Resonant Ionization Laser Ion Source (RILIS) Development on Lu and Pr

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Abstract

Resonance ionization laser ion sources are efficient and element selective ion sources, which are particularly well suited for radioactive ion beam facilities. Using TRIUMF’s off-line laser ion source test stand with a system of tunable titanium sapphire (Ti:Sa) lasers, laser resonance ionization schemes for lutetium and praseodymium have been investigated with a particular interest to autoionizing states. New ionization schemes via Rydberg states and autoionizing states were found. Their investigation and comparison of ion yields at the off-line test stand will be discussed, and the data of on-line Lu delivery will be presented.

Keywords: Resonance ionization spectroscopy (RIS), Lutetium, Praseodymium, Ti:Sa laser, Rydberg state, Autoionizing state

1. Introduction

Nuclear properties of rare-earth elements are interesting for astrophysicists due to their important role in \( r \)-process to form the rare-earth abundance peak in solar system \cite{1}. Furthermore with the magic number \( N=82 \) occurring in the mass range, the lanthanide isotopes provide a rich field for nuclear scientists to study the shell closure and the nuclear deformation. In recent years the application of lanthanides as radioactive imaging tracer and therapy treatment for tumors increases the attention on the scientific studies on these species. However as a group of neighboring elements with similar chemical properties, it is very difficult to obtain carrier free lanthanide isotopes in high purity without contamination from the adjacent bulk of other lanthanide isotopes \cite{2}. Similar problems hampered the nuclear study on lanthanide radioactive isotopes in RIB facilities due to surface ionized isobar combinations. Based on the electronic structure of different atomic species, the Resonant Ionization Laser Ion Source (RILIS) can selectively ionize the element of interest. With the aid of a high resolution mass separator, it inherently suppresses isobaric contaminations by relatively enhancing the ionization efficiency of the aimed element. However due to the low ionization potential of lanthanides (5.4-6.4 eV), the enhancement by the

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RILIS is not significant over surface ionization. Recently, the introduction of the ion guide laser ion source (IGLIS) at TRIUMF [3] and the laser ion source trap (LIST) at CERN [4] opened up the possibility of isobar-free RIB of lanthanides, and motivated the development of efficient laser ionization schemes on them.

Lanthanides with an open 4\textit{f} shell have complex electronic structures, which makes the theoretical calculation difficult and the experimental data scarce and fragmentary. However lutetium (Lu) as the last element in the lanthanide group is an exception. It has only one valence electron outside of filled 4\textit{f} and 6\textit{s} shells, which makes its atomic spectra outstandingly simple compared to other lanthanides. A series of works have done on Lu atomic structures since 1930, from traditional emission and absorption spectroscopy [5-8] to contemporary laser spectroscopy [9-10]. The spectroscopic work extended to autoionizing states (AI) afterward [11-14]. The majority of the studies on high-lying Rydberg states and AI states were made via laser resonance ionization spectroscopy (RIS), which gives helpful reference to our development work. In fact some RILIS schemes had been developed [15] in early days to apply to the determination of traces of Lu in a geological study [16]. The long-lived ^{176}\text{Lu}^{176}\text{Hf} radioactive decay system is a powerful tracer used in geology and astrophysics to date rocks and meteorite samples. With the high selectivity and sensitivity of the RIS method, the minimum detectable concentration can be down to $10^{-10} \%$ [16]. This is another strong motivation to develop efficient schemes for Lu. The scheme used in [16] is 451.982 nm + 460.688 nm via an AI state at 43831.6 cm$^{-1}$ (all the wavelengths shown in this paper are the values in vacuum). In this work different atomic transitions of Lu for the first excited step (FES) were attempted. The ion yield of our new developed schemes were compared with that of the scheme in [16].

Contrary to Lu, praseodymium (Pr) has a very complicated atomic structure with three 4\textit{f} and two 6\textit{s} outer electrons. The five valence electrons give a large number of electronic configurations, very rich fine structures and strong overlap of configurations with different parities. All of these complexities resulted in the limited knowledge on spectral lines and ambiguous assignments [17]. Although the study of Pr atomic spectra started in 1940’s [18], the bulk of the available data is still from the investigation before the 80’s [19]. Even till today the knowledge of atomic properties of high-lying Rydberg states and AI states are nearly unknown. The only one reported AI state study on Pr was made using RIS by O. Kujirai et al. in 2000 [20]. On the other side, the atomic properties of Pr transitions are of increasing interest due to new astronomical observations with high-resolution spectrograph and a large number of rare earth lines observed in chemically peculiar stars [21]. Measurements on odd-mass Pr isotopes indicate a shape transition as the neutron number increases from the magic number 82 to 90. This isotope chain provides a good candidate to test various nuclear models [22]. The measurement of the nuclear moment of ^{140}\text{Pr} was recently motivated to explain the counter-intuitive observation on the decay constant of the hydrogen-like ^{140}\text{Pr}^{58+} ions in the ESR storage ring [23]. The increasing needs for Pr isotope beams and the lack of atomic data reinforced the needs for the laser scheme development. Recently, Mainz University LARISSA group performed a laser ionization scheme development of Pr with a Ti:Sa laser system [24]. The resulting optimal scheme was 461.901 nm + 899.981 nm + 877.918 nm, which ionized Pr atoms via an AI state. Meanwhile, the RILIS group at ISOLDE established a scheme of 461.901 nm + 899.996 nm + 532 nm(Nd:YAG) as an efficient scheme for their dye laser system [25]. In this work, two different atomic transitions of Pr for the FES were tested. Especially, previously unexplored blue+blue schemes to Rydberg and AI states were developed.
2. Experimental Setup of Offline Developments

The schematic setup of the experiment is shown in Fig. [1]. Three Ti:Sa lasers were used in the experiments, one birefringent-filter (BRF) laser and two grating lasers. All three lasers are simultaneously pumped by a pulsed Nd:YAG laser (LEE laser LDP-100MQG) of 35 W power and 10 kHz repetition rate. The Ti:Sa lasers can provide 1-2 W output power with the tunable wavelength range of 700-980 nm. The BRF laser and one of the grating lasers are both followed by a frequency doubling unit, which can extend the laser wavelength range to 350-460 nm. The typical conversion efficiency of frequency doubling is 30%. The doubling unit following the grating laser was automatically controlled by a PC to phase-match the angle of the nonlinear doubling crystal (BBO or BIBO crystal) with the wavelength of the Ti:Sa laser. The wavelength of the lasers were measured by a wavemeter (High Finesse WS/6) with the precision of $10^{-6}$. It is routinely calibrated to a polarization stabilized HeNe laser with wavelength accuracy of $10^{-8}$ (Melles Griot 05 STP 901/903). A Nd:YVO4 laser (Spectra-Physics Inc. YHP-40) is employed for nonresonant ionization schemes. This laser has a maximum output power of $\sim$12 W at 1064 nm and $\sim$6.7 W at 532 nm, with a pulse length of $\sim$30 ns. The laser beams for consecutive excitation steps were overlapped via polarization beam splitters and dichroic mirrors. The temporal superposition of laser pulses was obtained by the intra-cavity Pockel cell Q-switches. All the laser beams were finally focused into the ion source to interact with the atomic vapor of the element of interest. The source in this experiment is an IGLIS source, which consists of a thermal-ion repeller and a radio-frequency quadrupole (RFQ) as an ion guide [3]. The IGLIS can be operated in two different modes: transmission mode and suppression mode. In transmission mode, the potential of the crucible is higher than those of the repeller and the RFQ. Therefore, all the ions generated in the high temperature Ta crucible - either thermal ions or laser ions - transmit. However in suppression mode, the repeller has a potential higher than the crucible, so that thermal ions are repelled and prevented from entering the RFQ. So in principle, only the laser ionized ions generated after the repeller will be guided and extracted. The extracted ions are accelerated to 10 keV, then vertically bent and decelerated into a commercial quadrupole mass spectrometer (EXTREL-QMS MAX300) for mass filtering. The QMS was equipped with a channel electron multiplier (CEM) to detect the ion signal. The setup has been described in more details in [26, 27].

3. Experimental procedure, Results and Discussion

The purpose of the off-line developments of Lu and Pr is to obtain better ionization schemes based on the Ti:Sa laser system. The direct benefit is to improve the efficiency of on-line beam delivery with TRILIS and other similar LIS facilities on these two elements. It also provides good reference schemes of Lu and Pr for any other application using laser ionization as a sensitive atom detection method, such as ultra trace analysis [16, 28]. As described in our previous work [27], no absolute ionization efficiency measurement is made in our off-line laser ionization scheme development due to the absence of a properly suppressed Faraday cup after the QMS. Thanks to the low ionization potentials of lanthanides, the surface ion yield can be used to normalize the ion yield of different laser ionization schemes, and therefore, makes the efficiencies of the these schemes comparable. Here we use the term - relative ionization efficiency - as the ratio of laser ion yield to surface ion yield. To make sure the surface ion yield to properly act as an normalizer, a constant temperature of the source must be maintained. Furthermore the spatial laser overlapping and pointing were carefully optimized for each scheme.
Figure 1: The TRILIS off-line experimental setup consists of a laser system for resonant ionization, an IGLIS source, a quadrupole mass spectrometer (QMS) equipped with a channel electron multiplier (CEM), and a computer based data acquisition system.

3.1. Off-line Relative efficiency comparison of lutetium RILIS schemes

A standard solution (Alfa Aesar Specpure, 1 µg/µl Lu₂O₃ in 5% HNO₃ solution) was loaded on a thin Zr foil. After drying out the water in a 110 °C oven, the foil was folded into a tiny piece and inserted to a Ta crucible. Lu atomic vapor was generated as the crucible being resistively heated. To keep the surface ionization efficiency constant during the experiment, the temperature of the crucible was kept at 1555 °C. The crucible temperature was estimated using the heating current via a calibrated temperature-current curve. Two types of temperature measurement devices, a Pyrometer (Mikron M90-R-2) and a two-color-ratio fiber-optic-infrared temperature-measurement system (Omega iR2C), had been used for calibration. The measurement precision is within 1.5%, and the measurement accuracy of two different devices is within 15%.

The investigated ionization schemes of Lu are shown in Fig. 2. In both, scheme A-1 and scheme A-2, Lu atoms were firstly excited from the ground state 5d₆s²D₃/₂ to an intermediate state of 5d₆s₆p²D₃/₂. The laser of this excitation step was provided by the frequency-doubled BRF laser. The laser for the second excitation step (SES) was the fundamental output or the frequency doubled output of the grating laser, for scheme A-1 and scheme A-2 respectively. The fundamental output of the grating laser has a continuously tunable wavelength range of 720-930 nm [29], which can excite the Lu atoms from the intermediate state into various even-parity Rydberg states. The obtained spectrum is shown in Fig. 3a. Three series of Rydberg states 6s²nd²D₃/₂, 6s²nd²D₅/₂ and 6s²ns³S₁/₂ were observed with clear regularity approaching the ionization potential (IP). The spectroscopic analysis and discussion of the Rydberg states is presented in [30]. In the obtained spectrum of this scheme, the highest ion yield was achieved by exciting the Lu atoms to an AI state at 43831.6 cm⁻¹. This AI transition has a linewidth of
Figure 2: Lutetium ionization schemes. $A_\text{E}$ is the Einstein A coefficient. The FES were all provided by the frequency doubled BRF laser. The SES and TES were provided by the grating lasers. The red colored line means the fundamental output of the laser was applied. The blue colored line means the frequency doubled output of the used laser. Scheme C is from [16] and has been used at ISAC for Lu yield measurement (Sect. 3.2).

2.5 cm$^{-1}$, which also gives a good stability against small frequency drifts during on-line RIS beam delivery. It is worth noting that this AI state is the same one used in [16], the scheme of which is marked as scheme C in Fig. 2.

In scheme A-2, the automatic phase-matching of the nonlinear crystal was employed, which enables a continuous wavelength scan of the frequency doubled output of the grating Ti:Sa laser. Due to the angle change of the nonlinear crystal during the wavelength scan and the loose restriction of the laser cavity in the grating incident plane, a regular manual correction of the laser spatial pointing was needed. The necessity of correction is referred to the significantly drop on the resonance signal and the visual offset of laser reflections on a reference screen. Normally the correction of the alignment was made by optimizing on a resonance signal every 10-15 nm. This resonance signal was used as a normalization to link the scans. The resulting spectrum is shown in Fig. 3.b. The scan covers the energy range of 51960 - 58008 cm$^{-1}$, across two ionic state limits 5d$^6$6s$^3$D$^1$ and 5d$^6$6s$^3$D$^2$. The detailed analysis of atomic spectroscopy is presented in [30]. The output power of the frequency doubled laser varied from 40 mW at two ends of 370 nm and 445 nm, and 200 mW at the middle wavelength of 420 nm. Due to the low output at the ends of the tuning curve, the effect of the laser power on the ion yield may be not negligible. Based on this condition, the best scheme in the spectrum of Fig. 3.b is the one via the AI state at 54199.68 cm$^{-1}$ with the linewidth of 0.4 cm$^{-1}$.

Scheme B is a three step scheme with nonresonant ionization. The FES excites Lu atoms from the ground state to the 5d$^6$6p$^2$F$^6_{5/2}$ state at 28020.11 cm$^{-1}$. The TES, namely the nonresonant ionization step, was provided by the 4.8 W Nd:YVO$_4$ at 532 nm. To search the best SES for this scheme, a wavelength scan of the fundamental output of the grating laser was performed. The resulting spectrum is shown in Fig. 3.c. The highest ion yield in the spectrum is given via an excited state at 40282.58 cm$^{-1}$, whose electronic configuration has not been clearly assigned.
Figure 3: Lutetium spectra: a) Scheme A-1 spectrum: three Rydberg series approaching the IP were observed. The AI state at 43831.6 cm$^{-1}$ provides the best ion yield in this spectrum. b) Scheme A-2 spectrum: Al Rydberg series approaching ionic states Lu$^+$ 5d6s $^3$D$_1$ and Lu$^+$ 5d6s $^3$D$_2$ were observed. The AI state at 54199.68 cm$^{-1}$ gives the best ion yield in this spectrum. c) Scheme B spectrum: eleven excited states were observed. The state at 40282.58 cm$^{-1}$ gives the best ion yield in this spectrum.
Scheme C had been developed and investigated in [12,13], and had been practically applied to ultratrace measurements in [16]. Measurement of this scheme was also performed in our experiments to compare its ionization efficiency with that of the new schemes. The FES of scheme C is from the ground state to \(^5S_6p^2D^\circ_{3/2}\) state at 22124.76 cm\(^{-1}\). And the SES is exciting Lu atoms further to the AI state at 43831.6 cm\(^{-1}\).

Table 1: Lutetium: the relative ionization efficiency \(\epsilon_{rel}\) comparison of the different schemes (Fig. 2). \(P_{sat}\) is the saturation power of the transition, and \(P_{op}\) is the laser power in operation when measuring the scheme efficiency. The \(\lambda_2\) for the FES are from NIST ASD [17], and the \(\lambda_1\) for the SES are from our measurements. The errors of the \(P_{op}\) are about \(\pm 2\) in the last digit. For all the measurements, the temperature of the crucible was kept at 1555 °C, corresponding to an crucible heating current of 180 A. The power of the 532 nm laser was 4.8 W.

| scheme | \(\lambda_2\) (nm) | \(P_{op}/P_{sat}\) (mW) | \(\lambda_1\) (nm) | \(P_{op}/P_{sat}\) (mW) | ionization | \(\epsilon_{rel}\) | \(\epsilon_{rel}\) via +532nm |
|--------|------------------|-----------------|------------------|-----------------|----------|-----------|----------------|
| A-1    | 337.746          | 30 / 6(1)       | 703.056          | 220 / 95(7)     | AI       | 3.0       | 7.5            |
| A-2    | 337.746          | 30 / 6(1)       | 406.642          | 79 / 6b         | AI       | 2.0       | 5.5            |
| B      | 356.887          | 110 / 1.9(3)    | 815.497          | 1300 / 61(8)    | Non      | 1.0       | 10             |
| C      | 451.982          | 145 / 8(2)      | 460.684          | 45 / 27(2)      | AI       | 1.5       | 7.0            |

\(a\) Two schemes use the same AI state at 43813.6(3) cm\(^{-1}\).
\(b\) The saturation power is too high to be accurately extracted from the measured saturation curves.
\(c\) The scheme has been investigated [12,13] and applied to ultratrace measurement [16]. On-line isotope yield using this scheme at ISAC is presented in Sect. 3.2.

To determine the saturation power of the transitions, the ion yield dependences on the laser powers were measured. For convenience, the laser power was measured on the laser table right after the telescope expansion. After that, the laser beam will still lose power by passing the combination mirrors, transportation prism and the vacuum window before it finally interacts with the Lu atoms. A typical transportation loss of \~50\% shall be taken into account. The exciting and ionizing lasers all overlap in the 3 mm diameter crucible. In the laser alignment prior to the experiment, the laser beams were focused as small as possible into the crucible region. During the experiment, a slight readjustment was attempted to maximize the ion yield. In principle, the maximum signal is achieved when the laser beams spatially match with the atomic vapor volume (3 mm diameter) at the saturated power. A function of \(I = I_0 + A(1 - e^{-P/P_{sat}})\) was applied to fit the measured data, where \(I\) is the ion yield, \(P\) is the laser power and \(P_{sat}\) is the saturation power. In some cases, Lu atoms may absorb one more photon from the resonant laser after being excited to the aimed state, and ionize nonresonantly if the total energy is over the IP. In these cases, a nonresonant term \(A' \ast P\) was added to the saturation function above. The measured saturation powers for the tested excitation schemes are listed in Tab. 1.

Tab. 1 also presents the measured relative laser ionization efficiency \(\epsilon_{rel}\) of the schemes. The \(\epsilon_{rel}\) was defined as the enhancement ratio of laser ionization over surface ionization. For easy comparison, the values were normalized to the \(\epsilon_{rel}\) of scheme B. The laser powers used in measuring the efficiencies are listed as \(P_{op}\). Comparing the \(P_{op}\) with the \(P_{sat}\) reveals the possibility to improve the \(\epsilon_{rel}\) by increasing the laser power. The 532 nm laser pronouncedly increased the \(\epsilon_{rel}\). With only the 532 nm laser into the source, the surface ionization of the Lu did not increase evidently, which seemed to imply the atom vapor density was not significantly boosted by the laser. Therefore, it was not a dominant contributor to the enhancement of \(\epsilon_{rel}\). However,
when adding the 532 nm laser to the AI scheme A-1, there were two distinguishable effects: one was immediately seen right after adding the laser, and the other one ramped up gradually in \( \sim 1 \) minute. Delaying the pulse of the 532 nm laser off the synchronization around more than 3 \( \mu \)s, both effects persisted. A similar phenomenon was also observed in Pr development, which is discussed later in this paper.

3.2. On-line lutetium RILIS test

We have applied the scheme C to an IGLIS source with a 10 \( \mu \)A proton beam hitting on a uranium carbide (UCx) target in June 2015. The generated radioactive isotopes effuse into the IGLIS source, where laser ionization occurs. The IGLIS source was set in a transmission mode [3]. The temperature of the UCx target was estimated by the heating current via the pre-measured temperature-current curves and the calculated power deposition from the proton beam. The yield of the Lu isotope was measured as an ion count on a downstream channeltron. The saturation powers measured on line were 10(1) mW and 33(2) mW for the FES and SES, respectively. The disagreement with the values obtained (Tab. 1) can be explained with the different transportation efficiency of the laser beams. The ion yields for different isotopes of Lu are shown in Tab. 2. The laser powers are 250 mW and 600 mW for the FES and SES respectively during the yield measurement. From the result, we can see the release of Lu isotopes from UCx target is not favored, especially for short lifetime isotopes. We did not observe any Lu\(^{+}\) release for the isotopes whose lifetime is shorter than 5 hours. Additionally, the surface ionized Lu\(^{+}\) was barely seen.

In June 2016, we applied the scheme C to a rhenium (Re) hot cavity RILIS source with a 60 \( \mu \)A proton beam on a Ta target. The release of Lu isotopes from this target is much better than from a UCx target. The temperature of the target was about 2300 °C. Here the ion yield was measured with a downstream channeltron and the ISAC yield station [31]. The investigated isotopes yields are listed in Tab. 3.

3.3. Temperature dependence of the ion yield via Rydberg states of lutetium

With the total excitation energy lower than the IP, the detailed ionization mechanism of Rydberg states is still an open question. For Lu a high ion yield peak is generated via the Rydberg state at 43717.68 cm\(^{-1}\), which is only \( \sim 45 \) cm\(^{-1}\) beneath the IP. The ion yield is outstandingly
Table 3: Lutetium: on-line ion yield from a Ta target with a Re hot cavity source bombarded with a 60 µA proton beam. Here, the ion yield was measured with the ISAC yield station through nuclear decay counting. All yields in this table was evaluated via characteristic γ lines.

| isotope | isomer | half life | laser off (s⁻¹) | laser on (s⁻¹) | enhancement ratio |
|---------|--------|----------|----------------|---------------|------------------|
| 164Lu   | g      | 3.14 m   | 2.1×10⁸        | 5.5×10⁸       | 2.6              |
| 166Lu   | g      | 2.65 m   | 1.6×10⁸        | 4.4×10⁸       | 2.8              |
| 166Lu   | m1     | 1.41 m   | 1.5×10⁸        | 1.7×10⁸       | 1.1              |
| 166Lu   | m2     | 2.12 m   | 7.5×10⁷        | 2.0×10⁸       | 2.7              |
| 167Lu   | g      | 51.5 m   | 8.6×10⁸        | 3.1×10⁹       | 3.6              |
| 167Lu   | g      | 5.5 m    | 2.0×10⁸        | 6.8×10⁸       | 3.4              |
| 168Lu   | m1     | 6.7 m    | 6.5×10⁸        | 1.7×10⁹       | 2.6              |
| 169Lu   | g      | 1.42 d   | 3.1×10⁹        | 2.3×10¹⁰      | 7.4              |
| 170Lu   | g      | 2.0 d    | 3.1×10⁹        | 1.4×10¹⁰      | 4.5              |
| 171Lu   | g      | 8.24 d   | 2.7×10⁹        | 2.0×10¹⁰      | 7.4              |
| 172Lu   | g      | 6.7 d    | 5.9×10⁸        | 3.9×10⁹       | 6.6              |
| 177Lu   | g      | 6.647 d  | 4.1×10⁷        | 6.5×10⁹       | 16               |
| 178Lu   | g      | 28.4 m   | 1.0×10⁷        | 4.2×10⁷       | 4.2              |

High compared to the neighboring Rydberg states, and more interestingly, it increases significantly (relative to that of the AI state at 43831.6 cm⁻¹) with the ambient temperature. A similar phenomenon was seen in the laser ionization spectroscopy of antimony [32]. The occurrence of this phenomenon in both cases coincides with the existence of a perturbation from doubly excited states. The mixture with the doubly excited valence states significantly decreases the lifetime of the state, e.g. the photoexcitation rate to the state, therefore prominently enhances the ion yield.

The detail of the perturbation is discussed in [30].

The interesting operational aspect for the RILIS is the extraordinary enhancement of ion yield when increasing the ambient temperature. The laser ionization spectra of high Rydberg states and the AI state at 43831.6 cm⁻¹ were obtained under different crucible temperatures. The AI resonance peak acts as a reference to normalize the Rydberg state spectra. The experimental results are shown in Fig. 4: R-1 is the perturbed Rydberg state at 43717.68 cm⁻¹, and R-2 is another perturbed Rydberg state at 43431.82 cm⁻¹. Unlike the very localized line-intensity change at R-1, the perturbation around R-2 is much broader, which indicates a strong perturbation. Despite the different magnitude of perturbation, the two perturbed Rydberg states both show dependence of the ion yield on the temperature, so do some other regular Rydberg states. Due to the broad perturbation around R-2, e.g. multiple Rydberg states are mixed with a doubly excited state. It is difficult to tell whether this temperature-dependence is strongly affected by the mixture of the doubly excited state, or only related to the binding energy. However, evident is that at higher temperature the ionization probability increases at higher binding energy range. This should either relate to the blue-shift of maximum emission of the black body radiation spectrum (λₘₚ∼1/T) with increased temperature, or be caused by the increase of the thermal kinetic energy of particles (Eₖ∼kT) in the collisions. More investigations are need to determine whether both mechanisms significantly contribute or only one dominates, and whether the leading mechanism changes when the Rydberg states mix with doubly excited states. Additionally, the total
Figure 4: Lutetium: the ionization via Rydberg states depends on the ambient temperature. The IGLIS was set in the transmission mode. The spectra at different temperatures have been normalized to the Al resonance peak.
photon emission from the black body radiation increases with temperature, so does the collision rate. However this effect should equally address on all Rydberg resonances. In conclusion, when applying the laser ionization schemes with Rydberg states the temperature must be considered as an important parameter affecting the ionization efficiency.

Proven the temperature effect on the ion yield of Rydberg states, the feasibility to use Rydberg-state RILIS schemes with an IGLIS was tested. The laser ionization spectra covering the high-lying Rydberg states and the 43831.6 cm$^{-1}$ Al state were measured at both transmission and suppression mode of IGLIS. To make the measurements comparable, the only difference of ion optics between the two modes is the increasing the repeller potential to +22 V in the suppression mode instead of -4 V relative to the crucible potential in the transmission mode. The crucible temperature was kept constant (1555 °C), so were all the laser settings. In the transmission mode, the majority of laser ionization happens in the hot crucible. However in the suppression mode, those ions are pushed backward by the potential of the repeller and not extracted. Only a small amount of ions (around 2 orders of magnitude less shown in the Fig. 5) generated after the repeller was guided by the RF and finally get detected. Approximately we can say the resonant ions signal observed in two modes are generated at different locations: inside the crucible and after repeller, for the transmission mode and the suppression mode, respectively. Inside the hot crucible, Rydberg atoms can easily get ionized by thermal photons and collisions. However after the repeller, both the density of thermal photons and the collision possibility drop significantly, so does the possibility of ionizing Rydberg atoms. Consequently as shown in Fig. 5 no Rydberg resonant peaks are observed when the IGLIS operated in the suppression mode.
An interesting phenomenon is that the perturbed Rydberg state R-1, or the component from the doubly-excited valence state, still ionizes at the IGLIS suppression mode. Assuming that the neutral atoms effuse from the 3 mm diameter hot crucible and form a beam with an opening angle $\sim 10^\circ$, the relevant ionization volume in suppression mode should locate directly downstream from the repeller electrode. However this region is not field-free. In this experiment, the repeller has a potential $+20$ V relative to the RFQ. And the RFQ has a $\sim 75$ V pp $0.3$ MHz square-wave alternative potential on the rods. According to the classical saddle point model [33], the ionization threshold $W_{th}(F)$ is lowered by the electric field:

$$W_{th}(F) = IP - 2\sqrt{\frac{Ze_{eff}e^2}{4\pi\varepsilon_0}} \sqrt{F},$$

(1)

where $IP$ is the ionization potential in zero field, $Ze_{eff}$ is the effective charge number of the core ($\approx 1$ for high Rydberg states), $e$ is the electric charge of the electron and $\varepsilon_0$ is the permittivity of the vacuum. From the formula, to shift the ionization threshold 50 cm$^{-1}$ below the IP, 75 V/cm is needed. This field strength was proven to reasonably exist in the suppression mode by SIMION simulation [34]. With the lowering of the ionization threshold, the doubly excited valence state at R-1 will be forced to become an AI state. This phenomenon of “forced autoionization” was observed at 200 cm$^{-1}$ below the IP of barium and was theoretically explained by Sandner et al. [35]. With the external electrical filed strength of 133 V/cm, a forced AI of Lu was observed by Maeda et al., which is exactly at the same energy position of R-1 [9]. The forced ionization spectrum they obtained agrees with our observation (Fig. 5). The onset of stark continuum at $W_{th}(F)$ was not evident in our spectrum due to the field inhomogeneity within the ionization volume.

3.4. Off-line Relative efficiency comparison of praseodymium RILIS schemes

A standard solution of Alfa Aesar Speccure (1 µg/µl Pr$_6$O$_{11}$ in 5% HNO$_3$) was deposited on a titanium (Ti) foil and then heated inside a Ta crucible. For the whole experiment, the crucible was kept in a same temperature of 1555 °C, corresponding to the crucible heating current of 180 A. The Pr laser excitation schemes studied in this work are shown in Fig. 7. For all the schemes A (A-1, A-2 and A-3), the Pr atoms were firstly excited into an intermediate state $4f^36s6p^4I^9/2$ [17] at 20190.85 cm$^{-1}$. From this state the excitation schemes using infrared (IR) + 532 nm, IR + IR and blue + 532 nm were investigated. The power of the 532 nm laser was 6.7 W. The experimental techniques of continuous infrared and blue scans were the same as described in Sect. 3.1. The resulting spectra are shown in Fig. 6.

The transitions that generated highest ion yield in each spectrum are marked in Fig. 6 and listed in Tab. 4 to compare the relative ionization efficiencies $\varepsilon_{rel}$. The values of $\varepsilon_{rel}$ were normalized to that of scheme A-1. In Fig. 6b and c, the upper states, giving best ion yield, are within the uncertainty of the best known IP value, therefore they could be Rydberg or AI states. The SES of scheme A-2 was chosen as 795.007 nm transition because this transition as the SES in scheme A-1 gives the highest ion yield. The corresponding upper state is 32769.35 cm$^{-1}$ (Fig. 6a). The spectral linewidth of the all the transitions for the best ion yield (including the two Rydberg/AI states) is 9-15 GHz, dominated by the laser linewidth.

Similar to Lu, the laser ionization of Pr was also significantly enhanced by adding the 532 nm laser with both “immediate” and “slow” effects. Unlike Lu, there was an increase of Pr$^+$ by only shooting 532 nm laser into the source. Due to the very complex atomic level structure of Pr, it is difficult to tell if it is the result of a thermal effect or an optical resonance. Another
Figure 6: Praseodymium spectra: a) Scheme A-1 spectrum: the intermediate state at 32769.35 cm$^{-1}$ gives best ion yield in this spectrum. b) Scheme A-2 spectrum: the Rydberg/AI state at 44149.54 cm$^{-1}$ gives best ion yield in this spectrum. The IP value with uncertainty [17] is marked. c) Scheme A-3 spectrum: the Rydberg/AI state at 44153.03 cm$^{-1}$ gives best ion yield in this spectrum. d) Scheme B spectrum: the intermediate state at 32343.04 cm$^{-1}$ gives best ion yield in this spectrum.
Figure 7: Praseodymium ionization schemes. $A_m$ is the Einstein A coefficient. The meanings of the dash line, solid line, line colors are the same as Fig. 2.

Table 4: Praseodymium: the relative ionization efficiency $\epsilon_{rel}$ comparison of the different schemes. The scheme details are shown in Fig. 7, the meanings of $P_{sat}$, $P_{opt}$ and $\lambda$ are the same as what described in Tab. 1. The $A_1$ for the FES are from NIST ASD [17], and the $A_2$ for the SES and the $A_3$ for the TES are from our measurements. The errors of the $P_{opt}$ are about ±2 in the last digit. For all the measurements, the temperature of the crucible was kept at 1555 °C, corresponding to an crucible heating current of 180 A. The power of the 532 nm laser was 6.7 W.

| scheme | FES | SES | TES | ionize | $\epsilon_{rel}$ | $\epsilon_{rel}$ |
|--------|-----|-----|-----|--------|-----------------|-----------------|
|        | $\lambda_1$ | $P_{opt}/P_{sat}$ | $\lambda_2$ | $P_{opt}/P_{sat}$ | $\lambda_3$ | $P_{opt}/P_{sat}$ | via | +532nm |
| A-1    | 495.274 | 390/(6(1)) | 795.007 | 1130/(460/90) | - | - | Non | 1.0 | 6.0 |
| A-2    | 495.274 | 390/(6(1)) | 795.007 | 1130/(460/90) | 878.704 | 480/(12(1)) | Ryd/Al | 5.2 | 12 |
| A-3    | 495.274 | 390/(19(3)) | 417.315 | 180|h a | - | - | Ryd/Al | 2.1 | 4.3 |
| B      | 491.539 | 515/(7(2)) | 833.401 | 1370/36(7) | - | - | Non | 4.3 | 13 |

a The saturation power is too high to be accurately extracted from the measured saturation curves.
interesting observation is that PrO$^+$ molecular ions ($IP_{PrO}=4.9$ eV [36]) were generated only using the 532 nm laser. Beside PrO$^+$, the molecular ions TiO$^+$ ($IP_{TiO}=6.8$ eV [37]) and ZrO$^+$ ($IP_{ZrO}=6.2$ eV [38]) were also observed from the Ti and Zr foil that were used as carriers for the AAS solution. The dependence of these molecular ion yields on the 532 nm laser power was studied (Fig. 8). To avoid the influence of plasma and thermal effect caused by the powerful 532 nm laser, IGLIS was set in the suppression mode: the repeller had $+3$ V relative to the source. A small amount of surface ionized Ti$^+$ was also observed in this mode due to the low suppression potential on the repeller relative to the big amount of Ti sample ($\sim 1 \times 1$ cm$^2$ 0.001 inch thickness Ti foil) in the crucible. The parabolic dependence of PrO$^+$ and TiO$^+$ on the laser power (linear in logarithmic scale in Fig. 8) indicates two-photon excitation with nonresonant ionization by the 532 nm laser [39]. The Pr$^+$ and Ti$^+$ ions, which were from the resonant one-photon excitation and the surface ionization respectively, did not show the dependence on the 532 nm laser.

4. Summary

Laser resonant ionization scheme developments of lanthanide elements Lu and Pr were performed at the off-line LIS stand of ISAC-TRIUMF. The relative laser ionization efficiencies of different laser schemes have been evaluated. Additionally, on-line tests of Lu schemes have been performed on two different types of targets (uranium carbide and tantalum) and two different types of ion sources (IGLIS and hot cavity RILIS). The temperature dependence of the laser resonance ionization efficiency via Rydberg states of lutetium has been studied. The validity to use Rydberg state schemes on IGLIS was investigated. The ionization mechanism of Rydberg
states, especially perturbed ones, was discussed. The generation of molecular ions PrO$^+$, TiO$^+$ and ZrO$^+$ by interaction with 6.7 W 532 nm laser light was observed. Their two-photon excitation character, a linear dependency on the square of the laser intensity, has been measured and discussed.

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