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# Upgrades at ClusterTrap and latest results

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ABSTRACT

For the last decade the production of polyanionic metal clusters in the gas phase and the investigation of their size- and charge-state dependent properties was the main objective of the ClusterTrap experiment. An upgrading of the ion-trapping devices extends the range of anionic charge states: a recently installed Penning trap with a 12-T superconducting magnet provides an increased mass and thus cluster-size range, crucial to reach higher anionic charge states by means of the electron-bath method. Its cylindrical Penning trap is characterized and compared with respect to the previous asymptotically hyperbolical setup. In addition, polyanionic cluster production in a linear radio-frequency quadrupole (RFQ) trap has been initiated. Preliminary results for gold-cluster polyanion production in the new Penning trap, the RFQ trap, as well as the combined use of these traps are presented.



## 1. Introduction

Atomic clusters are nano-scale molecular systems whose physical properties depend strongly on their size and charge state [1–5]. About two decades ago, the "ClusterTrap" [6–10] has been set up to investigate metal clusters by taking advantage of the ion-trap technique. The experiments include multiple preparation and reaction steps with extended observation times, while the ions remain levitated in free space [11–13]. To this end, a Penning trap with a 5-T magnetic field was used for storage and experimental manipulation of cluster ions [6,7].

For the last decade the major research focus at ClusterTrap was on the production and investigation of polyanionic metal clusters [14–18]. The electron-bath technique was introduced [19] to produce those highly negative charged species by sequential attachment of electrons to cluster monoanions, with both these species simultaneously stored in the Penning trap. However, two conditions have to be fulfilled to reach a certain charge state: first, the attaching electron needs to have enough kinetic energy to overcome the repulsive Coulomb potential of the already anionic cluster. Second, the cluster has to have a minimum size, i.e. number of atoms, to bind the excess electrons and thus to form a (meta-)stable polyanion. With growing charge state, both, the height of the Coulomb potential and the minimum cluster size increase [14,20–22]. However, both effects are in conflict with each other and thus the reachable polyanion charge state for a given cluster species is limited [16,23]. In short: the electron energy is determined by the trapping voltage, but with increasing trapping voltage – needed for overcoming higher Coulomb barriers – the maximum mass-over-charge ratio where ions can be stored is reduced [24].

There are three different strategies, which may also be combined, to bypass this limitation and to reach higher negative charge states. The first option trades on the Penning-trap storage limit, which increases for higher charge states. Hence, the trapping voltage may be stepwise increased during sequential electron attachment [23]. The two other options are more obvious. On the one hand, the storage limit of the Penning trap may be extended, i.e. by means of an increased magnetic field and/or a different trap geometry. On the other hand, the clusters might be pre-charged before being exposed to the electron-bath in the Penning trap. Both strategies initiated recent modifications of the ClusterTrap experiment, which are discussed in the following: the implementation of a cylindrical 12-T Penning trap and the production of cluster polyanions in a linear radio-frequency quadrupole (RFQ) ion trap.

## 2. Polyanion production in ion traps

The production of polyanionic clusters is discussed in this section, with a short review on the clusters' Coulomb potential and on the polyanion stability, and with emphasis on the production

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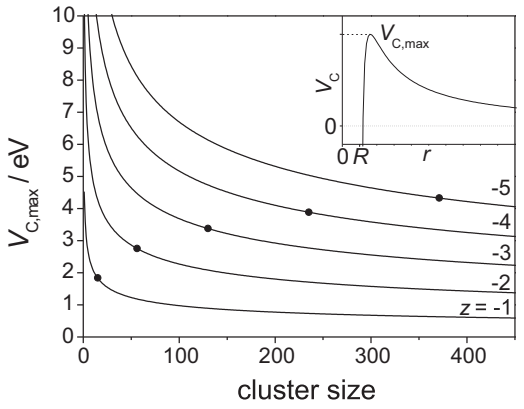


**Fig. 1.** Height of the Coulomb potential, $V_{C,max}$, as a function of gold-cluster size for charge states $z = -1, \ldots, -5$. The points indicate the calculated minimum cluster sizes 15, 56, 130, 235 and 371 for (meta-)stable clusters of charge states $z-1 = -2, \ldots, -6$, respectively. The inset illustrates the Coulomb potential $V_C$ as a function of distance $r$ from the center and the height, i.e. the maximum $V_{C,max}$.

methods in Penning traps and in RFQ traps. The stability of a polyanionic cluster depends on its ability to bind its excess electrons. From considerations of the electron affinity, the Coulomb potential and electron tunneling effects, it has been shown theoretically [25–28] and experimentally [20–22,29], that a minimum cluster size is required to produce a polyanion of a given (negative) charge state. The minimum cluster size increases with the charge state to be produced, i.e. larger and larger clusters are required to produce higher and higher (negative) charge states. More recently, the influence of internal cluster energies on the polyanion stability has been included in the discussion of the minimum cluster size [22].

In the conducting-sphere model, the electron affinity of a metal cluster with charge $Q = ze$ ($z < 0$),

$$EA(R,z) = W - \left(|z| + \frac{1}{2}\right)\frac{e^2}{4\pi\varepsilon_0 R}, \tag{1}$$

is approximated by the (bulk) work function $W$ of the respective element (for gold $W = 5.38$ eV [30]) and a size-dependent term [31]. The cluster radius $R(n) = R_a n^{1/3}$ depends on the number of atoms in the cluster, i.e. the cluster size $n$, and the atomic radius $R_a$ (for gold $R_a = 0.159$ nm [32]). Note, that for dielectric particles, a similar approach can be used, which includes the dielectric constant $\epsilon$ in the second term of Eq. (1) [33,34].

For emission of electrons from polyanionic clusters, tunneling through the Coulomb potential has to be taken into account due to the high repetition rate of tunneling tries. However, it can be neglected for the reverse process of electron attachment, because electrons with an energy too low to overcome the Coulomb potential have only a very low probability to attach during one of their rare encounters with the cluster. Thus, formation of a polyanion requires the additional electron to overcome the Coulomb potential (Fig. 1, inset) of the already $z$-charged precursor cluster with radius $R$,

$$V_C(r) = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{|z|}{r} - \frac{R^3}{2r^2(r^2-R^2)}\right), \tag{2}$$

given as a function of distance $r$ to the center of the cluster [35]. Fig. 1 shows the calculated height of the Coulomb potential, $V_{C,max}$, as a function of the cluster size, for gold clusters with precursor charge states $z = -1, \ldots, -5$. The points indicate the calculated minimum cluster sizes required to produce the next higher charge state, $z-1$, respectively [20]. In summary, Fig. 1 illustrates that for producing higher charge states, bigger clusters are required and, in addition, the attaching electrons have to overcome higher Coulomb potentials.

### 2.1. Polyanion production in a Penning trap

A Penning trap is a superposition of a homogeneous, static magnetic field $B$ and an electro-static quadrupolar field, arranged to confine charged particles of mass-to-charge ratio $m/Q$ to a defined volume in space. The electrostatic field is produced by a trapping voltage $U_0$ applied between a set of electrodes [11]. The respective electrostatic quadrupolar potential

$$U(r,z) = \frac{U_0}{2d_0^2}\left(z^2 - \frac{r^2}{2}\right) \tag{3}$$

is radially symmetric to the $z$-axis, i.e. to the direction of the magnetic field, and it is characterized by the parameter[1] [11]

$$d_0^2 = \frac{1}{2}\left(z_0^2 + \frac{r_0^2}{2}\right) \tag{4}$$

where $r^2 - 2z^2 = -2z_0^2$ and $r^2 - 2z^2 = r_0^2$ describe equipotential surfaces being separated by the potential difference $U_0$. For the special case $r_0^2 = 2z_0^2$, the respective potentials of these equipotential surfaces are $\pm U_0/2$ with respect to the potential in the center of the trap. Therefore, in the case of hyperbolically shaped traps, $r_0$ and $z_0$ are typically referred to as minimum distances of the respective electrodes to the trap center. The characteristic parameter $d_0$ relates to the angular frequency

$$\omega_z = \sqrt{\frac{QU_0}{md_0^2}} \tag{5}$$

of the axial ion motion in the trap, i.e. along the magnetic field lines. Further details of Penning trap theory are given in literature [11–13]. The present focus is on the storage limit of the Penning trap, considering fixed values for $B$ and $d_0$ without loss of generality. Then, for a given trapping voltage $U_0$ ion confinement is limited to a maximum value of the ions $m/Q$-ratio [24],

$$\left(\frac{m}{Q}\right)_{max} = \frac{d_0^2 B^2}{2U_0}, \tag{6}$$

or, for an ion species with given $m/Q$-ratio, the trapping voltage is limited to a maximum,

$$U_{0,max} = \frac{d_0^2 B^2 Q}{2m}. \tag{7}$$

Fig. 2 shows the maximum $m/Q$-ratio as a function of the trapping voltage $U_0$ for three sets of ($B$, $d_0$)-values. The selection includes both, the previous ($B = 5$ T, $d_0 = 14.14$ mm; dash-dotted line) and the new Penning trap ($B = 12$ T, $\tilde{d} = 26.65$ mm; solid line)[2] at the ClusterTrap setup, illustrating the gain in the mass limit by a factor of about 20.

Though the Penning trap has an upper $m/Q$-limit (Eq. (6)), there is no lower one, which would restrict the storage of very light-weighted particles. While trapping of electrons ($m_e/e \approx 5 \times 10^{-4}$ u/e) sometimes comes as an unwanted effect [36], it turns out to be most favorable for production of cluster polyanions. During application of the electron-bath method [19], cluster monoanions are stored simultaneously with electrons in the Penning trap for extended periods of time, causing stepwise electron attachment. However, the electron-bath method is limited to a maximum charge state due to two opposing effects [21,23]. On the

[1] Note, that in the description of hyperbolic RFQ-traps the definition of $d_0$ often differs from Eq. (4) by a factor of 1/2, i.e. $d_0^2 = z_0^2 + r_0^2/2$ [13].
[2] The characteristic parameter has to be corrected for the cylindrical trap, as discussed in Section 3.1.