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Infrared Photodissociation Spectroscopy of $\text{Ag}_n(\text{C}_6\text{H}_6)_m$ and $\text{Ag}_n(\text{C}_6\text{D}_6)_m$ Clusters: Evidence of Adsorption-Induced Symmetry Reduction in Benzene

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Introduction

Photodepletion spectroscopy has emerged in recent years as a powerful tool for probing the optical response of both neutral¹⁻¹¹ and charged¹²⁻²⁰ metal clusters. Comparison of measured spectra with theoretical predictions²¹⁻²³ has allowed for inferences about size-specific cluster structures. The bulk of cluster photodepletion spectroscopy studies to date have been performed in the visible and near-infrared region, thereby providing information on electronic transitions. Recently, there has been an increased interest in infrared photodissociation experiments involving vibrational transitions in cluster-adsorbate complexes. In particular, the infrared photodissociation spectra of $\text{Fe}_n(\text{CH}_3\text{OH})_m$ complexes and their deuterated analogs have been recorded²⁴⁻²⁸, as have the spectra of Ag_2NH_3 ²⁹, $\text{Fe}_2(\text{CH}_3\text{CH}_2\text{OH})_2$ ⁺³⁰, $\text{Cr}_3(\text{CH}_3\text{CH}_2\text{OH})$ ⁺³⁰, and $\text{Au}_4(\text{CH}_3\text{OH})_m^+$ ($m=1-3$)³¹.

The vibrations of benzene- h_6 and benzene- d_6 on single crystal metal surfaces have been thoroughly investigated using a number surface science techniques, including high resolution electron energy loss spectroscopy^{32,33}, reflection absorption infrared spectroscopy³⁴, unenhanced surface Raman spectroscopy^{35,36}, and surface enhanced Raman spectroscopy (SERS)³⁷⁻⁴⁰. On silver surfaces, it has been found that benzene adsorbs weakly, with vibrational frequencies that are shifted downward by approximately 5 cm^{-1} relative to those of gas-phase benzene.³⁷ Furthermore, modes which are inactive for gas-phase benzene are seen when the benzene is adsorbed to the surface, showing that although the interaction is weak, it is sufficient to lower the symmetry of the benzene from D_{6h} to C_{3v} (σ_d).³⁷ The orientation of the benzene relative to the surface remains a point of controversy. It seems likely, based upon SERS-detected temperature program desorption results, that the orientation depends upon the coverage.⁴⁰

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On bulk metals a surface selection rule comes into play: only those vibrational modes having a non-zero normal component of the dipole moment derivative are infrared active.⁴¹ This can be visualized by considering that for each dipole above the surface of a metal, there is an image dipole at an equal distance below the surface. Hence the bond-stretching vibration of an adsorbate on a metal gives rise a change in the image dipole. The effect of vibrations parallel to the surface is cancelled out by the change in the image dipole, while the effect of vibrations perpendicular to the surface is reinforced. It has been demonstrated that the surface selection rule applies to the vibrations of benzene on single crystal silver surfaces³⁵, but no studies investigating the applicability of the surface selection rule to metal clusters have been published. Indeed, the breakdown of the surface selection rule with decreasing cluster size could be used a measure of the metal→nonmetal transition in clusters of metallic elements.

Experimental Methods

The experimental apparatus and methods used for infrared photodissociation spectroscopy have been described in detail previously.²⁸ Briefly, silver clusters were generated by pulsed laser vaporization of a silver rod (details). Cluster cooling and growth occurred in helium carrier gas flowing within a 7.6 cm x 0.32 cm (length x i.d.) maintained near 70 K and at a pressure of 40-45 Torr. The silver cluster-benzene complexes were formed by adding a mixture of benzene in helium to the pure helium flow stream approximately 3 cm downstream of the target rod. The partial pressure of benzene- h_6 (benzene- d_6) was maintained at roughly 1 mTorr. Both C_6H_6 and C_6D_6 were obtained from Aldrich and used without further purification.

After spending ~1 ms in the flow tube, the silver cluster-benzene complexes (hereafter denoted Ag_nBz_m) underwent a mild supersonic expansion into vacuum through a 0.10 cm diameter orifice opening into a 15° (half angle) conical nozzle. They passed through a skimmer, forming a molecular beam, and a collimating orifice before entering the detection chamber. Here the beam was crossed at 90° by a collimated ArF (probe) laser capable of ionizing the clusters for time-of-flight (TOF) mass analysis. On every second ArF laser pulse, the molecular beam was irradiated by a counterpropagating line-tunable carbon dioxide (pump) laser. The relative depletion of the Ag_nBz_m species was found by dividing the TOF depletion spectrum, obtained when both the pump CO_2 and probe ArF lasers were fired, by the TOF reference spectrum, obtained when only the ArF probe laser was fired. Action spectra were normalized with respect to pump

laser power, obtained by reflecting a portion of the CO₂ laser output into a pyroelectric energy detector.

Results and Discussion

Reference and depletion TOF mass spectra of Ag_n(C₆H₆)_m for n=3-8 are shown in Figure 1. It is seen in Figure 1 that many of the mass peaks corresponding to cluster complexes, such as Ag₅(C₆H₆)₄ and Ag₇(C₆H₆)₂, are depleted when the pump laser is tuned to 985.6 cm⁻¹, indicating that a portion of the complexes have undergone photofragmentation. The assignment of this depletion feature is discussed below. Estimating the cluster-benzene bond energy at 0.4-0.6 eV (as measured in single crystal surface experiments³³) it is seen that absorption of several pump laser photons ($h\nu_{\text{pump}} \cong 0.1$ eV) are necessary to reach the cluster-benzene dissociation threshold. (The alternative explanation would be that benzene is bound much more weakly to a silver cluster than to a silver surface.) Quantum chemical calculations on small silver clusters indicate their binding energies lie in the region of 1-2 eV.^{42,43} Assuming that the complexes obey statistical unimolecular dissociation behavior, they will likely fragment by loss of benzene molecules rather than by loss of silver atoms.

It should be noted that while Ag₄, Ag₆, and Ag₈ are not ionized at 6.42 eV due to their relatively high ionization potentials, Ag₄(C₆H₆)_m (m≥1), Ag₆(C₆H₆)_m (m≥2), and Ag₈(C₆H₆)_m (m≥1) are observed in the mass spectrum. This result shows that when benzene molecules are attached to silver clusters, they have the effect of lowering the cluster ionization potentials. This trend has been observed in studies of benzene chemisorption on platinum clusters⁴⁴ and is consistent with other experiments showing that electron-donating adsorbates such as ammonia tend to decrease cluster IPs,⁴⁵ an effect analogous to the work function shifts accompanying adsorption of molecules on bulk metal surfaces. A more quantitative study of the effects of benzene adsorption on silver cluster ionization potentials will be published later.

Representative photodissociation action spectra are presented in Figures 2 and 3. Because of their high (D_{6h}) symmetry, benzene-h₆ and benzene-d₆ each possess only four infrared active vibrational modes: three doubly degenerate e_{1u} vibrations and one a_{1u} mode.⁴⁶ Of these only the ν₁₄ (e_{1u}) vibration of benzene-h₆ symmetry lies within the 920-1090 cm⁻¹ tuning range of the pump laser used in this study. In gas phase benzene-h₆ this mode is observed at 1038 cm⁻¹ while in benzene-d₆ it lies at 814 cm⁻¹. As shown in Figure 2, a depletion feature is observed for several

$\text{Ag}_n(\text{C}_6\text{H}_6)_m$ species near 1032 cm^{-1} , which we attribute to the ν_{14} mode of adsorbed benzene- h_6 . No corresponding depletion feature is observed in the spectra of the perdeuterated analogs, as expected for this assignment. The small magnitude ($\sim 6\text{ cm}^{-1}$) of the observed frequency shift with respect to the gas phase value is in line with the results of vibrational spectroscopy studies of benzene on bulk silver surfaces and indicates a weak cluster-benzene interaction.³³

In addition to the 1035 cm^{-1} feature, most of the $\text{Ag}_n(\text{C}_6\text{H}_6)_m$ species investigated display a second depletion feature near 986 cm^{-1} . This observation may suggest the presence of isomers in which the benzene interacts more strongly with the underlying silver cluster, reflected by a greater frequency shift from the 1038 cm^{-1} gas phase benzene value. We, propose, however, that this feature corresponds to the ν_2 vibration of benzene a_{1g} symmetry, which in the gas phase lies at 993 cm^{-1} . Although this vibrational mode is infrared inactive for gas phase benzene, the proximity of the molecule to the cluster surface effectively reduces the symmetry from D_{6h} to C_{6v} (or lower) in which case this mode becomes infrared active. The observation of depletion features in the corresponding $\text{Ag}_n(\text{C}_6\text{D}_6)_m$ complexes at $\sim 938\text{ cm}^{-1}$, 7 cm^{-1} to the red of the gas phase value for the ν_2 mode of C_6D_6 , confirm this assignment. These observations provide compelling evidence that the mode observed is the a_{1g} C-C breathing mode.

In addition, we observe small but measureable difference in the shifts from the gas-phase benzene frequencies for the various Ag_nBz_m clusters. For instance, the resonance in $\text{Ag}_5(\text{C}_6\text{H}_6)_3$ falls at 988 cm^{-1} and that in $\text{Ag}_5(\text{C}_6\text{D}_6)_3$ falls at 940 cm^{-1} , while the resonance in $\text{Ag}_5(\text{C}_6\text{H}_6)$ falls at 986 cm^{-1} and that in $\text{Ag}_5(\text{C}_6\text{D}_6)$ falls at 938 cm^{-1} . These small differences may be due to differences in the strength of interaction of the benzene molecules with the silver clusters, perhaps because of differences in the relative orientation of the molecules and the clusters.

Another observation from the photodissociation action spectra is that the feature corresponding to the e_{1u} mode is only seen for some of the complexes studied. In particular, it is present for $\text{Ag}_3(\text{C}_6\text{H}_6)_3$, $\text{Ag}_4(\text{C}_6\text{H}_6)_3$, $\text{Ag}_4(\text{C}_6\text{H}_6)_4$, $\text{Ag}_5(\text{C}_6\text{H}_6)_2$, $\text{Ag}_5(\text{C}_6\text{H}_6)_3$, and $\text{Ag}_5(\text{C}_6\text{H}_6)_4$. Since the e_{1u} mode is a linear combination of vibrations parallel to the surface, the absence of depletion for most clusters when the laser is tuned near 1035 cm^{-1} may indicate that the surface selection rule applies even to these very small clusters. However, it is also possible that the resonance is shifted below 1020 cm^{-1} , where there is a gap in the tuning range of the pump laser. Efforts to extend the tuning range of the pump laser into this frequency region by using $^{13}\text{CO}_2$ in the lasing gas mixture are currently underway. Another explanation for the absence of depletion of the smaller clusters lies in the mass balance of the photodissociation chain. When the larger

clusters are dissociated, complexes with fewer benzene molecules are formed. Thus, when a given complex Ag_nBz_m is irradiated, its intensity is decreased if there is absorption but it may also be simultaneously increased due to the absorption of radiation by complexes $\text{Ag}_n\text{Bz}_{m+p}$ ($p>0$). Therefore when the molecular beam contains clusters with more benzene molecules attached than in the complex of interest, there is a convolution of depletion and enhancement which may lead to only a small, undetectable net change in the intensity of this complex. Attempts to do this by reducing benzene coverage were largely unsuccessful because the overall signal of complexes with benzene attached decreased to a level where there was poor signal-to-noise for the spectroscopic measurements.

Summary

The observation of the a_{1g} C-C breathing mode of benzene in infrared photodepletion measurements of Ag_nBz_m clusters demonstrates that there is a reduction in the benzene symmetry when it is adsorbed on silver clusters. Furthermore, the absence of detection of the e_{1u} mode for most clusters investigated suggests that the surface selection rule may apply even in these very small systems. Experiments to further probe the infrared response of M_nBz_m (M = coinage metal) clusters are ongoing.

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Figure Captions

Figure 1. A portion of the reference (a) and depletion (b) TOF spectra for $\text{Ag}_n(\text{C}_6\text{H}_6)_m$, with mass peaks labeled according to (n,m). The flow tube/nozzle temperature was ~ 70 K. The depletion spectrum was recorded with $\omega_{\text{pump}} = 985.6 \text{ cm}^{-1}$.

Figure 2. Photodissociation action spectra of $\text{Ag}_3(\text{C}_6\text{H}_6)_3$, $\text{Ag}_4(\text{C}_6\text{H}_6)_4$, and $\text{Ag}_5(\text{C}_6\text{H}_6)_4$ in the range $1020\text{--}1060 \text{ cm}^{-1}$, demonstrating vibration of the a_{1g} mode at $\sim 1035 \text{ cm}^{-1}$.

Figure 3. Photodissociation action spectra of $\text{Ag}_5(\text{C}_6\text{H}_6)$, $\text{Ag}_5(\text{C}_6\text{H}_6)_3$, $\text{Ag}_6(\text{C}_6\text{H}_6)_2$, $\text{Ag}_7(\text{C}_6\text{H}_6)$, and $\text{Ag}_7(\text{C}_6\text{H}_6)_2$ in the range $982\text{--}990 \text{ cm}^{-1}$ and of the corresponding perdeuterated adducts in the range $932\text{--}946 \text{ cm}^{-1}$, demonstrating vibration of the a_{1g} mode.

Fig 1

Fig 2

Fig 3

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