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The Mainz Cluster Trap

Ion storage techniques at work in atomic cluster research

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Abstract. When cluster ions are stored by electromagnetic forces they are available in the gas phase for extended preparations and investigations. Over the last decade a Penning trap (Ion Cyclotron Resonance) apparatus has been constructed and further developed with respect to metal cluster research at the Institute of Physics at Mainz. It allows to capture and accumulate ion bunches injected from an external cluster source and to manipulate the ions' motion, i.e. select and center the clusters of interest. The interactions that have been investigated include those with inert and chemically reactive gases, photons and electrons. Multiple mass spectrometric steps such as fragment ion selection can be used to disentangle complex reactions or interfering reaction channels. A brief introduction into the principles of ion trapping and a short overview of the history and experimental setup at Mainz are given. The advantages of ion storage with respect to extended preparation of the trapped cluster ensemble and with respect to extended reaction periods are exemplified by measurements of the collision induced dissociation of Ag_{16}^{2+} and by time-resolved observation of the photodissociation of V_{12}^{+}. References are given both to the investigations performed at the Mainz Cluster Trap as well as to other experimental arrangements and measurements.

PACS. 36.40.Wa Charged clusters – 07.75.+h Mass spectrometry and related techniques

1 Introduction

Free atomic or molecular clusters, i.e. those in the gas phase as opposed to in matrices or on substances, have long been studied in beams [1]. Since in general the sources deliver a variety of clusters with respect to the number of their constituents, experiments on size-selected clusters are much facilitated by previous ionization and mass spectrometric separation. In a beam experiment a spatial section is devoted to such a selection event by use of mass spectrometric (MS) techniques. The final analysis after a reaction involves another MS step including additional hardware. Such types of experiments and setups are denoted MS/MS or MS^n if further steps are added [2].

In trap experiments the ions do not fly from a source to a detector through various selection and reaction devices, but are rather confined by electro-magnetic fields in a small spatial region.[1] The MS steps are separated in time rather than in space and the experiments consist of pulsed event sequences. Note that in contrast to beam experiments the addition of a new event requires no additional hardware. There is no limit as to how many events may be included in a sequence and different kinds of events are easily combined.

The left-hand column of Fig. 1 gives a list of reaction partners that have been (or will be) brought to interaction with stored metal clusters at the Mainz setup. Combinations are e.g. the production of multiply charged clusters by electron impact ionization or the synthesis of a cluster-ligand complex as a first step and another MS event for the probing of certain properties of interest. In general the experimental signature consists of the observation of a dissociation after a collision or photoabsorption. In most cases not only the depletion of the precursor ion signal, but also the appearance of the charged dissociation products can be observed. All product ions stay stored inside the trap after the dissociation; the trap essentially serves as a 4π detector.

The second main difference between trap and beam experiments lies in the maximum time period of a given event. In a beam the particles can be slowed down to some extend but will eventually reach the detector. Since clusters are heavy ion species this period is of the order of hundreds of microseconds or a few milliseconds. In ion traps, in contrast, they may be stored for durations several orders of magnitude longer, i.e. seconds or minutes. The storage period may be used for extended interaction (providing many collisions or continuous irradiation with

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[1] Experiments with clusters 'trapped' in storage rings (see e.g. [3]) will not be discussed in the present article.

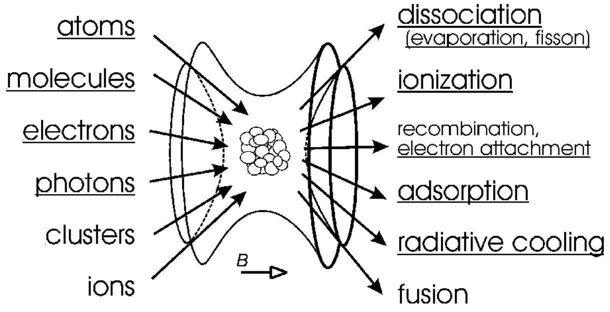

Fig. 1. Interaction partners (left column) and reactions (right column) of stored cluster ions (already studied at the Mainz Cluster Trap if underlined). Center: schematic drawing of a cluster ion stored in trap with hyperbolically shaped electrodes.

a light source) or extended 'reaction', i.e. interaction-free periods where the clusters can rearrange themselves with respect to their internal degrees of freedom.

The next section describes the techniques of ion trapping in a little more detail. It is followed by a brief account of the history and present status of the apparatus at Mainz and by the description of two measurements where the particular advantages of cluster trapping are exemplified. Finally, the earlier and present research activities at the Mainz Cluster Trap are summarized, with an outlook on some possible future experiments. References to cluster trap experiments by other groups are given along the way.

2 Ion trapping

2.1 Principles

Having said that much about the advantages of cluster ion trapping, how can it be accomplished? The objective is the storage of the clusters in a wall-less container. In the absence of any space charge potentials static electric fields are not sufficient for three-dimensional trapping. There are two main solutions to the problem of ion storage, the Penning trap and the Paul trap.

In the Penning trap [4], also called Ion Cyclotron Resonance (ICR) trap, a strong homogeneous magnetic field leads to the confinement in the two dimensions perpendicular to the field lines (radial) and the application of an additional electric potential restricts the ions' motion along the field lines (axial confinement). Both the magnetic and electric field are static. In contrast, the Paul trap [5] uses an electric potential only, which, however, has a strong time dependent component, and is therefore also called 'RF' trap (for 'radio frequency'). In the scientific community of analytical and ion-molecule chemistry the term 'ion trap' seems to be reserved to the Paul trap. In the present paper, however, we will use it in its literal, more general sense.

Ideally, the electric fields of both Penning and Paul traps are of quadrupolar geometry, i.e. they should be created by the application of appropriate potentials to hyperbolically shaped electrodes (see Fig. 1). In practice there is a variety of electrode forms in use [6]. To first order the potential at the center of the trap is still quadrupolar. Furthermore, the particular electrode shapes allow more efficient applications of further time varying electric fields which are used for the manipulation of the ion motion.

One difference between Penning and Paul traps is the polarity of simultaneously trapped ions. In its standard form the Penning trap stores either positive or negative ions whereas the Paul trap allows a simultaneous storage. Another difference lies in the range of cluster sizes. The Penning trap has an upper mass limit (see below) whereas the Paul trap can, in principle, operate at any cluster mass and very large particles have been stored even in its earliest days [7]. However, while the Paul trap has recently received lots of attention as an analytical device in general, it is still not much used in cluster science. An exception are the recent investigations of Parks *et al.* on fullerenes [8] including electron diffraction measurements [9].

There are other ion storage devices, such as the linear Paul trap, which is similar to a quadrupole mass filter and also allows extended ion storage if static electric trapping potentials are added on both ends. The latter device has been used by Wöste *et al.* [10]: After irradiation of stored cluster anions with ultra-short pump and probe laser pulses the respective cations are detected which results in valuable information about the structure and dynamics of the neutral (!) clusters. Gerlich has used RF traps of higher multipolarities to create very shallow trapping potentials. This allows the investigation of clusters at low temperatures [11]. Nevertheless, the bulk of cluster experiments with ion traps has been performed by the use of the ICR technique, which is described in some more detail in the following section.

2.2 Penning trap

As mentioned above, the combination of a static homogeneous magnetic field and a static quadrupolar electric field leads to both radial and axial ion confinement [4]. For an ideal trapping potential the ions' motion can be described in terms of three independent modes: (a) the cyclotron motion, the circular motion in the radial direction due to the Lorentz force, (b) the trapping motion, the axial oscillation due to the electric field, and (c) the magnetron motion, a slow circular drift around the trap's symmetry axis due to the crossed electric and magnetic fields.

Typical values for the respective resonance frequencies are given in Table 1. The magnetron frequency, ν_m, is small and almost mass independent. The trapping frequency, ν_t, (which is independent of the magnetic field) is higher and scales as one over the square root of the mass.[2] The cyclotron frequency, ν_r, is somewhat reduced with respect to its value in the absence of the electric trapping field, $\nu_\mathrm{c} = qB/(2\pi m)$, namely by just the value of the magnetron

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[2] In general mass spectrometric methods can not distinguish between different ion species of the same mass-over-charge ratio and 'mass' in this context should be read 'mass-over-charge'.

Table 1. Frequencies of motional modes for Au_n^+ and Penning trap parameters as given in Sect. 3.2.

n	ν_m [kHz]	ν_t [kHz]	ν_r [kHz]
4	0.80	12.45	96.65
20	0.83	5.57	18.66
100	1.11	2.49	2.78

frequency, $\nu_\mathrm{r} = \nu_\mathrm{c} - \nu_\mathrm{m}$. Nevertheless, the cyclotron motion is still most important with respect to mass selection and mass analysis, because ν_r covers the largest frequency range.

Since there is a hierarchy of frequencies [4] and $\nu_\mathrm{r} \geq \nu_\mathrm{m}$, Table 1 suggests that there is an upper mass limit [12]. For the trap parameters of Table 1 the largest singly charged gold cluster that can be stored has size $n = 122$. (In the case of a higher charge state the maximum size increases proportionally.) In addition to this theoretical upper mass limit, there is a further limitation which depends on how much kinetic energy the cluster is to have. For Au_{100}^+, as an example, already the room temperature energy of $kT = 1/40\,\mathrm{eV}$ corresponds to a cyclotron radius of almost a millimeter. While the theoretical mass range can be extended by lowering of the trapping voltage the cyclotron radius at a given energy is mainly determined by the magnetic field. Note that this feature also sets limits with respect to collision experiments of large clusters.

The ions' motion may be manipulated by the application of appropriate electric fields which are characterized by their frequency and multipolarity [13]. By use of dipolar fields the ion motion can be excited. This is frequently made use of for the excitation of the cyclotron motion, either to eject unwanted ion species or to bring those of interest to a defined cyclotron radius and energy, e.g. for collision studies. An azimuthal quadrupolar field at the sum frequency of $\nu_\mathrm{r} + \nu_\mathrm{m}$, i.e. at the 'true' cyclotron frequency, leads to the conversion of the magnetron motion into the cyclotron motion and vice versa [14]. This method allows ion confinement even in the presence of collisions with residual gas particles. Without quadrupolar excitation the ions are lost from the trap due to an increase in their magnetron radius. With quadrupolar conversion, however, the ions are centered in the middle of the trap [15].

The method of choice for broad-band mass analysis of ICR trapped ions in analytical applications is called Fourier Transform (FT-)ICR MS [6, 16]. It makes use of both the increased cyclotron radius and the coherence of the ions' motion after (in general broad-band) radial dipolar excitation. The ions' image charges, that are induced in the ring electrode segments, are picked up, amplified, digitized and subjected to an FFT algorithm [17]. Frequency-to-mass conversion yields an abundance spectrum of the ion distribution. An experiment in general consists of a series of such measurements as a function of the event parameters of interest, like e.g. the pressure of a gaseous reaction agent, cyclotron excitation amplitude, frequency of an applied laser pulse, or storage period after the interaction and before the FT-ICR analysis.

3 The Mainz apparatus

3.1 History

With no previous experience in FT-ICR, why then has Mainz been the site of recent cluster trap investigations? It was during the middle of the eighties that the first ideas of the use of a Penning trap for the study of cluster ions were developed at the Institute of Physics of the Johannes Gutenberg-Universität [18]. At that time H.-J. Kluge and his coworkers had just completed a Penning-trap setup for precision mass measurements of short-lived isotopes. This apparatus, later dubbed ISOLTRAP, had been installed [19] at the on-line mass separator ISOLDE at CERN/Geneva (for reviews see [20]). To optimize ion production/preparation and the actual mass measurement two Penning traps were connected. The transfer from one trap to the other had been demonstrated [21] and it was realized that the injection of cluster ions from an external source could be accomplished in the same way.

In addition to the technical similarities of trap investigations of clusters and nuclei, the latter and in particular metal clusters are closely related with respect to the underlying physics: Both systems can be modelled in first approximation as a finite number of fermions (nucleons or electrons, respectively) in a potential well, which leads to shell structures as observed in various cluster properties [22].

The detection scheme used at ISOLTRAP provided high mass accuracy for preselected atomic ions, but would not allow the conventional mass analysis that is necessary to investigate the properties of cluster ions. Therefore, FT-ICR was studied at Mainz which led to further understanding and development of this technique [23].[3]

After early FT-ICR observations of carbon and silicon clusters [26], the setup was modified by the addition of time-of-flight (TOF) mass analysis. This technique, in contrast to FT-ICR, is very sensitive and allows single ion counting of singly charged species. The tradeoff is a poor mass resolution, whereas that of FT-ICR MS is excellent [27]. However, the emphasis of the investigations at Mainz was to be on interactions with small cross sections and the possibility to work with only very few ions at a time.

Finally, three years ago, the complete system including the external cluster source, the Penning trap and the TOF section was presented [28] under almost the same title as the initial proposal [18]. Since then the system has been further developed and several investigations on metal clusters have been performed, some of which have been already reviewed [29].

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[3] In the meantime Smalley *et al.* had already succeeded in the injection of cluster ions into an FT-ICR system [24], followed by Irion *et al.* [25].

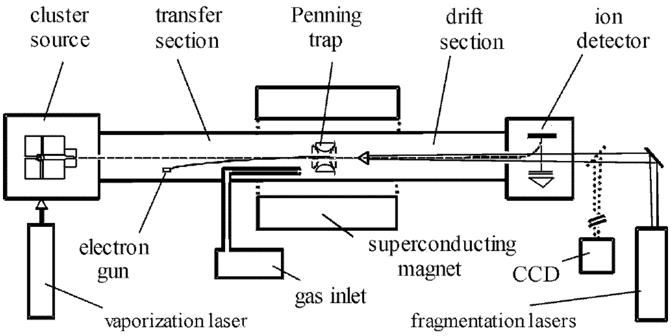

Fig. 2. Overview of the setup of the Mainz Cluster Trap.

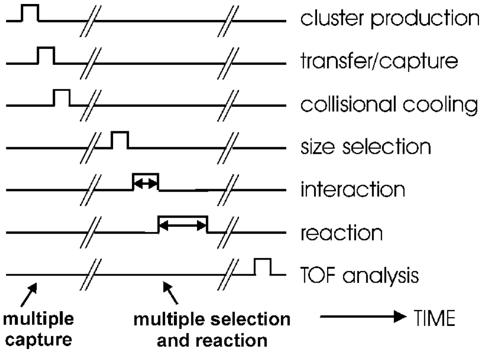

Fig. 3. Experimental sequence.

3.2 Experimental setup and procedure

Figure 2 gives an overview of the main elements of the present experimental setup: Cluster ion source, transfer section, Penning trap, drift section and ion detector, complemented by a gas inlet system, an electron gun and various pulsed lasers [28, 29]. Not shown are the vacuum equipment and the experimental control systems which include the electronics for trigger pulses, manipulation of the ions' motion and data acquisition, as well as the computers for on-line and off-line data evaluation.

The hyperbolic electrodes of the trap (inner diameter of the ring: 40.0 mm, distance between endcaps: 28.3 mm) sits in a superconducting magnetic ($B = 5\,\mathrm{T}$). A typical potential difference between endcaps and ring is 10 Volts. The ring is segmented for the application of rf signals to manipulate the ions' motion as described above.

A generalized event sequence is shown in Fig. 3. Metal cluster ions are produced by laser vaporization into adiabatically expanded helium [30]. They are transferred by static ion optical elements to the Penning trap where they are captured in flight [21] and stored for subsequent experiments. If desired, several bunches of cluster ions delivered by the source may be accumulated [31] and centered in the middle of the trap before the interactions and reactions of interest. These events may be repeated and combined as already mentioned above. Finally, the product ions are axially ejected from the trap and analyzed by TOF MS.

While systems with external cluster ion sources [24, 25, 32] are very versatile, there are alternative techniques of cluster ion production for trap investigations, such as 'direct' laser ablation in the immediate vicinity of an FT-ICR cell [33]. In some cases even the synthesis of atomic clusters from their constituents can be achieved by ion-molecule reactions [34].

4 Examples of extended cluster investigations

The following two examples demonstrate the advantages of (a) extended multi-step cluster preparation and (b) long–term observations of cluster reactions.

4.1 Multi-step cluster selection, MS^n

Figure 4 gives an example of extended ensemble preparation and can also serve as a partial illustration of the experimental sequence described above. Shown are TOF spectra at various stages of a Collision Induced Dissociation (CID) experiment: After several accumulation events and irradiation with an electron beam the silver cluster ensemble has a size distribution as in Fig. 4a. One particular cluster, Ag_{17}^{2+} is selected by the removal of all others (Fig. 4b). CID yields several product ions including (due to neutral atom evaporation) Ag_{16}^{2+}. (Fig. 4c). Thus it is possible to select Ag_{16}^{2+} unequivocally (Fig. 4d), which, upon renewed CID excitation, shows fission to Ag_{13}^{+} (Fig. 4e). In contrast, a selection at $n/z = 8$ immediately after the electron bombardment would have let to a contamination with the singly charged Ag_{8}^{+}, and its fragment ions after CID [35].

An experiment which pushed the MS^n ability of ICR traps to its limit has been reported by Irion *et al.* who have studied the chemical properties of iron clusters. By repeated chemical reaction combined with several selection and CID events they showed that Fe_4^+ has a special catalytic ability with respect to the formation of benzene from ethylene [36].

4.2 Time resolved photodissociation

Time is on the trapper's side. Figure 5 shows the intensity of precursor and product signals as a function of delay period after pulsed photoexcitation of size-selected V_{12}^{+}. The decay is a delayed **reaction** after a short-term interaction. The range of investigated storage durations extends over 4 orders of magnitude up to almost 100 ms. In this example the lifetime of V_{12}^{+} (respectively the risetime of V_{11}^{+}) is about 7 ms.

In contrast, Bondybey *et al.* have recently performed a very different kind of photodissociation of stored cluster ions which also shows the advantage of long storage durations. The **interaction** period itself was extended when they exposed water clusters to the ambient blackbody radiation and observed their decay on a time scale of seconds to minutes [32]. By extended interaction of stored niobium clusters with hydrogen (i.e. a chemical 'reaction') Smalley *et al.* found the existence of different cluster isomers [37].

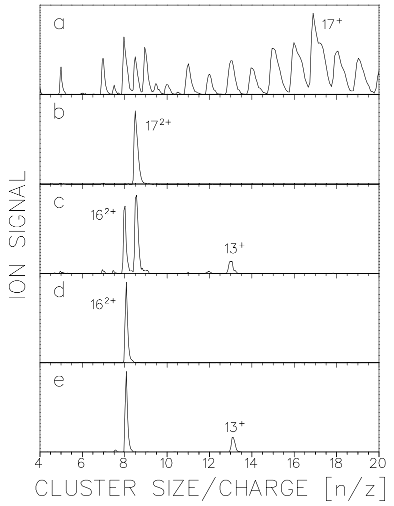

Fig. 4. Sequence of TOF spectra of silver clusters. For details see text.

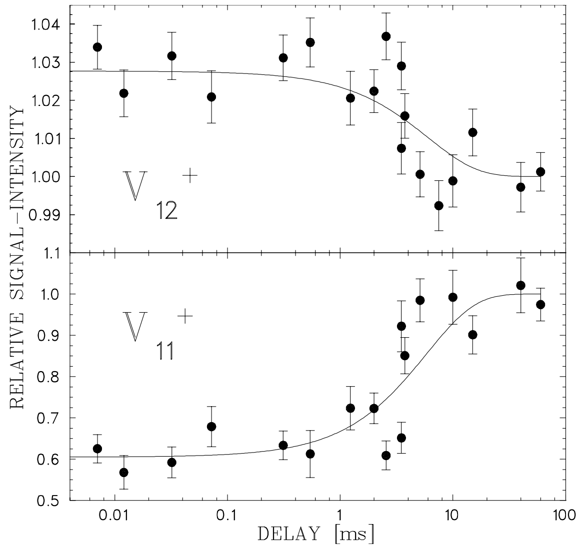

Fig. 5. Intensity of the V_{12}^+ and V_{11}^+ signals as a function of delay period between laser excitation of V_{12}^+ and mass analysis (normalized to long delay periods; $h\nu = 2.89$ eV, note that the absorption of two photons is necessary for the observation of a subsequent decay).

5 Previous, current and future studies

The following overview of investigations that have already been performed at the Mainz Cluster Trap shows its versatility and indicates what directions future experiments on trapped cluster ions may take.

When the system had just been built, the **further development of ICR techniques** made up an important part of the investigations. This included measurements regarding the transfer and accumulation of the clusters from the external ion source [31], the performance and limitations of the trap itself [12] and the introduction of the TOF detection scheme to ICR trapping [28]. The first looks into cluster properties were taken by CID [38] and chemical reactions [39] of singly charged gold clusters, Au_n^+.

After the introduction of electron impact ionization for the production of clusters **of higher charge state** [40] the CID measurements were extended to Au_n^{2+} and Au_n^{3+} [41]. Other elements were included in the investigations [42], in particular silver [35]. The method of **CID in the ICR trap** has been refined to yield not only the dissociation pathways but quantitative results with respect to the dissociation energies. The comparison of the experimental results for both different cluster sizes and charge states showed the strong influence of the number of atomic valence electrons on the stability of metal clusters [43].

The investigations with **chemical** directions have been continued with the study of the reaction of vanadium clusters, V_n^+, with molecular hydrogen [44]. In another series of measurements the CO stretching mode of methanol molecules on gold clusters was studied by IR photodetachment [45]. In combination with theoretical investigations the experimental resonance frequencies yield valuable insights into the structure of those complexes [46].

A second kind of **photodissociation** studies has already been shown above in the V_{12}^+ example: Gold and in particular silver clusters have been subjected to laser pulses in the visible and UV to observe their subsequent decay [47]. Its **photon flux dependence** allows the determination of absorption cross sections. The rate of the **delayed** dissociation carries information about the dissociation energy which can thus be determined with higher accuracy than by the CID studies.

A delayed reaction has also been observed when tungsten cluster anions were irradiated with pulsed laser light [48]: **Electron emission** leads to the loss of cluster signal as a function of time. Recently, electron emission has been observed after collisional activation [49]. These experiments will be extended to other elements where a competition between electron emission and dissociation is expected.

Clusters do have a third way to react to excess energy, **radiative cooling**. This process has been studied in the case of photoexcited vanadium clusters, V_{13}^+. The cooling rates can be inferred from the fragmentation yields after delayed two-photon two-color excitation, where the duration between the 'pump' and 'probe' laser pulses has been varied (again up into the tens of milliseconds) [50].

Furthermore, the abundance spectra after **electron bombardment** of mass-selected Ag_n^+ led to the discovery of a geometric shell at $n = 55$ in the vicinity of electric shells [51]. Finally, by use of the electron beam **gold cluster dianions** have been produced recently [52].

There are many ways (see Fig. 1) to combine the established techniques, e.g. time resolved photodissociation on multiply charged clusters, and to introduce new reaction partners, e.g. simultaneously trapped cluster cations and anions[4] or highly charged atomic ions for cluster fusion and charge transfer studies, respectively. Therefore, further exciting results and new insight in the properties of free clusters can be expected.

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[4] Pilot FT-ICR studies of simultaneously trapped fullerene cations and anions have already been performed successfully.

Many thanks go to all that have contributed to the Mainz Cluster Trap: Since H.-J. Kluge, who had intitiated the project, had left, the support of E.W. Otten and of the EXAKT group has been essential for the success of the experiments. St. Becker, M. Lindinger, G. Dietrich and J. Ziegler were the first to do their Ph.D. research with the instrument, along with numerous students that worked on their 'Diplom'. The Konstanz group of E. Recknagel/D. Kreisle has helped in the initial studies, in particular in supplying the cluster ion source, and H. Weidele came for several stays to Mainz. So did K. Dasgupta from Bombay, S. Kuznetsov from Moscow and P. Beiersdorfer from Livermore/CA. The Mainz Cluster Trap received financial support from the Deutsche Forschungsgemeinschaft, the Materialwissenschaftliches Forschungszentrum Mainz, the European Union, the Fonds der Chemischen Industrie, the Studienstiftung des deutschen Volkes (S.K.), and the Graduiertenkolleg Physik und Chemie Supramolekularer Systeme (C.W.).

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