Infrared Studies of the Interaction of Methanol with Cu_n, Ag_n, and Au_n

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Methanol (Me) adsorbs intact on copper, silver, and gold clusters at 70 K to form the complexes Cu_nMe_m, Ag_nMe_m, and Au_nMe_m, respectively. The infrared photodissociation spectra of the deuterium-substituted complexes $M_n(CD_3OH)_m$ and $M_n(CD_3OD)_m$ ($M_n = Cu_{3-11}$, Ag_{3-22}, and Au_{3-13}) have been recorded in the 9−11 μm region. The methanol C−O stretching band frequency is invariant with cluster size and depends only slightly on the metal of which the underlying cluster is composed, indicating that local interactions are responsible for the shift from the gas-phase value and that these interactions are similar for methanol adsorbed on clusters of all three metals. Progressive blue shifts of the depletion bands of Ag_nMe_m and Au_nMe_m with increasing m indicate a strong interaction among methanol ligands in these species.

1. Introduction

Most of what is known about bare coinage metal clusters, Cu_n, Ag_n, and Au_n, has emerged from studies of their physical properties. Measurements of ionization potentials and electron affinities, as well as observations of their relative unimolecular dissociation thresholds (i.e., "stabilities", as inferred from mass spectrometric abundance measurements), have revealed sudden discontinuities of these properties at certain cluster sizes.[1−14] It is now well established that these anomalies are attributable to delocalization of the metals' valence electrons throughout the volume of the "spherical" clusters and the resulting organization of electron levels into shells and subshells.[15−18] A smaller odd−even alternation effect in these properties that is not predicted for strictly spherical clusters has been shown to be due to the filling of electron levels in ellipsoidally distorted clusters.[15,19]

A large body of data regarding the chemistry of coinage metal surfaces has been collected through the application of modern surface science techniques.[20,21] While the surfaces of these metals are relatively unreactive compared to those of the open d-shell transition metals, they are not chemically inert. The use of copper-containing catalysts for the industrial production of methanol, and of silver catalysts for the production of ethylene oxide, provides examples where the surface reactivity of coinage metals can be of considerable practical importance.[22] In the presence of preadsorbed oxygen, methanol decomposes on coinage metal substrates, whereas in the absence of preadsorbed oxygen, methanol adsorbs reversibly.[23,24] Much less is known about the chemical properties of small coinage metal clusters, specifically whether the electronic shell filling phenomenon, which is dramatically manifested in coinage metal cluster *physical* properties, affects their *chemical* behavior as well. While an understanding of the chemistry of coinage metal clusters is far from complete, reactivity surveys have revealed many similarities of their reaction channels to those of the macroscopic metal surfaces.[25−35] Copper clusters, for example, are reactive toward carbon monoxide[26,30] and oxygen[29,36] but are essentially inert toward molecular hydrogen,[25,29] behavior which parallels that observed on bulk copper surfaces. However, underlying the overall similarities in their behavior, a size-dependent "fine structure" in their behavior can sometimes be observed. For example, studies of Cu_nCO^+ complexes found that those species possessing a closed electronic subshell, namely Cu_7CO^+ and $Cu_{17}CO^+$, were more stable toward collision-induced dissociation than their open-shell neighbors.[30] Flow tube kinetics studies of copper clusters by Winter et al. revealed that Cu_{20}, Cu_{40}, and Cu_{92}, which have closed electronic subshells, are less reactive toward molecular oxygen than their open-subshell neighbors,[36] behavior confirmed by Andersson et al. in beam-gas experiments conducted under single-collision conditions.[29] On the other hand, the binding propensity of water to copper clusters was found to be sensitive to geometric—rather than electronic—structure, in this case following the pattern of icosahedral shell and subshell closings of the underlying clusters.[36]

In this paper, we report the infrared molecular beam photodissociation spectra of complexes formed from the reaction of copper, silver, and gold clusters with methanol: Cu_nMe_m, Ag_nMe_m, and Au_nMe_m (Me = CD_3OH and CD_3OD). While this study is the first, to our knowledge, of neutral coinage metal cluster−methanol complexes, an investigation of the infrared photodissociation of $Au_4(CH_3OH)_m{}^+$ ($m = 1-3$) has recently been published.[33]

2. Experimental Methods

The experimental apparatus and methods used to record infrared photodissociation spectra have been described in detail previously.[37] Briefly, clusters of copper, silver, or gold atoms were generated by pulsed laser vaporization from a target of the corresponding pure metal within a continuous-flow cluster source. The flow tube where cluster growth occurred was maintained at 60−70 K. The copper target was fabricated of isotopically enriched ^{63}Cu. Methanol complexes of the coinage metal clusters were formed by adding a trace of CD_3OH or CD_3OD (Aldrich) in helium to the cluster source. The partial pressure of methanol in the flow tube was roughly 1 mTorr under typical conditions.

Following expansion through a 0.10 cm diameter orifice, a molecular beam containing the clusters was formed, which ultimately entered a detection chamber held at $<10^{-6}$ Torr. Here the beam was crossed at 90° by a collimated ArF (probe) laser ($h\nu = 6.42$ eV) which ionized the clusters for time-of-flight (TOF) mass analysis. Prior to every other ArF laser pulse,

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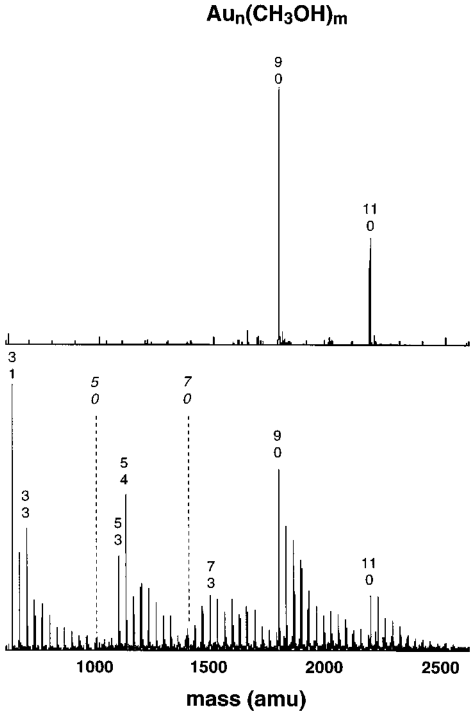

Figure 1. Photoionization time-of-flight mass spectrum of gold clusters at 193 nm (6.4 eV). Top trace: helium carrier gas only. Bottom trace: methanol added to carrier gas. Au_n and $Au_n(CH_3OH)_m$ complexes are labeled according to $^{n}_{m}$. The expected locations of bare Au_5 and Au_7 are indicated. Bare Au_3 (off scale in these TOF spectra) is also absent at this ionization wavelength.

a line-tunable, carbon dioxide (pump) laser irradiated the molecular beam in a collinear configuration. The interaction time of the molecular beam with the pump laser was approximately 200 μs. The relative depletion of the cluster complexes was measured by pulsing the pump laser at one-half the probe laser repetition rate and concurrently recording two TOF spectra: a *reference* TOF spectrum obtained with the ArF probe laser only and a *depletion* TOF spectrum obtained using both pump + probe lasers. The relative pump laser fluence $F(\nu)$ was measured by reflecting a portion of the CO_2 laser output into a pyroelectric energy detector. Effective cross sections $\sigma(\nu)$ were calculated from the measured depletion, $D(\nu)$, assuming a first-order saturation behavior: $D(\nu) = 1 - e^{-\sigma(\nu)F(\nu)}$. The validity of this approach for infrared multiphoton dissociation experiments such as those described here is discussed in ref 37.

3. Results

Photoionization Mass Spectra. A photoionization time-of-flight mass spectrum of $Au_n(CH_3OH)_m$ recorded at 193 nm (6.4 eV) is shown in Figure 1. For all three metals, we observe TOF peaks corresponding to methanol complexes of clusters that cannot be ionized at 193 nm in their bare form, demonstrating that adsorption of methanol onto the clusters effectively lowers their ionization potentials (IPs). For example, while Au_3, Au_5, Au_7, and Au_{10} are not observed in the 193 nm TOF mass spectrum due to their relatively high ionization potentials, their corresponding methanol complexes are abundantly present, as shown in Figure 1. The absence of methanol complexes of the even n gold clusters in this size range implies that their IPs are significantly greater than 6.4 eV. Similar IP-lowering effects were observed for $Cu_n(CD_3OD)_m$/$Cu_n(CD_3OH)_m$ complexes [$n = 4$, 6, and 8] and $Ag_n(CD_3OD)_m$/$Ag_n(CD_3OH)_m$ complexes [$n = 4$, 6, and 8].

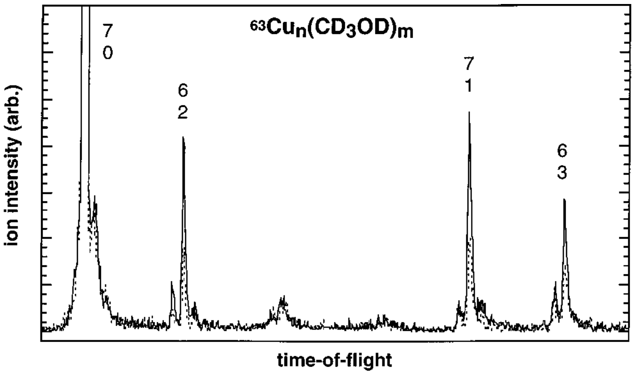

Figure 2. Photoionization time-of-flight mass spectrum of Cu_n and $Cu_n(CD_3OD)_m$ complexes at 193 nm. Solid trace: infrared pump laser off. Dashed trace: pump laser on, $\nu_{pump} = 957.8$ cm^{-1}. Note the presence of $Cu_6(CD_3OD)_m$ complexes. Bare Cu_2, Cu_4, Cu_6, and Cu_8 are not observed at 193 nm.

Infrared Photodissociation Spectra. The intense C−O stretching fundamental of methanol has the advantage of being sensitive to molecular interactions, displaying characteristic frequency shifts in response to adsorption onto surfaces,[38] ionic complex formation,[39] and hydrogen bond formation.[40−44] In this study we have used the deuterium-substituted species CD_3OH and CD_3OD ($\nu_{CO} = 985$ and 980 cm^{-1}, respectively[45]) in order to shift the depletion bands of interest away from the 990−1020 cm^{-1} tuning gap of the CO_2 laser, where the corresponding bands involving adsorbed CH_3OH and CH_3OD would be found.

The CO_2 laser-induced depletion of $Cu_n(CD_3OD)_m$ complexes from the molecular beam is illustrated in the TOF spectra shown in Figure 2. The photodissociation action spectra of selected $Cu_n(CD_3OH)_m$ and $Cu_n(CD_3OD)_m$ complexes in the region near the methanol C−O stretching fundamental are shown in Figures 3 and 4; the spectra of other complexes in the size range $n = 3$−11 were similar to those shown. For $Cu_n(CD_3OH)$ complexes, ν_{CO} appears around 965−970 cm^{-1}, 15−20 cm^{-1} to the red of the gas-phase value;[45] a red shift of similar magnitude is found for ν_{CO} in the $Cu_n(CD_3OD)$ species. The spectra of $Cu_n(CD_3OD)_2$ are essentially identical with those of the corresponding monoadducts, while those of $Cu_n(CD_3OH)_2$ complexes display a shoulder approximately 10 cm^{-1} to the blue of the main C−O stretch peak. The spectra of complexes containing three or more methanol molecules possessed poor signal-to-noise due to the low abundance of these species in the molecular beam and are not presented here. No other depletion bands were observed above the noise in the 920−1090 cm^{-1} region for either $Cu_n(CD_3OH)_m$ or $Cu_n(CD_3OD)_m$ complexes.

Photodissociation spectra of selected $Ag_n(CD_3OH)_m$ and $Ag_n(CD_3OD)_m$ complexes are shown in Figures 5 and 6; the spectra of other complexes in the size range $n = 3$−22 were similar. Depletion bands attributed to ν_{CO} are centered near 970 and 965 cm^{-1} for $Ag_n(CD_3OH)$ and $Ag_n(CD_3OD)$ complexes, respectively, about 15 cm^{-1} to the red of the corresponding gas-phase values of ν_{CO}. For $Ag_n(CD_3OH)_2$ and $Ag_n(CD_3OD)_2$ the position of the ν_{CO} depletion feature is shifted to the blue of the corresponding monoadduct band, ~15 cm^{-1} for $Ag_n(CD_3OH)_2$ and ~5 cm^{-1} for $Ag_n(CD_3OD)_2$. In addition, as shown in Figures 5 and 6, we observed in some cases smaller depletion features at 1060−1070 cm^{-1} for $Ag_n(CD_3OH)_m$ and 1040−1050 cm^{-1} for $Ag_n(CD_3OD)_m$. These bands correspond to the ν_6 and/or ν_{10} CD_3 bending modes[45] of CD_3OH ($\nu_6^{gas} = \nu_{10}^{gas} = 1068$ cm^{-1}) and CD_3OD ($\nu_6^{gas} = 1028$ cm^{-1}, $\nu_{10}^{gas} = 1069$ cm^{-1}).

Photodissociation spectra of selected $Au_n(CD_3OH)_m$ and $Au_n(CD_3OD)_m$ complexes are shown in Figures 7 and 8 for m

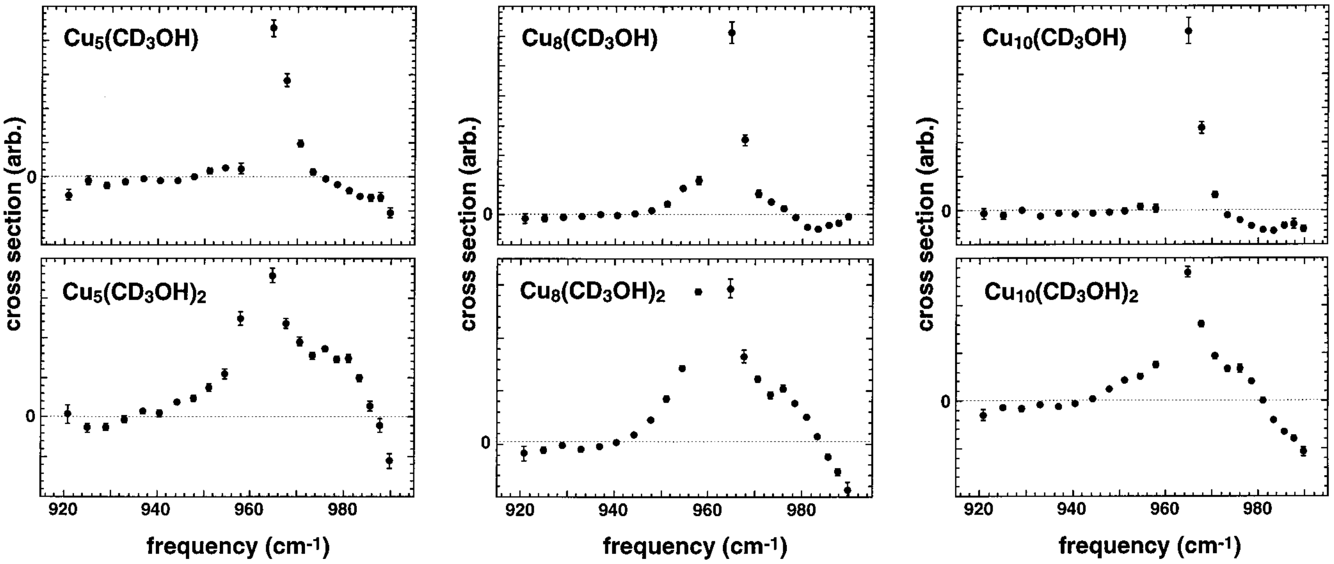

Figure 3. Infrared photodissociation spectra of representative $Cu_n(CD_3OH)_m$ complexes.

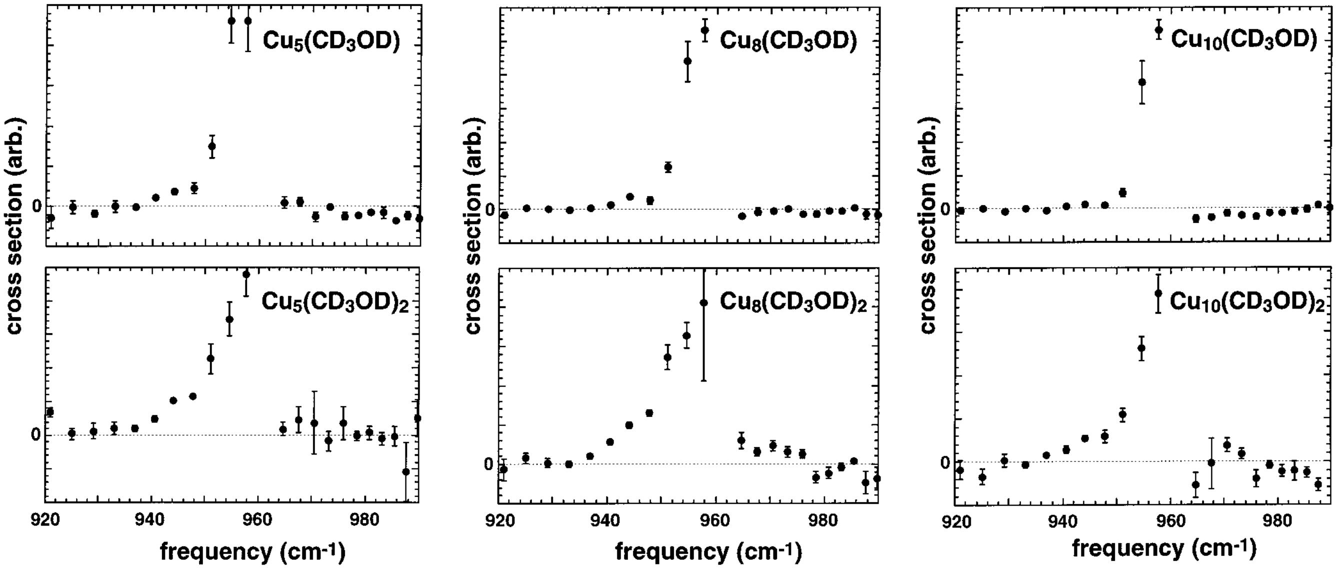

Figure 4. Infrared photodissociation spectra of representative $Cu_n(CD_3OD)_m$ complexes.

≤ 4; other complexes in the size range $n = 3-13$ produced similar spectra. For the monoadducts, $Au_n(CD_3OH)$ and $Au_n(CD_3OD)$, ν_{CO} is centered around 960 and 955 cm^{-1}, respectively, about 25 cm^{-1} to the red of the corresponding gas-phase values of ν_{CO}. A progressive broadening and blue shift of the C$-$O stretching depletion band are observed with increasing methanol coverage, with the band positions for $Au_n(CD_3OH)_m$ complexes shifting somewhat more with increasing m than those of $Au_n(CD_3OD)_m$ complexes. No other depletion bands were observed in the 920$-$1090 cm^{-1} region.

The observed depletion band frequencies for Cu_nMe_m, Ag_nMe_m, and Au_nMe_m (Me = CD_3OH and CD_3OD) are tabulated in Table 1.

TABLE 1: Frequencies ν_{CO} of the C$-$O Stretching Bands in Cu_nMe_m, Ag_nMe_m, and Au_nMe_m (Me = CD_3OH and CD_3OD)[a]

	$\nu_{CO}/\Delta\nu_{CO}$ (cm^{-1}) for m =			
	1	2	3	4
$Cu_n(CD_3OH)_m$	965/$-$20	965/$-$20 975/$-$10[b]		
$Cu_n(CD_3OD)_m$	960/$-$20	960/$-$20		
$Ag_n(CD_3OH)_m$	970/$-$15	985/0		
$Ag_n(CD_3OD)_m$	965/$-$15	970/$-$10		
$Au_n(CD_3OH)_m$	960/$-$25	970/$-$15	975/$-$10	985/0
$Au_n(CD_3OD)_m$	955/$-$25	960/$-$20	965/$-$15	970/$-$10

[a] The tabulated values are averages over n, rounded to the nearest 5 cm^{-1}. Also tabulated is $\Delta\nu_{CO}$, the displacement from fundamental of gas-phase CD_3OH (985 cm^{-1}) and CD_3OD (980 cm^{-1}). [b] Shoulder.

4. Discussion

Photoionization Thresholds. Several studies have demonstrated that adsorption of atoms or molecules onto metal clusters can significantly shift their IPs, an effect analogous to the work function changes, $\Delta\phi$, accompanying chemisorption and physisorption of atoms and small molecules on macroscopic metal surfaces. Simple electrostatic considerations show that a polar molecule adsorbed with its dipole moment directed toward (away from) the cluster will result in an IP decrease (increase).[46,47] The ability to photoionize methanol complexes of high IP clusters that could not be photoionized at the same wavelength in their bare form (e.g., see Figure 1) verifies that, as on the corresponding macroscopic coinage metal surfaces,

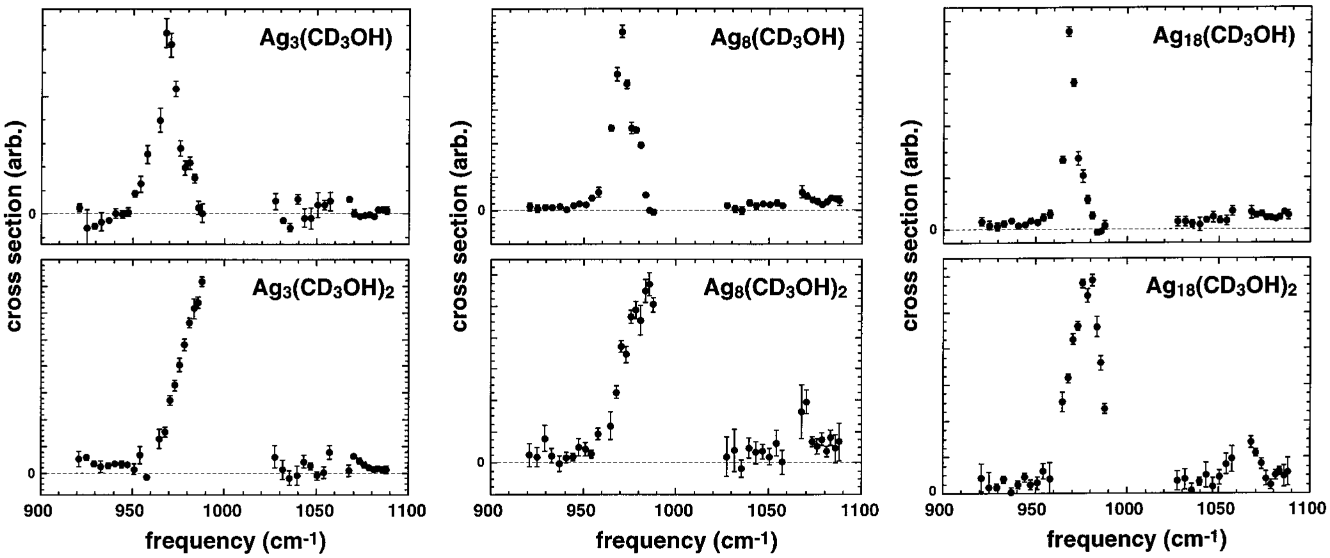

Figure 5. Infrared photodissociation spectra of representative $Ag_n(CD_3OH)_m$ complexes.

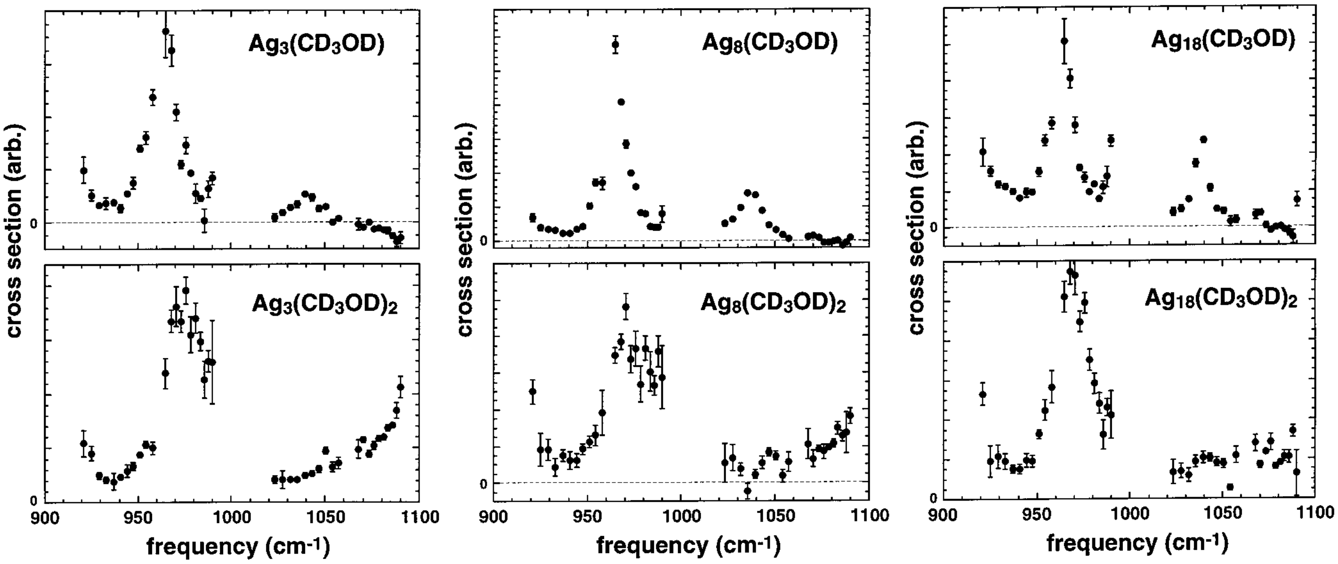

Figure 6. Infrared photodissociation spectra of representative $Ag_n(CD_3OD)_m$ complexes.

methanol adsorbs to these clusters dipole down, presumably through an oxygen atom lone pair.

Infrared Photodissociation Spectra. Surface studies have shown that methanol adsorbs to coinage metal surfaces with enthalpies in the range 9.5−16.7 kcal/mol (0.41−0.72 eV/molecule).[24,48] In a recent infrared photodissociation study, Dietrich and co-workers[33] modeled the fluence variation of the observed depletion of $Au_4(CH_3OH)_m^+$ at 10 μm ($h\nu = 0.1$ eV) and estimated that 3−4 photons were required to reach the dissociation threshold in this ionic cluster. Assuming that these results provide reasonable approximations to the copper−, silver−, and gold cluster−methanol bond dissociation energies, it becomes clear that the photodissociation process leading to desorption of methanol requires absorption of several infrared photons. Despite the multiphoton nature of the photodissociation process, we have shown[37] that the variation of depletion with fluence mimics one-photon photochemistry and is thus well described by first-order (sigmoidal) saturation behavior. This approximation breaks down, however, under reagent-rich flow conditions in which a broad distribution of complexes containing various number of adsorbates are produced. In this case, the stepwise photodissociation of high-*m* (i.e., adsorbate-rich) complexes can lead to suppressed or even "negative" net depletions in low-*m* complexes, resulting in distorted spectra.[37] Mass selection prior to photodissociation is one approach that has been used to overcome this problem in studies of molecular clusters.[42,49] The present study was conducted using sufficiently low methanol flows to ensure that the product distribution was narrow ($m \leq 4$) and skewed toward low *m*, thus minimizing the distorting effects of coupled photodissociation.

The observation that the positions of the strong ν_{CO} depletion features in cluster−CD_3OH and cluster−CD_3OD complexes are shifted approximately 5 cm^{-1} with respect to one another (just as with gas-phase CD_3OH and CD_3OD) verifies that methanol adsorbs intact on Cu_n, Ag_n, and Au_n, analogous to the reversible molecular chemisorption of methanol observed on the corresponding *clean* single-crystal surfaces.[23,24,38,50−57] The observation of the weak methyl bending modes in $Ag_n(CD_3OH)_m$ and $Ag_n(CD_3OD)_m$ complexes confirms the assignment. In contrast, methanol and other aliphatic alcohols have been found to react readily with oxygen-precovered surfaces of Cu, Ag, and Au to form surface-adsorbed methoxy, formate, or other species.[23,38,50−54,57−59]

Considering first those complexes containing only a single adsorbed methanol molecule, we note that the frequency of the C−O stretching fundamental of adsorbed methanol is slightly

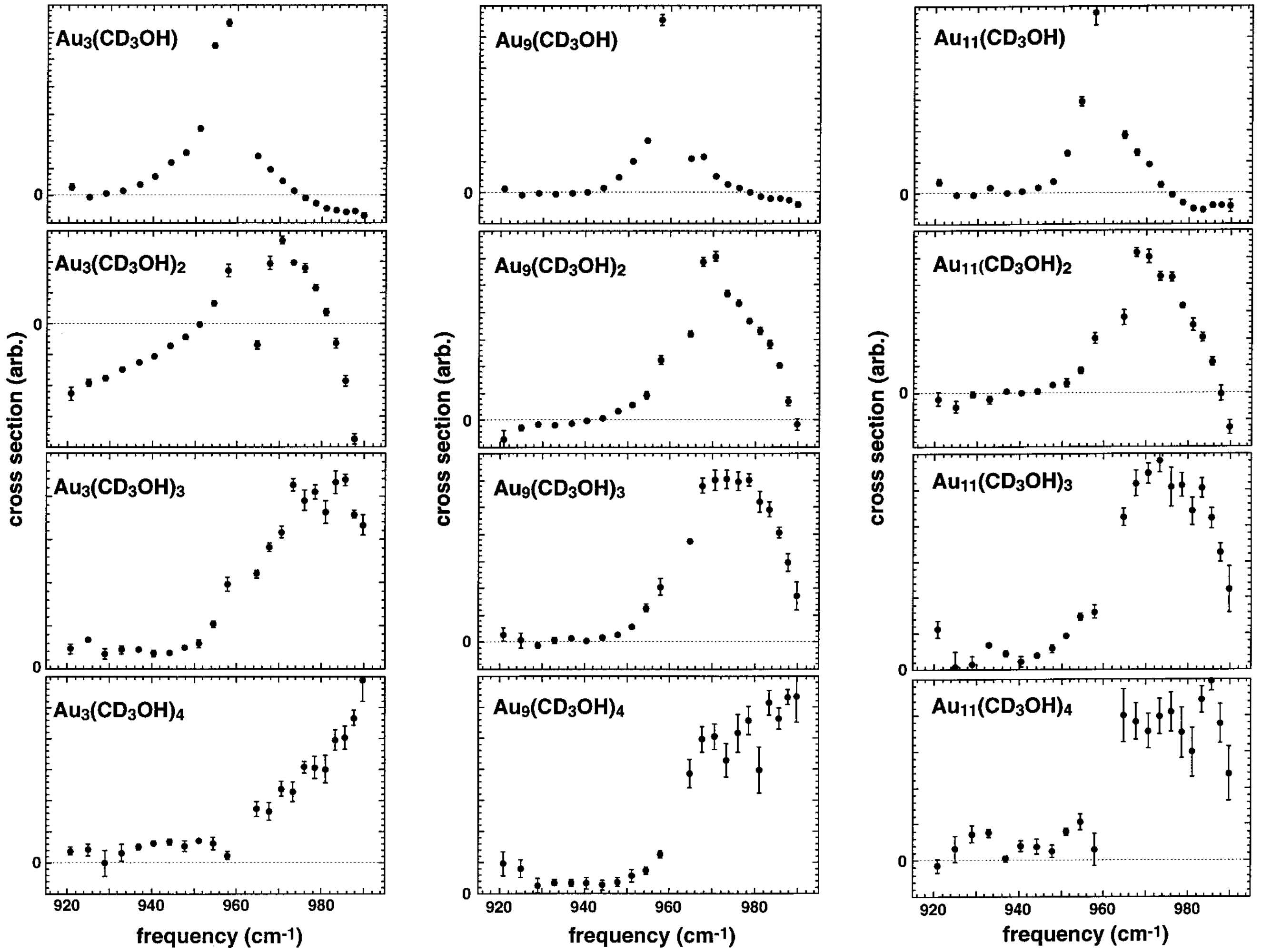

Figure 7. Infrared photodissociation spectra of representative $Au_n(CD_3OH)_m$ complexes.

different among copper, silver, and gold complexes, but for each metal ν_{CO} displays little variation with cluster size (n) throughout the size range investigated. The sensitivity of the stretching frequency to the metal of which the cluster is composed may be due to the orientation of the cluster−adsorbate bond, the strength of the cluster−adsorbate interaction, or both. Neither the electronic shell closing at $n = 8$ nor the odd−even modulation of cluster electronic structure (e.g., as is reflected in ionization potentials and electron affinities) is manifested in the cluster−methanol interactions, as measured by $\Delta\nu_{CO}$. This suggests that the cluster-methanol interaction responsible for the red shift in ν_{CO} is local, involving one or a few atoms of the metal cluster, rather than a global, involving the total valence electron population.

The spectra of complexes containing more than one adsorbed methanol molecule are now considered. First, the broadening and frequency shifts observed of ν_{CO} with increasing m in Ag_nMe_m and Au_nMe_m complexes are greater than those expected due to the band-distorting effects of sequential elimination of methanol at the low methanol coverages used here (vide supra) and are therefore judged to be genuine spectroscopic observations. Because the spectra of the monoadducts uniformly display single (rather than multiple) C−O stretch bands, we can assume either that the methanol molecules adsorb to a single type of site on the cluster surface or that ν_{CO} is independent of the type of surface site occupied. We propose that the observed changes in band position and/or width with increasing methanol coverage may be due to an interaction among the methanol molecules on the surfaces of the clusters. One possibility is that the observed shifts result from simple vibrational coupling among strongly bound (i.e., immobile) methanol molecules, akin to those observed in organometallic complexes and on surfaces.[60] A second possibility is that the methanol ligands, rather than being firmly bound to the cluster surface, are mobile, forming aggregates on the surface of the underlying metal cluster. The absence of two distinct peaks in the frequency range of the C−O stretching band indicates, however, that two interacting methanol molecules do not form a true hydrogen-bonded methanol dimer. For the isolated methanol dimer, two distinct C−O stretching bands are observed, with that of the proton-accepting methanol shifted by 25−30 cm^{-1} to the red of the C−O stretching band of the proton-donating methanol.[40−44] No such doublets are observed in the present spectra. It is notable that the progressive band shifts measured in $Au_n(CD_3OH)_m$ and $Au_n(CD_3OD)_m$ were also seen in $Au_4(CH_3OH)_m^+$ over the range $m = 1−3$.[33] These workers also rejected the existence of true methanol dimers within this complex for the reasons outlined above. The progressive shift of ν_{CO} to higher frequencies with increasing methanol coverage in Ag_nMe_m and Au_nMe_m complexes is consistent with the blue shift of 20 cm^{-1} in ν_{CO} (compared to ν_{CO}^{gas}) observed in electron energy loss spectroscopy measurements of a monolayer of CH_3OH on Ag(110) at 90−100 K [ref 38].

For $Cu_n(CD_3OH)_2$ complexes, the appearance of a shoulder rather than a uniform broadening of the depletion band with the addition of the second methanol molecule suggests that only a portion of the methanol pairs in the $Cu_n(CD_3OH)_2$ complexes

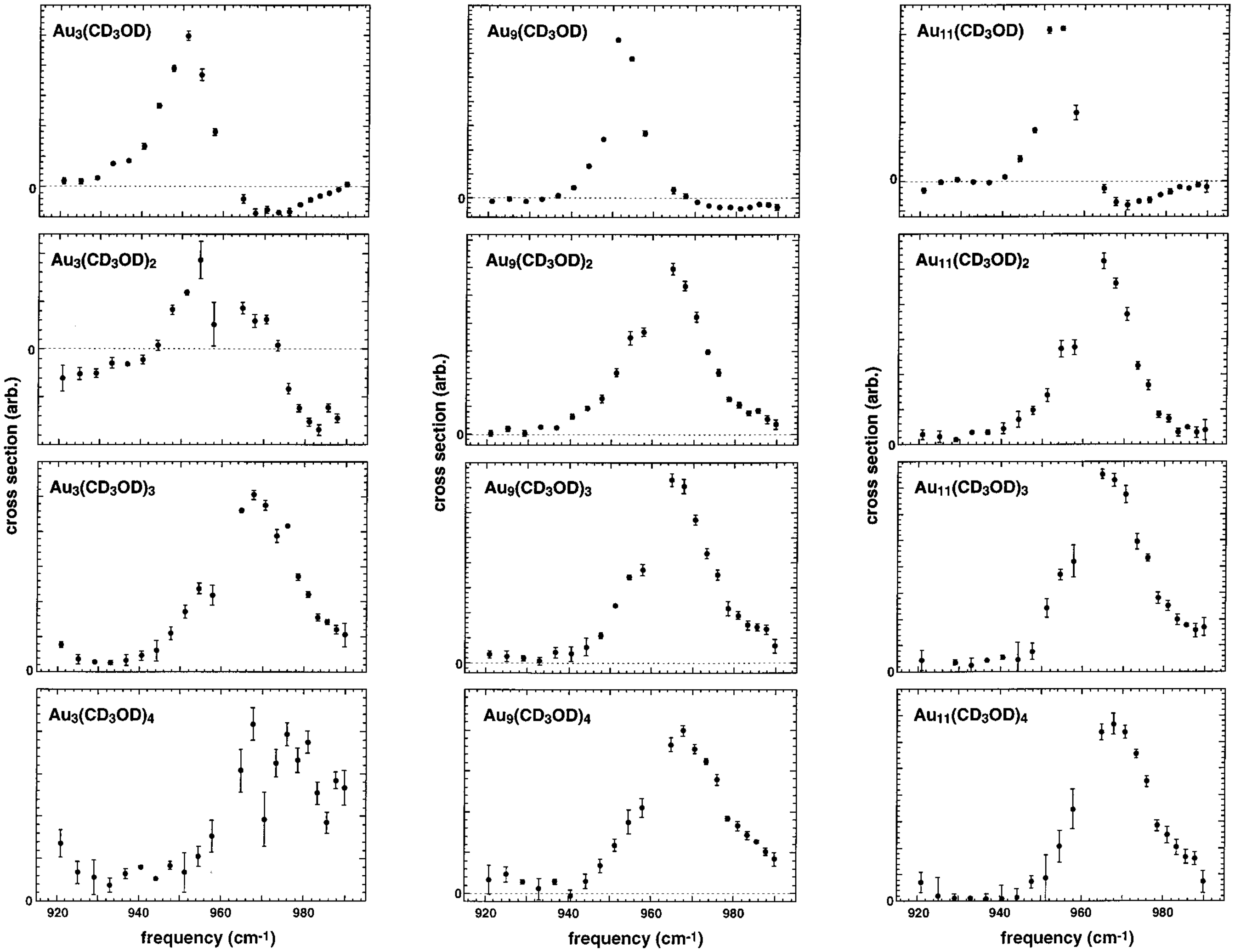

Figure 8. Infrared photodissociation spectra of representative Au$_n$(CD$_3$OD)$_m$ complexes.

interact strongly, perhaps due to lower mobility (i.e., stronger adsorption) as compared to methanol in the silver and gold cluster complexes. No such shoulder is observed in the spectra of Cu$_n$(CD$_3$OD)$_2$ complexes, although it is possible that such a feature may have fallen within the tuning gap in the pump laser around 960 cm^{-1}.

The similarity of the depletion band positions among clusters of a different size (n) implies an insensitivity of cluster–adsorbate interaction to the geometric structure of the underlying metal cluster. While there are no direct experimental determinations of the structures of copper, silver, or gold clusters beyond the trimers, quantum chemical calculations indicate that they exhibit a variety of dissimilar structures as a function of size, rather than a common structural motif.[61–72] A number of these theoretical studies have suggested the lowest energy structures for the smaller copper clusters[62,64,66,70,71] are similar to those of the corresponding silver clusters,[61,67,69,72] showing for example a transition from a two-dimensional "W" shape for the copper and silver pentamers to a three-dimensional pentagonal pyramid structure for the hexamers. Gold clusters have been studied less extensively, both experimentally and theoretically, but calculations suggest that they too undergo a 2D → 3D transition at the same size as copper and silver clusters.[64,65] In general, the bonding in gold clusters is stronger and the bonds are shorter compared to clusters of the lighter transition metals because of substantially enhanced relativistic effects. However, this does not appear to have a dramatic effect on the cluster–methanol interaction, as evidenced by the small variance in the C–O stretching band frequency.

5. Conclusions

The 193 nm photoionization TOF mass spectra together with the photodissociation spectra show that on Cu$_n$, Ag$_n$, and Au$_n$ methanol adsorbs intact. In particular, we observe no correlation of the methanol C–O stretching band position with the large electronic and geometric structure variations displayed by the underlying copper, silver, and gold clusters, confirming that the interaction responsible for the shift from the gas-phase value is local, involving one or a few atoms, rather than global. The blue shift and broadening of the C–O stretching band with increasing methanol coverage is attributed to a strong interaction among the methanol molecules.

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