On the origin of bonding and vibrational frequency shifts for CO adsorbed on neutral, cationic and anionic gold clusters

PS Bagus¹ and G Pacchioni²,³

¹Department of Chemistry, University of North Texas, Denton, Texas, USA
²Dipartimento di Scienza dei Materiali, Università degli Studi di Milano Bicocca, via R. Cozzi, 53, 20125 Milan, Italy

E-mail: gianfranco.pacchioni@unimib.it

Abstract. We report a detailed analysis of the electronic mechanisms which determine the bond strength and the vibrational frequency of CO molecules adsorbed on neutral or charged gold nanoparticles. To this end we have considered a simple cluster model, Au₅CO⁰(q = +1, 0, -1), and decomposed the Au-CO interaction energy into the sum of various contributions according to a Constrained Space Orbital Variation approach. While the adsorption energy is relatively insensitive to the value of q, the C-O stretch frequency, ω(CO), changes substantially, and allows the use of this molecule as a direct probe of the gold oxidation state. The results show that two major terms contribute to the red or blue shift of ω(CO) as a function of q: the interaction with the electric field associated to the charged nanoparticle (Stark effect) and the Au®CO π back donation. The CO®Au σ donation is about half as important as the π back-donation and all other terms are much less important.

1. Introduction

Gold nanoparticles deposited on the surface of transition metal or rare-earth oxides like TiO₂ or CeO₂ are active species in the conversion of CO to CO₂ as well as in other catalytic processes. This is different from bulk gold which is chemically inert and catalytically inactive. After the discovery of Haruta that, once prepared in the form of nanoparticles, gold becomes an active catalyst [1-4] a large number of studies has been made with the goal of elucidating the reasons for this special activity. There is ample consensus that this is related to the small dimensions of the metal particle; while particles of 2-3 nm in diameter are good catalysts, larger particles are inactive. Beside this aspect, however, the reasons for the enhanced activity are not yet fully clarified. Some authors believe that this is due to the relatively large number of low-coordinated sites at the surface of a nanoparticle; some experiments point to a special role of the oxide support; in other studies it has been proposed that the reason for the enhanced activity is the oxidation state of gold [5-18]; most probably, all these effects are important and act together, although their relative contribution can change from case to case. What is sure is that the activity of nanostructured gold depends on the preparation of the sample [4], on the form and nature of the oxide substrate and on the particle size and shape [2,3,19-22]. Among all these factors, the charge state of the gold nanoclusters is widely discussed and often controversial. Some studies suggest that the active catalyst is cationic gold [23-26], and that this “oxidation” occurs in the course of catalytic reactions in the presence of oxygen [27,28]. Other model studies, on the contrary, have shown that negatively charged gold clusters are chemically more active.

³ To whom any correspondence should be addressed
than their neutral counterparts [11,13,16,29,30]. In fact, the presence of an extra negative charge on a gas-phase as well as on a small supported Au cluster results in an easier breaking of bonds of adsorbed molecules, O2 in particular, and in an enhanced catalytic activity [31]. Cluster charging may occur in various ways, but in particular through the interaction with specific sites of the oxide surface such as oxygen vacancies and other point defects. The literature on charging of gold nanoparticles on MgO and TiO2 substrates is rather abundant and there is ample evidence that oxygen vacancies (F centers) act both as nucleation and activation centers for supported Au nanoparticles [11,13,16].

To study the effect of different charge states of a Au5q cluster (q = +1, 0, −1) on adsorbed molecules, we have analyzed in detail the electronic mechanisms contributing to the formation of a chemical bond between the Au particle and an adsorbed molecule. We have chosen CO because this is directly involved in the most widely studied reaction catalyzed by gold nanoparticles, CO + ½ O2 ® CO2, but also because CO is commonly used as probe molecule to verify the charge state of the metal particle. In particular, the charge state of Au particles has been related to shifts of the C-O stretch frequency [13, 32].

We have performed a Constrained Space Orbital Variation, CSOV, analysis [33-35] of the interaction energy and vibrational frequency, of CO adsorbed on a Au5 cluster model of Au nanoparticles. We have used this model to determine the different properties of cationic, neutral, or anionic gold. In particular, we have analyzed the relative importance of various bonding contributions as a function of q: the classical CO ® Au σ donation, the Au ® CO 2π* back donation, but also other important terms which are often neglected in the discussion of the origin of the vibrational shifts of adsorbed CO.

2. Computational method

The CSOV analysis is based on steps where the variation of only certain occupied orbitals is made using only certain unoccupied orbitals in the variational space [33-35]; thus, it is possible to associate each of the constrained variations with specific chemical and physical interaction mechanisms. When several effects make major contributions to the bonding, it is necessary to repeat certain steps in order to take into account the coupling of the different effects [36]. For the Au5–CO interaction, as we show below, several bonding mechanisms make important contributions to the interaction energy. Thus, we have repeated CSOV steps, as necessary, to reduce to a small level the non-additivity of the CSOV steps compared to the full variation [36]. Rather than report the contributions at each individual CSOV step, we have summed the contributions of steps with the same variational freedom and we describe this sum as the contribution of a particular CSOV mechanism. The order of the CSOV steps introduces normally small uncertainties in the magnitudes of the contributions of individual mechanisms to a given property [35]. In order to avoid artifacts related to these uncertainties, we have used exactly the same sequence and order of CSOV steps for all geometries and for all charge states of Au5CO considered. The CSOV analysis of the Au-CO interaction has been done at the Hartree-Fock (HF) level. However, to verify that the general conclusions at the HF level are not significantly modified by electron correlation effects, we have included these correlation effects using density functional theory (DFT). The comparison of the HF and DFT results shows essentially the same changes in all properties as a function of the charge state of the Au5CO cluster. This constancy allows us to use the CSOV results with confidence that they properly describe the properties of real Au nanoparticles. For the DFT calculations, we used the Becke’s three-parameter hybrid exchange functional [37] combined with the correlation functional of Lee, Yang and Parr [38], B3LYP.

Au5 has a square pyramidal shape, and CO has been adsorbed on the apical atom, Fig. 1. Of course this is not the only possible adsorption site, but is chosen here for comparative purposes. The conclusions of the paper are expected to be valid also for other sites. The Au-Au distances are taken from bulk gold, 2.88 Å. The gold skeleton was not allowed to relax, while the position of the CO adsorbate has been fully optimized.

We have used two different basis sets for these calculations. For basis set A, used for DFT and HF
calculations, the Au atoms were described with the small core, 19 electron, effective core potential, ECP, of Hay and Wadt [39] and an unsegmented \[5s6p3d/3s3p2d\] double-zeta basis set. The atoms of the CO molecule were described at the all electron level using a 6-311+G* basis set. For basis set B, used for HF and CSOV calculations, the Au atoms were described with the same ECP but a somewhat more flexible contraction of \[5s6p3d/3s4p3d\] was used for the Au basis set. The all electron C and O atoms were described with an unsegmented contraction of \[9s5p/4s3p\] [40,41] that is somewhat less flexible than the sets used for C and O in basis set A. The two basis sets provide a similar description of the adsorption properties (see below).

The harmonic vibrational frequencies, \( \omega_h \), were also calculated differently with basis sets A and B. For the HF and DFT calculations using basis set A, the frequencies of the normal modes are determined solving the full secular matrix [42] where the internal coordinates for the Au-CO frustrated translation and the C-O stretch were allowed to mix. For the HF and CSOV calculations with basis set B, these two internal coordinates were not allowed to mix. For the low energy Au-CO stretch, the C-O distance was fixed at \( r(C-O) = 1.14 \text{ Å} \) and the potential curve for CO moved rigidly with respect Au was determined. For the high energy C-O stretch, the position of the C-O center of mass was fixed as for \( r(Au-C) = 1.14 \text{ Å} \) and \( r(Au-O) = 3.26 \text{ Å} \) and the potential curve for the pure C-O stretch was determined. These potential curves were determined for the full HF energies and for the energies at the various CSOV steps. Dunham analyses [43] were performed to determine harmonic frequencies, \( \omega_h(Au-CO) \) and \( \omega_h(C-O) \), the equilibrium distances, \( r_e(Au-C) \) and \( r_e(C-O) \), and the dissociation energy, \( D_e \). We have used the internal coordinates to simplify the calculation of the CSOV \( \omega_h \). However, since the \( \omega_h(Au-CO) \) and \( \omega_h(C-O) \) differ by about an order of magnitude, there is very little mixing of the internal coordinates in the normal modes [44]. Thus, the frequencies obtained with the two approaches can be directly compared and we also use the notation \( \omega_h(Au-CO) \) and \( \omega_h(C-O) \) for the normal modes. Anharmonic contributions for free CO are small [45] and our test calculations show that they are also small and similar for the charge and neutral Au\(_5\)CO clusters.

The CSOV decomposition has been performed with a modified version of ALCHEMY [46]. The calculations at the DFT level were done using the Gaussian03 program package [47].

**Figure 1.** Structure of Au\(_5\)CO\(^q\) complex \((q = +1, 0, -1)\).

**Figure 2.** Plot of the bonding orbital responsible for the Au\(_5\) to CO 2\(\pi^*\) back donation.

3. Results and discussion

3.1 DFT versus HF results

We start our discussion by comparing the results of the calculations for Au\(_5\)CO\(^q\) \((q = +1, 0, -1)\) obtained at HF and DFT levels, Table 1. Quite surprisingly, the binding energy of CO to cationic, neutral, or anionic Au\(_5\) is very similar, about 0.5-0.6 eV at the HF level, and 1.3-1.4 eV at the DFT
level. Thus, the presence of a positive or a negative charge on the cluster does not affect in a dramatic way the bonding properties of CO. This is what is expected for an extended metal, while on a small cluster, where the charge is confined in a small volume, one would expect a larger effect. The fact that a similar binding is found for electronically quite different situations suggests the existence of compensating and canceling contributions to the bonding. Although the changes in $D_e$ for the differently charged states of Au$_5$CO are small, there are non-negligible changes in $r$(Au-C) and in $\omega$(Au-CO), Table 1, and these latter properties are also normally taken as indications of the bond strength. For example, $r$(Au-C) in Au$_5$CO$^+$, 2.18 Å, is considerably longer than in Au$_5$CO$^-$, 2.04 Å, but $D_e$ differs by only 0.04 eV (HF results, basis A); at the DFT level the differences in $r$(Au-C) are less pronounced, Table 1.

Furthermore, for this paper, the changes in the C-O distance and vibrational frequency as a function of cluster charge are very important. We give, in Table 1, the shifts in $r$ and $\omega$, denoted $\Delta r$(C-O) and $\Delta \omega$(C-O), taken with respect to the free gas-phase molecule computed at the same level of theory; these changes are reasonably large. The presence of a positive charge on Au$_5$ has the clear effect to reduce $r$(C-O) and increase $\omega$(C-O), Table 1; a negative charge on Au$_5$ reflects in longer $r$(C-O) and lower $\omega$(C-O). At first sight, significant differences exist between HF and DFT calculations, Table 1. In addition to the fact that the DFT $D_e$ is more than 0.75 eV larger than the HF values, the DFT Au-C distances are also considerably shorter and the CO vibrational frequencies are more red shifted compared to the HF ones, Table 1. However, a more careful analysis shows that the trends as function of $q$ are very similar for the HF and DFT calculations.

### Table 1. Properties of CO adsorbed on [Au$_5$$^q$] (q = +1, 0, −1)

| Method       | Au$_5$$^+$ | Au$_5$$^0$ | Au$_5$$^-$$ |
|--------------|------------|------------|-------------|
| $D_e$, eV     | 0.53       | 0.48       | 0.49        |
|              | HF basis A | B3LYP basis A | HF basis B |
| $r$(Au-C) Å  | 2.18       | 2.10       | 2.04        |
|              | HF basis A | B3LYP basis A | HF basis B |
| $\Delta r$(C-O) Å | −0.009 | −0.004   | +0.003     |
|              | HF basis A | B3LYP basis A | HF basis B |
| $\omega$(Au-CO) cm$^{-1}$ | 196 | 230 | 277 |
|              | HF basis A | B3LYP basis A | HF basis B |
| $\Delta \omega$(C-O) cm$^{-1}$ | +78 (−59) | +19 (−78) | −59 |
|              | HF basis A | B3LYP basis A | HF basis B |
| (a) Change in $\omega$(C-O) with respect to the free molecule (2432 cm$^{-1}$ HF basis A, 2212 cm$^{-1}$ DFT basis A, and 2285 cm$^{-1}$ HF basis B). In parenthesis are given the shifts going from Au$_5$CO$^+$ to Au$_5$CO$^0$, and from Au$_5$CO$^0$ to Au$_5$CO$^-$. |

At the HF level, with basis set A, $\omega$(C-O) in Au$_5$CO$^0$ is blue shifted by +19 cm$^{-1}$ with respect to free CO; in Au$_5$CO$^+$ the shift is much larger, +78 cm$^{-1}$, with a differential increase with respect to the neutral cluster of +59 cm$^{-1}$; in Au$_5$CO$^-$ $\omega$(C-O) is red-shifted by 59 cm$^{-1}$ with respect to gas-phase CO, with a differential shift $\Delta \omega$ = −78 cm$^{-1}$ compared to Au$_5$CO$^0$. These numbers are consistent with the experimental observations. All the reported data indicate that the frequency of CO on neutral gold is around 2110-2120 cm$^{-1}$ [13,32], with a small red-shift compared to free CO of about 20 cm$^{-1}$.
(ω(CO)_{gas-phase} = 2143 cm^{-1}); on oxidized Au particles the CO vibrational shift is of about +50/+60 cm^{-1} and the absolute frequency is up to 2170-2180 cm^{-1} [32]; on reduced (anionic) gold nanoparticles the frequency becomes 2060-2070 cm^{-1}, with a shift with respect to neutral gold of about −50/−70 cm^{-1} [11,13]. In this respect, the HF calculations on our Au_5 model produce results which are completely consistent with the experimental observations.

At the DFT level the trends are similar, but there is an additional rigid shift of all the CO frequencies to low wave numbers. On Au_5CO^0 the CO frequency is red-shifted compared to free CO by 45 cm^{-1}, about twice the experimental shift (= −20 cm^{-1}); in Au_5CO^- the blue shift is of +25 cm^{-1} only, with a differential increase of +70 cm^{-1} compared to the neutral cluster, consistent with both the HF and the experimental results; on the contrary, in Au_5CO^- ω(C-O) is shifted by −128 cm^{-1} with respect to free CO, a value which is clearly too large compared to the experiment and which reflects the tendency of DFT to overestimate the back donation of metals to the CO 2π* MO [48,49]. This is due to the well known problem of self-interaction in DFT, an effect which produces too small band gaps in solids and HOMO-LUMO gaps in molecules. The low energy of the 2π* MO of CO in DFT is the reason for the too large back bonding. However, the differential shift Δω(C-O) at the DFT level from Au_5CO^0 to Au_5CO^-, −83 cm^{-1}, is only slightly exaggerated compared to HF and experimental results.

The results obtained with the basis set B adopted for the CSOV analysis, Table 1, are very similar: in particular, the CO vibrational shifts are +63 cm^{-1} for Au_5CO^+, −11 cm^{-1} for Au_5CO^0, and −95 cm^{-1} for Au_5CO^-, with respect to free CO. These shifts are in line with the experimental measurements for CO on supported gold nanoparticles [32], so that the analysis of the origin of vibrational shifts can be considered as representative of the real situation.

### 3.2 CSOV analysis of the CO adsorption energy

In Table 2 we report the results of a CSOV decomposition of the interaction energy of CO with the Au_5 cluster for various values of q. We have performed the CSOV analyses using the same Au-C distance, 2.12 Å, and the same C-O distance, 1.14 Å, in the three clusters, in order to separate electronic from geometric effects.

| | Au_5CO^+ | Au_5CO^0 | Au_5CO^- |
|---|---|---|---|
| 1. FO | (−1.22) | (−1.25) | (−1.30) |
| 2. Au π back-donation to CO | +0.33 | +0.45 | +0.58 |
| 3. CO σ donation to Au | +0.56 | +0.52 | +0.48 |
| 4. Au polarization | +0.49 | +0.55 | +0.62 |
| 5. CO polarization | +0.27 | +0.17 | +0.11 |
| 6. Other terms | +0.10 | +0.10 | +0.10 |
| 7. Sum of terms 2-6 | +1.76 | +1.79 | +1.91 |
| 8. Non-additivity | +0.03 | +0.02 | +0.01 |
| 9. Full SCF | (−0.56) | (−0.56) | (−0.63) |

(a) The CO position above the surface for these decompositions is z(C)=2.12 Å and r(C-O)=1.14 Å. The difference between the various contributions and the Full SCF where no constraints are applied is given as “Non-additivity” and indicates the coupling of the different contributions not taken into account in the decomposition. For the first, or FO, CSOV step and for the Full SCF result, the value given in parenthesis is the total ΔE_{INT}.

In the first CSOV step, frozen orbital (FO), the HF orbitals of the separated systems CO and Au_5 are taken and an anti-symmetric wavefunction, which satisfies the Pauli Exclusion principle, is
constructed from these orbital sets [50]. No orbital relaxation is allowed at this step which gives the sum of the electrostatic interaction and the Pauli repulsion between the two subsystems. So, no chemistry occurs at this step, since no mixing of the occupied and virtual orbitals on the two interacting fragments is possible. The FO contribution is repulsive by about 1.2-1.3 eV, and is largely independent of the charge on the gold cluster, Table 2.

The second type of CSOV constraints allows the occupied Au₅ orbitals of π symmetry (or e in the C₅ᵥ point group of Au₅) to mix with the virtual π orbitals of the CO molecule. These constraints account for the π back donation from Au, which is mainly from the 5d orbitals of the apical Au atom, into the unoccupied CO 2π* orbitals, see Fig. 2. This bonding effect is the one that changes most with the charge on the gold cluster: 0.33 eV for Au₅⁺, 0.45 eV for Au₅⁰, and 0.58 eV for Au₅⁻, Table 2. In the third type of CSOV constraints, the occupied CO orbitals of σ (a₁) symmetry are allowed to mix with the virtual orbitals of Au₅. This mixing describes the CO → Au₅σσ⁻ donation, mainly occurring from the doubly occupied CO 5σ orbital. The contribution of this bonding mechanism is nearly the same, about 0.5 eV, in the three cases, Table 2.

In fourth type of CSOV constraints, the occupied and unoccupied orbitals of the Au₅ cluster are allowed to mix. This represents the polarization of the gold cluster in response to the presence of the CO molecule (intra-unit polarization). This term is comparable in size to the CO σ donation, about 0.5 eV, and it increases going from the cationic Au₅⁺ to neutral Au₅⁰ to anionic Au₅⁻. Therefore, the sum of the two intra-unit polarization effects, CO and Au₅, remains nearly constant: 0.76 eV for Au₅⁺, and 0.72 eV for Au₅⁰ and 0.73 eV for Au₅⁻. The contributions grouped as “Other Terms” in Table 2, involve σ back-donation from Au to CO and CO π donation to Au; these terms represent artifacts associated with the finite basis set size. These artifacts are small and they are the same for all three cases considered.

From the analysis it emerges that the sum of the bonding contributions of CO on the three Au₅⁰ clusters, terms 2 to 6, is similar, about 1.8-1.9 eV. This similarity arises because of canceling effects: on cationic gold both the CO polarization and the CO σ donation are larger, but the π back donation is considerably reduced; on anionic gold the situation is reversed, with a dominant π back donation, a smaller CO σ donation and negligible CO polarization. Non-additive contributions account for 0.02-0.03 eV only, so that by summing up the repulsive contribution of the FO term and the bonding mechanisms one recovers the Full SCF binding energy of about 0.6 eV, Table 2.

3.3 CSOV analysis of the CO vibrational frequency and equilibrium distance
In Table 3 we report the individual contributions to the shifts [51] of the C-O stretching frequency, Δωᵢ = [ωᵢ(Au₅C–O) – ωᵢ(C–O)], and the C–O equilibrium distance, Δrᵢ = [rᵢ(Au₅C–O) – rᵢ(C–O)], for q = +1, 0, –1. The individual contributions are denoted δωᵢ and δrᵢ to distinguish them from the total values of Δωᵢ and Δrᵢ. The δωᵢ and δrᵢ for the four largest contributions and the total Δωᵢ and Δrᵢ for the unconstrained SCF wavefunctions are given for the three Au₅CO⁰ clusters.

The FO charge superposition of Au₅ and CO involves no chemistry but it leads to large blue shifts in ωᵢ(C–O), +262 cm⁻¹ in Au₅CO⁺, +236 cm⁻¹ in Au₅CO⁰ and +214 cm⁻¹ in of Au₅CO⁻. These δωᵢ are accompanied by large reductions of rᵢ(C–O), Table 3. Two terms contribute to the large blue shift in the C–O ωᵢ: the first one comes from the Pauli repulsion of the CO lone pair and the ”rigid wall” formed by the Au₅ orbitals; this is sometimes referred to as the “wall effect” as discussed in [40]. However, a second contribution arises from the interaction of the CO moment with the electric field associated to the charge distribution of the gold cluster. The interaction of the cluster electric field is with the derivative of the CO dipole moment [40,52], which is large, in contrast to the dipole moment itself, which is small [45]. For Au₅ this additional term is not very large compared to the wall effect;
for charged clusters, however, the contribution of the electric field-CO dipole interaction, Stark effect, is much larger. A good estimate of the effect of the electric field, due to either Au$_5^+$ or Au$_5^-$, on $\delta\omega_c$ can be made by examining $\omega_c$(C-O) for a model system of a point charge, PC, and CO in a linear arrangement where the PC is placed at the center of charge of the Au$_5$ cluster. A PC = +1 at 3.7 Å from the C atom gives rise to a blue shift of +43 cm$^{-1}$ while a PC = −1 at 4.1 Å from the C atom gives rise to a red shift of −45 cm$^{-1}$. These shifts are larger than the changes in $\delta\omega_c$(FO) for the charged clusters from the value for the neutral cluster. The Stark contribution to a blue shift in $\omega_c$(FO) with Au$_5$CO$^+$ is offset by a smaller wall effect for Au$_5^+$ than for Au$_5^0$. The HOMO in Au$_5^0$ is an open shell e orbital occupied with 3 electrons. For Au$_5^+$, the HOMO contains only two electrons and hence the blue shift due to the surface wall is reduced. On the other hand, for Au$_5^-$, the HOMO is fully occupied and, hence, the blue shift of the wall is increased and this offsets the red shift due to the charge of the cluster. These two effects are the main reasons for the different values of $\delta\omega_c$ at the FO step as $q$ varies from +1 to −1.

**Table 3.** Development of the changes in the C-O stretch, $\omega_c$(C-O), and in the C-O equilibrium distance, $r_c$(C-O), between free CO and the Au$_5$CO$^q$ clusters with $q = +1$, 0, and −1; see text.$^{(3)}$

| CSOV Contribution | Au$_5$CO$^+$ | Au$_5$CO$^0$ | Au$_5$CO$^-$ |
|-------------------|-------------|-------------|-------------|
| 1. FO             | +262 cm$^{-1}$ | −0.029 Å   | +236 cm$^{-1}$ | −0.026 Å   | +214 cm$^{-1}$ | −141 Å   |
| 2. Au $\pi$ back-donation to CO | −75 cm$^{-1}$ | +0.00 Å   | −106 cm$^{-1}$ | +0.010 Å   | −53 cm$^{-1}$ | +0.006 Å   |
| 3. CO $\sigma$ donation to Au | −46 cm$^{-1}$ | +0.00 Å   | −47 cm$^{-1}$ | +0.005 Å   | −76 cm$^{-1}$ | +0.008 Å   |
| 4. Au polarization | −46 cm$^{-1}$ | +0.00 Å   | −47 cm$^{-1}$ | +0.005 Å   | −76 cm$^{-1}$ | +0.008 Å   |
| 5. Sum of terms 1-4  | +99 cm$^{-1}$ | −0.013 Å   | +24 cm$^{-1}$ | −0.005 Å   | −56 cm$^{-1}$ | +0.004 Å |
| 6. Total SCF ($\Delta\omega_c$ & $\Delta r_c$) | +63 cm$^{-1}$ | −0.009 Å   | −11 cm$^{-1}$ | −0.001 Å   | −95 cm$^{-1}$ | +0.008 Å |

(a) The sum of the four large contributions given and the total values of $\Delta\omega_c$ and $\Delta r_c$ for the full, unconstrained SCF solution for Au$_5$CO$^0$ are also given.

While the FO term leads to a very large blue shift of the CO frequency, all bonding mechanisms lead to a reduction of $\omega_c$(C-O) and to the elongation of $r_c$(C-O), Table 3. The first of these contributions in terms of importance is the Au $\pi$ back donation to CO. The change of $\omega_c$(C-O) due to the back donation changes considerably with the cluster charge, −75 cm$^{-1}$ for cationic gold, −106 cm$^{-1}$ for neutral gold, and −141 cm$^{-1}$ for anionic gold. Therefore, in Au$_5^+$ the $\pi$ back donation cancels to large extent the positive shift determined at the FO level, +236 cm$^{-1}$, while in Au$_5^-$ the sum of the first two CSOV steps still leads to a very large positive shift of nearly 200 cm$^{-1}$.

The other covalent bonding contribution in the Au-CO interaction is that corresponding to the CO → Au$_5^+$ $\sigma$ donation. Here the effect on $\omega_c$(C-O) is similar on the three clusters, being −42 cm$^{-1}$ in Au$_5$CO$^+$, −47 cm$^{-1}$ in Au$_5$CO$^0$, and −53 cm$^{-1}$ in Au$_5$CO$^-$. The reasons for the observed red shift at this step, which contradicts the usual assumption of a small blue shift associated with the removal of electrons from the slightly antibonding CO 5$\sigma$ orbital, have been discussed in ref. [40].

The polarization of the Au cluster lowers the CO frequency but to a different extent, depending on $q$. In particular, anionic gold is more polarizable and the contribution to $\omega_c$(C-O) is −76 cm$^{-1}$; for Au$_5^+$ this value is only −46 cm$^{-1}$ and neutral gold is in between, −59 cm$^{-1}$, Table 3. The contribution of the CO polarization to $\Delta\omega_c$ and $\Delta r_c$ is not shown in Table 3 because it is small and also because it is quite similar for all three states of Au$_5$. 


Ab initio Simulation of Crystalline Solids: History and Prospects

The sum of the major contributions to the CO vibrational frequency, CSOV terms 1-4, is therefore +99 cm\(^{-1}\) for Au\(_{5}^{+}\), +24 cm\(^{-1}\) for Au\(_{5}^{0}\), and −56 cm\(^{-1}\) for Au\(_{5}^{-}\), Table 3. These values can be compared with the \(\Delta \omega_{c}(C-O)\) obtained from a complete SCF calculation, +63 cm\(^{-1}\) for Au\(_{5}^{+}\), −11 cm\(^{-1}\) for Au\(_{5}^{0}\), and −95 cm\(^{-1}\) for Au\(_{5}^{-}\). This shows that the CSOV analysis reported in Table 3 captures the major ingredients of the vibrational shift of CO adsorbed on cationic, neutral or anionic gold. In all cases a large positive shift arises from the Pauli repulsion or “wall effect”, but this term is reinforced (Au\(_{5}^{+}\)) or attenuated (Au\(_{5}^{-}\)) by the electrostatic interaction between the electric field associated to the cluster and the CO dipole and multiple moments. The other term showing large changes as function of the cluster charge is the back donation from the Au orbitals to the CO 2\(\pi^{*}\) antibonding MO. This term is by far the most important chemical contribution: in anionic gold it is twice as large than in Au\(_{5}^{+}\), thus largely contributing to the final shift. The effect of CO donation is similar in the three cases, while the different polarization of the gold substrate as a function of q further contributes to the final shifts.

The physical and chemical changes in the Au-CO bonding with respect to cluster charge can be related to the changes in the C–O stretch by considering the contributions to \(\Delta \omega^{+}\) and \(\Delta \omega^{-}\) where

\[
\Delta \omega^{+} = \omega_{c}(CO;Au_{5}CO^{0}) - \omega_{c}(CO;Au_{5}CO^{+}) \tag{1}
\]

\[
\Delta \omega^{-} = \omega_{c}(CO;Au_{5}CO^{0}) - \omega_{c}(CO;Au_{5}CO^{0}) \tag{2}
\]

We have seen in the introduction that the CO vibrational frequency is normally taken as a measure of the nature and oxidation state of a gold nanoparticle, and that direct correlations are done between the cationic, neutral or anionic gold and the CO stretching frequency. The absolute values of \(\Delta \omega_{c}(C-O)\) computed at the HF or B3LYP levels, Table 1, show that there is a nearly linear relationship between the value of q and \(\omega_{c}(C-O)\): going from Au\(_{5}CO^{+}\) to Au\(_{5}CO^{0}\), the frequency decreases by 74 cm\(^{-1}\), and from Au\(_{5}CO^{0}\) to Au\(_{5}CO^{-}\) there is a further decrease with \(\Delta \omega^{-} = -84\) cm\(^{-1}\). These \(\Delta \omega^{\pm}\) are the HF results with basis set B; similar results are obtained with basis A or at the DFT level, Table 1. The question is therefore if this “constant” shift with the net cluster charge is due to a fortuitous cancellation of terms or rather reflects a regular change in the bonding mechanisms.

| Table 4. Development of the changes in \(\omega_{c}(C-O)\) between Au\(_{5}CO^{0}\) and Au\(_{5}CO^{+}\) and between Au\(_{5}CO^{0}\) and Au\(_{5}CO^{-}\); see text. |
|------------------|------------------|------------------|------------------|------------------|
| **CSOV Contribution** | \(\Delta \omega^{+} (\text{cm}^{-1})\) | **Percent Total** | \(\Delta \omega^{-} (\text{cm}^{-1})\) | **Percent Total** |
| 1. FO | −25 | 34% | −22 | 26% |
| 2. Au \(\pi\) back-donation to CO | −31 | 41% | −35 | 41% |
| 3. CO \(\sigma\) donation to Au | −14 | 18% | −17 | 20% |
| 4. Au polarization | −6 | 8% | −6 | 7% |
| 5. Sum of Terms 1-4 | −76 | - | −80 | - |
| 6. Total SCF | −74 | - | −84 | - |

(a) The largest CSOV contributions to \(\Delta \omega^{+} = \omega(C-O;Au_{5}CO^{+}) - \omega(C-O;Au_{5}CO^{0})\) and \(\Delta \omega^{-} = \omega(C-O;Au_{5}CO^{0}) - \omega(C-O;Au_{5}CO^{0})\) are given along with the percent of the total \(\Delta \omega^{\pm}\). Terms that contribute less than 5% to \(\Delta \omega^{\pm}\) are not listed.

To this end we have considered the \(\Delta \omega^{\pm}\) values for each bonding contribution going from Au\(_{5}CO^{+}\) to Au\(_{5}CO^{0}\) and from Au\(_{5}CO^{0}\) to Au\(_{5}CO^{-}\), Table 4. For the FO wavefunctions, \(\Delta \omega^{+} = -25\) cm\(^{-1}\) and \(\Delta \omega^{-} = -22\) cm\(^{-1}\); not surprisingly, the CO vibrational shift varies linearly with the cluster charge hence with the strength of the associated electric field. This term alone contributes to about 30% of the total relative shift induced by the different charges on the gold cluster. It is less intuitive that the change in \(\omega_{c}(C-O)\) associated to the \(\pi\) back-donation mechanism is also almost linear in q. This is the most
important term contributing to the total shift in $\Delta \omega_e(C-O)$, about 40%, being $\Delta \omega^+ = -31 \text{ cm}^{-1}$ and $\Delta \omega^- = -35 \text{ cm}^{-1}$. Therefore, the modifications in the CO stretching frequency as a function of the oxidation state of a gold nanoparticle are basically determined by these two terms, (a) the purely electrostatic change in field-dipole interaction (Stark effect) partly offset by the change in the surface wall with cluster charge and (b) the change in back donation which varies linearly with the net cluster charge. The remaining terms, CO polarization and CO to Au $\sigma$ donation are much less important as they do not contribute more than 25% of the total $\Delta \omega_e^\pm$ as function of $q$, Table 4. Notice that these four terms are determining the final full SCF $\Delta \omega_e^\pm$, Table 4, and that no other important contributions are missing from this analysis.

4. Conclusions
The charge state of gold nanoparticles is relevant for the understanding of their catalytic activity. CO is widely used as a probe molecule to deduce the oxidized or reduced state of the gold nanoparticle, by studying the changes in the infra-red absorption of the C-O stretching frequency. In this paper we have analyzed in detail the origin of the shift of the vibrational frequency of a CO molecule adsorbed on a small Au$_5^q$ cluster as a function of the net charge $q$. As a reference we have considered the free CO molecule but we have also analyzed the internal shifts in Au$_5^q$CO$^q$ as $q$ changes from +1 to 0 and from 0 to $-1$. The computational results correctly reproduce the trend observed experimentally of a red and blue $\omega(C-O)$ shift, respectively, for negatively positively charged gold; on neutral gold the shift compared to free CO is small. Two contributions are largely responsible for the large shifts in $\omega_e(C-O)$ for $q = \pm 1$: one is the purely electrostatic field-CO dipole interaction, or Stark effect, which is active when a net charge is confined in the small volume of the metal cluster; the Stark term raises the CO frequency for $q = +1$ and lowers it for $q = -1$. This effect, however, is expected to decrease rapidly for larger particles where the net charge is more delocalized and the center of charge of the cluster is likely to be further from the adsorbed CO molecule. The second term which shows the largest variation with the gold oxidation state is the $\pi$ back donation from Au to CO. For Au$_5^-$, this contribution to $\Delta \omega_e$ is twice as large as for Au$_5^+$, thus contributing to the final result of a red shift for reduced gold and a blue shift for oxidized gold. The CO $\sigma$ donation contributions to the shifts of $\omega_e(C-O)$ with charge state of the Au$_5$ are about half as important as the contributions from the $\pi$ back-donation. Other terms, like intra-unit polarization, are much less important.

Acknowledgments
One of us (PSB) wishes to acknowledge support from the U. S. National Science Foundation under grant NSF CHE06-51083. We acknowledge partial computer support from the National Center for Supercomputing Applications, Urbana-Champaign, Illinois. We thank Sabrina Sicolo for help in some of the calculations and we appreciate helpful discussions with Prof. H.-J. Freund. This paper is dedicated to Prof. C. Pisani in occasion of his 70th birthday. One of us (GP) is particularly indebted to Prof. Pisani for all his human support and scientific lessons.

References
[1] Haruta M, Kobayashi T, Sano H, Yamada N 1987 Chem. Lett. 405.
[2] Haruta M, Tsubota S, Kobayashi T, Kageyama H, Genet MJ, Delmon B 1993 J. Catal. 144 175.
[3] Hayashi T, Tanaka H, Haruta M 1998 J. Catal. 178 566.
[4] Haruta M 2002 Cat. Tech. 6 102.
[5] Chen MS, Goodman DW 2004 Science 306 252.
[6] Campbell CT 2004 Science 306 234.
[7] Rodriguez JA, Liu G, Jirsak T, Hrbek J, Chang ZP, Dvorak J, Maiti A 2002, J. Am. Chem. Soc. 124 5242.
[8] Lopez N, Janssens TVW, Clausen BS, Xu Y, Mavrikakis M, Bligaard T, Norskov JK 2004 J. Catal. 223 232.
[9] Boccuzzi F, Chiorino A, Manzoli M, Lu P, Akita T, Ichikawa S, Haruta M 2001 J. Catal. 202 256.
[10] Molina LM, Hammer B 2003 Phys. Rev. Lett. 90 206102.
[11] Yoon B, Häkkinen H, Landman U, Wörz AS, Antonietti J, Abbet S, Judai J, Heiz U 2005 Science 307 403.
[12] Chen MS, Cai Y, Yan Z, Goodman DW 2006 J. Am. Chem. Soc. 128 6341.
[13] Sterrer M, Yulikov M, Fishbach E, He yde M, Rust HP, Pacchioni G, Risse T, Freund HJ, 2006 Angew. Chemie Int. Ed. 45 2630.
[14] Yulikov M, Sterrer M, Heyde M, Rust HP, Risse T, Freund HJ, Pacchioni G, Scagnelli A 2006 Phys. Rev. Lett. 96 146804.
[15] Ricci D, Bongiorno A, Pacchioni G, Landman U 2006 Phys. Rev. Lett. 97 036106.
[16] Sanchez A, Abbet S, Heiz U, Schneider WD, Häkkinen H, Barbett RN, Landman U 1999 J. Phys. Chem. A 103 9573.
[17] Remediakis IN, Lopez N, NorskovJK 2005 Angew. Chem. Int. Ed. 44 1824.
[18] Wang JG, Hammer B 2006 Phys. Rev. Lett. 97 136107.
[19] Valden M, Lai X, Goodman DW 1998 Science 281 1647.
[20] Choudary TV, Goodman DW 2005 Appl. Catal. A: General 291 32.
[21] Lopez N, Norskov J 2002 J. Am. Chem. Soc. 124 11262.
[22] Sterrer M, Yulikov M, Fishbach E, Heyde M, Rust HP, Pacchioni G, Risse T, Freund HJ, 2006 Angew. Chemie Int. Ed. 45 2630.
[23] Yulikov M, Sterrer M, Heyde M, Rust HP, Risse T, Freund HJ, Pacchioni G, Scagnelli A 2006 Phys. Rev. Lett. 96 146804.
[24] Ricci D, Bongiorno A, Pacchioni G, Landman U 2006 Phys. Rev. Lett. 97 036106.
[25] Sanchez A, Abbet S, Heiz U, Schneider WD, Häkkinen H, Barbett RN, Landman U 1999 J. Phys. Chem. A 103 9573.
[26] Remediakis IN, Lopez N, NorskovJK 2005 Angew. Chem. Int. Ed. 44 1824.
[27] Wang JG, Hammer B 2006 Phys. Rev. Lett. 97 136107.
[28] Valden M, Lai X, Goodman DW 1998 Science 281 1647.
[29] Choudary TV, Goodman DW 2005 Appl. Catal. A: General 291 32.
[30] Lopez N, Norskov J 2002 J. Am. Chem. Soc. 124 11262.