

Zero electron kinetic energy spectroscopy of Au_6^-

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Zero electron kinetic energy (ZEKE) spectroscopy and photodetachment cross section measurements have been carried out on Au_6^- . The transition frequencies of ZEKE peaks and resonance peaks are nearly identical, consistent with the proposal that the excited negative ion of Au_6 has a geometry quite similar to that of neutral Au_6 , and supporting the picture of the resonances as weakly bound "surface states." From these studies the 0-0 transition frequency between Au_6^- and Au_6 is measured to be $16\,541 \pm 17\text{ cm}^{-1}$, and the vibrational frequencies for the neutral Au_6 ground state, the Au_6^- ground state, and the $(\text{Au}_6^-)^*$ anion excited electronic state are 107, 73, and 107 cm^{-1} , respectively. Lastly, we observe evidence for a previously unreported resonance transition to the excited anion which we suggest is the 0-0 transition of Au_6^- to $(\text{Au}_6^-)^*$.

INTRODUCTION

The electronic and geometric structure of small particles¹ is one of the most important questions in cluster research. In cases where it is possible to produce macroscopic amounts of particles such as C_{60} ,² a large number of experimental techniques become available for analysis. Unfortunately, in most instances monosized bare clusters can be produced only in small quantities and in the gas phase, since mass selection mandates cation or ion production. Even within these limitations, photodetachment spectroscopy³ is proving to be a powerful technique for probing the electronic and vibrational structure of small metal clusters, which together with theoretical calculations⁴ is now allowing insight into the geometry of small metal clusters.

In measurements of the photodetachment cross section of Au_6^- Taylor *et al.*⁵ observed a simple vibrational progression of autodetaching resonances. Two important questions arise from these studies. (i) What is the mechanism of autodetachment? (ii) Why is only one vibrational mode observed for Au_6^- ? Taylor *et al.* proposed that the decay mechanism is vibrational autodetachment from a weakly bound "surface state" of excited Au_6^- . From this proposal it follows that the observed vibrational structure of the excited state of the anion of Au_6 must be similar to that of the neutral ground state. In addition, from extended Huckel calculations for different Au_6^- geometries, Taylor *et al.* concluded that the most likely interpretation for appearance of only one vibrational mode was that Au_6^- possesses a highly symmetric planar ring structure similar to benzene.

In recent studies of Au_2^- using zero electron kinetic energy (ZEKE) spectroscopy⁶ we have obtained directly the vibrational frequencies of the ground states of Au_2^- and Au_2 .⁷ In further work, resonances were observed in the photodetachment cross section of Au_2^- .⁸ These resonances exhibited a vibrational spacing significantly different from both the neutral and anion ground state and thus are due to electronic autodetachment from an excited electronic state of the dimer anion. In this paper we present results from the ZEKE spectroscopy and photodetachment cross section

measurements on Au_6^- . From these measurements we are able to determine 0-0 transition frequency between Au_6^- and Au_6 , and the vibrational frequencies for the neutral Au_6 ground state, the Au_6^- anion ground state and the $(\text{Au}_6^-)^*$ anion excited state. In addition, we present evidence for a previously unreported resonance transition to the excited anion which tentatively has been assigned as the 0-0 transition of Au_6^- to $(\text{Au}_6^-)^*$.

EXPERIMENTAL APPARATUS

The experimental set up is described in detail in earlier publications.⁷⁻⁹ Briefly, neutral, positive, and negative charged metal clusters are produced by a pulsed laser vaporization metal cluster beam source. The metal cluster anions are accelerated with a pulsed electric field in a Wiley-McLaren time-of-flight mass spectrometer. At the end of the drift region photoelectrons are detached from a mass selected anion bunch by a tunable dye laser within an electrostatically and magnetically shielded area. The dye laser is frequency calibrated to known transitions in krypton.

In the ZEKE spectroscopy mode, electrons with kinetic energy $\approx 1.5\text{ meV}$ hit the walls of this field free region within $\sim 200\text{ ns}$. The remaining electrons (ZEKE electrons) are extracted by applying a small pulsed electric field ($\sim 1\text{ V/cm}$) perpendicular to the original beam direction. The electrons thus extracted are then detected by a channeltron. Spectra are obtained by recording the electron intensity as a function of photon energy. Peaks occur at photon energies identical to transitions between populated levels of the anion and the neutral. The intensities depend on the Franck-Condon factors and the population of the anion levels. To avoid saturation effects the spectra are taken at low laser flux, typically $\lesssim 1\text{ }\mu\text{J/cm}^2$. Saturation effects can be caused mainly by the existence of strong resonances, which at certain photon energies lead to detachment from such a large fraction of the anions that the anion density is depleted. In practice, even at the lowest laser flux, saturation effects could not be completely excluded (*vide infra*).

In the photodetachment cross section mode of oper-

ation, the pulsed extraction field is applied without any delay and thus all detached electrons irrespective of their kinetic energy should be collected. In this mode a steplike increase in electron signal occurs when the photon energy is sufficient to access another direct detachment transition from anion to neutral. At frequencies which overlap autodetaching resonances, sharp, narrow features are superimposed upon the total electron signal.

RESULTS

Figure 1(a) shows the measurement of the photodetachment cross section of Au_6^- in the wavelength range between 585 and 607.5 nm (2.12–2.04 eV). The scale is chosen to display clearly the signal maxima, but electron signal is observed over this entire range as well as to shorter and longer wavelengths at a low but detectable level. The positions of the main features are marked by letters and listed in Table I. No other sharp maxima (resonances) are found within the range from 670 to 575 nm (1.85–2.16 eV). The most striking feature is the progression of relatively intense peaks (A,B,D,F) with a nearly constant energy separation, 105 cm^{-1} (A–B), 107 cm^{-1} (B–D), 107 cm^{-1} (D–F). Note also that the peaks increase in intensity as the photon energy decreases. In addition, a series of smaller peaks (C,E,G) are observed with nearly the same spacing 102 cm^{-1} (C–E), 109 cm^{-1} (E–G), but shifted with respect to the main progression (A,B,D,F) by 73 cm^{-1} . The full-width at half-maximum (FWHM) of peak F is $\sim 8 \text{ cm}^{-1}$.

Figure 1(b) displays the spectrum of Au_6^- obtained in

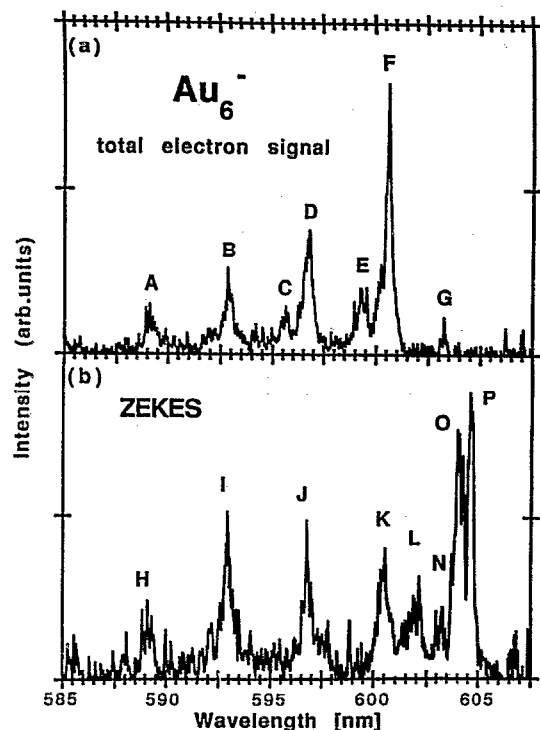


FIG. 1. (a) The photodetachment cross section of Au_6^- as a function of wavelength. (b) The ZEKE spectrum of Au_6^- over the same wavelength range as in (a).

TABLE I. Frequencies of the resonances in the relative cross section of photodetachment of Au_6^- [Fig. 1(a)] and of the features in the ZEKE spectrum [Fig. 1(b)]. The uncertainty in the frequencies is $\pm 4 \text{ cm}^{-1}$.

Resonance Fig. 1(a)	Position cm^{-1}	ZEKE feature Fig. 1(b)	Position cm^{-1}
A	16 966	H	16 969
B	16 861	I	16 860
C	16 785	J	16 753
D	16 754	K	16 649
E	16 683	L	16 606
F	16 647	N	16 577
G	16 574	O	16 551
		OP (dip)	16 541
		P	16 534

the ZEKE mode over the same wavelength range as Fig. 1(a). In this case only low energy electrons ($< 2 \text{ meV}$) are detected as a function of the dye laser photon energy. The detected electron signal is roughly three orders of magnitude lower in Fig. 1(b) than that in Fig. 1(a).¹⁰ In Fig. 1(b), a progression of peaks (H,I,J,K) is also observed. These peaks appear at almost the same energies as peaks A, B, D, and F, respectively, and thus have similar energy spacings, 109 cm^{-1} (H–I), 107 cm^{-1} (I–J), and 104 cm^{-1} (J–K), but they exhibit a significantly different intensity distribution. Another outstanding difference between the two spectra is the appearance of a series of features (L,N,O,P) at low frequency between 601 and 605 nm in Fig. 1(b), whereas in Fig. 1(a) only the weak feature G is present. The strong dip, between the features labeled O and P is shifted 108 cm^{-1} from K (or F).

DISCUSSION

Examination of the two spectra shown in Fig. 1 now allows the following conclusions to be drawn. First, the photodetachment cross section displayed in Fig. 1(a) is nearly identical to that reported by the Rice group.⁵ As they proposed, the peaks A, B, D, F appear as resonances and can be assigned to transitions from $v'' = 0$ of the Au_6^- ground electronic state into different vibrational levels v''' of an excited state of the anion (Au_6^-)*, i.e., $v'' = 0$ to $v''' = n$ transitions with a vibrational spacing of $\sim 107 \text{ cm}^{-1}$ for the anion excited electronic state.

As shown in Fig. 2, the peaks of the second, weaker progression C,E,G are assigned to “hot band” transitions from the first vibrational level of the anion to the anion excited state, i.e., $v'' = 1$ to $v''' = n$. The vibrational frequency of the anion ground electronic then equals the separation $F(v'' = 0 \rightarrow v''' = n) - G(v'' = 1 \rightarrow v''' = n) = 73 \text{ cm}^{-1}$.

Now we turn to the ZEKE spectrum in Fig. 1(b). In order to interpret this spectrum, we make the assumption that the measured electron signal arises from true ZEKE electrons, i.e., low energy electrons detached at photon energies corresponding to direct vibrational transitions between Au_6 and Au_6^- . As noted above, the energies of the peaks in the vibrational progression H, I, J, K in the ZEKE spectrum occur at nearly identical energy as the resonances A, B, D,

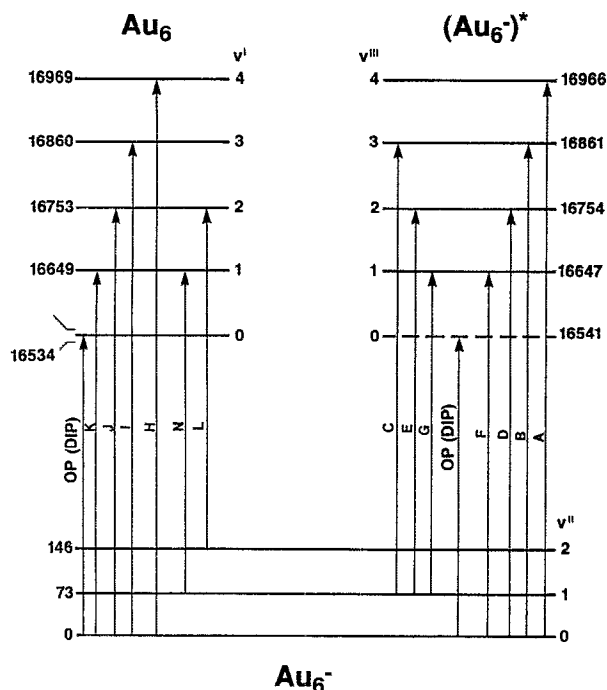


FIG. 2. Schematic energy diagram of transition frequencies from Au_6^- to Au_6 and $(\text{Au}_6^-)^*$. Labels correspond to values listed in Table I.

and F, respectively. Thus the vibrational spacing (107 cm^{-1}) of the neutral Au_6 is nearly equal to that of the Au_6^- excited state, suggesting nearly identical geometry for both Au_6 and $(\text{Au}_6^-)^*$ in agreement with the predictions of Ref. 5. This also suggests that the electron in $(\text{Au}_6^-)^*$ must be very weakly bound ($\leq 3 \text{ meV}$).

Next we note that peak O is shifted from K by 98 cm^{-1} and P is shifted from K by 115 cm^{-1} , but that the “dip” between them is shifted from K by 108 cm^{-1} , almost exactly the shift expected for the next vibrational transition toward lower energy, if it were part of the the series H, I, J, K, OP(dip).

In order to unravel this, we first note that if the features H,I,J,K,OP(dip) are part of a single vibrational progression, they would be expected to display a monotonic increasing intensity with increasing wavelength, similar to that observed in the resonance spectrum [Fig. 1(a)]. Instead, K and J are weaker than I (and features O and P). Such changes can be explained by saturation effects. At a photon energy corresponding to a resonance, e.g., 600.5 nm for resonance F, a large fraction of the anions will be excited by resonant transitions into the weakly bound $(\text{Au}_6^-)^*$ “surface state” with the neutral core in the $v' = 1$ state. The resonance decays by vibrational autodetachment into the neutral $v' = 0$ state emitting an electron with a kinetic energy corresponding to one vibrational quantum of neutral Au_6 . If the anion density is substantially depleted due to the strong resonance [note again the 2–3 orders of magnitude difference in signal levels between Figs. 1(a) and 1(b)], the measured intensity of the resonance will be lower than that expected for the true photodetachment cross section measurement. More importantly, depletion of electron signal also would be

expected in the direct channel (ZEKE spectrum) at photon energies corresponding to resonances, and this effect will be stronger the stronger the resonance. Thus at F, the strongest resonance observed, the most depletion would be expected at K in the ZEKE spectrum and the least at H which overlaps with the weakest resonance A. What at first appears to be an anomalous intensity distribution of the various peaks H, I, J, K can be accounted for by saturation effects due to fortuitous overlapping of resonance and direct detachment energies in Au_6^- .

However the most intense feature in the ZEKE spectrum occurs at the lowest frequency and is centered around the dip between the features O and P. Since OP(dip) occurs at precisely that frequency for which the next resonance towards lower energy would be expected, we propose that O, P, and OP(dip) are all due to a single feature, and that feature corresponds to the 0–0 transition between Au_6^- and $(\text{Au}_6^-)^*$. The dip is induced by saturation due to a very strong, but undetected, resonance in the photoabsorption cross section, namely the 0–0 transition between Au_6^- and $(\text{Au}_6^-)^*$. This resonance goes undetected by photodetachment spectroscopy (vibrational autodetachment) in Fig. 1(a), since it derives from the vibrational ground state of the excited anion $(\text{Au}_6^-)^*$. Such a state must decay via some other channel such as fragmentation or fluorescence, but importantly saturation effects due to it should also lower the anion density and cause a dip in the ZEKE spectrum. Thus the double peaked feature labeled by O and P is simply one feature corresponding to the 0–0 transition between Au_6^- and Au_6 centered near 15541 cm^{-1} . The dip is caused by a (previously undetectable) resonance at that particular energy and represents the 0–0 transition between Au_6^- and $(\text{Au}_6^-)^*$ also centered near 15541 cm^{-1} . This $v''' = 0$ state is shown as a dashed line in Fig. 2.

As can be seen in Fig. 2, the features observed in Figs. 1(a) and 1(b) can now be assigned. The series of features H, I, J, K, OP(dip) are assigned as direct vibrational transitions from the $v'' = 0$ level of the ground electronic state of the anion to $v' = m$ ($m = 4, 3, 2, 1, 0$, respectively) vibrational levels of the neutral ground electronic state of Au_6 . The feature OP(dip) thus corresponds to $\text{Au}_6^-(v'' = 0) \rightarrow \text{Au}_6(v' = 0)$ transition, i.e., the adiabatic electron affinity. Similarly, the peaks K, J, I, H are assigned as $\text{Au}_6^-(v'' = 0) \rightarrow \text{Au}_6(v' = 1, 2, 3, 4)$ transitions, respectively. The other features observable in the ZEKE spectrum can be explained as “hot bands,” $L [\text{Au}_6^-(v'' = 2) \rightarrow \text{Au}_6(v' = 2)]$; $N [\text{Au}_6^-(v'' = 1) \rightarrow \text{Au}_6(v' = 1)]$. The $\text{Au}_6^-(v'' = 1) \rightarrow \text{Au}_6(v' = 0)$ “hot band” expected at $\sim 16469 \text{ cm}^{-1}$ is missing (or very weak), as is the $\text{Au}_6^-(v'' = 3) \rightarrow \text{Au}_6(v' = 3)$ expected near 16641 cm^{-1} (or it is buried under K).

Thus all the features observable in the ZEKE and resonance spectra can be explained within the model presented above. However, could the occurrence of ZEKE peaks (H,I,J,K) at the same positions as the resonances (A,B,D,F) be an experimental artifact? Namely, could a “background” signal show up in the ZEKE spectrum because of the extraordinarily high signal of electrons of higher kinetic energy being created at the positions of the reson-

ances. The suppression of signal from electrons of higher kinetic energy by the electron spectrometer is unknown, but it is reasonable to assume that the suppression is higher the higher the kinetic energy. Also if vibrational autodetachment occurs largely by $\Delta v = -1$ transitions, the decay of a resonance at higher photon energy (e.g., peak H) should yield electrons with the same kinetic energy (or higher kinetic energy if $\Delta v > 1$ is possible) compared to resonances at lower kinetic energy (e.g., peak K). Thus, if the features H,I,J,K are due to "background" electrons from resonances A,B,D,F the suppression of electrons from A should be equal to or stronger than from F, which predicts that H-K should display an intensity distribution similar to that of A-F. This is not observed; K and J are significantly weaker than I, whereas F and D are stronger than B. It is difficult to understand the intensity distribution H,I,J,K assuming these peaks are simply experimental artifacts in the ZEKE spectrometer created by the presence of resonances. Thus it appears likely, as argued earlier, that resonances should decrease the intensity in the ZEKE spectra not enhance it, e.g., the origin of the dip between features O and P. In further support of this conclusion we note that in studies of Au_2^- no evidence of "background" electrons from resonances could be observed.

The appearance of lines in the ZEKE spectrum at the same energies as the resonances but with a different intensity distribution could be explained if an additional decay mechanism with different transition probabilities is also active. One known mechanism, rotational autodetachment,¹¹ occurs in excited anions and does produce low energy electrons. This mechanism presumably could produce peaks in the ZEKE spectrum at the same energy and with the same shape as those observed, but likely with an intensity distribution different from that produced by vibrational autodetachment. We cannot entirely exclude this possibility, since the detected electrons in the ZEKE spectrum arise from the low energy tail of the kinetic energy distribution of all electrons emitted from the resonances.

When dealing with weakly bound states close to the ionization or detachment threshold, field ionization can also be a source of low energy electrons. If the feature "OP" in the ZEKE spectrum is located below the detachment threshold, electrons may be detached by field ionization by the (1 eV) extraction pulse if the lifetime of this "surface state" is sufficiently long (> 200 ns). In this case "OP" would correspond to detachment from a highly excited state of the anion and not to the 0-0 transition. However the odd shape of the feature, e.g., the "dip" is difficult to understand within this picture.

Without further information about the Au_6^- system, we cannot completely exclude the possibility that electrons from rotational autodetachment and/or field ionization contribute somewhat to the ZEKE spectrum. On the other hand, in ZEKE spectrum electrons from direct transitions contribute without suppression to the signal and at a level three orders of magnitude lower than the resonance signal, it seems reasonable to interpret the peaks as direct transitions.

CONCLUSIONS

The coincidence, within our energy resolution, of the ZEKE peaks and the resonances are consistent with the picture of the resonances as weakly bound "surface states" with a neutral core very similar in geometry to that of the neutral Au_6 , thus supporting the picture that Au_6 is a very symmetric cluster.⁵ With this interpretation, the vibrational frequencies of the anion ground and excited electronic states and the neutral cluster are the following: Au_6^- , 73 cm^{-1} ; $(\text{Au}_6)^*$, 107 cm^{-1} ; Au_6 , 107 cm^{-1} .

The interpretation that the dip between O and P results from saturation effects due to a resonance which cannot decay by vibrational autodetachment suggests that the frequency of OP (dip), $16541 \pm 17 \text{ cm}^{-1}$ ($2.051 \pm 0.002 \text{ eV}$), be assigned as the 0-0 transition.

Somewhat surprising is the difference in the autodetachment mechanism between Au_6^- and Au_2^- . In the case of Au_2 , the anion excited state not only has a vibrational frequency very different from that of the neutral dimer, but decays via electronic autodetachment. In Au_6 , the vibrational frequency of the anion excited state and neutral Au_6 are identical and the excited anion decays by vibrational autodetachment. In addition, the Au_6^- electronic ground state has a substantially lower vibrational frequency than either the neutral or excited anion, suggesting a significant structural change upon electronic excitation or detachment. One possible explanation may be that Au_6^- has a distorted "flat" structure, or even a three-dimensional structure, whereas neutral Au_6 or Au_6^- in its excited state has the symmetrical "flat" structure. These two gold clusters serve as prime examples of the strong dependence of cluster properties on the size of the cluster thus once again demonstrating the novel nature of each different size cluster.

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¹⁰ The intensity ratio between the two spectra is somewhat uncertain, since the channeltron detection efficiency may be altered because different amplifications were used in the two modes of operation.

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