Eur. Phys. J. D **24**, 137–143 (2003)
DOI: 10.1140/epjd/e2003-00181-x

THE EUROPEAN PHYSICAL JOURNAL D

New approaches to stored cluster ions

The determination of dissociation energies and recent studies on dianionic metal clusters

L. Schweikhard[1,a], K. Hansen[2,3], A. Herlert[4], G. Marx[1], and M. Vogel[4]

[1] Institut für Physik, Ernst-Moritz-Arndt-Universität Greifswald, 17487 Greifswald, Germany
[2] Department of Physics, University of Jyväskylä, P.O. Box 35, 40014, Finland
[3] Chalmers University of Technology and Gothenburg University, School of Physics and Engineering Physics, 41296 Gothenburg, Sweden
[4] Institut für Physik, Johannes Gutenberg-Universität Mainz, 55099 Mainz, Germany

Received 10 September 2002

Abstract. Ion traps are "wall-less containers" which allow the extended storage of selected species. During the storage various interaction steps may be repeatedly applied. To this end no further hardware has to be added – in contrast to beam experiments. In this progress report two examples of recent developments are presented: the experiments have been performed with metal clusters stored in a Penning (ion cyclotron resonance) trap. A new experimental scheme has been developed which allows precision measurements of the dissociation energies of polyatomic species. It has been triggered by investigations on the delayed photodissociation of stored metal clusters. However, the technique is also readily available for application to a broad variety of different species and it is not even restricted to trapping experiments. The second development is more closely connected with ion storage in Penning traps: by application of an "electron bath" singly charged anionic clusters can be converted into multiply charged species. Subsequently, they are charge selected and investigated with respect to their reaction upon excitation. In particular, preliminary results indicate that dianionic metal clusters emit two electrons upon photoexcitation whereas the singly charged species show dissociation.

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

1 Introduction

The Cluster Trap is an ion trapping device devoted to the study of atomic clusters, *i.e.* systems that bridge the gap between isolated atoms and condensed matter [1]. The instrument consists of a Penning trap combined with an external cluster ion source and a time-of-flight (TOF) section for the detection and analysis of the reaction products. A description of the setup, including the application of gas pulses in the trap volume, was given by Becker *et al.* at a stage where the stored clusters were investigated mainly by collision induced dissociation [2]. A later addition provided the possibility of photoexcitation by laser irradiation [3]. To this end, the multichannel plate detector was removed from the setup's symmetry axis and an off-axis conversion electrode detector was added. This allowed time-resolved studies of delayed cluster dissociation and delayed electron emission from anionic clusters after pulsed photoexcitation [4–6].

The developments have been described in a number of detailed publications and summarized in several review articles [7–11]. The trapping of ions in "wall-less containers" has at least three main advantages with respect to alternative experimental techniques in research on free clusters: (i) ion traps allow the extended storage of clusters at rest in vacuum, *i.e.* with a minimum of interaction with the rest of the world. (ii) They have an intrinsic capability for mass spectrometry (MS): selected species may be isolated for further studies and a mass analysis of the final products can be performed either by the choice of the trapping parameters or by suitable manipulation of the ions' motional modes in the trap. (iii) Defined interactions of various kinds may be applied to the stored cluster ions. These interaction steps can be repeated several times and various different interaction events may be combined, as the charged interaction products stay trapped (as long as they are in the appropriate mass range).

Thus, a Penning trap like the Cluster Trap provides the possibility of many interesting investigations. Stored, size selected cluster ensembles can be probed by various interactions with neutral atoms or molecules (at different collision energies), by photons and by electrons [9]. This leads to processes such as adsorption, desorption/evaporation, fission, further ionization by electron

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[a] e-mail: `lutz.schweikhard@physik.uni-greifswald.de`

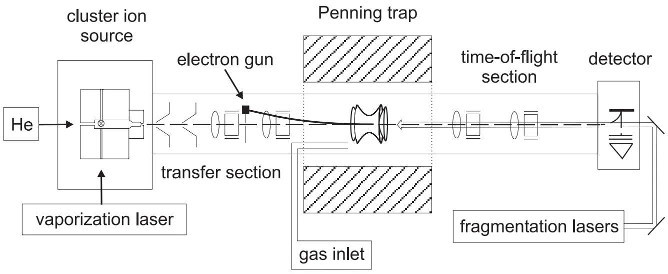

Fig. 1. Overview of the experimental setup.

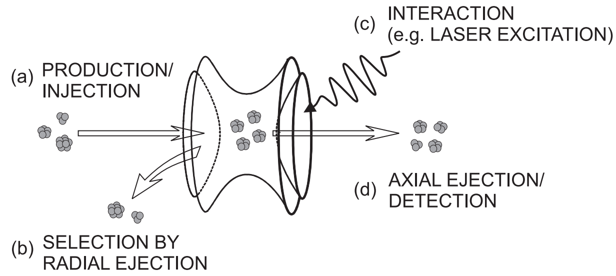

Fig. 2. Schematic drawing of Penning trap and indication of the main steps of a typical experimental sequence.

ejection (from cations), electron attachment (to anions) or photoemission (radiative cooling). These processes may be combined and further ones may be thought of (see outlook). In the following, the investigations are exemplified by recent developments in two lines of research: (a) production and investigation of multianionic metal clusters, (b) time-resolved decay studies of excited metal clusters.

While the setup described in this progress report is unique in several aspects (like the application of a Penning trap with TOF ion detection for cluster studies) it is only natural that some aspects have also been taken advantage of in other experimental arrangements: clusters have been studied in extended time ranges of seconds and longer at ion storage rings, too (see *e.g.* [12]). In these devices the clusters are not at rest in the laboratory frame, but for some kinds of experiments this, together with the large number of ions stored, may even be an advantage.

In general, due to its high resolving power FT-ICR MS (Fourier transform – ion cyclotron resonance mass spectrometry [13–15]) is the method of choice for the analysis of ions stored in a Penning trap and over the years several groups have reported such kind of cluster experiments, *e.g.* [16–18]. In contrast, the choice of TOF instead of FT-ICR MS at the Cluster Trap results in a loss of resolving power, since the storage but not the ejection of the ions from the trap has been optimized. However, it is still possible to distinguish between different cluster sizes and in contrast to FT-ICR MS the TOF MS provides ultimate sensitivity by single ion detection.

Furthermore, in addition to the Penning traps there are the Paul traps, where the storage is not provided by a static magnetic field (see below), but by time varying (radio frequency) electric fields. Depending on the particular purpose, one or the other kind of trap may be more suitable. As a particular highlight in Paul trap cluster physics, the electron diffraction measurements by Parks and coworkers are mentioned, which revealed the geometrical structures of small cesium iodide clusters. The experiments showed that in general the clusters' structures differ from CsI bulk structure, but also depend on the particular cluster size under investigation [19]. Linear rf traps are another possibility to store ions. Recently, a hexadecapole trap has been applied for extensive IR spectrometry of $V_4O_{10}^+$ [20,21].

In passing we mention some of the technical developments that were pioneered at the Cluster Trap: the capture of externally created cluster ions and in particular their accumulation [22] and the trapping conditions have been investigated in detail [23]. More recently, the studies have been extended to reactions where the charge state is changed, which can lead to previously unexpected ion loss [24].

Furthermore, it should be noted that not only are ion trap devices well-suited for cluster research, but that on the other hand clusters can play a significant role in precision mass spectrometry by use of ion traps: recently, carbon clusters have been introduced to ISOLTRAP, a Penning trap mass spectrometer for accurate mass measurements of short-lived nuclei [25]. There, clusters are applied as absolute reference masses and can also be used for consistency checks, *i.e.* for the determination of the uncertainty of the new experimental mass values [26].

2 Experimental setup and procedure

Figure 1 shows an overview of the experimental setup[1] with its main components: the cluster source, the Penning trap and the TOF section. Metal clusters are produced in a Smalley-type wire source [27]. So far, no postionization has been applied and only the ionic clusters that are delivered directly from the source have been transferred to the trap. Note, that the source provides only singly charged (either cationic or anionic) clusters. Directly produced clusters of higher charge have not been observed.

The Penning trap is a combination of a strong homogeneous magnetic field (5 tesla) for radial ion confinement and a quadrupolar axial electric field for ion confinement along the magnetic field lines [28]. Figure 2 schematically shows the shape of the trap's electrodes. The ion trajectories inside the trap are superpositions of the radial cyclotron and (low-frequency) magnetron modes and the axial oscillations between the endcap electrodes. In particular, the cyclotron motion is used extensively for the manipulation of the clusters' motion, since it is strongly mass and thus cluster-size dependent (to be exact, it is the mass-over-charge ratio that is relevant, as in general in mass-spectrometry investigations).

The main steps of an experimental sequence are indicated in Figure 2: (a) after the cluster ions have left

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[1] The Cluster Trap has been developed and operated for about a decade at Mainz and is presently built up again at Greifswald.

the source they are guided by electrostatic ion-optical elements to the trap. For in-flight capture the trapping potential is lowered on the source-side endcap and raised again once the clusters have passed a central hole in this electrode. During the trapping period a potential well of typically a few volts is applied.

(b) In contrast to the Paul trap, a Penning trap uses static trapping fields. However, the ring electrode is segmented into several pieces to allow the additional application of rf signals in various multipole configurations in order to manipulate the ion trajectories [29]. In particular, the cluster size of interest is isolated by ejection of all unwanted ions. To this end, a strong dipolar rf field is applied in the frequency range corresponding to their cyclotron frequencies.

(c) A defined interaction step is added for the actual investigation. This may involve collisions with inert gases, chemical reactions, electron impact ionization or electron attachment or photoabsorption at various wavelengths. In general, such an interaction step is followed by a reaction period, *i.e.* a delay in the sequence, where the clusters are stored without further interaction. The charged reaction products stay stored inside the trap which thus acts as a 4π detector. It also provides the possibility to use the reaction products for further investigations. As an example, after the production of doubly charged clusters from size selected singly charged clusters, it is possible to perform a second selection step, namely with respect to the charge state. Thus, both size and charge-state selected clusters have been produced by sequential selection-reaction-selection processes for species such as Ag_{18}^{2+} [30] or various dianions Au_{2n}^{2-} [31] where a single selection would have resulted in a contamination by the corresponding clusters of the same mass-over-charge ratio, Ag_{9}^{+} and Au_{n}^{-}, respectively.

(d) For mass analysis of the ion ensemble after interactions and reactions, the ions are axially ejected. In analogy to the in-flight capture, the trapping potential is lowered on the detector-side endcap and the ions leave the trap through a central hole of this electrode. They are accelerated to a few hundred eV and are guided through a drift tube to the conversion electrode detector. There, they are further accelerated to several thousand eV before they hit the aluminum conversion electrode, where either electrons are released in the case of cationic clusters, or Al^{+} ions are sputtered in the case of anionic clusters. The electrons (or aluminum ions, respectively) are then detected by a tandem micro-channel plate configuration. This geometry both allows single-ion counting and the application of various laser beams along the trap's axis.

Typically, a sequence takes about one or a few seconds and the number of clusters present in the trap at a given time, *i.e.* investigated during each sequence, is on the order of ten. To increase the statistical significance of the data, TOF spectra of several hundred sequences are added at a given set of experimental parameters before the parameter of interest is switched to the next value. In addition, reference sequences are introduced which are performed alternately with those of the actual measurement. Thus, important parameters, like the cluster production rate of the source, can be monitored quasi-simultaneously.

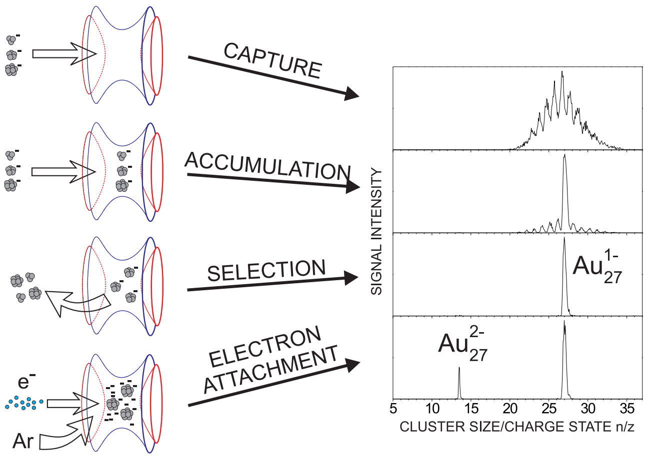

Fig. 3. Left side: cartoon of a typical experimental sequence. Right side: corresponding TOF spectra.

In Figure 3 (left) a typical experimental sequence is illustrated by schematical drawings of the capture, accumulation, size selection of Au_{27}^{1-} clusters and finally the attachment of an additional electron. The TOF spectra on the right side of Figure 3 are the result of the experimental sequence when terminated by TOF analysis at the corresponding stages. As mentioned above, the sequence can be continued by charge-state selection and storage of only the dianions for further investigation by use of collision-induced activation or photoexcitation.

3 Attachment of electrons to anionic clusters

Before these more complex experiments with repeated selection steps will be further discussed, the seemingly simple attachment of surplus electrons to anionic species is treated in a little more detail: in order to increase their charge state, the stored singly charged cluster anions are bathed in a sea of electrons. These electrons are the products of the ionization of atoms of an argon gas pulse which is applied to the trap volume simultaneously with a primary electron beam produced by an electron gun about half way between the cluster source and the Penning trap. The electron impact ionization of argon leads to an immediate ejection of the argon ions from the trap, whereas the electrons stay in the trap and may attach to the cluster ions.

The details of the electron attachment process are not yet fully understood. As has been shown recently for both gold clusters in the Cluster Trap as well as fullerenes stored and detected in a commercial FT-ICR mass spectrometer the well depth of the trapping potential plays a significant role [32]. Presumably the electrons have to have sufficient initial kinetic energy to overcome the Coulomb barrier of the clusters that are already charged.

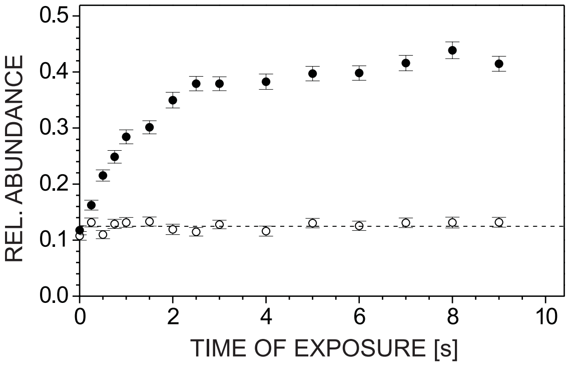

Fig. 4. Relative abundance of dianionic gold clusters Au_{27}^{2-} as a function of the time of exposure to an electron bath (full circles). Open circles: reference measurements where the electrons are released immediately after application of the electron beam.

In addition, it is found that the attachment requires a considerable storage period: Figure 4 shows the relative yield of dianions (with respect to the total number of cluster ions) as a function of the time of exposure to the electron bath. The electrons are created during a period of one second. Since the anions are already exposed to some electrons during this time there is an offset of about 0.1 in the relative abundance of the dianions. The data points indicated by full circles show how the dianion yield develops when the ions are exposed to the electron bath for up to 9 seconds. For comparison, an identical sequence has been performed alternately, where immediately after the creation of the electron bath the electrons are released from the trap. To this end, the trap is opened (see capture and ejection above) for about a microsecond. While the electrons leave, the ions due to their much higher inertial mass still remain inside the trap (suspended trapping [33]). As expected, their storage for up to 9 seconds neither increases nor decreases the relative abundance (open circles). In contrast, the dianion production continues in the electron bath for a few more seconds until it levels off at about 40% and remains constant. The termination of the electron attachment processes seems to be due to the cooling of the electron motion, *i.e.* eventually the electrons no longer have enough kinetic energy to overcome the monoanionic clusters' Coulomb barrier [32].

To summarize the present stage of knowledge about dianion production: the depth of the potential well and the duration of exposure to the electron both matter. The deeper and longer, respectively, the more clusters are converted from mono- to dianions. Even with this limited information further investigations can be performed and in particular the relative dianion yield can be measured as a function of cluster size when all other parameters are kept constant.

Such investigations have been performed for copper, silver and gold clusters and an overview is given in Figure 5. The broken vertical lines indicate the expected threshold sizes for the appearance of dianionic clusters according to a charged sphere model [34]. The experimental data roughly follow the expected trend. However, the yield function is much steeper in the case of gold than for silver or even for copper. Furthermore, significant sudden deviations from the general trend are observed, which have been related to the well-known electronic shell structure of simple metal clusters [34,35].

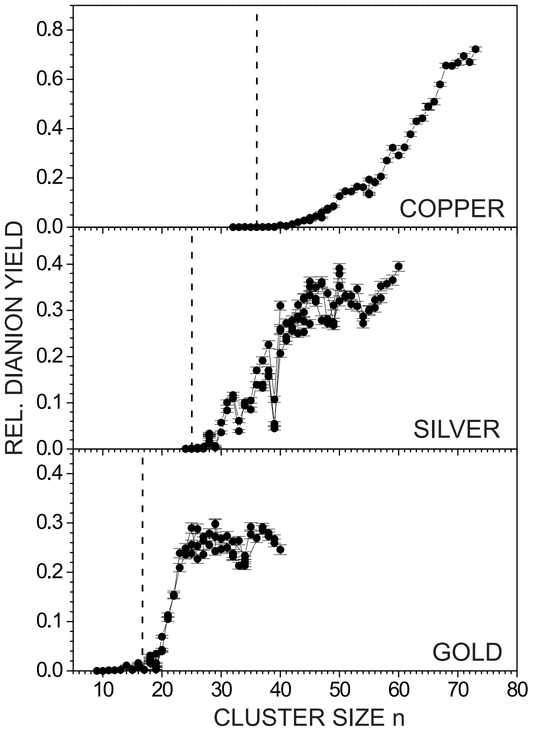

Fig. 5. Relative dianion yield as a function of cluster size at constant experimental conditions for copper, silver and gold clusters.

With regard to ion trapping, it is worth noting that the Penning trap allows the simultaneous trapping of particles as light as electrons and as heavy as, *e.g.*, Au_{27}^{-} (Fig. 3). Thus, a mass range of more than seven orders of magnitude is spanned which is not easily possible by other trapping methods. On the other hand, the Penning trap is unipolar in the sense that either positive or negative species can be trapped at a given time – the axial trapping well has to be reversed to switch between polarities. This is in sharp contrast to the Paul trap which does not necessarily distinguish between the sign of the electric charges.

4 Electron detachment from dianionic clusters

After dianions have been successfully created one may try to remove electrons from them. Note, that the removal of an electron still leads to an anion, *i.e.* the cluster stays trapped, as opposed to similar studies on singly charged species [5,6]. Initial investigations made use of collisional activation. However, it was realized that the ion trajectories after electron emission may easily increase

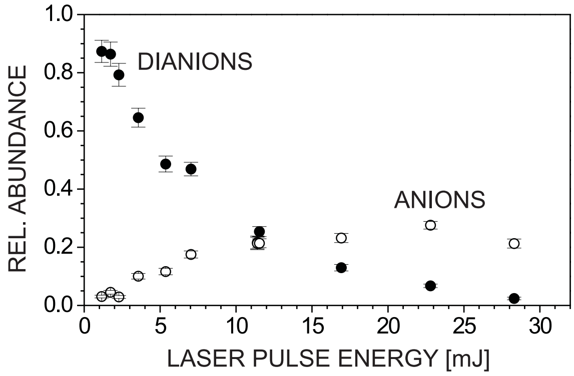

Fig. 6. Relative yield of dianions (full circles) and mono-anions (open circles) after photoexcitation of Au_{30}^{2-} clusters as a function of laser pulse energy (for 10-ns pulses at a wavelength of 355 nm).

beyond the trap dimension which leads to an immediate ion loss [24]. Thus, the experiments have shifted towards photoexcitation.

After laser irradiation of size and charge-state selected dianions Au_n^{2-} both mono-anions Au_n^{1-} and the next smaller dianions Au_{n-1}^{2-} have been observed. Thus, there is a competition between the emission of the second surplus electron and neutral monomer evaporation, where smaller clusters prefer electron emission and larger ones (above about $n = 50$) tend to evaporate atoms [11]. A closer look reveals that this is not the full story: as Figure 6 shows, the abundance of the mono-anionic Au_{30}^{1-} produced by electron detachment of Au_{30}^{2-} (which shows no significant monomer evaporation) does not match the loss of the Au_{30}^{2-} signal, *i.e.* ions are lost. This ion loss indicates that the dianions preferentially lose both surplus electrons. Without further experimental input, one may think that the dianions can lose one electron at a time in independent sequential electron-emission processes. However, reference measurements on the proposed first product Au_{30}^{1-} show that it rather evaporates a neutral monomer: $Au_{30}^{1-} \rightarrow Au_{29}^{1-} + Au$. Thus, the two electrons seem to be emitted by the dianion in a correlated fashion. This correlation may vary with respect to cluster size, element and the details of the excitation, but it seems to be a general feature of photoactivation of dianionic noble metal clusters.

5 Time-resolved photodissociation

The Cluster Trap has been used extensively for the study of the reaction of metal clusters upon photoexcitation. As compared to investigations by collision-induced activation, see *e.g.* [36–38], pulsed laser excitation has two main advantages: (i) the amount of energy deposited is quantized in relatively large steps (the photon energy) and is thus well defined. (ii) By use of pulsed lasers the time of excitation is also well-defined.

Thus, in addition to the determination of photoabsorption cross-sections or branching ratios of the dissociation pathways [39,40] the major interest of the measurements is on the time-resolved investigation of delayed dissociation processes: when a cluster absorbs a photon, the energy is rapidly distributed among the various degrees of freedom, in particular the modes of vibration. If the system consists of more than only very few atoms, it will not decay immediately, although the excitation energy exceeds the dissociation energy. For clusters of, say, 20 or more atoms, even a multiple of the dissociation energy is needed to place the decay within a typical experimental time window. If the appropriate excitation energy is chosen, an exponential decay of the precursor cluster and the corresponding appearance of the charged fragment can be observed. The time window of the Cluster Trap is in the range between about 10 μs and 100 ms.

In principle the known excitation energy and the observed decay constants should be enough information to determine the dissociation energy, *i.e.* the smallest amount of energy required to remove an atom (or dimer) from the cluster. However, none of the several theories that have been introduced and applied over the years to evaluate these kinds of unimolecular dissociations is able to represent the measured rate constants of a given cluster with a single value of the dissociation energy [41]. Instead, the value of the dissociation energy derived as described above depends on the excitation energy. This, at least, is the experimental evidence in the case of cationic gold clusters, which have been investigated extensively: for all the various statistical models used, the resulting value of the dissociation energy was not independent of the excitation energy for which the experiment was performed.

This is not likely to be a failure of the statistical description of the decay but rather expresses our ignorance about the details of the studied systems. Application of realistic models for unimolecular reactions require knowledge of level densities, equivalent to caloric curves for the clusters, as well as an assumption that radiative cooling does not occur. This information is not easily obtained.

A new method has been invented to circumvent these problems [41]: the experimental input from delayed decays is supplemented by measurements of rate constants for sequential decays. Delayed sequential decays are observed when the excitation energy is tuned to such a value that the first product after the decay of the precursor has enough energy to decay, too, and in particular to do it just in the experimental time window. Figure 7 shows an example of the simultaneous observation of single and sequential decay of Au_{25}^{+}, after the absorption of two and three photons (of wavelength 303 nm), respectively.

In general, separate measurement series are performed for the time-resolved studies of the sequential decay of the cluster of size n and the direct decay of the cluster of size $n-1$, as schematically depicted in Figure 8. When the excitation energies E_n and E_{n-1} required to observe the delayed decay from cluster $n-1$ to $n-2$ is the same in both cases, $E_n - E_{n-1}$ is essentially the dissociation energy of the cluster n. Thus, most systematic uncertainties are cancelled.

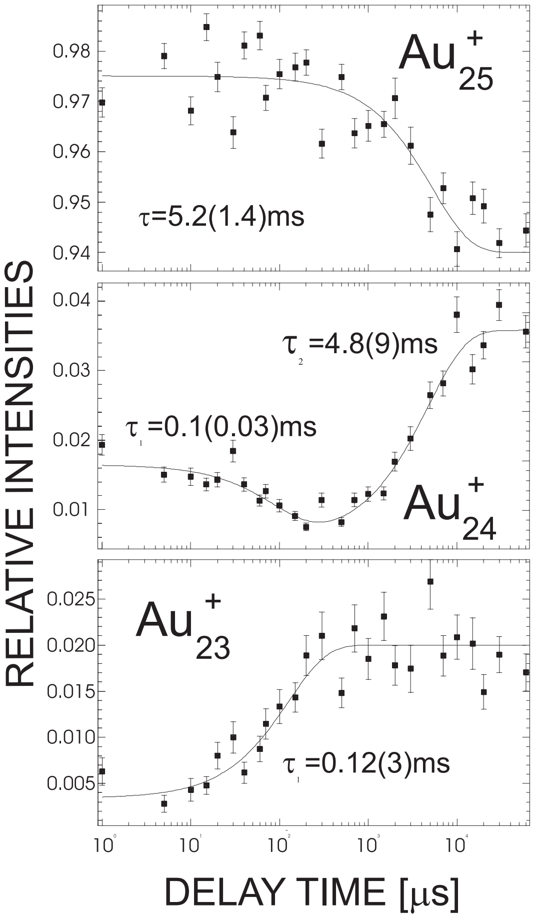

Fig. 7. Relative signal intensities of Au_n^+ (n = 23, 24, 25) as a function of the delay between laser excitation and TOF analysis. For details see text (adapted from [9]).

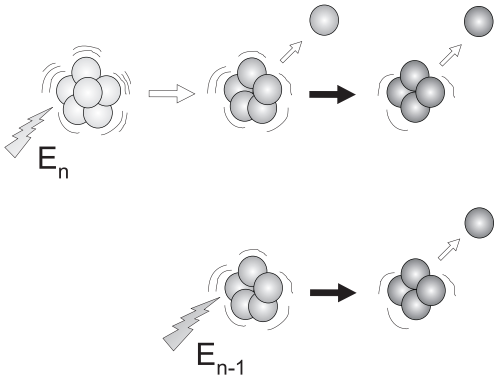

Fig. 8. Schematic drawing of the sequential and direct decay processes which are compared for the model-free determination of dissociation energies.

There is an alternative way to state the new method: the problem in determining the dissociation energy from a single decay is the fact that the remaining energy in the products is in general not experimentally accessible. In the sequential decay, this energy is measured by comparison with the energy required to excite the intermediate product in a separate direct dissociation measurement such, that it decays in the same way as in the sequential dissociation.

The new method works best if there is only one product with internal energy after the initial decay. Thus, it is well-suited for neutral monomer evaporation. It has been applied for dissociation energy studies of various gold clusters [41]. For some of these cases the method has also been modified: instead of the decay rate, any property can be used that shows a measurable dependence on the excitation energy. Thus, *e.g.* the decay branching ratio can be monitored, too [42]. In addition, not only the sequential and direct decay may be compared, but also longer decay chains have been investigated which yields additional information [43]. The various modifications of the new method allow cross checks of the resulting values of the dissociation energies, which are in very good agreement [44].

As a first application to other species, the new technique has recently been applied to V_{13}^+, which also decays by monomer evaporation. In this special case the dissociation energy is a valuable input number for the further evaluation of radiative cooling [45]. Furthermore, data from earlier measurements on silver clusters [46] are currently reevaluated with respect to the new method [47].

When the evaporated particle is a more complicated system, the method is not quite model-free any longer and the internal energy of this neutral evaporation product has to be inferred by other means. Nevertheless, the comparison of direct and sequential decay still allows valuable further investigations, as shown in the cases of dimer evaporation [48] and the detachment of methanol molecules that have been attached to small gold clusters [49].

6 Conclusion and outlook

The latest findings on polyanionic metal clusters and the time-resolved measurement of delayed dissociation at the Cluster Trap have been reviewed. Of particular interest are the decay pathways of activated dianions. In addition to the observation of neutral monomer evaporation and of the emission of single electrons, conditions have been found where the observations indicate a correlated two-electron emission. Furthermore, a method has been invented and applied to a series of gold clusters and to some other species of particular interest, where a combination of sequential and single dissociations upon photoexcitation at defined energies leads to a precise determination of dissociation energies. The technique circumvents the modelling of the details of the decays. Thus, the resulting values are model-free and can, in return, serve as benchmarks for future tests of the corresponding calculations. The new method, in particular in the branching ratio mode, is not restricted to ion trap experiments, but can be applied as well to, *e.g.* molecular beams. An extension to other polyatomic systems is straightforward and even other excitation schemes, such as collision or surface induced dissociation [50], may be considered. (However, note that in general for these methods the excitation energy is not as well defined as for the absorption of photons from a laser beam.)

On the other hand the potential of the trap is by no means restricted to the two types of experiments described above. As an example of other possibilities, multiply charged atomic ions could be stored simultaneously with size-selected trapped cluster ions, or alternatively, they could be shot at higher kinetic energies through the trap. Furthermore, stored multiply charged clusters (of either polarity) could be brought to interaction with neutral atoms or molecules.

In addition, the combined trap, a hybrid of Penning and Paul trap, as well as so-called nested traps allow the simultaneous storage of species of different polarities (see *e.g.* [51]). Thus size-selected both cationic and anionic clusters could be brought and kept together for interactions such as *e.g.* cluster fusion. If the charge states are selected properly, the reaction products may still be charged, *i.e.* stay stored inside the trap. Such kinds of reactions are interesting with respect to the study of the processes involved and also with respect to the products which may be species that have not yet been produced by other means.

The Cluster Trap is supported by the Deutsche Forschungsgemeinschaft, the European Union (network on Cluster Cooling), and the Fonds der Chemischen Industrie.

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