First experiments with a laser ablation source at the COALA setup

Laura Renth1 · Phillip Imgram1 · Jörg Krämer1 · Kristian König1 · Tim Lellinger1 · Bernhard Maass1 · Patrick Müller1 · Tim Ratajczyk1 · Wilfried Nörtershäuser1

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Abstract
A laser ablation ion source has been built and tested at the COALA beamline. Time-of-flight measurements for various elements are sufficiently accurate to confirm the production of the intended ion species. Furthermore, the isotope shift between $^{40}$Ca$^+$ and $^{44}$Ca$^+$ has been determined on these bunched beams by collinear laser spectroscopy and compared to previous measurements. The frequency of the $4s^2S_{1/2} \rightarrow 4p^2P_{1/2}$ transition has been determined to $\nu^0_{D1} = 75522766.8(15)$ MHz for $^{40}$Ca$^+$, as well as the corresponding isotope shift of $^{44}$Ca$^+$ to 848.1(23) MHz. This is in a good agreement to more accurate measurements performed in a recent ion trap experiment and demonstrates the strength of the collinear-anticollinear approach to reduce systematic effects caused by the broad velocity distribution generated in the ablation process.

Keywords Ion source · Laser ablation · Collinear laser spectroscopy · Isotope shift

1 Introduction

Collinear laser spectroscopy is a powerful tool to access atomic and nuclear properties of atoms, ions and molecules, see, e. g. [1] and references therein. If fast beams with narrow velocity spread are available, isotope shifts and hyperfine constants can be extracted with sub-MHz precision. Optical transition frequencies can be determined using simultaneous or subsequent measurements in collinear- and anticollinear alignment [2, 3]. However, the availability of these beams is limited by chemical processes in the ion source, prohibiting the production of many elements.

A new ion source based on laser ablation has been built and tested to provide more species to be investigated at the COllinear Apparatus for Laser spectroscopy and Applied
Fig. 1 Schematic representation of the COALA beamline. The ion beam passes several ion optical devices to be superimposed with the laser beams. The beam alignment can be controlled at the diagnostic stations. In the fluorescence detection region, resonant laser-ion interactions are driven by changing the ion velocity with a small scan voltage. The emitted fluorescence light is collected and guided to two photomultiplier tubes.

The COALA beamline at TU Darmstadt has been designed for high-precision collinear laser spectroscopy that tests atomic theory [6], to continue the development of the technique and to perform high-accuracy high-voltage metrology [7].

Figure 1 shows a schematic representation of the beamline where the laser ablation ion source is mounted on the left side. After production, the ions are accelerated to 15 keV, traverse several ion optical elements and are superimposed collinearly or anticollinearly with a laser beam of frequency $\nu_c$ or $\nu_a$, respectively. The resonant laser-ion interaction takes place in the fluorescence detection region, which is equipped with a combination of in-vacuum elliptical mirrors and light concentrators to guide the fluorescence light towards the photomultiplier tubes while suppressing laser-induced background. The resonance condition can be achieved by applying a scanning voltage to the fluorescence detection region, which alters the ion velocity $\beta = \nu/c$ and hence, the Doppler shift

$$\nu_{c/a} = \nu_0 \cdot \gamma [1 \pm \beta].$$ (1)
with $\gamma$ being the time-dilation factor $\gamma = (1 - \beta^2)^{-1/2}$. This allows running the laser at a fixed frequency being locked, e.g., to a frequency comb and scanning precisely across the resonance by amplifying an analogue voltage generated by the data acquisition system (DAQ). More details can be found in [4].

3 The laser ablation ion source

Figure 2a shows a schematic representation of the laser ablation ion source. The target (orange) consists of the pure metal to be ionized and is surrounded by a stainless steel tube to suppress electrical field penetrations. A pulsed laser beam (green) is focused with a lens through an aperture in a tube onto the target. The laser pulse ablates ions off the target, producing a plasma plume. On top of the tube, a lid with a 1 cm aperture can be mounted, which plays a significant role for the ion beam properties, which will be discussed below. The source is floated on a potential of typically 15 kV, allowing to generate a fast ion beam of corresponding energy. The ablation laser is a Quantel Centurion+ and provides up to 25 mJ per shot and a variable repetition rate from single shot up to 100 Hz at a wavelength of 532 nm. The beam profile of the ablation laser is shown in Fig. 2b. The laser spot is roughly rectangular and has a flat-top profile providing a more homogeneous energy density than a Gaussian profile. The spot size of the laser beam on the target could not be measured accurately but is estimated from previous measurements at a different installation with the same laser and a similar optical setup, to be in the range of 300–700 $\mu$m.

An ion current of 20 pA was measured at the end of the COALA beamline when the ablation laser was firing with a repetition rate of 100 Hz and a pulse energy of 8 mJ, corresponding to a fluence of approximately 4 J cm$^{-2}$ assuming a 500 $\mu$m diameter spot. While we have seen variations in resonance position ($\sim 40$ V) and resonance shape with time for an unstructured target, this became much more stable once the target was sanded to an even surface and positioned with an angle of 45° with respect to the laser pulse as shown in Fig. 2a. Under these conditions, the ion yield was quite stable over the time of at
least 14 measurements of the $^{40,44}$Ca$^+$ isotope shift taking about 10 hours, though a small degradation of the target could be observed.

With the lid at the target we observed stable ion currents for laser energies below 15 mJ (fluence of $\approx 8 \text{ J cm}^{-2}$). Whether instabilities observed at higher laser power are caused by an increase of emittance due to the higher energy deposited into the laser plume, by a change from normal to explosive vaporization [8] or by structural changes of the surface in the ablation process that lead to strongly varying preferred emission directions out of the crater, is not clear. For spectroscopy, we have therefore restricted the pulse energy to less than 15 mJ.

### 4 Time-of-flight measurement

Without the lid on top of the steel tube, the electric field at the target is high, and the ions are accelerated immediately after production. This results in very short pulses, as shown in Fig. 3, where a calcium resonance was recorded in anticollinear geometry. On the left, the number of registered photons is plotted colour-coded as a function of the scan voltage on the x-axis (being amplified by a factor of 50 before it is applied to the detection region) and the ToF on the y-axis. A trigger related to the laser pulse generation is used as the starting signal. On the right, the signal is projected on the time axis and exhibits a short pulse with a temporal full width half maximum of $\sim 300$ ns.

This configuration allows us to perform ToF measurements with a reasonable resolution. To avoid the necessity of resonant laser light for these measurements, the ion beam was adjusted to partly collide at the apertures of the fluorescence detection region. The light produced in this process was used to identify the arrival time.

ToF measurements were carried out for the elements boron ($A = 11$), aluminium ($A = 27$), calcium ($A = 40$), palladium ($A = 106$) and tantalum ($A = 181$) to confirm the production of the intended ion species. The laser energy was adapted between 9–15 mJ to exceed the ablation threshold for the different elements.

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1 In all cases the atomic number of the most abundant isotope is given, since the neighbouring isotopes can not be resolved.
The measured ToF is plotted with the square root of the ion’s mass as the x-axis in Fig. 4. The FWHM of the ToF spectra are taken as the uncertainties. As the energy-mass relation

\[ E_{\text{kin}} = \frac{1}{2} m \left( \frac{d}{t} \right)^2 \]  

leads to the linear dependency

\[ t = \sqrt{\frac{d^2}{2E_{\text{kin}}} \cdot \sqrt{m}}, \]  

a linear function is fitted to the data. The fit \( t_{\text{ToF}} = 3.7(3)\sqrt{m} - 0.3(16) \) with a correlation of \( R^2 = 0.97 \) shows that the measurements are sufficiently accurate to confirm the production of the intended ion species.

### 5 Ion source optimization for collinear laser spectroscopy

In collinear laser spectroscopy experiments, a narrow energy and velocity width is essential, whereas the temporal width of the ion bunch is less important for abundantly available stable isotopes. In this respect, the large spread along the voltage axis in Fig. 3 is detrimental for accurate measurements. Installation of a lid with a 1 cm aperture on the target drastically improved the energy distribution. This is visible in Fig. 5. Spectra were taken this time with laser beams superimposed with the ion beam in collinear and anticollinear geometry. Under these conditions, collinear-anticollinear laser spectroscopy is carried out for the isotopes \( ^{40}\text{Ca}^+ \) and \( ^{44}\text{Ca}^+ \).
Fig. 5  The upper plots show the time and frequency distribution of an exemplary measurement of collinear (a) and anticollinear (b) laser spectroscopy on $^{40}$Ca$^+$. All data points inside the black rectangle are used for the evaluation. The lower plots show the projection of the data points inside the black rectangle onto the frequency axis. A symmetric Voigt function is fitted to the data (red line). The FWHM of the spectra is 100 MHz corresponding to an energy width of 4.5 eV which is a factor of 20 smaller than in measurements without the lid. However, the bunch length is now 13 μs long. The zero-frequency position is chosen arbitrarily.

Figure 5a) shows the ToF and frequency distribution for an exemplary collinear measurement. On the upper part, the number of registered photons is plotted as in Fig. 3 but the scan voltage on the x-axis is now transformed to the frequency domain. The dominant part of the signal now covers a frequency span of 100 MHz, corresponding to an energy width of 4.5 eV, which is a factor of 20 smaller than in measurements without the lid. However, a small tail with an energy width corresponding to about 40 eV is still visible.

Since the lasers are referenced to a frequency comb, we can extract the ion energy from the total Doppler shift at the resonance position. Surprisingly, the center of the distribution shown in Fig. 3 is shifted by up to 700 eV towards higher energies than expected from the target voltage. The size of the shift depends approximately linearly on the energy of the laser pulse. It is important to note that the lid not only reduced the width but also shifts the resonance back into the position where it is expected from the potential applied to the target.

Three attempts to explain the energy shift and width will be discussed.

a) Field penetration
The energy spread of about 150 eV could be caused by the potential gradient in the front of the target since the ions can be generated somewhere in the laser plume. However, penetration of the extraction field to the target region will generate ions that are too low in energy, but cannot explain the excess energy. Moreover, this excess in ion energy depends approximately linearly on the laser pulse energy.

b) Plasma acceleration
Ion velocities of up to 40 km s$^{-1}$ corresponding to kinetic energies of 200 eV are observed from laser ablation of Al with 2.5 J cm$^{-2}$ of $\lambda = 355$ nm and 6 ns pulse length [9]. These conditions are not so different from those that we used and therefore could also explain the observed energy width. Ion acceleration in laser-induced plasmas has been explained by a so-called double layer, a self-consistent ambipolar electric field arising in the expanding plasma [10]. The double layer is formed as a result of the
spatial charge separation of the fast electrons and the slower ions, which are then accelerated by the heading electron cloud [11]. This also provides an explanation for the increasing energy excess with growing laser pulse energy. The relatively broad kinetic energy distribution reported for such laser processes [9] could cause the energy width observed in Fig. 3. But the effect of the lid cannot be explained so easily. Both, total energy and width might be reduced if a sufficiently high pressure builds up in the target region, allowing thermalization of the fast ions by collisions with atoms and ions produced in the ablation process. For such a scenario, the mean-free-path of the ions would have to decrease clearly below 1 cm, requiring an atom density of about $10^{17} \text{cm}^{-3}$. In [9] the generation of up to $10^{16}$ atoms per laser pulse is reported with about half the fluence of our experiment but on a four times larger spot. Other studies consistently report material ablation rates in the range of a few $\mu\text{g cm}^{-2}$ and plasma densities of more than $10^{16} \text{cm}^{-3}$. This is still below the density required for a thermalization but might also be strongly dependent on experimental conditions.

c) Increased target potential by electron emission

The excess energy of the ions, as well as the large energy width without the lid, could be explained by an increased positive potential of the target caused by a fast emission of electrons during laser pulse impact. Fast prompt electrons have been reported in laser ablation processes induced by UV [12] as well as infrared lasers [13] using fluences comparable to our study. The power supply provides maximum currents of 6 mA, corresponding to approximately $4 \times 10^7$ electrons/ns, whereas prompt electron ejection of the order of 11 A cm$^{-2}$ is reported in [12]. The effect of the lid could be that most of the electrons are collected again and quickly driven back to the target.

Currently (c) seems to provide the best explanation of the experimental findings. However, a definite conclusion which of these (or other) explanations are correct, requires a better understanding of the plasma processes and the energies of the appearing ions. Therefore more dedicated studies have to be performed. Even though we cannot give a final explanation for the reduction in energy width and the energy shift of the ions at this point, the fact itself is essential for the accuracy that can be achieved in laser spectroscopy as we will demonstrate next.

6 Transition frequency and isotope shift analysis

Even with the lid, the first ions that appear at the detection region still have a broad velocity distribution, and it is, therefore, useful to cut-off the ‘tail’ during the evaluation and only use the data of a 9 $\mu$s long time-gate from 26 $\mu$s to 35 $\mu$s, as indicated by the black rectangle in Fig. 5. The atoms generating the signal in this region still have varying energies, which is visible by the slight tilt to the right (higher energy) with increasing flight time. The corresponding anticollinear measurement shown in Fig. 5b) exhibits a symmetric structure that is mirrored in frequency space. This is advantageous for the determination of the rest-frame frequency since the systematic shift will largely cancel in the geometric average $\nu_c \cdot \nu_a = \nu_0^2$. We have carried out various fitting strategies: (a) Simple symmetric Voigt fitting, (b) dividing the 9 $\mu$s time-gate into four slices of 2.25 $\mu$s, fitted individually with a symmetric Voigt and averaging the individual results for $\nu_0$, (c) asymmetric Voigt caused by a side-peak, (d) same as (c) but now the side peak is constrained to have the same intensity ratio and distance in the collinear and anticollinear measurement. The central frequency $\nu_0$
The data points show the measured transition frequencies of $^{40}$Ca$^+$ for 14 combined sets of collinear and anticollinear measurements. The error bars include the statistical uncertainty and the uncertainty from the frequency shift with time-gate shifts. The weighted average of the transition frequency is shown as a red line. As a systematic uncertainty, the mean value of the frequency shifts for varying time-gates is shown as a red error band. The blue area around the mean transition frequency indicates the total uncertainty taken as the standard deviation of the mean of all measurements added linearly to the systematic uncertainty.

For the final evaluation, a symmetric Voigt function was fitted to the data of the reduced time-gate of 9 μs, corresponding to strategy (a). The tilted resonance structure mentioned above was considered for the uncertainty analysis. For this, the individual results of the 2.25 μs time-gates of fitting strategy (b) are used to calculate how much the transition frequency of each measurement shifts with the time-gate variation. This frequency shift is added as an individual systematic uncertainty linearly to the statistical uncertainty of each of the 14 measurements. The error bars plotted in Fig. 6 represent this total uncertainty and are used to calculate the weighted average as the mean transition frequency of all measurements, plotted as a red line. The individual, combined uncertainties obtained in this way do not represent the observed scatter of the data points. This is also reflected by the reduced $\chi^2$ of 3.9. A reason for this might be the often too small statistical uncertainties from the fitting routine. Therefore, we preferred to estimate the uncertainty of our final result from the distribution of the data points in Fig. 6 rather than from the standard uncertainty of the weighted average. The statistical uncertainty is taken as the standard error of the mean of all 14 measurements. Additionally, the mean of all 14 individual systematic uncertainties (represented by the red area around the mean transition frequency) was calculated and linearly added to the statistical uncertainty to obtain a conservative error estimation. This is represented by a blue error band in Fig. 6. The same procedure was applied for the 13 measurements of $^{44}$Ca$^+$. 

Fig. 6
Table 1  Measured transition frequencies of $^{40}$Ca$^+$ and $^{44}$Ca$^+$ and corresponding isotope shift. All values are in MHz

| Isotope | $\nu_D^{\text{Lit}}$ | Literature       |
|---------|----------------|-----------------|
| $^{40}$Ca | 755 222 766.8(15) | 755 222 765.896(88)[14] |
| $^{44}$Ca | 755 223 614.9(17) |                 |
| Isotope shift | 848.1(23) | 849.534(74)[15] |

The final values for $^{40}$Ca$^+$ and $^{44}$Ca$^+$ with corresponding uncertainties are listed in Table 1. The uncertainty of the isotope shift is determined by Gaussian error propagation.

7 Conclusion

The measurements on calcium are a demonstration of the usability of a laser ablation ion source for collinear laser spectroscopy as it has previously been reported in [5]. While in this previous work the frequency axis was corrected according to the time-of-flight information, we have used the collinear-anticollinear approach, assisted by a frequency comb, to measure the absolute transition frequencies. We demonstrated that the design of our ion source led to superior properties of the ion beam, especially in terms of a narrower energy width. However, the exact processes that take place and lead to these better properties are not fully understood and have to be investigated further. The higher population in this small velocity class increases the sensitivity to less abundant isotopes and allows a precise determination of the center frequency.

Collinear laser spectroscopy has been carried out for $^{40}$Ca$^+$ and $^{44}$Ca$^+$. The measured transition frequency of the $4s^2S_{1/2} \rightarrow 4p^2P_{1/2}$ transition of $^{40}$Ca$^+$ is in good agreement with former measurements [14]. The isotope shift between $^{40}$Ca$^+$ and $^{44}$Ca$^+$ has been extracted from the transition frequencies and is also in agreement with recent more precise experiments [15]. We have used simple Gaussian error propagation for the calculation of the isotope shift, even though there might still be a systematic correlated uncertainty. To remove remaining correlated errors requires a more sophisticated treatment of the statistical and systematic uncertainties than it was performed for this proof-of-principle study. Such a scheme has been adapted in [16] and is discussed there in more detail.

As the laser ablation ion source gives access to a wide range of ion species, it is of particular interest for elements that could not be investigated yet due to accessibility. In dedicated time-of-flight measurements, we could verify the production of various intended ion species in the range of boron to tantalum which will allow us to access these elements with laser spectroscopy.

However, the present design is ultimately limited by the high temperature caused by the laser ablation process. Improving the linewidth for collinear laser spectroscopy, therefore, requires to cool the ions further down before extracting them into the beamline. This is achievable by performing the ablation process in the presence of a background gas ($p \sim 100$ mbar), which reduces the temperature to room temperature. The ions are then extracted through a series of differential pumping stages, in which radio frequency funnels confine them radially. A setup using this technique was designed and assembled and first test measurements are currently performed [17].
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