Potential Energy Surfaces for Rh—CO from DFT Calculations

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ABSTRACT

We present potential energy surfaces for Rh—CO obtained from density functional theory for two electronic states of Rh—CO. We have performed local spin-density calculations including relativistic as well as gradient corrections. The construction of a reasonably accurate atom–atom potential for Rh—CO is not possible. We were much more successful in constructing the potential energy surfaces by representing the potential as a spherical expansion. The expansion coefficients, which are functions of the distance between the rhodium atom and the carbon monoxide center of mass, can be represented by Lennard-Jones, Buckingham, or Morse functions, with an error of the fit within 10 kJ/mol. The potential energy surfaces, using Morse functions, predict that the electronic ground state of Rh—CO is $^2\Sigma^+$ or $^2\Delta$. This is a linear structure with an equilibrium distance of rhodium to the carbon monoxide center of mass of 0.253 nm. The bonding energy is -184 kJ/mol. Further, Morse functions predict that the first excited state is $^4A'$. This is a bent structure ($\angle$Rh—CO = 14°) with an equilibrium distance of rhodium to the carbon monoxide center of mass of 0.298 nm. The bonding energy of this state is -60 kJ/mol. Both these predictions are in good agreement with the actual density functional calculations. We found 0.250 nm with -205 kJ/mol for $^2\Sigma^+$ and 0.253 nm with -199 kJ/mol for $^2\Delta$. For $^4A'$, we found 0.271 nm, $\angle$Rh—CO = 30°, with -63 kJ/mol. The larger deviation for $^4A'$ than for $^2\Sigma^+$ or $^2\Delta$ is a consequence of the fact that the minimum for $^4A'$ is a very shallow well. © 1994 by John Wiley & Sons, Inc.

Introduction

The interaction of carbon monoxide with a transition metal surface is of enormous technological importance and of great catalytic interest. Examples of where this interaction plays a crucial role are the Fischer-Tropsch synthesis of hydrocarbons,[1] the catalytic production of methane,[2] and automobile exhaust catalysis.[3] Because of this, the interaction between carbon monoxide and transition metals is both experimen-

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tally and theoretically intensively studied.[4] It is generally described by the Blyholder model. In this model, the bonding is the result of the (repulsive) donation of the 5σ orbital of carbon monoxide to empty metal levels and the (attractive) back donation from the metal to the empty $2\pi^*$ orbital of carbon monoxide.[5]

In theoretical studies, the chemisorption processes (assuming that the interaction of carbon monoxide with the surface is mainly of a local nature) has been investigated using various transition metal clusters to model the surface. The most commonly studied transition metals are nickel, copper, and platinum.[6] When one is interested in quantitative correct properties, the cluster model shows its limitations and care must be taken when comparing the results to experiments involving real surfaces. The calculated results will depend largely on cluster size, and the convergence as a function of cluster size is usually slow. Although these shortcomings of the cluster model are apparent, the model proves to be useful when one is interested in a qualitative description rather than quantitative accuracy. Also, the results of cluster calculations can often directly be compared with molecular beam experiments.[7] Because we only performed calculations with one transition metal atom, the calculated properties are quantitatively not correct for the carbon monoxide chemisorption on a surface. Nevertheless, it is possible to draw interesting conclusions from such model calculations, as has been shown in previous calculations using various *ab initio* methods.[8,9] We will focus on the interaction of carbon monoxide with rhodium using density functional theory (DFT).[10] Within DFT it is possible to obtain molecular properties which compare well with measured properties. Rhodium has a partial filled $3d$ shell, which is nearly degenerate with the $4s$ shell. This partially filled d shell gives rise to interesting catalytic properties. Carbon monoxide adsorbs molecularly on rhodium at room temperature, but dissociative adsorption occurs at reaction temperatures.[11] Because of this, rhodium is a catalyst for the synthesis of oxygenated compounds and hydrocarbons. Particular promoters, like ThO_2, MoO_3, and V_2O_5, enhance the selectivity to oxygenated compounds.[12] Rhodium is also used in catalysts for motor cars for the total oxidation of carbon monoxide by incomplete oxidation of hydrocarbons. These facts motivate experimental[13] and theoretical[8,14-17] studies of the rhodium–carbon monoxide system.

We will present an analytic potential energy surface (PES) for Rh—CO.[18,19] The concept of a PES, which is based on the assumption that in a molecule electronic motion and nuclear motion are separable, is one of the important ideas in chemical physics. Much research effort is directed both to determining PES from spectroscopic data and by the methods of quantum chemistry, and to using such surfaces for dynamical calculations and the simulation of spectra. In our understanding of the dynamics of chemical reactions, at the most qualitative level the activation barrier can be understood in terms of the variation of potential energy along the reaction coordinate. At a more detailed and quantitative level, the dynamics of a chemical reaction can be understood fully in terms of motion of the nuclei on a potential energy surface. Although methods are being developed which do not use the Born-Oppenheimer surface,[20] most theoretical treatment of the dynamics, whether classical, semiclassical, or quantum, still uses some form of PES. These potentials are used extensively in molecular dynamics (MD) studies. With MD methods we will be able to study, for example, the kinetics of carbon monoxide dissociation on a rhodium surface. These kinds of studies would be much more difficult, if not impossible, with the conventional cluster approach. An example of investigating the dynamics of a chemisorptive processes is a trajectory study of carbon monoxide on a small copper cluster.[21]

The PESs we will present here are only the first step in our attempt to describe the interaction of carbon monoxide with a rhodium surface. The interaction of carbon monoxide with only one rhodium atom is most likely not able to describe quantitatively the interaction of the substrate with the surface. We find, for example, that our PESs are not very anisotropic. For rhodium, however (like for most elements from the middle of the transition series), directional bonding is important. Preliminary calculations of carbon monoxide adsorption on some rhodium clusters indeed show larger anisotropy. We will try to achieve an improved PES by including results of the interaction of carbon monoxide with small and large rhodium clusters.[22] There are already some schemes available to incorporate an approximation to the many-atom interactions that are currently neglected by our PESs.[23] We expect that employing such a scheme to the PESs presented here will enable us to obtain a more quantitative PES for the interaction of carbon monoxide with a rhodium surface.

Theory

COMPUTATIONAL DETAILS

We performed, within the density functional formalism, spin-unrestricted calculations using the Vosko-Wilk-Nusair (VWN) local spin-density functional,[24] as implemented in the Amsterdam density-functional (ADF) program system developed by Baerends and co-workers.[25] ADF represents the molecular orbitals as linear combinations of atomic Slater-type orbitals (STOs), computes the integrals numerically,[26] and computes the bonding energies with the Ziegler transition state method.[27] The bonding energy ΔE_b is defined as the energy difference between the fragments (A and B) and the overall molecule (AB)

$$\Delta E_b = E(AB) - E(A) - E(B) \qquad (1)$$

It can be separated into two different contributions:

$$\Delta E_b = \Delta E_{steric} + E_{int} \qquad (2)$$

Here ΔE_{steric}, referred to as the steric repulsion, is the energy change due to superposition of the fragments A and B without changing their molecular orbitals. ΔE_{int}, the interaction energy, represents the energy change upon the formation of the molecular orbitals of A—B. The steric interaction can be split as

$$\Delta E_{steric} = \Delta E_{xrep} + E_{elstat} \qquad (3)$$

which are the exchange repulsion and the electrostatic interactions, respectively. This decomposition of the bonding energy can be useful for analyzing a chemical bond.[28]

To go beyond the local spin-density approximation (LSDA), we used gradient corrections (or nonlocal corrections) to the bonding energy by Becke[29,30] for the exchange and by Perdew[31] for correlation, or we used the correlation self-interaction correction of Stoll et al.[32,33] Relativistic corrections were included by using a relativistic core, including relativistic effects on the valence electrons as perturbation to first order.[34]

For rhodium we tested two different basis sets. In the first set, the electrons up to and including the $4p$ core were frozen, leaving nine valence electrons. The valence functions were of double-ζ quality with a triple-ζd. In the second set, the electrons up to and including the $3d$ core were frozen, leaving 17 valence electrons. In this set, the valence functions were of triple-ζ quality with a double-ζs function. The basis sets show only small differences. We thus decided to use the first one for all the further calculations because it is smaller. For carbon and oxygen, the $1s$ core was frozen. Here the valence functions are again of double-ζ quality. For all three atoms, a polarization function was added to the basis set. Single-ζ functions were used for core orthogonalization. Table I shows the exponents of the STO basis sets for rhodium, carbon, and oxygen we used.

THE REPRESENTATION OF THE POTENTIAL

There are a number of methods for constructing analytical potential energy surfaces (PES) for triatomic systems.[35] The simplest is the construction of an atom–atom potential (see Fig. 1 for the coordinates).

$$\Delta E_b = V_{RhC}(R_{RhC}) + V_{RhO}(R_{RhO}) + C \qquad (4)$$

We have added a parameter C in eq. (4) to de-

TABLE I.

Exponents of the Core and Valence STOs for Rhodium, Carbon, and Oxygen.

Type	Rhodium (DZP) ζ	Type	ζ	Carbon (DZD) Type	ζ	Oxygen (DZD) Type	ζ
1S	29.25 c	3D	11.00 c	1S	5.40 c	1S	7.36 c
2S	19.00 c	4D	1.30 v	2S	1.24 v	2S	1.70 v
3S	7.85 c	4D	2.50 v	2S	1.98 v	2S	2.82 v
4S	6.05 c	4D	4.40 v	2P	0.96 v	2P	1.30 v
2P	19.47 c	5S	1.05 v	2P	2.20 v	2P	3.06 v
3P	9.09 c	5S	1.95 v	3D	2.50 v	3D	2.00 v
4P	4.07 c	5P	1.45 v				

c: Core STO, single-ζ core function for core orthogonalization.; v: Valence STO.
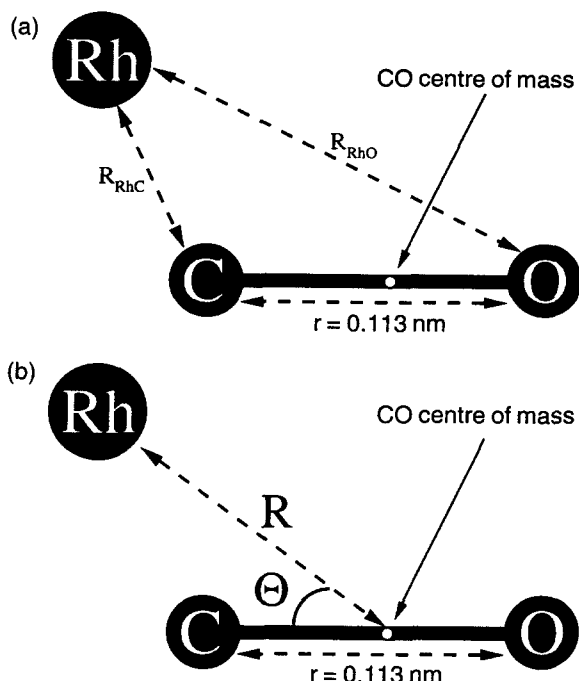
FIGURE 1. The Rh — CO system with the definition of (A) RR_{Rhc} and R_{Rho} to be used in the development of an atom–atom potential, and (B) R and Θ to be used in a spherical expansion.

scribe excited states. The second method is the spherical expansion. Fixing the carbon monoxide bond length, we can specify the Rh—CO system by a distance R and an angle Θ (Fig. 1). In general, an energy $V(R, \Theta)$ [e.g., the exchange repulsion, eq. (3), electrostatic interaction, eq. (3), orbital interaction, eq. (2), or bonding energy, eq. (1)) can then be expanded in an infinite sum of Legendre polynomials,

$$V(R, \Theta) = \sum_{l=0}^{\infty} a_l(R) P_l(\cos \Theta) \qquad (5)$$

Using a Gauss-Legendre (GL) quadrature[36, 37] of order n, we can compute all expansion coefficients exactly for $l = 0, 1, 2, \ldots, n - 1$. We use $n = 10$. This is slightly larger than necessary. Within the accuracy of our DFT calculations, an exact representation is obtained by restriction on the summation in eq. (5) to terms $l \leq 8$. The R dependence of the expansion coefficients is determined in a least-squares fit with weights. For the bonding energy, we tried three different functions: a Lennard-Jones form,

$$a_l(R) = \frac{A_l}{R^{12}} - \frac{B_l}{R^6} + C\delta_{0l} \qquad (6a)$$

a Buckingham form,

$$a_l(R) = A_l e^{-\alpha_l R} - \frac{B_l}{R^6} + C\delta_{0l} \qquad (6b)$$

and a Morse form

$$a_l(R) = A_l e^{-2\alpha_l R} - B_l e^{-\alpha_l R} + C\delta_{0l} \qquad (6c)$$

In our case, the least-squares fit with weights to obtain the parameters in these functions was done on the coefficients a_l calculated for 10 distances ($R = 0.150, 0.175, 0.200, 0.225, 0.250, 0.275, 0.300, 0.325, 0.350$, and 0.375 nm). The term $C\delta_{0l}$ in these functions originates from the fact that for $R \to \infty$ the excited state PES should converge to the excitation energy of rhodium from the ground state ^4F ($4d^85s^1$) to the first excited state ^2D ($4d^9$).

Results and Discussion

THE RHODIUM ATOM AND THE CARBON MONOXIDE MOLECULE

Before starting with DFT calculations on the Rh—CO system, some variations of DFT were tested on the rhodium atom/ion and the carbon monoxide molecule. We concentrated on the electronic ground state and excitation energies of rhodium atom, and the bonding energy, equilibrium distance, vibration frequency, and dipole moment of the carbon monoxide molecule. All these properties are experimentally well known. Our main results for a number of excitation energies and the ionization potential of the rhodium atom/ion are listed in Table II. The results for carbon monoxide are shown in Table III.

From Table II we can see that our unrestricted calculations, including relativistic corrections, are able to yield the correct ground state for the rhodium atom: Rh(d^8s^1; ^4F), whereas LSDA usually gives a $4d^9$ configuration as ground state.[38] This would lead to underestimates of the metal–carbon monoxide bonding energy.[39] The first-order relativistic approach used here is adequate for the calculation of bond energies in compounds containing elements as heavy as gold ($Z = 79$),[40] so we expect that the use of more sophisticated relativistic methods would not greatly alter our results. The result obtained without any gradient corrections shows little difference between the two states. When gradient corrections for the exchange (Becke) and correlation (Perdew) are included, the excitation energy improves. Re-

TABLE II.

Excitation Energies (in kJ / mol) for the Rhodium Atom and Ion Calculated at the Local (VWN) and Nonlocal (VWN + Perdew + Becke and VWN + Stoll + Becke) Level.

Atom / ion	Electronic config.	State	VWN	VWN Perdew Becke	VWN Stoll Becke	Exp.[a]
Rh	$s^1 d^8$	^4F	0	0	0	0
	$s^0 d^9$	^2D	3	12	7	34
	$s^2 d^7$	^4F	190	187	177	163
Rh$^+$	$s^0 d^8$	^3F	0	0	0	0
	$s^1 d^7$	^5F	209	207	199	206
IP			789	780	743	720

[a]Ref. 46, experimental values are averaged over J states.

TABLE III.

Equilibrium Distance (R_e), Dissociation Energy (D_e), Dipolemoment (μ), and Stretch Frequency (ω_e) for the Carbon Monoxide Molecule Calculated at the Local and Nonlocal Level.

LSD & corrections	R_e (nm)	D_e (kJ / mol)	μ (Debye)	ω_e (cm^{-1})
VWN	0.1130	-1247	0.05	2209
VWN + Perdew + Becke	0.1138	-1148	0.02	2146
VWN + Stoll + Becke	0.1144	-1151	0.04	2096
Experiment[a,b]	0.1128	-1077	0.11	2143[c]-2170[d]

[a]Ref. 42.
[b]D. R. Lide, Handbook of Chemistry and Physics, 71st ed., CRC Press, Boca Raton, FL, 1990.
[c]Measured.
[d]Harmonic; see K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure. Constants of Diatomic Molecules, Van Nostrand Reinhold, New York, 1979.

placing the Perdew correction with the Stoll correction lowers the calculated excitation energy somewhat. Table II also shows the excitation energies from the ground state to Rh($d^7 s^2$; ^4F), and from the ionic ground state Rh$^+$(d^8; ^3F) to Rh$^+$($d^7 s^1$; ^5F) and the ionization potential. In general, the best agreement is obtained when we use VWN with Stoll and Becke correction.

Table III shows the calculated equilibrium distance, dissociation energy, dipole moment, and stretch frequency for carbon monoxide. Except for the dissociation energy, these properties do not vary much with the various methods or corrections we used. The influence of relativistic corrections for light atoms such as carbon and oxygen is negligible. Spin-orbit effects do occur, but because our implementation only includes relativistic effects as a first-order perturbation on the core electrons, spin-orbit effects are neglected. The basis set effects in carbon monoxide were already studied in detail.[41] This demonstrated the need of adding a single 3d-polarization to get close to converged basis results. Using a triple-ζ (TZ) or quadruple-ζ

(QZ) basis for carbon monoxide did not have as much effect as adding a single 3d polarization function. Only for the dipole moment TZ or QZ bases are necessary. For the remaining calculations on Rh—CO, we have used VWN with Stoll and Becke correction.

THE RHODIUM–CARBON MONOXIDE SYSTEM

For 10 different distances (R = 0.150, 0.175, 0.200, 0.225, 0.250, 0.275, 0.300, 0.325, 0.350, and 0.375 nm), and for 10 different angles Θ, the cosines of which are the roots of the tenth-order Legendre polynomial,[36] we calculated for both electronic configurations the exchange repulsion [eq. (3)], the electrostatic interaction [eq. (3)], the orbital interaction [eq. (2)], and the bonding energy [eq. (1)]. The smallest distance (R = 0.150 nm) was chosen so that the interaction of carbon monoxide with the rhodium at each of the 10 angles Θ was repulsive. For small Rh—CO distances, the ground state is a doublet ($^2\Sigma^+$ or $^2\Delta$ for the linear geometry, $^2A'$ otherwise), corresponding to the $4d^9$ configuration

of rhodium. For larger Rh—CO distances, the quartet ($^4\Delta$ for linear geometries, $^4A'$ otherwise), corresponding to the $4d^85s^1$ configuration of rhodium, is the lowest. This is in agreement with the ground states of the rhodium atom and the carbon monoxide molecule separated at infinity. In contrast to earlier calculations by Koutecky et al., who found that the $^4\Delta$ state was repulsive at every distance,[8] we find the $^4A'$ state to be slightly bonding. Mains and White[15] have found an optimized linear geometry for the quartet, which they call ^4X, but they only report on the total energy.

The C—O distance (r) was fixed at 0.1128 nm[42] for all the calculations on the rhodium–carbon monoxide system. Neglecting different r's for carbon monoxide might be a source of error to the PES that we want to develop because the carbon monoxide bond is expected to relax upon the bond formation of carbon monoxide with the rhodium (because of the electron donation from rhodium into the $2\pi^*$ orbitals of carbon monoxide). Therefore, we tested the approximation of fixing r by calculating near the equilibrium geometry of the $^2\Sigma^+$ ground state of Rh—CO (the $^2\Delta$ state lies 7 kJ/mol higher near the equilibrium geometry) the formation energy of Rh—CO from the separate atoms for several C—O distances. We found that the carbon oxygen bond indeed relaxes significantly, from 0.1128 nm to approximately 0.117–0.118 nm. However, the change in bonding energy is relatively small. For geometries further away from the equilibrium geometry of the $^2\Sigma^+$ ground state (or the $^2\Delta$ state) of Rh—CO, we expect that the influence of CO relaxation is even smaller, concluding that we do not introduce a large error when we neglect this degree of freedom in our PES development. Also, at this moment we are not interested in the dissociation of carbon monoxide.

THE RHODIUM–CARBON MONOXIDE POTENTIAL ENERGY SURFACES

We tried to obtain an atom–atom potential [eq. (4), where both V_{RhC} and V_{RhO} are Lennard–Jones form functions, eq. (6a)] because they are widely used and more easy to apply in molecular dynamics (MD) calculations. The development of such an atom–atom potential was less successful than the results we obtained by representing the potential as a spherical expansion. The parameters for the atom–atom potential we obtained are shown in Table IV, and those for the spherical expansion in Tables V and VI. These results are obtained by a least-squares fit with weights. The weights are proportional to $e^{-E/\varepsilon}$, where $\varepsilon = 81$ kJ/mol. The weights were necessary because, especially for $R = 0.150$ nm and small or large Θ, the rhodium atom is close to either the carbon or the oxygen atom. This yields a strong repulsion, which would completely determine a fit without the weights. While using weights, the fit is only incorrect at the irrelevant geometries where there is an extremely strong repulsion. The value of ε is somewhat arbitrary. The initial value we used was 324 kJ/mol, but we also tried 243 kJ/mol, 162 kJ/mol, and 81 kJ/mol. We tried to find the best value for ε that gives a good fit around the minima and for large R, whereas all essential characteristics of the repulsive part of the PESs are retained. In the weighted fit of our atom–atom potential, $\varepsilon = 81$ kJ/mol seems to be the best value. For larger values of ε, we get a bad fit, whereas for smaller values of ε the repulsive part of the PESs vanishes completely. Despite the use of weights, the root-mean-square (rms) deviation of this Lennard–Jones type of fit was around 35 kJ/mol for the doublet and 9 kJ/mol for the quartet. For the doublet this is too large. Moreover, the equilibrium geometry for the doublet and the quartet is inaccurate. This can be seen from Table VII, which shows a poor comparison between the PESs and the actual calculated minima. Other analytical forms do not really yield a better result. It is possible to derive expressions, using variational calculus, for the optimal atom–atom potentials V_{RhC} and V_{RhO} in terms of the bonding energy ΔE_b by minimization of

$$\int dR_{RhC}\, dR_{RhO}\, w(R_{RhC}, R_{RhO})$$
$$\times [\Delta E_b(R_{RhC}, R_{RhO}) - V_{RhC}(R_{RhC})$$
$$- V_{RhO}(R_{RhO})]^2 \qquad (7)$$

TABLE IV.
Parameters for the LJ Expansion Functions.

Parameter	$^2A'$ state	$^4A'$ state
A_{RhC} (kJ / mol · nm^{12})	$1.302 \cdot 10^{-7}$	$8.502 \cdot 10^{-8}$
B_{RhC} (kJ / mol · nm^6)	$8.986 \cdot 10^{-3}$	$1.571 \cdot 10^{-3}$
A_{RhO} (kJ / mol · nm^{12})	$-4.553 \cdot 10^{-8}$	$-4.505 \cdot 10^{-8}$
B_{RhO} (kJ / mol · nm^6)	$-7.276 \cdot 10^{-3}$	$-1.039 \cdot 10^{-3}$

The value of C is 0 for $^4A'$ and 10 kJ / mol for $^2A'$. Root mean square errors are 35 and 9 kJ / mol for the doublet and quartet, respectively.

where $w(R_{RhC}, R_{RhO})$ is some weight function. The integral is over all realizable combinations of R_{RhC} and R_{RhO}. The resulting expressions can be evaluated numerically, yielding numerical representations for V_{RhC} and V_{RhO}.[43] We found that this procedure gave only potentials that were marginally better than the atom–atom Lennard-Jones, thus proving that an atom–atom potential is not suited for Rh—CO.

We tried with the functional forms of eqs. (6a)–(6c) to fit our data with a global rms error lower than 10 kJ/mol. The results for the separate contributions to the bonding energy [eqs. (2) and (3)] are not presented here because our attempts to fit these were not satisfactory. The exchange repulsion [eq. (3)] could be fitted to a high degree of

accuracy using

$$a_l(R) = A_l e^{-\alpha_l R} \qquad (8)$$

However, fits of the two other contributions to the bonding energy, the electrostatic interaction [eq. (3)] and the orbital interaction [eq. (2)], were less successful because we could not find a suitable functional form. The best rms error of both of these fits was well above 10 kJ/mol. There are functional forms that are derived for these interactions between systems at large distances,[44] but these need not be appropriate when the orbitals of rhodium and carbon monoxide overlap. Damping functions have been suggested to improve the description for small R.[45] However, we find that, at

TABLE V.
Parameters for the Buckingham Spherical Expansion Functions.

	$^2A'$ state			$^4A'$ state		
1	A (kJ/mol)	B (kJ/mol · nm⁶)	α (nm⁻¹)	A (kJ/mol)	B (kJ/mol · nm⁶)	α (nm⁻¹)
0	$4.495 \cdot 10^6$	$2.087 \cdot 10^{-2}$	$4.663 \cdot 10^1$	$9.525 \cdot 10^5$	$-7.161 \cdot 10^{-4}$	$4.097 \cdot 10^1$
1	$9.439 \cdot 10^5$	$3.653 \cdot 10^{-2}$	$3.788 \cdot 10^1$	$6.291 \cdot 10^5$	$2.211 \cdot 10^{-2}$	$3.846 \cdot 10^1$
2	$7.198 \cdot 10^6$	$2.857 \cdot 10^{-2}$	$4.626 \cdot 10^1$	$1.214 \cdot 10^7$	$6.097 \cdot 10^{-3}$	$5.109 \cdot 10^1$
3	$4.274 \cdot 10^5$	$1.347 \cdot 10^{-2}$	$3.728 \cdot 10^1$	$2.244 \cdot 10^5$	$5.912 \cdot 10^{-3}$	$3.582 \cdot 10^1$
4	$6.889 \cdot 10^5$	$8.120 \cdot 10^{-3}$	$4.069 \cdot 10^1$	$6.762 \cdot 10^5$	$-5.125 \cdot 10^{-4}$	$4.351 \cdot 10^1$
5	$9.060 \cdot 10^5$	$-1.219 \cdot 10^{-3}$	$5.978 \cdot 10^1$	$3.981 \cdot 10^4$	0	$3.602 \cdot 10^1$
6	$3.080 \cdot 10^5$	$-1.424 \cdot 10^{-5}$	$4.933 \cdot 10^1$	$4.631 \cdot 10^4$	0	$3.651 \cdot 10^1$
7	$1.566 \cdot 10^6$	$-1.193 \cdot 10^{-4}$	$6.701 \cdot 10^1$	$6.452 \cdot 10^5$	0	$6.068 \cdot 10^1$
8	$1.755 \cdot 10^6$	$-2.010 \cdot 10^{-4}$	$7.359 \cdot 10^1$	$1.005 \cdot 10^5$	$-1.209 \cdot 10^{-4}$	$5.341 \cdot 10^1$

The value of C is 0 for $^4A'$ and set to 33.77 kJ/mol for $^2A'$.[46] Root mean square errors are 13 and 10 kJ/mol for the doublet and quartet, respectively.

TABLE VI.
Parameters for the Morse Spherical Expansion Functions.

	$^2A'$ state			$^4A'$ state		
1	A (kJ/mol)	B (kJ/mol)	α (nm⁻¹)	A (kJ/mol)	B (kJ/mol)	α (nm⁻¹)
0	$1.865 \cdot 10^6$	$1.880 \cdot 10^4$	$2.166 \cdot 10^1$	$7.129 \cdot 10^7$	$-6.036 \cdot 10^5$	$3.873 \cdot 10^1$
1	$1.522 \cdot 10^4$	$2.236 \cdot 10^3$	$1.236 \cdot 10^1$	$1.868 \cdot 10^4$	$2.027 \cdot 10^3$	$1.404 \cdot 10^1$
2	$2.713 \cdot 10^6$	$2.338 \cdot 10^4$	$2.114 \cdot 10^1$	$4.296 \cdot 10^6$	$1.093 \cdot 10^4$	$2.292 \cdot 10^1$
3	$7.290 \cdot 10^4$	$2.250 \cdot 10^3$	$1.575 \cdot 10^1$	$7.951 \cdot 10^4$	$1.099 \cdot 10^3$	$1.613 \cdot 10^1$
4	$3.077 \cdot 10^5$	$3.456 \cdot 10^3$	$1.903 \cdot 10^1$	$4.298 \cdot 10^5$	$3.657 \cdot 10^2$	$2.028 \cdot 10^1$
5	$2.275 \cdot 10^6$	$-1.515 \cdot 10^4$	$3.298 \cdot 10^1$	$2.649 \cdot 10^5$	$-3.931 \cdot 10^3$	$2.606 \cdot 10^1$
6	$1.659 \cdot 10^7$	$-2.448 \cdot 10^5$	$4.808 \cdot 10^1$	$2.604 \cdot 10^5$	$-3.695 \cdot 10^3$	$2.562 \cdot 10^1$
7	$3.056 \cdot 10^7$	$-3.482 \cdot 10^4$	$4.525 \cdot 10^1$	$5.016 \cdot 10^6$	$-6.778 \cdot 10^3$	$3.836 \cdot 10^1$
8	$7.684 \cdot 10^5$	$-2.016 \cdot 10^3$	$3.355 \cdot 10^1$	$1.132 \cdot 10^6$	$-5.700 \cdot 10^3$	$3.648 \cdot 10^1$

The value of C is 0 for $^4A'$ and set to 33.77 kJ/mol for $^2A'$.[46] Root mean square errors are 11 and 10 kJ/mol for the doublet and quartet, respectively.

least for the electrostatic interaction, the interaction increases rather than decreases for decreasing distances. Because the knowledge of the separate contributions to the bonding of carbon monoxide on rhodium is not essential for our further study, we will focus only on the bonding energy.

The results of the fit of the total bonding energy with Buckingham [eq. (6b)] and Morse [eq. (6c)] are shown in Tables V and VI, respectively. These results are again obtained by a least-squares fit with weights. The weights are proportional to $e^{-E/\varepsilon}$, where $\varepsilon = 162$ kJ/mol for the Buckingham and $\varepsilon = 243$ kJ/mol for the Morse fit. Also in these cases we tried to use the largest value of ε that gives a good fit around the minima and for large R, whereas all essential characteristics of the repulsive part of the PESs are retained.

We also determined a fit of Lennard-Jones type [eq. (6a)], with $\varepsilon = 81$ kJ/mol, but the results for the doublet and quartet states of Rh—CO are rather poor. The rms error in bonding energy was 65 kJ/mol for the doublet state and 18 kJ/mol for the quartet state. The results using Buckingham or Morse functions are much better. For the doublet state we find rms errors of 13 and 11 kJ/mol, and for the quartet state we find rms errors of 10 and 10 kJ/mol, respectively for Buckingham (Table V) and Morse (Table VI). Note that for all potential forms the usual attractive part of the potential is sometimes used to fit repulsion. For the fit involving Buckingham functions, we were in some cases unable to use both terms to fit repulsion; in such cases the R^{-6} was removed from the fit (fixed to zero). Contour plots of the two potential energy surfaces which we obtained with the Morse fit [eq. (6c)] are shown in Figure 2. The difference between the two surfaces at infinite separation of the rhodium atom from the carbon monoxide molecule is set to exactly 33.77 kJ/mol. This is the experimental difference, averaged over J states, of Rh(d^8s^1; ^4F) and Rh(d^9; ^2D), and we fitted with this constraint.[46] The rms deviation for the Morse fit was the smallest, around 10 kJ/mol.

For the remaining part of this discussion, we will concentrate on the PES which we obtained by fitting to the Morse function (Table VI) because this gave the best fit. We will compare our results with quantum chemical calculations (Table VII). This PES predicts that the ground state of Rh—CO is $^2\Sigma^+$ or $^2\Delta$, the linear geometry, with a bonding energy of -184 kJ/mol and with an equilibrium distance of rhodium to the CO center of mass of 0.253 nm. The first excited state is predicted to be $^4A'$, a bent structure ($\angle$Rh—CO $= 14°$) with a
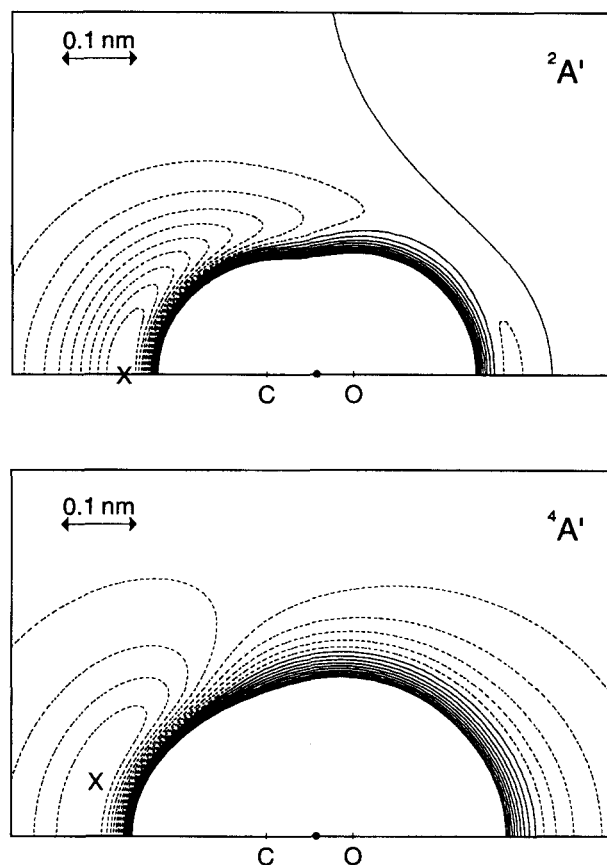

FIGURE 2. The potential energy surfaces (PES) for the doublet state and quartet state of Rh — CO. The PES for the doublet state goes to 33.77 kJ / mol at infinite Rh — CO separation; the PES for the quartet state goes to zero. The energy difference between two neighboring contours is 18 kJ / mol for the doublet and 6 kJ / mol for the quartet. The cross indicates the position of the minimum. Solid lines indicate positive energies, and dashed lines indicate negative energies relative to the rhodium atom and carbon monoxide molecule in their ground states.

bonding energy of -66 kJ/mol and with an equilibrium distance of rhodium to the carbon monoxide center of mass of 0.298 nm. Additional DFT calculations around the PES minima show that the fit is reasonable (compare the last two rows of Table VII). The geometry of the quartet minimum is shallow, and larger deviations between DFT and the PES than for the doublet are to be expected.

The values for the bonding energy of carbon monoxide to rhodium seem to be somewhat too large compared with experimental values for CO adsorption on single crystals of rhodium. On the Rh—CO molecule itself, only a few theoretical

TABLE VII.
Equilibrium Geometries and Binding Energies for Rh — CO; Results from Previous Studies and from This Study.

Method	Remarks	C—O (nm)	$^2\Sigma^+$ or $^2\Delta$ state[a] ($\Theta = 0°$)			$^4A'$ state		
			Rh—C (nm)	ΔE_b (kJ/mol)		Rh—C (nm)	Q	ΔE_b (kJ/mol)
SCF-CI	Ref. 8	0.116	0.205	−17		All	0°	Repulsive
HF	Ref. 14	0.1141[b]	0.1865[b]	−18		—	—	—
MP2	Ref. 14	0.1141[b]	0.1865[b]	−231		—	—	—
MP3	Ref. 14	0.1141[b]	0.1865[b]	−174		—	—	—
INDO	Ref. 16	0.1190	0.1898	−153		—	—	—
DFT	Ref. 17	0.1169	0.1758	−257		—	—	—
PES	Atom–atom	0.1128[c]	0.233	−153		0.277	0°	−15
PES	Lennard-Jones	0.1128[c]	0.180	−91		—	—[d]	−34
PES	Buckingham	0.1128[c]	0.185	−188		0.231	10°	−58
PES	Morse	0.1128[c]	0.188	−184		0.236	14°	−60
DFT	ADF	0.1128[c]	0.185	−205		0.218	30°	−63
DFT	ADF[e]	0.1128[c]	0.182	−199		—	—	—

[a]Ref. 14 reports that the ground state of Rh — CO is $^2\Delta$. All other studies predict the ground state of Rh — CO to be $^2\Sigma^+$.
[b]Geometry is optimized at the Hartree-Fock level only.
[c]The C — O distance was kept fixed, the optimized C — O distance is approximately 0.117 nm.
[d]The equilibrium geometry is at a very large R value. Because this is clearly not correct, we did not try to determine the equilibrium geometry accurately. Because the minimum in the PES is very shallow, the depth could be determined.
[e]Results for the $^2\Delta$ state; we found that this state is slightly higher in energy than the $^2\Sigma^+$ state.

investigations have been carried out, and it has not been observed yet experimentally. The initial heat of chemisorption of carbon monoxide was measured to be approximately −180 kJ/mol.[47] However, various studies indicate that this value might be too high. More recent measurements for the desorption energy of carbon monoxide from a one-fold site yielded a bonding energy of about −120 kJ/mol for the Rh(100) surface and about −130 kJ/mol for the Rh(111) surface.[48-40] Preliminary calculations of carbon monoxide adsorption on large rhodium clusters give a lower adsorption energy, in agreement with experimental results. Hence, we feel confident that our results for one rhodium atom are fair.

It seems that there are no reliable ab initio results available for comparison with our DFT results. Former ab initio calculations give puzzling results. The calculations by Koutecky et al.[8] as well as by McKee and Worley[14] (who report the $^2\Delta$ state as the ground state) show also a much smaller value for the carbon monoxide bonding energy on rhodium. The first study, a nonempirical valence-only self-consistent field SCF configuration interaction (CI) procedure with inclusion of electron correlation effects according to the multireference double excitations (MRD) CI procedure, showed a bonding energy of only −17 kJ/mol. This is almost the same result as the second study, which

showed that at the Hartree-Fock (HF) level, while using a relativistic effective core potential (RECP) for rhodium, the bonding energy of carbon monoxide on rhodium is −18 kJ/mol. Adding electron correlation via Møller-Plesset perturbation treatment increases the bonding energy to −231 kJ/mol (MP2) and −174 kJ/mol (MP3). All electron and RECP HF studies for the $^2\Sigma^+$ and $^4\Delta$ states of Rh —CO have also been presented by Mains and White,[15] but no correlation effects were included in their calculations. Their unrestricted Hartree-Fock (UHF) dissociation energy into CO and the ^2D atom is only 7 kJ/mol. Unlike the other theoretical studies we know of, they also report on a quartet state, which they labeled ^4X. Their optimum geometry is, however, linear. The intermediate neglect of differential orbital (INDO) calculations of Estiu and Zerner[16] yield a bonding energy of −153 kJ/mol, after they corrected the result by 240 kJ/mol to account for the overestimation of bonding energies by the INDO method. Finally, the DFT calculation of Pápai et al.[17] resulted in a bonding energy of −257 kJ/mol. Their method, implemented in the deMon program,[51] uses Gaussian-type orbitals (GTOs). The results they find for Rh, Rh$^+$, and Rh—CO compare reasonably with ours. In general, the DFT results show somewhat larger bonding energies than the other calculations. At the optimized geometries for

Rh—CO, we found for the doublet ($^2\Sigma^+$) a steric repulsion of 604 kJ/mol and an orbital interaction of -809 kJ/mol [eq. (2)] resulting in a total bonding energy of -205 kJ/mol. For the quartet ($^4A'$), we calculated 246 kJ/mol for the steric repulsion and -310 kJ/mol for the orbital interaction, yielding a total bonding energy of -64 kJ/mol. Both these bonding energy decompositions are relative to the unrestricted fragments in their ground state. For the rhodium atom, this is the ^4F state and for the carbon monoxide molecule it is the $^1\Sigma^+$ state.

Table VII also gives the Rh—C and the C—O bond lengths. The C—O bond length indicates to some extent the amount of rhodium to carbon monoxide backbonding. Typical Rh—C bond lengths are in the range 0.178–0.201 nm.[52] This is in good agreement with the Rh—C bond length of 0.185 nm that we found for the $^2\Sigma^+$ ground state and the 0.188 nm that we found for the $^2\Delta$ state. The ab initio study by McKee and Worley[14] found the $^2\Delta$ state as ground state with an optimum Rh—C bond length of 0.1865 nm, but there the C—O bond length had increased to only 0.1142 nm. The INDO calculations of Estiu and Zerner[16] yield an Rh—C distance of 0.1898 nm together with a C—O distance of 0.1190 nm. The DFT calculation of Pápai et al.[17] resulted in an optimized Rh—C distance of 0.1758 nm with a C—O separation of 0.117 nm. In our calculations, the C—O bond length increases to 0.117–0.118 nm.

Conclusions

We have calculated two PESs for the interaction of carbon monoxide with a rhodium atom using DFT. The PESs correspond to the electronic ground state at short and large Rh—CO distances, respectively. At short distances the system is a doublet, and at large distances it is a quartet. It was necessary to do unrestricted calculations, which include gradient as well as relativistic corrections. It could be proven that atom–atom potentials were not appropriate to describe this system. The PESs could be fitted best with a spherical expansion and Morse forms for the expansion coefficients.

It seems that no reliable ab initio result for Rh—CO is available for comparison and for judging the performance of our DFT results. The two previous ab initio studies[8, 14] give puzzling results. We found somewhat larger bonding energies than most previous calculations. This may be due to the common overestimation of bonding energies in

DFT, even though we have included gradient corrections. Our results agree reasonably well with previous DFT calculations on Rh—CO.[17] We think, however, that we cannot exclude the possibility that other calculations may have underestimated the correlation in Rh—CO. The large contributions of the different orders of perturbation theory[14] seem to point in that direction. The INDO results[16] seem to be in remarkable agreement with both DFT calculations on Rh—CO.

Preliminary calculations (using the same methods as in this article) on the interaction of carbon monoxide with some rhodium clusters show reasonable agreement with experiments, substantiating our results for Rh—CO. Comparing the same calculations with predictions by the PESs presented here, it seems that our PESs are not anisotropic enough. This shows the need to improve the PESs presented here. Using the results for the interaction of carbon monoxide with rhodium clusters, we want to incorporate the many-atom interactions that are currently neglected by our PESs in an approximate way. We expect that this will enable us to obtain a more quantitative PES for the interaction of carbon monoxide with a rhodium surface.

Acknowledgments

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