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Nuclear Instruments and Methods in Physics Research A 487 (2002) 618–651

NUCLEAR INSTRUMENTS & METHODS IN PHYSICS RESEARCH Section A

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SMILETRAP—A Penning trap facility for precision mass measurements using highly charged ions

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Received 7 November 2001; accepted 29 November 2001

Abstract

The precision of mass measurements in a Penning trap increases linearly with the charge of the ion. Therefore we have attached a Penning trap, named SMILETRAP, to the electron beam ion source CRYSIS at MSL. CRYSIS is via an isotope separator connected to an ion source that can deliver singly charged ions of practically any element. In CRYSIS charge state breeding occurs by intense electron bombardment. We have shown that it is possible to produce, catch and measure the cyclotron frequencies of ions in the charge region $1+$ to $52+$. The relevant observable in mass measurements using a Penning trap is the ratio of the cyclotron frequencies of the ion of interest and ion used as a mass reference. High precision requires that the two frequencies are measured after one another in the shortest possible time. For reasons of convenience the precision trap operates at room temperature. So far it has been believed that warm traps working at 4 K are required for high mass precision with exactly one ion in the trap at a time. In this paper we demonstrate that mass precision of a few parts in 10^{10} also can be obtained in a warm trap at a pressure of about 5×10^{-12} mbar by stabilizing the pressure in the He-dewar, the trap temperature and the frequency synthesizer. In order to reduce the influence of changes of the magnetic field to a level below 10^{-10}, the scanning of the frequencies close to the resonances of both the ion of interest and the reference ion is done in a total time <2 min. Trapping of ions is a statistical procedure, allowing more than one ion to be trapped in each measurement cycle. However, after completing the measurements it is possible to reject all information except for events based on 1 and 2 trapped ions. The procedures of producing, transporting, catching, exciting and measuring the cyclotron resonance frequencies of highly charged ions and the mass reference ions with the time-of-flight method are described. In routine measurements with 1 s excitation time lasting for about 24 h, atomic masses can be determined at an uncertainty of about 1 pbb. In the case of q/A doublet measurements a mass uncertainty close to 0.1 ppb can be obtained as illustrated by a mass measurement of $^{4}He^{2+}$. The mass measurements so far performed are either related to fundamental constants or to masses the accuracy of which is needed for some current questions in physics. © 2001 Published by Elsevier Science B.V.

PACS: 32.10.Bi; 07.05.Dz; 07.05.Hd

Keywords: Mass measurements; Penning trap; Highly charged ions; Fundamental constants

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0168-9002/01/$ - see front matter © 2001 Published by Elsevier Science B.V.
PII: S0168-9002(01)02178-7

1. The development of mass spectrometry

From the very first mass measurements on an atomic scale by J. J. Thomson [1] in the beginning of the 20th century the precision has increased dramatically. In Thomson's cathode ray tube, mass spectra appeared as parabolas on a photographic film due to the large energy spread of the ions created in a high-voltage discharge tube used as ion source. With the vacuum technology available at that time it was impossible to avoid appreciable amounts of hydrogen in the ion source. Thus, in the mass spectra not only protons and H_2^+ ions but also H_3^+ ions appeared due to frequent collisions of H_2^+ ions. As a matter of fact H_3^+, a molecular ion sometimes used in our investigations, was discovered in such spectra.

Measurements on the mass of hydrogen reflect in a illustrative way the development of precision mass spectrometry. By combining electric and magnetic fields, Aston could reduce the influence of the energy spread of the ions. In 1927 he reached a mass uncertainty of about 10^{-4} in various determinations described in Ref. [2]. In this paper he also reported a value of the mass of atomic hydrogen of 1.007 78 u, a value related to 1/16 of the mass of natural oxygen which at that time was used as the mass unit. A number of different magnetic mass spectrometers combined with electrostatic devices were later developed by Mattauch, Nier, Dempster, Duckworth and their collaborators and many other physicists [3] with a rapidly increasing precision. Using these classical mass spectrometers, uncertainties as low as 10^{-7} were reported at the end of the 60s. In particular, the Manitoba group [4] made a considerable development work. At the end of the 80s a mass uncertainty of a few times 10^{-8} was often reported. This group, in particular, developed a method, in which differences of masses being mass doublets, could be measured very accurately [5].

In 1960 L. G. Smith designed his *mass synchrometer*, which was the first mass spectrometer applying frequency measurements. In a paper [6] published in 1971 he gave a review of the development of the accuracy in measurements of the mass of atomic hydrogen performed by various groups. During the period 1957–1971 the mass uncertainty of atomic hydrogen was improved from 1.007 824 663(2 0 0) u to 1.007 825 029 (5) u, the latter value reported by Smith himself (now 1 u= 1/12 of the mass ^{12}C). In 1971 Smiths measurement of the hydrogen mass represented an impressive accuracy, though he seems to have underestimated the systematic uncertainties by a factor 3 [7]. A modified version of this spectrometer (MISTRAL) has recently been installed in the ISOLDE facility at CERN which is suitable for measuring atomic masses of radioactive isotopes with short half-lives. With this spectrometer measurements of the masses of sodium and other light elements with half-lives in the region of 30 ms [8] have recently been reported at an uncertainty of about 10^{-6}.

Smiths accuracy level could only be considerably improved by introducing entirely new technology. This occurred when Penning traps entered the field of precision mass spectrometry at the end of the 80s. In the pioneering work of the Seattle group [9] the electron and proton masses could be compared at an uncertainty of about 10^{-8}.

Measurements of the atomic hydrogen mass using Penning traps have been made by the Seattle group [10] and by the MIT group [11] reporting the values 1.007 825 032 57(99) u and 1.007 825 031 6(5) u, respectively. The MIT-value corresponding to a proton mass 1.007 276 466 3(5) u was thus an improvement by another order of magnitude as compared to the value obtained by Smith. The Seattle group [12] has improved their measurement on the proton mass reporting in 1998 a value of 1.007 276 466 89(13) u by implementing a new and much more stable magnet.

Mass measurements in a Penning trap can be performed in a non-destructive way by measuring the three respective characteristic frequencies (Eqs. (8)–(10)) using the same single ion during the entire measurement. The cyclotron frequency can also be directly determined by using many ions in a destructive way as we have done. In this case the final result is based on the use of about 20 000 different ions of the same species. The final mass value is thus based on using thousands of ions one at the time in the trap. In each case a well defined ion is used for a certain time t. The MIT and Seattle groups used a non-destructive determination of the

cyclotron frequency of one and the same ion for relatively long times. In the Seattle measurements t for H^+ ($q/A = 1$) respectively C^{6+} ($q/A = 1/2$) ions could be as large as 1–2 days. In the MIT experiments using a variety of light singly charged organic molecules t could be lowered to about 10–15 min, which considerably reduces the correction for changes in the magnetic field. In our measurements t is only about 45 s. The Seattle group [12] could recently reduce the problem of long-term magnetic field variation by a newly designed very stable magnet. With this new device the group has been able to measure the ^{16}O mass at an uncertainty close to 0.01 ppb.

In a sequence of measurements performed at LEAR, CERN, aiming at a test of the CPT theorem for a system containing three strongly interacting quarks, G. Gabrielse et al. [13] have measured the ratio of the proton and antiproton masses reaching in 1997 an accuracy close to 10^{-9}. In the last sequence of measurements the proton was replaced by H^- that brought the uncertainty in the mass ratio of the proton and antiproton to a value as low as 9×10^{-11}, achieved just before the shut down of LEAR [14]. The H^- ion and the antiproton were used in a non-destructive way. The time between measurements of the cyclotron frequencies of the two species was a few hours.

The Seattle and the MIT groups produced the relevant ions inside their traps. In the CERN experiments the antiprotons were delivered by LEAR and thus produced outside the trap and the proton and H^- produced in the trap. In these three experiments the ions were cooled before being excited resulting in an impressive resolving power. As will be shown in the next section the mass increases linearly with the charge of the ion. The highest charge states used by the MIT- and the Seattle groups are 3+ (^{133}Cs; [15]) and 8+ (^{16}O; [16]) respectively while we so far have trapped ions with q up to 52+.

In 1987 the Mainz group installed a Penning trap facility (ISOLTRAP) at ISOLDE, CERN, for the determination of the atomic masses of radioactive singly charged ions [17]. This was the first Penning trap experiment using *externally* produced singly charged ions (in a destructive way). Since the start of this project in 1987, masses of more than 100 radioactive isotopes have been determined at an uncertainty of about 10^{-7}. From our experiences it can be concluded that it should be possible to improve the accuracy in these measurements by one order of magnitude.

During 1990–1992 the upper part of present trap system (Fig. 1) now located at the Manne Siegbahn Laboratory was assembled at the Physics Department of the Johannes Gutenberg University in Mainz [18]. It was connected to a laser ion source providing singly charged atomic ions and light carbon and silicon cluster ions. The trap performance for *singly* charged ions is illustrated by a mass measurement of ^{28}Si at an uncertainty of 10 ppb [19], which at that time was an improvement. This measurement is part of an international effort of finding a new definition (a silicon single crystal) for the kilogram based entirely on atomic quantities. Since then the accuracy of the ^{28}Si mass has been further improved [11,20] as discussed in Section 8.4.

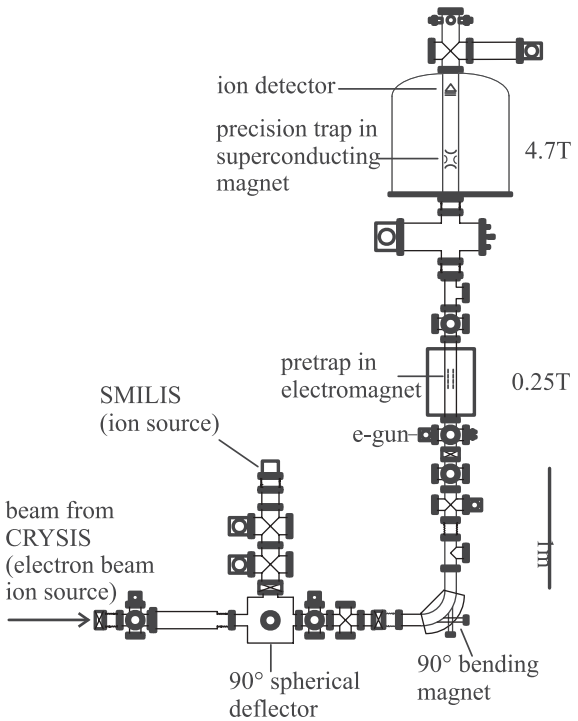

Fig. 1. The SMILETRAP mass spectrometer at the Manne Siegbahn Laboratory in Stockholm.

In the beginning of 1993 the trap system was attached [21] to the electron beam ion source CRYSIS at the Manne Siegbahn Laboratory. In addition, an external ion source (SMILIS) for singly charged ions was connected to SMILETRAP (Fig. 1).

This paper describes the merits and the limitations of a method to reach high precision in mass determinations by using highly charged ions (HCI) in a warm Penning trap that is directly connected to an electron beam ion source (EBIS; in Stockholm named CRYSIS). It will be shown that a mass uncertainty close to 0.1 ppb can be obtained in measurements where q/A is the same for the two ions whose cyclotron frequencies are to be compared in spite of the fact that a room temperature bore of the superconducting coil is used.

2. Merits of highly charged ions

The cyclotron frequency ν of a single ion with rest mass m and charge qe moving perpendicular to a magnetic field B is given by

$$\nu_c = qe\,B/(2\pi\,m). \tag{1}$$

Though this situation never can be achieved in laboratory experiments this simple formula can be used to discuss the merits of HCI. Let us assume that it is possible to measure this cyclotron frequency somehow (see Section 5.3). In any frequency determination, involving a resonance phenomena, the figure of merit can be defined as $m/\Delta m = \nu/\Delta\nu$, i.e. the mass resolving power. There are three obvious ways of increasing the resolving power and thereby the precision.

Firstly it is evident from Eq. (1) that the highest possible magnetic field should be used since the cyclotron frequency increases linearly with the field strength. We are using a 4.7 T superconducting coil. Now reliable commercial coils working at 9 T are available and thus a factor 2 in precision can be gained with such a magnet. More important is that for the same precision the running time can be reduced, which is important since many Penning traps are located in accelerator laboratories with limited access to required beam time. Secondly the width $\Delta\nu$ of the cyclotron resonance can also be decreased. The RF-excitation of ions in a Penning trap is a Fourier limited process. The relation between $\Delta\nu$ and the observation (excitation) time Δt for such a process is given by [17]:

$$\Delta\nu\,\Delta t \approx 0.8. \tag{2}$$

In our mass measurements we frequently used excitation times of 1 s corresponding to $\Delta\nu \sim 1$ Hz. For ions with $q/A = \frac{1}{2}$, ν is about 36 MHz corresponding to a mass resolving power $m/\Delta m = \nu/\Delta\nu = 6 \times 10^7$. It should be possible to define the resonance to within 1% of $\Delta\nu$. In this case it should be possible to reach a statistical accuracy of about 0.1 ppb. This fact is behind our use of H_2^+ as mass reference, since several light elements can be fully stripped resulting in a value of q/A of $\frac{1}{2}$ or close to this value.

Longer excitation times than 1 s are possible, but were until recently difficult to apply due to several restrictions, as for example, ion interaction with rest gas molecules (insufficient vacuum) and fluctuations of the magnetic field.

Finally, much more efficient, than a somewhat higher magnetic field and longer excitation times, in particular, for heavier ions, is the use of a high ion charge q. This fact, of course, requires a device for the production of such ions (CRYSIS). The accuracy in mass determinations of a certain isotope is thus expected to increase linearly with the charge q of the ion since the cyclotron resonance frequency increases with q. An accuracy increase using this fact can be between one and almost two orders of magnitude for heavy atoms. It is this property of HCI that we are exploring with SMILETRAP.

3. Mass determinations using highly charged ions

Mass measurements in a Penning trap are based on a comparison of the cyclotron frequencies of the ion of interest and that of a mass reference ion. If the reference ion is denoted by subscript 1 and the ion whose mass is to be measured by subscript 2 the following relation is obtained:

$$\nu_1/\nu_2 = (q_1/q_2)(m_2/m_1). \tag{3}$$

It is here assumed that the change in the magnetic field can be neglected during the time the cyclotron frequencies of the two ion species are measured. This condition is only fulfilled if measures are taken to stabilize the B-field (Section 6) and measure the cyclotron frequencies of the two ion species as close as possible in time (Section 6).

The ideal mass measurements are performed by using various charge states of ^{12}C as mass references because of the definition of the atomic mass unit. The charge of the ^{12}C ion is chosen such that the measurement as much as possible is done with ions being q/A-doublets. As mass references in an attempt to measure the proton mass we have also used light ions whose masses [11] are known to about 0.1 ppb. As a very convenient intermediate mass reference H_2^+ ions produced in the cylindrical retardation trap (Fig. 1) are frequently used (in a few cases also H_3^+ produced in SMILIS). The H_2^+ ion has namely $q/A = 0.5$ like several fully stripped light ions making doublet mass measurements possible.

The relevant observable in mass measurements in a Penning trap is thus ν_1/ν_2, i.e. the ratio between the cyclotron frequency of the reference ion and that of the highly charged ion. This fact reduces the systematic uncertainties considerably, since often the two frequency measurements are performed in identical ways. Therefore, the systematic frequency uncertainties often are of the same size and to a great extent cancel in the frequency ratio. Since the measurement gives the mass of the HCI, the atomic mass is obtained by correcting for the missing q electrons ($m(e)$ is the electron mass) and their binding energy E_B. When H_2^+ ions are used as mass reference, the mass of the neutral atom to be determined is obtained from the following relations:

$$m(\text{neutral atom}) = m(\text{HCI}) + q\, m(e) - E_B \tag{4}$$

$$m(H_2^+)/m(\text{HCI}) = [1/q(\text{HCI})[\nu(\text{HCI})/\nu(H_2^+)] \tag{5}$$

$$m(H_2^+) = m(p)\, C. \tag{6}$$

where $C = 2.00\,544\,600\,52$ is a constant that can be calculated at an uncertainty below 0.1 ppb (see Section 7.8). The electron binding energies are discussed in Section 7.7.

In several measurements we have also determined the frequency ratio $\nu(^{12}C^{q+})/\nu(H_2^+)$. Dividing this frequency ratio by $\nu(\text{HCI})/\nu(H_2^+)$ it is possible to calculate $\nu(\text{HCI})/\nu(^{12}C^{q+})$ and thus use a carbon ion as mass reference with a charge that as much as possible provides a q/A-doublet.

4. Equations of ion motion in an ideal penning trap

Eq. (1) represents a condition that cannot be realized in laboratory experiments. The magnetic field confines the ions only in a plane perpendicular to the magnetic field. But injected ions have a velocity component also along the magnetic field. Therefore, trapping of ions is done by introducing two retardation electrodes separated by a distance $2z$, which limits the ion motion in the direction of the magnetic field. These two electrodes are both required to have surfaces of hyperboloidal shape as well as an additional ring placed as shown in Fig. 2. The ring is also segmented in order to allow RF excitation of the trapped ion. The electrodes and the ring create an electric quadrupole field that together with the B-field makes the ions move with three independent motions. It is also possible to create an electric quadrupole field with a set of cylindrical electrodes as applied in our retardation trap (Fig. 1) placed in front of the hyperboloidal precision trap (Section 5.3). Fig. 3 shows a simplified picture of the three eigen-motions with the respective frequencies ω_+ (the reduced cyclotron frequency), ω_- (the magnetron frequency) and ω_z (the axial frequency). The following relations hold between these three frequencies [26]:

$$\omega_z = (q\, U/m\, d^2)^{1/2} \tag{7}$$

$$d^2 = 1/2(z_0^2 + r^2/2)$$

$$\omega_+ = \omega_c/2 + (\omega_c^2/4 - (\omega_z/2)^2)^{1/2} \tag{8}$$

$$\omega_- = \omega_c/2 - (\omega_c^2/4 - (\omega_z/2)^2)^{1/2} \tag{9}$$

$$\omega_c = \omega_- + \omega_+ \tag{10}$$

$$\omega_c^2 = \omega_-^2 + \omega_+^2 + \omega_z^2. \tag{11}$$

In SMILETRAP the magnetic field is about 4.7 T. This means that the axial frequency ν_z is

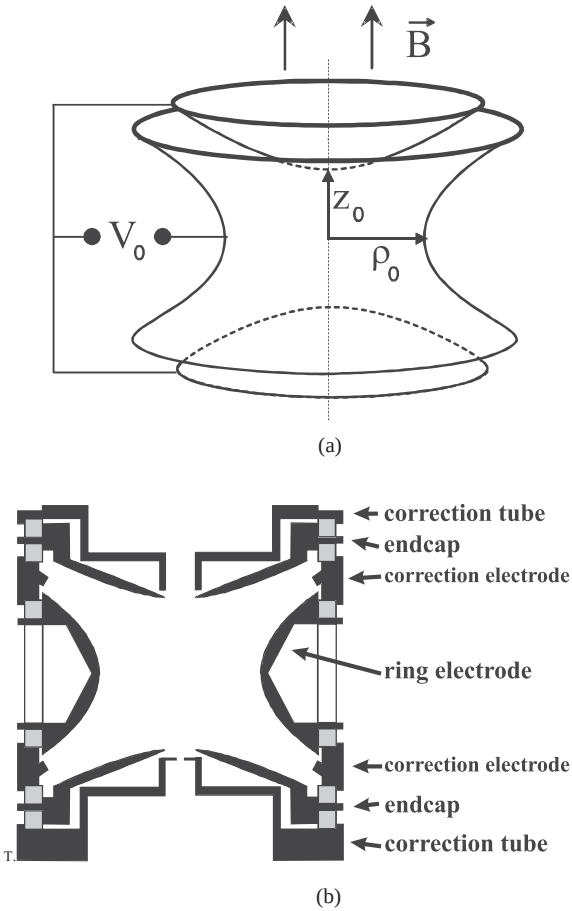

Fig. 2. (a) A schematic picture of a hyperbolic Penning trap similar to that used in the SMILETRAP project and ISOLTRAP, ISOLDE CERN. The voltage and dimensions of the SMILETRAP trap is $V_0 = 5\,\mathrm{V}$, $Z_0 = 11.2\,\mathrm{mm}$, $r_0 = 13,0\,\mathrm{mm}$, $B = 4.7$. (b). The two hyperbolic end caps have holes (diameter 5 mm) for ion entrance and exit. A carefully selected voltage (5.74 V see Fig. 15) is applied to the two correction tubes as to optimize the electric quadrupole field. The finite size of the trap is compensated by applying a voltage of 2.4 V on two rings, each one located above and below the hyperbolic ring.

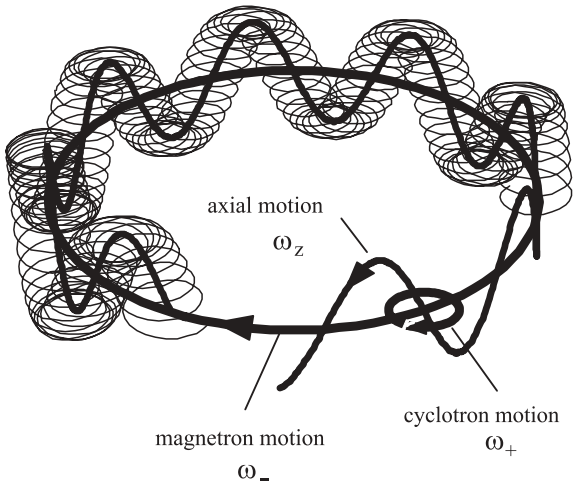

Fig. 3. Simplified picture of the three Eigen-motions in a Penning trap.

about 240 kHz and the reduced cyclotron frequency ν_+ as well as the cyclotron frequency is close to 36 MHz for ions with $q/A = \frac{1}{2}$, while the magnetron frequency ν_- is close to 820 Hz.

The reduced cyclotron frequency ω_+ can be determined by observing the mirror currents in the hyperboloidal ring of the trap and the axial frequency by observing the resonance frequency of the ion oscillating between the two end caps. The magnetron frequency is low and it is enough to calculate its value. It has an obvious advantage to measure all characteristic frequencies this way. The procedure allows consistency checks, for example, performed by measuring the frequencies at different values of the trap voltage U. We measure directly ω_c, a method that also allows consistency checks by measuring the cyclotron resonance frequency of ions of the same elements with a few neighboring charge states. This feature is illustrated by the mass determination of ^{36}Ar which is based on measuring the cyclotron frequencies of four charge states; 16+, 15+, 14+ and 13+ (Section 8.5). The atomic mass has to be independent of the charged state of the ion if there are no serious hidden systematical errors.

Eq. (11) is rather insensitive to misalignment between the symmetry axis of the trap and the magnetic field, a very attractive feature. A drawback with this method of determining the cyclotron frequency by measuring the ring mirror currents used by the MIT and Seattle groups, is that the trap dimension d has to be small (a few mm). This is due to the fact that the oscillating ions are part of a resonance circuit where the trap capacity enters. In order to get a reasonably strong

signal the trap has to have small dimensions. Another disadvantage is that the resonance condition is fixed for each ion species. Thus it is not easy to make fast changes of ions which is very important in order to avoid frequency shifts due to changes of the magnetic field. Our trap and the ISOLTRAP have dimensions as large as 22 mm (end cap distance), a size that allows very accurate mechanical manufacturing. A large trap also dramatically reduces the frequency shifts arising from an imperfect electric quadrupole field (Section 6.3).

When detecting mirror currents exactly one ion produced in the trap itself is used in a non-destructive way. It is important that the two ions whose cyclotron frequencies are to be compared move in the same region of the magnetic field. Since they may be ionized at different radii, cooling is important which forces the ions to the trap center. As will be shown in Section 6.4, our frequency ratios are based on the use of tens of thousands ions, which in doublet measurements, as an average, are localized in the same region of the magnetic filed. This fact gives rise to the same frequency shift for the two ion species and thus they cancel in the frequency ratio.

Due to the fact that cold traps have a temperature of 4 K there is no risk for rest gas interaction because of the extremely low temperature. However, H_2^+ cannot be used as a mass reference when claiming mass uncertainties of about 0.1 ppb or less, since it is not known in which vibrational state the single H_2^+ ion is excited. In our case the mass measurements are based on a large number of measurements with about one ion at the time in the trap (a destructive method) each ion in one of the possible vibrational states. Therefore the average energy of the vibrational states of H_2^+ is the relevant number and it is experimentally known (see Section 7.8). In our much bigger trap its also easier to achieve a good electric quadrupole field over a larger volume and therefore the cooling requirements are less critical. It should already here be mentioned that the influence of the magnetic field in-homogeneity can be considerably reduced if the ions of the two ion species as an average move in the same trap region (discussed in Section 6.2).

In our mass measurements we determine directly the cyclotron frequency ω_c by connecting a frequency synthesizer to four of the eight electrodes of the segmented ring. Sometimes it is also useful to drive the dipole frequency (two of the segments used) or the axial frequency ω_z (see Section 5.4) in order to remove contamination ions (cleaning). In the latter case the RF is applied to the end caps.

5. Experimental set up and sequence of measurements

The SMILETRAP—experiments involve mainly the following parts;

- an electron beam ion source CRYSIS connected to an isotope separator for production of HCI,
- an ion transport system,
- a charge selection magnet,
- a retardation trap where also H_2^+ ions can be produced as a mass reference,
- beam elements between the retardation trap and the precision trap,
- a hyperboloidal Penning trap where the precision mass measurements are done by exciting the ions and detecting their time-of-flight (TOF).

In the following it will be shown how these parts of the SMILETRAP facility are used in the experiments.

5.1. Production of highly charged ions

CRYSIS has a construction similar to most other electron beam ion sources. The main features of CRYSIS have been published in Refs. [28,29]. The EBIS concept, invented by E. D. Donets [30], is based on the ability of an electron beam to remove several electrons from atoms or ions trapped radially by the coulomb interaction between a narrow beam of electrons and the ions. The electrons have an energy of 15–20 keV and the electron beam is on all the time during ion production. Leaving CRYSIS the electrons hit a cooled collector after being retarded to an energy of 5 keV.

Axial trapping of the ions is done by applying suitable voltages on a set 33 cylindrical electrodes (each one 50 mm long with an inner diameter 9 mm) arranged in 5 groups and centrally located, occupying a total length of 1.6 m. A strong magnetic field (5 T is possible but usually 2 T is used), generated by a superconducting coil, forces the electrons into an intense beam with a diameter of only a few tenths of a mm.

A gas of neutral atoms or molecules, or injected singly charged ions are bombarded by DC electrons for a time defined as the *confinement time*, that gives a charge distribution of HCI which is requested by the user. Frequently this confinement time is about 1 s. By lowering the trapping potential applied to the electrodes the ions are then extracted as a pulse having a width of about 100 μs corresponding to the time it takes to empty the trap.

The highest charge states achievable depends on the energy of the electron beam. At present the highest energy reached is 35 keV, which for example is sufficient for removing all electrons except the two electrons in the K-shell of Xe. The highest charge achievable is limited by ion heating caused by elastic collision with electrons in the beam. The highest electron current tested is 1.3 A (DC). However, the energy spread and thus the emittance of the extracted ion beam increases with the electron current. Experience has shown, that beam currents of about 100 mA produce the best intensity of trapped ions in SMILETRAP. At this current the beam energy spread is about 15 eV. This information is obtained by varying the potential of the pretrap relative to that of CRYSIS. The width of the distribution of captured ions as a function of this potential difference was measured with a channeltron detector, placed between the two Penning traps. Using cooling with helium in CRYSIS it was shown that the energy spread was reduced to 8 eV as shown in Fig. 4.

There are two ways of injecting species into CRYSIS. In cases were monoisotopic (or almost monoisotopic) gases with high enough vapor pressure are available, gas injection directly into CRYSIS is used. When using this injection the gas is fed into CRYSIS up-stream in the trap region consisting of the first three electrodes. During a

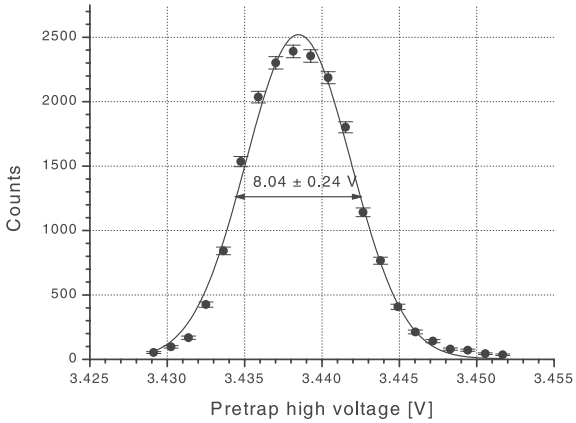

Fig. 4. The number of trapped ions as a function of the potential of the pretrap. The half-width gives the energy spread of the ion beam, in this case of $^{76}Se^{25+}$, after cooling of the ions with alpha particles by adding helium gas in CRYSIS during the ion creation. The number of ions is measured by a channeltron detector ~0.5 m above the pretrap.

certain time defined as *the injection time* (usually about 100 ms) the electron beam hits atoms, molecules or ions in this trap region. Then by adjusting the potentials of these electrodes the ions are moved to a larger trap consisting of the other 30 electrodes. Ions of low charge states are not allowed to enter this region where ions of higher charges are stored during the entire confinement time, frequently being about 0.5–1 s. Then the potential barrier trapping the ions is lowered and the ions are ejected into the beam line. Before the next CRYSIS cycle starts all electrodes are set to values such that all ions that might be left are ejected. It should be pointed out that molecules do not survive this procedure, a feature that, for example has been used for the mass determination of ^{3}H, ^{12}C, ^{28}Si, cases in which gaseous $^{3}H_2$, $^{12}CH_4$, $^{28}SiH_4$ molecules were introduced into CRYSIS via a needle valve.

The experiments with HCI are always performed with an isotope of well-defined mass number and charge. Therefore, in many experiments singly charged ions to be injected into the CRYSIS for the production of HCI are produced in a plasma ion source named CHORDIS (Fig. 5) constructed by DANFYSIK. The ion source can be run with gases, evaporation of solids in an oven

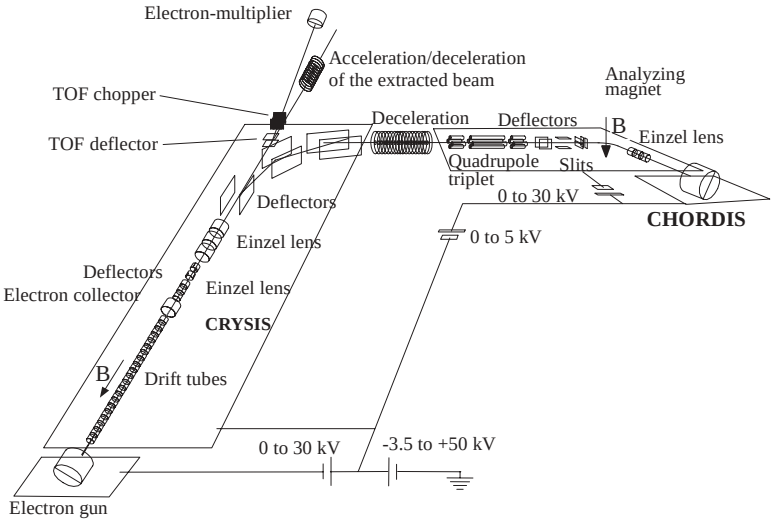

Fig. 5. The equipment for injecting singly charged mass separated ions into CRYSIS for the production of highly charged ions. All optical elements and deflectors that are used are indicated.

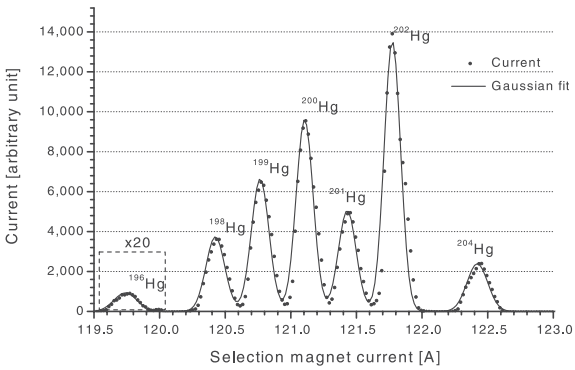

Fig. 6. The mercury mass spectrum recorded about 0.5 m in front of the exit/entrance of CRYSIS with a thin wire. As seen the injected isotopes are well separated. The intensity for each isotope agrees with the tabulated values of the natural abundance, even for the rare isotope ^{196}Hg.

or in a sputtering mode thus being able to produce singly charged ions of practically any element. The ions are first mass separated and then injected into CRYSIS. The operation of CRYSIS for various types of experiments is described in [29]. Fig. 6 shows the mass spectrum of mercury obtained by sweaping the beam across a very thin wire located about 0.5 m in front of the entrance to CRYSIS. As seen the mass resolution and beam purity is very good.

The charge distribution of the HCI wanted by the user can be checked in a flight-time device directly attached to CRYSIS. After completed adjustments of the charge distribution the ion pulses are sent to the user. Each pulse contains about 10^8 charges corresponding, for example, to 2 million 50+ ions.

5.2. Transport and handling of ions from CRYSIS to the traps

The transport distance from CRYSIS to SMILETRAP is about 20 m and is done with conventional beam transport devices, including strip detectors and electrostatic lenses located in suitable positions. The ions are charge selected by a 90° double focusing magnet. Fig. 7 shows the charge distribution of ^{208}Pb ions measured in the focal plane of this magnet by varying the magnet current. The charge selected ions then pass an aperture in the focal plane of the magnet and are focused into a cylindrical trap (pretrap).

Ions from CRYSIS or SMILIS (the ion source for production of singly charged light ions; Fig. 1) are extracted at a potential of 3.4 kV. As the precision trap is operated close to ground potential, the ions captured in the precision trap have to be retarded in the pretrap. This trap consists of 7

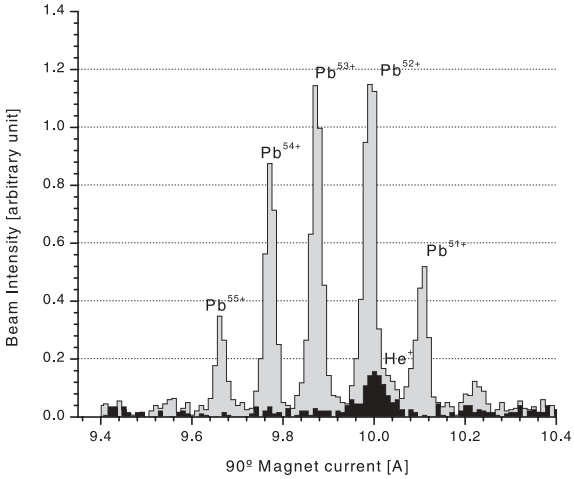

Fig. 7. The charge spectrum of ^{208}Pb measured at the entrance of the SMILETRAP retardation trap. By blocking the lead beam injected into the ion source the background of ^{4}He ions is seen which were used for cooling the ^{208}Pb ions in CRYSIS. It is thus possible to separate ions of close lying charge states. The position of the $^{4}He^{1+}$ peak was used for charge identification of ^{208}Pb ions.

cylindrical electrodes with an inner diameter of 10 mm. The magnetic field is 0.25 T and generated by a warm coil. The trapping potential varies between 2.2 and 5 V. Capture of the ions is achieved by quickly lowering the lower end cap potential for a few seconds to let the ions enter the trap. The ions when captured have a transportation energy of $3.4 \times q$ keV. We do not like to operate the precision trap at a voltage of 3.4 kV. Therefore the ions are brought to ground potential in the pretrap by rapidly ramping its potential to zero in a time of about 30 ms. The ions are so to speak brought to a zero potential level by a rapid electric elevator device. The ions are then ejected out from the pretrap by applying a short negative pulse on the upper end cap. The drift tube potential between the traps is –1 kV.

The pressure in the pretrap is about 10^{-10} mbar. At this pressure there may be a risk that HCI interact with the rest gas which lowers the charge of these ions. However, this effect can be entirely neglected for a storage time of 30 ms, i.e. the time the HCI spend in the first trap during the retardation process.

H^+ and H_2^+ ions are produced in the retardation trap by bombarding the rest gas by 3.4 keV electrons. As the TOF of two hydrogen ion species are well resolved either one of the two ion species can be selected by proper timing and sent to the precision trap. The production of H_2^+ ions offers a very convenient mass reference ion that is, in particular, useful for precision measurements when the two ion species have the same $q/A = \frac{1}{2}$.

The distance between the two traps is about 3 m and here the ion beam position is controlled by deflectors and lenses. The voltages on these beam elements have to be adjusted to the value of q/A for the two ion species. In order to find the optimal settings each voltage can be scanned automatically using the new control program (Section 5.4).

A Micro Channel Plate detector is placed at the entrance of the precision trap. This detector is used for counting the number of ions in each pulse. Before the ions enter the precision trap they have to pass an aperture with a diameter of 1 mm preventing ions with too large initial radial energy to enter the trap and limiting the volume that the ions occupy in the precision trap. There the coldest ions are selected by ramping the trap potential temporarily from 5 V to <0.1 V. After this ion evaporation procedure about 1–2 ions as an average are left in the trap. The ion motion is then excited by a quadrupole RF-field during 1 s at frequencies close to the cyclotron frequency of the ion. The ions are then expelled (Fig. 8) from the trap and the flight time to a channel plate detector is measured (Fig. 9). As seen from the figure ions with the same q/A have cyclotron frequencies which are very similar.

The ion economy in this selection procedure is very low. Out of a few million ions leaving CRYSIS only up to a few thousand are caught in the pretrap. The loss is mainly due to the fact, that the dimensions of the trapping region in the pretrap is only a few mm. This corresponds to an ion flight time <1 μs, as compared to the ion pulse length of about 100 μs. Furthermore, all ions from CRYSIS are not able to enter the pretrap because of poor phase space conditions of the beam. Usually we catch a few thousand ions. Of these ions about 30 are able to enter the precision trap. After the boil off procedure usually as an average 1–2 ion remains trapped. The selection of cold ions in three steps (first in CRYSIS, then in the pretrap

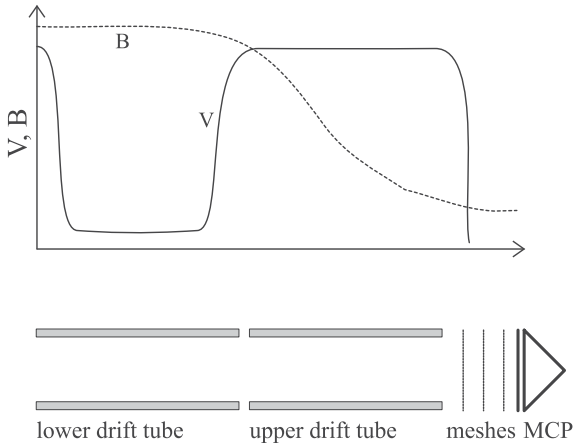

Fig. 8. The drift tube section located above the precision trap. In front of the multi-channel plate detector there are three meshes where a blocking potential can be applied for measurements of the kinetic energy of the ions for the determination of the relativistic mass increase achieved during excitation.

and finally in the precision trap) is very important for the precision that was achieved in this way, rather than using conventional cooling of one single ion in the trap.

5.3. Excitation of ions and time-of-flight detection of the cyclotron resonance frequency

Already when the ions enter the precision trap they have a radial motion caused by the fact that the beam is slightly convergent when entering the trap, that gives rise to a magnetron motion. The ions are excited in the precision trap by applying a quadrupole RF-frequency on four of the segmented ring electrodes. The process of converting an initial magnetron-like motion to pure cyclotron motion is described in Ref. [17].

The cyclotron resonance is recorded by measuring the ion TOF [31]. In the inhomogeneous magnetic fringe field the ions are subject to a force caused by the magnetic field gradient acting upon the magnetic moment of the ion. The radial energy corresponding to the circular ion motion is here transferred to longitudinal kinetic energy. Thus ions in resonance have received maximum energy during excitation and therefore fly faster than the ions off resonance. After a flight distance of about 50 cm the ions are detected by a micro-channel plate detector, that has an efficiency of 0.5 for hydrogen ions [32], which is reduced to 0.40 by the three meshes placed in front of the detector and used for measuring the ion energies. For HCI the corresponding detection efficiency is estimated to be close to 1 [33] but reduced to about 0.8 because of the grids.

The TOF is recorded for 21–25 equidistant frequencies close to the resonance value. Using 1 s excitation time it takes about 45 s to make 2 scans of these frequencies for each ion species. The ion exchange time takes only a few seconds and the total cycle is thus <2 min. It takes <20 cycles to

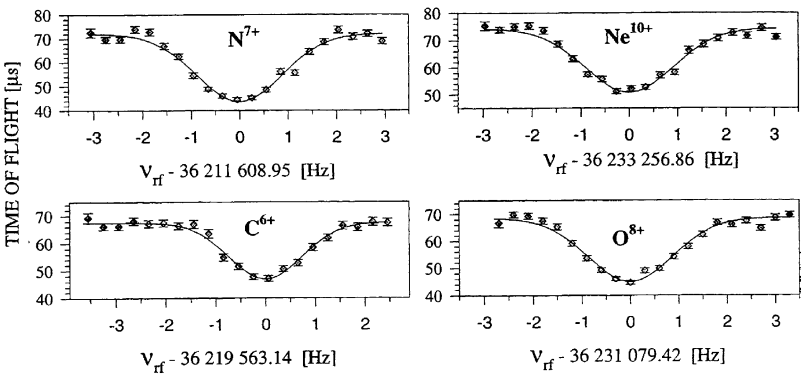

Fig. 9. Ion time-of-flight as a function of the applied cyclotron frequency of light bare nuclei having $q/A = \frac{1}{2}$ and therefore very similar values of the cyclotron frequencies. The time-of-flight at resonance ($t_{\min}$) and off resonance (t_0) define the so-called time-of-flight effect $100(t_0 - t_{min})/t_0\%$.

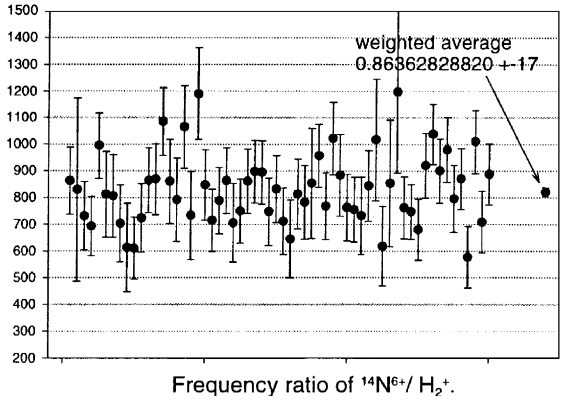

Fig. 10. The frequency ratios of H_2^+ and $^{14}N^{6+}$ ions measured during one week of running. As can be seen the long-term stability of the measured frequency ratio is very satisfactory.

visually observe convincing resonance curves of the two ion species and about 24 h to get a statistical uncertainty of 0.5 ppb for ions with $q/A = \frac{1}{2}$.

The minimum of TOF defines the cyclotron resonance that in the central part has a shape that can be approximated by a Gaussian. The reduction in TOF at resonance is considerable, typically 30%. Fig. 9 shows the cyclotron resonances recorded for the bare nuclei of ^{12}C, ^{14}N, ^{16}O, and ^{20}Ne. Fig. 10 shows the ratio of the cyclotron resonance frequencies of $^{14}N^{6+}$ and H_2^+ over one week of running time. As seen the reproducibility is very satisfactory also for experiments lasting for weeks.

In front of the detector three meshes are placed which can be used to determine the ion energy both before and after excitation by retarding the ions, a procedure enabling correction for the relativistic mass increase (Section 7.6).

In most experiments we have used an excitation time of 1 s. As shown in Section 6.3 the pressure in the precision trap is about 5×10^{-12} that allows excitation times of 3 s using up to 60+ ions with only small charge exchange losses. In future experiments the excitation time will be increased.

5.4. The control system

Though the control system implemented in 1992 was very powerful, it was written in the C++ programming language. It proved, however to be too costly to maintain and improve. The requirement for a new program were the following:

- high realibility and efficiency,
- new features (new devices, more control…),
- easy to upgrade in the future by non-specialists,
- short development time (< 1 man year).

For these reasons we have chosen to develop a LabVIEW program running on a standard personal computer.

This new control system has been fully operational since August 1999. It controls 10 GPIB devices, 28 analog outputs signal (for control of electrodes and deflectors), 16 analog inputs (for vacuum, temperature, LN_2 level monitoring). It is possible to scan all the parameters both in 1D and 2D to help the user to define the best voltage settings for optimum capture efficiency of the ions in the retardation trap and the precision trap.

All the controls and the status of the experiment are displayed on a user-friendly interface. The average ion number in the trap and the cyclotron resonance frequency of the two ion species can be observed during different stages of the experiments. The center of the resonance is here approximated with a Gaussian. A new program for more accurate off-line data analysis has also been implemented.

6. The real trap versus the ideal trap

In the discussion of Penning trap properties we have so far identified a number of measures which have to be taken for reaching highest possible precision. The order given is related to the magnitude of the effects in terms of changes in the cyclotron frequency.

a. A very stable trap temperature close to the trap is required. Changes cause magnetic field disturbances due to the susceptibility of the construction material, in particular, that one of the precision trap and the stainless steel vacuum tube enclosing the trap volume. The effect if not corrected could be as large as 600 ppb for a temperature variation of $\pm 1^\circ$C).

b. A stable magnetic field requires a stable helium pressure in the dewar in which the superconducting coil is emerged. This effect is very sensitive to changes in weather conditions and could amount to 10 ppb and even larger.
c. The electric quadrupole field has to be optimized because the trap has a finite size and ion entrance and exit holes. The total effect could be about 10 ppb.
d. The magnetic field has to be made as homogeneous as possible. If not optimized there could be a frequency shift of about 10 ppb.
e. The E- and B-field have to be well aligned due to possible q/A dependent frequency shifts.
f. In mass measurements aiming at a mass accuracy close to 0.1 ppb it is necessary to stabilize also the frequency synthesizer, an effect if not taken care could amount to a frequency uncertainty of about 0.5 ppb.
g. The excited ion should not interact with other ions during excitation. Therefore, it is important that the trap pressure is so low that there will be no interaction with rest gas molecules during the excitation time. Therefore we have developed a method to measure the trap pressure. The interaction with ions of the same kind is discussed in Section 7.4. It is also important to control the amount of impurity ions originating from CRYSIS with the same value of q/A as the ion of interest.

In the following it will be shown how these requirements were met by various technical measures.

6.1. Stabilization of the trap temperature

The laboratory temperature is regulated within 0.5° for long periods but there are sometimes sudden large changes in the temperature. Therefore a temperature-regulated system that forces air to circulate in the space between the magnet bore and the vacuum chamber was installed (Fig. 11) some years ago that made the trap stable within a few tenth of a degree. However, that is not good enough. The old system was improved and two temperature probes were installed close to the trap, one for measuring the trap temperature and one for regulations.

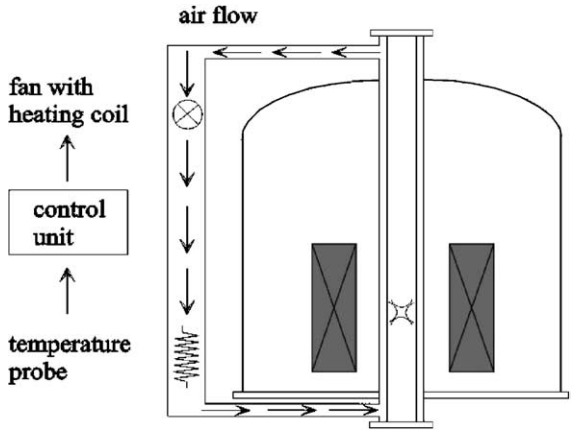

Fig. 11. With a PID regulator the temperature of the trap is held within ± 0.03°C using a PT100 probe to measure the temperature close to the trap and a used hair dryer as a heater. A strong fan forces air to circulate in a isolated closed loop around the trap.

As is seen in Fig. 12 there is a strong correlation between the temperature and the measured H_2^+ resonance. A change in temperature by 1°C corresponds to a cyclotron frequency change by as much as 11 Hz. The FWHM width of the resonance is about 1.0 Hz at an excitation time of 1 s. To improve the precision in the measurements and/or shorten the time, that it takes to get data with sufficient statistics, the excitation time should be increased to above 1 s. The sharper resonance that will result and the smaller window over which the frequency is scanned, the more important it is to set a limit to the maximal allowed temperature drift (both the absolute drift and the drift rate) . If the drift is too big the resonance will leave the scanned frequency window and the measurement must be restarted. Also if the drift rate is too high the resonance will disappear in the background. With the regulating system (Fig. 11) we can now stabilize the vacuum tube temperature below and above the trap within <0.03°C. In order to achieve even a higher degree of temperature stability an active correction device of the magnetic field has also been designed. The trap temperature is used as a B-field probe to control

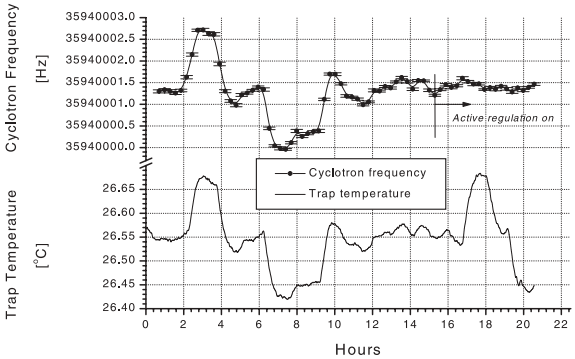

Fig. 12. The lower curve shows the trap temperature as a function of time and the upper curve the variation of the cyclotron resonance frequency of H_2^+ ions during the same time. During the measurement the locking point of the temperature regulator was changed $\pm 0.01°C$, one time in each direction. Note the strong correlation between the measured frequency and the temperature. After 16 h we turned on the active field regulation where we apply a current, proportional to the temperature, through a coil that removes the remaining fluctuations in the temperature. Even when we again change the temperature by $\pm 0.01°C$ the measured frequency is constant.

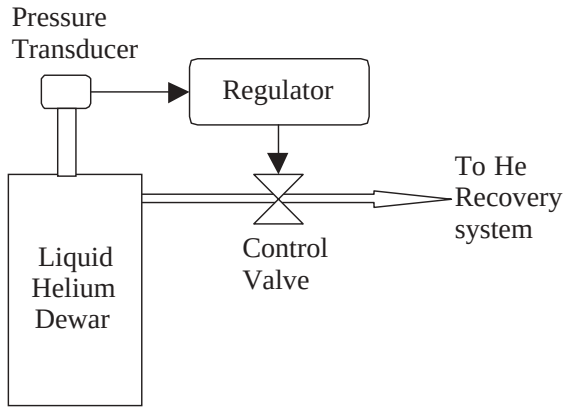

Fig. 13. A scheme of the liquid helium pressure regulation system. The pressure transducer is an absolute pressure meter with no significant temperature dependence. The regulation electronics opens and closes a needle valve so that the pressure inside the magnet dewar is held within 0.1 mbar. The regulated pressure is roughly 80 mbar above normal air pressure.

the current in a warm correction coil. This system is very efficient and reduces further the remaining temperature variations (Fig. 12).

6.2. Stabilization of the helium pressure

The pressure of liquid He dewar is regulated within ± 0.05 mbar by the simple system shown in Fig. 13. In order to be able to monitor the air pressure, a barometer was also installed. Fig. 14 shows the air pressure changes during a severe hurricane that passed over Sweden at the beginning of December 99. With this system installed we have not been able to see any correlation between the air pressure and the magnetic field.

6.3. Optimization of the electric quadrupole field

If the electric field deviates from the quadrupole shape there may be unwanted frequency shifts in the cyclotron frequency. Near the trap center the electric potential $V(r,\theta,\varphi)$ in polar coordinates can be expanded in Legendre polynomials where odd terms are zero and thus:

$$V(r,\theta,\varphi)] = V_0/2\Sigma\, C_k(r/d)^k\, P_k(\cos\theta).$$

Limiting the summation to the first three non-zero terms, the first one corresponds to the electric quadrupole potential wanted and the second and third term to respectively the octupole and dodecapole potentials, which should be as small as possible. It can be shown [17,26] that the last two potentials lead to cyclotron frequency shifts given by

$$\Delta\nu_c^{(4)} = (3C_4V_0/4d^4B)[\rho_-^2 - \rho_+^2]$$

$$\Delta\nu_c^{(6)} = (15C_6V_0/8d^6B)[3z^2(\rho_-^2 - \rho_+^2) + (\rho_-^4 - \rho_+^4)]$$

V_o is defined in Fig. 2a, ρ_- and ρ_+ are the radii of the magnetron and modified cyclotron motions. In a recent work [27] the frequency shifts have been determined for a similar but smaller trap ($d = 7.3$ mm as compared to 15.2 mm in our case). Both have similar shapes and are made by the workshop of the Physics Department, Johannes Gutenberg University in Mainz. The two frequency shifts $\Delta\nu_c^{(4)}$ and $\Delta\nu_c^{(6)}$ are in this work estimated to be $<10^{-12}$ for a q/A doublet measurement and $<10^{-10}$ when the ratio q/A of the two ion species differ by a factor 2. Our adjustments of the electric quadrupole field

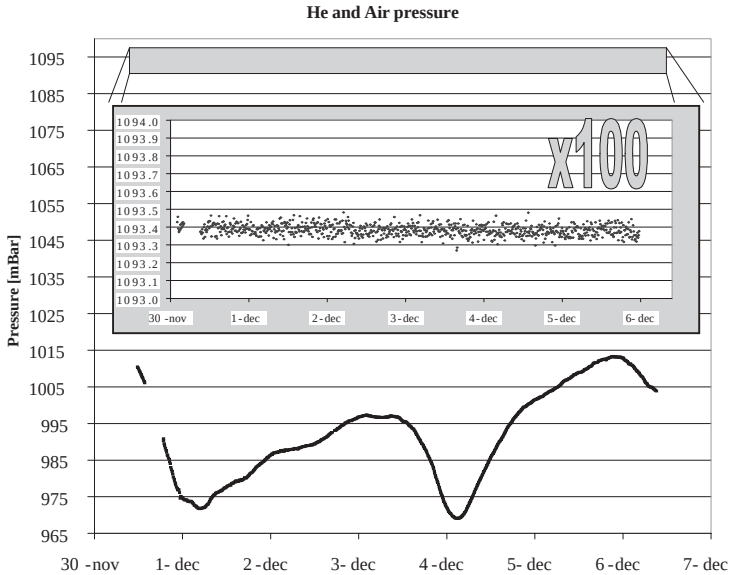

Fig. 14. The air and helium pressure (lower and higher curve respectively) during the passage of two strong low-pressure centers. As seen the helium pressure is constant even during these unusually large changes in air pressure.

described below are likely to be as accurate as described in Ref. [27]. Considering the fact that the two frequency shifts decreases as d^4 and d^6, respectively, we conclude that these frequency shifts should be negligible in measurements claiming mass uncertainties of 0.1 ppb.

The electric field in a real trap deviates from the ideal quadrupole field due to the fact that the trap has finite extension and the end cap electrodes have holes for the entrance and exit of the ions. These imperfections can be compensated by applying suitable voltages on the correction rings and the tubes as indicated in Fig. 2. The potential for the correction rings was set at 3.4 V according to calculations. The potential on the tubes inserted for correction of the disturbing effects of the ion entrance and exit holes, however, was much more critical. Even a small change causes a large effect on the axial frequency and therefore this fact was used to tune the electric quadrupole field. The tuning can be done by measuring a quantity defined as the *time of escape effect* (TOE-effect). The time t taken for trapped ions to leave the trap after the start of the ejection ramp is measured here. Ramping is a procedure in which the potential difference between the end electrodes and the ring is continuously decreased. The ramping is large enough to completely empty the trap. If the applied RF field is in resonance with the ions their axial amplitude will increase. Therefore they will leave the trap earlier after the ramp starts and get a shorter time of escape. Thus this procedure is an indirect measurement of the average axial amplitude of the ions. The better the trap electric field is, the more effective the excitation works and thus the ions leave the trap earlier that gives rise to a shorter TOF. This procedure is done for a number of tube voltage settings. For each voltage V applied a resonance-like curve (Fig. 15a) is obtained in which the time-of-escape (TOE) effect is defined as $100(t_0 - t_{\min})/t_0$ (t_0 defined in the figure). As is seen from Fig. 15b the optimal tube voltage is 5.74 V. At this voltage the electric field is closest to an ideal quadrupole field. Adjusting the tube voltage this way resulted in a dramatic change of the axial resonance width from 1000 to 10 Hz at an excitation time of 100 ms.

The potential 2.3 V on the correction ring for finite size was obtained both from numerical

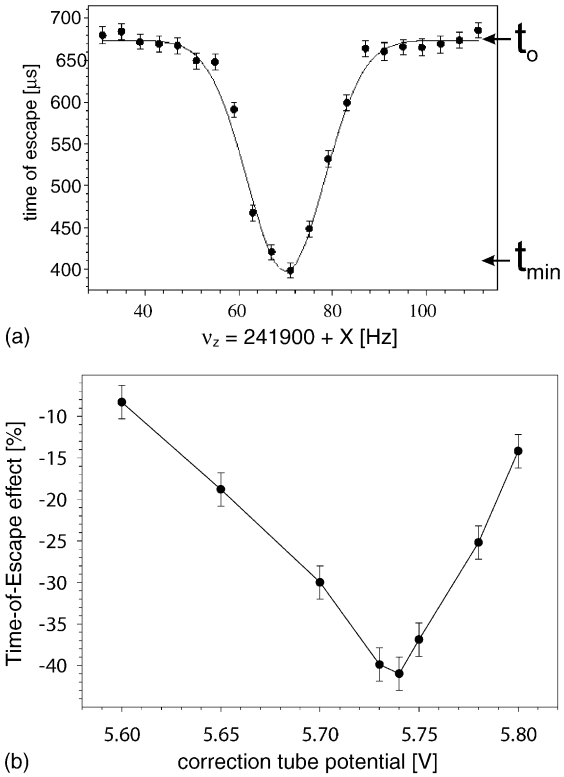

Fig. 15. (a)The time of escape for H_2^+ from the trap as a function of axial frequencies at an excitation time of 0.5 s at a fixed tube voltage. (b) The time of escape effect 100 $(t_0\text{-}t)/t_0$ for different tube voltages. The most ideal electric quadrupole field is clearly obtained for a tube setting of 5.74 V.

calculations [17] and using the TOE method discussed above. It was experimentally found that the ions only were slightly affected by this voltage.

6.4. Optimization of the magnetic field

After installation of the trap the magnetic field of the main superconducing coil was mapped with NMR probes. With this information the currents in the superconducting shim coils were adjusted to give as homogenous field as possible. It was shown that the inhomogeneities are smaller than $10^{-8}/\text{cm}^3$. However, the installation of the trap affected the magnetic field mainly because of the susceptibility of the construction material. Therefore, using trapped H_2^+ ions, an additional optimization was performed with a warm coil mounted in between the bore and the vacuum tube using. The least shift in ν_+ for different axial amplitudes gave the optimum shim current.

An inhomogenous magnetic field increases the resonance width. So, for example, at an excitation time of 1 s when ions with $q/A = \frac{1}{2}$ occupy a radial region where $\Delta B/B$ is as large as 10^{-8}, the additional frequency width becomes 0.36 Hz as compared to the expected width of about 0.9 Hz. But it also causes a frequency shift. The axial component of the magnetic field can be given by [26,17]

$$B_z = B_0(1 + \beta_2(z^2 - \rho_-^2/2))$$

where β_2 is the quadrupole strength of the magnetic field and z and ρ_- (the magnetron radius) give the position of the ions in the trap. As a consequence there is a frequency shift of the size

$$\Delta\nu_c^B = \beta_2 B_0 q(z^2 - \rho_-^2)/m$$

β_2 is not easy to determine experimentally. This may seem to be a serious limitation. However, notice that what matters is the ratio of this frequency shift for the two ion species. In this ratio $\beta_2 B_0 q/A$ cancels in doublet measurements and left is $(z^2 - \rho_-^2)$ that is depending on the position of the two ion species in the trap. The aperture in front of the precision trap should define this position, which as a statistical average of a large number of ions should be the same for the two ion species if they are injected in the same way. This is indeed the case for ions with the same q/A. This is an unexpected advantage of using results of a large number (about 20 000) of ions measured one at a time rather than having one single ion in a long sequence of measurements.

In a few experiments we have noticed that the HCI have resonance width larger than expected. Therefore, it is very essential to accept only data for which the frequency widths are the same for the two ion species. We have set a limit and reject data for which $\Delta\nu > 1.1$ Hz. The cyclotron radii are only of the order of a few μm which are only slightly changed by excitation. However, a higher energy spread may affect the ion optical action on the ions between the two traps, This may increase the entrance angle to the trap and force as an

average the ions to move in a wider radial range. However, it has to be admitted that the cause for larger resonance widths that sometimes are observed is not fully understood.

The influence of the term $(z^2 - \rho_-^2)$ is of course reduced by forcing the two ion species to the trap center by cooling. It remains to be shown how far we can go in accuracy without cooling the trapped ions.

6.5. Determination of the rest gas pressure

Our measurements so far have been restricted to an excitation time of 1 s. In order to achieve higher precision it is necessary to increase the excitation time. Therefore it is important to know when interaction of the excited ion with the rest gas molecules sets a precision limit. The main charge exchange reaction involved is the following:

$$X^{q+} + H_2 \Rightarrow X^{(q-1)+} + H_2^+. \tag{12}$$

The trap pressure should be so low that this reaction does not occur. It is, therefore, very important to be able to measure the pressure in the trap. Since a direct measurement with a vacuum gauge is not reliable at pressures close to 10^{-12} mbar we used an indirect method.

The principle is to trap a highly charged ion X^{q+} (for example $^{76}Ge^{22+}$ [34]) for a certain time (Δt) and then to drive a strong dipole excitation only of this selected ion. The frequency should be set to the resonant frequency of the initial charge state q^+. In this way only this ion picks up radial energy that is transformed to axial energy in the magnetic fringe field. Thus the flight time of this excited ion is much shorter than the non-excited ions and its TOF is resolved from those of the other ions.

The TOF spectrum thus reveals to what extent the highly charged ion has captured an electron from the rest gas molecules. In this case the $X^{(q-1)+}$ ion (and other possible impurity ions) cannot be excited. Therefore the TOF is much longer for the impurity ions than the one of the ion X^{q+}.By determining the ratio

$$\kappa = \frac{N(X^{q+}, \Delta t = t_2)}{N(X^{q+}, \Delta t = t_1)}$$

it is then possible to estimate a maximum value of the H_2 pressure in the trap using the following equation:

$$P(\mathrm{mBar}) = \frac{-2 \times 10^4 \ln(\kappa) \mathrm{RT}}{v\sigma(\Delta t)N}. \tag{13}$$

Here R(J/mol K) is the molar gas constant, T(K) is the gas temperature, v (cm/s) is the velocity of the HCI, σ(cm^2) is the charge exchange cross section, and N is the Avogadro constant.

The cross sections for the charge exchange reaction have been taken from [35] and a ion energy of $1q$ eV has been assumed.

For the experiment (Fig. 16) with $^{76}Ge^{22+}$ the obtained ratio was $<8.8(4.1)\%$ for $t_1 = 0.1$ s and $t_2 = 3.7$ s, which corresponds to a pressure $<6.4(3.6) \times 10^{-12}$ mbar. This value is quite good since we are using a warm bore and since the precision trap is not easily pumped down due to small apertures. Assuming that this value is correct we have estimated the corresponding half-lives for various ions and the capture rate for the excitation times of 1 and 3 s (Fig. 18 and Table 1). We thus conclude that the pressure in our trap is not a limiting factor for excitation times of 3–5 s. However, it is always possible to apply a 'cleaning' pulse during the excitation in order to get rid of the unwanted charge states. To reduce the pressure still more the vacuum tube has to be more efficiently baked out. The most radical solution is to use a cold system. There are, however several projects that can be investigated with the present performance. As seen in Fig. 17 it should be possible to make experiments with ^{238}U ions having q in the region 50+ to 60+ without any serious losses at an excitation time of 3 s.

6.6. Stabilization of the frequency synthesizer

The commercial frequency synthesizer used has a guaranteed stability of about 10^{-8}/day. Considering the improvements described in this paper that was not enough for the most accurate measurements. Therefore it has been connected to a 10 MHz GPS frequency standard. The frequency stability is now 2×10^{-12}/day. The short-term stability (100 s) is 5×10^{-11}. This is about the time it takes to scan the cyclotron

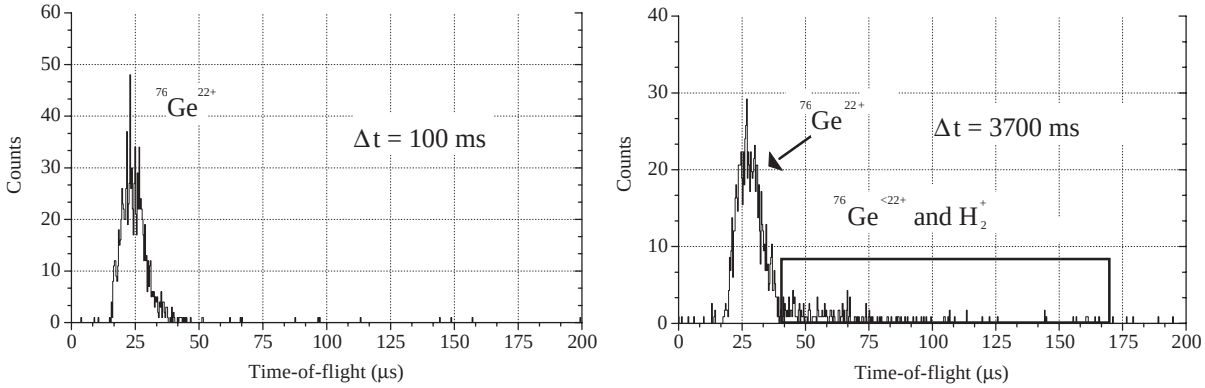

Fig. 16. Time-of-flight spectra for short and long confinement times in the precision trap. Indicated in the figure to the right are the expected positions of $^{76}Ge^{21+}$ and H_2^+ ions. The number of events in this flight-time region gives an upper limit of charge exchange between $^{76}Ge^{22+}$ and the rest gas molecules.

Table 1
Capture rates of highly charged ions from H_2

Ion	Capture rate after 1 s (%)	Capture rate after 3 s (%)
$^{4}He^{2+}$	0.8	2.5
$^{14}N^{7+}$	1.4	4.3
$^{40}Ar^{18+}$	2.6	7.6
$^{76}Ge^{22+}$	2.5	7.2
$^{86}Kr^{26+}$	2.9	8.4
$^{208}Pb^{46+}$	4.0	11.6
$^{238}U^{56+}$	4.9	14.1

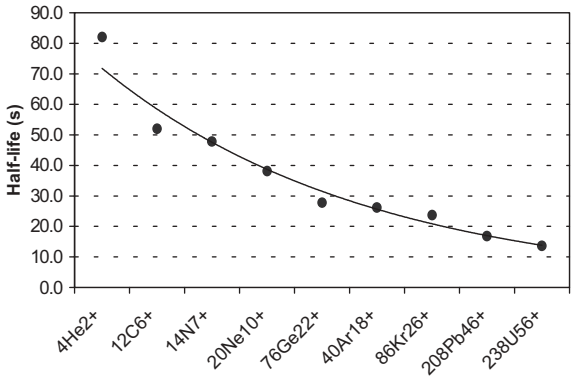

Fig. 17. Calculated half-lives of some highly charged ions in our trap at a pressure of about 5×10^{-12} mbar.

frequencies of the two ion species. Thus the remaining errors of the frequency synthesizer are not a problem even for the most accurate measurements.

7. Accuracy limitations

There are several sources of error to be considered due to limitations in our experimental equipment and procedures which can cause frequency shifts and thus give rise to systematic uncertainties

1. Instabilities in the magnetic field
2. Instabilities in the trap voltage
3. Ion interaction with the mirror charge in the ring of the precision trap
4. Ion–ion interaction
5. Ion-rest gas interaction
6. Relativistic mass increase
7. Uncertainty in the total binding energy of the HCI
8. Uncertainty in the mass of the reference ions
9. Trap misalignment

Before discussing the different sources of systematic uncertainties we would like to emphasize that the relevant observable in our measurements is the frequency ratio of the two ion species. Each frequency is associated with a set of frequency shifts $\varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \cdots$. The real

observable R is then:

$$R = (\nu_1 + \varepsilon_1^1 + \varepsilon_2^1 + \varepsilon_3^1 + \cdots)/(\nu_2 + \varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_3^2 + \cdots).$$

If the time between the two frequency measurements is very short the quantity R can be considered as a direct determination. If the two frequency measurements are performed in a similar way the shifts in R cancel to a great extent even those ones whose origin are not known. This is the main reason that our measurement cycle is as short as 2 min.

In the following we discuss the most obvious sources of frequency uncertainties.

7.1. Instabilities in the magnetic field

Changes of the magnetic field can cause both a frequency shift and an increase in the resonance width, both effects hampering the mass precision.

The natural decay of the current in our superconducting coil is $\ll 0.1$ ppb/h. Therefore, this effect can be entirely neglected considering the fact that the measuring cycle usually is about 1.5 min. Other sources for the change of the magnetic field are discussed in Section 6, where it is concluded, that after stabilization of the trap temperature and the helium pressure the frequency shifts due to changes in the magnetic field is $\ll 0.1$ ppb.

7.2. Trap voltage

Since we measure directly the cyclotron resonance frequency that is independent of the trap voltage, (compare Eqs. (7–11)) this source of possible frequency shift should be very small. The possible influence of trap voltage variations was checked the following way. In one cycle the potential on one end electrode of the trap was constant and 5 V, while in the next cycle it was changed in steps during a frequency ratio determination of two subsequent measurements of the cyclotron frequency of H_2^+ ions. It was found that a voltage change of 100 mV caused a frequency shift of 1.3×10^{-9}. The stability of the end cap voltage supply was certainly much < 5 mV and therefore this kind of frequency shift should be $\ll 0.1$ ppb.

7.3. Ion interaction with the mirror charges in the ring electrode

As shown in a work by R. D. van Dyck Jr. et al., [36] the interaction with the trapped ions and their mirror charges in the ring electrode, cause a negative shift of the reduced cyclotron frequency ω_+, while there is a positive shift in the magnetron frequency ω_-. The shift for ω_+ was found to be -0.29 ppb per charge for protons and -3.33 pb for $^{12}C^{4+}$. The effect scales linearly with the total mass of the trapped ions and as d^{-3}, where d is the trap dimension. It is also shown that the shift is not present in the sum frequencies, i.e. in the cyclotron frequency. It is pointed out that the mirror charge interaction is negligible for a large trap like for example ours that is 10 times larger than the one used by the Seattle group. Since we drive the cyclotron frequency the effect should not be present in our experiments. The trap field U/d may be changed by the presence of additional charges. While ω_+ and ω_- depend on U/d this is not the case for ω_c. Thus, one of the advantages of our method is that mirror charge interaction should not influence the measurements.

7.4. Ion–ion interaction

There may be frequency shifts depending on the number of trapped ions, due to other effects than interaction with mirror charges. During the excitation time the ions, the mass of which is to be determined, can interact both with other ions of the same kind or with impurity ions. Impurities with the same q/A can come from CRYSIS. There is also a risk that the ion with charge q may interact with ions with charge $q-1, q-2$, etc. created by charge exchange with the rest gas. As evident from Fig. 16 this is not the case with the present trap pressure. We have also shown that it is possible to check the maximum amount of impurities of the type $q-1, q-2$, etc. by driving the dipole frequency for charge q and then observe the TOF spectrum in which ions with q is resolved from any other ions (Fig. 18). In certain experiments we have applied cleaning of charges $q-1$ and $q-2$, for example $^{28}Si^{13+}$ and $^{28}Si^{12+}$ produced by charge exchange of $^{28}Si^{14+}$ with H_2

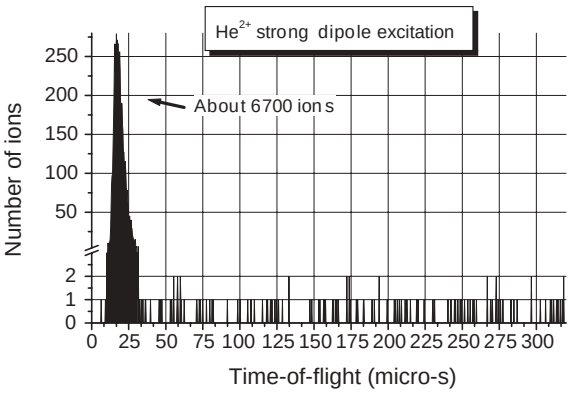

Fig. 18. Strong dipole excitation is applied to $^4He^{2+}$ ions after a confinement time of 1 s. As seen in the time-of-flight spectrum there is about 1 count per channel above 35 μs corresponding to the detector background. By comparing the background intensity with the intensity corresponding to dipole excited $^4He^{2+}$ it is possible to set a limit for impurity ions. From this number it can be concluded that a frequency shift due to impurity ions in this case is $\ll 0.1$ ppb.

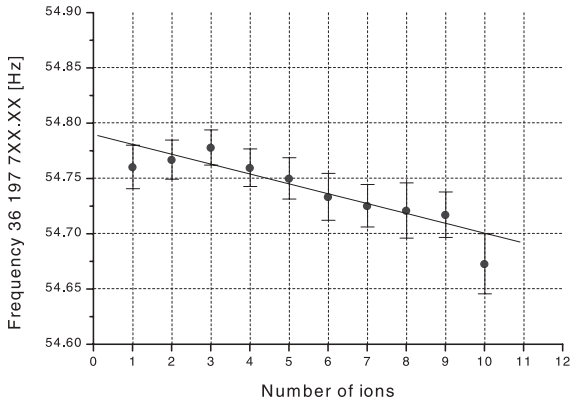

Fig. 19. The measured cyclotron frequency of He^{2+} ions for different number of simultaneous trapped ions. As a compromise between statistics and precision we only accept events with 1 or 2 ions in the trap. The mass uncertainty caused by this effect is about 0.1 ppb.

molecules, by driving these ions to the end caps applying the corresponding axial frequencies.

The number of trapped ions in each measuring cycle varies statistically and is measured by the channel plate detector used for the ion TOF determination after excitation. After a run it is possible to investigate the frequency shifts caused by as an average 1, 2, 3, etc. simultaneously trapped ions. If there are more than one trapped ion these ions may interact with themselves. It has been concluded from calculations by the Mainz group [37], that the true cyclotron frequency is not affected if a few ions of the same species present in the trap. However, this does not seem to be the case as shown in our experiments.

In the off-line data analysis it is possible to determine the cyclotron frequencies for a given number of simultaneously trapped ions and it has been observed that there is a frequency shift that increases almost linearly with the ion number. As an example Fig. 19 shows this effect for different number of trapped ions $^4He^{2+}$ ions. Based on such measurements with ions of different charge states it is concluded that the frequency shift is proportional to the total charge of the trapped ions. For $q = 1+$ the effect is –0.127(14) ppb per charge while for higher charges ($q = 2+$ *to* 42+) the effect is reduced to $-0.016(10)$ ppb per charge. The difference between these two sets of data can partly be explained by the different detection efficiency for the two kinds of ion species.

It is evident that one should not use data based on the presence of many ions simultaneously trapped. As a compromise between accuracy and statistics we base the cyclotron frequencies for high charges on 1 and 2 ions and for H_2^+ on 1–3 ions also taking the detection efficiency into account.

It can be concluded that the ion number selection done this way gives corrections in the frequency ratio of the two ion species that are <0.1 ppb and can be neglected.

In SMILETRAP impurity ions with the same q/A as the ion to be measured can be introduced in the precision trap from CRYSIS, for example He^{2+}, $^{14}N^{+7}$ and $^{16}O^{8+}$ (water molecules, helium leaks, vacuum leaks). This risk is illustrated by a measurement of the mass of C^{6+} in which there was a contamination of He^{2+} as high as 30%. This large impurity caused a frequency ratio shift as high as 7 ppb. The $^{12}C^{6+}$ resonance width was also 1.5 times larger than expected. In order to minimize this effect CRYSIS is usually warmed up before being used by us. We have also observed

that the impurities are much less when 1+ ions are injected into CRYSIS. As mentioned above we now also check the amount of impurities, a method that now can set an uncertainty limit of impurities to a value $\ll 0.1$ pp (Fig. 18).

7.5. Ion interaction with the rest gas

Since we are not using a cold bore at liquid helium temperature there is a risk that the HCI undergoes charge exchange with rest gas molecules in particular H_2. As shown in Figs. 16 and 17 this is not the case with the present trap pressure and a frequency shift due to this effect can be neglected at an excitation time of 1 s.

7.6. Relativistic mass increase

The mass of the excited ion increases quadratically with the excitation time as seen in Fig. 20. As a first approximation for the relativistic correction the average mass increase is estimated. The check of this effect is based on direct simple measurements of the kinetic energy of the ejected ions both before and after excitation. Three meshes are placed in front of the channel plate detector on which a retardation potential can be applied. The number of ions is measured as a function of the retardation voltage. After differentiation the experimental data thus obtained gives the energy distribution of the ions and thus their average energy (Fig. 21). The energy distribution is measured both before (E_i) and after (E_f) excitation, since there is a possibility that some ions entering the superconducting coil may have a direction which is not colinear with the axis of the magnetic field. Thus they may in this way acquire some radial energy in addition to the energy obtained during excitation.

With a good approximation the average energy E_{av} achieved during excitation can be shown to be [38]

$$E_{av} = [E_i + E_f + 1/2(E_i\, E_f)]/3. \tag{14}$$

It is also possible to construct a useful graph for the relativistic correction by plotting the measured ion energies as a function of the ion TOF for a number of different runs. This means that the

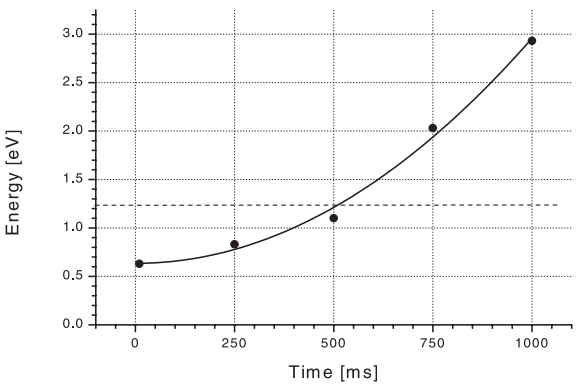

Fig. 20. The energy of H_2^+ ions as a function of excitation time t at fixed amplitude. As seen the energy increases as t^2 as expected. At $t = 0$ the ions have an initial E_i Eq. (14).

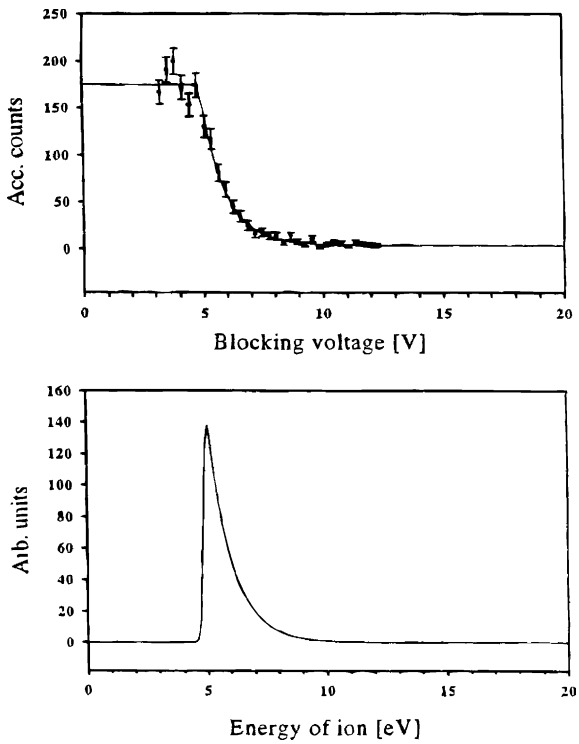

Fig. 21. The upper curve shows the number of ions hitting the multi channel plate detector as a function of the blocking voltage applied on the meshes in front of the detector. The lower curve shows the upper curve differentiated that gives the energy distribution of the ions from which their average energy can be calculated. The average ion energy is measured both before and after excitation from which the energies E_i and E_f appearing in Eq. (14) can be calculated.

correction for relativistic mass increase can be directly obtained from this empirical curve since the average flight time is always recorded in each run. The average relativistic correction in the frequency ratios is usually <0.3 ppb, which can be corrected for with an uncertainty of about 0.1 ppb.

In principle the resonance width should increase during excitation because of the relativistic mass increase. However, a mass increase of 10^{-9} ppb corresponds only to about 36 mHz for ions with $q/A = \frac{1}{2}$ as compared to a width of about 1 Hz at an excitation time of 1 s.

7.7. The total electron binding energy in HCI

As mentioned earlier the total electron binding energies were calculated by summing up the relevant experimental ionization energies tabulated, for example, by Kelly [22]. For ions with $Z<20$ the uncertainty in E_B is $<10^{-11}$. As has been discussed in Section 2, for heavier atoms calculated [23] electron binding energies have to be used. They are claimed to have an uncertainty of about 100 eV [24]. For closed electron shells and for these shells having one additional or one missing electron relativistic calculations can be made with an uncertainty of about 20 eV [25]. Therefore, we always select ion charges q corresponding to filled electron shells and sometimes charges $q-1$ and $q+1$. For intermediate or heavy ions this effect contributes to a mass uncertainty of about 0.2 ppb.

7.8. Uncertainties in the mass of the reference ion

By definition 1/12 of the ^{12}C is exactly 1 mass unit. The masses of the other reference ions ^{14}N (0.086), ^{16}O (0.13; 0.01 by the Seattle group), ^{20}Ne (0.12), ^{28}Si (0.071) and ^{40}Ar (0.088) that sometimes are used as mass references have all been accurately measured [11] by the MIT-group (relative accuracy in units of ppb within brackets) at uncertainties close to 0.1 ppb.

H_2^+ and H_3^+ molecules are useful mass references and it is important to know the ratio of the masses of these ions and the mass of the proton. H_2^+ is a convenient mass reference in $q/A = \frac{1}{2}$ doublet measurements. It can also be used as an intermediate mass reference when q/A for the two ion species differ. As emphasized in doublet measurements the accuracy is set by the uncertainty of the proton mass that now is 0.13 ppb [12]. Below we show that the ratio between the H_2^+ and H_3^+ masses and proton mass can be calculated at an uncertainty <0.1 ppb.

7.8.1. $m(H_2^+)/m(p)$

This mass ratio is calculated in the following way, where all quantities are given in eV:

$$m(H_2^+) = 2m(p) + m(e) + E_I(H_2) - 2E_I(H) - E_B(H_2)$$

$$m(H_2^+)/m(p) = 2 + m(e)/m(p) - [2E_1(H) + E_B(H_2) - E_1(H_2)]/m(p)$$

$m(e)/m(p) = 1/1836.1526646(58)$; [39] $E_I(H)$ is the ionization energy of atomic hydrogen = 13.598 11(8) eV [40], $E_B(H_2)$ the binding energy of H_2 = 4.476 eV [40], $E_I(H_2)$ the ionization energy of $H_2 \rightarrow H_2^+$ = 15.4256 [39] $+\Delta E$ eV.

For the conversion between eV and atomic units we have used the value 1 MeV = 1073544.38(8) nu (7).

The ionization energy 15.4256 eV refers to removing the electron from the ground state of H_2 to the ground state of H_2^+. At room temperature the H_2 molecules are in the vibrational ground state. By bombarding the rest gas by 3.4 keV electrons the neutral H_2 molecules are ionized to H_2^+. However in this process other vibrational states than $v=0$ can be populated in H_2^+. In order to calculate the average energy ΔE of vibrational states populated this way one has to know the energies of the vibrational states and the population probability of these states. The vibrational energies are given by the semiempirical formula [41]:

$$E(v) = k_1(v + 1/2) + k_2(v + 1/2)2,$$
$$k_1 = 0.2848\ \text{eV}; k_2 = -0.007687\ \text{eV}.$$

It has been shown [42,43] that the population distribution is independent of the energy of the electrons ionizing the neutral hydrogen molecule. Using the empirical population probability and Eq. (4) the average energy ΔE of the populated

vibrational levels is found to be 0.74 eV. The maximum population lies between $v = 2$ and 3 but levels with v up to about 17 are also populated. These vibrational levels are stable since the H_2^+ molecule does not have any electric dipole moment. Collisional depopulation may occur but not [43] for our relatively short excitation times of about 1 s and at the pressure of about 5×10^{-12} mbar in our precision trap.

Inserting the numerical values given above the following ratio between the H_2^+ and the proton mass is obtained:

$$C_2 = m(H_2^+)/m(p) = 2.000\,544\,600\,49(<6).$$

The uncertainty in the average vibrational energy 0.742 eV is estimated to be <0.07 eV since both the experimental [42] and theoretical [43] values of the population probability agree within a few percent for the most frequently populated vibrational levels. A conservative estimate [44] of the uncertainty in ΔE corresponds to $< 3 \times 10^{-11}$ in the mass ratio $m(H_2^+)/m(p)$.

Inserting the accepted value 1.007 276 466 89(13) u for the proton mass the mass of H_2^+ becomes 2.015 101 497 03(27) u.

7.8.2. $m(H_3^+)/m(p)$

Considering a fusion between the H_2^+ molecular ion with the hydrogen atom the following relation is obtained:

$$\begin{aligned} m(H_3^+) &= zm(H_2^+) + m(H) - E_B(H_3^+)_I \\ &= C_2 m(p) + m(p) + m(e) - E_B(H_3^+) - E_I(H) \\ &= m(p)[1 + C_2] + m(e) - E_B(H_3^+) - E_I(H) \end{aligned}$$

Inserting the numerical value of C_2 obtained above, the molecular binding energy $E_B(H_3^+)_I$ 6.1595 eV [45] of the H_3^+ molecule and the ionization energy of the hydrogen atom one obtains:

$$C_3 = m(H_3^+)/m(p) = 3.001\,089\,196\,45.$$

The H_3^+ molecule does not have any long-lived states above the vibrational ground state comparable with the excitation times of about 1 s and, therefore, there is no need for correction of possible population of vibrational levels in the value of the molecular binding energies. The uncertainty in the constant C_3 is thus $<3 \times 10^{-11}$.

7.9. Trap misalignment

There is a frequency shift depending on the angle between the magnetic and electric field axis (the geometrical trap axis) that can be shown [26] to be

$$\Delta\nu_c = 2.25\,\nu_-\,\sin\theta^2.$$

When aligning the trap with an electron beam it was concluded that the angle θ is $<5 \times 10^{-3}$ radians (5 mm in 1 m). Inserting here the approximate value of $\nu_- = 820$ Hz and $\theta = 5$ mrad one obtains a shift in the cyclotron frequency of 46 mHz. This corresponds to a relative shift of 1.3 ppb for ions with $q/A = 0.5$, for example $^{12}C^{6+}$. For a $^{12}C^{4+}$ ion with $q/A = 0.33$ the corresponding shift is about 1.9 ppb. In the frequency ratio this corresponds to a shift of which cannot exceed 0.6 ppb.

From a sequence of measurements aiming at a determination of the proton mass using light ions as mass references a maximum shift of –1.03(43) ppb was observed for ions with q/A in the region 0.2–0.5. Experiments were also done with hydrogen ions aiming at setting experimental limits for the possible shifts due to misalignment. The cyclotron frequencies of hydrogen ions externally ($_{ext}$) produced in SMILIS were compared with that of H_2^+ ions internally ($_{int}$) produced in the pretrap. The frequency ratios are compared with the calculated values given in Table 2.

The average deviation from the three measurements is -0.23 ± 0.92 ppb. The statistics are not good enough for setting a conservative limit of the q/A-asymmetry effect. The cyclotron frequency is proportional to q/A. Therefore, when possible the experiments should be done with ions which are q/A doublets since the shift then is the same for the two ions meaning that the frequency ratio for the two ions does not change. For ion species which are not q/A doublets we cannot exclude a frequency ratio shift close to 1 ppb.

7.10. Total mass uncertainties

The total mass uncertainties appearing in a SMILETRAP mass determination have to be

Table 2
Comparison of measured and calculated frequency ratios for hydrogen ions ($q = 1$)

Ion pair	Mass ratio	Measured frequency ratio (ion_{int} to ion_{ext})	Calculated frequency ratio	Deviation ppb
P_{ext}, $H_{2\,int}^{+}$	0.50	2.000 544 598 90(1 1 1)	2.000 544 600 49	-0.81 ± 0.55
$H_{2\,ext}^{+}$, $H_{2\,int}^{+}$	1.00	1.000 000 00034(59)	1.000 000 000 00	$+0.34 \pm 0.59$
$H_{3\,ext}^{+}$, $H_{2\,int}^{+}$	0.67	0.666 606 178 49(30)	0.666 606 178 33	$+0.24 \pm 0.45$

Table 3
Mass uncertainties (ppb) in the determination of the masses of $^{4}He^{2+}$,$^{3}He^{2+}$ and $^{76}Ge^{22+}$

	^{4}He	^{3}He	$^{76}Ge^{22+}$
Reference mass (the proton)	0.18	0.18	0.14
Relativistic mass increase	0.10	0.45	0.10
Ion number dependence	0.10	0.10	0.25
q/A-asymmetry	0.10	0.77	1.03
Magnetic field drift	<0.06	<0.06	<0.06
Contaminant ions	<0.10	<0.10	0.25
Total systematic uncertainty	<0.26	<0.92	<1.15
Statistical uncertainty	0.18	0.18	0.71
Total uncertainty	0.31	0.94	1.35

analyzed from case to case. As an example the mass uncertainties (in ppb) in the measurements of a q/A-doublet (^{4}He) and two non-doublet measurements (^{3}He and ^{76}Ge) are presented in Table 3. In all three cases H_2^+ was used as a mass reference.

From the results presented in Table 4 we have several arguments that our uncertainty assignments are correct. In what we consider to be a routine measurement of the masses of ^{20}Ne and ^{40}Ar using two charge states we agreed with the much more accurate measurements of the MIT-group [11] within <1 ppb, where our uncertainty limit was set by statistics. Furthermore, in a determination of the mass of ^{28}Si with a statistical uncertainty of 0.25 ppb we deviated only 0.3 ppb from the accurate value of the MIT-group [11]. In addition, we measured the proton mass using various charge states of ^{12}C, ^{14}N, ^{20}Ne, ^{28}Si and ^{40}Ar as mass references. A value [46] of 1.007 276 466 72(16) u was obtained where the uncertainty is only due to statistics. The value deviates only 0.17 ppb the accurate value 1.007 276 466 89(13) determined by the Seattle-group [12].

8. Examples of mass determinations

8.1. Present accuracy of stable isotopes and summary of results

The recent technical improvements of SMILE-TRAP allow mass uncertainties of about 1 ppb in routine measurements of light ions lasting for about 20 h. In doublet mass measurements with $q/A = 0.5$ uncertainties of a few times 10^{-10} can be achieved. There are several hundred stable isotopes many of them having a mass uncertainty $\gg 1$ ppb (Fig. 22). It would be rather meaningless to systematically improve hundreds of mass values only in order to make the mass tables more attractive. We have, therefore, given priority to mass measurements which may shed light on the technology of our method of determining atomic masses and fundamental questions in physics in which accurate mass values are of decisive importance.

In Table 4 we have summarized the results of some relevant mass determinations with mass

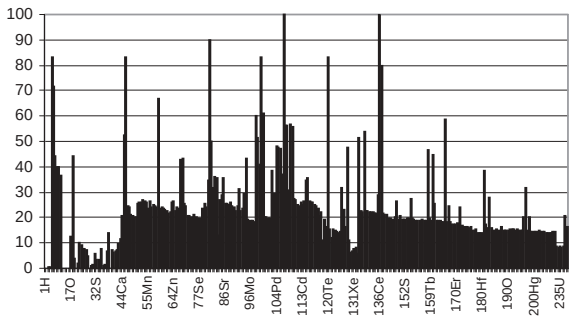

Fig. 22. Uncertainties of atomic masses in ppb published in 1995 [7]. As seen, most stable isotopes in the entire nuclear chart has a mass uncertainty exceeding our precision of at least 1 ppb. Therefore we have given priority to masses which are related to some urgent problems in various fields of physics.

Table 4
Summary of mass determinations made in SMILETRAP

Isotope	q +	Atomic mass (u)	Uncertainty (ppb)	References
^{1}H	1	1.007 276 466 66(35)	0.35	[46]
^{3}H	1	3.016 049 278 4(29)	0.96	[a]
^{3}He	2	3.016 029 323 5(28)	0.93	[47]
^{4}He	2	4.002 603 256 8(13)	0.33	[46]
^{20}Ne	9, 10	19.992 440 186(14)	0.70	[b]
^{22}Ne	9, 10	21.991 385 115(19)	0.86	[b]
^{28}Si	12, 13, 14	27.976 926 531 (14)	0.50	[20]
^{36}Ar	13, 14, 15, 16	35.967 545 105(15)	0.42	[b]
^{40}Ar	14, 16	39.962 383 122(40)	1.0	[b]
^{76}Ge	22, 23	75.921 402 758(96)	1.3	[33]
^{76}Se	24, 25	75.919 213 795(81)	1.1	[33]
^{86}Kr	26	85.910 610 729(1 1 0)	1.3	[b]
^{133}Cs	36, 37	132.905 45159(41)	3.1	[48]
^{198}Hg	52	197.966 768 4(6)	3.0	[c]
^{204}Hg	52	203.973 494 2(6)	2.9	[c]

[a] Preliminary result.
[b] T. Fritioff, and G. Douysset, Determination of the atomic masses of ^{22}Ne, ^{36}Ar and ^{86}Kr, submitted to Nuclear Physics A.
[c] To be submitted to Nuclear Physics.

numbers from 1 to 204 and with q from 1 to 52. As can be seen a mass uncertainty of 1 ppb can be obtained in routine measurements even for ion pairs which are not q/A-doublets. For heavy atoms the uncertainties are increased partly due to the fact that $q/A = 0.25$, which means a frequency drop to about 19 MHz and thereby a drop by a factor 2 in precision.

In the following the mass determinations referred to in Table 4 are commented from light to heavy atoms.

8.2. The proton and helium masses

One of the very first projects at SMILETRAP was an effort to determine the proton mass using H_2^+ as a proton carrier and HCI of ^{4}He, ^{12}C, ^{14}N, ^{20}Ne, ^{28}Si and ^{40}Ar as mass references. The masses of ^{14}N, ^{20}Ne, ^{28}Si and ^{40}Ar have been measured by the MIT-group [11] at an uncertainty close to 0.1 ppb and a value of the ^{4}He mass has been reported by the Seattle group at an uncertainty of 0.25 ppb [10] (Fig. 23).

In 1997 C. Carlberg [46] presented a value of the proton mass determined by the SMILETRAP-collaboration by comparing the cyclotron frequencies of H_2^+ and those of HCI of the elements

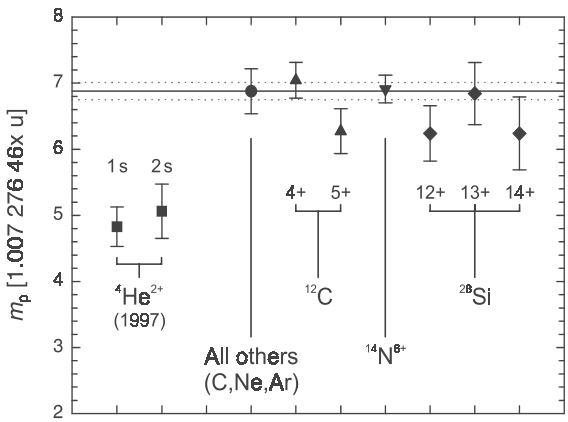

Fig. 23. In a series of experiments we used various highly charged ions of the elements indicated in the figure as mass standards in a determination of the proton mass. H_2^+ ions were used as a carrier of the proton. Indicated with a solid line is the presently accepted proton mass. As seen our value of the proton mass is close to the accepted value except when the alpha particle is used as mass standard. This observation could either be due to a wrong accepted helium mass or an unknown systematic error in our determination of light masses. The accepted Helium mass was proved to be wrong by a large amount.

quoted above. A consistent value of about 1.007 276 466 72(16)(86) for all mass references was found except for ^{4}He which gave an unreasonably

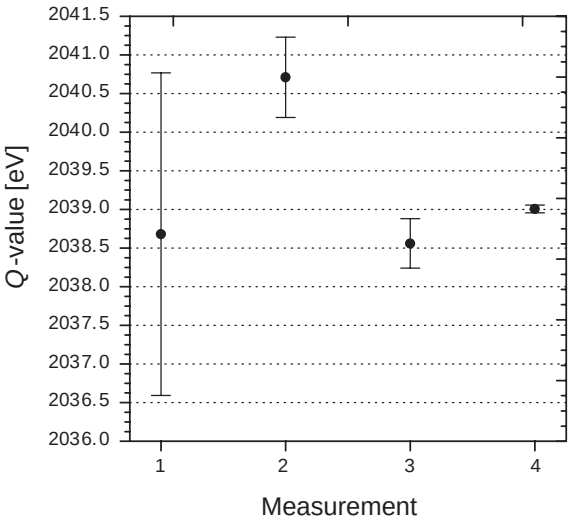

Fig. 24. Different ^{76}Ge double beta decay Q-value determinations. (1) Deduced from Audi et al. [17]; (2) Ellis et al. [13]; (3) Hykawy et al. [14]; (4) Our recent measurement, 2000.

low value of the proton mass indicating that the ^{4}He mass might be wrong (Fig. 24). The relatively large systematic uncertainty of 0.86 ppb in our measurement was mainly caused by uncertainties in the correction of frequency shifts due to ion number dependence and q/A asymmetry between the two ion species used. The helium mass anomaly also contributed to assigning maybe an overestimated maximum systematic error.

After the technical improvements presented in Section 6 had been implemented we returned to a measurement of the ^{4}He mass. The H_2^+ ion was again chosen as carrier for the proton, because it offers a perfect mass doublet measurement with the alpha particle. It was found in earlier measurement that one has to avoid $q/A = \frac{1}{2}$ impurities that could have been produced in the electron beam ion source CRYSIS. In order to check the possible presence of such impurities the alpha particles were excited with its dipole frequency and then the TOF spectrum was analyzed. The $^4He^{2+}$ peak is then entirely resolved from the impurity ions. It could be concluded (Fig. 18) that the amount of impurities was low enough that a possible frequency shift due to impurity ions could be entirely neglected.

Table 5
Comparison between our helium masses and the accepted values

	$m(^4\text{He})$ u	$m(^3\text{He})$ u
SMILETRAP	4.002 603 256 8(13)	3.016 029 323 5(28)
Accepted values	4.002 603 249 7(10)	3.016 029 309 70(86)

We also measured the mass of ^{3}He. The results [47] are given in Table 5.

The mass of ^{4}He was thus determined with an uncertainty of 0.3 ppb, which as a matter of fact, is the most accurate mass determination that we have performed so far. The uncertainty in the ^{3}He mass is larger due to the fact that we may have a q/A asymmetry effect in this non-doublet measurement, that so far is not corrected for. As seen from Table 2 our helium mass values deviate from the accepted values dominated by the measurements of the Seattle group [10]. We were informed by R. S. van Dyck Jr. that the large deviation might be due to an error in their measurements caused by a daily variation of the magnetic field that at the time of the measurements was not known by the group. With a much more stable magnet he has recently re-measured the ^{4}He-mass confirming our value. After the technical improvements discussed in this paper were implemented we have compared the cyclotron frequencies of H_2^+ with $^{12}C^{6+}$ from which we obtained a proton mass 1.007 276 466 66(35) only somewhat lower than the value 1.007 276 466 89(13) reported by Van Dyck Jr. et al. [12].

The difference between the masses of ^{3}He and the ^{3}H gives the Q-value of the tritium beta-decay that, if measured sufficiently accurate, may be used in future experiments aiming at finding a finite rest mass for the electron antineutrino mass. Therefore, we have also measured the tritium mass using a source, in which the tritium is trapped in a uranium bed. The tritium is released by warming up the metal and fed into CRYSIS as gaseous $^3H_2$. In CRYSIS these molecules are entirely dissociated and $^3H^+$ ions are sent to SMILETRAP. A preliminary value for the tritium mass is 3.016 049 278 4(29) u that together with our helium mass gives a Q-value of 18 587.9(3) eV for the beta decay

of tritium. The uncertainties will be reduced by a factor 3 after measuring the ^{3}He mass using singly charged ions. It should be pointed out that this is the first time that an EBIS has run with radioactive ions. The main reason that CRYSIS was used to produce 1+ ions of tritium was the fact that tritium molecules do not survive the intense electron bombardment and thus a beam of pure $^{3}H^{1+}$ ions is extracted. Furthermore, due to the high ionization efficiency of CRYSIS very small amounts of tritium gas is consumed.

8.3. ^{20}Ne and ^{22}Ne

The mass of ^{20}Ne was measured to check our total uncertainty budget in routine measurements dominated by limited statistics. We agree with the very accurate value of the MIT-group within 1 ppb, a fact supporting our uncertainty assignments. ^{22}Ne was the first case for which we tested on-line isotope enrichment. The accurately measured value of the mass of ^{20}Ne [11] was used as an accurate mass reference.

8.4. ^{28}Si, ^{29}Si and ^{30}Si

Already Maxwell suggested that the definition of the kilogram should be based on atomic quantities. The Pt-Ir kilogram is a rather arbitrary standard and suffers a loss of weight each time it is cleaned. It has been suggested to replace this standard with a macroscopic piece of a super-clean Si-single crystal having spherical shape. Several such crystals have been made in Australia and used at PTB in Braunschweig, Germany [49]. It is claimed that the same crystal could be used both for improving the Avogadros number and as a kilogram standard. Knowing its macroscopic radius to be determined by an interference method and its lattice constant, it should then be possible to count the number of Si atoms with a high accuracy. Given this number of silicon atoms, it should be multiplied with the atomic average weight of Si. But all atoms are not ^{28}Si, the mass of which has been measured by the MIT-group [11] at an uncertainty as low as 8×10^{-11}. The masses of ^{29}Si and ^{30}Si have been assigned uncertainties of about 0.75 ppb, but these values are indirectly derived. Some problems can be overcome by using pure ^{28}Si. It is, however, difficult to enrich ^{28}Si to the desired high abundance. Furthermore, the single crystals made from this material, however, do not have the required quality. Therefore natural silicon has to be used. The abundance of the three Si-isotopes has to be known very accurately as well as their masses. The abundance has been measured by neutron irradiation by the PTB-group.

A SMILETRAP measurement of the ^{28}Si mass at an uncertainty of 1 ppb is described in a thesis of Johannes Schönfelder ([20] see Table 3) using natural SiH_4 in CRYSIS. The agreement between our value and that of the MIT group is very good. The deviation is only $+0.3\ \pm0.16$ ppb. Here the uncertainty in our measurements is only due to statistics. The agreement could be fortuitous, but it indicates that our systematic uncertainties are indeed <1 ppb. An estimate of the systematic uncertainty can be obtained in calculating the proton mass by comparing the cyclotron frequencies of H_2^+ ions and ions of different charges of ^{12}C (4+, 5+, 6+) and ^{28}Si (12+, 13+, 14+) as mass references. A proton mass of 1.007 276 466 52 u is then obtained with a statistical uncertainty 0.25 ppb. Assuming a systematic uncertainty 0.25 ppb the total uncertainty in the determination of the proton mass determined this way is 0.35 ppb. The deviation between our measurement and the best value 1.007 276 466 89 (13) u of the proton mass is thus -0.37 ± 0.39 ppb, a reasonable agreement suggesting that the total uncertainty in our ^{28}Si mass should be <0.50 ppb. This comparison could not be made at the time of our measurement since the uncertainty in the proton mass at that time was too large (0.50 ppb).

Using SMILETRAP it should be possible to determine the masses of all three silicon isotopes at an uncertainty of about 0.2 ppb Though the mass of ^{28}Si has been measured [11] with high accuracy, it is important that at least two groups using different methods agree about its value.

8.5. ^{36}Ar

Since the nucleus of this atom is a mirror nucleus with the same number of neutrons and

protons it is of special interest in nuclear structure physics. However, it is not obvious, that the accurate mass value that traps can provide will be relevant in nuclear physics because of the relatively crude nuclear models. When we started our measurements the mass of ^{36}Ar was known at a much lower accuracy than that for ^{40}Ar. We also took the opportunity to check the mass consistency when using several charge states (13+, 14+, 15+, 16+) of the same isotope. Highly enriched ^{36}Ar was injected directly into CRYSIS. The mass agreement using four different charge states is excellent. A test was also made to use natural argon in the CHORDIS ion source. It was concluded that the intensity of both ^{36}Ar and ^{38}Ar would be enough for mass measurements in spite of their very low abundance (0.34 and 0.063% respectively).

Ion	Mass (u)
$^{36}A^{13+}$	36.967 545 075(32)
$^{36}A^{14+}$	36.967 545 115(28)
$^{36}A^{15+}$	36.967 545 112(26)
$^{36}A^{16+}$	36.967 545 106(23)

The uncertainty given is only statistical. The weighted average of the ^{36}Ar mass based on the four charge states with total uncertainties is given in Table 3. The new value of the ^{36}Ar mass has been used [50] as mass reference in ISOLTRAP measurements in which masses of short-lived argon isotopes have been measured. It was shown that the isobaric multiplet mass equation breaks down for mass 33.

8.6. ^{76}Ge and ^{76}Se (determination of the Q-value the double beta-decay of ^{76}Ge)

The project was stimulated by experiments [51] searching for the ($0\nu2\beta$) monochromatic electron peak, which if present would violate the standard model. It is even important to set a lower limit for its appearance. The position of this peak is given by the Q-value of the ^{76}Ge beta decay, i.e. the mass difference between ^{76}Ge and ^{76}Se. There were two measurements [52,53] of this Q-value published by the same group based on results from using a conventional mass spectrometer arriving at Q-values which did not agree within the respective uncertainties. We were asked by groups studying the double beta decay to check this Q-value. Our project was delayed several years because of the difficulty in developing a suitable ion source technique for the two elements. $^{76}Ge^{1+}$ ions were finally successfully produced by using a sputtering target in the CHORDIS ion source. We reached an accuracy of 1 ppb for the masses of the two atoms, which represents a 17-fold mass improvement. However, in the mass difference the systematic uncertainties practically cancel giving a Q-value of 2039.005(50) keV, a more than 6-fold improvement (Fig. 24) in accuracy, however confirming the last reported value. Thus the uncertainty 50 eV of the Q-value is only a small fraction of the resolution of the Ge-detectors used. Therefore, the new Q-value can be used with great confidence for locking the position of electron peak in the search for the possible sophisticated mode ($0\nu2\beta$) of the double beta decay of ^{76}Ge. With the present detector resolution this accuracy cannot be exploited but it is important that two groups agree using very different experimental methods. Furthermore, it is not excluded that future detectors may be developed with higher energy resolving power.

8.7. ^{86}Kr

The mass of ^{86}Kr was determined at an early stage as a test of the improved SMILETRAP performance. First a measurement with $^{86}Kr^{29+}$ ions was made [54] improving the mass value from 85.910 615 0(50) u to 85.910 609 8(12) u. In a later measurement mass separated $^{86}Kr^{1+}$ ions were injected into CRYSIS. Neon-like ions ($q = 26+$) were delivered to SMILETRAP since the electron binding energy for this charge has been calculated with high accuracy [25]. The mass obtained is 85.910 610 729(1 1 0) u, an improvement by an order of magnitude.

8.8. ^{133}Cs

In a paper [48] on the mass of ^{133}Cs we described an effort [55] to improve the fine structure

constant α [56] in a way independent of QED. The method is obvious after rewriting the expression for α

$$\alpha^2 = (2R\infty/c)(h/m_e) = (2R\infty/c)(h/m_{Cs})(m_{Cs}/m_p)(m_p/m_e). \quad (15)$$

We determined (m_{Cs}/m_p) at an uncertainty of about 3 ppb. This measurement was done before the technical improvements described in Section 6 was implemented. The value is good enough to get an uncertainty in α, twice lower than that obtained by comparing the famous determination of g-2 with the prediction of QED, provided the other ratios are known with the same accuracy. The largest uncertainty (about 20 ppb) so far is in the measurements of h/m_{Cs}, a value that is obtained by measuring the recoil of the Cs atom after it has absorbed a laser photon whose frequency is known at a very high accuracy. Somewhat later the ^{133}Cs mass was measured even more accurately by the MIT group [57], but it should be noted that we directly determined the mass ratio of ^{133}Cs and the proton.

8.9. ^{198}Hg and ^{204}Hg

Since about two decades there has been an anomaly in the mass tables of Audi and Wapstra [7]. The extrapolations from heavier and lighter atoms suggested masses for all stable Hg- isotopes that differed by almost 100 ppb from the values measured by the Manitoba group [58]. In the experiments aiming at testing the mass values of ^{198}Hg and ^{204}Hg we fed into CRYSIS singly charged Hg-ions produced by evaporation in the CHORDIS ion source. The confinement time in CRYSIS was about 2 s. Note that the natural abundance of these two isotopes only is 10.0 and 6.9% respectively. We benefited very much from the fact that the total charge that the electron beam can trap is relatively independent of the isotopic abundance. Fig. 6 shows the mercury mass spectrum measured about 50 cm before the entrance to CRYSIS. As seen the mass resolution is good and the background very small. It was possible to transport the ion pulses of the HCI to the entrance of the retardation trap without serious losses. However, we first had great difficulties in getting the ions into this trap. Almost a factor 10 was missing in intensity. By feeding in helium into CRYSIS we evidently were able to cool the HCI by alpha-particles improving the phase space of the beam considerably. In this way sufficiently many 52+ ions were caught. Charge 52+ was selected since the number of electrons represents an ion with a closed nickel-like electron shell for which the electron binding energy can be accurately calculated [25]. In running times of about 12 h we confirmed the Manitoba results and improved the mass uncertainty by a factor 2.5 (Fig. 25). Evidently the masses of heavier and lighter isotopes on which the mass extrapolations were made are wrong. Thus there is no mercury mass anomaly any longer. But the main result is that we have shown that it is possible to trap and measure the mass of an ion with such a high charge as 52. This result is promising for experiments planned at GSI (Darmstadt) aiming at measuring the masses of very highly charged radioactive and stable isotopes (the so-called HITRAP-project) for example, $^{238}U^{92+,\,91+,\,90,\,89+}$ as well as g-factors of hydrogen-like heavy ions.

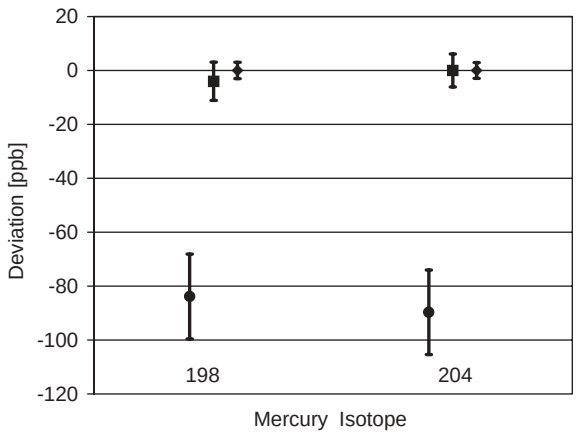

Fig. 25. The deviation between our result and the two earlier mass values of the isotopes of ^{198}Hg and ^{204}Hg determined by, from left to right in each group, Audi/Wapstra, Manitoba, and our value. In the figure zero deviation is the value obtained by us. As clearly visible the direct mass measurements by us and the Manitoba group agree perfectly with each other.

9. Future and outlook

There are a few obvious measures to be taken which would improve the performance of SMILETRAP.

a. Increase of the excitation time
b. Implementation of the Ramsey fringe technique
c. Cooling of the ions in the pretrap
d. Combining SMILETRAP with an electron beam ion trap (EBIT) at a 250 kV platform.

9.1. Increase of the excitation time

The objective for future measurements is among other things to decrease further the uncertainties in the mass determinations as well as to reach the present accuracy in a shorter time, since our experiment take place in a laboratory with scheduled use of its facilities including CRYSIS. At present a statistical uncertainty of ~ 0.5 ppb using an excitation time of 1 s can be reached in about 24 h for ions with $q/A = 0.5$ (longer for lower q/A- ratios). If the data collection time is longer a statistical uncertainty close to 0.1 ppb can be reached. One way to reduce the time it takes to gather data is to increase the excitation time. This was not possible until recently, mainly because of B-field instability. Today an excitation time of 2–3 s seems possible. This would reduce the time necessary to achieve a ~ 0.5 ppb uncertainty to 7.5 h for ions with $q/A \approx 0.5$. Depending on the objective of the experiment, it would be possible, during a typical run week when everything works, to measure several species with a statistical accuracy of 0.1 ppb. (Fig. 26).

9.2. Application of Ramsey excitation

Another very attractive possibility to reach higher precision is to apply a Ramsey excitation scheme, which has been tested by the ISOLTRAP group [59]. Instead of using a constant excitation, the ions are excited by several short pulses being in phase. Ramsey fringes will then be observed in the TOF. This procedure has also been tested (Figs. 26 and 27) by us using three 100 ms long pulses separated by 350 ms (i.e. 1 s total cycle time) leading to promising results. Setting the frequency window in such a way, that it covered the central peak and the two neighboring side bands, three well-separated peaks are observed whose widths became narrower (FWHM ~ 0.6 Hz). The line shape for dipole Ramsey excitation was successfully applied for fitting the Ramsey fringes. With the frequency window covering only the central fringe and one of the neighboring side band fringes, altogether containing 31 frequencies, a precision improvement by a factor 2.5 was obtained for H_2^+ ions (Fig. 27). It seems likely that increasing the excitation to 2 s a precision gain by a factor 4 will be achieved, i.e. reaching a value of 10^{-10}. It is evident that this precision will, in particular, be competitive for ions with $q > 10$.

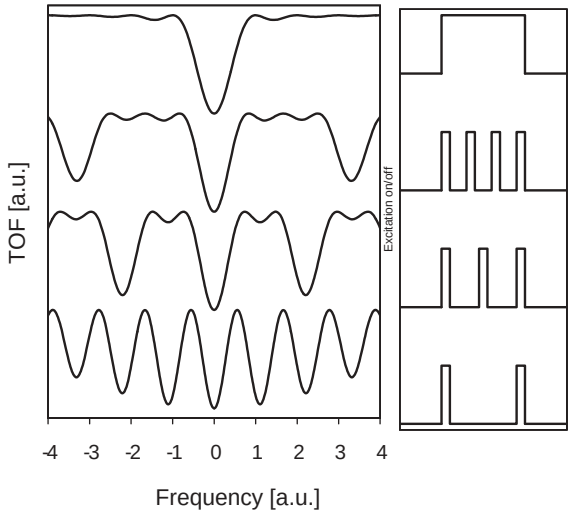

Fig. 26. Theoretical resonance curves for normal excitation and different Ramsey patterns with four, three and two pulses.

9.3. Cooling

It remains to show how far in accuracy we can go by ion selection rather than cooling. As shown in Section 6.4 the destructive method of using the ions means that averaged over a large amount of scans (about 20 000) the two ion species occupy the same trap region and therefore the magnetic field inhomogenuity is not so critical. If necessary both

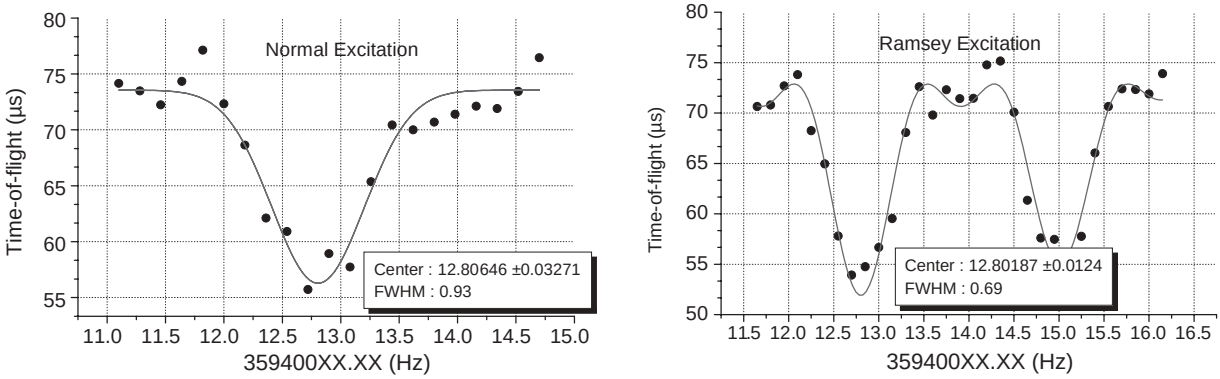

Fig. 27. The cyclotron resonance for H_2^+ ions using normal excitation with one long RF-pulse (left) and Ramsey excitation with three equally long pulses (right) each of 100 ms separated by 350 ms. The total time in the trap is in both cases 1 s. The Ramsey resonance shows only the center dip (left) and the first sideband (right). The FWHM of the center Ramsey fringe is $<75\%$ compared to the normal excitation and the center in this example is determined with a 2.5 times lower uncertainty.

resistive and electron cooling ought to be tested. In the case of resistive cooling the cooling time t_0 defined as the time to reduce the ion energy by $1/e$ is

$$t_0 = 4m\, z_0^2/q^2 R \tag{16}$$

Here m is the mass of the ion, q its charge, z_0 half the distance between the end caps and R the resistance in the tuned oscillating circuit. As seen the cooling time decreases with q for a certain value of m/q.

Electron cooling in the retardation trap requires additional electrodes to create a so-called nested trap. We have also observed effects of ion–ion cooling, a method that requires more systematic studies. With the present technology we have about 30 ions in the precision trap before the ion evaporation process starts. With a new electron gun in CRYSIS it is estimated that the ion intensity will increase by a factor of 10. Starting with more ions in the pretrap as well as in precision trap is likely to lead to more efficient ion–ion cooling.

9.4. Ion production in a short EBIS or an EBIT (Electron beam ion trap)

The EBIS that we have used for production of HCI has the drawback that its length of 1.6 m is large as compared to the dimensions of the retardation trap resulting in large ion losses. Also it has been a limitation that we are not the only users of CRYSIS. Therefore an attractive future solution would be a dedicated source. This could either be a shorter warm EBIS (warm in order to avoid memory effects of accumulated species). It could also be an EBIT that is nothing but a short EBIS, the length only being a few centimeters comparable to the size of the retardation trap. In order to reach the highest possible charge states the device has to be set at a platform voltage of about 250 kV. Such a system means a considerable investment but the total facility for stable ions is compatible with the ambitious HITRAP project at GSI.

10. Conclusions

It should be emphasized that the SMILETRAP facility is the only one that has measured masses of ions with $q \gg 8+$. At the accelerator facility GSI in Darmstadt there is a recently approved project named HITRAP that aims at producing very HCI of radioactive as well as stable isotopes, as for example ^{238}U ions with the three highest charge states. These ions are produced at very high energies and slowed down, first in the storage ring ESR and then further retarded in some decelerator device. Our experience of catching and measuring

masses of HCI is also of interest for this ambitious project.

We have convincingly shown that it is possible to exploit the precision merits of using HCI in accurate mass determinations.

The electron beam ion source CRYSIS has successfully supplied the wanted HCI. It has been shown that the duoplasmatron ion source CHORDIS can produce singly charged ions of practically any elements for injection into CRYSIS. This procedure is rather independent of the isotopic abundance since the electron beam can only accept a certain amount of charges.

The cyclotron resonances of the ions produced in CRYSIS and H_2^+ ions in the pretrap are determined by measuring their time-of-flight after excitation. This procedure allows a switching time between ion species of a few seconds only. A total cycle time as short as 2 min using excitation times in the region 1–3 s is possible. Approaching an uncertainty in mass determinations of 0.1 ppb, we have so far not seen limitations in using the time-of-flight method for the determination of the cyclotron frequencies.

The high accuracy close to 0.1 ppb recently achieved for mass doublets is to a great extent due to the measures taken to stabilize the helium pressure and the trap temperature. After these improvements an accuracy level was reached that made it justified to connect the frequency synthesizer to a GPS-receiver in order to improve its frequency stability.

A warning often expressed by leading groups in precision mass spectroscopy was that cooling of the ions would be absolutely necessary in order to reach high accuracy. However, we have shown, much to our own surprise, that our 4-step selection of the coldest ions delivered from CRYSIS is an unexpected promising alternative. The first energy selection is done in CRYSIS by the fact that the trapping voltage is about 30 eV (no cooling with helium). With helium cooling we could accept a trapping voltage of 70 eV. The second energy selection is done in the retardation trap with a small entrance angle and low trapping voltage. The final selection is achieved by the aperture placed at the entrance of the precision trap and by the following ion evaporation. Furthermore, a selection is made by keeping the two traps at potentials which only differ by about 2 V. This measure limits the number of ions which have gained radial energy before excitation to enter the precision trap.

The two ion species to be compared are used in a so-called destructive way. This means that after loading the trap, 21 frequencies close to the resonance frequency, were applied twice for each of the two ion species. This procedure is due to the fact that we are using a warm bore and thus the ions cannot be kept in the trap for long times because of the interaction with the rest gas molecules. This procedure has some unexpected advantages. Firstly the results are based on a large number of ions and this means that one can use the experimental values of the average vibrational energies of the H_2^+ mass reference ions. Furthermore, cooling of the ions is not so urgently needed, because the two ion species occupy as an average the same volume of the magnetic field. Therefore, the frequency shifts of the two ion species due to in-homogeneity of the magnetic field cancel in the frequency ratio.

Mass doublet measurements with $q/A = \frac{1}{2}$ are associated with the risk of frequency shifts due to impurities from CRYSIS, having the same value of q/A, as that for the ion whose mass is to be measured. Knowing the impurity species the impurity ions can be removed by driving their axial frequencies. We have shown that it is simpler to check the presence of impurity ions by driving the dipole resonance of the ion of interest and than analyze the time-of-flight spectrum.

When planning mass determinations of intermediate and heavy atoms we were first worried about the absence of experimentally determined ionization energies from which the electron binding energies could be accurately calculated. By the accurate calculations of binding energies for filled electron shells performed by the groups of E. Lindroth and P. Indelicato [25] this is not any longer a problem, when mass uncertainties of about 0.2 ppb or larger is enough. As a matter of fact it is now a challenge to increase the precision in our mass determinations to about 0.1 ppb also for heavy atoms and rather aim at checking their

relativistic multiconfigurational calculations including QED.

The precision achieved shows, furthermore, that our methods of optimizing the electric quadrupole field as well as the magnetic field, results in a relatively large trap region, where these fields are close to the ideal ones. The large size of the trap also allows a rather perfect mechanical precision of the shapes of the hyperboloidal electrodes that simplifies the efforts to get a good electric quadrupole field. This may be an additional reason for the progress in precision.

Though the precision depends on q/A of the ion, even a greater surprise is that we have been able to make precision measurements also of the lightest atoms. SMILETRAP was rather constructed in order to benefit from the precision increase of ions with very high charges. Our measurements of the masses of ^{3}He, ^{4}He and ^{3}H remind of an old experience in precision physics. At least two groups have to agree on the value of an interesting observable, if possible obtained in different ways, before it can be safely accepted.

Acknowledgements

We gratefully acknowledge the support from the Knut and Alice Wallenberg Foundation, The Carl Trygger Foundation, The Bank of Sweden Tercentenary Foundation, The Swedish Natural Research Council, The European Community Science and TRM-Programs and The Manne Siegbahn Laboratory.

In particular, we appreciate the confidence that the Wallenberg Foundation has shown us from the start of the SMILETRAP project, which in the beginning looked rather hypothetical with several seemingly week features.

The upper part of SMILETRAP is more or less a copy of ISOLTRAP at CERN. We are very much indepted to Prof. H.-J. Kluge and Prof G. Bollen for their continued interest and support, in particular during the building up period at the University of Mainz.

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