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Charge-changing reactions and their influence on the ion motion in a Penning trap

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Abstract. Charge-changing reactions can lead to a significant change of the ion motion which may result in the loss of the ions from the trap. For the present experiments singly charged gold clusters from an external laser vaporization source have been transferred into a Penning trap and transformed into dianions by use of an electron bath of simultaneously stored electrons. The dianions have been investigated by collisional activation and laser excitation where electron emission has been observed as a cooling mechanism. Electron emission doubles the value of the cyclotron radius and in addition, the ions acquire a finite magnetron radius. This leads to an extension of the radial distance of the ion motion from the trap’s axis by a factor of about three.

INTRODUCTION

The Penning trap is a versatile tool for the investigation of charged particles [1], including atomic clusters. Recently, it has been shown that the trap can be employed for the production of multiply charged anionic metal clusters [2–4]. The properties of these new particles are currently examined by use of laser excitation and collisional activation. As will be shown, especially in the latter case care has to be taken when charge-changing reactions are involved. These can lead to significant changes of the motion of the trapped ions and may cause their loss from the trap. In the following the influence of electron emission from doubly charged gold cluster anions in case of collisional activation is described in more detail.

ION MOTION IN THE PENNING TRAP

We start with a brief review of the basics of a Penning Trap [1]. For axial ion confinement in a harmonic potential, a potential $U_0$ is applied between a ring electrode and two endcap electrodes, all of which have a hyperbolic shape. A particle of mass $m$ and charge $q$ is therefore trapped and performs an axial oscillation (trapping motion) at the frequency

$$\omega_z = \sqrt{qU_0 \over md_0^2}$$

where the trap dimension $d_0$ is defined as in ref. [1]. Radial confinement is achieved by use of a homogeneous magnetic field $\vec{B}$ where the field lines are parallel to the
electrodes' symmetry axis. In the absence of the electric potential the ion performs a cyclotron motion at the frequency

\[ \omega_c = \frac{qB}{m}. \]  

But the crossed electric and magnetic fields lead to a splitting of the radial motion into two modes (see Fig. 1 (left)): the high frequency cyclotron motion at the reduced cyclotron frequency

\[ \omega_+ = \frac{\omega_c}{2} + \sqrt{\left(\frac{\omega_c}{2}\right)^2 - \frac{\omega_0^2}{2}} \]  

and the low frequency magnetron motion (drift motion) around the trap axis at the frequency

\[ \omega_- = \frac{\omega_c}{2} - \sqrt{\left(\frac{\omega_c}{2}\right)^2 - \frac{\omega_0^2}{2}}. \]  

The amplitudes and phases of the three harmonic motional modes (axial, cyclotron and magnetron) are independent of each other and are only determined by the "initial conditions". In Fig. 1 (right) four different trajectories are shown in a projection on the radial plane.

**METAL CLUSTER DIANIONS: EXPERIMENTAL RESULTS**

A detailed description of the experimental setup has been given elsewhere [5–7]. Singly charged metal cluster anions of various sizes are produced in an Smalley-type laser vaporization source [8, 9] and transferred into a Penning trap. After in-flight-capture the cluster size of interest is selected by radial ejection of all unwanted ions from the trap. An external electron beam is applied while argon gas is pulsed into the trap volume. Thus,
by ionization low energy electrons are produced which stay trapped. The simultaneously stored cluster anions are therefore subjected to an electron bath and electrons may attach producing cluster dianions [2, 3]. Note, that the trap allows the simultaneous storage of electrons and negatively charged gold clusters (e.g. Au$_{28}^{1-}$ with $n=28$ atoms), while the mass-over-charge ratio of these particles differs by seven orders of magnitude. In a second selection step an ion ensemble of specific charge state can be prepared for further experiments. Finally, the trap is emptied by axial ejection into a drift section and

FIGURE 2. TOF spectra of the experimental sequence of dianion production: (a) selection of singly charged cluster anions, (b) application of electron bath, (c) selection of dianions.

FIGURE 3. Relative abundance of gold cluster dianions Au$_{22}^{2-}$ (top, full circles) and Au$_{28}^{2-}$ (bottom, full circles) as a function of collisional activation. Note, that for the singly charged cluster anions the scale is decreased by one order of magnitude.
FIGURE 4. Relative abundance of cluster anions \( \text{Au}_{28}^{1-} \) after collision induced dissociation of \( \text{Au}_{28}^{1-} \) (top) and \( \text{Au}_{14}^{1-} \) (bottom). For the latter open circles represent \( n = 14 \), open squares \( n = 13 \), open triangles \( n < 13 \) and full circles the sum of all ion signals.

Reactions during the storage period are analyzed by time-of-flight mass spectrometry. In Fig. 2 several spectra of the production sequence are shown for the case of \( \text{Au}_{28}^{2-} \): (a) capturing and size selection, (b) after reaction with the electron bath and (c) selection of dianions.

In order to study the properties of the size and charge-state selected gold-cluster dianions, collisional activation is applied as previously investigated for singly charged species [10]. The ring electrode of the Penning trap is segmented to perform a dipolar rf-excitation at the reduced cyclotron frequency \( \omega_{\pm} \). This leads to an increase of the radius \( r_{\pm} \) of the cyclotron motion (proportional to the amplitude of the rf-excitation) and therefore to an increase of the kinetic energy of the cluster dianions. When argon gas is pulsed into the trap volume the dianions collide with the gas atoms and part of

**FIGURE 5.** TOF spectra before (top) and after (bottom) photoexcitation of selected gold cluster dianions \( \text{Au}_{28}^{2-} \).
the kinetic energy is transformed into internal excitation energy. In Fig. 3 the relative abundance of \( \text{Au}_{28}^{2-} \) (top) and \( \text{Au}_{28}^{2-} \) (bottom) is plotted as a function of the excitation of the cyclotron radius. The dianion signal (full circles) disappears, but almost no product signal is observed, in particular with respect to singly charged cluster anions (open circles). For comparison Fig. 4 shows the analog result for CID measurements of \( \text{Au}_{28}^{1-} \) and \( \text{Au}_{14}^{1-} \), i.e. of singly charged gold-cluster anions of the same mass and cyclotron frequency as \( \text{Au}_{28}^{2-} \), respectively. Compared to these measurements on singly charged cluster anions the \( \text{Au}_{28}^{2-} \) signal is disappearing at a much smaller cyclotron radius.

In case of photoexcitation, the cluster dianions remain in the center of the trap volume when they are excited with a single pulse of a frequency tripled Nd:YAG laser (\( \lambda = 355 \) nm). In Fig. 5 the spectra before (top) and after the excitation (bottom) of \( \text{Au}_{28}^{2-} \) are shown. Only the singly charged species \( \text{Au}_{28}^{1-} \) appear in the spectrum as a product signal, which is interpreted as the result of electron emission.

EXPLANATION: THE EFFECT OF CHARGE-CHANGING REACTIONS

In order to explain these observations the influence of the electron loss on the ion motion is studied in more detail. Consider the simple initial conditions of a finite cyclotron radius \( \rho_+ \) and no magnetron motion (\( \rho_- = 0 \)) for an ion of mass \( m \) and charge state \( z = -2 \). The loss of an electron changes the charge state from \( z = -2 \) to \( z' = -1 \) and therefore cuts the cyclotron frequency by a factor of almost two (\( \omega_+ \approx \omega_+/2 \)). But there is no significant change of the velocity, \( v' \approx v \), thus

\[
v' \approx \omega'_{+} \rho_{+} \approx \omega_{+} \rho_{+} \approx v.
\]

FIGURE 6. Radial ion motion of a dianion which loses an electron for the initial conditions of a finite cyclotron radius \( \rho_+ \) and no magnetron motion (\( \rho_- = 0 \)).
Therefore, the loss of charge leads to an instantaneous increase of the cyclotron radius $p_+$ by a factor of about two:

$$\rho_+^\prime \approx 2\rho_+.$$  (6)

At the same time the center of the ion motion is shifted and the magnetron radius is increased from $\rho_- = 0$ to $\rho_+^\prime \approx \rho_+$. Thus, the maximum extension of the radial ion motion $\rho_+^\prime + \rho_-^\prime$ is about three times as large as before the loss of the electron (see Fig. 6). However, the Penning trap has finite radial dimensions. Thus, after the electron loss the ion will collide with the ring electrode, if its initial cyclotron radius exceeds 1/6 of the free diameter of the ring electrode.

In conclusion, charge-changing reactions may lead to drastic changes of the ions' motion in a Penning trap. In particular, the decrease of the charge state can result in severe ion loss.

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