

Dimer dissociation energies of small odd-size clusters Au_n^+

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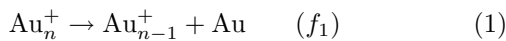
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Abstract. The dimer dissociation energies of gold cluster ions Au_n^+ , $n = 9, 11, 13, 15$ have been determined with an extension of a recently developed model-independent method. Monomer-dimer decay pathway branching ratios provide the energy dependent process which is needed in this method. The measured values are $D_2(\text{Au}_9^+) = 3.66(8)(9)$ eV, $D_2(\text{Au}_{11}^+) = 4.27(11)(8)$ eV, $D_2(\text{Au}_{13}^+) = 4.50(9)(7)$ eV and $D_2(\text{Au}_{15}^+) = 4.29(10)(6)$ eV.

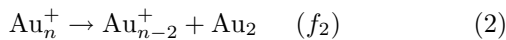
PACS. 36.40.Qv Stability and fragmentation of clusters – 36.40.Wa Charged clusters

1 Introduction

Neutral dimer evaporation from small, odd-size cluster ions and anions of monovalent metals is known to compete with neutral monomer evaporation [1–13]. This competition is a result of the odd-even variations in the stability of the clusters and is observed as a finite branching into both monomer and dimer channels in the unimolecular decay of some small clusters. For cluster cations of group-11-elements, such as gold, the branching ratio f_2/f_1 between the two channels



and



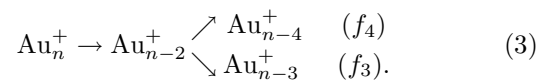
is known to depend on the excitation energy [14]. Here, f_1 and f_2 denote the relative fragment yields for neutral monomer and neutral dimer evaporation, respectively. The evaporation of neutral dimers from excited clusters is generally preferred due to the larger phase space [15], but is in most cases suppressed by a dissociation energy, $D_2(n)$ which is higher than the monomer value, $D_1(n)$.

Thus, knowledge of both the monomer and dimer dissociation energies is essential for a description of the fragmentation behaviour since the competition between the two possible decay pathways is to a large extent determined by the values of these energy barriers. It is particularly relevant for small gold clusters since monomer dissociation energies have been determined with good precision and the observed branching ratios have so far defied any attempt of an explanation [14]. The problem has

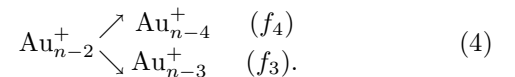
also been demonstrated for the monomer evaporation from gold cluster cations where unimolecular rate theory fails to describe the observations quantitatively, occasionally seriously [16]. The results presented here will not solve this problem but will provide a stronger basis for a future solution.

The monomer dissociation energies were found by application of a recently developed model-independent experimental method [16,17]. The method is based on comparison of the direct dissociation, $B \rightarrow C$, with the sequential process, $A \rightarrow B \rightarrow C$, and yields the dissociation energy of the system A . In the original version [16] the rate constant of the process $B \rightarrow C$ serves as a measure of the energy content of the species B in the sequential decay in the sense that if the rates are equal, so are the excitation energies. The method is not limited by the choice of rate constants as energy gauges; any measurable, energy-dependent quantity can be used, *e.g.* decay pathway branching ratios [17].

In the following, we apply a procedure that allows to experimentally determine the dimer dissociation energy $D_2(n)$ of a cluster by a measurement of the monomer-dimer branching ratio. The decay investigated is the sequential dissociation process



The measuring process is the single-step decay



The branching ratio depends monotonously on the excitation energy [14]. When the branching ratios f_4/f_3 of the

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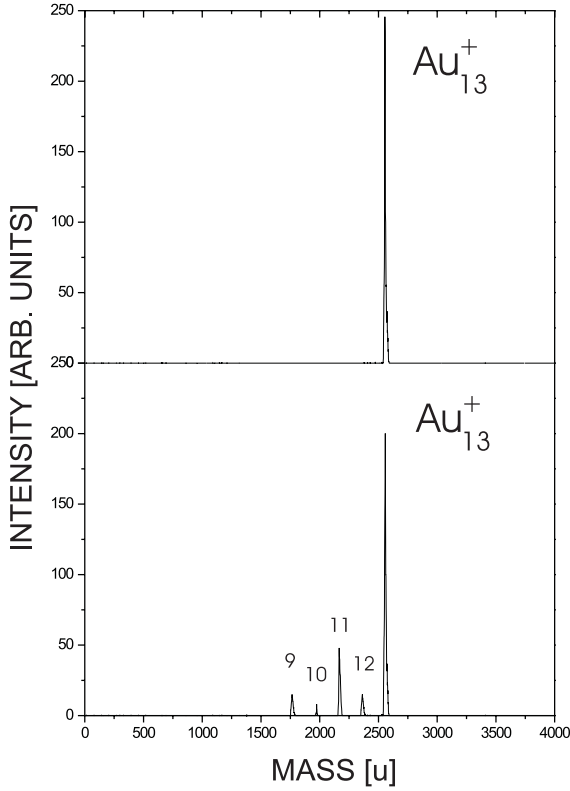
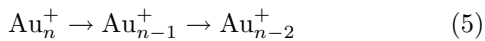


Fig. 1. Abundance spectra of size-selected Au_{13}^+ clusters before photoexcitation (top spectrum) and 100 ms after photoexcitation with a single 10 ns laser pulse at $\lambda = 266$ nm and a pulse energy of $50 \mu\text{J}$ (bottom spectrum).

relative yields in the fragment channels Au_{n-4}^+ and Au_{n-3}^+ are identical in the two reactions, the energy content of the intermediate product Au_{n-2}^+ is also identical.

Apart from reaction (3) the sequential monomer evaporation



occurs with finite branching ratio. Since the measured products Au_{n-3}^+ and Au_{n-4}^+ do not include products from reaction (5) it will cause no background.

2 Experimental setup and procedure

A detailed description of the experimental setup has already been given in [18] and the references in [16]. The experimental sequence begins with the cluster ion production in a Smalley-type laser vaporization source [19,20], followed by a transfer to the Penning trap [21] where the clusters are stored and the cluster size of interest is selected by resonant ejection of all other species. The selected clusters are centered radially in the trap by use of Ar gas [22] which also acts to thermalise the clusters to room temperature [16]. After centering they are photoexcited by a single 10 ns pulse of a Nd:YAG laser or, in some cases, a Nd:YAG pumped dye laser. After a storage period of 100 ms the abundances of the cluster ion ensemble

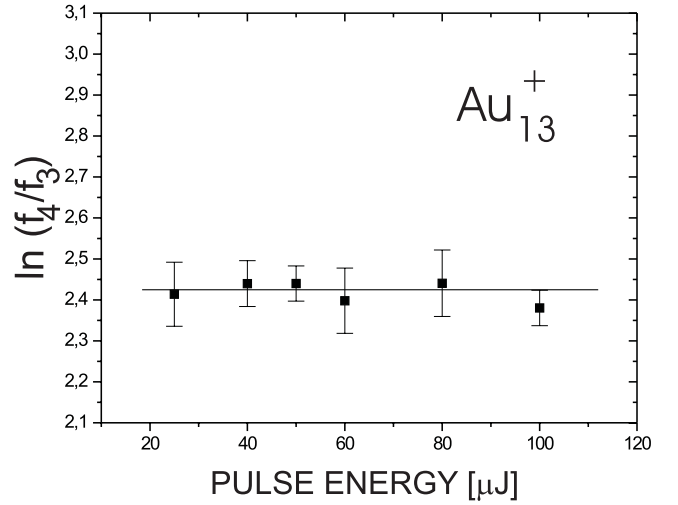


Fig. 2. The branching ratio f_4/f_3 between Au_9^+ and Au_{10}^+ intensities in the Au_{13}^+ decay *vs.* the laser pulse energy.

is measured by ejection into a time-of-flight (TOF) mass spectrometer [18].

Figure 1 illustrates the photodissociation of Au_{13}^+ : the mass spectra show trapped, size-selected Au_{13}^+ clusters before photoexcitation (top spectrum) and 100 ms after photoexcitation with a single 10 ns laser pulse at $\lambda = 266$ nm and a pulse energy of $50 \mu\text{J}$ (bottom spectrum). Au_{13}^+ clusters that have absorbed a single photon of 4.66 eV evaporate neutral monomers and dimers resulting in Au_{12}^+ and Au_{11}^+ signals in the product mass spectrum. Those Au_{13}^+ clusters that have absorbed two photons of 4.66 eV each also produce Au_{12}^+ and Au_{11}^+ clusters but still have enough internal energy for a further evaporation. Au_{12}^+ is an odd-number cluster with respect to valence electrons and evaporates a monomer [13]. Au_{11}^+ clusters evaporate neutral monomers and dimers resulting in Au_{10}^+ and Au_9^+ signals in the product mass spectrum.

Background from three-photon processes can be excluded if the laser pulse energy is kept low enough. This has been checked in a measurement of the fluence dependence. Figure 2 shows the branching ratio f_4/f_3 of Au_9^+ and Au_{10}^+ intensities as a function of the laser pulse energy in the low-energy region between $20 \mu\text{J}$ and $100 \mu\text{J}$ per pulse. Obviously, the branching ratio does not depend on the laser pulse energy, which indicates that higher-order photon processes are negligible.

3 Results and discussion

Figure 3 shows the branching ratio between Au_5^+ and Au_6^+ in the one-step decay of Au_7^+ (squares) and in the two-step decay of Au_9^+ (triangles) measured at several values of the photoexcitation energy. There is an energy shift of 4.59(08) eV between the corresponding curves which both result from a linear fit of the measured $\ln(f_4/f_3)$ as a function of photoexcitation energy. If a hypothetical branching in equation (3) to a trimer evaporation channel

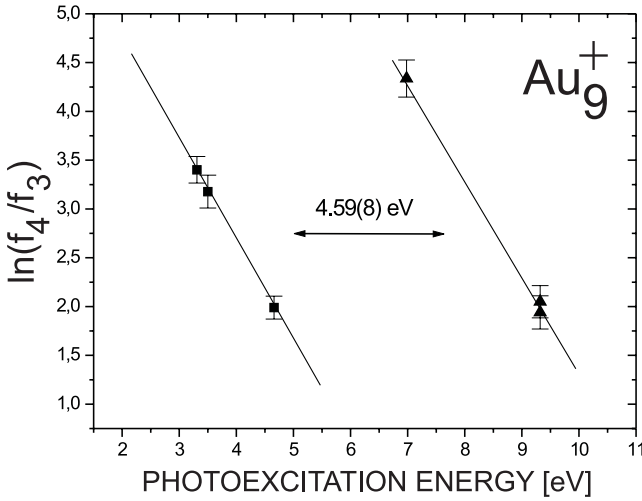


Fig. 3. Branching ratios between Au_5^+ and Au_6^+ intensities in the one-step decay of Au_7^+ (squares) and in the sequential decay of Au_9^+ (triangles).

were included the lines would no longer be parallel. Any significant contribution from such channel can therefore be excluded. The assumed linear behaviour is justified by the results in [14]. From the energetic shift, the dimer dissociation energy $D_2(\text{Au}_n^+)$ is found as

$$D_2(n) = E_n - E_{n-2} + (E_n^{\text{th}} - E_{n-2}^{\text{th}}) - E_{\text{KER}} - E_{\text{ROT}} - E_{\text{VIB}}, \quad (6)$$

where E_{KER} is the translational kinetic energy of the evaporated dimer in the primary process, E_n^{th} the initial room temperature thermal energy and E_n the photoexcitation energy. E_{ROT} and E_{VIB} are the rotational and vibrational energies of the dimer [15]. The rotational energy is $E_{\text{ROT}} = k_{\text{B}}T$ and the vibrational is $E_{\text{VIB}} = k_{\text{B}}T - \hbar\omega_2/2$. The latter results from the high temperature expansion of the standard canonical partition function result for a harmonic oscillator. It is calculated as $-(1/Z) dZ/d\beta$ ($\beta \equiv 1/k_{\text{B}}T$). With the harmonic oscillator partition function $Z = 1/(1 - \exp(-\beta\hbar\omega_2))$ the result is $E_{\text{VIB}} = \hbar\omega_2 \exp(-\beta\hbar\omega_2)/(1 - \exp(-\beta\hbar\omega_2))$ which in the high temperature limit $\beta\hbar\omega_2 \ll 1$ can be approximated by the stated result. An analogous term is present for E_{ROT} also but is so small that it can safely be ignored.

The dimer vibrational frequency is $\omega_2 = 3.597 \times 10^{13} \text{ s}^{-1}$ [23]. The cluster temperature is determined from the extrapolated bulk heat capacities as described in [24], evaluated at an energy equal to the total excitation energy minus the dissociation energy, *i.e.* it is the product cluster temperature. One unit of k_{B} is subtracted from the heat capacity in accordance with the result in [25].

The contribution from the thermal energy difference $E_n^{\text{th}} - E_{n-2}^{\text{th}}$ is small. With the Debye vibrational spectrum the value per vibrational degree of freedom is 0.020 eV. The experimental bulk heat capacity gives 0.021 eV. Adopting the latter the difference in energy between parent and product is $E_n^{\text{th}} - E_{n-2}^{\text{th}} = 0.126(6) \text{ eV}$.

The kinetic energy release E_{KER} is a measurable quantity but the setup used in the present experiment does not allow such a measurement. It is therefore necessary to find the value by theoretical considerations. The kinetic energy in the outgoing channel can be decomposed into the thermal value and a contribution from a possible reverse activation barrier. Since almost all metals have bulk sticking coefficients of unity (Zn is an exception), this may be expected to hold here also. In a few cases the kinetic energy release has been measured for metal clusters, and these results show no reverse barrier [26–28]. The first two references deal with sodium clusters of different sizes. The latter is a measurement which yields, among other things, a limit on a combination of radiative cooling and kinetic energy release for monomer evaporation from cationic gold clusters in the size range relevant here. The measurements indicate that the average kinetic energy can be accounted for by purely thermal values consistent with the simple picture suggested here [28].

For sticking coefficients of unity the most transparent formulation of theories of rate constants are the ones based on detailed balance, in particular when dealing with kinetic energy release distributions. Assuming a geometric capture cross section gives a value of twice the product cluster temperature, $2k_{\text{B}}T$ [29]. If also the attractive polarisation potential is included the value is reduced slightly [15]. This potential is fairly weak but since the kinetic energies are on the order of the temperature the effect is not always negligible. A formula which takes this into account is given in [28], in terms of the value of the polarisation potential V_r at the cluster surface and the product cluster temperature. It applies also to dimer evaporation when the polarisability of the gold dimer is used. This may be assumed to be about twice the value of the gold atom, $6.48 \text{ \AA}^3$ [30]. This is overestimating the value slightly but only marginally if judged by a comparison with the alkali metals. The contact radius can be defined similar to the one for the monomer and reads $r_{n-2,2} = \pi r_{\text{S}}^2((n-2)^{1/3} + 2^{1/3})^2$, where r_{S} is the Wigner-Seitz radius of gold, $1.59 \text{ \AA}$ [30].

For $n = 9$ the resulting value is

$$\begin{aligned} D_2(\text{Au}_9^+) &= 4.59(8) \text{ eV} + 0.126(6) \text{ eV} \\ &\quad - 0.41(4) \text{ eV} - 0.33(3) \text{ eV} - 0.32(2) \text{ eV} \\ &= 3.66(8)(9) \text{ eV}. \end{aligned} \quad (7)$$

The same procedure has been applied to determine the dimer dissociation energies of the clusters Au_{11}^+ , Au_{13}^+ and Au_{15}^+ . Table 1 summarizes the resulting values for $E_n - E_{n-2}$ and $D_2(n)$. The uncertainty on the energetic difference $E_n - E_{n-2}$ is the statistical uncertainty from the uncertainties of the measured branching ratios. The uncertainties on the resulting dissociation energies are the statistical uncertainty and the sum of the systematic uncertainties of the difference of initial room temperature thermal energies, the kinetic energy release and the vibrational and rotational energies.

The case of Au_{15}^+ deserves special attention because the monomer dissociation energies $D_1(\text{Au}_{15}^+)$ and $D_1(\text{Au}_{14}^+)$

Table 1. Dimer dissociation energies of Au_n^+ ($n = 9, 11, 13, 15$).

n	$E_n - E_{n-2}$ [eV]	$D_2(n)$ [eV]
9	4.59(8)	3.66(8)(9)
11	4.91(11)	4.27(11)(8)
13	4.99(9)	4.50(9)(7)
15	4.72(10)	4.29(10)(6)

are known with a high precision from earlier model-free measurements [16]. With these values it is possible to calculate the dimer dissociation energy $D_2(\text{Au}_{15}^+)$ from a thermodynamic cycle. The energy necessary to evaporate a neutral dimer is identical to the energy necessary to evaporate two monomers sequentially and to subsequently form a dimer from these two monomers:

$$D_2(n) = D_1(n) + D_1(n-1) - D(2) \quad (8)$$

with the dissociation energy values $D_1(\text{Au}_{15}^+) = 3.52(13)$ eV, $D_1(\text{Au}_{14}^+) = 3.18(11)$ eV [16] and the neutral dimer separation energy $D(2) = 2.29(2)$ eV [23] the resulting dimer dissociation energy is $D_2(\text{Au}_{15}^+) = 4.41(19)$ eV. This value is in good agreement with the directly determined value of $D_2(\text{Au}_{15}^+) = 4.29(10)(06)$ eV and corroborates the values calculated for the corrections in equation (6).

4 Conclusion

The model-independent determination of dissociation energies of polyatomic particles by use of sequential decays has been extended to the case of dimer evaporation. It has been applied to gold cluster ions Au_n^+ ($n = 9, 11, 13, 15$). The method makes use of energy-dependent decay pathway branching ratios which serve as a measure of the energy content of the intermediate product after dimer evaporation from the precursor. The value of the dimer dissociation energy as determined by these new measurements is in excellent agreement with the combined values of the corresponding monomer dissociation energies which are known from previous experiments.

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