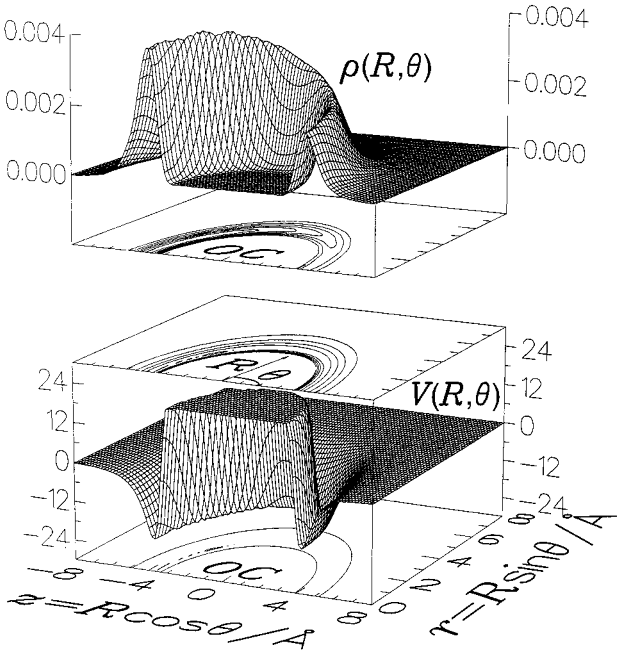

Figure 1. Top: calculations of 3D atomic-density distributions for the He atom relative to the CO-fixed z axis (see text for details) and 2D representation of the same density; bottom: 2D and 3D representation, also in cylindrical coordinates as above, of the PES employed in the present work. The Jacobi coordinates and the CO position are marked for clarity. In the lower diagram a 2D representation is also shown of the bound-state contour energies at the classical turning points.

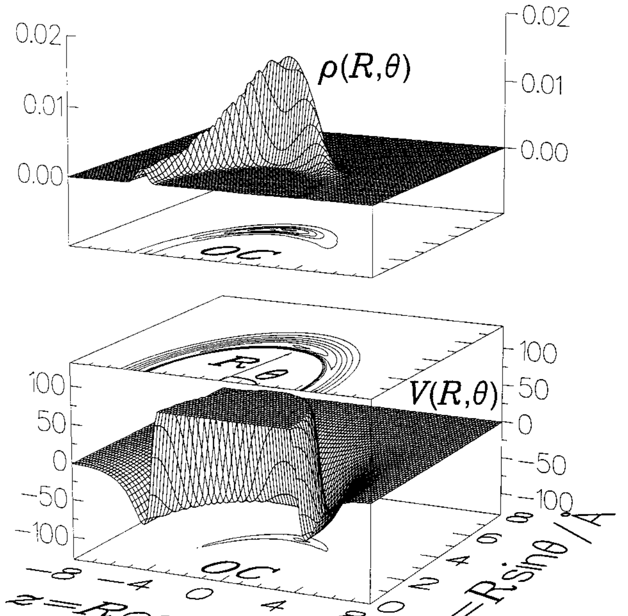

Figure 2. As for Figure 1, but for the Ar–CO system.

hand, the present DMC approach requires little extra effort as the size increases.[22, 28] Furthermore, the DMC technique is also useful in obtaining position correlation functions between atomic partners in the cluster, in visualizing the structural aspects of the complex, and in carrying out such calculations for larger systems.[22] In the present case of a single rare gas adduct to a CO molecule, two-dimensional density distribution $\rho(r,z)$ histograms have been calculated in cylindrical coordinates. The z axis of the cylinder coordinate system coincides with the CO bond and the polar radius $r = R\sin\theta$ (with R,θ the Jacobi coordinates) defines the perpendicular distance of the Rg to the bond axis. The origin coincides with the c.o.m. of the molecule, and the carbon atom is on the positive z axis. The particle density is computed as a function of r and $z = R\cos\theta$ by averaging over walks with descendant weighting according to Equation (6).

$$\rho(r,z) = \frac{1}{2\pi}\sum_i \left\langle \frac{\delta(r_i - r)}{r}\, \delta\,(z_i - z) \right\rangle_{\text{walks}} \tag{6}$$

The calculation therefore accounts for the cylindrical symmetry of the complex around the overall rotational angle φ. The computed quantities of Equation (6) are shown in the upper parts of Figures 1 and 2 for the He–CO and the Ar–CO complexes, respectively.

Discussion of Results

As mentioned before, the computed DMC histograms in Cartesian coordinates are proportional to the spatial density of the bound wavefunction for all the N nuclei interacting in the system at hand. By taking advantage of adiabatic decoupling, we can separate the internal vibrational motion of the molecular atoms from the relative dynamics of the three particles, leaving the one-particle density of the Rg component with respect to the position of the diatomic species as structural information. This density distribution corresponds to the $(J = 0, j = 0)$ rigid rotor bound state furnished by the alternative expansion methods.[13, 35] The well-known method of describing nuclear motions in weakly bound vdW complexes involves a set of coordinates related either to a space-fixed (SF) or a body-fixed (BF) frame of reference.[39, 40] Such expansions are then employed to yield variationally computed transition matrix elements, with either Hamiltonian (BF or SF), which are in turn compared either with sequences of spectroscopic transitions between triatomic bound states or with line-broadening features due to metastability effects and predissociation mechanisms.[20, 21] In such analysis, however, the total wavefunctions of the various bound states are rarely analysed and the highly delocalized character of the more floppy complexes like He–CO is only obliquely described by taking the view that it contains a nearly free rotating CO partner.[14–16, 34–37] The more direct view provided by the present DMC calculations allows us to confirm earlier results and directly focuses on the atomic motion of the Rg adduct within the complex. By choosing cylindrical coordinates referred to a fixed CO molecule ($J = 0$, $j = 0$ bound state in the SF representation), the DMC density is in fact readily able to provide the spatial density for that part of the wavefunction which is associated with either the He or Ar atomic partners in the VdW complexes.

The top part of Figure 1 shows such a density distribution for the He atom. The following observations can easily be made:

1. The distribution is very broadly shaped over nearly the whole region around the CO monomer, with only a slight increase of amplitude on the oxygen side (θ approaching 180°) but being essentially constant from $\theta \approx 120°$ onwards.
2. Although the density distribution of the He atom is seen to decrease as the angle θ varies from 180° toward 0°, the actual density values for the other linear O-C-He geometry remain high, indicating that there is a large probability for the Rg adduct to exist in that configuration.
3. The He atom is therefore highly delocalized, both in R and θ, and the average position of the helium is different from the one suggested by the single configuration of the BO potential minimum. This point could be further understood by looking at the shape of the angular potential when the Rg adduct is kept at the distances R of its radial potential minima as the angle θ is changed (minimum energy path). This is shown in the upper part of Figure 3, where such a profile is compared with the position of the lowest bound state (straight line) given by the DMC calculations. The absence of a local anisotropy barrier explains the high delocalization of the He atom with respect to the molecular partner at the bound-state energy. Thus the adduct appears to be kept together mainly by long-range dispersion forces.

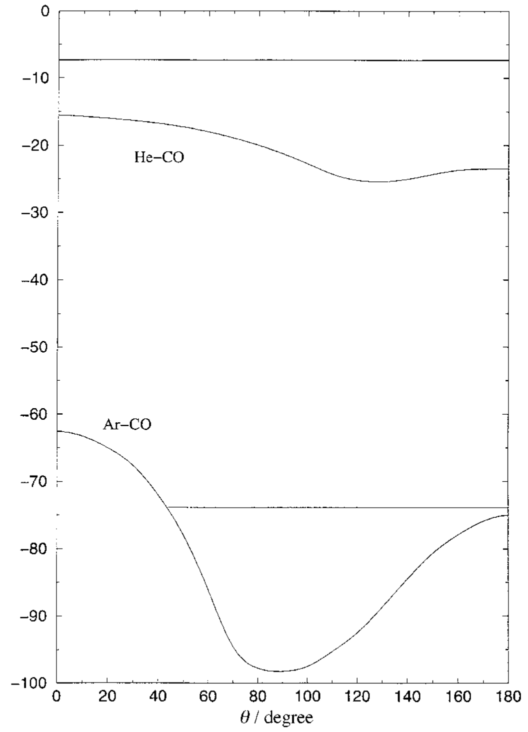

Figure 3. Minimum energy profiles for motion of the rare gas atoms around CO as a function of the angular coordinate $\theta = \arccos(R \times r_{eq})$ discussed in the main text. Top: angular variation for the He–CO system, with the position of the lowest bound level (6.65 ± 0.007 cm^{-1}) marked as a horizontal line; bottom: same representation for the Ar–CO system, where the bound state is located at -73.93 ± 0.01 cm^{-1}.

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The above results are indeed in accord with earlier calculations for the bound, total wavefunctions obtained by diagonalizing the SF Hamiltonian on a basis of rovibrational functions.[13] The results of Moszynski et al. for ($j = 0$, $J = 0$) in fact show a substantial delocalization both in R and θ and the presence of a total symmetry for the wavefunction fairly close to, albeit still different from, the spherical limit. This is also indicated by the DMC density plot of Figure 1.

The power of the present approach is further illustrated by repetition of the same calculations for the Ar–CO complex, for which previous computations of the bound triatomic wavefunctions exist.[34, 35] For this system the variational problem of determining bound and metastable states becomes numerically more demanding than for He–CO.[39] On the other hand, once the PES is available, the DMC evaluation of its ground bound state is not computationally more difficult than that of the He complex.

The Ar adduct spatial density distribution with respect to the fixed CO molecule ($j = 0$, $J = 0$ in the SF parlance) is shown in the upper part of Figure 2, while the angular behavior of the PES profile at the R values of the minima as θ changes are depicted in the lower part of Figure 3.

1. The Ar atom density around the CO partner clearly peaks at the T-shaped geometry ($\theta \approx \pi/2$) and is more narrowly distributed along R; that is, the localization in space of the argon adduct is stronger than for He.
2. The lowest bound state is noticeably localized in the attractive well (the ZPE is about 30% of the well depth, compared with about 70% in the case of He–CO), and is below the barrier for rotation on the carbon end: the corresponding CO motion, therefore, is more that of a hindered rotor within the complex but still retains some features of a nearly free internal rotor.[35]
3. The Ar adduct is here seen to exhibit a nonvanishing density for the collinear structure of Ar-O-C, that is, it shows a sizeable probability of existing above the orientational barrier, as suggested by the DVR calculations[35] and by the position of the bound state in Figure 3. Compared with the He adduct, the asymmetric density distribution of Ar atom along the CO molecule is now more marked.
4. There is a noticeable probability that the Ar atom will tunnel through the end-carbon rotational barrier, thereby reaching the linear O-C-Ar configuration, a feature also discussed when comparing calculations to experiments.[35]

A further qualitative indicator of the differences in behavior can be seen by looking at the associated wavelengths of the triatomic pseudoparticles bound in the lowest states of the complex systems. The value of λ for He–CO is about 4.8 Å, to be compared with the λ_{ArCO} value of about 0.7 Å; in other words, the behavior of the latter system is much more classical than that of the former. However, as the ZPE value for the Ar–CO is about twice that of He–CO ($\approx 30\,\mathrm{cm^{-1}}$ versus $\approx 16\,\mathrm{cm^{-1}}$) the local velocities are nearly the same: about 2 Å$\,\mathrm{ps^{-1}}$ for He and about 3 Å$\,\mathrm{ps^{-1}}$ for Ar.

Conclusion

The present DMC calculations based on realistic PES's from our ab initio DFT calculations[33, 38] have allowed us to examine quite directly the quantum features of nuclear delocalization in weakly bound vdW complexes of three component atoms. As it turns out, the method confirms the highly delocalized nature of the lowest bound state of He–CO found in earlier calculations[13] and also allows us to extend the results to a different complex, Ar–CO, without increase of computational effort. In the latter case the present calculations are in agreement with the latest ab initio results on the location of its bound triatomic states;[35] this finding confirms the accuracy of the present stochastic treatment. The interesting feature of these DMC calculations is that they directly underline the dynamic nature of the structures in the two clusters and the quantum delocalisation of the He and Ar atoms within the systems. In both cases, in fact, the floppy character of the vdW complexes already pointed out in previous studies[13, 16, 34, 35] is confirmed by the DMC results. Although the rather dubious validity of invoking a specific structure to describe the highly delocalized He–M bound states has been mentioned before in several instances,[13–21] the DMC quantum density distributions provide an additional, and very instructive, representation for such molecular quantum states.

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