Radium ionization scheme development: The first observed autoionizing states and optical pumping effects in the hot cavity environment


⁎ Corresponding author at: Accelerator Science Division, TRIUMF, Vancouver BC V6T 2A3, Canada.
1 Present address: Accelerator Science Division, TRIUMF, Vancouver BC V6T 2A3, Canada.
E-mail address: tdaygoodacre@triumf.ca (T. Day Goodacre).

A R T I C L E   I N F O

Keywords:
RILIS
ISOLDE
Radium
Autoionizing states
Laser ionization

A B S T R A C T

This paper reports on resonance ionization scheme development for the production of exotic radium ion beams with the Resonance Ionization Laser Ion Source (RILIS) of the CERN-ISOLDE radioactive ion beam facility. During the study, autoionizing states of atomic radium were observed for the first time. Three ionization schemes were identified, originating from the 7s 2 1 S0 atomic ground state. The optimal of the identified ionization schemes involves five atomic transitions, four of which are induced by three resonantly tuned lasers. This is the first hot cavity RILIS ionization scheme to employ optical pumping effects. The details of the spectroscopic studies are described and the new ionization schemes are summarized.

1. Introduction

The principal ion source of the ISOLDE radioactive ion beam facility [1] based at CERN is the Resonance Ionization Laser Ion Source (RILIS) [2,3]. The RILIS uses tunable lasers to excite valence electrons by targeting sequential atomic resonances before a final ionizing transition, typically either to an autoionizing state or non-resonant excitation to the ionization continuum. The selectivity of the ionization mechanism is a result of the element unique nature of atomic energy levels. However, it also follows that an “ionization scheme” of sequential resonances has to be tested and developed for each element that the RILIS is applied for. Excitation to an autoionizing state is typically the preferred method of ionization in resonance ionization spectroscopy (RIS) [4]. This is because the cross-section for a resonant transition can be orders of magnitude greater than for non-resonant excitation to the ionization continuum.

Despite having no stable isotopes, optical spectroscopy of atomic radium has been ongoing for > 100 years [5]. However, prior to this work no autoionizing states had been identified. Here we present the results of ionization scheme development for atomic radium including three new ionization schemes, the first identification of autoionizing states of atomic radium and the first harnessing of optical pumping effects within a hot cavity RILIS ionization scheme.

1.1. Radioactive ion beam production at ISOLDE

ISOLDE is an ISOL type [6] radioactive ion beam facility. A pulsed 2 μA average power “driver beam” of 1.4 GeV protons from the CERN
of use for medical applications [16] which continues to the present day. $^{226}$Ra is used to treat castration-resistant prostate cancers with metastases [17,18] and there is current interest in using $^{226}$Ra as a generator for $^{226}$Ac, which is considered to be particularly promising for medical applications [19]. Radium isotope collections have been undertaken at ISOL facilities as a result of this interest [20]. Dedicated facilities, applying ISOL principles for medical isotope production, are currently under development [21,22]. The application of a RILIS in such cases offers the possibility for increasing both the purity and the efficiency of collections.

2. Radium ionization at ISOL facilities

2.1. Surface ionization

The efficiency of surface ionization in the hot cavity environment has been discussed in detail in [9,23,24]. The ionization potential is a good guide to the comparative susceptibility of an element to surface ionization, however, the excited states of the atom and ion must also be considered [26]. This leads to an effective ionization potential ($IP_{\text{eff}}$) which can be calculated as

$$ Q_s = \sum \gamma_j \exp(-E_j/kT), $$

where $Q_s$ is a partition function accounting for the influence of the ground or excited states $j$ of the atom ($x = a$) or the ion ($x = i$), $\gamma_j$ is the degeneracy of the atomic or ionic state, $E_j$ is the excitation energy of a particular state, $k$ is the Boltzmann constant and $T$ is the temperature.

In the case of radium, $IP_{\text{eff}} = 5.14$ eV at 2060°C.

Based on the equations and ion survival probability in a tungsten hot cavity discussed in [25], the surface ionization efficiency of radium in a tantalum hot cavity (work function $\phi = 4.25$ eV [27]) can be estimated to be 5%. This could be considered to be a conservative estimate due to the increased electron emission from tantalum compared to tungsten, however, given the number of uncertainties such an approach is justified. Efficiencies of surface ionized radium calculated from ISOLDE yields [28] support the feasibility of the estimation.

2.2. RILIS ionization

Based on the Boltzmann equation, 99.7% of radium atoms are in the ground state at 2060°C, hence all of the ionization schemes investigated originated from the $7s^2\ 5S_0$ atomic ground state. The application of a RILIS for the ionization of radium was previously demonstrated at the TRIUMF-ISAC Facility [29], applying a $\{8s,|\lambda_8\rangle|\lambda_8\rangle = (483$ nm)/818 nm)/532 nm) ionization scheme with a non-resonant final excitation step [30]. A factor of three increase of the surface ionized signal was reported when applying the ionization scheme to ionize radium extracted from a pre-irradiated target heated to ≈1000°C.

For this study, literature data [5] was used to identify the first two transitions of an alternative ionization scheme better suited for use at the ISOLDE RILIS due to the avoidance of the 483 nm first step (that requires the operation of a Ti:Sa laser beyond its typical operational range or a UV pumped dye laser). This alternative ionization scheme employs a 714 nm first step and a 784 nm second step, exciting to the $7s^2\ 5S_0$ state at 26,754 cm$^{-1}$, which is ≈15 819 cm$^{-1}$ (≈632 nm) from the ionization potential at 42.573.36 (2) cm$^{-1}$ [31]. Further information on these transitions is presented in Table 1.

Excitation to a state within the energy of a ≈632 nm photon from the ionization potential, enabled fundamental light from the RILIS dye lasers to be used as a final excitation step to probe the ionization continuum for autoionizing states.
A schematic of the experimental setup, the lasers used for this experiment are highlighted. A detailed discussion of the experimental setup is included in the text.

3. Experimental setup

The ISOLDE RILIS is depicted in Fig. 1. A system of three dye lasers and three Titanium:Sapphire (Ti:Sa) lasers are used in combination with 2ω, 3ω and 4ω harmonic generation to produce laser light with wavelengths spanning between 210 nm and 950 nm for multi-step resonance ionization. The lasers are typically pumped with 532 nm light, produced by frequency tripling the light from a Nd:YAG laser. The dye lasers are typically pumped with 355 nm light and are overlapped by using a master clock to synchronize the output of the pump lasers. The laser light is stabilized in both position and wavelength, a more detailed description of the RILIS laser system can be found in [3].

Following two-step (714 nm|784 nm) resonance excitation to the 7s8s 3S1 state, dye lasers were used to scan the excitation energy band from the ionization potential to 45 094 cm-1 (632 nm to 545 nm). Ionization in this case was achieved via (714 nm|784 nm|545 nm- 632 nm dye scan). Three resonances were observed at wavelengths of 558 nm, 581 nm and 615 nm, additional details of the transitions are given in Table 1. The peaks in the spectra were fitted using either Voigt, Breit-Wigner-Fano or Inverse Polynomial peak functions. The different line shapes were the result of differing relative contributions from the spectral laser line shape, Doppler broadening of the atomic line, saturation effects and for the observed autoionizing states, asymmetric Fano Profiles. The scans of these resonances are presented in Fig. 2. The two resonances observable on the higher energy tail of the 558 nm autoionizing resonance are highlighted. The uncertainties of the 558 nm and 581 nm transitions are dominated by the widths of the autoionizing resonances and are typically overlapped by using a master clock to synchronize the output of the pump lasers. The laser light is stabilized in both position and wavelength, a more detailed description of the RILIS laser system can be found in [3].

The lasers used in the ionization scheme development reported here are highlighted in Fig. 1. Two Ti:Sa lasers were used to produce the light for the first and second excitation steps. Dye lasers operated with ethanol solutions of either Fluorescein 27, Rhodamine 6G or DCM dyes were scanned to search for autoionizing resonances, accessed via ionization schemes of (714 nm|784 nm|545 nm - 632 nm dye scan). The laser light was focused using optics within the RILIS laser room and directed to converge inside a tantalum hot cavity surface ion source coupled to a UC5 target. Based on off-line calibration, the target and tantalum hot cavity were maintained at 1950 °C and 2060 °C respectively throughout these measurements. In the case of radium, since no stable isotope exists, the atoms were produced on-line at ISOLDE.

During the scans of the final excitation step, the wavelength of the laser light was measured using a HighFinesse/Ångstrom WS7 wavelength meter while the ion current on mass A = 226 was measured using a Faraday cup inserted downstream of the mass separator magnet, as depicted in Fig. 1.

4. Results and discussion

4.1. The search for autoionizing states

Following two-step (714 nm|784 nm) resonance excitation to the 7s8s 3S1 state, dye lasers were used to scan the excitation energy band from the ionization potential to 45 094 cm-1 (632 nm to 545 nm). Ionization in this case was achieved via (714 nm|784 nm|545 nm - 632 nm dye scan). Three resonances were observed at wavelengths of 558 nm, 581 nm and 615 nm, additional details of the transitions are given in Table 1. The peaks in the spectra were fitted using either Voigt, Breit-Wigner-Fano or Inverse Polynomial peak functions. The different line shapes were the result of differing relative contributions from the spectral laser line shape, Doppler broadening of the atomic line, saturation effects and for the observed autoionizing states, asymmetric Fano Profiles. The scans of these resonances are presented in Fig. 2. The two resonances observable on the higher energy tail of the 558 nm autoionizing resonance are highlighted. The uncertainties of the 558 nm and 581 nm transitions are dominated by the FWHM of the resonances and the associated possibility for variations in the laser power over the range of the scan due to wavelength dependent dye efficiencies.

All three of the resonances were initially identified as autoionizing states, with full width at half maxima (FWHM) of 62 (0.7) cm-1, 90 (1) cm-1 and 2.28 (3) cm-1 respectively (no attempt was made to deconvolve the ~12 GHz linewidth of the dye lasers or account for...
power broadening). Autoionizing resonances with both comparable and greater FWHM have been observed for other elements such as the alkaline earth metal homologue barium [32]. However, an unexpected insensitivity to blocking either of the first two steps was observed when the \(714 \text{ nm} | 784 \text{ nm} | 615 \text{ nm}\) ionization scheme was tested at the CRIS beamline [11], where a charge exchange cell is used to neutralize ions before re-ionization. Following an additional review of the literature, it was realized that the 615 nm line was a known transition from the \(7s7p \, ^{3}P_{2}\) metastable state. On the CRIS beamline, the metastable state is understood to have been populated during the charge exchange process [33], while during hot cavity RILIS operation it could only be significantly populated via a decay from the \(7s8s \, ^{3}S_{1}\) state, as from the Boltzmann equation the thermal population of the \(7s7p \, ^{3}P_{2}\) state at 2060 °C is just 0.02 %. This is the first time optical pumping has been observed in hot cavity RILIS operation. Similar non-laser driven transitions within resonance ionization schemes have been observed in other laser-atom interaction environments [34], where the intermediate non-laser driven stage was reported to be resulting from interactions with a buffer gas.

Excitation from \(7s7p \, ^{3}P_{2}\) to \(7p^{2}P_{2}\) with 615 nm light results in an excited state \(\approx 9632 \text{ cm}^{-1}\) below the ionization potential. Thus it was unexpected that applying the \(714 \text{ nm} | 784 \text{ nm} | 558 \text{ nm}\) ionization scheme (ionizing via an autoionizing state) and applying the \(714 \text{ nm} | 784 \text{ nm} | 993 \text{ nm decay} | 615 \text{ nm, 714 nm, 784 nm}\) ionization scheme (which relies on photons with energies matching preceding transitions for the final ionizing transition) yielded a similar factor of 3–4 increase in the ion rate. Due to time constraints, further investigations were limited to these two ionization schemes corresponding to the highest ionization efficiency. The sensitivity to the timing overlap of the pulsed laser light and the saturation of the transitions were investigated to clarify the situation.

### 4.2. Timing scans

In order to demonstrate optical pumping within the hot cavity environment, the 615 nm laser pulses were delayed with respect to the temporally overlapped 714 nm and 784 nm pulses while monitoring the ion current on the Faraday cup inserted downstream of the dipole mass separator. The variation in ion current with the time delay of the 615 nm laser pulses is presented in Fig. 3, together with the results of delaying the 558 nm transition in the same manner for comparison. The comparative insensitivity of the \(714 \text{ nm} | 784 \text{ nm} | 993 \text{ nm decay} | 615 \text{ nm, 714 nm, 784 nm}\) ionization scheme to the timing overlap of the final step with the first two transitions, can be understood as resulting from the decay from the \(7s8s \, ^{3}S_{1}\) state to the \(7s7p \, ^{3}P_{2}\) state, from which there is no allowed transition path to the \(7s^{2}S_{0}\) atomic state.

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**Fig. 2.** The ionization schemes investigated during the radium ionization scheme development and scans of the resonances. Levels labeled AIS are identified to be autoionizing states, the dashed line labeled IP represents the first ionization potential of atomic radium. Based on the observations summarized in Section 4.4, 615 nm light is the dominant ionization step for electrons populating the \(7p^{2}P_{2}\) excited state. This is reflected by the solid arrow for a 615 nm excitation step from \(7p^{2}P_{2}\).

**Fig. 3.** The change in ion current with a variation in the synchronization of the second and third step transitions. An off-set of \(\approx 100 \text{ ns}\) with respect to the timing of the second step transition is the result of the laser pulse timing being measured at different locations. Further details are discussed in the text.
ground state. However, the comparatively small reduction in ionization efficiency when delaying the 615 nm transition from the first two excitation steps by 1 μs also indicates that the 615 nm transition is the dominant ionization step from the 7P 23P 2 excited state. Thus the ionization scheme can be considered to be (714 nm|784 nm|993 nm dec|615 nm|615 nm).

### 4.3. Saturation measurements

Saturating the transitions of an ionization scheme maximizes its efficiency and reduces the impact of any potential deterioration in laser power over the course of an experiment. Saturation measurements of the 714 nm, 784 nm, 558 nm and 615 nm transitions were made by varying the laser power of each transition individually, while monitoring the ion current. The results are presented in Fig. 3. The variation in the error bars on specific measurement points is the result of the measurements taking place at different times, with differing ion currents.

The saturation measurements presented in Fig. 3 were fitted using Eq. 3, a commonly used function [36,37] which relates the ion current to the laser power delivered for each resonant transition

\[
I = B + M (P_{1/2sat} / (P_{1/2sat} + 1)),
\]

where \(I\) is the ion current, \(B\) is the background ion current when the transition is blocked, \(M\) is the maximum ion current achievable with a fully saturated transition, \(P\) is the laser power delivered to the laser-atom interaction region and \(P_{1/2sat}\) is the laser power required to achieve 50 % of \(M\). The equation assumes the dominant contribution to the ionization process is from resonant excitation.

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The uncertainties in the \(P_{1/2sat}\) values are dominated by the uncertainty in the transmission of the laser light to the hot cavity. The transmission efficiency is assumed to be constant during the saturation measurement therefore it was not included as an uncertainty on each measurement point but rather in the error in the value for \(P_{1/2sat}\), with a transmission efficiency of between 40 and 60 %. The plots shown in Fig. 3 assume a 50 % transmission efficiency.

The 714 nm, 784 nm and 615 nm transitions were demonstrated to be deeply saturated with the available laser power; while the 558 nm transition was found to be on the edge of saturation reaching approximately 0.78 M with an estimated 2.8 W of laser light delivered to the ion source. By extrapolating from the saturation fit, doubling the laser power delivered to the laser-atom interaction region would increase the saturation level to 0.87 M. Based on the saturation measurements, it is clear that the (714 nm|784 nm|993 nm dec|615 nm|615 nm) ionization scheme offers the greatest operational stability for on-line radioactive ion beam production.

The significant population of the 7s7p 3P 2 state, highlights the potential limitation to some RILIS ionization scheme efficiencies due to the decay of excited states within the time frame of the applied ionization scheme. For a given pulse length, such losses would make it additionally challenging to saturate a transition.

### 4.4. An enhanced cross-section for excitation from 7P 2 to 49 193.7 cm⁻¹

The timing synchronization scans presented in Fig. 3 demonstrate that the 615 nm transition (exciting from the 7P 2 to 49 193.7 cm⁻¹) was the dominant ionization step, despite there being a comparable number of 714 nm and 784 nm photons (capable of exciting from the 7P 2 state to 46 940.5 cm⁻¹ and 45 695.8 cm⁻¹ respectively). This suggests a significantly increased cross-section for excitation from 7P 2 to 49 193.7 cm⁻¹ compared to either 46 940.5 cm⁻¹ or 45 695.8 cm⁻¹. Given that the 615 nm transition is the dominant ionization step, the inference of an enhanced cross-section for excitation to 49 193.7 cm⁻¹ is supported by the deep saturation of the influence of 615 nm photons presented in Fig. 4. By comparison, non-resonant final step transitions in RILIS ionization schemes using a dedicated 532 nm frequency-doubled Nd:YVO₄ Blaze laser [14] are not typically saturated despite delivering an estimated 24 W of laser light to the laser-atom interaction region. Applying a fourth laser, as part of a (714 nm|784 nm|993 nm dec|615 nm|605 − 625 nm) ionization scheme, could clarify whether the efficiency of the (714 nm|784 nm|993 nm dec|615 nm|615 nm) ionization scheme is the result of an autoionizing state in the vicinity of 49 193.7 cm⁻¹.

### 4.5. On-line application

Following the ionization scheme development reported here, RILIS ionization of atomic radium has been successfully applied on two occasions to produce radioactive ion beams for experiments on the CRIS beam line [10]. Based on the enhancement and the degree of saturation, the (714 nm|784 nm|993 nm dec|615 nm|615 nm) ionization scheme was identified as optimal for on-line RILIS operation.

For future on-line operation, the application of a fourth laser producing 558 nm light to additionally target radium atoms in the 7s8s 2S 1 excited state, may result in an enhanced overall efficiency. This would correspond to the simultaneous application of ionization schemes of (714 nm|784 nm|993 nm dec|615 nm|615 nm) and (714 nm|784 nm|558 nm). A similar approach is commonly applied for the ionization of elements such as indium, aluminium and gallium at the ISOLDE RILIS, where there is a significant percentage of the atomic population existing in a low lying thermally populated atomic level (at ~ 2000 °C) [3].

The ionization schemes presented here include excitations via s→p transitions, which exhibit the necessary sensitivity to nuclear structure effects for future in-source resonance ionization spectroscopy experiments. The applicability of the 714 nm line for such investigations has already been demonstrated [38].

### 5. Conclusion

Three ionization schemes for atomic radium were developed. Autoionizing states of atomic radium were observed for the first time, found to be at 43 951 (6) cm⁻¹ and 44 686 (4) cm⁻¹ and accessed via ionization schemes of (714 nm|784 nm|581 nm) and (714 nm|784 nm|558 nm) respectively. The optimal ionization scheme of (714 nm|784 nm|993 nm dec|615 nm|615 nm) was found to provide an enhancement factor of 3.8 with respect to surface ionization in a tantalum hot cavity heated to 2060 °C. This ionization
scheme includes five atomic transitions in the process of exciting to 49 193.7 cm$^{-1}$. It is the first time that optical pumping has been employed in a hot cavity RILIS ionization scheme. All of the laser driven excitation steps were found to be deeply saturated, suggesting an enhanced cross-section for atomic excitation from the 7p$^2$P$_2$ excited state to 49 193.7 cm$^{-1}$.

Following this ionization scheme development, RILIS ionization has been successfully applied on two occasions to increase the yield of exotic radionuclides for experiments on the CRIS beam line at ISOLDE. In addition to offering the possibility of increasing the yield of radionuclide beams, the new ionization schemes enable the possibility for signal identification and the future application of surface ion suppression techniques. The first (714 nm) excitation step, common to all of the ionization schemes, is sufficiently sensitive to nuclear structure effects to enable future in-situ resonance ionization spectroscopy experiments at the ISOLDE RILIS.

Acknowledgements

This project has received funding through the European Union’s Seventh Framework Programme for Research and Technological Development under Grant Agreements 262010 (ENSAR), 267194 (CофUND), and 289191 (LA.NET). This work was supported by the ERC Consolidator Grant No. 648381; the IUAP-Belgian State Science Policy (BRIX network P7/12), FWO-Vlaanderen (Belgium) and GOAs 10/010 and 10/05 and starting grant STG 15/031 from KU Leuven; the Science and Technology Facilities Council Consolidated Grant No. ST/ F012071/1, Continuation Grant No. ST/J000159/1 and Ernest Rutherford Grant No. ST/L002868/1; and the European Unions Horizon 2020 Framework through ENSAR2 No. 654002. We acknowledge the financial aid from the Ed Schneiderman Fund at New York University.

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