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Theoretical Study of Gold−Carbonyls Interaction in $Au(CO)_n$ ($n = 1-3$) Complexes

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We studied the dependence on the attraction between gold(0) and carbonyls in $Au(CO)_n$ ($n = 1-3$) complexes using ab initio methodology. Oscillations in the equilibrium Au−C distance, as well as in the interaction energy, are sensitive to the electron correlation potential. These effects were evaluated using several levels of theory, ranging from MP2 to CCSD(T). The long-distance behavior of the AuCO interaction is related to simple induction and dispersion expressions involving the individual properties of both gold and carbonyl. The dispersion interaction is the principal contribution to the stability at long distances and an important term at short distances.

Introduction

Metal surfaces and complexes formed with transition metals (M) can absorb small molecules (L), e.g., carbonyl, water, ammonia, and hydrocarbons. This adsorbtion should receive considerable attention because of its relevance in bond activation and other catalytic processes.[1−5] Spectroscopic data such as vibrational (IR and Raman) and UV−visible absorption spectra and electron spin resonance (ERS) studies have been provided.[6,7]

It has been shown that $M(L)_n$ complexes could be generated in matrix isolation at cryogenic temperatures. This is the case for the metal atoms of group 11. It has been observed that they react with carbonyls to produce $M(CO)_n$ (M = Cu, Ag, Au; $n = 1-3$) complexes[8−10] (matrix isolation) as carbonyl−metal surfaces.[11,12] These complexes may be considered as the smallest models to study the interactions between the metallic surfaces and carbonyls.[13] Schwerdtfeger and Bowmaker[14] studied the stability and structure of open-shell monocarbonyl compounds MCO in the ground state $^2A_1$ at Hartree−Fock and Møller−Plesset second order (MP2) levels. They reported a dissociation energy for AgCO less than 1 kJ/mol, while those of the metal−carbonyl interactions in CuCO and AuCO as relatively weak, with dissociation energies of about 30 kJ/mol. This interaction has been established to be of van der Waals type. It is also possible to find such van der Waals interactions in other systems, for example, the $M(C_2H_4)_n$ complexes (M = Cu, Ag, Au; n = 1, 2[15−17]).

The dispersion forces that are essential in the stabilization of the complexes are not found at the HF (Hartree−Fock) level. Therefore, it is necessary to use at least MP2-level methods for the complete description of the dispersion forces, which are included among the correlation effects.[18,19] However, depending on the chemical system, the MP*n* energies and several other properties, namely, distance, frequencies, and so on, display rapid or slow convergence and monotonic or oscillatory decay.[20] Moreover, for the particular case of weak van der Waals interactions, we have found an oscillatory energy convergence.[17,18] Bearing this in mind, it might

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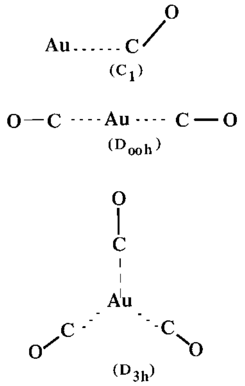

Figure 1. Assumed structure of the Au(CO)$_n$ (n = 1−3) complexes.

be convenient to restrict the use of MPn theory and instead use the coupled cluster method with perturbative treatment of triple excitations to achieve a higher degree of accuracy.[20]

The van der Waals systems are frequently classified on the basis of the leading stabilization energy term. According to this criterion, they can be denominated as ionic, electrostatic, hydrogen-bonded, or charge-transfer complexes.[19] The intermolecular interactions in general can be analyzed in terms of electrostatic, induction, short-range Pauli repulsion, and dispersion.[21] Here, we are interested in understanding the nature of the intermolecular forces that contribute to stabilize the AuCO system.

In the present work, we undertake a theoretical study of the Au(CO)$_n$ (n = 1−3) complexes (Figure 1). We first examine the influence of the ab initio methods and the explicit influence of relativity in the ground state ($^2A_1$). To our knowledge, no ab initio molecular orbital calculations on Au(CO)$_2$ and Au(CO)$_3$ have been reported so far. Moreover, we try to identify the dominant contributions to the attraction forces by considering the long-range limits using AuCO as a model.

Computational Details and Theory

Quantum Chemical Methods. The calculations were done using Gaussian 98.[22] The 19-valence-electron (VE) quasi-relativistic (QR) pseudo-potential (PP) of Andrae[23] was employed for gold. The f orbitals are necessary for the weak intermolecular interactions, as it has been demonstrated previously for the gold atom.[24,25] We employed two f-type polarization functions. This is desirable for a more accurate description of the interaction energy. Also, the carbon and oxygen atoms were treated by 4-VE and 6-VE,[23] respectively. For these atoms, double-ζ basis sets were used,[23] adding one d orbital polarization function.

We fully optimized the geometries for the Au(CO)$_n$ (n = 1−3) complexes at the MPn (n = 2−4), CCSD, and CCSD(T) levels. The interaction energy $V(R)$ for the complexes were obtained according to eq 1; a counterpoise correction for the basis-set superposition error (BSSE)[23] on ΔE was thereby performed.

$$\Delta E = E_{\mathrm{AB}}^{(\mathrm{AB})} - E_{\mathrm{A}}^{(\mathrm{AB})} - E_{\mathrm{B}}^{(\mathrm{AB})} \qquad (1)$$

The optimized geometries, interaction energies, $V(R_e)$, force constants, and frequencies for the AuCO complex are shown in Tables 1 and 2. In these tables, we have not included the results obtained at the MP3 and CCSD levels, because at such levels of calculation stabilizing interactions are not obtained.

Theory of Intermolecular Forces. We can partition the interaction energy of the eq 1 as

$$\Delta E = \Delta E(\mathrm{HF}) + \Delta E(\mathrm{corr}) \qquad (2)$$

where ΔE(HF) is the interaction energy evaluated from a self-consistent-field (SCF) supermolecule calculation at the Hartree−Fock (HF) level. The second term, ΔE(corr), is the electron correlation energy, which is a useful approximation to the dispersion energy at MPn, CCSD, and CCSD(T) levels.[19,27]

On the other hand, the total intermolecular potential V_{int}[21,28] can be partitioned into different contributions at long ranges (eq 3),[29] where the overlap between the molecular charge clouds is insignificant. The four terms are the short-range

$$V_{\mathrm{int}} = V_{\mathrm{short}} + V_{\mathrm{elect}} + V_{\mathrm{ind}} + V_{\mathrm{disp}} \qquad (3)$$

(V_{short}), electrostatic (V_{elect}), induction (V_{ind}), and dispersion (V_{disp}) contributions. At short distances, repulsive effects appear because the electron clouds of the species penetrate each other and bring about charge overlap and long-range contributions. At long-range, the electrostatic and induction terms are classical. Furthermore, the dispersion (London) term also has long-range character. It is attractive, but requires a quantum mechanical interpretation.[29]

The Hartree−Fock term (ΔE(HF)) is associated with the sum of short-range (V_{short}), electrostatic (V_{elect}), and induction (V_{ind}) terms, while the ΔE(corr) electron correlation term is associated with dispersion (V_{disp}).[29] Hence, our aim is to find a relationship between the intermolecular potential in the long distance ($R_{\mathrm{Au-C}}$) Au−CO with the properties of the isolated Au and CO through the dipole moment (μ), quadrupole moment (θ), polarizability (α), and first ionization potential (IP_1). The latter property was obtained from Koopmans' theorem.[30] These properties are given in Table 3 for each system studied at the HF, MP2, MP4(SDTQ), and CCSD(T) levels.

The interaction of the Au−CO (Figure 1) will be studied using the specific configuration given for Au and CO with respect to their dipole moment, as shown in Figure 2.[21] The θ angle (i.e., the angle formed between Au and CO) values depend on the methodology used, namely, MP2, MP4, and CCSD(T). In this case, both Au and CO do not have any formal charge, so a long-range electrostatic energy vanishes. Thus, the induction and dispersion terms remain. The induction energy (eq 4) results from the interaction of the dipole of CO with the polarizability of Au. This term is attractive, but since the CO dipole moment is very small, then it is not a dominant

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Table 1. Optimized Au−C and C−O Distances, R_e, for the Complexes at Different Levels of Calculations[a]

species	method	Au−C	C−O	∠AuCO	$-V(R_e)$	F(Au−C)	F(C−O)
AuCO (C_1)	MP2	197.5	115.2	152.9	26.4 (52.1)	1.02	16.41
	MP4	199.8	116.0	154.4	24.3 (51.1)	0.97	14.51
	CCSD(T)	205.9	114.6	150.6	13.5 (36.8)	0.67	17.35
$Au(CO)_2$ ($D_{\infty h}$)	MP2	190.5	116.0	180.0	73.6 (130)	7.67	14.53
	MP4	194.8	116.4	180.0	44.2 (78.1)	7.25	14.68
	CCSD(T)	196.4	115.8	180.0	23.3 (41.1)	5.06	16.52
$Au(CO)_3$ (D_{3h})	MP2	196.1	115.5	180.0	86.4 (168)	8.57	16.51
	MP4	200.7	116.1	180.0	57.1 (111)	8.04	14.54
	CCSD(T)	201.4	115.2	180.0	30.6 (59.3)	6.35	16.40
CO ($C_{\infty v}$)	MP2		114.4				17.99
	MP4		115.1				16.20
	CCSD(T)		114.1				18.57
CO	expt[8]		112.8				19.01

[a] Distance R_e in pm; angles α_e in degrees; interaction energy $V(R_e)$ with BSSE and in parentheses without BSSE in kJ/mol; force constants F(Au−C) and F(C−O) in mdyn/Å.

Table 2. Vibrational Frequencies of AuCO[a]

compound	method	ν_1	ν_2	ν_3
AuCO	MP2	180	346	2036
	MP2+3f[14]	186	370	2042
	MP4	178	338	1915
	CCSD(T)	168	286	2093
	expt[8]			2040
CO	MP2			2132
	MP2[14]			2126
	MP4			2023
	CCSD(T)			2165
	expt[31]			2143−2140

[a] ν_1 is the Au−C−O bend, ν_2 is the M−C stretch, and ν_3 is the C−O stretch. All values are in cm^{-1}.

Table 3. Finite Field Calculations (au) of Electric Properties of Gold and Carbonyl at HF, MP2, MP4(SDTQ), and CCSD(T)

properties	Au	CO
μ(HF)	0	0.1213
μ(MP2)	0	0.1116
μ(MP4)	0	0.0712
μ(CCSD(T))	0	0.0476
α(HF)	49.3029	9.4981
α(MP2)	27.4687	9.8213
α(MP4)	32.8112	9.7788
α(CCSD(T))	37.8030	9.7410
$\alpha_\parallel-\alpha_\perp$(HF)	0	4.1098
$\alpha_\parallel-\alpha_\perp$(MP2)	0	4.5399
$\alpha_\parallel-\alpha_\perp$(MP4)	0	4.4486
$\alpha_\parallel-\alpha_\perp$(CCSD(T))	0	4.5035
θ(HF)	0	1.6052
θ(MP2)	0	1.5592
θ(MP4)	0	1.5888
θ(CCSD(T))	0	1.6007
IP_1(HF)	0.2920	0.5545
IP_1(MP2)	0.2920	0.5523
IP_1(MP4)	0.2919	0.5541
IP_1(CCSD(T))	0.2919	0.5532

term. The dispersion term makes an important contribution to the intermolecular potential, and it is attractive between Au and CO at long and short distances. The London approximation is given in eq 5. The leading dispersion term behaves as $V_{disp} = -C_6/R$.[6]

$$V_{ind} = -\frac{1}{2}\alpha^{Au}\left(\frac{\mu^{CO^2}(3\cos^2\theta + 1)}{R^6} + \frac{12\mu^{CO}\Theta^{CO}\cos^3\theta}{R^7}\right) \quad (4)$$

$$V_{disp} = -\frac{3IP_1^{\,Au}IP_1^{\,CO}}{2(IP_1^{\,Au} + IP_1^{\,CO})R^6}\left(\alpha^{Au}\alpha^{CO} + \frac{1}{3}\alpha^{Au}(\alpha_\parallel - \alpha_\perp)^{CO}\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)\right) \quad (5)$$

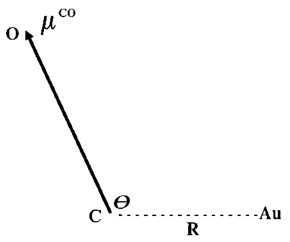

Figure 2. Definition of coordinates for the CO and Au interaction.

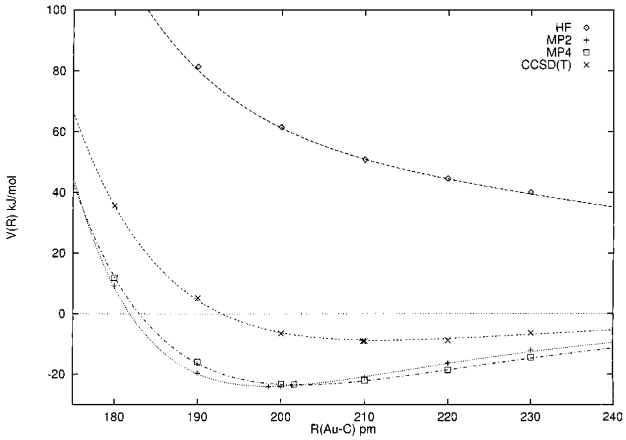

Figure 3. Calculated Au−CO potential curves $V(R)$ at the HF, MP2, MP4, and CCSD(T) levels.

Results and Discussion

Short-Distance Behavior. The results obtained in this work for the AuCO (C_1) complex are similar to those of Schwerdtfeger et al.[14] at the HF and MP2 levels. A bent structure for the AuCO complex is also obtained at the MP4 and CCSD(T) levels. The linear structure is only 2.4, 2.0, and 3.5 kJ/mol above the bent arrangement using MP2, MP4, and CCSD(T), respectively. At the HF level, the Au−C interactions are found to be repulsive for the complexes, and no real chemical bond is established. Figure 3 shows the interaction energy potential as a function of the Au−C distance using different electron correlation methods. Similar results for $Au(CO)_2$ and $Au(CO)_3$ complexes were also obtained. The first complex shows a linear structure ($D_{\infty h}$), while the second adopts a trigonal planar geometry (D_{3h}). We found an oscillatory trend in the interaction energy of both complexes, as well as in other properties such as Au−C distance, independently of the methodology used.

One may expect that the inclusion of f functions on gold should reduce the BSSE. However, as it is appreciated in Table 1, the interaction energies without BSSE are strongly overestimated. This is in agreement with the suggestion made by Schwerdtfeger et al.[14] The BSSE can increase in these systems due mainly to the shorter Au−C distance and the increase of the BSSE in CO.

The carbonyl moiety is expected to be weakly perturbed when complexing with gold in the ground state ($^2A_1$). For instance, we have found that the C−O bond is slightly longer in the $Au(CO)_n$ ($n = 1-3$) complexes when compared with that of free CO. This increase in distance can be attributed to weak interactions. However, there is no experimental evidence on the geometrical parameters due to the absence of crystal structures for these complexes. Moreover, there are experimental estimates of force constants for C−O stretching and vibrational frequencies in the AuCO complex. As force constants depend on the matrix used (Ne, Ar, Kr, or Xe), the experimental magnitudes for C−O vary between 15.93 and 16.18 mdyn/Å. The free carbonyl has an experimental force constant of 19.01 mdyn/Å,[8] very close to that calculated theoretically (see Table 1). Once the complexes are formed, there is a trend to reduce this property.

We have calculated the frequencies of the AuCO complex at different levels (see Table 2). In this table, some frequencies available from experiments (matrix isolation) have been included in order to be compared with our theoretical results. The values derived from the CO ν_3 stretching frequency decrease due to CO binding with gold atom. This can be observed both theoretically and experimentally, when we compare with the free carbonyl.[31] However, it is possible to observe a strong oscillation in this property according to the calculation method used. MP4 tends to underestimate, while CCSD(T) tends to overestimate the frequencies. MP2 calculation provides better results. The IR intensity of the gold−carbon stretching mode is very small, and the Au−C−O bending mode is quite weak; therefore it is not possible to observe them experimentally.

We have considered the effect of the electron correlation in the Au−CO complex at the MP4(SDQT) and CCSD(T) levels (see Figure 4). A strong oscillation at the equilibrium distance Au−C(R_e) as well as in the interaction energy can be seen upon changing the electron correlation potential. Figure 4 also shows the minimal interaction energies in $Au(CO)_n$ complexes for each methodology. At HF level calculations, we have taken the Au−C distance obtained at the MP2 level as reference since no minimum is obtained with this methodology. This interaction energy obtained at the MP2 level, ΔE(MP2), nearly vanishes at the MP3 and CCSD levels. However, at the MP4(SDQT) and CCSD(T) levels, this energy is recovered. The triple excitations in CCSD(T) strongly contribute to that energy at approximately a third of the MP2 result. A similar trend is observed in the $Au(CO)_2$ and $Au(CO)_3$ systems.

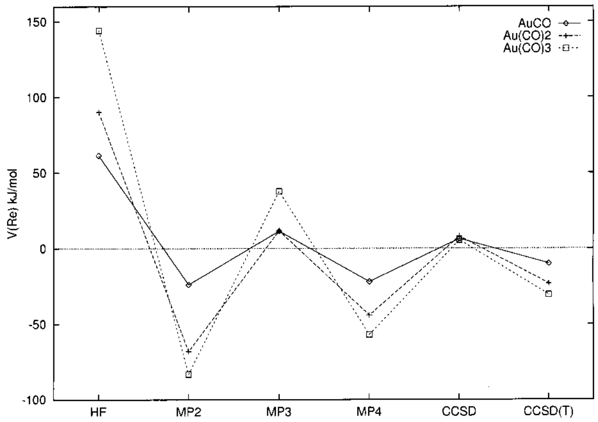

Figure 4. Effect of the method used on the minimal interaction energy $V(R_e)$.

Table 4. NBO Analysis of the MP2 Density for $Au(CO)_n$ ($n = 1-3$), CO, and Au

	atom	NBO charge	NBO electron configuration
AuCO	Au	0.0273	$6s^{1.14}\ 5d^{9.75}\ 6p^{0.06}\ 6d^{0.01}$
	C	0.5165	$2s^{1.48}\ 2p^{1.90}\ 3s^{0.06}\ 3p^{0.03}\ 3d^{0.01}$
	O	−0.5437	$2s^{1.71}\ 2p^{4.80}\ 3d^{0.03}$
$Au(CO)_2$	Au	0.3407	$6s^{0.85}\ 5d^{9.59}\ 6p^{0.21}\ 6d^{0.02}$
	C	0.3771	$2s^{1.32}\ 2p^{2.23}\ 3s^{0.02}\ 3p^{0.04}\ 3d^{0.01}$
	O	−0.5474	$2s^{1.70}\ 2p^{4.81}\ 3d^{0.03}$
$Au(CO)_3$	Au	0.5668	$6s^{0.55}\ 5d^{9.60}\ 6p^{0.28}\ 6d^{0.02}$
	C	0.3642	$2s^{1.42}\ 2p^{2.14}\ 3s^{0.03}\ 3p^{0.04}\ 3d^{0.01}$
	O	−0.5531	$2s^{1.70}\ 2p^{4.82}\ 3d^{0.03}$
CO	C	0.6305	$2s^{1.64}\ 2p^{1.68}\ 3s^{0.02}\ 3p^{0.01}\ 3d^{0.01}$
	O	−0.6305	$2s^{1.74}\ 2p^{4.86}\ 3d^{0.03}$
Au	Au	0.0000	$6s^{1.0}\ 5d^{10.0}$

In general, the Au−C interaction analysis shows that for many systems the convergence of the perturbation theory is oscillatory, indicating that higher order terms may be important.[32,33] This oscillation occurs in transition metal systems, particularly when ($n - 1$)d to ns excitations are involved.[32] This is especially stressed for the case of gold.

The natural bond orbital (NBO)[34] population analysis results for the complexes are shown in Table 4. This analysis is based on the correlated densities. The data show a small charge transfer from gold toward the carbonyl (0.0273*e*) in the AuCO complex. This would suggest a weak interaction in the complex with a dative interaction, similar to that found in the classical Dewar−Chatt−Duncanson model.[35,36] The gross population per atom shell shows that 6s and 6p orbitals belonging to gold tend to take advantage of this charge transfer by increasing their occupation. However, 5d orbitals are depopulated. In this complex hybridization between Au and CO orbitals does not exist. Moreover, electron paramagnetic resonance (EPR) results[9] fully support the conclusion that the unpaired spin is mostly located at the gold atom.

On the other hand, both $Au(CO)_2$ and $Au(CO)_3$ complexes showed charge transfer from gold toward the carbons of carbonyls of 0.3407*e* and 0.5668*e*, respectively. In other words, the main feature is the donation from the 6s orbital of the Au atom to a 2p orbital on C.

Long-Distance Behavior. The long-distance attraction between Au and CO is shown in Figures 5 and 6,

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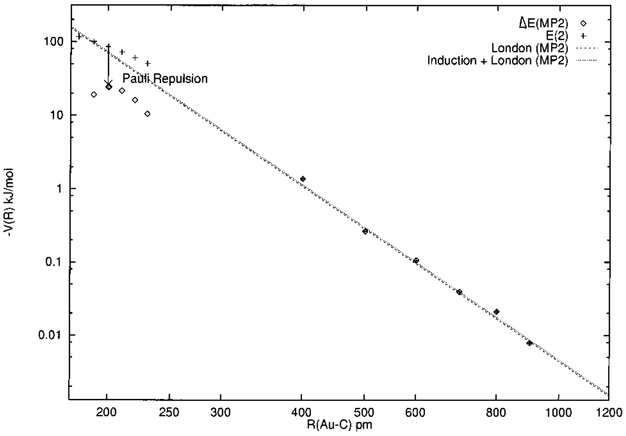

Figure 5. Interaction energy, $V(R)$, of the long-range behavior at the MP2 level.

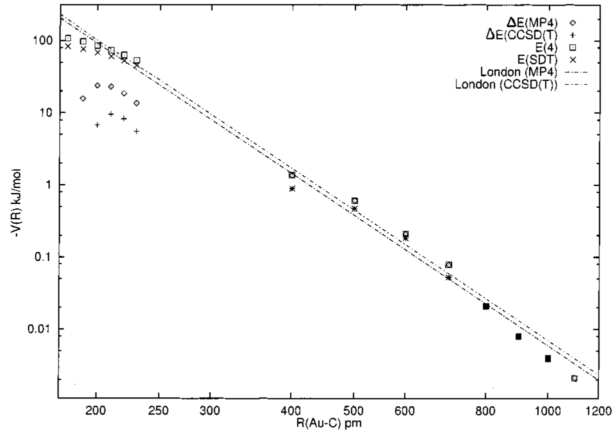

Figure 6. Interaction energy, $V(R)$, of the long-range behavior at the MP4 and CCSD(T) levels.

together with MP2, MP4, and CCSD(T) results for the AuCO complex. Energy minima occur at R_e (Table 1). At these distances the attractive and repulsive dV/dR terms tend to cancel mutually. The main repulsive term, the Pauli repulsion, already occurs at the HF level. When we included electron correlation at the MP2, MP4, and CCSD(T) levels, several energy minima are generated. At this level of calculations, the difference (from the HF contribution) is dominated by the repulsive Pauli and induction terms.

Table 5. Dispersion Coefficients C_6 (in 10^{13} kJ mol^{-1}/pm^6) for AuCO

method	ΔE(corr)	London
MP2	604	446
MP4(SDTQ)	630	578
CCSD(T)	656	683

The long-range behavior can be compared with the sum of the induction and dispersion terms, which were estimated with eqs 4 and 5, respectively. The induction term is small and attractive, without any effect at all distances (see Figure 5). This is because the dipole moment of carbonyl is relatively small. The dominant long-range force is expected to be a London-type dispersion force. The extrapolation from large values R to R_e tends to be an attractive dispersion term (as R^{-6}), being the main contribution to the Au−CO attraction. We can see from Figures 5 and 6 a good relationship between the dispersion (or London) formula (eq 5) and the contribution of the electron correlation term. The effective C_6 coefficients are shown in Table 5.

Conclusions

The present study provides further information about the nature of the interactions in Au(CO)$_n$ complexes. We have found that the energy interaction is mainly due to an electronic correlation effect. This energy shows a strong oscillation upon changing to higher levels of electron correlation, when going from MP2 to MP3, MP4(SDQT) and from CCSD to CCSD(T) models. The AuCO system shows an R^{-6} behavior at large distances. This result provides proof that the binding in Au(CO)$_n$ complexes is essentially due to dispersion forces. Moreover, the NBO analysis in the AuCO complex showed a small charge transfer from Au toward the carbonyl, but we cannot understand this dative interaction as similar to that proposed in the Dewar−Chatt−Duncanson model. Otherwise, the HF calculations should show an energy minimum.

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