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Infrared Photodissociation Spectroscopy of Copper Carbonyl Cations

A. D. Brathwaite, Z. D. Reed, and M. A. Duncan*

Department of Chemistry, University of Georgia, Athens, Georgia 30602, United States

Ⓢ Supporting Information

ABSTRACT: Copper carbonyl cations of the form $Cu(CO)_n^+$ ($n = 1-8$) are produced in a molecular beam via laser vaporization in a pulsed nozzle source. Mass-selected infrared photodissociation spectroscopy in the carbonyl stretching region is used to study these ions and their argon "tagged" analogues. The geometries and electronic states of these complexes are determined by the number of infrared-active bands, their frequency positions, and their relative intensities compared to the predictions of theory. $Cu(CO)_4^+$ has a completed coordination sphere, consistent with its expected 18-electron stability. It also has a tetrahedral structure similar to that of its neutral isoelectronic analog $Ni(CO)_4$. The carbonyl stretch in $Cu(CO)_4^+$ (2198 cm^{-1}) is blue-shifted with respect to the free CO vibration (2143 cm^{-1}), providing evidence that this is a "non-classical" metal carbonyl.
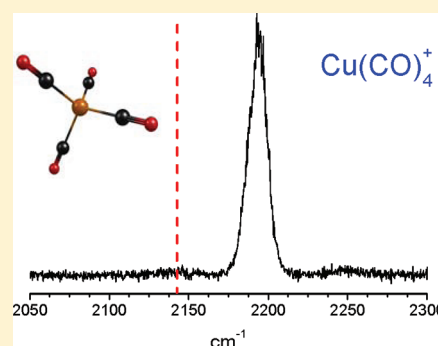
■ INTRODUCTION

Transition metal carbonyls are ubiquitous in inorganic and organometallic chemistry, where they provide prototypical examples of metal−ligand bonding and have applications in catalysis.[1−4] Transition metal carbonyls also provide models of more complex systems such as chemisorption on the surface of metals[5] or the binding at active sites of metallo-proteins.[6] In all these contexts, the carbonyl stretching frequency (ν_{CO}) provides a sensitive indicator of the metal−ligand bonding geometry and the chemical environment of these systems.[1−9] The spectroscopy of neutral metal carbonyls is well-known, but these studies have been extended to cations only recently.[9,10] In the present work, we use infrared spectroscopy in the C−O stretching region to investigate the carbonyl complexes of copper cations in the gas phase.

Metal carbonyl ions have been studied extensively in the gas phase using mass spectrometry.[11−17] Their structures and bonding have also been investigated with theory.[8−10,18−22] Reactions involving metal carbonyl ions have been well characterized and the dissociation energies of many metal cation-CO complexes have been measured.[14−17] However, there is significantly less data on the spectroscopy of these species. Stable neutral transition metal−carbonyls have been studied using infrared spectroscopy in both the gas phase and condensed phase environments.[23−27] In an effort to investigate isoelectronic analogues, various charged metal carbonyls have been produced in the condensed phase as salts with counterions, and studied using spectroscopy.[28−31] Unsaturated metal carbonyl ions have been produced in rare gas matrices and studied with infrared spectroscopy.[9,18] Photoelectron spectroscopy of mass-selected anions has provided information about the ground states of neutral carbonyls, including unsaturated species.[32−35] Multimetal atom cluster carbonyls have been studied by photodissociation spectroscopy with infrared free electron lasers.[36−39] In all of these systems, the C−O stretch vibrations vary systematically depending on the metal atom, charge, electronic structure, and bonding configuration. These effects have been studied extensively with theory.[8,9,18−21]

The shifts of metal carbonyl vibrational frequencies compared to that of the free CO molecule are usually discussed using the Dewar−Chatt−Duncanson complexation model.[1−9,19,21,22] In this framework of metal carbonyl bonding, two main interactions influence the vibrational frequencies. The first is σ donation, in which the carbonyl donates electron density from its highest occupied molecular orbital (HOMO) along the metal−CO bond axis into empty metal d orbitals. Because this HOMO has partial antibonding character, this strengthens the bond and tends to increase the vibrational frequency. The second interaction is π back-bonding, in which partially filled metal d orbitals donate charge into the antibonding lowest unoccupied molecular orbital (LUMO) on CO. Back-bonding is facilitated because the metal d orbitals overlap spatially with the CO antibonding orbital. Electron density in this orbital weakens the bond and reduces the vibrational frequency. In classical metal carbonyls, π back-bonding usually dominates over σ donation and the C−O stretch is lower (i.e., red-shifted) than that of the free CO molecule (fundamental = 2143 cm^{-1}).[40]

Most transition metal carbonyls follow the classical bonding model, but some of these systems exhibit so-called "nonclassical" bonding. This occurs when there are filled d orbitals and the metal is unable to accept or donate charge effectively.[9,19−22,41] In these systems, electrostatic polarization can also play a role in the metal−ligand interaction.[9,19−22,41] Several investigators have recognized the importance of such polarization,[19,21,22] noting that the CO$^+$ cation has a higher vibrational frequency (fundamental = 2184 cm^{-1})[40]

than the corresponding neutral. It has been suggested that polarization by cation binding gives CO a partially positive charge and redistributes the otherwise imbalanced electron density in its bond.[21] This strengthens the bond and results in a higher C—O frequency. A blue-shifted C—O stretch is therefore the signature of these nonclassical carbonyls. Unfortunately there are few spectroscopic studies of gas phase carbonyl cations in which these interactions have been explored.

Our research group has studied the infrared spectra of various metal cation carbonyl complexes in the gas phase using mass-selected ion photodissociation spectroscopy.[10,42−44] Although many of these systems had carbonyl stretches that were slightly red-shifted or had nearly no shift with respect to isolated CO, the $Au(CO)_n^+$ system exhibited blue-shifted CO vibrations, as expected for a nonclassical system.[42] In the present study, we apply the same methods to study cationic copper carbonyls, $Cu(CO)_n^+$ for $n = 1−8$. $Cu(CO)_4^+$ is predicted to be stable, as it satisfies the 18-electron rule and is isoelectronic to the well-known neutral $Ni(CO)_4$. $Cu(CO)_n^+$ complexes have been studied in strongly acidic media,[45] where the $[Cu(CO)_n]^−[AsF_6]^+$ ($n = 1−3$) salts were synthesized and characterized using IR and Raman spectroscopy.[46] This study concluded that $Cu(CO)_2^+$ and $Cu(CO)_3^+$ have $D_{\infty h}$ and D_{3h} symmetry, respectively and that the ions have blue-shifted CO frequencies. Copper carbonyl cations have also been studied in the gas phase, where the dissociation energies of $Cu(CO)_n^+$ ($n = 1−4$) species were measured by Armentrout and co-workers.[14c] The bond energy of $Cu(CO)_3^+$-CO was determined to be 0.55 eV (4440 cm^{-1}), demonstrating that up to four CO ligands are directly coordinated to the central copper ion. $Cu(CO)_n$ neutrals and ions have also been isolated and studied with infrared spectroscopy in rare gas matrices.[18b] Here we report infrared photodissociation spectroscopy in the gas phase for both the small unsaturated complexes $Cu(CO)_n^+$ ($n = 1−3$), and the larger complexes at and beyond the filled coordination ($n = 4−7$). Density functional theory (DFT) calculations are carried out to aid in the interpretation of the experimental spectra.

■ EXPERIMENTAL SECTION

$Cu(CO)_n^+$ ions are produced in a pulsed nozzle laser vaporization source using the third harmonic of a pulsed Nd:YAG laser (355 nm; Spectra-Physics GCR-150). The laser is focused onto a rotating and translating 1/4 in. diameter metal rod mounted on the front of a pulsed nozzle (General Valve Series 9) in the so-called cutaway configuration.[47] The expansion gas is pure carbon monoxide (National Specialty Gas) at a backing pressure of 150 psi. Cluster ions of the form $Cu(CO)_n^+Ar$ are produced using gas mixtures of 10% CO in argon. The expansion is skimmed into a second chamber where positive ions are pulse-extracted into a homemade reflectron time-of-flight mass spectrometer.[47] Ions of a specific mass are selected by their flight time using pulsed deflection plates located at the end of the first flight tube. These ions are excited in the turning region of the reflectron with the tunable output of an infrared Optical Parametric Oscillator/Amplifier (OPO/OPA) system (LaserVision) pumped by a Nd:YAG laser (Spectra Physics Pro 230). This system provides infrared light in the region 2000−4000 cm^{-1} with a line width of about 1 cm^{-1}. When the output of the infrared laser is on resonance with a vibration of the complex, absorption and intramolecular vibrational energy relaxation (IVR) take place on a time scale much smaller than the residence time in the reflectron (1−2 μs), leading to dissociation of the complex.
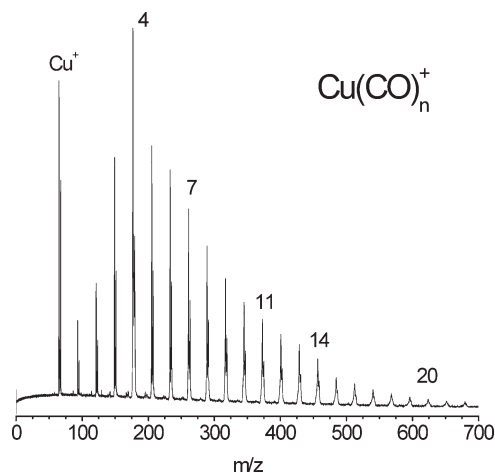

Figure 1. The mass spectrum of $Cu(CO)_n^+$ complexes produced by laser ablation of a copper rod in an expansion of carbon monoxide.

Infrared spectra are obtained by monitoring the appearance of one or more fragment ions as a function of the laser wavelength.

In support of the experimental studies, DFT calculations were carried out to determine the structures and spin configurations of $Cu(CO)_n^+$ and $Cu(CO)_n^+Ar$ complexes, considering the singlet and triplet states of each cluster size. The calculations were performed using the B3LYP functional[48,49] as implemented in the Gaussian 2003 computational package.[50] The Wachters + f basis set[51] was used for Cu atoms, the DZP basis set[52] was used for carbon and oxygen atoms, and the 6-311++G** basis set was used for argon. The same functional and similar basis sets were used previously by Schaefer and co-workers to calculate the structure and infrared spectra of binuclear copper carbonyls.[53] In the present work, the computed frequencies are scaled by a factor of 0.971 and are given a 3 cm^{-1} full width at half-maximum (fwhm) Lorentzian line shape for comparison to the experimental spectra. We derived this scaling factor by calculating the frequencies of the well-known stable neutral metal carbonyls, $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$, and finding the average value needed to make their experimental and calculated frequencies coincide.

■ RESULTS AND DISCUSSION

A mass spectrum of the $Cu(CO)_n^+$ complexes produced by our source is shown in Figure 1. All peaks are doubled because of the 63 and 65 amu isotopes of copper. The most intense peak corresponds to $Cu(CO)_4^+$, indicating that this complex is formed preferentially and suggesting that it may have enhanced stability. This cation is expected to be stable, as it satisfies the 18-electron rule and is isoelectronic to the stable neutral $Ni(CO)_4$. $Cu(CO)_n^+$ complexes out to $n = 20$ or more are observed. The CO ligands in these larger complexes cannot possibly all be directly coordinated to the central metal ion. Instead, larger complexes likely have "external" COs not bound directly to the central metal ion, but coordinated to other carbonyls via weaker electrostatic forces.[10] The formation of these larger complexes is possible because of the cold supersonic expansion conditions, and they are not likely to be stable at room temperature. Further insight into the relative stability and coordination of these complexes can be obtained by their fragmentation behavior. Small $Cu(CO)_n^+$ complexes ($n = 1, 2$) do not fragment

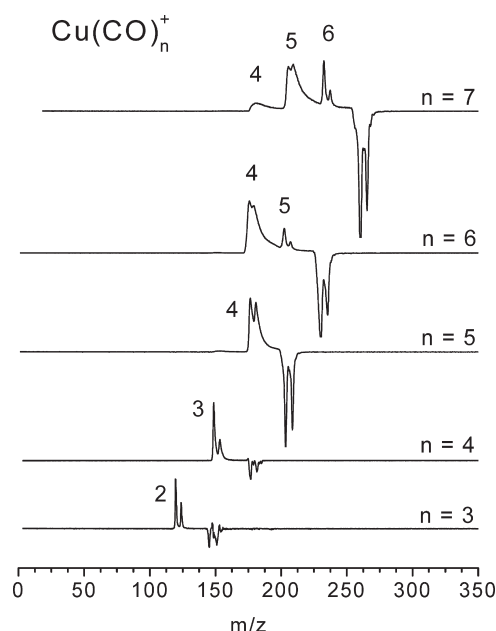**Figure 2.** The photofragmentation mass spectra of $Cu(CO)_n^+$ species, showing the fragmentation channels resulting from infrared excitation near the carbonyl stretch. The negative peak represents the depletion of the mass-selected parent ion, while the positive peaks represent the resulting fragments.

Figure 3. The infrared photodissociation spectra of the small $Cu(CO)_n^+(Ar)$ complexes, detected by the elimination of argon. The dashed red line indicates the frequency of gas phase CO.

when excited with infrared light, consistent with the bond energies (1.54, 1.78 eV, respectively for the elimination of the last CO from n = 1, 2), measured previously by Armentrout and co-workers.[14c] These bond energies are much greater than the energy of IR photons in the CO stretching region (2200 cm^{-1} is approximately 0.27 eV). Therefore it is not surprising that no fragmentation is observed for these complexes. Larger complexes do dissociate, and the infrared induced fragmentation mass spectra for $Cu(CO)_n^+$ (n = 3−7) complexes are shown in Figure 2. These data are collected by taking the difference between the mass spectra for a selected complex obtained with the photodissociation laser on versus off, when the IR wavelength is adjusted to the most intense resonance for each cluster size. The negative peak indicates depletion of the parent ion via dissociation, whereas the positive peaks indicate the fragment ions produced. The n = 3 and 4 complexes are not expected to dissociate in the infrared because of the high binding energies measured for these complexes (0.78 and 0.55 eV, respectively).[14c] The signal detected is likely due to multiphoton absorption or from a fraction of the ions containing residual internal energy from the growth process. Multiphoton absorption is not expected to be very efficient at the low laser pulse energies used here (about 1 mJ/pulse), but can be detected if the IR oscillator strength is high. Residual internal energy from inefficient cooling of a fraction of the clusters could add together with the photon energy, making photodissociation possible below the threshold for cold clusters. Clusters larger than n = 4 are expected to dissociate via a single photon process, and indeed the signal levels here are greater. The fragmentation of all of these larger species terminates at n = 4, consistent with the stability of this core ion and the presence of only weakly bound external carbonyl ligands beyond this size. This confirms our expectation that the tetra-coordinate complex has a filled coordination. As shown in the figure, the mass peaks for complexes larger than n = 4 show
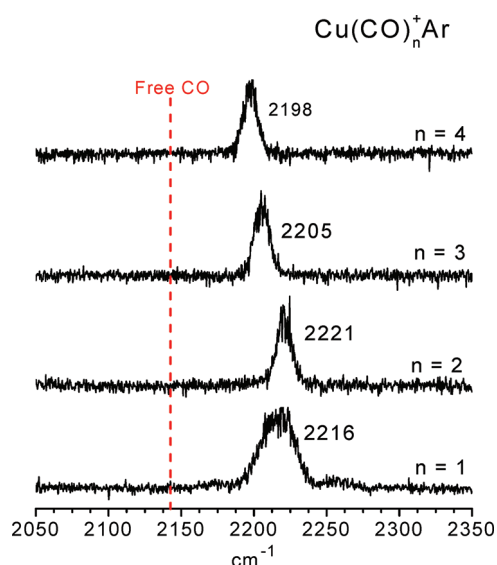
substantial tailing in time. This kind of "metastable" dissociation is well-known in time-of-flight mass spectrometry, and indicates that the dissociation takes place on a time scale comparable to the residence time in the reflectron ($\sim$1 μs). It is interesting, however, that we have not seen such behavior for any other metal carbonyl that we have studied. Instead, other systems appear to dissociate promptly on a time scale much faster than this. It is not clear why copper carbonyl cations would dissociate more slowly than other similar systems.

To examine the spectroscopy of these systems, we measure the wavelength dependence of these fragmentation processes. As noted above, the energy of IR photons near the CO stretching region is not sufficient to cause efficient dissociation of the smaller clusters. We therefore employ the rare gas "tagging" technique to enhance the dissociation yield for these systems.[47,54−57] We produce mixed complexes of the form $Cu(CO)_n^+Ar$, which can fragment by eliminating argon after photoexcitation of the ligand vibrations. The effect of tagging on the spectrum of these complexes is a valid concern. In some systems argon can bind strongly and act essentially as a ligand, causing the spectrum to be perturbed in comparison to that for the same cluster without tagging. The argon binding energy in these complexes has not been measured, but is calculated in the Cu−Ar$^+$ diatomic to be 0.405 eV (3270 cm^{-1}).[58] Although this is more than the energy of an IR photon in the CO stretching region, the binding of argon in the mixed complexes is expected to be lower than this value (see computational results below). The presence of CO ligands usually results in dilution of the charge-induced dipole interaction. Previous experience with similar systems indicates that tagging usually has a negligible effect on the structure and spectrum of these complexes.[10,42−44,47] However, we exercise due caution in interpreting these spectra and conduct computations on both the tagged and neat complexes to evaluate these effects.

Figure 3 shows the spectra of the n = 1−4 complexes measured by tagging with argon. Tagging with a single argon is sufficient to achieve efficient photodissociation for all complexes. The dashed vertical line indicates the position of the free CO stretch at 2143 cm^{-1}. All the spectra for the $Cu(CO)_n^+Ar$ complexes feature
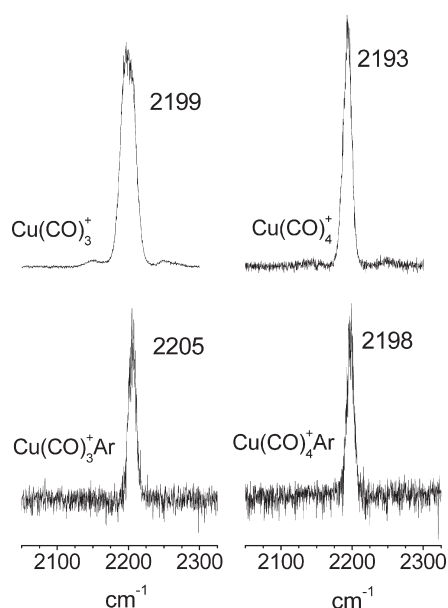
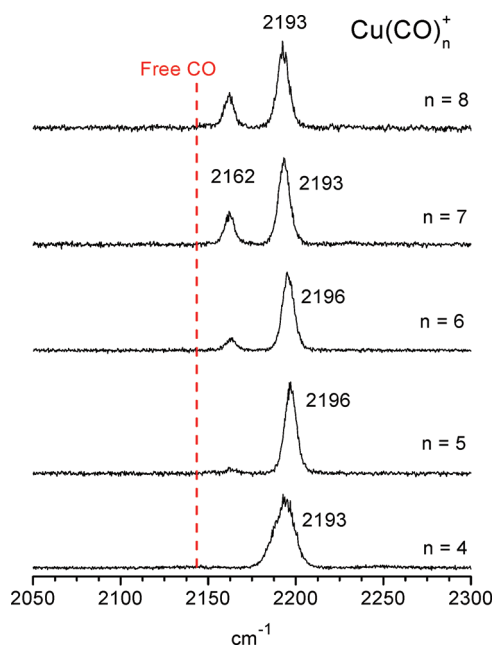**Figure 4.** The infrared spectra of $Cu(CO)_3^+$ and $Cu(CO)_4^+$ and their corresponding argon tagged analogues.

Figure 5. The infrared spectra of the $Cu(CO)_n^+$ complexes detected in the loss of CO mass channel.
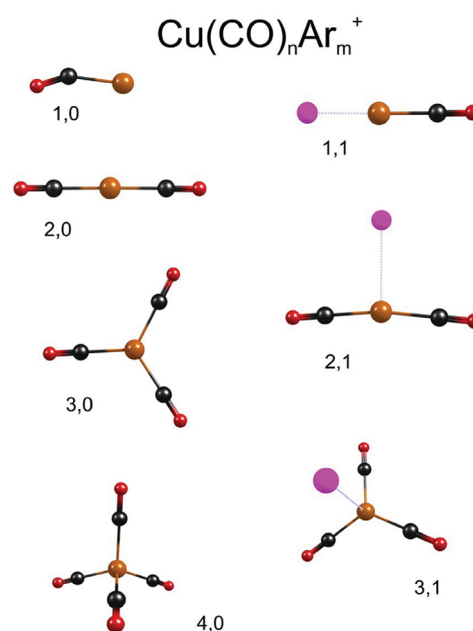

Figure 6. The structures for copper cation carbonyls resulting from DFT computational studies.

We investigate these structures, as well as ligand binding energies and spin states in the computational work described below.

Complexes containing three or more carbonyls dissociate without tagging. Though relatively inefficient, photodissociation via loss of CO was observed for the $n = 3$ and 4 complexes, allowing a comparison of neat and tagged spectra for these species, as shown in Figure 4. The tagged ion spectra have lower signal levels because the densities of these ions are much less than those of the corresponding neat species. In both examples the peak positions in the tagged spectra are shifted by approximately 5 cm^{-1} to the blue from those in the neat complexes. Also, for both sizes, the neat spectra are broader than those obtained with tagging. This is understandable because of the higher binding energies of these ions, which limit single-photon dissociation unless the complex has significant internal energy. Because the untagged spectra are biased toward hotter molecules, the tagged $n = 3$ and 4 complexes are expected to give the most accurate representation of their spectra.

Spectra for the $n = 4-8$ complexes, obtained by monitoring the loss of CO ligands, are shown in Figure 5. Each of these has a single band that is shifted by approximately 50 cm^{-1} to the blue from the free-CO stretch, in about the same position as the bands in the spectra for the $n = 1-4$ complexes measured with tagging. The neat $Cu(CO)_5^+$ complex and the tagged $Cu(CO)_4Ar^+$ complex have essentially the same spectra, consistent with the weak binding interaction expected for argon and the second-sphere CO. For each of the complexes larger than $n = 4$, a second weaker band near 2162 cm^{-1} is observed that increases in intensity with cluster size. Consistent with previous observations for other metal ion carbonyls,[10,42-44] we assign this band to the vibration of external CO molecules. The single band in the C—O stretching region, along with the external CO band that appears after this size, are both consistent with a tetra-coordinate $Cu(CO)_4^+$ as the core ion. Clusters larger than $n = 4$ have the spectrum of this core ion that is progressively solvated by external CO molecules. The solvation interaction changes the position of the $n = 4$ complex band only slightly.

an intense single band that is shifted to higher frequency than this value, consistent with our expectations for nonclassical behavior. The band obtained for $Cu(CO)^+Ar$ is weaker and broader than those for the larger complexes, suggesting that its dissociation is not as efficient. This is not surprising, as the argon binding to a monoligand complex is likely to be relatively strong, and therefore single photon dissociation may not be possible. Photodissociation of species in which the energetics are marginal may be biased toward warmer molecules containing residual internal energy, thus causing the greater line width.[47] The single-band spectra seen for each of these complexes immediately suggest high symmetry structures.

Table 1. Structures, Electronic Ground States and Relative Energies for Cu(CO)$_n^+$ Complexes Computed Using DFT

complex	spin state	symmetry	relative energy (kcal/mol)
Cu(CO)$^+$	singlet	C_s	0.0
	triplet	C_s	+80.0
Cu(CO)$_2^+$	singlet	$D_{\infty h}$	0.0
	triplet	C_{2v}	+106.8
Cu(CO)$_3^+$	singlet	D_{3h}	0.0
	triplet	D_{3h}	+114.5
Cu(CO)$_4^+$	singlet	T_d	0.0
	triplet	D_{4h}	+79.2

Table 2. Computed Binding Energies in kcal/mol for the "Last" Ligand in Cu(CO)$_n^+$ and Cu(CO)$_n$Ar$^+$ Complexes

complex	E[Cu(CO)$_n^+$ −CO]	E[Cu(CO)$_n^+$-Ar]
Cu(CO)$^+$	38.24	
Cu(CO)Ar$^+$		16.3
Cu(CO)$_2^+$	45.35	
Cu(CO)$_2$Ar$^+$		1.01
Cu(CO)$_3^+$	21.47	
Cu(CO)$_3$Ar$^+$		0.97
Cu(CO)$_4^+$	17.01	
Cu(CO)$_4$Ar$^+$		0.23
Cu(CO)$_5^+$	3.74	
Cu(CO)$_6^+$	3.65	

To gain further insight into these spectra, we have performed DFT calculations on the Cu(CO)$_n^+$ complexes for $n = 1-8$. Complete details on the calculated structures, energetics and spin states are provided in the Supporting Information for this paper. We have investigated various isomers and spin states for each complex, and have also included the corresponding argon tagged complexes in the smaller cluster sizes. Figure 6 shows selected structures resulting from these calculations, and Tables 1 and 2 show the most relevant numerical data. All the structures calculated to be stable minima are consistent with those determined previously by Andrews and Zhou.[18b] The $n = 1$ complex is slightly bent, the $n = 2$ species is linear, the $n = 3$ has a D_{3h} structure and the $n = 4$ species is tetrahedral. The complexes for $n > 4$ have essentially the structure of the $n = 4$ core ions with weakly attached external CO molecules. The addition of argon induces a noticeable change in the structures of the $n = 1$ and 2 complexes, but there is no significant perturbation in the other sizes, except for the triplet species, as noted below. Tagging causes the $n = 1$ complex to go from bent to linear, and the $n = 2$ complex to go from linear to slightly bent with C_{2v} symmetry. These perturbations in the smaller complexes are not surprising because of the relatively high Cu$^+$−Ar binding energy noted above.[58] In these smaller complexes, the argon essentially occupies a vacant ligand site. The efficiency of photodissociation in these complexes can be explained to some extent by these theoretical results. The calculated intensities of the CO stretches are generally quite high (>250 km/mol; see Supporting Information), explaining the possibility of multiphoton absorption suggested for some species. Also, external or second-sphere CO molecules which appear after $n = 4$ are calculated to be bound by about 1300 cm^{-1}. Although DFT is not expected to handle weak electrostatic bonding interactions accurately, the values calculated suggest that one-photon elimination of CO should be possible for the larger complexes. The argon binding to the $n = 1$ complex is quite high (16.3 kcal/mol), consistent with it acting essentially as a ligand, and explaining the difficulty in eliminating it with IR excitation. The binding energies of argon to all the other clusters are quite low, consistent with the ease of photo-elimination of argon from these species.

A comparison of the band positions measured in the present work to those in previous experiments and to those computed by theory is presented in Table 3. As shown, theory finds high symmetry structures consistent with the single band spectra measured, and reproduces all the experimental CO frequencies within a few cm^{-1}. In the case of the tagged complexes, theory seems to sometimes overestimate the perturbation caused by argon, resulting in band positions that are lower than those measured experimentally. This is particularly evident in the $n = 3$ and 4 complexes, where the experiment measures spectra both with and without argon tagging. The agreement with theory here is better for the neat species than it is for the tagged ones. Also, the computed trend for tagged versus neat spectra is backward. For both the $n = 3$ and 4 species, tagging is predicted to cause a small red shift, but in the measured spectra the argon complex bands are slightly blue-shifted with respect to those of the neat species. These effects are not extremely large, and are attributed to the deficiencies of DFT for handling bonding interactions involving weak electrostatic interactions. We have seen these effects in several other metal carbonyl systems studied previously.[44] The band positions of the complexes measured by Souma in acidic media,[45] and those measured by Strauss from salts with counterions present,[46] are noticeably lower than those measured in our experiment or those measured by Andrews via matrix isolation, particularly in the smaller complex sizes.[18b] The Souma experiment for the $n = 4$ complex is in closer agreement with our data. Also, the acidic media and condensed phase frequencies appear to increase with cluster size, whereas those measured in our work and also that by Andrews decrease with size from $n = 1-4$. These observations suggest that the condensed phase environment causes some perturbation of the vibrations. The band positions here for argon-tagged Cu(CO)$_3^+$ and Cu(CO)$_4^+$ are remarkably similar to those measured for the same ions by Andrews and co-workers in a neon matrix (2205 vs 2211 cm^{-1} and 2198 vs 2202 cm^{-1}, respectively).[18b] These same investigators calculated harmonic frequencies for the Cu(CO)$_n^+$ complexes at the DFT/BP86/6-311+G* level (for $n = 1-4$). Their computed values (2208, 2228, 2203, 2167 cm^{-1} for $n = 1-4$ respectively) differ somewhat from our B3LYP values obtained using a larger basis set and scaling.

For each of these clusters, only the spectra corresponding to the singlet species agree with the experiment. Computations were conducted on the triplet species having the nominal d^{9}s^1 orbital occupation, but the relative intensities and band positions in those spectra do not coincide with the experiment, as shown in Table 3. Triplet state species for the $n = 1-3$ clusters have essentially the same structures as the corresponding singlets, giving rise in each case to a similar single-band spectrum. However, the spectra for the triplet state complexes are strongly red-shifted to the edge of the range under investigation (1977 cm^{-1}, 2021 and 2043 cm^{-1}, and 2070 cm^{-1} for $n = 2-4$ respectively). The tagged $n = 3$ species has a different structure as a triplet, with a second weak vibrational band in addition to the strongest one, and the band positions fall in the

Table 3. Vibrational Frequencies (in cm^{-1}) Computed (Scaled by 0.971) and Measured for Singlet and Triplet States of Cu(CO)$_n^+$ and Cu(CO)$_n$Ar$^+$ Complexes, along with Comparisons to Previous Experiments[a]

complex	this exp	this theory	Andrews exp[18b]	Straus exp[46]	Souma exp[45]
Cu(CO)$^+$	2240.6	2234.4	2178	2160	
triplet	2155.6				
Cu(CO)Ar$^+$	2216	2225.2			
triplet	2217.9				
Cu(CO)$_2^+$	2218.3	2230.4	2164		
triplet	2013.6				
Cu(CO)$_2$Ar$^+$	2221	2213.8			
triplet	1977				
Cu(CO)$_3^+$	2199	2197.1	2211.3	2183	2177
triplet	2093				
Cu(CO)$_3$Ar$^+$	2205	2194.7			
triplet (C_{2v})	2021, 2043				
Cu(CO)$_4^+$	2193	2186	2202.1		2185
Cu(CO)$_4$Ar$^+$	2198	2185			
triplet	2070				

[a] All complexes have a singlet ground state unless otherwise noted.

Table 4. Comparison of Experimental Frequencies and Calculated Oscillator Strengths for the Isoelectronic Analogues Mn(CO)$_6^+$ and Cr(CO)$_6$, Co(CO)$_5^+$ and Fe(CO)$_5$, Cu(CO)$_n^+$ and Ni(CO)$_4$

complex	experimental frequency (cm^{-1})	oscillator strength (km/mol)
Mn(CO)$_6^+$	2115[a]	1061
Cr(CO)$_6$	2002.9[b]	1861
Co(CO)$_5^+$	2140, 2150[c]	644, 761
Fe(CO)$_5$	2013, 2034[d]	1268, 1456
Cu(CO)$_4^+$	2198	279
Ni(CO)$_4$	2056[e]	986

[a] Reference 44c. [b] Reference 27. [c] Reference 44a [d] Reference 23 and 24. [e] Reference 25.

for the neutrals indicate that the π back-bonding interaction is the most important consideration in these systems. However, the charge on the metal ions contracts the valence electrons, limiting their back-donation, and the red shift is less for cations than for their corresponding neutrals. This is completely consistent with conclusions from other previous systems.[10,21] The present case of copper ions provides an extreme case of these interactions, as both the charge and the filled shell act to contract the d electrons. σ donation is not possible because of the filled d shell, but the polarization interaction is strong, resulting in the blue-shifted vibration seen.

The dependence of π back-bonding on charge has been documented and discussed previously for the isoelectronic series Ni(CO)$_4$, Co(CO)$_4^-$, and Fe(CO)$_4^{2-}$, in which the CO stretching frequencies are 2056, 1946, and 1799 cm^{-1} respectively.[25,28,30] In this series, the anions have more charge density, hence they have greater π back-bonding, and larger red shifts. Our results in the present study enable us to add a cationic metal—carbonyl to this isoelectronic series, and the frequency of Cu(CO)$_4^+$ at 2198 cm^{-1} fits in this trend seamlessly. All of these data and our comparisons above are completely consistent about the importance of π back-bonding on the red shifts of carbonyl stretching frequencies.

The data presented in Table 4 also allow comparisons of IR intensities for the CO vibrations of neutrals versus cations. The right column shows the IR intensities for each of these metal carbonyls in our present computational work. As shown, the neutrals have substantially more intense vibrations than the cations. This trend is surprising, as the IR oscillation strength depends on the dipole derivative, and this is often enhanced when the motion in question involves a charge. For example, we have recently shown that the O—H stretches in metal—water complexes are much stronger in the cations than in the free water molecule, and those for the doubly charged complexes were much stronger than in the singly charged complexes.[59] It is not immediately obvious why the trend appears to be reversed in these carbonyl systems.

A final interesting issue here is the behavior of the external CO molecules in these systems. As noted above, the $n = 1-4$ complexes here have vibrations that are strongly shifted from the frequency of gas phase CO, as are the vibrations of most all carbonyls bound directly to metal. However, the frequency of the external CO molecules here is also shifted compared to gas phase CO. The band at 2162 cm^{-1} observed for all the larger clusters is blue-shifted by about 19 cm^{-1}. This is consistent with previous observations for this type of second sphere CO vibration in

same range as that of the singlet. Because of the strong frequency shifts predicted for the smaller complexes in the triplet states and the large energy differences favoring the singlets, we conclude that all of these complexes have singlet spin states as expected for the d^{10} ground state configuration.

It is interesting to compare cationic metal carbonyls to their neutral analogues. The Cu(CO)$_4^+$ complex is found here to have the same tetrahedral structure and singlet ground state as the isoelectronic Ni(CO)$_4$. However, the difference in the vibrational frequencies of this isoelectronic pair is striking. The charged Cu(CO)$_4^+$ complex has a frequency of 2198 cm^{-1}, which is blue-shifted by over 100 cm^{-1} from that of Ni(CO)$_4$ (2056 cm^{-1}).[25] The difference between ionic carbonyls and their neutral counterparts has been discussed previously by our group.[10,42-44] Table 4 presents a comparison of the closed shell cation carbonyls studied recently by our group to the corresponding well-known neutrals. Like the present Cu(CO)$_4^+$ and Ni(CO)$_4$ comparison, in each case the expected cation species has the filled coordination and same structure as the corresponding isoelectronic neutral. Fe(CO)$_5$ and Co(CO)$_5^+$ both have trigonal bipyramidal structures, whereas Cr(CO)$_6$ and Mn(CO)$_6^+$ are both octahedral. In the same way seen here for Cu(CO)$_4^+$ versus Ni(CO)$_4$, the neutral iron and chromium carbonyls have vibrational frequencies that are significantly different from their isoelectronic cations. The two IR bands for Fe(CO)$_5$ at 2013 and 2034 cm^{-1} compare to those of Co(CO)$_5^+$ at 2140 and 2150 cm^{-1}. In the case of Cr(CO)$_6$, the single IR band at 2003 cm^{-1} compares to that of Mn(CO)$_6^+$ at 2115 cm^{-1}. In each case, the red shift of the carbonyl stretching frequency is much greater for the neutral complexes. As discussed earlier, the carbonyl shift results from the combined effects of σ donation, electrostatic polarization, and π back-bonding. σ donation and electrostatic polarization should be stronger for cations, as these cause charge transfer from the CO toward the metal, while π back-bonding should be stronger for neutrals, as it involves transfer of charge in the other direction. The significant red shifts

analogous $Co(CO)_n^+$ and $Mn(CO)_n^+$ complexes,[10,44] but completely different from the behavior seen for other metal ligand complexes. In the case of metal$-CO_2$ complexes, for example, external CO_2 molecules have also been detected, but their asymmetric stretch vibrations fall at virtually the same frequency as the isolated gas phase molecule.[60−62] This unusual behavior of solvating CO molecules has been discussed in our previous metal carbonyl cation studies.[10,42−44] In a model computational study by Goldman and Krogh-Jespersen,[21] it was shown how a polarization of CO can be caused by a nearby charge, and that this causes a blue-shift in the C$-$O stretching frequency. This interaction is in fact exactly the same effect as the electrostatic polarization that occurs for closed shell nonclassical metal ions, leading to their blue-shifted CO frequencies.[21,22,42,43] When CO is external to metal, it does not experience such a strong polarization as it does when it is bound directly to a cation. Instead, it experiences a more modest polarization from the core metal ion complex, in this case the $Cu(CO)_4^+$, which leads to a smaller blue shift. Presumably, if even larger complexes could be studied that contain third-sphere (or greater) CO molecules, the polarization would be even smaller and the CO frequency would eventually be more like that of the isolated CO molecule. However, the IR intensity of these far-external molecules would also likely be reduced further as well. Thus far, we have not detected any evidence for these CO molecules in such outer shells.

CONCLUSION

Copper carbonyl cations of the form $Cu(CO)_n^+$ ($n = 1−8$), and their argon-tagged analogues, $Cu(CO)_nAr^+$, were produced and studied with mass-selected infrared photodissociation in the carbonyl stretching region. The geometries and electronic states of these complexes are determined by examining the distinctive patterns provided by the number of infrared-active bands, their frequency positions and relative intensities, and comparing them to the predictions of theory. All $Cu(CO)_n^+$ complexes were found to have a d^{10} singlet ground state configurations. All of the small complexes studied have a single IR-active band, indicating a high-symmetry structure, and all of these bands are shifted to higher frequency than the free-CO vibration. $Cu(CO)_4^+$ has a completed coordination sphere, consistent with its expected 18-electron stability. It also has a tetrahedral structure similar to that of its neutral isoelectronic analog $Ni(CO)_4$. Whereas the carbonyl stretch in $Ni(CO)_4$ is significantly red-shifted compared to the free-CO vibration, the band in $Cu(CO)_4^+$ (2197 cm^{-1}) is strongly blue-shifted due to charge induced reduction in the π back-bonding. Like the Au^+ systems studied previously, copper cation forms nonclassical carbonyls.

ASSOCIATED CONTENT

Ⓢ Supporting Information. The full details of the DFT computations done in support of the spectroscopy are presented here, including the structures, energetics, and vibrational frequencies for each of the complexes considered. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: maduncan@uga.edu.

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