Laser resonance ionization for ultra-trace analysis on long-lived radioactive isotopes

CHRISTOPHER GEPPERT[1,*] and KLAUS D A WENDT[2]

[1]Institut für Kernchemie, Johannes Gutenberg-Universität, Fritz-Straßmann-Weg 2,
D-55128 Mainz, Germany
[2]Institut für Physik, Johannes Gutenberg-Universität, Staudingerweg 7,
D-55099 Mainz, Germany
*Corresponding author. E-mail: C.Geppert@gsi.de

Abstract. Benefiting from the continuous laser developments, resonance ionization can be applied for a variety of experiments on radioactive isotopes, e.g. as a laser ion source for producing pure beams of short-lived isotopes at on-line facilities. In this paper the application of a compact set-up for resonance ionization mass spectrometry for ultra-trace analysis of the long-lived isotope Ca-41 is described. With this set-up a purely optical selectivity of 3×10^9 and an overall detection efficiency of $1.2(4)\times10^{-5}$ are demonstrated.

Keywords. Resonance ionization; laser spectroscopy; ultra-trace analysis; Ca-41.

PACS Nos 32.80.Rm; 07.75.+h; 42.62.Fi

1. Introduction

Since the first operation of the laser by Theodore Maiman 50 years ago [1], optical spectroscopy and in particular resonance ionization spectroscopy (RIS) has benefited tremendously from the continuous laser developments which took place during the last decades. Based on the technology of early laser systems like gas lasers, the development of broadband-tunable dye-solution-based lasers provided enormous and highly valuable contributions to laser application in spectroscopy as far as resolution and sensitivity are concerned. This rendered possible atomic and nuclear structure experiments of so far unreached precision. In the eighties of the last century, Ti:sapphire laser systems were evolved, representing alternative tunable laser systems opening up a new window towards shortest pulses down to the fs-range. The largest breakthrough of laser systems for daily applications was reached with the commercial production of semiconductor diode lasers. Both solid-state laser system lasers (Ti:sapphire and semiconductors) enabled the cross-over of the resonance ionization technique from delicate and dedicated experiments to routine operation units for a highly efficient and simultaneously highly selective ionization process.

Christopher Geppert and Klaus D A Wendt

The study of *short-lived* radioactive isotopes is one of the domains, which requires a reliable and versatile source of ionization. A resonance ionization laser ion source (LIS) which is a multi-step resonant excitation and ionization process by high-repetition rate pulsed lasers, as first suggested by Kluge an co-workers [2], is employed in a large number of on-line facilities worldwide. While the first LIS was based on copper vapour laser-pumped dye laser systems [3,4], modern Nd:YAG laser-pumped Ti:sapphire laser systems were recently tested, at the RISIKO off-line mass separator (Mainz, Germany) and installed at ISAC/TRIUMF (Vancouver, Canada), Holyfield Research Ion Beam Facility/ORNL (Oak Ridge, USA), IGISOL (Jyväskylä, Finland) and the future SPIRAL2 Facility at GANIL (Caen, France) [5].

Parallel to this development, resonance ionization spectroscopy was applied for the trace analysis of *long-lived* radioactive isotopes, with lifetimes in the range of several thousand years and above, in environmental and analytical samples. Depending on the isotopic abundances and thus the ratios under investigations, either pulsed or cw lasers were employed. For detecting Pu-239, a three-step excitation scheme driven by high-repetition rate Ti:sapphire lasers in combination with a time-of-flight mass separator was used at the Mainz University [6]. This experiment demonstrated a detection limit less than 1 femtogram Pu-239 in various environmental samples.

For RIS investigations on isotopic ratios below the separation capability of conventional mass spectrometers, narrow-bandwidth cw lasers are applied in high-resolution resonance ionization. The detection of ultra-trace isotopes with isotopic ratios less than 1×10^{-9} relative to the most abundant stable isotope become accessible, resolving the isotope shift of spectral lines. At Mainz University, two widely identical RIS experiments for the ultra-trace detection of Ca-41 and U-236 are developed. Both isotopes are formed by the capture of thermal neutrons stemming either from cosmogenic or terrestrial sources and thus are extremely rare with abundances less than 10×10^{-12} relative to the most prominent natural isotope Ca-40 or U-238, respectively.

Detection of both Ca-41 and U-236 is relevant for dosimetry, e.g. for waste identification and analysis of nuclear contaminations of waste from nuclear facilities [7]. Because of their low abundance in environmental samples, they are also ideal candidates for tracer studies. Motivated by the Chernobyl reactor accident in 1986, U-236 is envisioned as tracer for migration studies of uranium species in nature. Regarding bio-medical studies, Ca-41 is the ideal tracer for investigating the calcium metabolism in the human body because of its low natural abundance. Its long lifetime of 1.03×10^5 years allows for administration of Ca-41 as *in-vivo* tracer. A successful osteoporosis study, involving the RIS set-up described here, has been conducted within the EU network project OSTEODIET [8].

## 2. Experimental set-up for high-resolution resonance ionization mass spectrometry

Both cw laser systems used for ultra-trace analysis of U-236 and Ca-41 are rather similar; the latter is fully specified and is described here. The aim of the experimental design is to develop a compact table-top RIS experiment which allows for

routine measurement of extreme isotopic ratios. Figure 1 shows the corresponding diode laser system which fits on a 1.2×0.6 m laser breadboard. The excitation scheme shown in the inlet of figure 1 represents the result of previous extensive studies for an efficient and selective excitation and ionization scheme in calcium [9–11]. Three single-mode diode lasers in Littrow-type cavities are used for providing laser light for the resonant excitation steps. Beam splitters are employed to create partial beams which are merged by dichroic mirrors and polarization beam splitter cubes and in this way coupled into an actively scanning $\sim$300 MHz Fabry–Perot interferometer (FPI). The diode lasers are stabilized using fringe-offset locking [12] in reference to a two-mode stabilized He:Ne laser. In order to minimize temporal drifts, the FPI is made of low-temperature expansion coefficient Invar and was temperature-stabilized within a hermetically sealed housing. This way the stability of the diode laser wavelengths is limited by the stability of the reference laser, which is specified to be $<2 \times 10^{-9}$/h. By the precise knowledge of the free spectral range of the FPI, fringe-offset locking additionally allows for a controlled scanning of the laser frequency. Therefore, the free spectral range of the FPI is determined by resonance ionization laser spectroscopy on the hyperfine structure of ionic cesium Cs-133 to a value of 298,111(12) MHz. For the measurement of isotope ratios the laser frequency of all the three excitation steps in calcium can be tuned by computer control onto the isotopic shifts in these transitions synchronously within 200 ms. A quasi-cw 35 W CO_2 laser is used for efficient non-resonant ionization of calcium atoms from the 15 f Rydberg-level into the continuum.
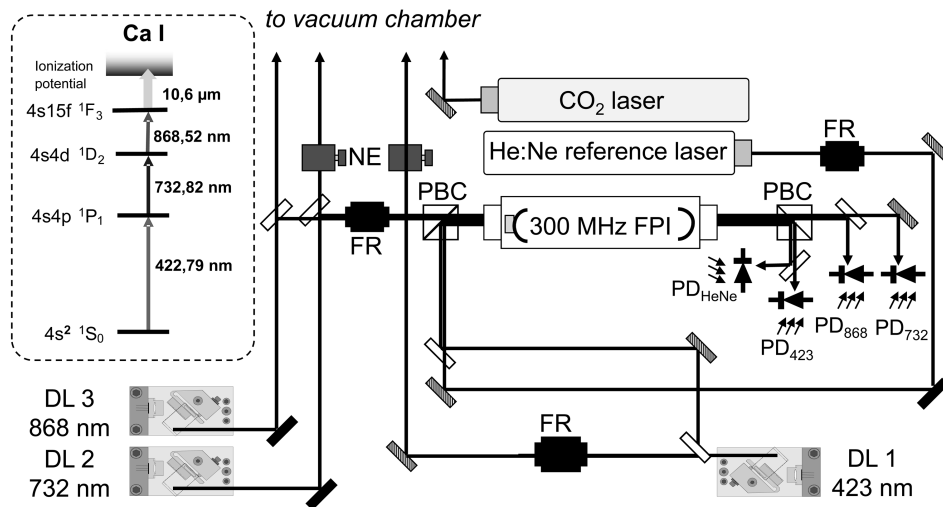

Figure 1. Scheme of the RIS laser system for the three-step excitation scheme of Ca as shown in the inlet. Partial beams of three diode lasers (DL) and a reference laser are coupled through Faraday rotators (FR) and polarizing beam splitter cubes (PBC) into a Fabry–Perot interferometer (FPI) and subsequent photodiodes (PD). The diode laser beams are coupled through noise eaters (NE), if commercially available, before being guided to the vacuum chamber for laser spectroscopy.

Two types of samples are employed: for specification measurements, metallic calcium grains containing about 1×10^{20} atoms have been inserted in the atom source. For analytical measurements, known amount of calcium is dissolved in 3 M HNO_3 solution and is pipetted on a titanium foil. After careful evaporation of the liquid components, the solid residue is enclosed by 3-fold folding of the titanium foil. The samples are evaporated in a collimated beam by resistive heating of a graphite furnace with an inner channel diameter of 2.4 mm and a channel length of 25 mm. By applying a negative offset potential on the graphite furnace, surface ions are suppressed by the grounded entrance aperture of the ion optics. As shown in figure 2, the effusing atomic beam is perpendicular overlapped with the resonant and the non-resonant laser beams. For momentum cancellation and the corresponding Doppler reduction, the infra-red diode laser beams are anti-collinearly aligned to the blue laser beam. The photoions are extracted with an energy of ~ 5 eV and focussed by an Einzel lens onto an electrostatic 90° quadrupole deflector. Thereby dominant
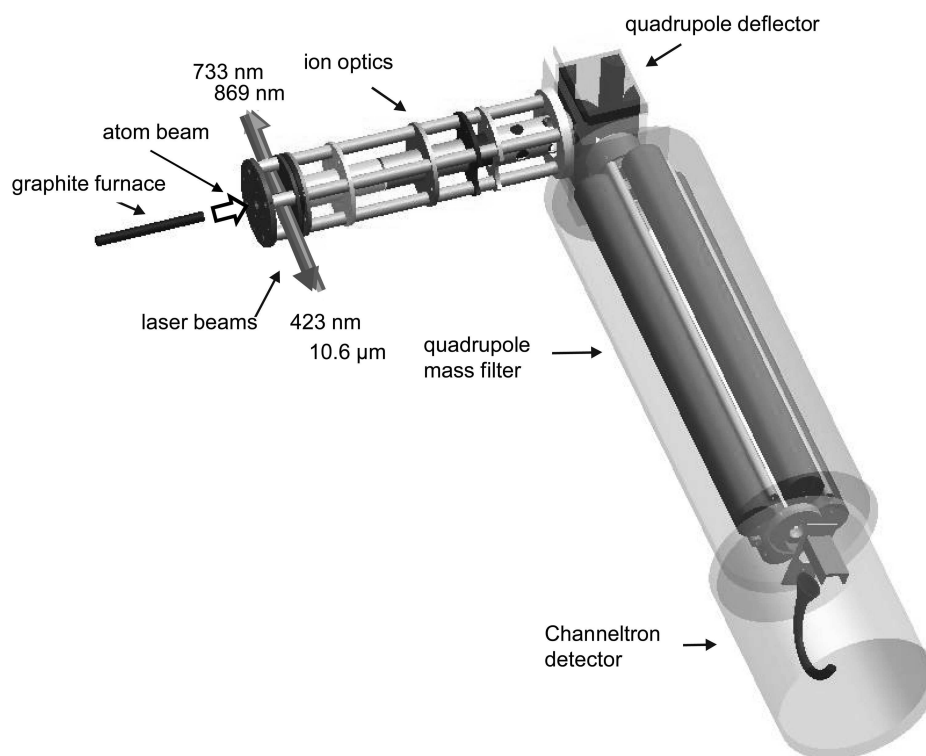
Figure 2. Simplified drawing of the main vacuum chamber and ion optics components for the ultra-trace isotope RIS. A collimated atomic beam formed by the graphite furnace is transversally overlapped with the laser beams. The created photoions are extracted and focussed by simple ion optics into an electrostatic quadrupole deflector and mass analysed in a subsequent quadrupole mass filter. The transmitted ions are detected by an off-axis Channeltron detector.
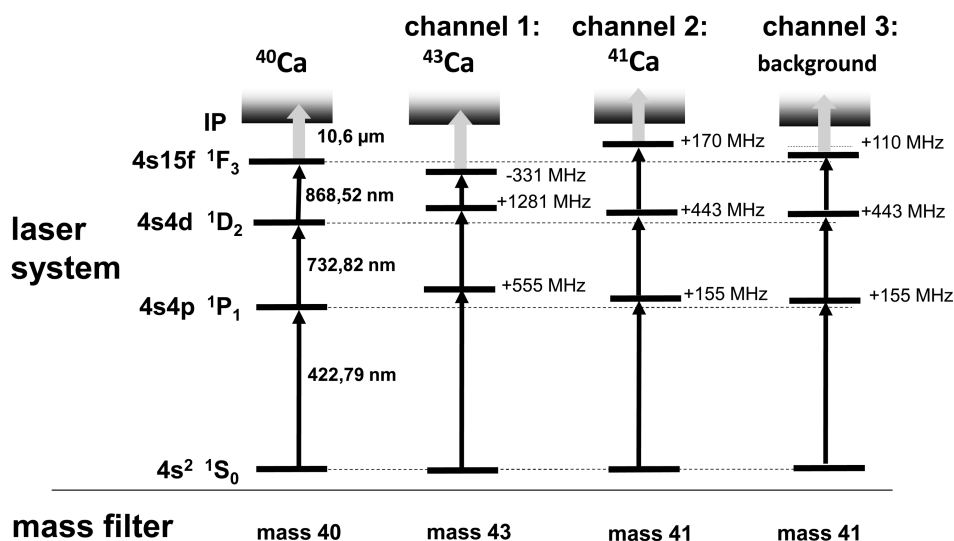
Figure 3. Scanning procedure for automated isotope ratio measurements. Whereas at the beginning the laser system and mass filter are tuned onto Ca-40, they are switched afterwards into three subsequent channels, exhibiting with typical integration times of 2 s in a fast sequence.

background sources like collisional charge exchange among isobars in the atom/ion beam or neutral atoms hitting the ion detector are suppressed. A commercial ABB EXTREL MEXM-64 quadrupole mass filter provides mass separation. Values of up to 1×10^8 in the suppression of the neighbouring half-mass are achieved towards either lower or higher mass [13]. The transmitted ions are finally detected by an off-axis Channeltron operated in counting mode.

For analytical measurements of isotopic ratios, the laser frequencies are initially tuned into resonance with the most abundant isotope Ca-40. As depicted in figure 3, the mass filter and ion optics are then optimized for maximum ion beam transmission. All lasers are adjusted afterwards for the isotopic shift in the respective resonant transitions and the mass filter is set to the reference isotope, i.e. Ca-43. Subsequently, all lasers and the mass filter are rapidly tuned to Ca-41 by computer control. For a later background subtraction a third channel accounts for isobaric contaminations and remaining ion signal from the neighbouring isotope Ca-40 with the lasers off-resonance. The detected ion current of all channels is integrated. Depending on the sample size and isotopic ratio a measurement takes between 5 and 45 min.

3. Specification measurements on Ca-41

3.1 *Selectivity of the RIS set-up*

To determine the optical isotopic selectivity of the three-step laser resonance ionization, a sample of metallic calcium is used. As the major isotopic contamination

is caused by the most abundant and neighbouring isotope Ca-40, the mass filter is fixed on mass 40 for both traces shown in figure 4. In the upper trace all laser frequencies and the mass filter are tuned onto Ca-40. While the first and second excitation steps are fixed, the upper trace in figure 4 shows the scan of the third excitation step over the resonance frequency. The abscissa is normalized on the count rate in three-step resonance of Ca-40. The measured data points are well reproduced by a Gaussian fit (solid line) exhibiting an experimental linewidth of 23 MHz FWHM. In the lower trace of figure 4 the first two excitation-step laser frequencies have been detuned by the isotopic shift for Ca-41 while the mass filter is still fixed on mass 40. The wavelength of the laser for the third excitation step is scanned by 1.2 GHz around the centre frequency of the third excitation step in Ca-40. The intersection point at +170 MHz indicates the laser frequency position where the count rate of Ca-41 will be recorded (shown in figure 3). With this specification the count rate of Ca-40 is reduced down to a value of 3×10^{-10} relative to the resonance position of Ca-40, which corresponds to an optical selectivity of 3×10^{9}.

Background effects, e.g. the formation of calcium hydroxides (Ca-40H) after ionization, do not allow to simply multiply the neighbouring mass suppression of the mass filter and the optical selectivity to calculate the resulting total selectivity and detection limit for this resonance ionization approach. At the current evolution stage of the set-up, characterized by the installation of the electrostatic quadrupole deflector, the lowest detection limit has been deduced from measurements on analytical samples to be 2×10^{-13} in the isotopic ratio of Ca-41/Ca-40. Thus this compact table-top resonance ionization set-up is not capable of accessing the
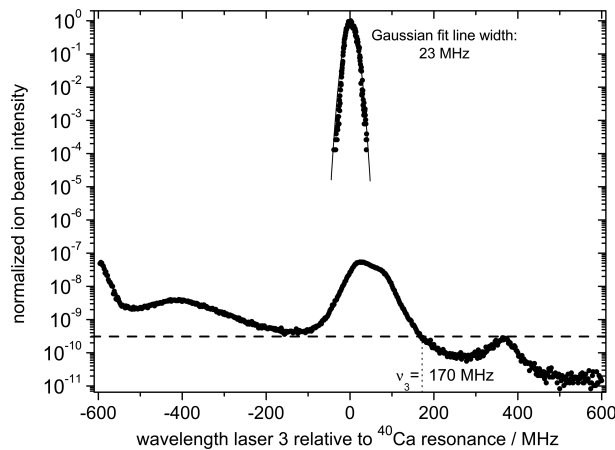
Figure 4. Measurement of the optical selectivity. In the upper trace the first two excitation steps are tuned in resonance to Ca-40 and the third resonant excitation step is scanned over the resonance of Ca-40. Mass filter is set to mass 40. Normalized on this count rate, the first two excitation-step lasers are tuned to Ca-41 in the lower trace. Still the mass separator is set on mass 40. The third laser is scanned in wavelength over 1.2 GHz. The resonance position of Ca-41 is also indicated.
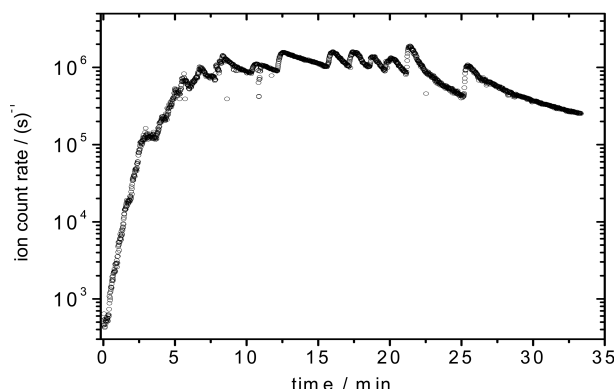
Figure 5. Efficiency measurement on an analytical sample with quantified calcium content. While the resonance ionization set-up is set on Ca-43 the sample is evaporated and the ion count rate integrated over time. The fins on the underlying structure are caused by step-wise increase of the heating temperature of the atomizer furnace.

isotopic ratio of Ca-41 in nature ($\sim 1 \times 10^{-14}$), but is predestinated for a large variety of tracer studies, where the Ca-41 ratio is inherently raised above the natural level.

3.2 *Overall detection efficiency*

The efficiency is the crucial parameter for determining the amount of sample which is required for a given measurement. For determining the overall efficiency in this experimental set-up, an analytical sample with a quantified amount of calcium in natural isotopic composition is inserted in the atomizer furnace and evaporated. During step-wise increase of the temperature of the furnace, the system is permanently tuned to Ca-43, as shown in figure 5, and the ion count rate is integrated. Starting from the initial $1.5(2) \times 10^{17}$ atoms of Ca-total, the amount of detectable Ca-43 is calculated from the natural isotopic ratio and from previous studies on the fraction of ions in the strongest hyperfine structure (HFS) component. After 35 min of heating, 1.5×10^9 atoms of Ca-43 (including dead time corrections) have been detected. Taking into account the uncertainty of the number of ions in the strongest HFS component and the uncertainty in the initially inserted number of ions, this corresponds to an overall detection efficiency of $1.2(4) \times 10^{-5}$.

4. Status and outlook

The applicability and accuracy of this set-up has previously been demonstrated on reference samples [14] provided by the European Institute for Reference Materials and Measurements (IRMM). Furthermore, additional comparison measurements provided excellent agreement with two different alternative ultra-trace detection

methods for Ca-41, i.e. accelerator mass spectrometry [15] and atomic trap trace analysis [16]. Transferring this set-up from prototype status into routine operation, the set-up recently provided analytical support within a European Network on osteoporosis research. After having successfully demonstrated the feasibility of laser-based ultra-trace analysis of Ca-41 this way, the resonance ionization set-up for Ca has been reconverted for ultra-trace detection on U-236, which is the ongoing activity at Mainz University.

References

[1] T H Maiman, *Nature* **187**, 493 (1960)
[2] H-J Kluge, F Ames, W Ruster and K Wallmeroth, Laser ion sources, in *Proceedings of the Accelerated Radioactive Beams Workshop* edited by LBaJM D'Auria (Parksville, Canada, 1985)
[3] ISOLDE Collaboration: V I Mishin, V N Fedoseev, H-J Kluge, V S Letokhov, H L Ravn, F Scheerer, Y Shirakabe, S Sundell and O Tengblad, *Nucl. Instrum. Methods Phys. Res.* **B73**, 550 (1993)
[4] V N Fedoseyev, G Huber, U Köster, J Lettry, V I Mishin, H Ravn and V Sebastian, *Hyperfine Interactions* **127**, 409 (2000)
[5] C Geppert, *Nucl. Instrum. Methods Phys. Res.* **B266**, 4354 (2008)
[6] C Grüning, G Huber, P Klopp, J V Kratz, P Kunz, G Passler, N Trautmann, A Waldek and K Wendt, *Int. J. Mass Spectrometry* **235**, 171 (2004)
[7] P Müller, B A Bushaw, K Blaum, S Diel, C Geppert, A Nähler, N Trautmann, W Nörtershäuser and K Wendt, *Fresen. J. Anal. Chem.* **370**, 508 (2001)
[8] E Denk *et al*, *Anal. Bioanal. Chem.* **386**, 1587 (2006)
[9] W Nörtershäuser, N Trautmann, K Wendt and B A Bushaw, *Spectrochim. Acta* **B53**, 709 (1998)
[10] B A Bushaw, W Nörtershäuser and K Wendt, *Spectrochim. Acta* **B54**, 321 (1999)
[11] P Müller, B A Bushaw, W Nörtershäuser and K Wendt, *Euro. Phys. J.* **D12**, 33 (2000)
[12] W Z Zhao, J E Simsarian, L A Orozco and G D Sprouse, *Rev. Sci. Instrum.* **69**, 3737 (1998)
[13] K Blaum, C Geppert, P Müller, W Nörtershäuser, E W Otten, A Schmitt, N Trautmann, K Wendt and B A Bushaw, *Int. J. Mass Spectrometry* **181**, 67 (1998)
[14] C Hennessy, M Berglund, M Ostermann, T Walczyk, H A Synal, C Geppert, K Wendt and P D P Taylor, *Nucl. Instrum. Methods Phys. Res.* **B229**, 281 (2005)
[15] C Geppert, P Müller, K Wendt, C Schnabel, H A Synal, U Herpers and S Merchel, *Nucl. Instrum. Methods Phys. Res.* **B229**, 519 (2005)
[16] I D Moore, K Bailey, J Greene, Z T Lu, P Müller, T P O'Connor, C Geppert, K D A Wendt and L Young, *Phys. Rev. Lett.* **92**, 153002-4 (2004)