Charge Exchange and Metastability of Small Multiply Charged Gold Clusters

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(Received 5 October 1988)

Charge-exchange and fragmentation cross-section measurements on $Au_2{}^{2+}$, $Au_3{}^{2+}$, $Au_4{}^{2+}$, and $Au_4{}^{3+}$ are presented. Limits on the cluster electron affinities are obtained in terms of the ionization energies of Ar, N_2, Kr, CO, Xe, and O_2. Fragmentation cross sections, largely independent of the gas species, are comparable to those for charge exchange. The metastability of $Au_2{}^{2+}$ is shown to be implied by the lower bound on its electron affinity.

PACS numbers: 36.40.+d, 82.30.Fi

It is of interest to understand the stability and metastability of multiply charged metal clusters. From elementary considerations,[1] there exists a critical cluster size $n_c(z)$ below which the Coulomb energy of the total charge z exceeds the cluster binding energy. Early experiments[2] suggested this size could be observed directly in cluster mass spectra, with clusters smaller than $n_c(z)$ rendered unobservable by their spontaneous decay. However, the many observations of clusters well below predicted[3] critical sizes, among these $Mo_2{}^{2+}$ (Ref. 4), $Au_3{}^{2+}$ (Ref. 5), $Ge_4{}^{3+}$ (Ref. 6), and $Hg_5{}^{2+}$ (Ref. 7), indicate that such a simple picture of multiply charged clusters may be incomplete.

Delley[8] was among the first to point to the possibility of metastable multiply charged clusters. Short-range bonding forces may overcome the slowly varying Coulomb repulsion, giving a local energy minimum. Recent theoretical studies of $Mg_n{}^{2+}$ (Ref. 9), $M_2{}^{2+}$ (Ref. 10), where M is a transition metal, and $Be_n{}^{2+}$ (Ref. 11) have found such metastable minima, in some cases[10,11] with spontaneous decay probabilities which are virtually zero on practical time scales. However, aside from observations *per se,* little experimental data concerning the electronic structure of small multiply charged metal clusters, and none pertaining to their metastability, have been available.

Here, charge-exchange and fragmentation measurements on $Au_2{}^{2+}$, $Au_3{}^{2+}$, $Au_4{}^{2+}$, and $Au_4{}^{3+}$ are reported. The clusters $Au_3{}^{2+}$ and $Au_4{}^{3+}$, having mass-to-charge ratios $M/z=\frac{3}{2}$ and $\frac{4}{3}$ (in units of $M_{\mathrm{Au}}/|e|$), respectively, are identifiable with a mass spectrometer. Identifying $Au_{2n}{}^{2+}$ is problematic because it is indistinguishable from $Au_n{}^{+}$ using conventional mass spectrometry. Previous observations[4,12] of doubly charged dimers have relied on resolving isotopically mixed species. The only previous observation of a doubly charged metal dimer is by Tsong,[4] who resolved isotopically mixed $Mo_2{}^{2+}$ from Mo^+. This technique is not amenable to Au, which has only one natural isotope. In the present case $Au_2{}^{2+}$, whose existence is unanticipated[10] due to the closed-shell configuration of the separated ions, is detected by observing $Au_2{}^{+}$ resulting from the charge-exchange reaction

$$Au_2{}^{2+}+X\rightarrow Au_2{}^{+}+X^{+}\,, \qquad (1)$$

where X, the target gas, is Kr, Xe, Ar, CO, O_2, or N_2. The reaction (1) (and related reactions with $Au_4{}^{3+}$ and $Au_3{}^{2+}$) proceed only for gases whose ionization potentials lie below a (cluster-dependent) threshold, giving limits on the cluster electron affinities. From the lower limit on its electron affinity, $Au_2{}^{2+}$ is shown to be metastable.

The measurements are carried out in a tandem triple-quadrupole mass spectrometer[13] on clusters produced by a liquid-metal ion source.[14] In the tandem mass spectrometer the first quadrupole selects a particular M/z for experimentation. The clusters interact with the target gas in the second quadrupole, which is operated as a nonselective ion guide. The gas pressures are measured with an ionization gauge (Balzers IMR-132) and are corrected for sensitivity to different gases following the manufacturer's recommendation. The third mass spectrometer analyzes the charge-exchange and fragmentation products. Ion kinetic energies are typically 10 eV. The flight time of Au^+ between source and detector is approximately 500 μsec. The ion detector consists of an aluminum conversion dynode and a secondary-electron multiplier. Individual ion pulses are discriminated, converted to logic pulses, counted, and logged onto a computer.

The liquid-metal ion source produces intense fluxes of ions, e.g., up to 4 nA of Au^+ and 50 pA of $Au_3{}^{2+}$. The intensities of the doubly charged clusters fall rapidly with cluster size, with $Au_7{}^{2+}$ being unobservable. Au^{3+} and $Au_4{}^{3+}$ are the only triply charged species observed. The low abundance of $Au_4{}^{3+}$ in the beam, 10^{-3} that of $Au_3{}^{2+}$, may account for its not having been previously observed.

Figure 1 shows a spectrum of the products formed when $Au_4{}^{3+}$, selected by the first quadrupole, interacts with Kr at 5×10^{-5} mbar. Because of the multiple charge of the parent cluster, the spectrum shows

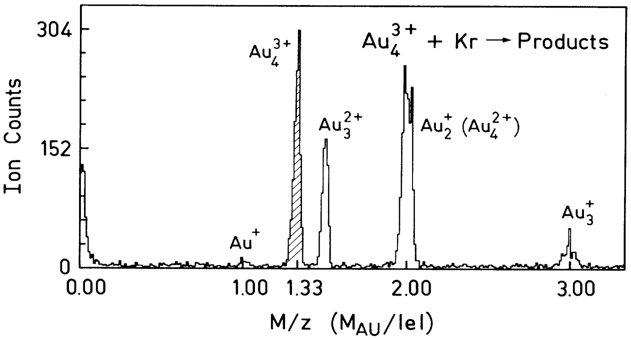

FIG. 1. Mass spectrum showing $Au_4{}^{3+}$ (shaded) and the products resulting from its interaction with Kr. Fragment ions of $M/z < \frac{4}{3}$ possess insufficient kinetic energy to pass through the spectrometer and therefore are not observed.

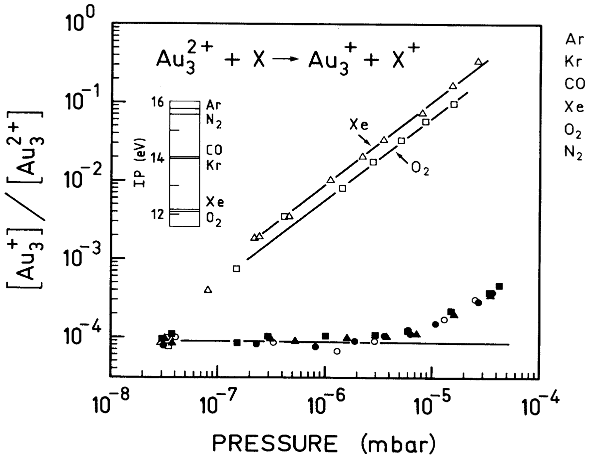

FIG. 2. Pressure dependence of the charge-exchange signal of $Au_3{}^{2+}$ with Ar, Kr, CO, Xe, O_2, and N_2. Inset: Ionization potentials (IP) of the target gases.

daughter ions of $M/z > \frac{4}{3}$. Identification of the parent is assured by the fragmentation pattern; $Au_3{}^{+}$ and $Au_3{}^{2+}$ defining lower bounds for the parent mass and charge, respectively. As discussed below, the peak at $M/z = 2$ appears to be largely due to a charge-exchange reaction.

Measurements similar to that shown in Fig. 1 have been made for the various multiply charged clusters as a function of pressure for different target gases. The results for the charge-exchange reaction of $Au_3{}^{2+}$ are shown in Fig. 2. At the background pressure of 3.5×10^{-8} mbar a small exchange signal is observed due to the residual vacuum background. With increasing pressure of both Xe and O_2, the exchange signal is found to increase linearly with pressure over 3 orders of magnitude.

From these data, the measured charge-exchange cross section of $Au_3{}^{2+}$ with Xe is 0.85×10^{-14} cm^2. The systematic error in this value might be as large as a factor of 2. Under identical conditions, the cross section measured for Au^{2+} with Xe is 0.78×10^{-14} cm^2. The magnitude of the cross section is comparable to that reported for charge exchange involving singly charged clusters.[15] For Kr, CO, Ar, and N_2, no pressure dependence of the charge-exchange signal is found below 10^{-5} mbar. A background signal, related to a slowing of the ions by the gas and their interaction with the vacuum background, is observed above 10^{-5} mbar. The cross sections for Kr, CO, Ar, and N_2 are less than the limiting value of 1.3×10^{-17} cm^2.

Excitation of metal clusters above their dissociation threshold generally results in rapid fragmentation. Therefore for $Au_3{}^{+}$ to be observed, electron transfer must be to a state below its dissociation limit. Adopting the interpretation that the drop between the cross sections of Xe and O_2 and those of Kr, CO, N_2, and Ar is governed primarily by the availability of final states[16] (i.e., energy conservation prevents charge exchange in the latter cases), the ionization energies[17] of Xe (12.12 eV), and Kr (14.00 eV) provide limits for the electron affinity of $Au_3{}^{2+}$. The calculated[18] ionization energy of $Au_3{}^{+}$ (14.91 eV) is in reasonable agreement with the experimental limits. The vertical electron affinity is generally less than the vertical ionization energy, since structural changes usually accompany a change of charge state.[11]

Simultaneous measurements of the fragmentation reaction

$$Au_3{}^{2+} + X \rightarrow Au_2{}^{+} + Au^{+} + X \qquad (2)$$

are performed by detecting the $Au_2{}^{+}$ fragment. In the absence of gas a spontaneous fragmentation signal is observed. Taking into account the flight time between the first and third quadrupoles and fitting to an exponential decay law, a cluster lifetime of approximately 200 msec is obtained. The fragmentation cross sections (for Xe, 0.80×10^{-14} cm^2) vary less than a factor of 3 between the gases and show no correlation with their ionization energies. The comparable magnitudes of the fragmentation cross sections for all the gases suggest that fragmentation is not due to excess energy from electron transfer. Since the parent cluster may be in an excited vibrational state, the above lifetime and cross sections should be considered as lower and upper bounds, respectively. A more comprehensive summary of the fragmentation results will appear elsewhere.[19]

Figure 3 shows the clear signature of $Au_2{}^{2+}$ given by the charge-exchange reaction when $M/z = 1$ is selected by the first quadrupole and $M/z = 2$ is selected by the third. The signal is normalized to the $Au_3{}^{2+}$ intensity (measured separately for each point) to correct for long-term beam fluctuations. The relative charge-exchange cross sections between $Au_2{}^{2+}$ and Xe, O_2, Kr, and CO vary by less than a factor of 5, while for Ar and N_2 they are below the background level. The ionization

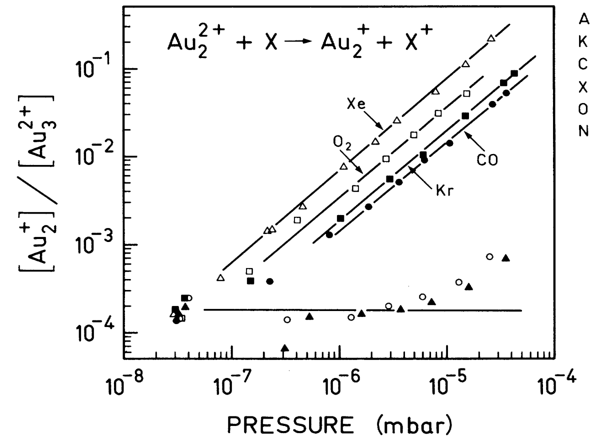

FIG. 3. Charge-exchange signal of Au_2^{2+}. The signal is normalized to the Au_3^{2+} intensity (measured separately) to correct for beam intensity fluctuations.

potentials[17] of CO (14.01 eV) and N_2 (15.58 eV) are therefore limits to the electron affinity of Au_2^{2+}.

Measurements on Au_4^{3+} are complicated by the overlap of the charge-exchange product Au_4^{2+} and a fragmentation product Au_2^+ at $M/z=2$. The cross section to produce $M/z=2$ varies by less than a factor of 3 between Xe (3.27×10^{-14} cm^2), Kr, O_2, and CO, but drops significantly for Ar (0.17×10^{-14} cm^2) and N_2 (0.082×10^{14} cm^2). This suggests that charge exchange is responsible for a majority of the $M/z=2$ signals in the former cases. It is interesting that the cross section for fragmentation into Au_3^{2+} (for Xe, 0.6×10^{-14} cm^2) shows little dependence on the target gas, while the cross section to produce Au_3^+ is appreciable only for CO, Kr, Xe, and O_2. The latter result suggests that this fragmentation channel accompanies charge exchange. The ionization potentials of CO and N_2 are taken as limits for the electron affinity of Au_4^{3+}. The predicted[18] ionization energy of Au_4^{2+} (20.6 eV) is substantially above the upper limit. The disagreement may imply that charge exchange is accompanied by a substantial change of cluster geometry.

No evidence for a charge-exchange reaction of Au_4^{2+} with the target gases is found, though the fragmentation reaction resulting in Au_3^+ has a cross section which varies by less than a factor of 4 with the target gas. This implies that charge exchange is not involved in the fragmentation process and that the electron affinity of Au_4^{2+} lies below the ionization energy[17] of Xe (12.13 eV). The predicted[18] ionization energy of Au_4^+ is 13.23 eV.

The metastability of Au_2^{2+} is implied by the lower bound found above for its electron affinity. This can be shown using the measured[17] ionization potentials of Au and CO, $V_{IP}(Au)=9.22$ eV and $V_{IP}(CO)=14.01$ eV, and the calculated[20] binding energy of Au_2^+, $E(Au_2^+)=-1.71$ eV. The uncertainty in $E(Au_2^+)$ might be as large as 1.0 eV (the binding energy of Au_2 calculated by the same technique[20] is -1.58 eV, 0.73 eV greater than the experimental value, -2.31 eV). Combining these results as shown schematically in Fig. 4 implies that $E(Au_2^{2+}) > 3.1 \pm 1.0$ eV. A positive lower bound for the binding energy implies metastability. For reference, the Coulomb energy of two point charges is also plotted in Fig. 4. It is perhaps important to note that quite a strong interaction between the ions is not ruled out. Enough is not presently known to permit similar analyses for the larger clusters.

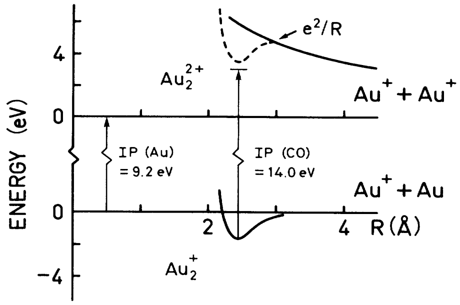

FIG. 4. The relationship between the lower limit on the electron affinity of Au_2^{2+} (the ionization potential of CO) and its positive binding energy. The energy scales are relative to the respective separated fragments. The bond length of Au_2 (Refs. 19 and 20) is 2.47 Å. For comparison, the Coulomb energy of two point charges is also plotted.

The nature of the bonding in the small multiply charged Au clusters is not simply understood. Clearly, the standard picture of an *s*-electron bound metal dimer (e.g., Na_2) fails in the case of Au_2^{2+}. This suggests the bonding of the small multiply charged Au clusters is neither analogous to that in the bulk nor to that in neutral clusters. Liu *et al.* (Ref. 10) have treated the binding of doubly charged transition metal dimers in a tight-binding framework. On that basis also, little bonding between Au^+ ions (of $5d^{10}$ configuration) is expected, since bonding and antibonding orbitals are equally occupied. Relativistic effects,[18] which strongly hybridize *s* and *d* levels, may alter this interpretation.

To summarize, charge-exchange and fragmentation measurements on Au_2^{2+}, Au_3^{2+}, Au_4^{2+}, and Au_4^{3+} have been reported. Limits on the electron affinities of the clusters, obtained in terms of the ionization energies of Xe, O_2, Kr, CO, Ar, and N_2, are in reasonable agreement with available calculated results. Au_2^{2+}, whose existence is unanticipated, was observed indirectly by employing a charge-exchange reaction. The metastability of Au_2^{2+} has been shown from the lower bound on its electron affinity.

Dr. W. A. de Heer, Dr. S. Mukherjee, Dr. F. Spiegelman, and Professor J. Buttet contributed especially valuable comments. S. Fedrigo participated in aspects of the liquid-metal ion source construction.

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