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The ILIAS project for selective isobar suppression by laser photodetachment

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Abstract

Laser photodetachment is the process when the extra electron of a negative ion is removed by means of laser radiation. This can happen only if the photon energy is larger than the electron affinity of the ion. The process can be used in mass spectrometry to selectively suppress unwanted isobars, provided that the electron affinity of the unwanted isobar is lower than that of the isobar under investigation.

At the Ion Laser InterAction Setup (ILIAS) at the University of Vienna laser photodetachment of negative atomic and molecular ions is studied and its applicability for selective isobar suppression in accelerator mass spectrometry (AMS) is evaluated. The setup provides mass separated beams of negative ions with energies up to 30 keV. Negative ions are produced in a Middleton type cesium sputter ion source, mass selected and overlapped with a strong continuous wave laser beam. In order to extend the interaction time of ions and laser, the ion beam is decelerated to thermal energies in a gas-filled radio frequency quadrupole cooler. For an appropriate choice of the photon energy, unwanted isobars are neutralized while the isobar of interest is unaffected and remains negatively charged.

A description of the ILIAS setup and results from the commissioning phase of the RFQ cooler are presented. Up to 8% ion beam transmission could be achieved after a recent redesign of the extraction system. Furthermore first results of photodetachment experiments of $^{63}Cu^-$ within the RFQ cooler are presented.

Introduction

Accelerator mass spectrometry (AMS) is a highly sensitive tool for the detection of isotopic ratios at the ultra-trace level [1], but the method is limited for certain isotopes by the presence of interfering isobars (i.e. ions with almost the same mass as the ion of interest). Molecular isobars can be efficiently removed by dissociation in the stripping process in a tandem accelerator. Atomic isobars, i.e. atoms with same mass number, are more difficult to separate. There are some fortunate cases (notably ^{14}C, ^{26}Al, ^{129}I) where the stable isobars do not form negative ions, and are thus efficiently suppressed by using a source for negative ions. In some cases the use of special negative molecular ions helps to suppress interfering isobars by orders of magnitude (e.g. suppression of the isobar $^{41}KH_3^-$ against $^{41}CaH_3^-$ or $^{182}WF_5^-$ against $^{182}HfF_5^-$). The generally applicable techniques for discrimination against isobars in AMS make use of differences in energy loss in matter to discriminate isobars. The efficiency depends strongly on the $\Delta Z/Z$ and the available particle energy, which is in the range of some MeV for typical AMS facilities. It is therefore limited to light ions. ^{60}Fe is the heaviest radionuclide that can be separated from its stable isobar ^{60}Ni ($\Delta Z/Z=1/14$) via their different energy loss in matter and is measured routinely at some laboratories, while ^{53}Mn can be separated from ^{53}Cr ($\Delta Z/Z=1/24$) only at two facilities worldwide [2,3]. Despite explorative effort, the separation of heavier radionuclides at ultra trace levels from their isobars by means of energy loss in matter has not yet been achieved.

Interfering isobars can be efficiently suppressed by chemical processing because the chemical properties of neighboring elements are usually quite different. However, this holds only for element ratios of about six orders of magnitude. Once the interfering isobar is reduced to the ppm level (10^{-6}), further chemical processing introduces as much contamination as it removes.

In order to extend the range of radionuclides accessible to AMS, an additional element-selective filter can be introduced to the low energy part of an AMS machine where one usually deals with negative ions. Two promising methods are currently under investigation: chemical reactions of the ions with a suitable gas in a reaction cell and laser photodetachment in a gas-filled RF-quadrupole. Information on isobar suppression by anion-gas reactions in reaction cells and their application in AMS can be found e.g. in [4,5]. This work deals with the latter case, i.e. the interaction of anions with laser photons. The decisive process is laser photodetachment, which is the removal of the extra electron of an anion due to the absorption of a photon.

In the fragile quantum system of a negatively charged ion, the extra electron is loosely bound to the neutral core atom or molecule. In the interaction of the negative ion with a photon the electron can be detached if the photon energy exceeds the electron affinity of the respective atom or molecule. This is a non-resonant threshold process, which is described in the vicinity of the threshold by the Wigner law [6]:

$$\sigma(E) \propto (E - EA)^{l+1/2} \qquad \text{for } E \geq EA$$

and

$$\sigma(E) = 0 \qquad \text{for } E < EA$$

Here $\sigma(E)$ is the cross section, E represents the photon energy, EA is the electron affinity and l the angular momentum of the outgoing electron. The electron affinity depends solely on the electronic structure of the atom or molecule and consequently on the nuclear charge. Different isotopes (and molecules with different isotopic compositions) therefore possess the same electron affinity - small isotope shifts below 1 meV [7] can be neglected for the purpose of this work. If the electron affinity of the unwanted isobar is lower than the electron affinity of the ion of interest, the photon wavelength can be chosen such that only the interfering species is neutralized while the ion of interest remains negatively charged (Figure 1).

Proof of principle of this so-called optical filtering was shown in demonstration experiments for the cases $^{36}Cl–^{36}S$ [8] and $^{59}Ni–^{59}Co$ [9]. However, the reported isobar suppression was far from being useful for AMS measurements. The measured photodetachment cross sections are in the order of 10^{-17} cm^2. As practically 100% of the interfering ions have to be removed, interaction times between the ions and the laser beam in the order of milliseconds have to be achieved given the currently available laser power. First attempts towards extending the interaction time were made by Liu *et al.* [10-13] by slowing down the ions in a gas-filled radio frequency ion beam cooler. By reducing the ion energy in the RFQ close to thermal energies, the interaction time between the ions and the photons was increased while maintaining a manageable interaction length. The cooled ions were confined to a small volume around the longitudinal axis, which resulted in an increased overlap between the laser and ion beams. In this way a suppression of the unwanted species of more than four orders of magnitude was reported [14].

For the application of our proposed scheme of selective isobar suppression some isobar systems with AMS relevance have already been identified. The atomic ion $^{14}C^-$ and its two molecular isobars $^{13}CH^-$ and $^{12}CH_2^-$ form a simple system to study the behavior and separation of molecular negative ions. Furthermore, all electron affinities of this system are known (C^-: 1.262118(20) eV corresponding to a wavelength of 982.3494(16) nm, CH^-: 1.238(8) eV or 1001(6) nm, CH_2^-: 0.652(6) eV or 1901(17) nm [15]). A second promising candidate is the separation of ^{60}Fe from the stable isotope ^{60}Ni. In this system the electron affinities of the two anions are not favorable (Fe^-: 0.151(3) eV, Ni^-: 1.15716(12) eV [15]), but if one uses the molecular hydrides this is reversed (FeH^-: 0.934(11) eV, NiH^-: 0.481(7) eV [15]). The use of hydrides for ion beam injection during ^{60}Fe AMS has already been demonstrated [16]. The ultimate goal for the application of our scheme is the separation of ^{182}Hf from the stable isobar ^{182}W. It has been shown in earlier studies [17-20] that ^{182}W can

be suppressed in the ion source by extracting the molecules $^{182}HfF_5^-$ and $^{182}WF_5^-$. Electron affinities of these molecules are currently unknown. However, studies performed at the University of Gothenburg have shown that a suppression by laser photodetachment should be possible using a suitable laser at the fourth harmonic wavelength of a Nd:YAQ laser at 266 nm [21].

Methods

In 2010 the ILIAS (Ion Laser InterAction Setup) was initiated at the Isotope Research group of the Faculty of Physics at the University of Vienna. A single cathode SNICS II cesium sputter ion source from National Electrostatics Corporation (NEC) provides atomic and molecular negative ion beams with energies up to 30 keV. A 90-degree double focusing magnet follows the ion source to provide mass selected beams for injection into the RFQ cooler. The cooler consists of four rods in a quadrupole configuration. Radio frequency is applied to these rods to confine the ions in the radial direction. The cooler device can be set to high voltage (up to 30 kV) to electrostatically decelerate the ions. A lens system is installed to focus the ions into the quadrupole structure, which is filled with helium buffer gas. By collisions of the ions with the gas atoms, the ion motion is being damped and the ion energy is reduced to thermal energies. Collisional detachment of the negative ions in the cooler is prevented as long as the residual collisional energy between the ion and the helium atom is lower than the electron affinity of the ion. Slightly tilted electrodes at DC voltage are mounted between the quadrupole rods, to produce a small longitudinal guiding field that drags the ions slowly through the cooler. Inside the cooler the ions are overlapped with a continuous wave laser beam for photodetachment. After passing the cooler the ions are accelerated to a kinetic energy of up to 30 keV. The ions pass a 4-way quadrupole switch where they are deflected by 90 degrees. After a short straight section a second electrostatic bender is used to deflect the ions again by 90 degrees. In the straight section between the two deflectors the ions can be

overlapped again with a laser beam either in a collinear or in a crossed-beam setup. Any neutrals produced by laser photodetachment along the second overlap can be detected by the neutral particle detector, which is installed behind the second deflector. This detector consists of a conductively coated glass plate where the impinging neutral particles produce secondary electrons. These electrons are guided by an electric field to a Channeltron Electron Multiplier (CEM). A more thorough description of this scheme and the neutral particle detector can be found in [22,23]. A sketch of the whole setup is shown in Figure 2.

The vacuum system is an important part of the RFQ cooler. The electrode structure is mounted in a tube, which is filled with the helium buffer gas used for collisional cooling. The gas pressure in this region typically is 0.1 mbar. The neutralization of the negatively charged ions in the quadrupole region is of minor concern, as the center of mass energy of the collisions of the ions with the buffer gas atoms is small compared to the electron affinity of the respective atom. However, outside the cooler where the ions move with keV energies, a good vacuum is of importance in order to limit the losses due to collisional detachment of the negative ions. Critical points in this respect are the deceleration and acceleration sections at the entrance and exit of the cooler where the buffer gas leaks out from the cooler tube through the entrance and exit apertures. In our design, two aperture lenses are used to focus the ions into the 3 mm diameter entrance aperture. The size of this aperture is a compromise between an efficient injection of the ions into the cooler and a reduction of the buffer gas leakage to a minimum. The exit of the cooler imposes a similar design with a 3 mm exit aperture and two re-acceleration lenses. A system of three turbomolecular pumps provides the required pumping power. One large pump with 1300 l/s pumping speed is installed at the central part of the cooler and two pumps with 650 l/s each are mounted at the entrance and exit regions. In this way vacuum levels below 10^{-6} mbar can be achieved in the entrance and exit sections for

a helium buffer gas pressure of 0.1 mbar in the active cooler region. The calculated values together with actual measurements are given in Figure 3.

The radio-frequency quadrupole consists of four circular rods of 10 mm diameter and a length of 80 cm, made from stainless steel. The radius r_0 of the inscribed circle of the four rods is 4.37 mm. The rods are held in place by specially designed ceramic spacers made of Macor®. The guiding electrodes are also fixed to these ceramic spacers.

The radiofrequency for the quadrupole electrodes is delivered by a 400 W solid-state RF amplifier model 1040L from Electronics & Innovation, Ltd. This device is able to produce RF power in the frequency range of 10 kHz to 5 MHz and does not need a matched load. The quadrupole electrodes represent mainly a capacitive load of about 300 pF, which can efficiently be driven by this amplifier. The RF input to this amplifier is provided by a function generator from Stanford Research Systems, model DS345.

There are two laser systems available: a 10 W fiber coupled diode laser with a nominal wavelength of 984 nm (CNI Laser 9800-10000-F-AC) and a Coherent Verdi V18 with a peak output power of 18 W at a wavelength of 532 nm. The laser beam is tuned through the entrance and exit apertures by maximizing the output power measured after the cooler. Up to 12 W of continuous wave laser beam (532 nm) were transmitted through the cooler system.

Measurements and Results

Laser photodetachment of C^- has been performed in a crossed beam configuration in order to test the neutral particle detector. A good overlap between the ion beam and the laser beam was achieved by inserting a stainless steel cube with two crossing holes of 3 mm diameter into the beam line. The laser beam was tuned through the cube by measuring the laser intensity leaving the vacuum chamber with a power meter whereas the ion beam was tuned by measuring the beam current with a Faraday cup after the interaction region. The advantage of the crossed beam configuration compared to a collinear configuration is that there is no Doppler shift. Identification of an atomic ion species is possible by scanning the photon

energy along the threshold region for the photodetachment process and thereby determining the electron affinity of the atom. For the photodetachment measurement the 10 W diode laser with a nominal wavelength of 984 nm was used. By varying the diode temperature, the output wavelength of the laser system can be changed by 16 nm. In this way a scan over the onset of the photodetachment threshold of C^- was performed. The experimental data in the threshold region together with a fit to the Wigner law for an s-electron is given in Figure 4. The electron affinity of C^- measured with our setup shows a reasonable agreement with the published value of 1.262118(20) eV [24], bearing in mind that our measurement was limited to four data points.

For performance tests with the cooler $^{63}Cu^-$ was extracted from a pure copper cathode in the ion source. The electron affinity of copper is 1.23578(4) [24] corresponding to a wavelength of 1003.29 nm. The corresponding anion can easily be detached by the photons of the 532 nm laser. During first experiments with the ion beam cooler presented here, an adequate extraction system was not yet installed. Due to a repulsive potential in the exit region, any cooled ion beam could not be extracted from the RFQ. However, a metallic sleeve was mounted onto a ceramic spacer at the end of the quadrupole structure (depicted in Figure 2) and the negative ion current hitting this sleeve could be measured with a low-noise current preamplifier (Stanford Research Systems model SR570). Although this arrangement was an ad-hoc solution due to the incomplete ion extraction system at that time, it turned out to have the advantage that it allowed studying the cooling and detachment process independently from extraction.

Figure 5 shows a typical photodetachment measurement at a certain buffer gas pressure. The laser beam is switched on and off periodically to account for variations of the ion beam current out of the ion source. The dependence on the helium buffer gas pressure is depicted in Figure 6. When increasing the pressure, the ions are stopped earlier in the buffer gas and thus

have a longer residence time in the cooler. Additionally the cooling effect is stronger leading to a closer confinement of the ions to the longitudinal axis. Both effects increase the ion-laser interaction time and thus the probability for photodetachment. The trend towards higher photodetachment efficiency with increasing buffer gas pressure is clearly reflected in the experimental data. The energy of the ions when entering the quadrupole region was about 150 eV.

After removal of the insulator spacer with the metal sleeve and completion of the extraction section including all lenses, it is now possible to extract cooled ion beams from the RFQ. Very recently, an encouraging ion beam transmissions of 8% through the cooler system could be measured when injecting currents of 1 μA $^{63}Cu^-$.

Conclusions

In first experiments we were able to show that photodetachment of negative ions inside a gas-filled radio frequency quadrupole with a high-power continuous wave laser beam is a promising technique for isobar suppression. A neutralization of more than 98% of the injected ions has been demonstrated. This value is limited by the noise in detection, and we expect substantial improvement with redesigned extraction optics. So far the extraction of cooled ion beams was possible with a transmission of up to 8%. Ongoing modifications of the injection and extraction lens systems are expected to further improve this value.

After solving these technical issues on the test bench, the ILIAS is going to be installed on the low-energy side of the AMS facility VERA.

The demonstration of efficient isobaric suppression could lead to a whole new world of isotopes available for AMS measurements which are currently inaccessible even for machines of large terminal voltage due to the presence of stable atomic isobars.

Acknowledgments

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List of figure captions

Figure 1. The photodetachment cross-section of the isotope of interest and an unwanted isobar is shown. By choosing a suitable photon energy it is possible to only photodetach the interfering isobar while leaving the ion of interest unaffected.

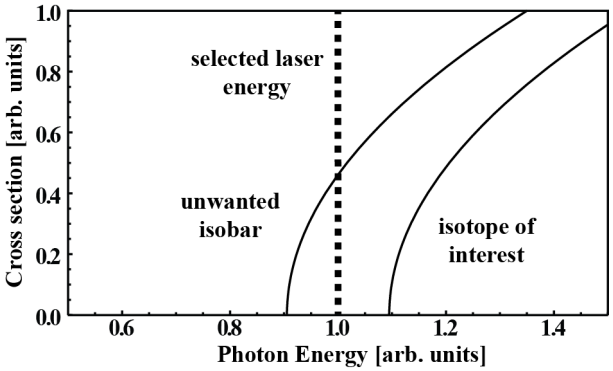
Figure 2. Layout of the ILIAS facility at the University of Vienna.

Figure 3. Vacuum system of the RFQ cooler. The pressure values in bold are the design values and the numbers in italics are the actual measured values.

Figure 4. Photodetachment cross-section around threshold for the laser photodetachment of C^-. The cross-haired points are the measurement points together with the uncertainty. The solid line is a fit according to the Wigner law for an outgoing s-electron.

Figure 5. Typical photodetachment measurement of $^{63}Cu^-$ with a 532 nm laser beam at 12 W laser power at a helium buffer gas pressure of 0.03 mbar. The energy of the ions entering the quadrupole was about 150 eV. The laser beam was continuously switched on and off during the measurement. The vertical axis shows the ion current measured on the extraction sleeve.

Figure 6. Photodetachment of $^{63}Cu^-$ with a 532 nm laser beam at 12 W laser power at different helium buffer gas pressures. The vertical axis shows the ion current measured on the extraction sleeve inside the quadrupole. The increasing photodetachment efficiency with increasing buffer gas pressure is clearly visible. Above 0.07 mbar nearly complete neutralization of the ions could be achieved.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0.0
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Photon Energy [arb. units]
selected laser energy
unwanted isobar
isotope of interest

Figure 1

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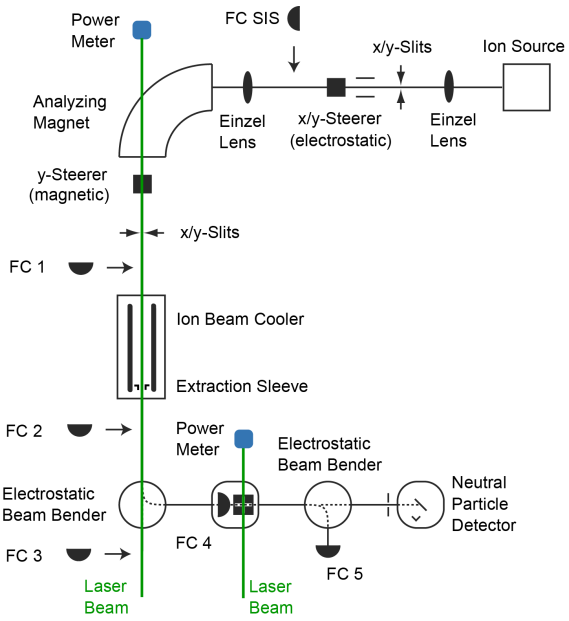
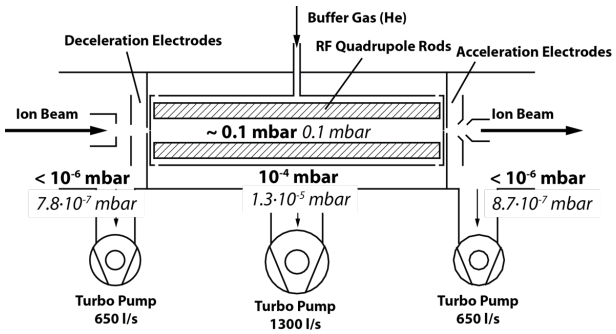


Figure 2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10-4 mbar
1.3·10-5 mbar
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Turbo Pump
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Turbo Pump
650 l/s

Figure 3

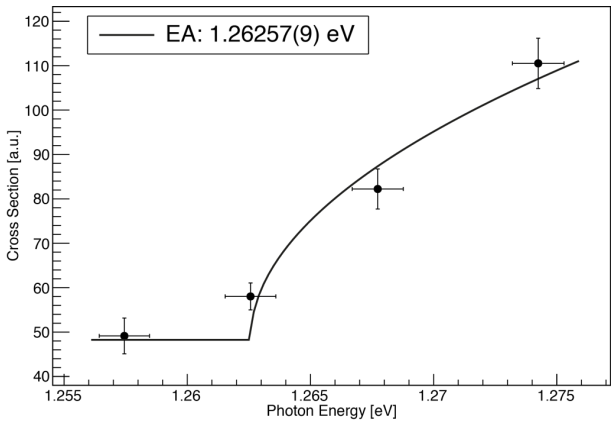
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Figure 4

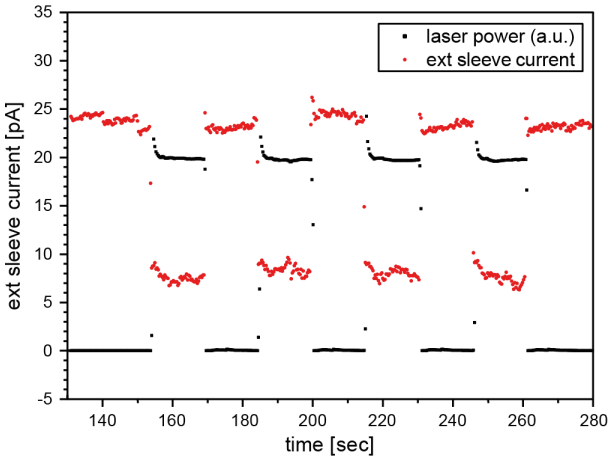
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Figure 5

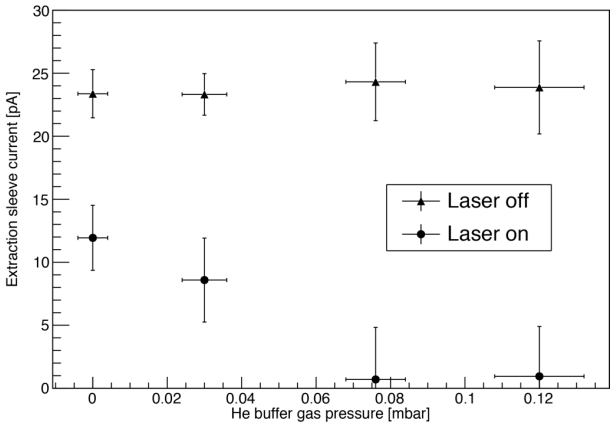
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Figure 6