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Carbon clusters for absolute mass measurements at ISOLTRAP

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Abstract. The cyclotron frequencies of singly charged carbon clusters C_n^+ ($n \geq 2$) were measured with the Penning-trap mass spectrometer ISOLTRAP at ISOLDE/CERN. The present limit of mass accuracy $\delta m/m = 1.2 \cdot 10^{-8}$ and the extent of the mass-dependent systematic shift $(\delta m/m)_{\rm sys} = 1.7(0.6) \cdot 10^{-10}/\,{\rm u} \cdot (m - m_{\rm ref})$ of the setup were investigated for the first time. In addition, absolute mass measurements by use of pure clusters of the most abundant carbon isotope ^{12}C are now possible at ISOLTRAP.

PACS. 21.10.Dr Binding energies and masses – 36.40.Wa Charged clusters

1 Introduction and motivation

The discovery and synthesis of C_{60} and C_{70} [1–3] and the possibility to produce them in macroscopic amounts [4] has opened the way for a variety of techniques to use these fullerenes for fundamental research and technological developments [5].

As pointed out before [6], carbon clusters provide the reference of choice for precision mass spectrometry since the atomic mass standard is based on the mass of ^{12}C. Free carbon cluster ions C_n^+ with $n \geq 2$ can be produced by nanosecond pulsed laser ionization and fragmentation of C_{60} [7]. The possibility of using carbon clusters as mass references in high-accuracy on-line mass measurements at ISOLTRAP [8], thereby eliminating the uncertainty of the mass of the reference ion by definition, leads to a number of advantages and applications:

- Not only direct but also absolute mass measurements can be performed,
- more reference masses which are at most six mass units away from the isotope of interest,
- determination of the upper limit of the mass-dependent systematic error per mass unit difference between the investigated and the reference ion, which has been evaluated for the ISOLTRAP mass spectrometer to be $(\delta m/m)_{\rm sys} \approx 2 \cdot 10^{-9}/\,{\rm u}$ [9],
- tests of the present limit of accuracy for mass measurements which is up to now only conservatively estimated to be $\delta m/m \approx 1 \cdot 10^{-7}$ [9] under standard measurement conditions.

Thus, the trapping and excitation of carbon cluster ions are a prerequisite for higher-precision and absolute atomic mass measurements on short-lived isotopes by ISOLTRAP.

2 Experimental setup and procedure

ISOLTRAP is a tandem Penning-trap system for high-precision on-line mass determination of short-lived isotopes located at ISOLDE/CERN [10]. The masses are measured by the determination of the cyclotron frequencies of ions confined in Penning traps [8]. A schematic of the layout of ISOLTRAP together with the cluster ion source, which is vertically mounted under the first Penning trap, is shown in fig. 1. The overall setup is described in detail in several previous publications [8,11,12], therefore only a brief description will be given here.

The carbon cluster ions are produced by use of nanosecond laser desorption, fragmentation and photoionization of C_{60} at 532 nm. To this end, the frequency-doubled beam of a Q-switched Nd:YAG laser (Quantel Brilliant B, LOT; repetition rate: 10 Hz; pulse duration: 6 ns) is focused on a C_{60} pellet (purity: $C_{60} > 99.4\%$ [4]), which is set to an accelerating voltage of 2.8 kV. The focal spot area of the laser is $\sim 0.1\,{\rm mm}^2$ with a typical

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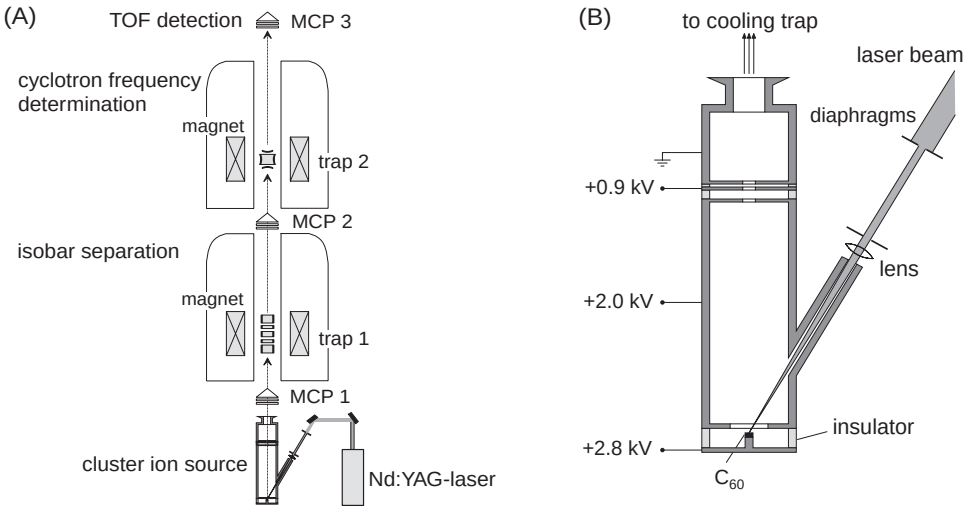

Fig. 1. (A) Schematic overview of the experimental apparatus; (B) detail of the carbon cluster ion source.

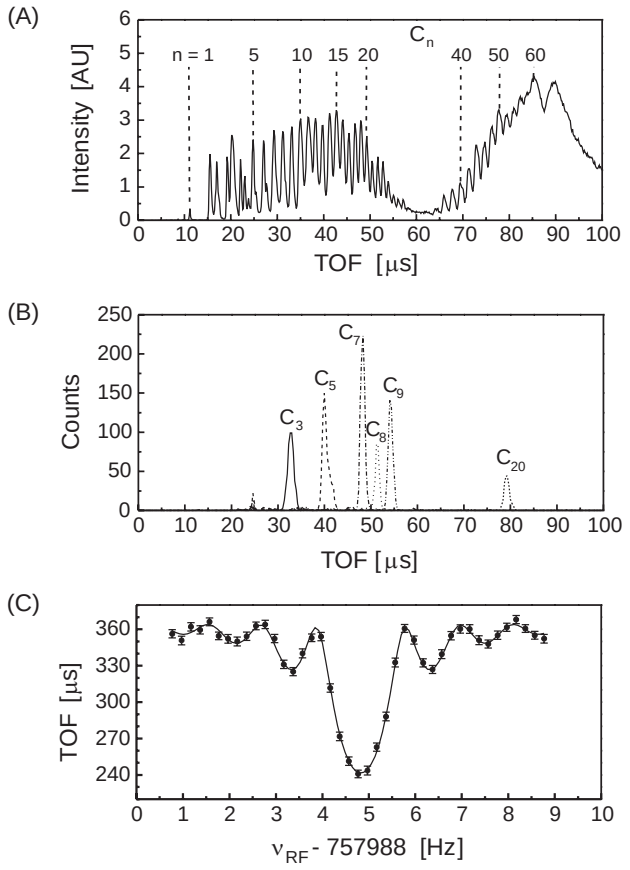

Fig. 2. (A) Time-of-flight (TOF) mass spectrum of carbon cluster ions using nanosecond laser desorption of C_{60} at 532 nm and $\sim 10\,\mathrm{J/cm^2}$ laser fluence. (B) Superposition of six TOF spectra of different carbon cluster ions after 100 ms cooling time and mass separation. (C) Cyclotron resonance curve of C_{10}^+ with a fit of the theoretically expected line shape to the data points.

pulse energy of 10 mJ at 532 nm. Details of the carbon cluster ion source are shown in fig. 1(B). Desorption and ionization of C_{60} sets in at a laser fluence of $\sim 5\,\mathrm{J/cm^2}$. At higher fluences the intensity of C_{60}^+ increases strongly and small amounts of lighter carbon cluster ions are produced by fragmentation. A typical time-of-flight mass spectrum on MCP 1 at a laser fluence of $\sim 10\,\mathrm{J/cm^2}$ is shown in fig. 2(A). The main features are the high-mass, even-carbon-numbered fragments (fullerene fragments C_{34}–C_{58}), the low-mass fragments $\leq C_{27}$, and the gap between C_{27} and C_{34}.

The cluster ions are injected into the cylindrical first Penning trap, where they are stored and purified from contaminant ions. To this end, a mass selective buffer gas cooling technique with He as buffer gas and an azimuthal radio-frequency (RF) field are applied [13]. A resolving power of about $1 \cdot 10^5$ can be achieved [11]. The ions are then extracted and transferred to the second trap. Time-of-flight signals of mass-separated carbon cluster ions ejected after 100 ms cooling time are shown in fig. 2(B), recorded with an insertable MCP detector located between both traps (MCP 2).

This second trap is a precision Penning trap placed in the homogeneous field of a 5.9 T superconducting magnet and is used as a mass spectrometer [8]. A mass measurement consists of a series of trial excitations of the cyclotron motion, each excitation followed by axial ejection of the ions and time-of-flight analysis of the absorbed energy [14]. The determination of the time of flight on MCP 3 as a function of the frequency ν_{RF} of the applied azimuthal RF field leads, due to the increase of energy in resonance, to a characteristic cyclotron resonance curve [15]. This is shown in fig. 2(C) for the example of C_{10}^+. The mass of an ion is obtained by the comparison of its cyclotron frequency $\omega_{\mathrm{c}} = q/m \cdot B$ (m: mass; q: charge; B: magnetic-field strength) with the cyclotron frequency of a known reference mass.

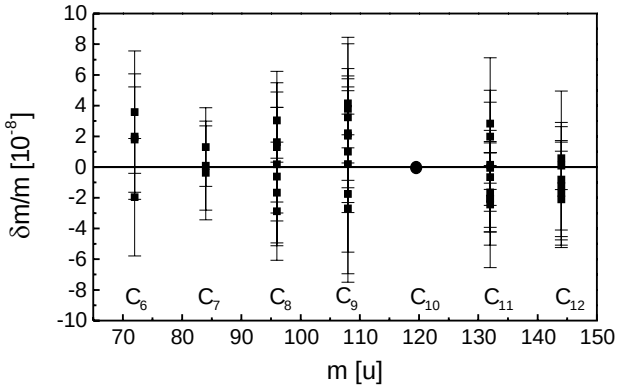

Fig. 3. Relative deviation of the measured carbon cluster mass values (squares) from the known mass values with C_{10}^+ (circle) as mass reference.

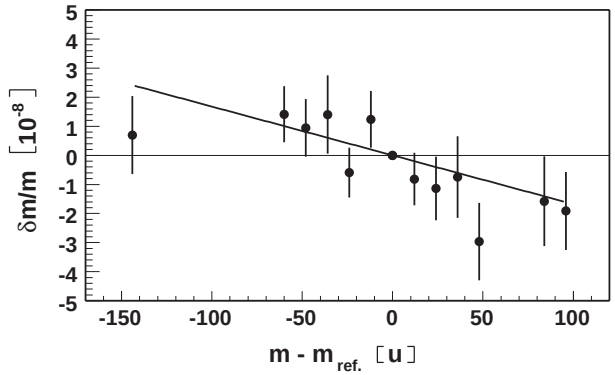

Fig. 4. Relative deviation of the measured cluster mass values from the known mass values for all cross-reference measurements as a function of the mass difference between the investigated and the reference ion.

3 Measurements

A cyclotron frequency is obtained by fitting the theoretically expected line shape [15] of a cyclotron resonance curve to the measured resonance curve as shown in fig. 2(C). To convert the measured cyclotron frequency into a mass value, the magnetic-field strength has to be known. It is calibrated by the cyclotron frequency of a reference cluster ion which is determined before and after each mass measurement. Hence, every second measurement is a reference measurement to minimize the effects of the magnetic-field fluctuations. Here, for the first series of the measurements C_{10}^+ and for the second and third series of the measurements C_{12}^+ and C_{20}^+ were chosen as the reference cluster ion. Each cyclotron resonance measurement with ~ 3000 detected ions lasted 15-60 minutes, depending on the production rate of the cluster ions and the excitation time ($T_{\mathrm{RF}} = 0.9$–$3.0\,\mathrm{s}$) used in the precision trap. The resonance width $\Delta\nu_{\mathrm{FWHM}}$, which is approximately equal to the inverse of the excitation time, determines the resolving power $R = \nu_{\mathrm{c}}/\Delta\nu_{\mathrm{FWHM}}$ of the spectrometer. For the carbon cluster mass measurements reported here the ISOLTRAP spectrometer was operated with a resolving power of $R = 0.6$–$3 \cdot 10^6$, which allows mass determination within a statistical mass accuracy $\delta m/m$ of a few 10^{-8} in each single measurement.

4 Results

For all singly charged carbon clusters C_n^+ with $2 \leq n \leq 20$ we were able to measure the cyclotron frequencies, as shown explicitly in the example of C_{10}^+ given in fig. 2(C). For carbon clusters with $n > 20$ the production rate was too low to measure the cyclotron frequency within one hour. Thus, nearly the whole mass spectrum of the chart of nuclei can be covered up to the mass number $A = 240$ and it is always possible to choose a reference carbon cluster ion with a mass number close to that ion under investigation. The deviation of the determined mass values of the carbon clusters C_n under investigation from the known mass value is plotted as a function of the mass in fig. 3. For this set of measurements C_{10}^+ was used as reference to calibrate the magnetic field. In all cases the relative deviation is less than $4 \cdot 10^{-8}$. This scatter is mainly caused by magnetic-field fluctuations. The mean uncertainty with 5-10 measurements per cluster size is $1.2 \cdot 10^{-8}$. Two more sets of measurements were performed with C_{12}^+ and C_{20}^+ as reference, so that an overall mass range of $\sim 250\,\mathrm{u}$ was covered. All carbon cluster cross-reference measurements are combined in fig. 4. The error bars represent the weighted mean errors from the single measurements. The fitted straight line does not exclude a mass-dependent systematic effect. The observed mean deviation is $1.7(0.6) \cdot 10^{-10}/\,\mathrm{u} \cdot (m - m_{\mathrm{ref}})$. The origins of this mass-dependent systematic error are probably still uncorrected imperfections in the trapping electric field or deviations from the ideal trap geometry [8].

5 Conclusions and outlook

The presented results show that carbon clusters can easily be used with benefit as mass references for absolute mass measurements with Penning-trap systems. This was demonstrated for the first time. The mass-dependent systematic shift per mass unit difference between the investigated and the reference ion was determined to be $1.7(0.6) \cdot 10^{-10}/\,\mathrm{u}$, which is more than an order of magnitude lower than the previously estimated upper limit of $2 \cdot 10^{-9}/\,\mathrm{u}$ [9]. Due to the fact that even with carbon cluster ions composed only of the most abundant isotope ^{12}C it is always possible to choose a reference mass which is at most six mass units away from the ion under investigation, the mass-dependent systematic error of our setup can be practically neglected. A correction of this mass-dependent systematic error is also possible. The limit of mass accuracy was determined to be $\delta m/m = 1.2 \cdot 10^{-8}$, again one order of magnitude better than the previously estimated limit of mass accuracy [9]. To increase the precision of ISOLTRAP further improvements are under way, as for example the installation of a magnetic-field stabilization system.

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