and will be of use in estimating barriers to intramolecular electron transfer. Spectra in applied magnetic fields have been obtained but have proven less than optimal for purposes of interpretation owing to the presence of impurity subspectra M1 and M2. Considerations, as to cause of the localized valence nature of $[Fe_2S_2(SR)_4]^{3-}$ will be presented upon completion of these studies.

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Chemisorption of Halogen on Copper and Silver Clusters

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Abstract: We report He I photoemission spectra for chemisorption of halogen on Ag and Cu clusters of different sizes. The spectral shape shows a strong size dependence for Cl/Ag, but little size dependence is noted for Cl/Cu. This effect is explained in terms of the orbital interactions between p orbitals of the halogen and d orbitals of the metal cluster. The predominant effect of cluster size on Cl-chemisorbed spectra persists up to a mean particle size of 30–40 atoms. Computations by extended Hückel procedures reproduce the experimental trends and allow assignment of the bonding and antibonding peaks in the experimental spectrum. Small silver clusters are more reactive than bulk films or single crystals for the decomposition of $CHCl_3$, leading to Cl overlayer formation.

The ultraviolet photoemission spectra (UPS) using He I and He II have been reported for a number of metal clusters.[1-6] These studies have shown that the measured density of states (DOS) depends markedly on the size of the cluster. These UPS results agree with a similar effect found for transition metals by using ESCA spectroscopy.[7,8] Many photoemission studies have now indicated that transition- or noble-metal clusters containing 100–150 atoms or more are required for bulklike spectra. Since this measurement primarily reflects the density of states of the cluster, it is of some interest to learn how the chemical properties of the metal cluster change with size.

Chemisorption is a tool whereby the chemical interaction of an adsorbate with a metal cluster can be measured. Grunze[3] studied the chemisorption of CO molecules on Pd particles of various sizes and found that the molecular orbitals of CO shift closer to the Fermi energy (E_F) of the metal as particle size increases. This facilitates interaction with d states of Pd closer to E_F. This shift in CO molecular orbitals was attributed to either an increasing relaxation energy of CO or a Pd work function change, but the two possible causes could not be separated.

We previously observed that the orbital spectrum of a chemisorbed species depends upon the size of the metal cluster support.[9] This was shown for I_2 chemisorbed on silver clusters. The UPS He I spectrum of the chemisorbed I shows two peaks whose intensity ratio is dependent upon the size of the silver cluster. This effect was interpreted in terms of the ability of the silver cluster to transfer electrons to the halogen. Larger clusters generally have smaller ionization potentials,[10] and thus electron transfer should be easier from the large clusters. This trend of decrease in ionization potential vs. increase in cluster size is reported in the ab initio calculations of Bauschlicher et al.[11] for Be clusters and Melius et al.[12] for Ni clusters. It has been found in experimental measurements for Na clusters by Herrmann et al.[13]

The present work extends our investigation to other adsorbates (Cl) and to other metal clusters (Cu). This study was prompted by the significant degree of interaction of halogen p orbitals with metal d orbitals that we observed in prior studies. The p orbitals of halogen are positioned below the d band of Cu and predominantly above the d band of Ag, as deduced from photoemission studies on these ordered surfaces.[14,15] Thus, it is of interest to learn how these interactions are modified by cluster size for the two extreme cases.

Experimental Section

The clusters were prepared inside the spectrometer by evaporation from thermally heated tungsten sources using high-purity wires. The substrate was carbon prepared by prior evaporation onto mica by using the technique and equipment described by Hamilton et al.[16] Upon introduction into the spectrometer, the carbon film was ion-etched with Xe to remove traces of O_2 or S. These samples remained clean for a few days before use as substrates for the evaporated metal.

The metal coverage was monitored by Auger spectroscopy[17] and with a quartz crystal oscillator. These data were calibrated by using neutron activation analysis to ensure proper determination of the amount of material deposited. The change in frequency of the quartz oscillator was proportional to the film thickness. These evaporated metal deposits on amorphous carbon have been characterized by electron microscopy.[16] The size distribution of the particle diameters was determined as a function of metal coverage so that a mean particle size can be associated with each deposit. The shape of the particles was shown to be hemispherical with a small flattening. Thus, the mean number of atoms in a cluster could be determined for a given metal coverage. In the following discussions we associate a mean size with particular spectra based upon this analysis although it must be remembered that an actual particle

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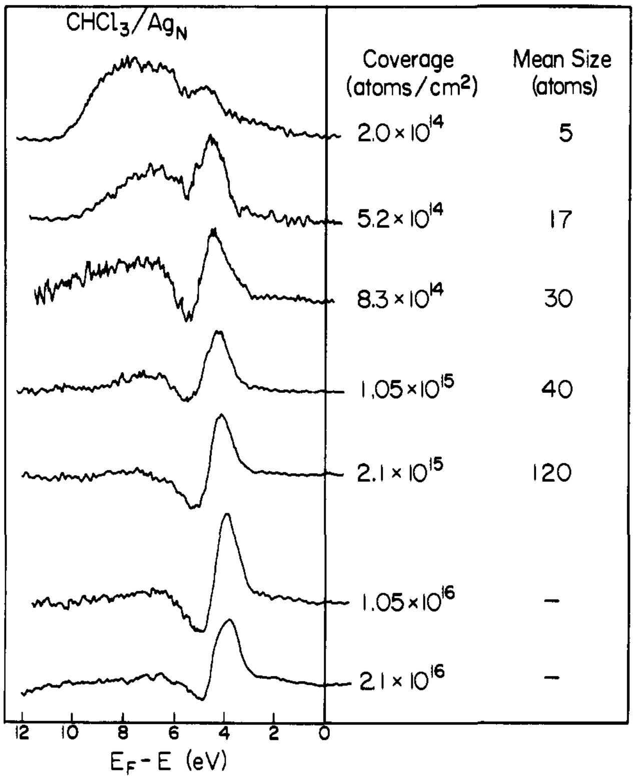

Figure 1. The UPS He I difference spectra for Cl chemisorption on silver clusters vs. silver coverage and mean size. The difference curve results from subtracting spectra before and after chemisorption of $CHCl_3$ on silver clusters.

size distribution exists rather than a single size.

Gaseous $CHCl_3$ was obtained from the vapor phase in equilibrium with liquid. After several freeze-pump-thaw cycles, vapor was admitted to the chamber with all electron guns turned off and the ion pump isolated from the chamber. Exposure levels were monitored with an ionization gauge.

All photoemission spectra were recorded by using He I emission. The photons were incident upon the sample at ~70° from the sample normal, which was aligned with the analyzer axis. The double-pass cylindrical mirror analyzer was operated at a resolution of 0.16 eV for photoemission. Typically 50–100 scans were signal-averaged over 30 min to reduce noise levels. These spectra were stored on tape for data manipulation.

Auger spectra were taken to ensure cleanness of the metal deposits. These were not recorded until after photoemission was completed. Using AES, we found that exposure of Cu single crystals or clusters to $CHCl_3$ produced a halogen layer with no detectable C fragments on the surface.[15] Of course, it is possible that some level of C below AES detection limits could be deposited on the surface of the metal. For Ag single crystals[14] the situation is more ambiguous because of the coincidence of a minor Ag peak with the C peak in the AES spectrum. We are sure that principally halogen is deposited on the Ag surface, but we cannot eliminate the possibility that small amounts of C are also deposited. Evidence for halogen deposition on the metal surface includes the observation that the Ag/C signal ratio measured by AES decreases ~10% after chemisorption.

Results

Exposure of clean silver clusters to $CHCl_3$ produces a layer of Cl on the cluster surface. We measured the photoemission He I spectra before and after chemisorption of $CHCl_3$; Figure 1 shows these difference spectra for several metal coverages. We note two peaks in the halogen spectrum that change in intensity as the silver coverage changes. The low-binding-energy peak gains in intensity as the coverage increases, just as was observed for I_2 chemisorption.[9] In addition, there is a shift in halogen peak position with size. The low-binding-energy peak shifts from 4.4 eV at the lowest coverage to 3.9 eV at the highest silver coverage. The spectral shape becomes constant in the region 8×10^{14}–1.0×10^{15} atoms/cm^2, which corresponds to hemispherical particles containing on the mean average 30–40 atoms.[16] All of these spectra correspond to halogen saturation coverage on the cluster (i.e., 1000-L exposure by $CHCl_3$), which is monitored by Auger spectroscopy. The Cl/Ag signal ratio measured by this technique was 0.65 at a silver coverage below 1×10^{15} atoms/cm^2 and showed a small decrease with increasing silver coverage.

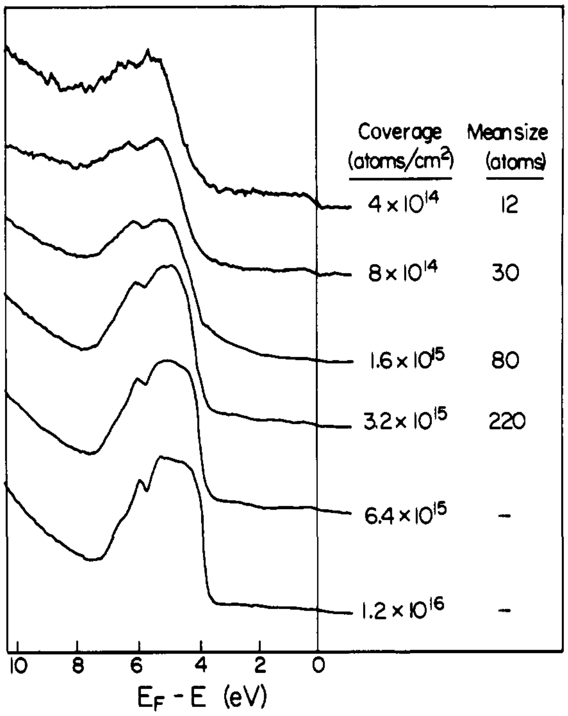

Figure 2. The UPS He I difference spectra for Ag clusters evaporated onto carbon for various silver coverages and mean size.

Experiments in which Cl_2 was the gaseous reactant in place of $CHCl_3$ gave the same behavior as with $CHCl_3$ (Figure 1). Thus, if any C was deposited along with Cl during exposure of Ag to $CHCl_3$, it had minor influence on the difference spectra.

The He I photoemission spectra of clean silver clusters evaporated onto carbon are shown in Figure 2. Here we observe coverage-dependent effects which are consistent with measurements at variable photon energies.[6] The d threshold is particularly sensitive to cluster size. It is much sharper and shifted to lower binding energy for larger cluster size. From measurements at the half-maximum we estimate a shift of 0.7 eV from the lowest to the highest coverage in Figure 2. This effect plays a role in the Cl difference spectra shown in Figure 1. Note that the negative component in the difference curves (Figure 1) appears only at the high coverage range, whereas at lower coverages a nonnegative portion exists. This region occurs at the top of the d band of silver and shows up only at higher coverages, because the silver d-band threshold has shifted 0.7 eV toward smaller binding energies. Thus, no Ag d states are present for possible attenuation. We interpret the two peaks in the halogen difference spectrum as resulting from the strong interaction of p orbitals with the silver d orbitals.

Copper clusters chemisorb Cl during exposure to $CHCl_3$, as detected by AES and discussed earlier for ordered surfaces.[15] Figure 3 shows the difference spectra for copper clusters obtained by subtracting spectra before and after chemisorption of $CHCl_3$. All UPS spectra are reported at saturation coverage of Cl on the cluster (500-L $CHCl_3$ exposure) which gives Cl/Cu Auger signal ratio of 1.2. The 60-eV Cu Auger transiton is considered. We find a major peak at ~7 eV in Figure 3 that shifts 0.9 eV toward lower binding energy as copper coverage increases. This peak is predominantly due to halogen p orbitals. There is a significant negative portion of the difference spectra that arises in the energy range at the top of the Cu d band. This negative component becomes more pronounced as the copper coverage increases.

The difference spectra for Cu clusters deposited on C are shown in Figure 4. Here we observe the s states extending from the Fermi energy to ~2 eV, at which point the d states begin. There

Table I. Position of d Edge (d), Position of the Cl Adsorbate Peak (p^d), and Change in Work Function ($\Delta\Phi^{Cl}$) for $CHCl_3$ Chemisorption on Ag and Cu Clusters

Ag				Cu			
coverage, atoms/cm^2	d, eV	$\Delta\Phi^{Cl}$, eV	p^d, eV	coverage, atoms/cm^2	d, eV	$\Delta\Phi^{Cl}$, eV	p^d, eV
2×10^{14}	5.8	0.0	4.4	8×10^{14}	4.1	0.1	7.1
5×10^{14}	5.6	0.1	4.4	1×10^{15}	3.8	0.1	6.8
1×10^{15}	5.5	0.2	4.2	2×10^{15}	3.2	0.2	6.5
2×10^{15}	5.3	0.3	4.0	4×10^{15}	3.1	0.4	6.2
5×10^{15}	5.2	0.9	3.9	1×10^{16}	2.6	0.8	6.2
1×10^{16}	5.1	0.9	3.9				

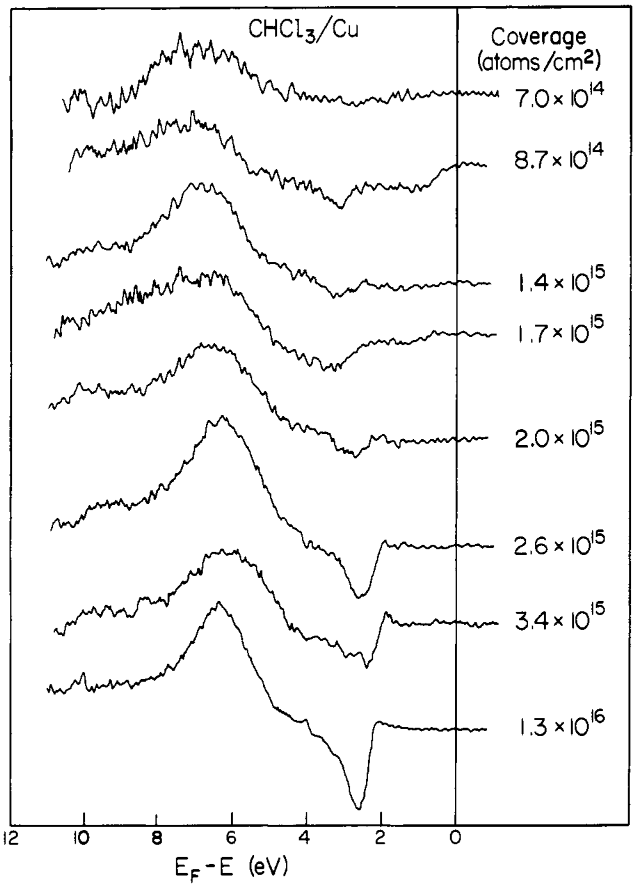

Figure 3. The UPS He I difference spectra for Cl chemisorption on Cu clusters for various copper coverages.

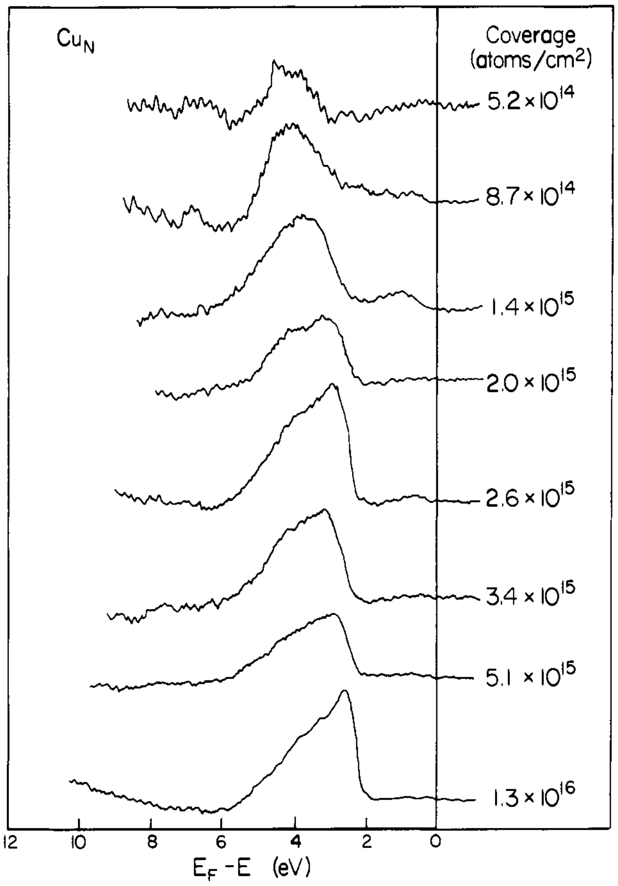

Figure 4. The UPS He I difference spectra for Cu clusters evaporated onto carbon for various copper coverages.

is a significant size dependence of these spectra. At low coverage the d states consist of basically one peak with the appearance of a shoulder region at higher coverage. The d peak threshold shifts 1.5 eV toward lower binding energy and attains a greater slope as coverage increases. These changes require a coverage of 2.6×10^{15} atoms/cm^2 to attain bulk values.

The work function increases upon $CHCl_3$ chemisorption for silver and copper clusters. The work function change is monitored by the change in width of the photoelectron energy distribution curve (Table I). We find an increase in work function for Cl chemisorption that becomes greater as the metal coverage increases. These data indicate that as the fraction of surface covered by metal increases, the electron-withdrawing properties of Cl become more apparent. Table I also shows the position of the leading edge of the d band (at half-maximum) and the peak position of the low-binding-energy Cl-induced peak as a function of metal coverage. These data indicate a decrease in binding energy of both quantities, but they do not seem to scale with the work-function change.

The reactivity of small Ag clusters was measured as a function of gas exposure. We exposed different coverages of silver prepared on carbon to various levels of $CHCl_3$ gas and subsequently recorded the Auger spectrum. Figure 5 is a plot of Cl/Ag signal

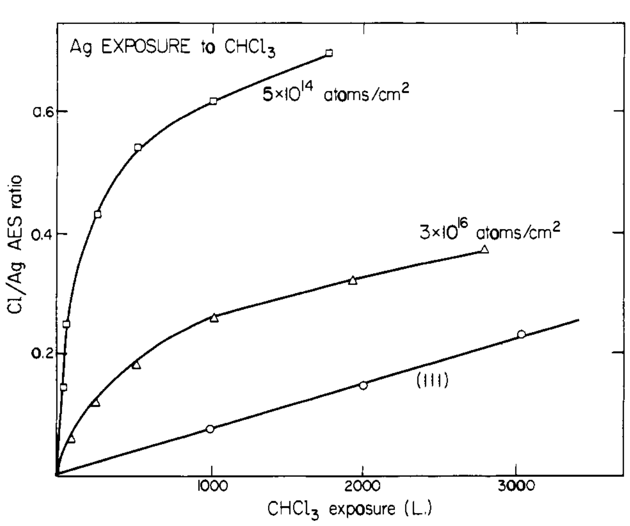

Figure 5. The Cl/Ag signal ratio measured by AES for evaporated clusters of silver and (111) silver crystals vs. $CHCl_3$ exposure in Langmuir units (1 L = 10^{-6} torr s).

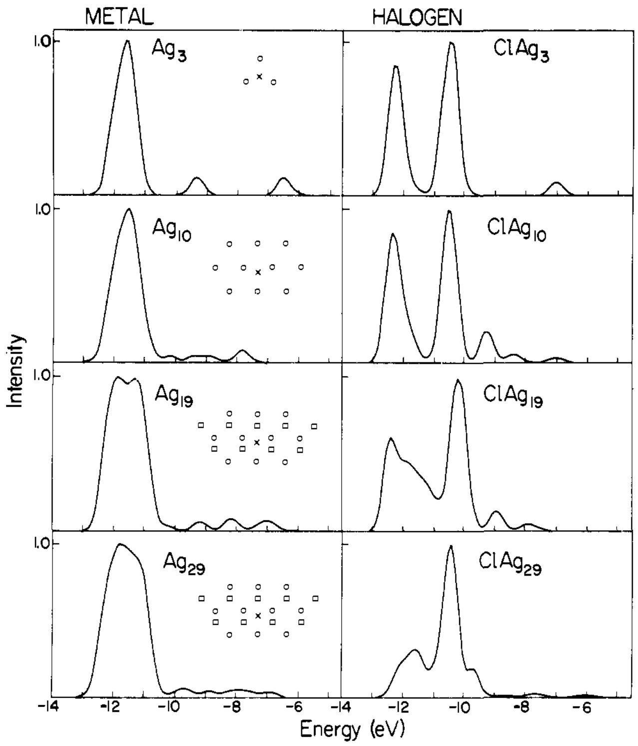

Figure 6. The calculated DOS of free Ag clusters and the Cl component of chemisorbed Cl on these clusters for various size clusters. The geometry of the cluster is sketched (O = Ag positions in first and third layers, □ = Ag positions in second layer, and X = Cl position over triangle center).

ratio as a function of gas exposure. These data show that low coverages of silver attain more quickly a higher level of Cl coverage on the cluster. We have also plotted some data for exposure of a (111) Ag crystal surface to $CHCl_3$.[14] Here the rate of buildup of Cl/Ag is even lower, although with continued exposure the curve attains the same shape in each case. We note that because the Auger technique samples a few layers of Ag while only one layer of Cl is measured, a lower Cl/Ag signal ratio is expected on continuous thick films than on small particles for the same overlayer coverage. Using the escape depth of 10 Å for Ag Auger electrons and taking a hemispherical shape, we estimate a factor of 4 would be expected for this effect. This factor cannot account for the much greater initial rate of Cl buildup on the small Ag particles that is shown in Figure 5. Thus, we must conclude that small Ag particles are more reactive than larger particles or films of silver for the $CHCl_3$ decomposition reaction.

We have compared the rate of $CHCl_3$ decomposition on small copper clusters supported on C with the rate on single crystals. No significant differences were noted. The difference in behavior of rate of $CHCl_3$ decomposition for Ag and Cu clusters vs. the corresponding single-crystal surfaces may be related to the features in Figures 1 and 3. The Cl-induced spectrum is a much more sensitive function of metal cluster coverage (size) for Ag compared to Cu. Perhaps the factors leading to changes in the adsorbate spectrum with cluster size are similar to the factors leading to a dependence of $CHCl_3$ decomposition rate on cluster size.

We have computed DOS curves for Cl adsorbed to copper and silver clusters as a function of the cluster size. This allows us to identify the important orbital interactions and determine qualitatively how the orbital spectrum of chemisorbed Cl should change with size. For calculation details, see the Appendix. In Figure 6, we have compared the computed DOS for Ag_N clusters with the projected component of DOS on chemisorbed Cl. We have considered a planar Ag_3 and Ag_{10} model with the addition of second and third planes in a close-packed arrangement to form Ag_{19} and Ag_{29}, respectively. For Ag_3 and Ag_{10}, the halogen component of DOS splits into two roughly equal parts located on either side of the Ag d states. The two parts consist of bonding (p + d) or antibonding (p − d) combinations of atomic orbitals. As the cluster size increases, the low-binding-energy peak begins to dominate in intensity. This effect correlates with the greater width of d states for the larger clusters. This is interesting, since the only change from the Ag_{10} geometry on going to Ag_{19} or Ag_{29} is the addition of a second and third layer of atoms, respectively. Apparently a greater d bandwidth is a factor leading to the change in intensity of the two halogen components of DOS. This explanation correlates with the argument presented before dealing with the change in ionization potential of the clusters.

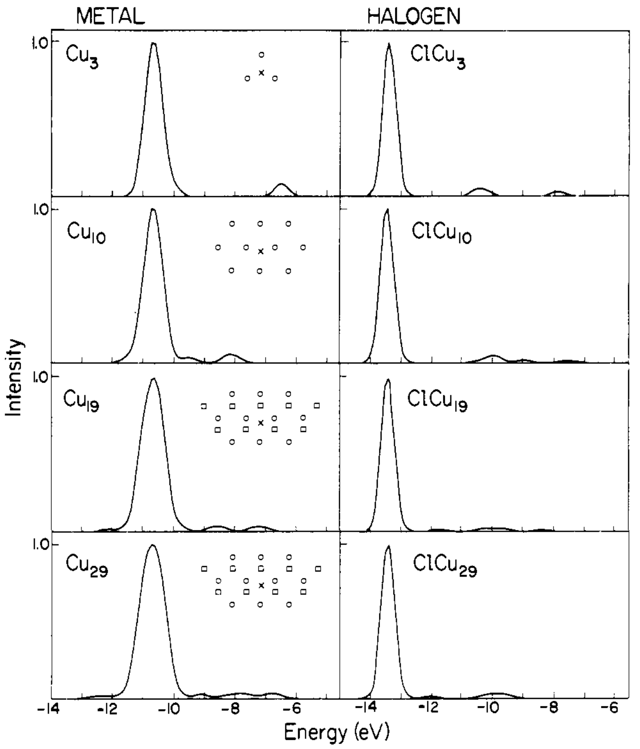

Figure 7. The calculated DOS of free Cu clusters and the Cl component of chemisorbed Cl on these clusters for various cluster sizes. The geometrical arrangement is the same as in Figure 6.

Halogen chemisorption on copper clusters of various sizes is much simpler than on silver clusters. Our calculated results in Figure 7 indicate that only one main halogen peak persists at all cluster sizes. This situation is created because the halogen p–metal d orbitals are more separated in energy for copper than silver. Thus, the weaker interaction for copper fails to lead to significant splitting of the halogen p orbitals. The small peaks which exist at lower binding energy relative to the main peak are due to interactions with the s orbitals, a fact that also accounts for the same type of behavior observed with silver clusters.

Discussion

The UPS spectra of copper and silver clusters show variations with size[1,6] that may be understood in terms of their electronic structure. The broadening in the d-band region reflects changes that have been computed previously[10] and are generally expected. These results show that a particle of ~150 atoms of silver is required for a bulklike UPS spectrum. This result compares well with a separate result obtained from an electron microscopic and photoemission study of Pd clusters evaporated onto silica.[18] An estimated 250-atom cluster was needed to observe metallic photoemission properties.

Chemisorptive properties of small metal particles depend upon the size of the particle. We find that the orbital spectrum of halogen (Cl) is dependent upon the size of the silver particle to which it is chemisorbed. A particle size of ~30–40 atoms is required for this spectrum to reach a limiting shape. This result

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suggests that rather large clusters are required to model chemisorption involving the strong interactions present in the halogen–silver system.

The interactions between different halogen atoms and metal clusters may be understood on the basis of second-order perturbation theory.[19] Here we have that

$$\epsilon_i = \epsilon_i^0 + \sum_{j \neq i} \frac{|H_{ij}|^2}{\epsilon_i^0 - \epsilon_j^0} \qquad (1)$$

where ϵ_i is the energy level after interaction, ϵ_i^0 is the energy before interaction, and H_{ij} is the matrix element connecting different orbitals. Clearly the strongest interactions will take place for $\epsilon_i^0 = \epsilon_j^0$. This is just the case for the p orbitals of Cl and the d orbitals of silver. For Cl interacting with Cu, the orbitals are spaced further apart, leading to a weaker orbital interaction in which the shape of the chemisorbed Cl spectrum is not sensitive to size. Of course, in all cases there is an interaction between halogen p orbitals and s orbitals of the metal. This interaction is less apparent in our experiments because in the UPS technique s orbitals have a relatively small cross section. Nevertheless, the positive region in the halogen difference curves on the low-binding-energy side of the d band is caused by this type of interaction.

Silver particles chemisorb $CHCl_3$ with a rate that is size dependent. For Ag clusters, the small particles attain a coverage of Cl at an initial rate 10–100 times greater than on films or single crystals. This behavior may be due to the lower coordination number on such particles and is consistent with the smaller binding energy per atom computed for small particles.

Frequently in chemisorption calculations a small cluster is used to represent the surface, as discussed recently by Moskovits.[20] This approximation greatly simplifies the computations by treating the adsorbate–surface interaction as local and assuming that long-range effects are unimportant. The present experimental results, however, show that for halogen chemisorbing on noble metals, as many as 30–40 substrate atoms may be required for the UPS spectrum to be constant. This result suggests that UPS is a sensitive technique for measuring the range of the adsorbate–metal interaction. This situation is somewhat different from the conclusions reached for CO bonding in $Rh_6(CO)_{16}$ and CO chemisorbed on Pd(111) and other metal surfaces.[21] The latter experiments were performed by UPS, and the similarity of the CO spectra in each case led to the conclusion that the CO bonding was local. Possibly the different bonding modes of halogen vs. CO are responsible for this effect. Of course, studies of the CO vibrational frequency on matrix-isolated clusters and single-crystal surfaces have also given some contrasting results.[20,22] The frequency of CO vibration on matrix-isolated Cu_n (n = 1–4) approaches the frequency of CO on large supported clusters, suggesting short-range interaction. Yet, in contrast with Cu, the infrared spectrum of CO on small matrix-isolated Pd clusters differs markedly from that for CO on large supported clusters or CO chemisorbed on single-crystal surfaces of Pd. These examples point out the difficulties in making generalizations regarding the nature of chemisorptive bonding.

Recent theoretical work by Van Der Avoird et al.[23,24] has shed light on the degree of localization expected in chemisorption of H atoms on transition metals. This work has shown that the calculation of metallic properties requires much larger clusters than are required for chemisorption. This result seems to be confirmed by these experimental studies.

The change in shape of the chemisorbed halogen spectra as a function of metal cluster size is observed experimentally and matched computationally. The origin of this effect can be traced to the electronic properties of the metal cluster. The large cluster has a smaller ionization potential, which facilitates electron transfer to the halogen. In addition, the bandwidth of the cluster plays a role in determining the strength of the interaction. This effect is illustrated in Figure 1, which shows that significant changes in the orbital spectrum of halogen are due to cluster growth by addition of atoms that do not directly interact with the chemisorbed species. Clearly, the strength of interaction, as measured by the orbital mixing, leads to the bonding and antibonding orbital peaks.

There is a shift in the position of the chemisorbed halogen spectrum with metal cluster size, as noted in the text. This shift is toward lower binding energy as the cluster is enlarged. Several factors could be involved in such a shift. One is the extramolecular final-state relaxation energy, which would be expected to increase as the metal cluster size increases and binding energy decreases. A second factor would be the charge on the halogen or silver. The charge transfer from silver to halogen should increase with cluster size since larger metal clusters have a smaller ionization potential. This would have the effect of decreasing the halogen p-orbital binding energy relative to the metal d-orbital binding energy, an effect which is consistent with our calculations and experiments. It is not possible to completely separate the relaxation energy and charge-effect arguments at this time. However, we believe the changes in shape of the halogen spectra must be accounted for in terms of initial-state effects, since final-state effects could not account for changes in orbital mixing.

Acknowledgment. I am grateful to Lou Gerenser for helpful conversations and the collaborations which initiated this project.

Appendix

The extended Hückel calculations[25] for halogen adsorbed to metal clusters were performed in the standard manner. We use K = 1.75 in the off-diagonal formula for Hamiltonian matrix elements

$$H_{ij} = \tfrac{1}{2} K S_{ij} (H_{ii} + H_{jj}) \qquad (2)$$

with the parameters for Cu and Ag that were used before.[10] Self-consistency was achieved by iteration on the H_{ii} element of Cl. We used

$$-H_{ii} = 12.0 + 2Q \qquad (3)$$

to achieve a self-consistent charge on Cl. The component of the halogen DOS was obtained through a Mulliken-type analysis. We compare this component of the DOS to the difference spectra with the understanding that the difference spectra contain information due to changes in position of the metal orbitals as well as features due to halogen. Thus, only the portions of the difference spectra corresponding to halogen features are compared with the computed results.

The self-consistent computational procedure reflects the dependence of halogen and metal energy levels on charge as in eq 2. This dependence allows for stabilization of the energy level in the presence of a positive charge and destabilization due to a negative charge. This effect is well known from the core shifts reported in X-ray photoemission. Thus, with this model we can qualitatively understand the spectra of chemisorbed species and the dependence on cluster size through the charge transferred.

These calculations emphasize only the halogen p–metal d orbital interactions because these are the dominant features present in the UPS spectrum. In fact, electron transfer from metal s orbitals to halogen p orbitals occurs, and we have noted some features of this interaction in Figure 3. This electron transfer, although it originates from metal s orbitals, manifests itself in features of the p–d orbital interactions because the charge transfer affects positions of atomic energy levels and the resulting molecular orbitals as may be seen by considering eq 1.

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