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A PENNING TRAP FOR STUDYING CLUSTER IONS

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Abstract: We propose to use a Penning trap for spectroscopy of stored cluster ions. A similar device has been built by us for the purpose of mass measurements of short-lived nuclei produced at the on-line isotope separator ISOLDE/CERN. A resolving power of 500,000 in a mass measurement of ^{39}K and an accuracy of 2×10^{-7} for the $^{85}\text{Rb}/^{39}\text{K}$ mass ratio were obtained. An efficiency for in-flight capture as high as 70% was achieved. A method of very high sensitivity is realized since typically only 10 to 100 ions are stored in the trap. We intend to perform laser spectroscopy on trapped Na cluster as a first application of the trap technique.

1. INTRODUCTION

Although enormous progress has been made in cluster spectroscopy during the past years, only very little is known about, for example, electronic structures of clusters, life times, and reaction, catalysis, or electron detachment processes. The reasons can be found in essentially two general drawbacks of all techniques applied so far to the study of clusters:

(i), the limited time of observation because atomic or ionic beams are used,

(ii), the difficulty of preparing a sample of one specific cluster size with sufficient purity and abundance.

Both problems can be solved by confining and accumulating the cluster ions of the wanted size in an ion trap. The device best suited for this purpose is the Penning trap where a combination of static magnetic and electric fields is used to establish a three-dimensional trapping potential: In such a trap [1], [2] the cluster ions would be almost at rest in space, confined in a small volume, essentially free of any undesired perturbation, and at hand for almost infinite times limited only by the life time of the cluster itself. The high resolving power of mass measurements in a Penning trap would allow a precise identification of the cluster size and even enable studies of isotope effects if they exist at all.

In the past many experiments made use of the ion trap technique for the investigation of charged particles and led to a variety of high-precision experiments [3]. These experiments include laser spectroscopy on single ions [4], [5], accurate mass measurements [6], [7], ultra-high resolution microwave spectroscopy [8], and determination of the g factors for the electron and positron [9], which represents the most accurate fundamental constant known today.

All charged particles investigated so far in an ion trap were created inside the potential well produced by the quadrupole field. However in case of cluster ions it is desirable to produce these species by well established techniques [10] outside the trap, eventually to separate them in mass and to guide them with high efficiency into a trap.

Recently we reported on the first in-flight capture of ions in a Penning trap starting from a continuous ion beam [11]. Simultaneously and independently Alford et al. [12] were successful in capturing bunches of cluster ions in a similar device which differs from our set up mainly with respect to the geometry and the detection scheme of the cyclotron resonance.

In the following, our method and our apparatus will be described which was developed for precise mass measurements of short-lived isotopes. Emphasis will be put on the discussion of the geometry of the Penning trap, the harmonic motion of the charged particles in the trap, and the detection scheme which differ from those described in [12]. The performance of the existing device and finally its potential for a future application for cluster spectroscopy will be discussed.

2. PRINCIPLE OF A PENNING TRAP

Fig. 1 shows the essential layout of a Penning trap. In the homogenous magnetic field B directed along the z axis particles with charge e and mass m perform a cyclotron motion with a frequency given by

$$\omega_c = (e/m) B . \quad (1)$$

In order to obtain a restoring force along the z axis in addition to the confinement by the magnetic field in x - y direction, a positive potential for positively charged ions is applied to the upper and lower electrodes (so-called endcaps, see Fig. 1) relative to the ring electrode. Due to the special (hyperbolical) shape of the electrodes the motion of a stored ion in the z direction is decoupled from those in the x - y directions and furthermore all motions are harmonic. They can be separated into an oscillation ω_z along the z direction and the modified cyclotron frequencies ω_+ and ω_- . These frequencies deviate from the pure cyclotron frequency ω_c due to the presence of the electrostatic field. The harmonic oscillations are described by the frequencies

$$\omega_z = \sqrt{2eU/mr_0^2} \quad (2)$$

$$\omega_+ = \omega_c/2 + \sqrt{(\omega_c^2/4 - \omega_z^2/2)} \quad (3)$$

$$\omega_- = \omega_c/2 - \sqrt{(\omega_c^2/4 - \omega_z^2/2)} . \quad (4)$$

The voltage U and the radius r_0 are explained in Fig. 1. In case of an ion with mass $m = 40$ amu, $B = 5.87$ T, $U = 8$ V and $r_0 = 0.8$ cm the frequencies are $\nu_c = 2253$ kHz, $\nu_z = 124$ kHz, $\nu_+ = 2250$ kHz, and the magne-

tron frequency $\nu_- = 3.4$ kHz almost independent of the mass of the stored particle.

Note that ω_z as well as the modified cyclotron frequencies depend on the voltage U applied to the electrodes. These frequencies correspond to one-quantum transitions in the harmonic oscillators. However, the sum frequency $\omega_+ + \omega_-$ equals to ω_c . This frequency depends only on B (see Eq.(1)) and represents a two-quantum transition. Although the ω_c resonance has a small strength because it is a two-quantum transition, it has the advantage of being independent of the trapping voltage. Even more important, this resonance is in contrast to ω_+ insensitive to space charge effects caused by a larger number of stored ions and is not very much influenced by imperfections of the hyperbolical shape of the electrodes caused, for example, by the necessary holes for capture and ejection of the ions.

3. DETECTION OF THE CYCLOTRON RESONANCE BY TIME OF FLIGHT

In resonance the trapped ions gain energy out of the applied radio frequency (RF) field. This is detected by a time-of-flight method [6]. The charged particles are ejected out of the trap by applying an electrical pulse to the ring electrode. For a short time the potential between the endcaps and the ring electrode is lowered so that the ions with highest energy can just escape the trap. These ions drift to a channel plate detector and their time of flight is determined. This procedure is repeated by continuously lowering the trapping potential as shown in Fig. 2 until the trap is empty. The mean time of flight as a function of the RF frequency shows a resonance which gives the mass of the stored ions (Fig. 3).

The basic principle of this detection technique is easily understood. In resonance the cyclotron orbit becomes larger. As a consequence the orbital magnetic moment μ_L increases, leading to a higher energy of the charged particle in the magnetic field. If the ions are ejected out of the trap into a region of lower magnetic field, the ions experience a force $\mu_L \delta B / \delta z$ in the direction of magnetic field gradient. Conservation of energy demands that the radial energy $\mu_L B$ is transformed into longitudinal kinetic energy. This is just the reverse of the magnetic-bottle effect. Hence in resonance the ions reach the detector faster than out of resonance.

Fig. 4 shows the time-of-flight effect for the case of a mixture of N and N_2 ions. If the frequency $\nu_c(N_2)$ is applied, the mean time of flight is shifted to smaller values. This is seen in the bottom part of Fig. 4 which shows the difference between the time-of-flight pattern in and off resonance.

The change in the mean time of flight has to be kept small if high resolution of the mass determination is required. Hence the change in time of flight seen in Fig. 4 amounts only to a few percent. If the strength of the RF field is increased, the ν_c resonance is power broadened. Finally at very high RF power, the ions gain such a high orbital energy that they can no longer escape through the hole of the ion trap. In this case, they strike the electrodes and are lost (Fig. 5). This effect can be used for purification of the sample, i.e. to get rid of unwanted contaminating species in the trap.

4. EXPERIMENTAL SETUP

The experimental setup for the mass measurements is shown in Fig. 6. The apparatus consists of an alkali ion source, a Penning trap (trap 1) placed in the pole gap of an electro magnet, a transfer line with a number of electrostatic lenses and deflectors, a Penning trap (trap 2) placed in the stable and homogeneous field of a superconducting magnet, a drift tube and finally a channel plate detector.

The first trap is essentially a bunching device to collect the continuous beam of the ion source. The second trap is used for high-precision measurements of the cyclotron frequency. Hence ultra-high vacuum, excellent homogeneity of the magnetic field and perfect geometry of the second trap are essential. Since the operating conditions of a bunching trap are incompatible with those of a precision trap, the layout of Fig. 6 was chosen with two completely separated traps connected only by a transfer tube. This configuration allows efficient differential pumping between traps 1 and 2 and the installation of electro-optical devices for steering the ion beam.

BUNCHING TRAP: Alkali ions delivered by the ion source are implanted into a tungsten foil mounted in one endcap of the Penning trap, then surface ionized by heating the foil, trapped [13], [14], and finally ejected by a sudden change of the trapping potential. In case of the study of cluster ions this trap can be abandoned because it is possible to create cluster ions directly in a bunched mode.

TRANSFER TUBE: After leaving the trap the ion bunch is accelerated to 1 keV by some electrodes. A system of electrostatic lenses guides the bunch into the fringe field of the superconducting magnet in such a way that the radial energy is not increased. Extensive electro-optical calculations have

been performed to find an optimum design [15]. This is most important for mass measurements, which require a very small energy spread of the trapped ions. The transmission of the transfer tube has been measured to be 80 % (including the transmission through the holes in the endcaps of trap 2). At the entrance of trap 2 the length of the bunch is shorter than 30 μ s.

PRECISION TRAP: Here the bunched ion beam is captured in flight by retarding it to a few eV just before entering the trap. The potential of the lower endcap of trap 2 is switched to the potential of the ring electrode just at the moment the ion bunch arrives. When the ions pass the center of trap 2 the potential of the endcap is raised again and the ions can no longer escape. More details of the apparatus built for mass measurements are given in Ref. [11].

5. PERFORMANCE

TRAPPING EFFICIENCY: It has been determined that up to 70% of an ion bunch ejected out of trap 1 can be retarded and captured in flight in trap 2. More details can be found in Ref. [11].

RESOLUTION: A resolving power of 500,000 has been observed in a mass measurement of ^{39}K . Here a line width of 4.4 Hz was obtained at a resonance frequency of 2.3 MHz (Fig. 3). Studies to increase further the resolving power are under way.

ACCURACY: The ratio of the cyclotron frequencies of, for example, the Rb/K pair coincide with the tabulated mass ratio within 2×10^{-7} . This devia-

tion corresponds approximately to the statistical uncertainty of the centroid of the resonance (Fig. 3) which is about 10% of the line width. Therefore the ratios of unknown to previously-known masses can be determined with an accuracy of the order of 2×10^{-7} .

STORAGE TIME: The storage time of our Penning trap has not yet been investigated systematically. We can give only a lower limit: Up to a delay of 1.5 s in respect to the capture of the ions in trap 2 no decrease in the number of stored ion was observed. It can be expected that the life time of the charged particles is much longer because the ions already survived a large number of oscillations (see Eqs. (3) - (5)) during this time of storage. The storage time depends strongly on the vacuum in the apparatus which was $< 10^{-9}$ mbar in the experiments reported here.

SENSITIVITY: Typically 10 to 100 ions were stored in trap 2 at a time. Since the detection scheme used by us is destructive, the trap has to be refilled after each cycle. This involves filling the trap, inducing the RF, ejecting the ions, and measuring the time of flight. The cycle time is about 0.5 s. For the mass measurement of ^{39}K (Fig. 3) 100 cycles per frequency value were performed, corresponding to a total time of 20 min needed for the measurement of the ^{39}K mass.

6. DISCUSSION

It is very attractive to apply the Penning trap technique to the study of clusters. In comparison to investigations on atomic or ionic beams one gains several orders of magnitude in observation time by using stored cluster ions. The ultra-high mass resolution achievable will even permit investigations of clusters of very large size. These advantages, together with the possibility of preparing pure samples of one cluster size only, lead us to expect that new fields in cluster spectroscopy will open up. All those techniques developed for the study of atomic ions can, in principle, be applied also to a study of cluster ions. These methods include cooling of the ions in the trap, detection of their motion, investigations using single ions, ultra-high resolution spectroscopy, and spectroscopy in the microwave as well as in the optical region. A quite comprehensive overview on the status of trapping atomic ions can be found in the contributions to the 1984 International Conference on Atomic Physics [16], [17], [18].

We intend to combine a Penning trap with a cold metal cluster beam produced in a supersonic expansion. Bunched ions can be obtained by pulsed photoionization. The time-of-flight technique can be used to pre-purify the cluster bunch in respect to mass before the clusters are captured in the Penning trap. It should also be possible to accumulate a larger number in the trap than obtained by a single injection. For this purpose the potential of the ring electrode can be continuously decreased while the lower endcap is pulsed with constant amplitude in order to allow the pass of additional bunches. In this way, stacks of cluster bunches can be accumulated in the trap.

As we discussed briefly in the Introduction, a large number of experiments can be performed with stored clusters. The most challenging might be to investigate Na clusters by laser spectroscopy and to search for optical resonances. Recently, Knight et al. [19] found peaks in the mass spectra of Na clusters at cluster sizes of $n = 8, 20, 40, 58,$ and 92 . These "magic" numbers can be explained in a one-electron shell model in which independent delocalized atomic 3s electrons are bound in a spherically symmetric potential well [19]. The calculation yields discrete electronic energy levels and a shell structure which reproduces the peaks observed in the mass spectra. The authors conclude that the good correspondence between the experimental results and the model calculations suggests that there are no perturbations large enough to distort the main features of the level structure. Hence, discrete resonances should also be observable by laser spectroscopy stored Na ions. Such an experiment which presents a stringent test of the model seems only feasible using the trapping technique.

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Figure Captions

- Fig. 1 Scheme of a Penning trap. The shapes of the electrodes are hyperbolical with rotational symmetry around the z axis which is also the direction of the magnetic field. The distance of the endcaps $2z_0$ is related to the minimum radius of ring electrode by $r_0^2 = 2z_0^2$.
- Fig. 2 Timing sequence for trapping charged particles, inducing the radio frequency, and for ejection of the ions. This sequence was used for mass measurements in a Penning trap using the time-of-flight technique.
- Fig. 3 Cyclotron resonance of potassium ions as obtained by the mean time of flight as a function of the frequency of the applied RF field. The resolution observed is 5×10^5 .
- Fig. 4 Time-of-flight spectrum of N and N_2 ions. At $t = 0$ the ions are ejected out of the trap and are then detected by the channel-plate detector. Top: Spectrum obtained with the radio frequency off resonance. Middle: Spectrum obtained in resonance at $\nu = \nu_c$. Bottom: Difference spectrum obtained by subtracting the spectra in resonance and off resonance.

Fig. 5 Time-of-flight spectrum as in Fig. 4 but for He ions. In this case, the radio frequency power is much higher. Hence a large fraction of the ions do not reach the detector when the resonance frequency ν_c is induced.

Fig. 6 Experimental set up for direct mass determination of externally created ions.

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Fig. 2

cyclotron frequency

Fig. 4

Fig. 6