INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS B: ATOMIC, MOLECULAR AND OPTICAL PHYSICS

J. Phys. B: At. Mol. Opt. Phys. **36** (2003) 1073–1083 PII: S0953-4075(03)55270-1

Model-independent determination of dissociation energies: method and applications

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Received 23 October 2002, in final form 8 January 2003
Published 24 February 2003
Online at stacks.iop.org/JPhysB/36/1073

Abstract

A number of methods are available for the purpose of extracting dissociation energies of polyatomic particles. Many of these techniques relate the rate of disintegration at a known excitation energy to the value of the dissociation energy. However, such a determination is susceptible to systematic uncertainties, mainly due to the unknown thermal properties of the particles and the potential existence of 'dark' channels, such as radiative cooling. These problems can be avoided with a recently developed procedure, which applies energy-dependent reactions of the decay products as an uncalibrated thermometer. Thus, it allows a direct measurement of dissociation energies, without any assumption on properties of the system or on details of the disintegration process. The experiments have been performed in a Penning trap, where both rate constants and branching ratios have been measured. The dissociation energies determined with different versions of the method yield identical values, within a small uncertainty.

1. Introduction

The dissociation energy is one of the fundamental parameters in the characterization of polyatomic particles, like molecules, polymers or clusters, since it determines the thermal stability of such systems. Defined as the minimum energy necessary to induce fragmentation, it is of obvious interest for, e.g., chemical reactivity studies and the study of the stability of clusters. A number of experimental techniques have been designed to measure this quantity. In one of the most generally applicable methods, a certain excitation energy is imparted into the system, in order to measure the decay of the particle, primarily by emission of heavy particles (atoms or larger fragments), which is often the lowest energy decay channel. In general, this

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decay proceeds delayed with lifetimes that depend on the excitation energy. Thus, time-resolved measurements yield unimolecular rate constants, k, which can be related to the activation energy for the process, which in the simplest case is just the dissociation energy, by theoretical expressions for k. The Penning trap which has been used in the studies presented here is well suited for these kinds of experiments; the very large range of time constants that can be measured should guarantee a precise determination of the dissociation energy.

A detailed study on gold cluster ions [1] has shown that the inversion of measured rate constants yields the unsatisfactory result that the resulting dissociation energy depends not only on details of the modelling but, more seriously, also on the value of the excitation energy at which the rate constants have been measured. The analysis can either be done with the transition state (RRKM) [2] or the detailed balance (Weisskopf) equation [3, 4]. It can be shown that these two theories are indeed equivalent if one takes proper care to include the phase space in the reaction coordinate in the transition state theory [5, 6]. Unfortunately, this does not fix the functional form of the rate constants, since these expressions require that two sets of level densities are known (before and after decay) as well as the transition state or, equivalently, the capture cross section for the inverse process. At least in the case of metal clusters, the latter is of minor importance, and can often be safely assumed to have a classical value with a sticking coefficient of unity. However, the level densities are often unknown, and realistic models differ mainly in the assumptions on this point [7–11]. In addition to this uncertainty, the amount of radiative cooling is very often unknown, and measured rate constants may represent a combination of unimolecular rate constants and radiative energy loss [12]. As an example, the power radiated from a gold cluster at a temperature of 2000 K exceeds 600 eV s^{-1} (calculated as described in section 5 of [6] for a plasmon damping of $\gamma = v_F/r_N$, where v_F is the Fermi velocity and r_N the radius of the cluster). By analogy with the V_{13}^+ case [12], the loss of less than an electronvolt of energy is expected to be sufficient to quench the evaporative decay. Hence radiative effects may be important for decays which occur on the millisecond timescale and potentially even for shorter times. To varying degrees, analogous problems with modelling also arise in the interpretation of thermochemical [13] and collision-induced-dissociation measurements [14].

It is therefore not surprising that the analysis of the gold cluster rate constants yields inconsistent results for the dissociation energy. In the following, a procedure is presented and applied that circumvents model-related problems and allows a direct experimental determination of dissociation energies. The technique is free of assumptions on the system or on how the decay proceeds, except for numerically small corrections on the order of the thermal energy per particle, which furthermore are observable in principle. It was first applied to the gold clusters which were observed to cause the above mentioned problems in the traditional analysis. Variations and applications of the new procedure are described.

2. General concept

The basic idea of the method [1] is to compare the excitation energy E_A of a sequential decay,

$$\mathrm{A} \rightarrow \mathrm{B} \rightarrow \mathrm{C} \tag{1}$$

with the corresponding energy E_B of the single decay,

$$\mathrm{B} \rightarrow \mathrm{C} \tag{2}$$

leading to the same final product. When the single-decay process (2) depends in a measurable way on the excitation energy of B, it can be used as an uncalibrated thermometer for B, i.e. as a measure of how much energy is left in the intermediate product B after the first step of the sequential reaction (1). When the two excitation energies, E_A and E_B, are chosen to produce the same reading of the thermometer, the difference in excitation energies, $E_A - E_B$, is a direct measure of the energy consumed in the first step of the sequential decay, which is essentially the dissociation energy of A. The procedure is reminiscent of earlier investigations on cluster heat capacities [15]. In these experiments a heat bath temperature and a photoexcitation energy were tuned to give the same total energy content of a cluster, as measured by the number of evaporated atoms.

In the most basic application of the method to gold clusters [1], the sequential process is

$$\mathrm{Au}_n^+ \rightarrow \mathrm{Au}_{n-1}^+ \rightarrow \mathrm{Au}_{n-2}^+, \tag{3}$$

the thermometer process is

$$\mathrm{Au}_{n-1}^+ \rightarrow \mathrm{Au}_{n-2}^+ \tag{4}$$

and the rate of unimolecular decay serves as the energy-dependent experimental quantity. The neutral fragments are not indicated, if no ambiguity is caused. Experimentally, it was found that the time evolution of the relative fragment yields, in either process, is well represented by a single exponential, from which the decay rate can be determined. The first step of the sequential decay in equation (1) is very rapid compared with the second process. This facilitates the determination of the rate constant for the last decay, but is not a requirement for the method. When E_n and E_{n-1} denote the total initial excitation energies for the sequential and the thermometer process, respectively, the dissociation energy of Au_n^+ is obtained as

$$D(n) = E_n - E_{n-1} - E_{KER}, \tag{5}$$

where E_{KER} is the small part of the initial excitation energy, E_n, carried away as translational kinetic energy of the departing fragments of the first process (KER for kinetic energy release), which is lost for the thermometer process. This energy is a stochastic quantity. It may, for example, be obtained from the accompanying recoil [16–18]. No values are available for gold clusters, but they are expected to be so small that a calculation based on estimated quantities is sufficient. This expectation is confirmed by data obtained in one of the modified versions of the method (see below under multisequential decay). For gold clusters, the value is close to $2k_BT$, where T is the microcanonical temperature [4]. The precise value, as used in the following, is calculated according to the prescription given in [19].

Since E_n is given by the sum of the photoexcitation energy and the small initial room temperature thermal energy, $E_n = E_{ph,n} + E_{th,n}$, equation (5) can be written as

$$D(n) = E_{ph,n} - E_{ph,n-1} + (E_{th,n} - E_{th,n-1}) - E_{KER}. \tag{6}$$

For gold clusters the thermal energy at room temperature is approximately 0.021 eV per vibrational degree of freedom [1], and thus the difference in thermal energies of the precursors in the sequential process and the thermometer process can be estimated to $E_{th,n} - E_{th,n-1} = 0.063$ eV. The combined systematic uncertainty of this value and that of the KER is about two orders of magnitude smaller than the dissociation energy itself.

3. Experimental implementation

As an example, figure 1 shows the observed decay rate constants of Au_{16}^+ as a function of the photoexcitation energy. The data are based on energy- and time-resolved photodissociation measurements on size-selected cluster ions stored in a Penning trap [20, 21]. The clusters are produced in a Smalley-type laser vaporization source as ions, transferred into the trap and stored. During storage, the ions are radially centred with inert gas pulsed into the trapping region. The gas also ensures the thermalization to room temperature [1]. After photoexcitation,

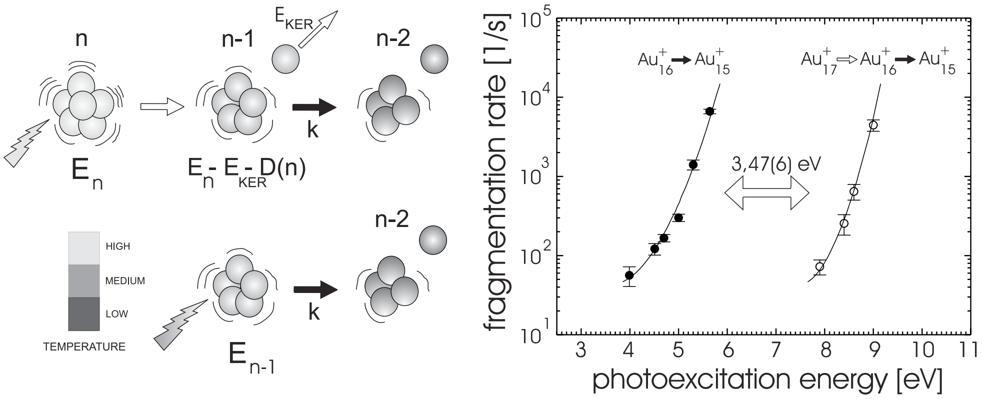

Figure 1. Left-hand part: schematic representation of the method described in section 2. Right-hand part: rate constants for the unimolecular dissociation $\mathrm{Au}_{16}^+ \rightarrow \mathrm{Au}_{15,}^+$ as a function of photoexcitation energy, for size-selected Au_{16}^+ clusters (full symbols) and for sequential decays of size-selected Au_{17}^+ clusters (open symbols). The curves are fits to the data with the exponential of a second order polynomial. Figure taken from [1].

the clusters are stored for a variable period before they are ejected and analysed by time-of-flight mass spectrometry. By variation of the delay between excitation and detection the decay can be followed time resolved, and thus unimolecular rate constants can be determined [22]. Details of the set-up and procedure are given in [23, 24].

In figure 1 the full symbols are the measured rate constants of the decay $\mathrm{Au}_{16}^+ \rightarrow \mathrm{Au}_{15}^+$ and the open symbols those of the last step of the sequential decay $\mathrm{Au}_{17}^+ \rightarrow \mathrm{Au}_{16}^+ \rightarrow \mathrm{Au}_{15}^+$. The displacement of the two curves by $E_{ph,17} - E_{ph,16} = 3.47(6)$ eV corresponds to the dissociation energy of Au_{17}^+ given by $D(17) = E_{ph,17} - E_{ph,16} + \Delta E_{th} - E_{KER} = 3.37(9)$ eV, where the uncertainty is dominated by the statistical uncertainty of the data. The uncertainties of the dissociation energies may seem surprisingly small. This result is mainly due to the fact that the rate constants depend strongly on the excitation energy, and that the projection on the energy axis can therefore be determined quite precisely. A detailed account of the calculation of the uncertainties is given in [19].

4. Variation I: branching ratios as thermometers

As mentioned in section 2, the choice of the uncalibrated thermometer is free, with the only requirement that the experimental observable is sensitive to the excitation energy of system B. The example shown in figure 1 uses the energy dependence of the rate constant. However, for gold cluster ions (among others), it is also possible to use the branching ratio between neutral monomer and neutral dimer evaporation as a thermometer [25]. This allows an independent check of the values obtained with the rate constant thermometer. The sequential process, with an initial excitation energy E_n and relative fragment yields f_1 and f_2,

$$\mathrm{Au}_n^+ \rightarrow \mathrm{Au}_{n-1}^+ \begin{array}{ll} \nearrow \mathrm{Au}_{n-2}^+ & \quad (f_1) \\ \searrow \mathrm{Au}_{n-3}^+ & \quad (f_2) \end{array}, \tag{7}$$

is compared with the single decay,

$$\mathrm{Au}_{n-1}^+ \begin{array}{ll} \nearrow \mathrm{Au}_{n-2}^+ & \quad (f_1) \\ \searrow \mathrm{Au}_{n-3}^+ & \quad (f_2) \end{array}, \tag{8}$$

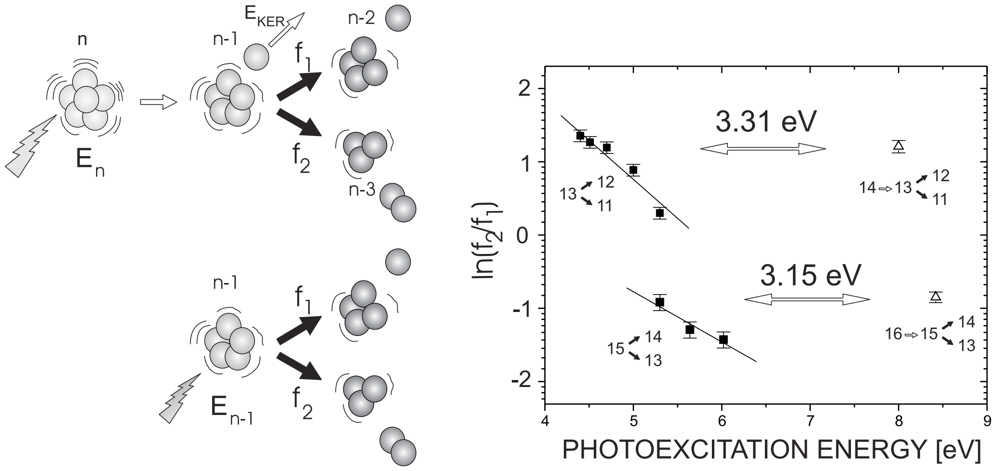

Figure 2. Left-hand part: schematic representation of the method described in section 4. Right-hand part: logarithm of the branching ratio, f_2/f_1, as a function of the photoexcitation energy for the decays of Au_{14}^+ and Au_{16}^+. Full symbols correspond to single-step decays; open symbols correspond to sequential processes. Figure adapted from [25].

with the initial excitation energy E_{n-1}. The excitation energies are adjusted to produce the same branching ratio, f_2/f_1, for both decay chains. Figure 2 shows the examples of Au_{14}^+ and Au_{16}^+. The fit of a straight line to the data can be discussed. However, the combined set of data for several cluster sizes is consistent with a linear behaviour [26].

In full analogy to section 2, $E_n - E_{n-1}$ is translated via equation (6) into the corresponding dissociation energy of the system Au_n^+. The energetic differences of 3.31(5) eV for Au_{14}^+ and 3.15(7) eV for Au_{16}^+ shown in figure 2 lead to the dissociation energies $D(14) = 3.24(7)$ eV and $D(16) = 3.03(9)$ eV. The uncertainties are again dominated by the statistics of the data.

A very interesting feature of this variant is that it is not necessary to measure decays time-resolved. The branching ratio can either be measured at a finite time after excitation or as the asymptotic value. This permits the method to also be used with molecular beam set-ups, where the range of ion flight times is much more restricted than the storage time in a trap.

5. Variation II: multisequential decays

The method presented in sections 2 and 4 can be extended to longer decay chains [19]. This allows checks on the value of the KER and the radiative energy loss in the first decay of the chain. The extension discussed here is based on three-step multisequential dissociation processes A → B → C → D, which are compared to sequential processes B → C → D. As in section 2, the last step occurs delayed, with a measurable rate constant, which serves as an uncalibrated thermometer for the energy content of B. The three-step decay chain is $\mathrm{Au}_n^+ \to \mathrm{Au}_{n-1}^+ \to \mathrm{Au}_{n-2}^+ \to \mathrm{Au}_{n-3}^+$, initiated by a photoexcitation energy of $E_{ph}(n, n-3) = E_{ph}(n_{initial}, n_{final})$. The corresponding two-step dissociation $\mathrm{Au}_{n-1}^+ \to \mathrm{Au}_{n-2}^+ \to \mathrm{Au}_{n-3}^+$ thus starts with the photoexcitation energy $E_{ph}(n-1, n-3)$. When the rate constants for the final steps are identical, the dissociation energy of Au_n^+ is, in analogy to equation (6),

$$D(n) = E_{ph}(n, n-3) - E_{ph}(n-1, n-3) + (E_{th,n} - E_{th,n-1}) - E_{KER,n}(n, n-3), \qquad (9)$$

where $E_{KER,n}(n, n-3)$ is the KER of the decay from Au_n^+ to Au_{n-1}^+ in the decay chain $n \to n-3$.

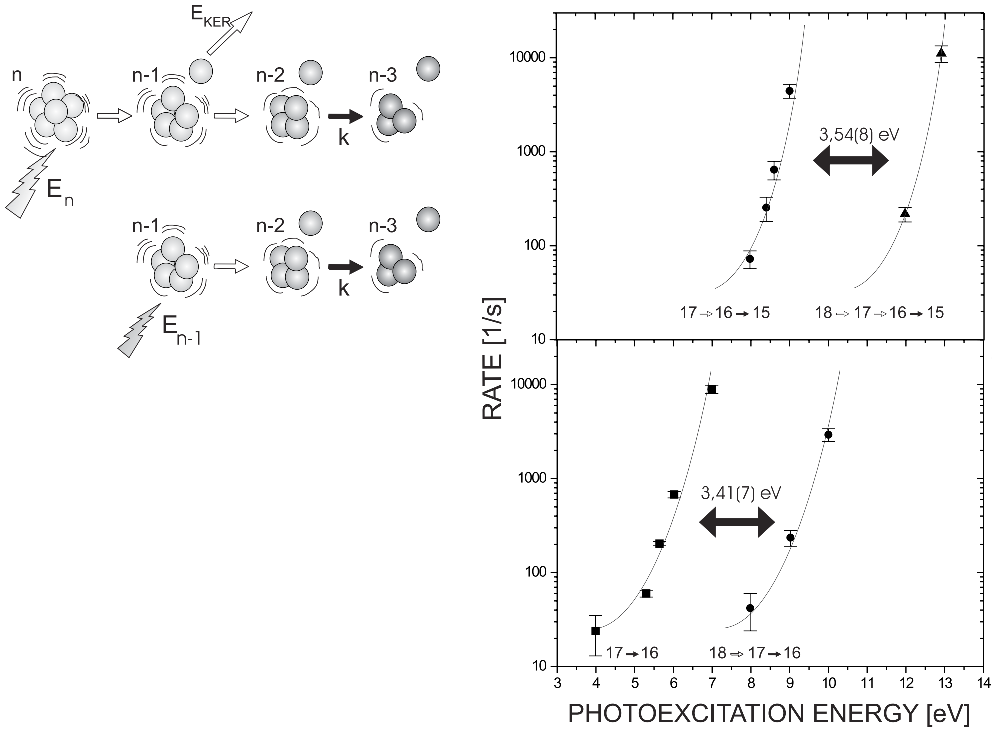

Figure 3. Left-hand part: schematics of the model-independent determination with multisequential dissociation as described in section 5. Right-hand part: corresponding measurements of the rate constant as a function of photoexcitation energy for Au_{18}^{+} with multisequential decays (top) and sequential decays (bottom).

The shifts in photoexcitation energy for the multisequential processes differ from those previously found for sequential dissociation in section 2 in two respects: first, in multisequential dissociation the E_{KER} of the first decay is higher, due to the higher initial excitation energy. In the case shown in figure 3 this excess KER is $3.54 - 3.41$ eV $= 0.13$ eV. This information can be used to determine the energy dependence of the KER, although with large relative uncertainty. Note that this determination is performed without detection of the emitted particle, and without measuring any recoil energy.

Second, if any radiative cooling occurs before the first decay in the sequential process, it is likely to be strongly reduced in the multisequential decay, since the evaporative rate constant is expected to increase much more rapidly with excitation energy than the radiated power [4]. The net result of these two differences is to give an experimental measure for the difference of the KER in the first decay from cluster size n to $n - 1$ and the amount of radiative cooling of the cluster of size n in the two-step decay chain. For all five cluster sizes investigated, this difference is consistent with the theoretically expected KERs and no radiative cooling [4, 19].

6. Comparison of results

A comparison of the values measured so far for the monomer dissociation energies of gold cation clusters with the various methods outlined above is given in figure 4. The agreement between data measured with the three different methods reviewed is very satisfactory.

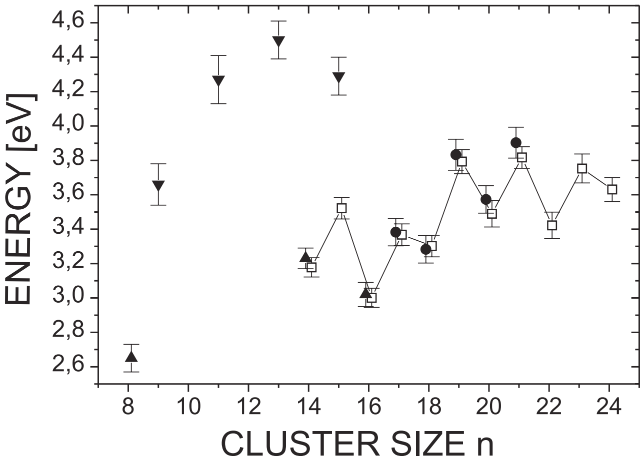

Figure 4. Dissociation energy as a function of cluster size for Au_n^+. Open squares represent values from the method described in section 2 [1], full triangles values from the variation with branching ratios [25] as described in section 4 and full circles values from multisequential measurements [19] as described in section 5. Full, inverted triangles are dimer dissociation energies from [41], as described in section 7.

One interesting aspect of these results is the pronounced odd–even staggering, which can be related to the electronic structure of the clusters, in the simplest version as described by the jellium model and the effect of deformations of open shell clusters [27]. A similar picture is found in abundance spectra, which display very strong odd–even effects [28]. However, the behaviour for gold clusters differs from that of the paradigmatic alkali clusters, where the shell closings are the dominating features in the abundance spectra [29, 30]. For both gold and the two other coinage metals, Cu and Ag, the odd–even variations in the abundances are comparable to the abundance variations across the shell closings [31]. The data in figure 4 suggest that this behaviour can be traced to the thermal stability of the clusters in a very direct way.

7. Application to dimer dissociation energies

Dimer evaporation is known to compete with monomer evaporation in unimolecular reactions of clusters of several different metals [26, 32–40], a feature whose energy dependence has already been described and used in section 4. For the Au_n^+ cluster sizes which show a finite branching into both channels ($n = 7, 9, 11, 13, 15$), the measurements give a ratio of dimer to monomer yields which decreases almost exponentially with excitation energy [26]. Neither the trend nor the absolute magnitude of the branching ratios is yet understood on the basis of unimolecular rate theory. An important ingredient in the theoretical study is the value of the dissociation energy for dimer evaporation from cluster size n, $D_2(n)$. It can in principle be calculated with a Born–Haber cycle [41] from sequential monomer dissociation energies and the binding energy of the neutral dimer, all of which are known quantities. However, given the discrepancy between the expected and measured branching ratios, a direct measurement is highly desirable.

Such a measurement has been performed in complete analogy to the variant described in section 4. The decays investigated are the sequential process (see figure 5)

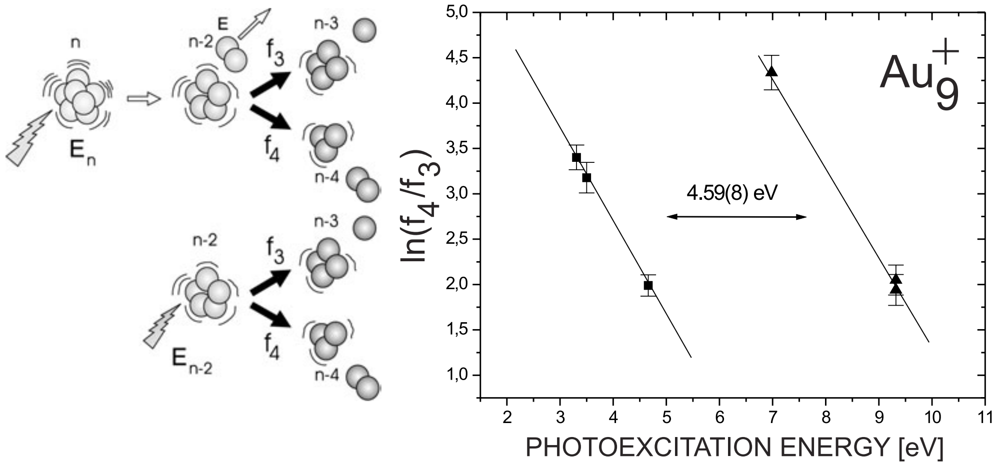

Figure 5. Left-hand part: schematic drawing of the method described in section 7. Right-hand part: branching ratios between Au_5^+ and Au_6^+ intensities in the one-step decay of Au_7^+ (squares) and in the sequential decay of Au_9^+ (triangles).

$$\mathrm{Au}_n^+ \rightarrow \mathrm{Au}_{n-2}^+ \begin{array}{ll} \nearrow \mathrm{Au}_{n-4}^+ & (f_4) \\ \searrow \mathrm{Au}_{n-3}^+ & (f_3), \end{array} \tag{10}$$

and the thermometer process

$$\mathrm{Au}_{n-2}^+ \begin{array}{ll} \nearrow \mathrm{Au}_{n-4}^+ & (f_4) \\ \searrow \mathrm{Au}_{n-3}^+ & (f_3). \end{array} \tag{11}$$

From the measured energetic shift, the dimer dissociation energy $D_2(n)$ is found as

$$D_2(n) = E_{ph,n} - E_{ph,n-2} + (E_n^{th} - E_{n-2}^{th}) - E_{KER} - E_{ROT} - E_{VIB}, \tag{12}$$

where the new features are the rotational energy, E_{ROT}, and the vibrational energy, E_{VIB}, of the evaporated dimer. These values can be estimated from detailed balance arguments to be $E_{ROT} = k_B T$ and $E_{VIB} = k_B T - \hbar\omega_2/2$, where the temperature is the microcanonical temperature of the product cluster, as for the translational kinetic energy, E_{KER} [4, 41]. For Au_{15}^+, this procedure gives $D_2(15) = 4.29(12)$ eV, where the statistical and systematic uncertainties have been added in quadrature. This value may be compared with the one obtained from a Born–Haber cycle: $D_2(15) = D_1(15) + D_1(14) - D(2)$, where $D(2)$ is the binding energy of the neutral gold dimer of 2.29(1) eV [42]. The monomer dissociation energies of Au_{15}^+ and Au_{14}^+ are known from previous measurements [1]. Inserting the numbers gives $D_2(15) = 3.52(13)$ eV + 3.18(11) eV − 2.29(01) eV = 4.41(17) eV, in excellent agreement with the model-independent value.

8. Perspectives

In the application of the method to dimer dissociation energies, the correction to the observed energetic shift in order to get the dissociation energy is larger than for the previously described applications. This obviously renders the method less assumption free. But, since the gold dimer is a well characterized species, the problem is much less severe than it would seem at first glance. It is in fact possible to obtain a good deal of information when the first decay involves the dissociation of a molecule with a larger number of degrees of freedom, as long as it is well characterized with respect to thermal properties, as e.g. in the case of the detachment of a methanol molecule from a gold cluster [44]. The methanol molecule is well known and the vibrational level density can be calculated [19]. The reaction

$$\mathrm{Au_8^+CH_3OH} \rightarrow \mathrm{Au_8^+} + \mathrm{CH_3OH} \rightarrow \mathrm{Au_7^+} + \mathrm{CH_3OH} \tag{13}$$

was compared with

$$\mathrm{Au_8^+} \rightarrow \mathrm{Au_7^+}. \tag{14}$$

Both the last decay in (13) and the decay in (14) were measured time resolved at different excitation energies. The first decay in (13) leaves the bare cluster with a relatively broad distribution of excitation energy due to the small and comparable heat capacities of the methanol molecule and the cluster. The decay of the product therefore does not proceed as a single exponential. With the measured energy-resolved decay constants from reaction (14), both the yield of $\mathrm{Au_7^+}$ and the shape of the decay curve as a function of time can be used to fit the cluster–molecule dissociation energy, $D = 0.35(5)$ eV. The relative accuracy is lower than for monomer evaporation. However, the fit is also sensitive to the thermal properties of the gold cluster (the level density, to be specific), since they determine the partition of the excitation energy between the free cluster and molecule. When the methanol–cluster complex absorbs a photon, the molecule is detached with 100% efficiency, due to the very low binding energy of the molecule to the cluster. The resulting $\mathrm{Au_8^+}$ may then fragment to $\mathrm{Au_7^+}$ or it may not, according to whether the amount of energy carried away by the methanol molecule leaves the cluster with enough energy for the process. The quantum efficiency of the fragmentation of $\mathrm{Au_8^+}$ is therefore known from the measured abundances of $\mathrm{Au_8^+}$ and $\mathrm{Au_7^+}$. The yield of $\mathrm{Au_7^+}$ from the naked $\mathrm{Au_8^+}$ is determined partly by the rate constant for the process equation (14) and the measurement time, and partly by the energy distribution of the $\mathrm{Au_8^+}$ cluster. Only the latter is unknown, and the yields therefore provide a measure of the distribution against which assumed distributions can be tested. The technique is therefore potentially useful for measurements of relative level densities. For the case of $\mathrm{Au_8^+}$, the data could be fitted with a level density extrapolated from the bulk values, with a simple scaling with the number of vibrational degrees of freedom [44]. The sensitivity of the method is still untested and at present it is not clear whether it will be sufficient e.g. to predict rate constants.

9. Summary

Several variations of a model-free determination of cluster dissociation energies have been presented. The results for gold clusters have shown consistency in all measured cases and the precision has reached the 1–2% level. The agreement between different determinations demonstrates that for gold clusters the details of the excitation process are not relevant on the microsecond and millisecond timescale, and illustrates that the choice of the uncalibrated thermometer can be made by convenience. For example, the use of branching ratios circumvents the necessity to measure rate constants and thus allows us to also apply the method to processes outside the experimental window for time-resolved observations. Other variations provide experimental measurements of other quantities of the decay process than dissociation energies, e.g. the energy dependence of the KER and limits on any competing radiative cooling channel. The idea can also be applied to decays where both fragments have a number of internal degrees of freedom. In addition to binding energies, this will provide information about thermal properties of the least known species.

Recently, the method has also been applied to silver clusters [45] and to the determination of the dissociation energy of $\mathrm{V_{13}^+}$, a model system for the study of radiative cooling processes [12]. This study is very sensitive to the dissociation energy and gains much from its precise determination [46].

In summary, the novel method allows us to measure precise values of dissociation energies, which are among the most fundamental characteristics of any polyatomic particle. In addition to the values as such, the accurate knowledge of the dissociation energies opens up new paths to investigate other particle properties and processes such as level densities and radiative cooling. In the present example, the studies have been performed with atomic clusters. However, the method is not resticted in this respect, and can be applied to other polyatomic particles as well. The reaction under investigation may not even be dissociative in nature. Any process which is followed by a second, energy-dependent process can be investigated as described above. Thus, the full potential of the new method still has to be explored.

Acknowledgments

This work was funded by the DFG, the EU networks ‘Eurotraps’ and ‘Cluster cooling’, the Fonds der Chemischen Industrie and the Academy of Finland under the Finnish Center of Excellence Programme 2000–2005 with a grant to KH.

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