

Electronic shell closings in metal cluster plus adsorbate systems: Cu_7^+CO and Cu_7^+CO

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(Received 31 May 1991; accepted 2 August 1991)

INTRODUCTION

One of the most striking experimental observations in studies of bare metal clusters is the appearance of electronic shell closings.¹ These shell closings, which for spherical clusters appear for 2, 8, 18, 20, 34, 40, etc., valence electrons, give particularly large stabilities and thus abundancies of the corresponding clusters. From these stabilities also follow high ionization potentials, low electron affinities, and minima in the reactivities to molecules like O_2 , H_2 , N_2 , etc.^{2,3} The electrons contributing to the shell closings of a cluster should be more or less delocalized and thus be part of the conduction band of the metal. For alkali metal clusters it is therefore clear that only the single outermost s electron of every atom will contribute. For transition metals the number of electrons per atom which will contribute to the cluster shells is less obvious, but normally there will only be one electron also for these systems. Exceptions to this rule could be atoms like cobalt and iron which have $d^n s^2$ atomic ground states and for this reason some atoms in the cluster may contribute two electrons.³ Copper clusters, which are studied in the present paper, are quite similar to the alkali clusters and should contribute one electron per atom. It can therefore be expected that of the smaller clusters, Cu_8 and Cu_9^+ should be among the most stable copper clusters.

In organometallic chemistry electronic shell closings have always played a significant role in the rationalization of the stabilities of certain transition metal complexes. Most well known of these shell closing effects is the 18 electron rule which explains the stability of large numbers of metal complexes, for example metal carbonyls like $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, and $\text{Cr}(\text{CO})_6$. These shell closings occur around the transition metal atom and it is in this context important how the ligand electrons are counted. For CO only two electrons, the carbon lone pair electrons, are considered to contribute to the shell closing around the metal atom.

In the present study the interaction between cationic copper clusters and a single CO molecule is investigated both experimentally and theoretically. These systems are neither of bare cluster type or of the normal type encountered in organometallic chemistry. Of particular interest in this case is to see if shell closing effects occur also for these mixed systems. These systems are considered mixed since the electrons contributing to the electronic shells should

come both from the cluster (the majority) and from the ligand (two electrons). The specific question asked is whether Cu_7^+CO is more stable than other Cu_n^+CO clusters in this size region. This same sort of picture where some of the electrons of the adsorbate fit into the electronic structure of "bond-prepared" clusters has been brought out in recent cluster modeling of metal surfaces.⁴

Results both from experiments and calculations will be presented. The corresponding study for the neutral clusters, where Cu_6CO is compared to other Cu_nCO clusters, is made only theoretically. On the experimental side the study is extended to clusters of 21 atoms in size, and clusters of gold are briefly considered as well.

The rates of association reactions between cationic copper clusters and CO have already been studied recently by Leuchtner, Harms, and Castleman.⁵ No indication of shell closing effects was noted. This is in sharp contrast with their earlier results on O_2 reactions with aluminum cluster ions² where such closed-shell species as Al_{13}^- (40 valence electrons) were found to be strikingly inert. We suspect their inability to observe shell closing effects in the $\text{Cu}_x^+ + \text{CO}$ experiments was due to the absence in this case of a substantial activation barrier to reaction. Under their relatively high pressure, low temperature experimental conditions, all clusters larger than 5–7 atoms reacted, and there was little ability to differentiate one chemisorbed cluster from another. The new experimental results presented below focus on relative binding energies as a function of cluster size, rather than reaction rates. They therefore provide a more direct test of theoretical predictions of stability.

COMPUTATIONAL AND EXPERIMENTAL DETAILS

The calculations for the neutral and cationic Cu_nCO systems were performed in the following way. In all calculations the valence electrons were correlated using the size-consistent modified couple pair functional (MCPF) method⁶ based on self-consistent-field (SCF) orbitals. In the first step of the calculations, the geometry of the bare cluster was optimized. This was done in the same way as was done recently for anionic and neutral copper clusters⁷ and the structures for the neutral clusters were taken from that study. Only topologically different clusters were considered and the bulk Cu–Cu distance was used throughout.

All copper atoms were modeled as one-electron systems using effective core potentials (ECPs)⁸ and core polarization potentials (CPPs).⁹ In the next step CO was attached to the cluster. The basis set for carbon and oxygen used was Huzinaga's (9s,5p) set¹⁰ generally contracted to [3s,2p] and with a *d* function added. Various possible chemisorption sites were investigated and it was found that only on-top chemisorption is relevant for these clusters. For on-top chemisorption the binding copper atom has to be modeled at the all-electron level and in this case the 3*d* electrons are counted as valence electrons in the correlation treatment. For this atom Wachter's basis set¹¹ was used including the usual two diffuse 4*p* functions and a diffuse 3*d* function, forming a generally contracted [5s,4*p*,3*d*] set. All distinct on-top chemisorption sites were investigated for all clusters. The geometry changes of the clusters when CO is chemisorbed are not expected to be significant on a qualitative scale since the chemisorption energy is so small, and such changes were therefore not investigated.

Experiments on these same positive copper clusters ions were performed on the Fourier transform ion cyclotron resonance (FT-ICR) cluster beam apparatus described extensively in earlier publications.^{12,13} The clusters were prepared by laser vaporization of a copper target disc in a pulsed supersonic nozzle, cooled in a supersonic expansion, and directly injected into the ion trap of the cluster FT-ICR apparatus. After sufficient cluster ions had been accumulated in the trap (typically 15 beam pulses at 10 s⁻¹), they were thermalized for 3 s by collisions with argon buffer gas at 1 × 10⁻⁶ Torr. The CO reaction gas was then pulsed into the ICR cell at a pressure of 1 × 10⁻⁶ Torr for a sufficient time to produce the desired extent of reaction, normally 1–3 s. The result of the reaction was then probed by measurement of the FT-ICR mass spectrum. Relative stability of the Cu_{*n*}⁺CO reaction products was determined by gentle excitation of the cyclotron motion (using SWIFT excitation¹³) while the ICR trap contained argon gas to serve as a collision partner. The relative ease of removal of the chemisorbed CO molecule from the clusters by this collision induced dissociation (CID) process thereby provided a measure of the relative stability of the Cu_{*n*}⁺CO clusters.

RESULTS AND DISCUSSION

The results of the calculations for the chemisorption energy of CO on neutral and cationic copper clusters up to 10 atoms are given in Table I. The most important result in this table is that the energies have clear maxima at Cu₆CO for the neutral clusters and at Cu₇⁺CO for the cationic clusters. The simple explanation for these results is that shell closings including 8 electrons have occurred for these cluster systems, where 6 electrons come from the cluster and 2 electrons come from CO. The shell closing effect is particularly marked if these clusters are compared to larger clusters, for which the CO lone pair electrons have to be added to an orbital outside the closed shells. The effect is less marked in a comparison to smaller clusters since the

TABLE I. Chemisorption of CO on singly ionized and neutral copper clusters, energies in eV.

Cluster	Neutral	Cation
Cu ₁	0.10	1.18
Cu ₂	0.60	1.06
Cu ₃	0.93	1.00
Cu ₄	1.03	1.04
Cu ₅	0.46	1.19
Cu ₆	1.06	1.23
Cu ₇	0.59	1.42
Cu ₈	0.44	0.93
Cu ₉	0.72	0.88
Cu ₁₀	0.31	0.66

lone pair electrons can then be added to the unfilled 1*p* shell of the cluster. Also, for the smaller cationic clusters there is a compensating effect in that CO gets closer to the delocalized positive charge on the cluster. For the smallest system with only one atom this positive charge leads to a very large difference compared to the neutral system, whereas for the largest systems studied the additional binding due to the charge is less marked.

The shell closing effect occurring for the cations at Cu₇⁺CO is clearly seen also in the calculated LUMO (lowest unoccupied molecular orbital) energies of the bare clusters. The virtual orbital energies for Cu₅⁺–Cu₉⁺ are –4.4 eV (5 atoms), –4.1 eV (6), –4.4 eV (7), –3.1 eV (8), and –3.2 eV (9). There is thus an increase in the virtual orbital energy of about 1 eV between Cu₇⁺ and Cu₈⁺ as a result of the shell closing. A picture of the chemisorption of CO where the carbon lone pair of electrons add in the LUMO is the obvious rationalization for the correlation between the absolute values of the LUMO energies and the association energies in Table I.

Figure 1 presents some of the typical results from experimental measures of the chemisorbed copper cluster cations. The top panel shows the observed mass spectrum of the copper clusters as initially injected. Here the injection parameters were chosen to select only those copper clusters in the size range from 6–13 atoms. The middle panel shows the change in this mass spectrum brought about by a 1.1 s exposure to CO reactant gas at 1 × 10⁻⁶ Torr. The formation of chemisorbed products having one CO attached to the cluster is evident here for all Cu_{*n*}⁺ clusters, although it is clear that Cu₇⁺ has the greatest effective reactivity at these pressures. The effect of chemisorption of a small amount of background H₂O is also evident in this panel for some of the clusters. In the bottom panel of Fig. 1, the most direct measure of the relative stability of these clusters is provided by the results of the CID experiment. Here all clusters and their reaction products throughout this region of the mass spectrum were excited in the presence of argon buffer gas. After thermalization, the FT-ICR mass spectrum here reveals that all the chemisorbed species have desorbed from the clusters, except Cu₇⁺CO, and to a smaller extent, Cu₆⁺CO. This is in excellent agreement with the calculated stabilities of Table I.

Similar experiments in the 14–24 atom size range for

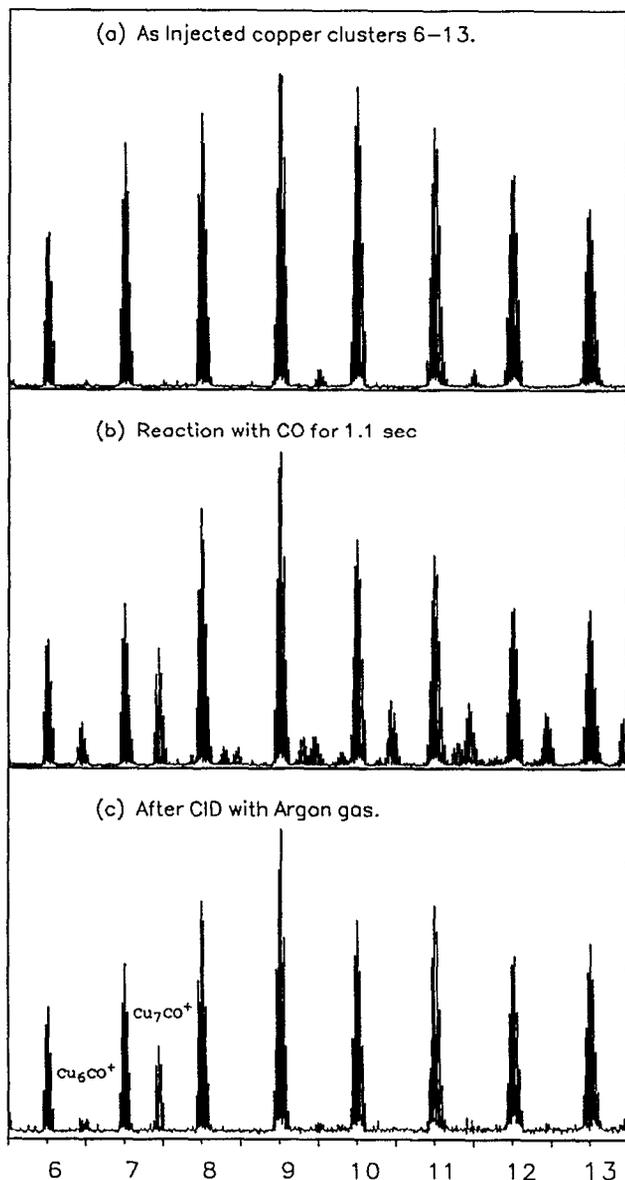


FIG. 1. CO chemisorption experiment on copper clusters in 6-13 atom size range: (top) mass spectrum of Cu_n^+ as injected into FT-ICR trap, (middle) mass spectrum after exposure to CO reactant gas at 1×10^{-6} Torr for 1.1 s, (bottom) resultant FT-ICR mass spectrum after CID with argon at 1×10^{-6} Torr. Note special stability of $\text{Cu}_7^+ \text{CO}$.

positive copper clusters were found to show that $\text{Cu}_7^+ \text{CO}$ is indeed the most stable reaction product in this region. Here, however, the effect was found to be somewhat less clear than in the size range around Cu_7 . As shown in Fig. 2, $\text{Cu}_7^+ \text{CO}$ appears to be simply the maximum of a series of relatively stable clusters ranging from $\text{Cu}_{13}^+ \text{CO}$ through $\text{Cu}_{15}^+ \text{CO}$. Photoelectron spectra of the negative ion forms of the bare copper clusters in this size range [1c] showed evidence for shell closing effects both at 18 and at 20.

More recent photoelectron spectroscopy studies of other coinage metal clusters¹⁴ have shown the shell closing effects to be much more clear in this size region for gold. Here the closings at 8 and 20 electrons are dramatically

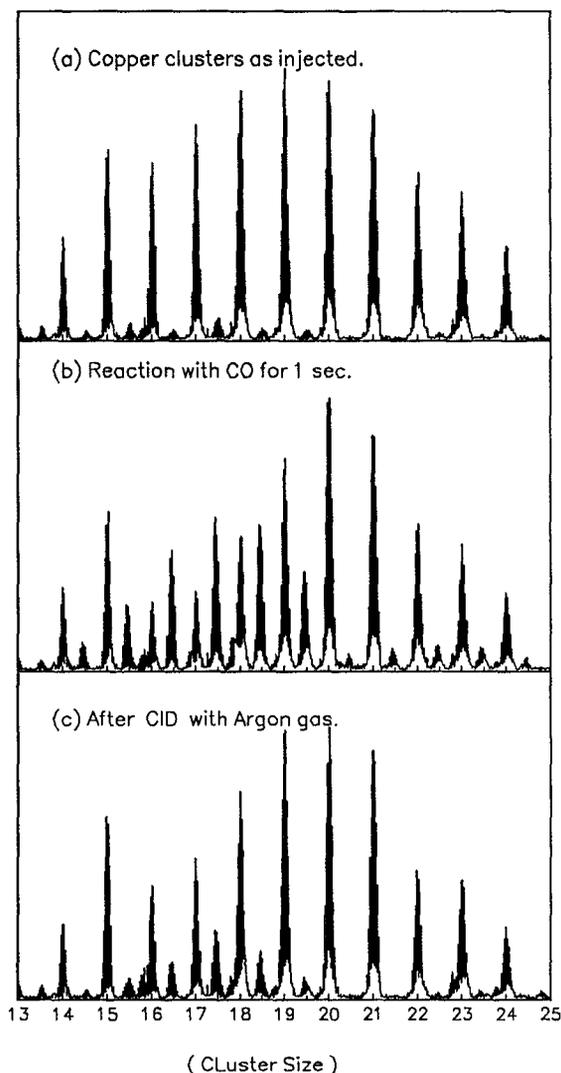


FIG. 2. CO chemisorption experiment on copper clusters in 14-24 atom size range: (top) mass spectrum of Cu_n^+ as injected into FT-ICR trap, (middle) mass spectrum after exposure to CO reactant gas at 1×10^{-6} Torr for 1 s, (bottom) resultant FT-ICR mass spectrum after CID with argon at 1×10^{-6} Torr. Note special stability of $\text{Cu}_7^+ \text{CO}$.

evident. Accordingly, FT-ICR survey experiments for CO chemisorbed positive gold clusters similar to those of Fig. 1 were found to reveal excellent accord with the expectations of the above simple theory: $\text{Au}_7^+ \text{CO}$ and $\text{Au}_{13}^+ \text{CO}$ were quite evidently the most stable chemisorbed clusters. Figure 3 shows, for example, the result of a reaction and CID experiment in the vicinity of Au_{20}^+ .

It will be interesting to see how far this concept of shell closing and the participation of extra electrons donated in the process of chemisorption will continue to be useful. Even in the more complicated case of clusters such as Co_n with an unfilled 3d band, it is conceivable that the largely 4s/4p-derived band of states continues to exhibit shell structure, and this may be manifest both in the reactivity of the bare clusters, and the stability of their chemisorbed products.³

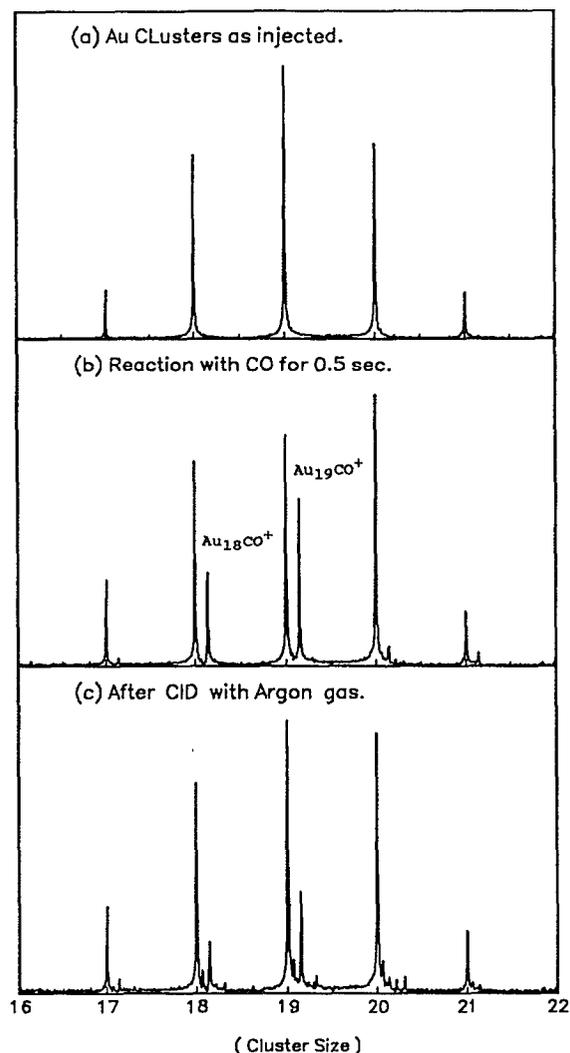


FIG. 3. CO chemisorption experiment on gold clusters in 17–21 atom size range: (top) mass spectrum of Au_n^+ as injected into FT-ICR trap, (middle) mass spectrum after exposure to CO reactant gas at 1×10^{-6} Torr for 0.5 s, (bottom) resultant FT-ICR mass spectrum after CID with argon.

ACKNOWLEDGMENTS

This research was supported (in Sweden) by the NFR, and (in Texas) by the U.S. Department of Energy, Division of Chemical Sciences, and the Robert A. Welch Foundation.

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