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Laser desorption/ionization cluster studies for calibration in mass spectrometry

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Abstract. Precise mass calibration is mandatory in many fields of mass spectrometry. We have performed laser desorption/ionization cluster studies with a MALDI-TOF mass spectrometer on gold and fullerene targets to produce atomic clusters. These investigations demonstrate that clusters are ideally suited for this purpose. Pulsed N_2-laser and Nd:YAG-laser ablation was used to produce positively as well as negatively charged clusters. Earlier observations of dianionic metal clusters are confirmed. First results from the tandem Penning trap mass spectrometer ISOLTRAP using carbon clusters as mass references show how carbon clusters can be applied to precision mass spectrometry by providing absolute mass standards.

PACS. 07.75.+h Mass spectrometers – 32.10.Bi Atomic masses, mass spectra, abundances, and isotopes – 36.40.Wa Charged clusters – 82.80.Ms Mass spectrometry (including SIMS, multiphoton ionization and resonance ionization mass spectrometry, MALDI)

1 Introduction

Atomic clusters are the mass reference of choice for calibration purposes in mass spectrometry. In the following we consider two applications in very different fields, accurate mass spectrometry of short-lived nuclei and conventional mass spectrometry of heavy molecules.

The nuclear mass is among the most fundamental values of any atomic nucleus. After the "mass defect" was observed it was soon realized that it involves the binding energy of the nuclear constituents and is an utmost indicator of the stability of the nucleus. Since the atomic mass standard u is defined as 1/12 of the mass of ^{12}C [1] carbon clusters provide the best reference for accurate atomic mass measurements.

ISOLTRAP has measured about 200 masses with a relative accuracy $\delta m/m$ below 10^{-7} by the determination of the cyclotron frequencies of ions confined in a Penning trap. Recently, the possibility to apply carbon clusters as mass references in accurate high-precision on-line mass measurements with the tandem Penning trap mass spectrometer ISOLTRAP [2,3] at ISOLDE/CERN [4] at Geneva has been demonstrated [5]. To convert the measured cyclotron frequency into a mass value, the magnetic field strength has to be known. In the past it has been calibrated by the cyclotron frequency of a reference ion with a very well-known mass, *e.g.* ^{85}Rb or ^{133}Cs. Now a new magnetic field calibration method by use of singly charged carbon clusters C_n^+ (n up to 20) is in use. There are several advantages of the recent development: any uncertainty of the reference mass is eliminated by definition while systematic deviations from the true mass value increase with the difference between the measured and the reference mass [6]. The reference masses are at most six mass units away from the nuclide of interest. And, as a further advantage, cluster in general allow by use of cross-reference measurements internal checks against systematic errors. They are thus similar to multiply charged atomic ions, but in a different mass-over-charge range.

Atomic clusters may also be a useful tool in conventional analytic mass spectrometry, *e.g.* of heavy organic molecules. In this case clusters of a heavy monoisomeric element, such as gold, are of particular interest. Here, the analyte of interest would be mixed with a gold complex, placed on a probe and investigated with the mass spectrometer as an internal standard, *i.e.* measured simultaneously with the analyte. This technique of sample preparation may allow for very precise and fast molecular weight determination of organic molecular ions. Alternatively, gold samples may be deposited next to the analyte of interest in order to quickly switch between mass measurements of the analyte and the gold cluster reference without change of the experimental conditions. As reported below, first results on negative gold clusters Au_n^- with n up to 55 were obtained with a conventional

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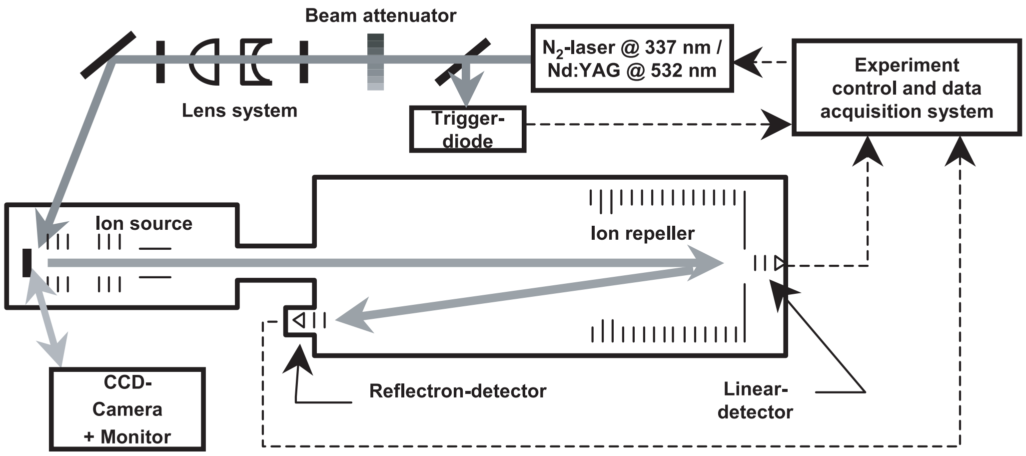

Fig. 1. Overview sketch of the experimental setup for MALDI-TOF mass spectrometry. Either a second harmonic of a Nd:YAG laser beam at 532 nm or a N_2 laser at 337 nm was used to achieve laser desorption and ionization. The apparatus can be used in the linear as well as in the reflectron modus.

apparatus for matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry [7].

2 Experimental setup and procedure

In the context of the applications described above we have studied the cluster production by use of a MALDI-TOF apparatus (Bruker Analytical Systems, Model: REFLEX III) at the institute of Physics of the University of Mainz. The experimental setup is schematically shown in Figure 1. Desorption and ionization and in the case of C_{60} fragmentation is induced either by a N_2 laser at $\lambda = 337$ nm or by a Nd:YAG laser at $\lambda = 532$ nm with pulse lengths of a few ns. The excitation occurs over a region of 10^4 μm^2 and laser irradiances are typically in the range of 10^6–10^7 W/cm^2. Both the linear and the reflectron mode were used depending on the resolution required.

A sketch of the ISOLTRAP setup is shown in Figure 2. Ions coming from the on-line isotope separator ISOLDE are injected into a first cylindrical Penning trap after the preparation in a radio-frequency quadrupole trap (not shown in the figure). The first Penning trap is used for the cooling and isobaric cleaning of the ion bunches.

The actual mass determination is carried out in a second Penning trap. To this end, the cyclotron frequency ω_c of an ion with charge q and unknown mass m in a magnetic field of magnitude B: $\nu_c = (1/2\pi)(q/m)B$ is determined [2] by ejecting the ion and measuring the time-of-flight to the micro-channel-plate (MCP) detector MCP5 as a function of the frequency ν_{RF} of the applied azimuthal quadrupolar radio-frequency (RF) field [8]. For the calibration of the magnetic field the cyclotron frequency of a stable ion with well-known mass, the so-called reference ion, is measured. To produce carbon cluster ions for mass references the frequency-doubled beam of a Nd:YAG laser is focused on a C_{60} pellet. The charged fullerene fragments C_n^+ are then electrostatically accelerated to 2.8 keV and transferred towards the preparation Penning trap. From this point on, the measurement procedure is identical to that described above for the short-lived ions delivered from ISOLDE.

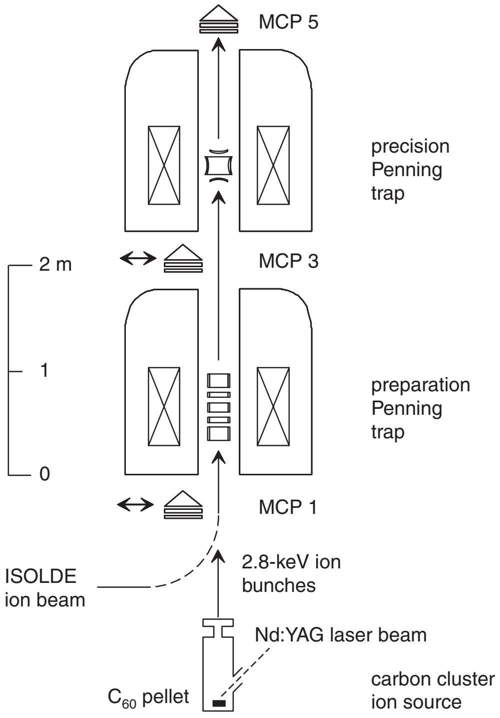

Fig. 2. Schematic drawing of the mass spectrometer ISOLTRAP including the preparation and precision Penning trap, as well as the new carbon cluster ion source. The latter is mounted about 2 m below the preparation Penning trap. To monitor the ion transfer and to record the time-of-flight resonance for the determination of the cyclotron frequency micro-channel-plate (MCP) detectors are used.

3 Results and discussion

Several experiments were performed at the MALDI-TOF apparatus at Mainz. When a gold foil is used as a target spectra such as the one shown in Figure 3a can be obtained. The Au_n^- cluster span a range from $n = 1$ to above $n = 50$. Hence, gold clusters can be used as mass markers up to 10 000 atomic mass units equally spaced by ≈ 197 u. In addition to this demonstration of pulsed laser ablation of gold clusters there are some observations worth

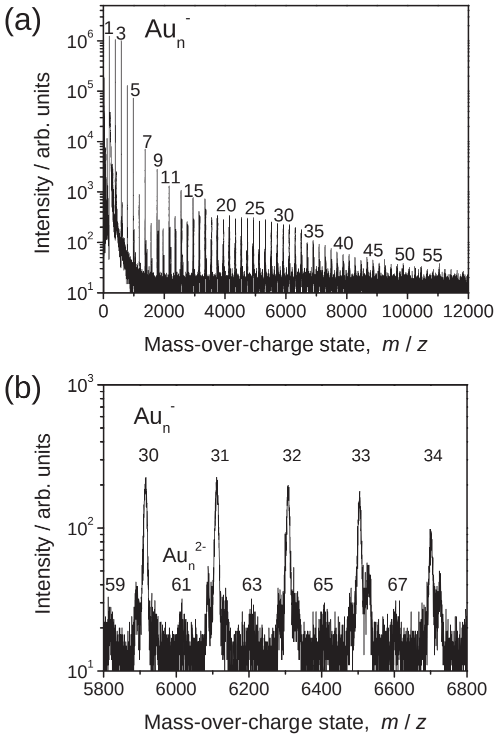

Fig. 3. Time-of-flight spectrum of Au_n^- clusters after N_2-laser desorption/photoionization at 337 nm with a laser fluence of 1 J/cm^2. In (a) the total spectrum from $n = 1$ up to $n = 55$ is shown, while (b) shows an enlarged part of (a). The spectrum was obtained by integrating 1000 individual laser shots.

mentioning: in the size range of up to ≈ 20 atoms there is a strong odd-even effect in the relative intensities of the monoanionic and monocationic (not shown) gold clusters. This feature is well-known from earlier gold cluster mass spectra [9,10] and decay studies [11,12]. In addition, dianionic gold clusters are observed. As shown in Figure 3b in the region around $m/z = 6000$ signals of odd-size Au_n^{2-} clusters (with $n = 60$) appear between the larger signals of the monoanions. This observation confirms recent reports by Stoermer *et al.* [13] who also obtained dianionic metal clusters by laser irradiation of a target in high vacuum. Note that the intensities of the Au_n^{2-} clusters are similar if not higher than the intensities of the monoanionic clusters of the same size. Further studies concerning pulsed N_2 and Nd:YAG laser ablation of various metal targets (Ag, Pb, Pt) are underway.

For the production of carbon clusters $C_n^{+/-}$ either a fullerene target or a Sigradur® target was tested. The latter (purchased from HTW GmbH, Thierhaupten, Germany) consists of pure carbon. It has ceramic properties and is obtained by thermal decomposition of a synthetic resin. Figure 4 shows a mass spectrum of C_n^+-clusters with n up to 25 obtained with a Sigradur® target. Even at a low laser fluence of 0.1 J/cm^2 the production rate for clusters $3 \leq n \leq 11$ was high enough to saturate the micro-channel-plate detector. The intensity of the small cluster sizes with $n < 5$ was several orders of magnitude higher in the case of Sigradur® than for a C_{60} target.

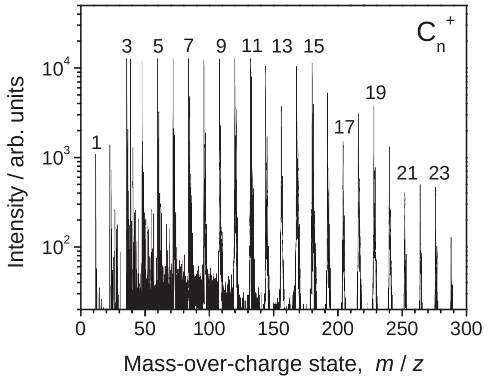

Fig. 4. Time-of-flight spectrum of C_n^+ clusters after N_2-laser desorption/photoionization at 337 nm with a laser fluence of 0.1 J/cm^2 (Sigradur® target). The spectrum was obtained by integrating 10 individual laser shots.

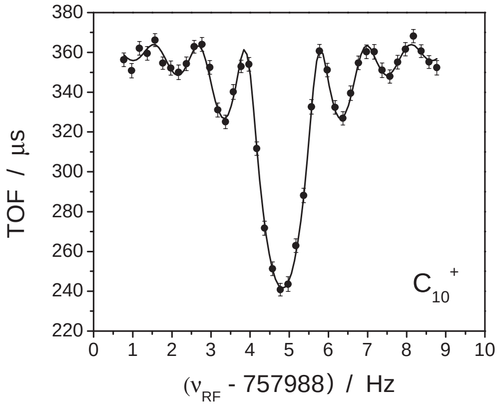

Fig. 5. Cyclotron resonance curve of C_{10}^+. The solid line is a fit of the expected line shape to the data points [14]. The excitation time was 1.2 s, the FWHM is ≈ 1 Hz.

In parallel with these preliminary studies with gold and carbon clusters to determine *e.g.* the cluster production as a function of laser power carbon clusters were already applied as mass references at ISOLTRAP. As one of the major questions it was studied, whether carbon cluster ions can be stored for several hundred milliseconds in the precision Penning trap in order to measure their cyclotron frequency. It was possible to determine the cyclotron frequency of carbon cluster ions C_n^+ with n up to 20. As an example Figure 5 shows a cyclotron resonance of C_{10}^+. The solid line is a fit of the expected line shape [14] to the data points. The duration of the quadrupolar excitation was varied between 900 ms and 3 s, corresponding to resolving powers $\Delta\nu/\nu$ (FWHM) between 6×10^5 and 3×10^6.

To determine the limit of mass accuracy which could be achieved with ISOLTRAP more than 100 cross-reference mass measurements, *i.e.* experiments where carbon clusters were used both as the reference ion and as the ion of interest, were carried out [15]. The deviation of the measured mass from the true known value yielded in a mass accuracy limit of ISOLTRAP measurements of

$\delta m/m < 8 \times 10^{-9}$, which is about an order of magnitude smaller than previously estimated [2].

4 Conclusion and outlook

The trapping and excitation of carbon cluster ions is a prerequisite for higher-precision and absolute mass measurements on short-lived nuclides by ISOLTRAP. Laser desorption/ionization is a means to produce these clusters.

Further investigations indicate that Sigradur® may be better suited for the production of small carbon clusters $C_{n\leq 20}$ and thus may replace the current fullerene target used at ISOLTRAP.

In addition, it can be expected that the use of atomic clusters will continue to be an important aspect of the development and application of mass spectrometry.

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