

Vibrational autodetachment spectroscopy of Au_6^- : Image-charge-bound states of a gold ring

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One of the most striking spectral experiments performed thus far with negative molecular ions has been the high resolution vibrational autodetachment study of dipole-bound negative ion states of such species as acetyl fluoride enolate.^{1,2} Here sharp spectral features carrying detailed rovibrational information are readily detected by scanning a dye laser and detecting the electrons detached by coupling of excited vibrations of the molecular core to the extra electron in its diffuse, dipole-bound orbital. As is often the case in spectroscopy, it is the weakness of the coupling interaction that makes this vibrational autodetachment spectroscopy so useful. This communication deals with a similar situation, except here the molecular core does not have a strong dipole moment. Instead it involves metal clusters with no permanent dipole moment whatsoever. Nonetheless, weakly bound negative ion states were found, and at least for one cluster, Au_6^- , the vibrational autodetachment spectrum was highly informative.

For sufficiently large metal clusters there will exist a set of weakly bound states for an outer electron bound by attraction to the image charge induced in the metal cluster. Such image-charge-bound (ICB) levels have been studied extensively for electrons above flat, metal surfaces,^{3,4} where the potential of the interaction of the electron with its image charge varies as $1/Z$, where Z is the distance above the surface, and the resultant bound level spectrum is much like that of the hydrogen atom. For a large, roughly spherical metal cluster the potential for this simple polarization interaction will scale as $1/R$ for distances from the surface of the cluster much smaller than the cluster radius, evolving asymptotically to a $1/R^4$ functional form (charge induced dipole) at long distances. Stimulated by rough calculations which indicated that this image charge potential may be deep enough to support bound states for metal clusters as small as 10 Å diameter, we initiated a search for such states in mass-selected clusters of simple, nearly free electron metals such as gold and silver. By scanning a dye laser near the wavelength region for threshold photodetachment we hoped to detect photoelectrons evolving from these states either as a result of resonant 2-photon detachment (R2PD) or through autodetachment from vibrational levels built on these ICB states.

The metal cluster photoelectron spectroscopy apparatus used in this study has been discussed in detail elsewhere.⁵⁻⁸ From previously recorded extensive ultraviolet

photoelectron spectra (UPS) of mass-selected copper, silver, and gold negative cluster ions⁸ we selected Au_6^- as the target of our first attempt to observe ICB states. The reason for this choice is evident in Fig. 1, which shows the UPS of this cluster taken with an F_2 excimer laser (7.9 eV) as the photon source. UPS of such negative cluster ions is particularly revealing in cases where the corresponding neutral cluster has a closed shell singlet ground state with a large highest (lowest) occupied molecular orbit (HOMO–LUMO) gap. The negative ion then has a single electron in what was the LUMO of the neutral cluster, and the UPS pattern will show a single feature at the photodetachment threshold corresponding to the removal of this LUMO electron followed by a substantial energy gap before the more deeply bound electrons from the HOMO and lower valence band orbitals are evident. The UPS pattern shown here in Fig. 1 for Au_6^- is an extreme example of this simple situation. The small feature seen near 2.0 eV is due to removal of the single extra electron from the LUMO. The 2.5 eV gap between this small feature and the first strong features near 4.5 eV is the largest we have seen in any cluster. It indicates that the Au_6 neutral cluster has a closed shell singlet ground state, with the first excited electronic state (corresponding to a HOMO→LUMO promotion) 2.5 eV higher in energy.

The position of the first small feature at 2.0 eV provides a direct measure of the vertical detachment energy. Any weakly bound excited electronic states of the Au_6^- ion such

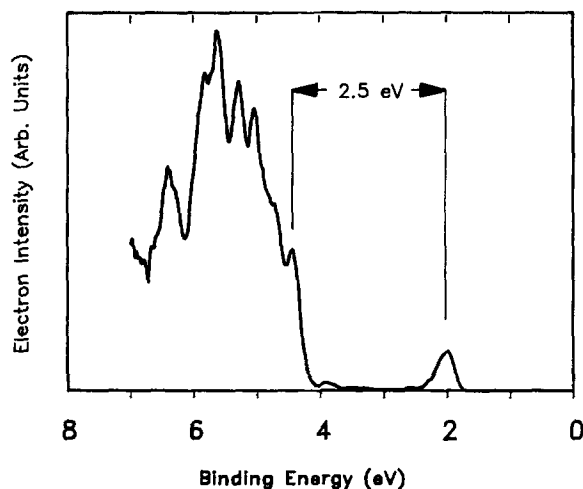


FIG. 1. Ultraviolet photoelectron spectrum of Au_6^- taken with a F_2 photodetachment laser at 7.9 eV.

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as the ICB states we were seeking would therefore correspond to a single electron with an energy slightly less than 2 eV, orbiting around a closed shell Au_6^- neutral cluster with no energetically accessible excited electronic states. Since a major decay mechanism for ICB states above metal surfaces involves the production of electron-hole excitations in the metal,⁴ the inaccessibility of these in the Au_6^- cluster should help to extend the lifetime of these weakly bound excited states.

Figure 2 shows the photoelectron spectrum (PES) of this Au_6^- cluster taken with a pulsed dye laser tuned to 6010 Å, a photon energy which is just slightly above the threshold for photodetachment predicted by the small initial feature at 2.0 eV seen in the UPS data of Fig. 1. Note that the horizontal axis for this figure is simply the translational energy of the photodetached electron. As is evident in Fig. 2 there are two distinct distributions. The majority of the photoelectrons arrive at the detector with translational energies below 0.10 eV. Measurements of the intensity of these low energy photoelectrons as a function of the dye laser fluence (in the range of 0.05 to 10.0 mJ cm^{-2} in a 20 ns pulse) showed them to result from a one-photon excitation of the Au_6^- cluster. However, the PES data of Fig. 2 show there to be another distribution of photoelectrons in a narrow energy region around 2.0 eV. They were found to scale with the square of the dye laser fluence and must therefore result from a two-photon excitation of the cluster—most likely a sequential R2PD process involving excitation to a bound intermediate level of substantial lifetime followed by excitation to the detachment continuum.

Figure 3 shows the intensity of these one-photon and R2PD photoelectron signals from Au_6^- as a function of the dye laser wavelength. The one-photon spectrum seen in the top panel of Fig. 3 shows a clear progression of peaks equally spaced at an interval of 108 cm^{-1} . Replicate measurements of this spectrum with differing choices of the precise range of photoelectron energies detected within the overall

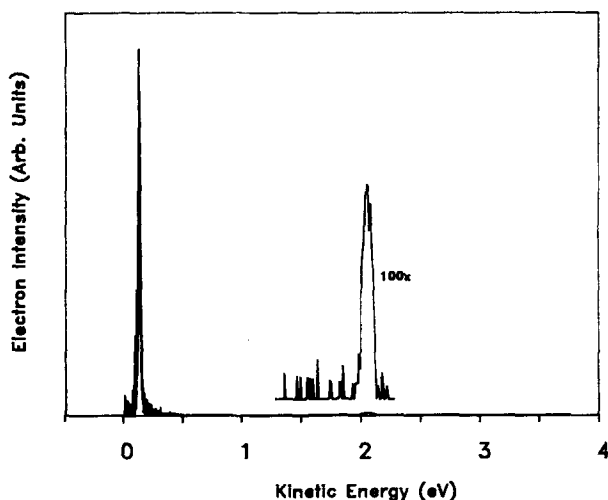


FIG. 2. Photoelectron spectrum of Au_6^- taken with a dye laser at 6010 Å (2.06 eV, 0.2 mJ cm^{-2} per 20 ns duration pulse), slightly above the photodetachment threshold.

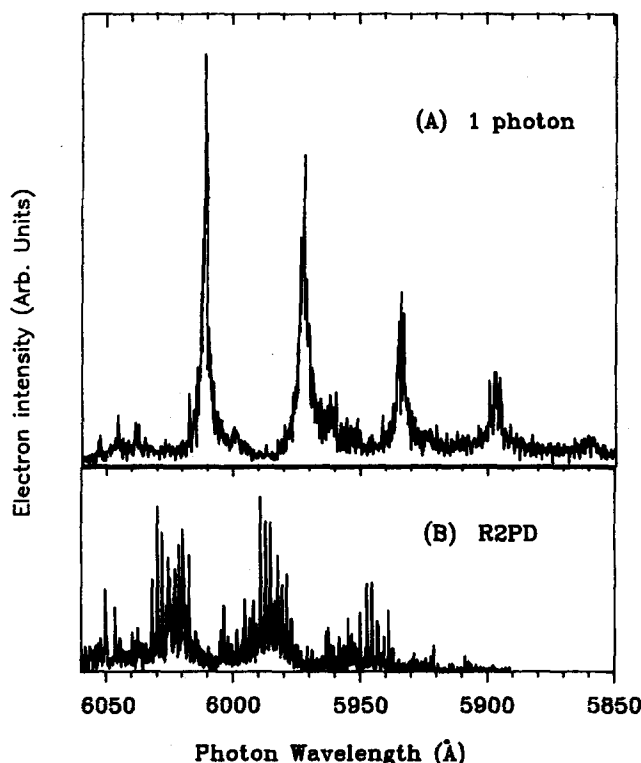


FIG. 3. Near-threshold photodetachment spectrum for (A) photoelectrons arriving with energies in the 0.1–0.2 eV range; (B) photoelectrons with energy between 2.1 and 1.9 eV arising from a 2-photon R2PD excitation of the Au_6^- cluster.

low energy PES distribution showed their peak positions were insensitive to the photoelectron energy being monitored. They must therefore be due to direct optical transitions to an excited electronic state of the Au_6^- ion. Since the spectral peaks are evenly spaced, we assign them as a progression in a totally symmetric vibrational mode of the Au_6^- cluster. Since the vibrational frequency of the Au_2 dimer⁹ is 190 cm^{-1} , and the Debye frequency of bulk gold crystals¹⁰ is 114 cm^{-1} , it is reasonable that Au_6^- would have vibrational frequencies of this magnitude. In order to be observed in this photoelectron-detected spectral experiment, these excited vibrational levels must be undergoing vibrational autodetachment before the clusters drift out of the source region of the cluster UPS apparatus (roughly $1 \mu\text{s}$).

The full width at half maximum (FWHM) for the first prominent peak at 6011 Å is 5 cm^{-1} . As is evident in Fig. 3(A), the higher members of the progression appear successively wider. We suspect this width is due to a combination of lifetime broadening via vibrational autodetachment and extensive vibronic coupling to underlying states (see below). Careful scans at a stepsize of 0.05 cm^{-1} reveal extensive fine structure within the overall 5 cm^{-1} wide profile. The spectrum shown in Fig. 3(A) was recorded with a dye laser fluence of 0.05 mJ cm^{-2} in a 20 ns pulse. At a fluence of 0.2 mJ cm^{-2} the peak at 6011 Å was observed to broaden due to saturation of the strongest fine structure features in the center of the band, indicating absorption cross sections well over 10^{-16} cm^2 . The electronic transition to this excited state is therefore strongly allowed.

The Au_6^- cluster therefore appears to have enough symmetry to permit only a single totally symmetric mode, with a frequency of 108 cm^{-1} . The weak, barely resolved satellite peak seen near 6000 \AA , 32 cm^{-1} blue of the major peak at 6011 \AA was observed to grow in intensity along with the rest of the unresolved spectral intensity in this region as the nozzle conditions were changed to provide less vibrational cooling. Similar weak features appear 32 cm^{-1} to the blue of each major peak in Fig. 3(A). We believe, therefore, that this is hot band structure. The position of the weak feature at 6038 \AA also fits well as a member of a hot band progression. If this assignment is correct, the frequency of the totally symmetric mode is reduced to 76 cm^{-1} in the ground state.

Observation of just a single vibrational progression for this six atom cluster is an intriguing result. There are 12 vibrational modes in Au_6 . Since we are dealing with an allowed electronic transition where only totally symmetric vibrational modes will be active, the fact that only one mode is seen in progressions sharply reduces the number of candidate structures for the Au_6 cluster. For six atoms there are only two reasonable structures with sufficient symmetry to give just a single totally symmetric mode: the O_h octahedron and the D_{6h} ring. Extended Huckel (EH) calculations¹¹ show that the O_h structure will have an open-shell ground electronic state—with the negative ion having 5 electrons in a 3-fold degenerate HOMO. The UPS data of Fig. 1 rule this structure out. Even with extensive distortion away from perfect O_h symmetry, EH calculations show it would be impossible to open up a HOMO–LUMO gap anywhere near the observed 2.5 eV. Spin–orbit coupling is large in gold, and one might argue that this is enough to split the degeneracy and quench the Jahn–Teller instability. But relativistic calculations have shown that the HOMO remains degenerate and unfilled.¹² On the other hand, the D_{6h} ring structure is in excellent agreement with the new spectra: it has just a single totally symmetric mode and EH calculations show it will have a large HOMO–LUMO gap.

Normal mode calculations for the D_{6h} gold ring predict the a_g symmetrical breathing motion to be the highest frequency mode of the molecule. EH calculations reveal that the analogy to benzene may actually be rather interesting. Because of the relativistic contraction of the $6s$ atomic orbital and the high spin–orbit splitting of the $5d$ levels, there is a substantial amount of s – d hybridization in the bonding orbitals of gold clusters, just as there is in bulk gold.¹³ Whereas EH calculations for simple s -orbital metal clusters such as Na_6 show the capped pentagon to be more stable than the D_{6h} ring,¹⁴ our EH calculations for Au_6 suggest the $6s$ – $5d$ hybridization is sufficient to make the D_{6h} ring the most stable by roughly 40%. The capped pentagon structure is found in these calculations to be the next best choice, and it also has a large HOMO–LUMO gap. However this pentagonal gold “crown” has two totally symmetric modes (the breathing mode, and the up/down motion of the cap atom). Since both these motions affect the bond distance between the cap atom and those in the ring, and the LUMO of this molecule is antibonding between these atoms, both totally symmetric modes of the gold crown should have been evident in the spectrum.

We note that the reconstruction observed for clean gold surfaces is thought to be driven by the decrease of the kinetic energy of the valence electrons when their geometrical confinement is relieved.¹³ A gold ring of the proposed structure would very efficiently allow such stabilization.

The assignment of the 1-photon spectrum of Fig. 3(A) to an allowed electronic transition from Au_6^- in the form of a D_{6h} ring, has some interesting consequences. The molecular orbital pattern of this molecule will be like the π -orbital pattern of benzene. In the ground electronic state of the negative ion the extra electron will occupy the e_{2g} LUMO of the closed shell neutral, resulting in this state having overall ${}^2E_{2g}$ electronic symmetry (note that spin–orbit coupling is probably strong enough here to quench the Jahn–Teller instability of this state¹⁵). The lowest ICB state of this cluster will have the extra electron promoted to a diffuse $n = 1$, $\Lambda = 0$ orbital with no angular nodes. The symmetry of this state in D_{6h} symmetry will be ${}^2A_{1g}$, so it is forbidden in electric dipole ($E1$) transitions from the ${}^2E_{2g}$ ground state. The first allowed ICB state will be one with a single angular node, corresponding to the extra electron orbiting around the closed shell neutral cluster in the plane of the ring with $n = 1$, $\Lambda = 1$. The symmetry of this state will be ${}^2E_{1u}$, and it should be strongly allowed in $E1$ transitions from the ground state. Rough calculations indicate this $\Lambda = 1$ state is very close to the vacuum level. Therefore, it seems reasonable at this point to tentatively assign the spectrum shown in Fig. 3(A) to the ${}^2E_{1u} \leftarrow {}^2E_{2g}$ (ICB \leftarrow valence) electronic transition of Au_6^- in the form of a D_{6h} gold ring.

Since the $E1$ forbidden ${}^2A_{1g}$ $n = 1, \Lambda = 0$ ICB state is expected to be bound by less than 0.1 eV, it should be in this same spectral region, and it is reasonable to expect some intensity will be borrowed from the allowed ${}^2E_{1u}$ state through extensive vibronic coupling involving the e_{1u} vibrational mode. Evidence for this state is found in the R2PD excitation experiments. The lower panel of Fig. 3 shows the wavelength dependence of the R2PD photoelectron signal. Though far weaker than the 1-photon spectrum, this R2PD spectrum is rich in detail. Many of the peaks in this spectrum have widths on the order of 0.3 cm^{-1} , which is the resolution of the pulsed dye laser. On the other hand there appears to be extensive broadening of some of the peaks, and the unresolved spectral activity on the baseline appears to be real signal, well above experimental noise. Although not shown in Fig. 3(B), this R2PD spectrum was found to continue to longer wavelengths, the last major feature appearing near 6250 \AA , which we tentatively assign as the vibronic origin of the ${}^2A_{1g} \leftarrow {}^2E_{2g}$ electronic transition. Throughout this range of the R2PD spectrum is highly complex, although clumps of major features can be discerned to form a progression with a spacing of roughly 108 cm^{-1} .

The fact that the R2PD spectrum is weakest in the region of the main peaks in the 1-photon spectrum suggests that here the coupling between the states may be so large that the lifetime becomes too short for efficient photodetachment with the 2nd photon. R2PD excitation selects those states which have borrowed sufficient oscillator strength from the ${}^2E_{1u}$ state to be seen without becoming so efficiently coupled that the lifetime is excessively shortened. Additional compli-

cations in this R2PD spectrum may arise from the presence of a second ${}^2A_{1g}$ ICB state (the one with $n = 2$, $\Lambda = 0$), which crude calculations for this gold ring indicate may be bound by a few meV, as well as the underlying quasicontinuum built on the ground and excited valence states of the negative ion. Studies are now underway to determine the lifetime of these levels and to attempt to unravel at least partially the complicated vibronic spectral pattern.

In summary, vibrational autodetachment spectra of Au_6^- clusters have been observed for an excited electronic state. Combined with the UPS studies, the spectral results are consistent with autodetachment from the totally symmetric breathing mode of Au_6^- in the form of a D_{6h} ring. In addition, R2PD excitation spectra have been obtained for a second and possibly a third weakly bound state having many long-lived vibrational levels. While rough calculations support the assignment of these spectra as excitations from a ${}^2E_{2g}$ ground state to a few ICB states (two $\Lambda = 0$ states with ${}^2A_{1g}$ symmetry and one $\Lambda = 1$ state of symmetry ${}^2E_{1u}$), more experiments and detailed calculations will be necessary to establish this assignment firmly.

Such ICB states may be common for a wide variety of metal and semiconductor clusters. We have made spot checks for similar behavior in 8th and 20th clusters of gold, and in the 6th, and 8th cluster of silver. Spectral features were seen in all cases, but these were never as sharp and well resolved as reported here for the very special case of Au_6^- . We suspect much of this apparent broadening is due to the presence of multiple active modes in the spectrum of these clusters combined with sequence congestion and lifetime broadening due to incomplete cooling of the clusters. Such spectra may be dramatically improved when the clusters are cooled to very low internal temperatures. The current 1- and 2-photon spectra of Au_6^- provide tantalizing incentives to push cluster beam technology yet a bit further, and to consider the detailed molecular physics of cluster ICB states in general.

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