# IR Photodissociation Spectroscopy and Theory of $Au^+(CO)_n$ Complexes: Nonclassical Carbonyls in the Gas Phase

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$Au^+(CO)_n$ complexes are produced in the gas phase via pulsed laser vaporization, expanded in a supersonic jet, and detected with a reflectron time-of-flight mass spectrometer. Complexes up to $n = 12$ are observed, with mass channels corresponding to the $n = 2$ and $n = 4$ showing enhanced intensity. To investigate coordination and structure, individual complexes are mass-selected and probed with infrared photodissociation spectroscopy. Spectra in the carbonyl stretching region are measured for the $n = 3-7$ species, but no photodissociation is observed for $n = 1, 2$ due to the strong metal cation-ligand binding. The carbonyl stretch in these systems is blue-shifted 50−100 $cm^{-1}$ with respect to the free CO vibration (2143 $cm^{-1}$), providing evidence that these species are so-called "nonclassical" metal carbonyls. Theory at the MP2 and CCSD(T) levels provides structures for these complexes and predicted spectra to compare to the experiment. Excellent agreement is obtained between experiment and theory, establishing that the $n = 3$ complex is trigonal planar and the $n = 4$ complex is tetrahedral.

## Introduction

Transition metal-carbonyl chemistry has a long and rich history that spans well over a century. Many examples of transition metal−carbonyl complexes have been synthesized and characterized throughout inorganic and organometallic chemistry, and some of these systems are used for homogeneous catalysis.[1,2] At a more fundamental level, transition metal carbonyls are important models for complex systems such as chemisorption on metal surfaces[3] or the binding of small molecules at the active sites of metallo-proteins. Infrared and Raman vibrational spectroscopy of metal carbonyls provides a convenient probe of their chemical environment.[4] Gas-phase metal carbonyl ions have been studied extensively in mass spectrometry,[5−7] and the structures and bonding of these ions have been investigated with theory.[6−20] The reactions of carbonyl ions have been well characterized, and bond energies have been determined,[21−31] but there is much less data on their spectroscopy. However, recent experiments have employed photoelectron spectroscopy to study a variety of metal carbonyl anions, providing vibrational information for the corresponding neutral ground states.[32−36] Infrared spectroscopy of unsaturated neutral metal carbonyls isolated in rare gas matrices have been reported,[7,37−39] and infrared photodissociation measurements have been described for metal cluster carbonyl cations using free electron lasers.[40−45] In the present study, we employ new optical parametric oscillator infrared lasers to investigate the unusual carbonyl complexes of atomic gold cations.

The bonding in transition metal carbonyl compounds is often understood using the classic Dewar−Chatt−Duncanson complexation model.[1,6,7,46−47] In this picture of so-called "classical" metal−carbonyl bonding, two general types of interactions contribute to the formation of the metal−CO bond. The CO contributes electron density from its HOMO on-axis, forming the dative $\sigma$ bond and removing bonding density from the carbonyl orbitals. $\pi$ back-bonding occurs by donation of electron density from the partially filled d shells of the metal into the LUMO of CO. In classical metal carbonyls then, the C−O stretching frequency is lowered and its bond lengthened because of the loss of bonding electron density and the gain of antibonding electron density in the LUMO on CO. The majority of transition metal carbonyl complexes follow this classical behavior. In contrast to this, examples are known of "nonclassical" carbonyl bonding, which usually occurs for systems with filled d electron shells that are not able to donate or accept charge efficiently.[17−18,48−51] The noble metal *atomic* ions are known to form such nonclassical carbonyls in the condensed phase.[48−51] Noble metal *cluster* complexes with carbonyls have been studied in the gas phase by Meijer and co-workers using multiphoton infrared spectroscopy with a free electron laser (FEL).[42−44] However, there is no previous gas-phase spectroscopy for the atomic $M^+(CO)_n$ species of these metals.

Haruta's discovery[52−56] of the ability of gold nanoparticles on a metal oxide support to oxidize CO at low-temperature has stimulated many investigations into the properties of gold clusters supported on metal oxide surfaces.[57−62] In all of these studies, a common theme has been the cooperative effects of the metal cluster and its support. Related to this, both gas-phase experiments and theory have documented the unusual catalytic activity found for small gold clusters and how this varies with cluster size and charge state.[63−73] The intrinsic reactivity of the pure metal cluster system or its support without the metal is difficult to distinguish with experiments or theory. However, gas phase measurements of isolated metal systems may be able to provide needed insight in this area.

Condensed-phase vibrational spectra of cationic gold carbonyls show a marked increase in the stretching frequency of metal-bound CO compared to free gas-phase CO (fundamental = 2143 $cm^{-1}$), earning these compounds the designation as nonclassical carbonyls, as noted above.[6−20,48−51] Numerous

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theoretical studies have discussed the origins of this vibrational blue shift, which appears to be found for only a few systems, including the noble metals.[6−20] Several groups have collected infrared spectra for cationic, neutral and anionic gold-carbonyl clusters frozen in rare-gas matrices.[37−39] Infrared spectra were recorded for CO bound to cationic gold clusters, $Au_n^+$ ($n$ = 3−20) in the gas-phase by Meijer and co-workers.[42−43] In the only other gas-phase spectroscopy, microwave spectra have been obtained for the corresponding neutral gas-phase complexes OCAuX ($X$ = F, Cl, Br, and I).[74,75]

Our research group has studied a number of transition metal cation-ligand systems with infrared photodissociation spectroscopy to investigate their bonding and structure. In particular we have measured infrared spectra for several different metal cations with multiple $CO_2$ ligands.[76−77] We have studied acetylene bound to $Ni^+$ to determine the coordination number as well as the structures of these small clusters.[78] Using the organic carbonyl acetone, we have measured the shifts associated with the carbonyl stretch upon binding to cations such as $Mg^+$, $Al^+$, and $Ca^+$.[79] Furthermore, we have measured infrared spectra for $N_2$ complexes (isoelectronic with CO) with $V^+$ and $Nb^+$.[80] In the present study, we investigate the nonclassical $Au^+(CO)_n$ ($n$ = 3−7) species in the gas-phase using these same methods. Experimental IR spectroscopy is interpreted with ab initio calculations to reveal the structure and bonding in these systems.

## Experimental Section

Gold−carbonyl cation complexes are produced by pulsed laser vaporization (355 nm; Nd:YAG laser) of an 1/8″ gold rod sample mounted in a rotating rod, pulsed nozzle source.[77] The rod holder used in these experiments has the so-called cutaway design.[77] The expansion gas is a mixture of 2% CO in Ar, by partial pressure. Depending on source conditions, various $Au^+(CO)_n$ cluster size distributions are produced. These complexes are detected and mass-selected with a reflectron time-of-flight mass spectrometer, as described previously.[77] Mass spectra are recorded with a digital oscilloscope (LeCroy "WaveRunner" LT342) connected to a PC computer via a GPIB interface. Tunable infrared radiation is produced with a specially designed infrared optical parametric oscillator/amplifier (OPO/OPA) system (LaserVision) pumped with a Nd:YAG laser (Continuum 9010). The line width of the OPO is about 0.3 cm$^{-1}$, and its pulse energy is 1−2 mJ/pulse in the wavelength region of this experiment. Excitation of the mass-selected ions takes place in the turning region of the reflectron, and fragment mass analysis occurs in the flight tube section located after this. Monitoring the fragment ion yield as a function of the infrared frequency generates the infrared spectra in the carbonyl stretching region (2140−2270 cm$^{-1}$).

All calculations were done using the GAMESS[81,82] program suite with the MacMolPlt[83] program used to visualize the molecules. Calculations were performed employing the aug-cc-pVDZ[84] (abbreviated here as ccd), aug-cc-pVTZ[85] (cct), or aug-cc-pVQZ[84] (ccq) basis sets on carbon and oxygen atoms. The gold atom was treated with 19 explicit electrons using the (SBKJC)[85] effective core potential (ECP) with scalar relativistic corrections augmented with a 3f/2g set of polarization functions with f function exponents of 2.00, 0.84 and 0.31, and g function exponents of 1.90 and 0.69, and one set of s and p diffuse functions with exponents of 0.01. Spherical Gaussian functions were used. Second-order perturbation theory (MP2)[86−89] or coupled cluster (CCSD(T))[90] levels of theory were used. The molecules were considered in their full point group symmetries. Molecules were tightly optimized[91−93] with the largest component of the gradient required to be less than $1 \times 10^{-5}$ Hartree/bohr, using MP2 analytical gradients and CCSD(T) numerical gradients.

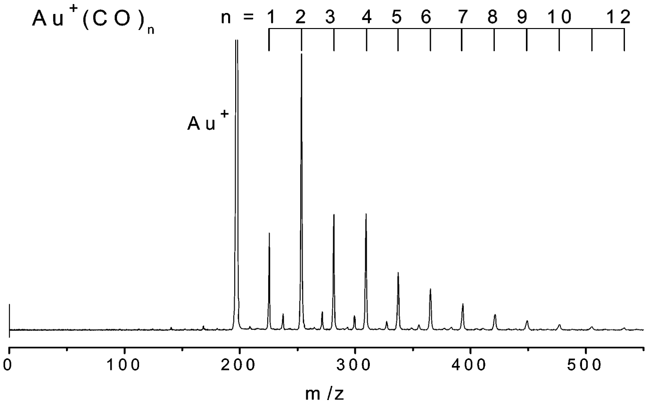

**Figure 1.** Mass spectrum of $Au^+(CO)_n$. The $Au^+$ cation is off-scale, while the small series not labeled is $Au^+(H_2O)(CO)_n$.

Normal-mode analyses[94] were performed using MP2 semi-numerical Hessians and fully numerical CCSD(T) Hessians. Hessians were calculated using double differencing of the energy with 0.01 Bohr displacements from the equilibrium geometry in both positive and negative directions. Anharmonic frequency calculations were performed using the vibrational self-consistent field (VSCF) method.[95] A grid of 16 points was created for each normal mode by making 8 displacements from the equilibrium geometry in both the positive and negative directions. To account for mode−mode coupling, simultaneous displacements from the equilibrium geometry were made along two normal mode displacement vectors; this generates a two-dimensional grid of 16 × 16 points. Electronic structure calculations were performed at each of these points. Anharmonic vibrational frequencies were calculated using a second-order perturbation theory correction for the vibrational self-consistent field calculation.

## Results and Discussion

The laser vaporization source efficiently generates different sizes of gold-carbonyl cations as well as other species with much lower concentrations. Figure 1 shows a mass spectrum of $Au^+(CO)_n$, for n up to 12, where the gold cation peak is off-scale. Depending on source conditions, cluster sizes up to $n = 24$ can be grown, but for this study, the focus is on $n < 7$. The small peaks interspersed between the $Au^+(CO)_n$ peaks are $Au^+(H_2O)(CO)_n$. The salient feature of the mass spectrum is the significantly enhanced intensity for the $n = 2$ mass channel, which occurs independent of source or mass spectrometer focusing conditions. The $n = 4$ mass peak is also somewhat more intense than others near it. These observations suggests that the $n = 2$ or perhaps $n = 4$ complexes are more stable than their neighbors, as would be the case if these are the preferred coordination numbers for gas-phase gold cations.

To investigate the cation coordination in more detail, we measured the fragmentation behavior of these complexes via photodissociation mass spectra. For these measurements, a particular mass channel was selected and the infrared laser scanned in the region where the C−O stretching resonances are expected, until a photodissociation signal was found. Mass spectra were then recorded with the photodissociation laser off and then subtracted from spectra recorded with the laser on. The resulting difference spectrum shows the breakdown of a parent channel into one or more fragment channels. In the case

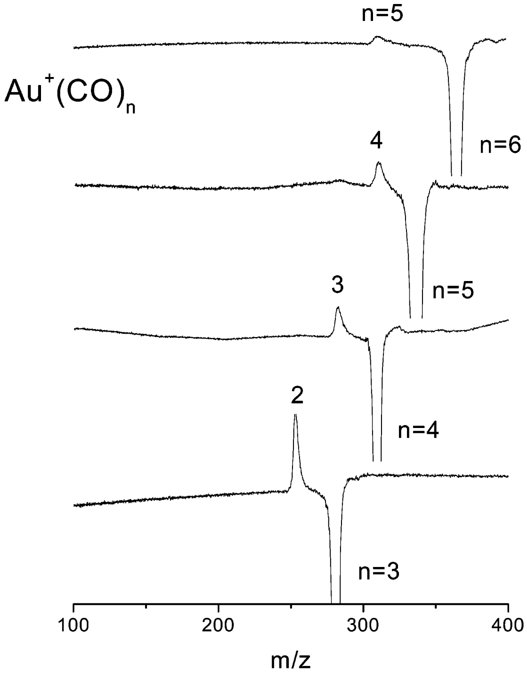

**Figure 2.** Photodissociation mass spectra of Au$^+$(CO)$_n$ ($n$ = 3−6). The parent ion mass peaks are all offscale in the negative direction, while the positive peaks at lower mass are those from the fragment ions. The numbers to the left of the positive peaks indicate the fragment ion formed. Each parent channel fragments by loss of CO. No photodissociation is observed for $n$ = 1 and 2.

of the $n$ = 1 and 2 complexes, no fragmentation signal could be found. We expect that these clusters have IR-active vibrations somewhere in this region, and strong resonances are indeed predicted by theory (see below). The absence of any photodissociation therefore indicates that the cation-carbonyl bonds are too strong to be broken by the infrared excitation at this energy. We therefore conclude that the Au$^+$−(CO) and (CO)Au$^+$−(CO) bond energies are well in excess of the infrared photon energy that would excite the C−O stretches in these complexes, i.e., greater than 2200 cm$^{-1}$ (6.3 kcal/mol). The larger complexes with more CO ligands do give a photodissociation signal, as shown in Figure 2 for the $n$ = 3−6 species. As indicated, there is only one fragment channel for each of these clusters, and that is the loss of a single CO ligand. The laser pulse energy employed here is low (about 1 mJ/pulse, in an unfocused 2−3 mm diameter spot), and these fragmentation channels vary with the laser pulse energy consistent with a single photon process. Therefore, we can conclude that their CO binding energies are less than the photon energy used for each cluster. As shown below, this is about 2200 cm$^{-1}$ (6.3 kcal/mol). The only previous experimental information on these bond energies comes from the work of Schwarz and co-workers.[31] They found a bond energy for Au$^+$(CO) of 1.95 eV (45.0 kcal/mol), consistent with the lower limit obtained here for this ion.

To measure vibrational spectra for these complexes, we record the wavelength dependence of their fragmentation yields. Because the $n$ = 1 and 2 complexes do not photodissociate by eliminating CO, we cannot study these systems in this way. The usual method for investigating strongly bound systems like these is rare-gas "tagging," in which a more weakly bound rare gas atom is added to the complexes to enhance the photodissociation yield.[76−79,96,97] We were able to tag both Au$^+$(CO) and Au$^+$(CO)$_2$ with a single argon atom, producing small amounts of the desired tagged complex ions. However, fragmentation could also not be observed for these tagged complexes. The binding energy of Ar to Au$^+$ in the diatomic ion has been calculated by Pyykko to be ~2600 cm$^{-1}$.[98] In light of this strong Au$^+$−Ar interaction, it is understandable that photofragmentation of Au$^+$(CO)−Ar or Au$^+$(CO)$_2$−Ar may not be efficient near 2200 cm$^{-1}$. A more weakly bound spectator ligand should make it possible to obtain photofragmentation. However, in several attempts, we were unable to successfully tag any Au$^+$(CO)$_n$ species with neon atoms. We therefore were unable to obtain any spectra for the $n$ = 1 and 2 complexes.

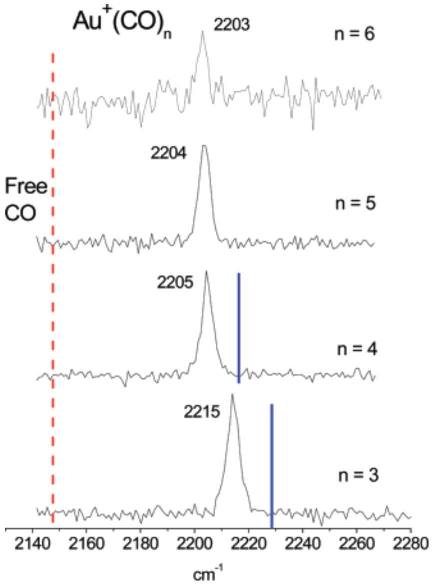

**Figure 3.** Infrared photodissociation spectra of Au$^+$(CO)$_n$ ($n$ = 3−6). The dashed red line indicates the position of the free C−O stretch (2143 cm$^{-1}$), while the blue lines for $n$ = 3 and 4 indicate the calculated frequencies. No photodissociation is observed for $n$ = 1 and 2.

The $n$ = 3−6 complexes do fragment in the 2200 cm$^{-1}$ region, and the resonance-enhanced photodissociation spectra for these complexes are presented in Figure 3. In this figure, the fundamental frequency for the C−O stretch in the isolated CO diatomic molecule (2143 cm$^{-1}$)[99] is indicated with a vertical dashed red line. All of these complexes have spectra with a single peak that is shifted significantly to higher frequency than the C−O stretch in free-CO. The single peak in the C−O stretching region suggests that these complexes have high symmetry, with equivalent CO ligands. Otherwise, more than one IR band would be detected here. We can thus suggest that the $n$ = 3 complex should be trigonal planar and that the $n$ = 4 complex should be square planar or tetrahedral, etc. The $n$ = 3 complex has its band at 2215 cm$^{-1}$, which is shifted 72 cm$^{-1}$ to the blue from the free-CO band. This is the largest blue shift seen here. The $n$ = 4−6 complexes have their bands at almost the same positions. The 2205, 2204, and 2203 cm$^{-1}$ resonances are blue-shifted by 62, 61, and 60 cm$^{-1}$, respectively. As noted earlier, blue-shifted CO vibrations have also been documented previously for the condensed phase Au$^+$(CO)$_n$ complexes and for complexes isolated in rare gas matrices. In the condensed phase, the measured blue-shifts are 52 and 68 cm$^{-1}$ for the $n$ = 1 and 2 complexes, respectively.[48] Our gas-phase spectra begin with the $n$ = 3 complex, so a direct comparison is not possible, but clearly the qualitative trend of blue-shifted CO stretches is maintained. In matrix-isolation studies, shifts of 60 and 50 cm$^{-1}$ were observed for the $n$ = 3 and 4 complexes, respectively.[7] Here, we have a direct comparison to our values of 72 ($n$ = 3) and 62 cm$^{-1}$ ($n$ = 4). It is reasonable to find shifts of 5−10 cm$^{-1}$ caused by the matrix environment, and therefore, this agreement is rather good.

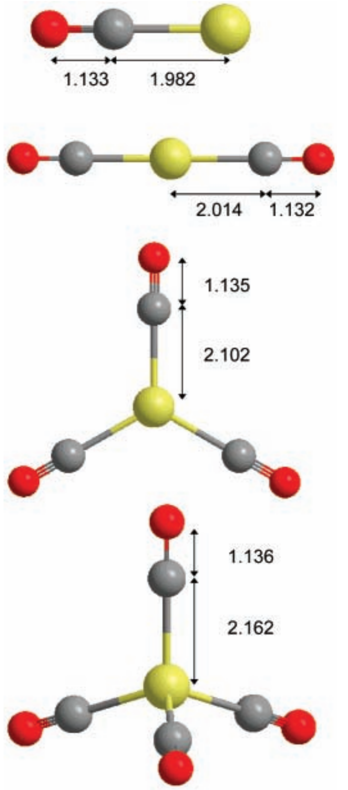

**Figure 4.** Optimized geometries at CCSD(T) level of theory with the ccd basis set on C and O atoms of (a) $Au^+(CO)$ in $C_{4v}$, (b) $Au^+(CO)_2$ in $D_{4h}$, (c) $Au^+(CO)_3$ in $D_{3h}$, (d) $Au(CO)_4$ in $T_d$ point group. The bond distances are in angstroms.

In data not shown, we have also measured a very noisy spectrum for the $n = 7$ complex. Presumably, this complex has one external ligand not coordinated to the gold cation. In previous studies of metal ion-$CO_2$ complexes, we have seen an "unshifted" vibrational band signaling the presence of such external ligands.[76,77] However, in this case, the $n = 7$ spectrum has only one blue-shifted band at 2201 $cm^{-1}$, which is at essentially the same position as the band in the $n = 6$ spectrum. There is no band near the position of the free C−O stretch that would indicate an external molecule. However, because CO has only a small dipole moment, the IR intensity of such a band would be quite low, and it is possible that we would miss it because the signal levels are so small in that spectrum. We also did not see unshifted vibrations in our previous studies of metal ion−$N_2$ complexes,[80] again because the vibrations for ligands not attached to metal have virtually no IR intensity.

To further investigate the origins of these blue-shifted spectra and to determine the structures of the complexes that might be consistent with these shifts, we performed calculations at various levels of theory. The calculations were performed using the same basis set for Au in all cases, while the C and O basis set was varied from ccd to cct to ccq. CCSD(T) optimized molecular geometries employing the ccd basis set are given in Figure 4. As shown in the figure, the optimized structures for both the $n = 1$ and $n = 2$ complexes are linear. The $n = 3$ complex has a trigonal planar structure, and the $n = 4$ complex is found to be tetrahedral. In each complex, the C−O bond distance is slightly longer than it is for the CO diatomic ($r_e = 1.128$ Å).[99] The $Au^+$-C bond distance is about 2 Å, increasing from the shortest value of 1.982 Å for the $n = 1$ complex up to the longest value of 2.162 Å for the $n = 4$ complex.

**TABLE 1: Differential Binding Energies of $Au^+(CO)_n$, $n = 1-4$, in kcal/mol**[a]

| | differential binding energies (kcal/mol) | | | | |
|---|---|---|---|---|---|
| molecule | ccd/ MP2 | cct/ MP2 | ccq/ MP2 | ccd/ CCSD(T) | cct/ CCSD(T) |
| $Au^+(CO)$ | 51.37 | 49.82 | 51.19 | 45.89 | 43.92 |
| $Au^+(CO)_2$ | 58.50 | 56.19 | 56.17 | 51.93 | 49.63 |
| $Au^+(CO)_3$ | 12.52 | 10.73 | | 8.76 | |
| $Au^+(CO)_4$ | 13.27 | 11.80 | | 9.20 | |

[a] Calculations were done at MP2 or CCSD(T) levels of theory using ccd, cct, or ccq basis sets on C and O atoms.

Table 1 presents calculated differential binding energies for these $Au^+(CO)_n$ ($n = 1-4$) complexes. According to these results, $Au^+$ has a quite high affinity for binding the first and second CO molecules, with binding energies in the vicinity of 50 kcal/mol. The $n = 2$ complex has a slightly greater binding energy for its outer CO than the $n = 1$ complex. This kind of increase in bond energy upon addition of a second carbonyl ligand has been seen and discussed previously by Armentrout and co-workers.[21−27] A significant decrease in the binding energy occurs here for the $n = 3$ and 4 complexes, whose outermost CO ligands are computed to be bound by about 10 kcal/mol. The highest differential binding energy, which occurs for the second CO, and the dramatic decrease in binding energy after this, suggests that the preferred coordination number for $Au^+$ in these complexes is two CO ligands, consistent with our experimental findings discussed above. This same value for the coordination number of gold cations has been suggested in previous work on condensed phase complexes, and it has been discussed in terms of an s−d($\sigma$) hybridization model.[9,10,12,14] Such hybridization minimizes the $\sigma$ repulsion between the filled ligand orbitals and those on the metal, thus enhancing the strong electrostatic component in the binding for the first and second ligand. Back-bonding into the $\pi^*$ orbital on CO is also enhanced by this hybridization configuration. However, addition of a third or fourth CO ligand makes the s−d hybridization much less effective, and there is a dramatic drop in the binding energy, as seen here.

The computed binding energies for these complexes are in reasonable qualitative agreement with our experimental data. We find that the binding energy of the outermost CO ligands in the $n = 1$ and 2 complexes is greater than the 2200 $cm^{-1}$ photon energy, which then places a lower limit on this binding of 6.3 kcal/mol. The computed values in the 40−50 kcal/mol range at different levels of theory are all consistent with this limit, but much higher in value. For the $n = 1$ complex, the present computed value is in good agreement with the previous experimental result of Schwarz (1.95 eV; 45.0 kcal/mol)[31] and in good agreement with the previous computed value reported by Dargel et al. (2.08 eV; 48.0 kcal/mol)[8] at the CCSD(T) level. Our theory here is also consistent with our experiment in the qualitative suggestion that the binding energy drops significantly after $n = 2$ for the $n = 3$ and 4 complexes. However, the quantitative values for the binding energies, which are 8−10 kcal/mol at different levels of theory, are higher than our experimental values. Because we observe efficient photodissociation for the $n = 3-6$ complexes at about 2200 $cm^{-1}$, we can place a firm upper limit on the outermost CO binding energy of 6.3 kcal/mol.

To improve the computed thermochemistry, the CCSD(T)/cct differential binding energies can be estimated by assuming that improvements due to the use of larger basis sets (e.g., cct vs ccd) and improvements due to the use of higher levels of theory (e.g., CCSD(T) vs MP2) are approximately independent of each other. This assumption is fundamental, for example, in the popular GN methods of Pople and co-workers.[100] Using the

**TABLE 2: Experimental and Calculated Vibrational Frequencies for $Au^+(CO)_n$ ($n$ = 1−6) in $cm^{-1}$[a]**

| | theory | | | | | | |
|---|---|---|---|---|---|---|---|
| molecule | ccd/ MP2 | cct/ MP2 | ccq/ MP2 | ccd/ CCSD(T) | cct/ CCSD(T) | ccq/ CCSD(T) | experiment |
| CO | 2114 | 2122 | 2129 | 2144 | 2154 | 2164 | 2170 |
| CO anharm | 2088 | 2096 | 2102 | 2118 | 2128 | 2138 | 2143 |
| $Au^+(CO)$ | 2189 | 2194 | 2204 | 2247 | 2257 | | |
| $Au^+(CO)$ anharm | 2157 | 2162 | | 2216 | 2225 | | 2195[b] |
| $Au^+(CO)_2$ | 2207 | 2216 | 2226 | 2269 | 2280 | | 2211[b] |
| $Au^+(CO)_3$ | 2163 | 2173 | - | 2229 | | | 2215 |
| $Au^+(CO)_4$ | 2149 | 2160 | - | 2218 | | | 2205 |
| $Au^+(CO)_5$ | | | | | | | 2204 |
| $Au^+(CO)_6$ | | | | | | | 2203 |

[a] Experimental data for CO are taken from the NIST database.[99] Photodissociation for $n$ = 1, 2 was not observed. Calculations were done at MP2 or CCSD(T) levels of theory using ccd, cct, or ccq basis sets on C and O atoms. Except as noted, the calculations are harmonic with no vibrational scaling applied. [b] Reference 48, in a superacid matrix.

values in Table 1, this approach reduces the $n = 3$ and $n = 4$ differential binding energies to ∼5 and ∼5.2 kcal/mol, respectively, which are well within the experimental range. Further improvement to the ccq basis set is expected to have a small effect in the same direction. So, the experiment and theory here both support the dramatic drop in the ligand binding for the third and fourth CO, as suggested by the s−d hybridization model.

The most quantitative comparison between theory and experiment is in the vibrational frequencies for these complexes. Table 2 shows the values computed at different levels of theory and the comparison of these values to the experimental frequencies of the C−O stretching mode in CO and for the various $Au^+(CO)_n$ complexes. The accuracy of the calculated MP2 vibrational frequencies for CO improves somewhat by improving the basis set from ccd to ccq, with the biggest improvement obtained from ccd to cct. The accuracy of the calculations improves by going from MP2 to CCSD(T), as one might expect. The CCSD(T) predicted frequencies are nearly independent of basis set. This suggests that one can achieve satisfactory accuracy at a relatively low computational cost by doing CCSD(T) with a modest basis set, such as ccd.

The basis set choice has a negligible effect of 1−3 $cm^{-1}$ on the accuracy of the calculated frequency shifts for $Au^+(CO)_n$, $n = 1-4$. Although both MP2 and CCSD(T) correctly predict the trend in the magnitude of the frequency shifts, the MP2 calculations are only qualitatively correct; this suggests the necessity of doing CCSD(T) calculations to get within 10 $cm^{-1}$ of experiment. Including the anharmonicity in the frequency calculations should additionally improve the accuracy; however, there are no available experimental data for $Au^+(CO)$,and the high computational cost of VSCF calculations for $Au^+(CO)_n$, $n = 3$ and 4, is difficult to justify if the gain in accuracy is small. The frequency for $Au^+(CO)$ at the highest level here (2225 $cm^{-1}$) is slightly higher than that computed previously by Neumaier et al. (2211 $cm^{-1}$) at the DFT-BP86 level,[69] and much greater than that obtained by Lupinetti et al. (2177 $cm^{-1}$) using a combination of CCSD(T) and MP2.[10]

Analysis of the calculated and experimental data shows that the C−O stretching frequency is higher in the bound than in the free CO molecule, with an interesting dependence of the magnitude of the frequency shift on the number of CO molecules bound to $Au^+$. This trend in computed $\Delta\nu$ can be summarized as $Au^+(CO)_2 > Au^+(CO) > Au^+(CO)_3 > Au^+(CO)_4$. The frequency of the C−O stretch increases upon binding of CO to $Au^+$ by about 100 $cm^{-1}$. There is an additional increase of about 25 $cm^{-1}$ upon binding of the second CO to $Au^+(CO)$, leading to an increase of about 125 $cm^{-1}$ in the C−O stretching frequency in $Au^+(CO)_2$ compared to that in the free CO molecule. However, the magnitude of the computed shift in the C−O stretching frequency is significantly reduced to ∼ 85 $cm^{-1}$ by the binding of the third CO. Binding of the fourth CO molecule leads to a very small change of less than 10 $cm^{-1}$, suggesting that there is a leveling off of the magnitude of the C−O frequency shift in $Au^+(CO)_n$.

Unfortunately, as noted above, we are not able to measure spectra here for the $n = 1$ and 2 complexes. However, these species have been studied previously in the condensed phase environment of a superacid matrix by Willner and Aubke.[48] In this environment, the CO stretching frequencies found for the $n = 1$ and $n = 2$ complexes were 2195 and 2211 $cm^{-1}$, which are both considerably lower than the values computed here. However, it is not clear what effect, if any, the superacid matrix has on these spectra. The computed vibrations can be compared directly to our gas-phase experiment in the case of the $n = 3$ and 4 complexes. At the highest level of theory (ccd/CCSD(T)), the harmonic frequency computed for the $n = 3$ complex is 2229 $cm^{-1}$, compared to the experimental value of 2215 $cm^{-1}$. For $n = 4$, the computed value is 2218 $cm^{-1}$ versus the experimental value of 2205 $cm^{-1}$. As indicated, these unscaled harmonic values are each slightly higher than the experimental values. However, the approximate value of the blue-shifted vibrations is reproduced, as is the trend of a larger shift for the $n = 3$ complex. We can use the $Au^+(CO)$ data, where both harmonic and anharmonic values were computed, to derive a scaling factor to apply to correct the larger complex spectra for the effects of anharmonicity. If we do this, we obtain a scaling factor of 0.986. Applying this to the ccd/CCSD(T) frequencies computed for the $n = 3$ and 4 complexes produces scaled frequencies of 2197 and 2186 $cm^{-1}$, which are unfortunately lower than and even further away from the experimental values. Therefore, there is no advantage to scaling the computed frequencies.

The shifts to higher vibrational frequencies occurring in these nonclassical systems have been discussed extensively in the literature.[6] The binding interaction is expected to involve $\sigma$-donation from the $5\sigma$ carbonyl HOMO and $\pi$ back-donation into the $2\pi^*$ LUMO. As noted for other metal carbonyl complexes, the back-donation is expected to be a much more significant factor in bond energies and frequency shifts.[6] However, because of the $d^{10}$ configuration and the charge on the metal, back-donation here is inefficient. Early proposals for the origin of the shift to higher C−O stretching frequencies claimed that the $5\sigma$ orbital of CO has partial antibonding character.[6] If this is true, then OC → $Au^+$ $\sigma$ donation would remove the density in this orbital, thus strengthening the bond and driving the C−O stretch to higher values, as seen experimentally. However, using a combination of CCSD(T) and MP2 methods, Lupinetti et al. investigated this proposal carefully with studies that compared the effect of placing a charged atom at either of the two ends of the carbonyl.[10] They found that attachment at the oxygen end did not produce the same frequency shift as attachment at the carbon end. The purported removal of 5$\sigma$ antibonding character should have been possible in either configuration, thus refuting this explanation. Instead, Lupinetti et al. suggested that an electrostatic orbital polarization effect is responsible for the C−O blue shift.[10] In the isolated CO, the bonding orbitals in the valence shell have more electron density on the oxygen, and are thus unbalanced, which limits the effectiveness of the binding. However, attachment of an ion on the carbon end of CO induces a polarization that effectively balances the orbital density on both atoms, thus enhancing the binding. This is the effect that is now generally attributed to cause the C−O stretch to shift to higher frequencies in these nonclassical systems.[6,10] Consistent with this suggestion, the $HCO^+$ ion, which also cannot have $\pi$ back-donation, is calculated to have a blue-shifted C−O stretch, but the $HN_2^+$ complex, which has exactly balanced charge on its “ligand”, does not (it is predicted to be red-shifted).[6] To test these ideas further, it would be interesting to study the corresponding $Au^+(N_2)_n$ complexes. According to the present model, the N−N stretch in these systems would shift in the opposite direction to the C−O stretches seen here. Likewise, the corresponding *neutral* $Au(CO)_n$ complexes (which have not been studied) would have limited back-donation, but no ability to polarize the CO ligands, and so we might predict hardly any shift relative to free CO for these systems.

It is interesting to compare the vibrational shifts seen here for the atomic gold cation complexes to those documented previously for gold *cluster* ions. Fielicke et al. previously investigated the gold cluster cation complexes containing 3−10 atoms[42] and the corresponding gold cluster anion clusters containing 3−14 atoms.[43] In these systems with different numbers of carbonyl ligands, the cations were found to have C−O stretching frequencies that were higher than the free molecule, while the anions were found to have C−O frequencies lower than the free molecule. The anions have additional electron density, making $\pi$ back-bonding possible, which then places electron density in the $\pi^*$ LUMO of CO, driving the frequency to lower values. This is the pattern seen for classical carbonyls of most other metals. In the cluster cations, however, the same kind of blue shift seen here is observed, but its magnitude is less. For example, the C−O stretch for $Au_3^+$ occurs at 2180 $cm^{-1}$.[42] Apparently, when the charge in a cluster cation is shared over more atoms, the polarization effect noted above is diluted, and the blue shift in the C−O frequency is less in the cluster complex than it is in the atomic ion complex. Consistent with this charge dilution effect, the blue shift is gradually less as larger gold cluster carbonyls are studied.[42]

## Conclusions

Complexes of $Au^+(CO)_n$ have been generated with a laser vaporization source and investigated with infrared photodissociation spectroscopy and theoretical calculations at the MP2 and CCSD(T) levels of theory. Mass spectra and photodissociation patterns indicate that gas-phase gold-carbonyl complexes have a preferred coordination number of two, consistent with the pattern of binding energies computed. The vibrational spectra of $Au^+(CO)_n$, $n = 3-6$, all exhibit significant blue-shifts from the free carbon monoxide stretch, as observed previously in both condensed phase measurements and matrix-isolation studies, indicating nonclassical carbonyl behavior. No gas-phase experimental data is available for the $n = 1$ and 2 complexes. Single bands are observed for each of the complexes studied in the C−O stretching region, consistent with high-symmetry structures. Calculations done at the CCSD(T) level of theory with cct basis sets for C and O atoms yields best agreement with the experimental vibrational frequencies. More importantly, theory and experiment are in excellent agreement on the values and the trends of the vibrational shifts. We can therefore conclude that $Au^+(CO)_3$ has a trigonal planar structure and $Au^+(CO)_4$ has a tetrahedral structure.

The picture of the bonding in these complexes is therefore one of a dative interaction in which the lone pair density from the carbonyl ligand is nominally donated into the empty s orbital of the $Au^+$ ion. s−d hybridization minimizes the ligand repulsion, enhancing the binding strength. This interaction saturates at two ligands, as discussed previously. The dominant effect of the electrostatic bonding polarizes the CO ligand, shifting its vibrational frequency to values higher than those in the free CO molecule. These effects have been discussed at length in previous theoretical work, and they have been documented experimentally for the ionized $Au^+(CO)_2$ complexes in the condensed phase with counterions present. However, this combined experimental and computational study documents the expected trend in the bond energies and provides the first view of the frequency shifts for the larger $n = 3-6$ complexes. The blue shifts in these vibrations for atomic gold cation complexes are greater than those seen previously for carbonyl complexes of gold cluster cations.

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