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Efficient three-step, two-color ionization of plutonium using a resonance enhanced 2-photon transition into an autoionizing state

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Abstract. Resonance ionization mass spectrometry (RIMS) has proven to be a powerful method for isotope selective ultra-trace analysis of long-lived radioisotopes. For plutonium detection limits of 10^6 to 10^7 atoms have been achieved for various types of samples. So far a three-step, three-color laser excitation scheme was applied for efficient ionization. In this work, a two-photon transition from an excited state into a high-lying autoionizing state, will be presented, yielding a similar overall efficiency as the three-step, three-color ionization scheme. In this way, only two tunable lasers are needed, while the advantages of a three-step, three-color excitation (high selectivity, good efficiency and low non-resonant background) are preserved. The two-photon transition has been characterized with respect to saturation behavior and line width. The three-step, two-color ionization is a possibility for an improved RIMS procedure.

PACS. 82.80.Ms Mass spectrometry (including SIMS, multiphoton ionization and resonance ionization mass spectrometry, MALDI) – 32.80.Rm Multiphoton ionization and excitation to highly excited states (e.g., Rydberg states) – 32.80.Dz Autoionization

1 Introduction

The detection and classification of long-lived plutonium isotopes at the ultra-trace level (fg/g) is important due to the release of plutonium into the environment. The main plutonium sources are fallout of nuclear weapons tests, various kinds of accidents as well as leakages from nuclear power plants and reprocessing facilities. The determination of the isotope composition allows an assignment of the origin of the plutonium since each source shows a unique isotope signature [1,2]. Compared to radiometric methods, mostly used in plutonium analysis, RIMS does not depend on the half-life or decay mode of the isotope. For example, α-spectroscopy of the long-lived isotopes ^{242}Pu and ^{244}Pu cannot be performed at ultra-trace levels. Furthermore, the energy resolution of most α-detectors is not good enough to distinguish between ^{239}Pu/^{240}Pu and ^{238}Pu/^{241}Am. ^{241}Pu, as a β-emitter, is not detectable by α-spectroscopy at all.

The difference between RIMS and other mass spectrometric methods [3] is the resonant laser ionization process, leading to a high selectivity. At least three photons of visible or near-infrared laser light are necessary to provide enough energy to overcome the ionization limit of plutonium. A two-step ionization scheme using ultra-violet photons would induce a background from non-resonant ionization of molecules present in the sample and thus in the interaction region of the atomic beam and the laser light. The result is a reduced detection limit. The three-step excitation scheme with lower-energy photons avoids such non-resonant background nearly completely and, moreover, improves the selectivity via the additional transition. By populating an autoionizing state or a Rydberg state with subsequent field-ionization (Figs. 1b and 1c), the ionization efficiency is improved by a factor 10−100 in comparison to non-resonant ionization into the continuum.

While extensive spectroscopic data on bound state transitions of the plutonium atom are available [4,5], very little is known on the spectra above the ionization limit, which has been determined by means of resonance ionization spectroscopy. In this context the work of Worden et al. [6] on the analysis of Rydberg series should be mentioned, where also a number of autoionizing states and some two-photon resonances have been reported, but were not investigated in detail. In a more recent experiment [7] two-photon transitions into autoionizing states have been studied in nickel atoms. However, it should be noted, that the laser intensities required for these measurements were

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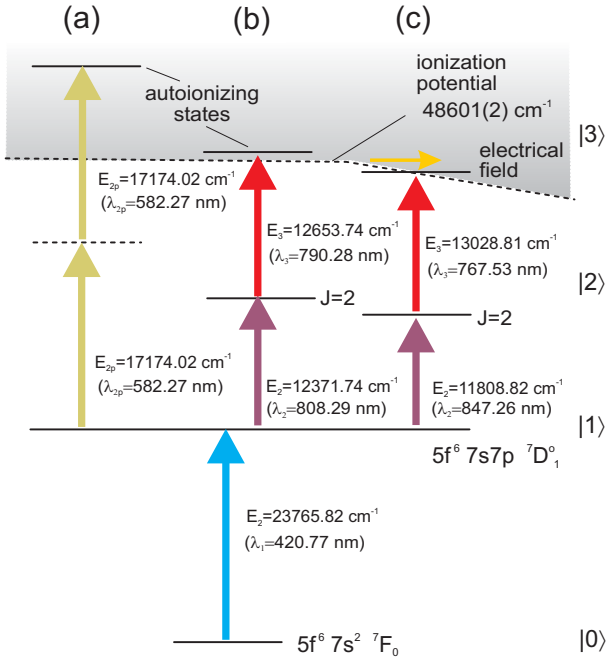

Fig. 1. Multi-step ionization schemes for efficient resonance ionization of plutonium. The most efficient excitation scheme for RIMS used three resonant steps so far, with the 3rd step leading to an autoionizing state (b) or to a Rydberg state, subsequently ionized by an electrical field (c). A similar efficiency can be achieved by a 2-photon transition into an autoionizing state (a).

2−3 orders of magnitude higher than the intensities used in this work.

An extensive study of autoionizing states for the application in three-step excitation schemes [8] reveals several strong two-photon transitions into autoionizing states. This work presents an excitation scheme (Fig. 1a) with a two-photon transition into an autoionizing state, yielding ionization efficiencies of the same order of magnitude as those of three-step schemes as used thus far for routine measurements. In this way, the complexity of the laser set-up and the tuning procedure is significantly reduced. Furthermore, the background problems of a simple two-step ionization process are avoided.

2 Experimental set-up

The RIMS apparatus (Fig. 2), used for the measurement of environmental samples as well as for spectroscopic studies on actinides [9], consists of three tunable titanium:sapphire lasers, pumped by a pulsed Nd:YAG laser and a reflectron type time-of-flight mass spectrometer (TOF) [10]. Additionally it is possible to overlap the titanium:sapphire laser beams from the opposite side with a tunable dye laser beam, obtained by a copper vapor laser pumped dye laser. This allows various combinations of the different laser systems and thus more flexibility for spectroscopic experiments. A neutral atomic beam of the analyte is evaporated from a resistively heated tantalum

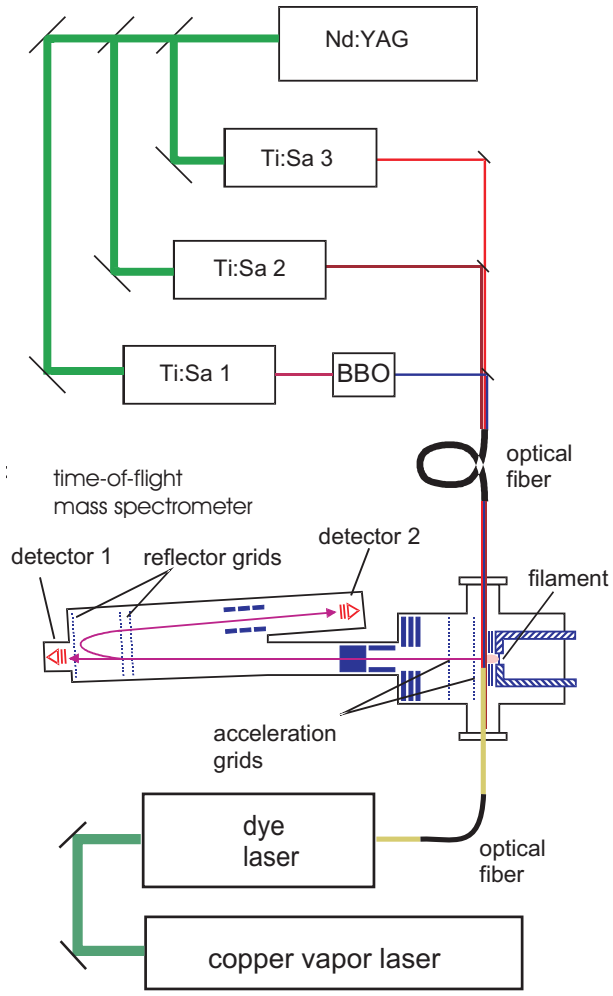

Fig. 2. Experimental set-up for RIMS. A pulsed laser system using titanium:sapphire lasers as well as a dye laser can be combined in various configurations. A reflectron type time-of-flight mass spectrometer is used for mass selective ion detection.

foil. More details on the sample preparation process are found in [11]. The atomic beam is intersected perpendicularly by the laser beams, transported to the interaction region via optical multi-mode fibers. The lasers are focused on the atomic beam with a typical beam diameter of 3 mm. The ions, which are produced in the interaction region are extracted by a pulsed electrical field. After a TOF mass separation they are counted by micro-channel plate detectors. With the ion reflector and a pulsed acceleration field a mass resolution of $m/\Delta m \approx 600$ has been achieved. For this arrangement an overall efficiency of approximately 10^{-4} can be estimated [12], including neutral atomization, thermal ground state population, spatial and temporal overlap of the atomic beam and the laser beams, transmission through TOF and detection efficiency.

Two laser systems have been used in this work. One works with the three tunable titanium:sapphire lasers [10], pumped by a high repetition rate 50 W Nd:YAG laser (Clark ORC 1000). The other system uses a dye laser (Lambda Physik FL2001), pumped by a 40 W copper

vapor laser. In both systems a repetition rate of the pump lasers of 7 kHz was applied. The pulse duration of the titanium:sapphire lasers is 70 ns with pulse energies of $< 250\ \mu$J. This corresponds to a maximum average output power of 1.7 W. The tuning range is 750−880 nm or 375−440 nm, respectively, with frequency-doubling. The dye laser covers the range of 520−850 nm and produces similar pulse energies at higher intensities due to the pulse duration of 20 ns.

The experiments to study autoionizing states, discussed shortly in Section 3, were performed with a synthetic sample of 5×10^{13} atoms of ^{244}Pu. The first and the second excitation step were provided by the titanium:sapphire lasers, whereas a dye laser was used to scan for autoionizing states. A sample of 3×10^{11} atoms of ^{244}Pu was used to characterize a two-photon transition (Sect. 4). The well-known three-step excitation schemes $\lambda_1 = 420.77$ nm, $\lambda_2 = 808.29$ nm, $\lambda_3 = 790.28$ nm (Fig. 1b) and $\lambda_1 = 420.77$ nm, $\lambda_2 = 847.26$ nm, $\lambda_3 = 767.53$ nm (Fig. 1c) served as a reference on the ionization efficiency.

3 Autoionizing states of plutonium

The efficiency and selectivity for multi-step excitation is considerably improved by the ionization via narrow autoionizing or Rydberg states, applying laser systems with high repetition rates and moderate intensities (10−100 kW/cm^2). With the set-up described in Section 2 saturation factors of 1−3 can be obtained in three-step, three-color ionization schemes for plutonium (Figs. 1b and 1c).

Several extensive searches for autoionizing states in plutonium have been performed with the aim to find strong transitions which are accessible by laser systems such as titanium:sapphire lasers, dye lasers or diode lasers. The experimental procedure is as follows: after transferring the atom in two resonant steps to a highly excited state it is ionized by a third laser, which can be scanned over a wide frequency range, as is the case for the FL2001 dye laser.

Figure 3 shows four scans of the ionization laser, using different excitation energies for the second step E_2 into the excited state $|2\rangle$. Not all the tested excitation schemes have shown good results in terms of ionization efficiency. The density of autoionizing states has been low and the spectra show mostly weak, broadband resonant structures. But there appear also some strong narrowband resonances in these scans (highlighted in Fig. 3). However, those are not the result of a one-photon transition from state $|2\rangle$ into an autoionizing state $|3\rangle$, but of a two-step, one-color transition from state $|1\rangle$ (Fig. 1a), because they do not disappear, if the laser light for the second step E_2 is switched off. Thus the spectra in Figure 3 represent a mix of rather weak and broad three-step, three-color and some strong and narrow three-step, two-color resonance structures. One of the two-color resonances with the two-photon transition energy of $E_{2p} = 17174.02(2)$ cm^{-1} ($\lambda_{2p} = 582.27$ nm) was investigated in more detail.

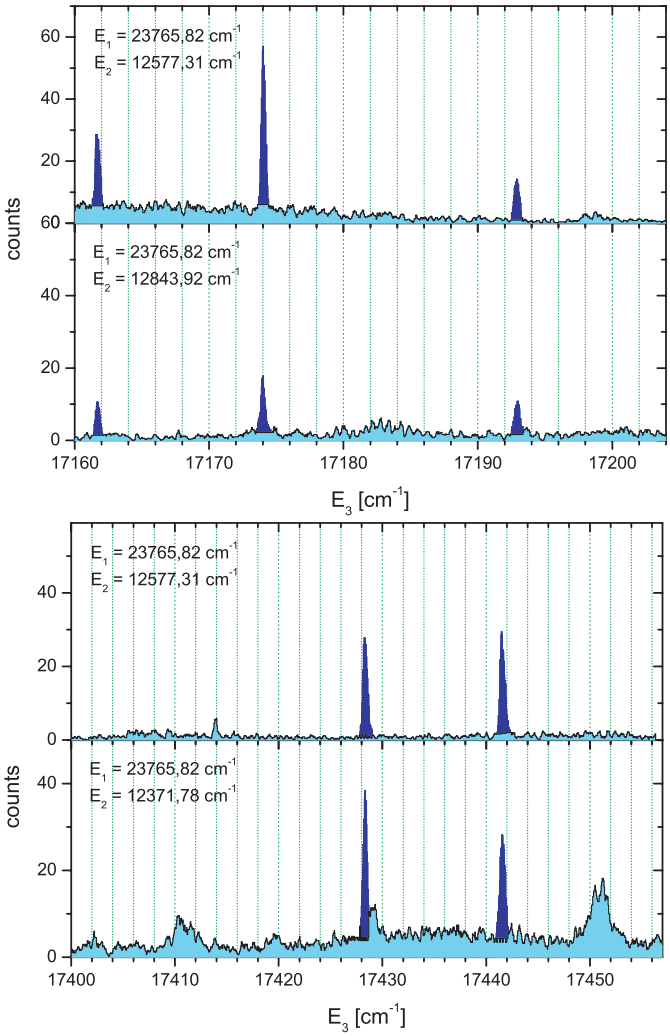

Fig. 3. Autoionizing states in plutonium. The scans of the ionization laser in different three-step excitation schemes show a number of resonances. However, some of those — indicated by a different color — are the result of two-photon transitions starting from the first exited state. Only the underlying broadband resonant structures are due to the three step ionization.

4 Two-photon transition in plutonium

The probability of a two-photon transition in an atomic level system depends on the composite transition matrix element A_{if} and the two-photon excitation intensity I_{2p} [13]. The total two-photon transition rate W_{fi} is given by:

$$W_{fi}(\nu_{if} = 2\nu_{2p}) = \frac{5.55}{\Gamma_{fi}} |A_{if}|^2 I_{2p}^2 \qquad (1)$$

$$A_{if} = \sum_k \frac{\langle f|z|k\rangle\langle k|z|i\rangle}{h(\nu_{ki} - \nu_{2p})}. \qquad (2)$$

This is the special case for the resonance condition $\nu_{if} = 2\nu_{2p}$. The dipole transition matrix elements $\langle f|z|k\rangle$ are expressed in units of the Bohr radius a_0, the energies $h\nu$ in Rydberg R$_0$ and the laser intensities I_{2p} in W/cm^2.

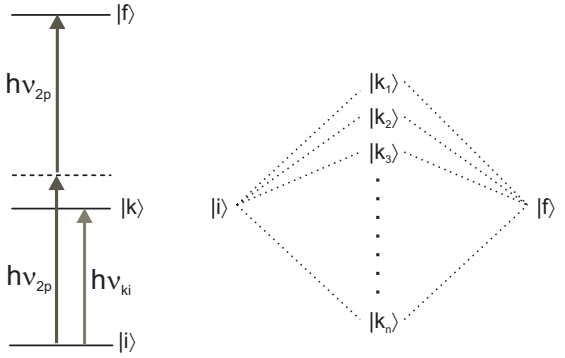

Fig. 4. Schematic view of a two-photon transition $|i\rangle \rightarrow |f\rangle$ with the energy $2h\nu_{2p}$. The transition rate is enhanced by intermediate states $|k\rangle$. In the special case of an ensemble of n $|k\rangle$-states with similar properties (absorption cross-section and detuning) the two-photon transition rate W_{fi} is enhanced by a factor of approximately n^2.

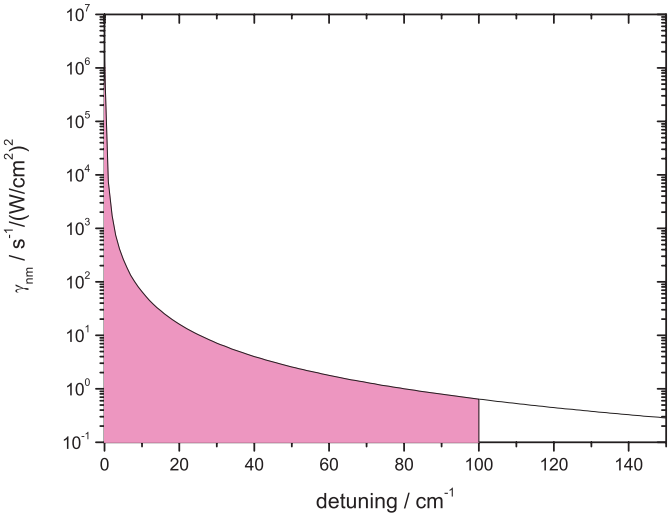

Fig. 5. Simulation of the strength of a two-photon transition γ_{nm} (Eq. (4)) with $\lambda_{2p} = 582.27$ nm. An estimate, considering the available laser intensity yields a range of approximately ± 100 cm^{-1} (highlighted), where intermediate states, that contribute substantially to the overall two-photon transition rate, should be located.

Γ_{fi} is the homogeneous line width of the $|i\rangle \rightarrow |f\rangle$ transition. The value of A_{if} depends very much on the absorption cross-sections of the $|i\rangle \rightarrow |k\rangle$ and $|k\rangle \rightarrow |f\rangle$ transitions, where $|k\rangle$ are intermediate states (see Fig. 4). If there are one or more intermediate states with transition frequencies ν_{ki} close to the two-photon resonance frequency ν_{2p} the two-photon transition rate can be enhanced so much that it is similar to those of one-photon transitions.

The transition rate of the dipole transition matrix elements $\langle n|z|m\rangle$ in units of a_0 can be expressed in terms of the spontaneous emission rate A_{nm} [14]:

$$|\langle n|z|m\rangle|^2 = 4.94 \times 10^{-16}\, \lambda^3 A_{nm}. \tag{3}$$

The transition wavelength λ is defined in nm and A_{nm} is expressed in s^{-1}. Equation (1) can also be written as a transition strength

$$\gamma_{fi} = W_{fi}/I_{2p}^2, \tag{4}$$

which can be simulated by choosing a plausible value for A_{nm}. Those are not known for plutonium, but strong transitions in atoms have very often A_{nm}-values of 10^8 s^{-1} or higher [15]. For example, the first excitation step of the excitation schemes shown in Figure 1 ($\lambda_1 = 420$ nm) is such a strong transition [16]. For uranium, as an actinide element with spectroscopic properties similar to plutonium, lifetimes of 50−100 ns (which correspond reciprocally to the sum of all A_{nm}) for high-lying valence states have been reported [17]. Therefore $A_{nm} = 10^7$ s^{-1} is a reasonable estimate for the simulation of γ_{fi}, shown in Figure 5.

γ_{fi} depends strongly on the detuning of the intermediate state from the two-photon resonance $\lambda_{2p} = 582.27$ nm and varies about 10 orders of magnitude over a detuning range of ± 5000 cm^{-1}. It can increase significantly, if there is more than one intermediate state $|k\rangle$ contributing to W_{fi}. For example, a number of n intermediate states $|k\rangle$ with comparable absorption cross-sections and a similar detuning should enhance the two-photon transition rate W_{fi} by a factor of approximately n^2.

The average laser fluence for the two-photon excitation step, available during this experiment, was $I_{2p} \approx 3$ W/cm^2 (repetition rate 7 kHz, laser pulse width $t_{pulse} = 20$ ns). With the assumption $W_{fi} \approx t_{pulse}^{-1}$ it is possible to combine these values with the estimate for γ_{fi} and equation (4). This yields a range of approximately ± 100 cm^{-1} around $h\nu_{2p}$, where an intermediate state $|k\rangle$ should be located in order to contribute substantially to the overall two-photon transition rate (see Fig. 5).

However, a condition of the simple two-photon transition model is, that the gap between ν_{2p} and ν_{ki} has to be substantially larger than the two-photon excitation line width $\Delta\nu_{2p}$ [18]:

$$|\nu_{ki} - \nu_{2p}| \gg \Delta\nu_{2p}. \tag{5}$$

In our experiment the line width of the scanning dye laser was $\Delta\nu_L = 3.3$ GHz. Taking into account that the laser intensities do not cause extreme saturation broadening, condition (5) holds, if the difference $|\nu_{ki} - \nu_{2p}|$ is larger than the laser bandwidth $\Delta\nu_L$.

The two-photon transition in plutonium investigated in this work (Fig. 1a) starts from the resonantly excited bound state $5f^6 7s7p\ ^7\mathrm{D}_1^\mathrm{o}$ and leads to an autoionizing state at $E_{a.i.} = 58113.86(3)$ cm^{-1} above the ground state $5f^6 7s^2\ ^7\mathrm{F}_0$. Its transition strength is close to the strengths of two efficient one-photon transitions to autoionizing states in plutonium. The ionization efficiency of the two-photon excitation scheme ($\lambda_1 = 420.77$ nm; $P_1 = 35$ mW, $\lambda_{2p} = 582.27$ nm; $P_{2p} = 320$ mW) (Fig. 1a) was directly compared with the efficiency of a three-step, three-color excitation scheme ($\lambda_1 = 420.77$ nm; $P_1 = 35$ mW, $\lambda_2 = 847.26$ nm; $P_2 = 770$ mW, $\lambda_3 = 767.53$ nm; $P_3 = 620$ mW) (Fig. 1c) by alternating between the two ionization paths and monitoring the ion signal at mass 244. The comparison of the accumulated ion counts for each

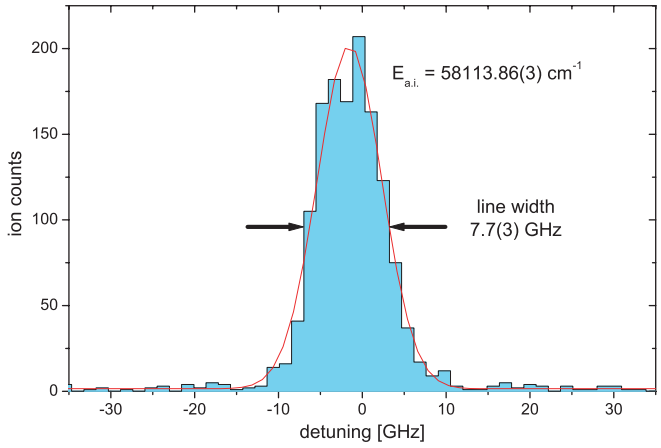

Fig. 6. Three-step, two-color ionization of plutonium. A scan of the ionization laser reveals an autoionizing state with a measured line width of 7.7(3) GHz at $E_{a.i.}$ = 58113.86(3) cm^{-1} above the $5f^6 7s^2\ {}^7\mathrm{F}_0$ ground state. Starting from the $5f^6 7s7p\ {}^7\mathrm{D}_1^o$ intermediate level at E_1 = 23657.82 cm^{-1}. $E_{a.i.}$ is populated via a two-photon transition (E_{2p} = 17174.02(2) cm^{-1}).

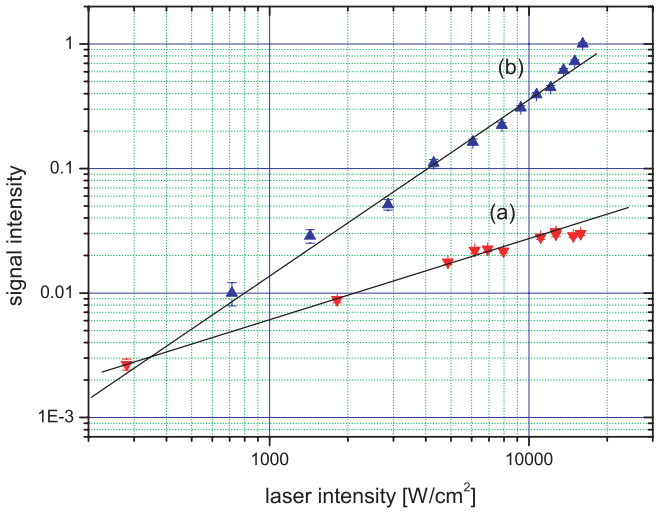

Fig. 7. Ion signal as a function of laser intensity. (a) The λ_3 = 790.28 nm single-photon transition into an autoionizing state shows a linear dependence on the laser intensity until saturation effects become relevant at higher laser powers. (b) As predicted by the theory the rate for a 2-photon transition is proportional to the square of the laser intensity, indicated by the higher slope in the logarithmic presentation.

ionization path enabled the determination of the relative ionization efficiency. A value for the ratio of efficiency of 0.29 has been found. Taking into account the overall detection efficiency of the three-step, three-color excitation (Fig. 1c) of $\varepsilon = 4 \times 10^{-5}$ [10] an overall efficiency for the two-photon excitation scheme of $\varepsilon_{2p} > 10^{-5}$ results.

The measured line width of the two-photon transition, which exhibits a Gaussian line form, is $\Delta\nu_{2p}$ = 7.7(3) GHz (Fig. 6). This is compatible with the laser line width of 3.3 GHz and the Doppler broadening of the atomic plutonium beam of $<$ 1 GHz. The conditions for Doppler-free two-photon excitation are not fulfilled in this case, because there are no counter-propagating light waves and the excitation line width is larger than the Doppler-broadening. The resonance enhancement factor, i.e. the ratio of the signal intensity at the resonance peak to the non-resonant background, for this transition is ≈186. This is almost one order of magnitude higher than the signal/background ratios observed for autoionizing states in three-step, three color configurations, where the laser light of the first (resp. second) excitation step can contribute via non-resonant ionization from the highest excited state to an increased background. This is not possible in the three step, two-color excitation scheme since there is no accessible intermediate state from which non-resonant ionization could occur.

We also examined the two-photon ionization efficiency as a function of laser intensity. This measurement can be compared with a saturation intensity measurement of a one-photon transition from a second excited state into an autoionizing state (λ_1 = 420.77 nm, λ_2 = 808.29 nm, λ_3 = 790.28 nm). Figure 7a shows — as expected from the theory — a linear dependence on the laser intensity as long as the saturation effects at higher laser powers are not relevant. In contrast the two-photon transition (Fig. 7b) shows a linear dependency to the square of the intensity. This proves — according to (1) — that it is in fact a two-photon transition and even though there has to be a substantial resonance enhancement due to the proximity of intermediate states, condition (5) is fulfilled. Even at the maximum laser intensity there are no saturation effects observed.

5 Conclusion

A strong two-photon transition into an autoionizing state has been found, specified and implemented in a three-step, two-color excitation scheme for the resonance ionization of plutonium. By comparison with a well established three-step, three-color excitation scheme it is demonstrated, that the ionization efficiency is similar and should be sufficient for the application of this scheme in ultra-trace analysis of plutonium with RIMS. It is an important aspect in the context of the ongoing development of a simplified RIMS procedure.

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