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Determination of a three-step excitation and ionization scheme for resonance ionization and ultratrace analysis of Np-237

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ABSTRACT

The long-lived radio isotope ^{237}Np is generated within the nuclear fuel cycle and represents a major hazard in the final disposal of nuclear waste. Related geochemical research requires sensitive methods for the detection of ultratrace amounts of neptunium in environmental samples. Resonance ionization mass spectrometry (RIMS) has proven to be one of the most sensitive methods for the detection of plutonium. A precondition for the application of RIMS to ultratrace analysis of neptunium is the knowledge of an efficient and selective scheme for optical excitation and ionization. Therefore, a multitude of medium to high-lying atomic levels in neptunium was located by applying in-source resonance ionization spectroscopy. By using excitation via six previously known first excited, intermediate levels of odd parity, a set of twelve so far unknown high-lying levels of even parity were identified and studied further for their suitability in resonant excitation/ionization schemes. Autoionizing resonances for efficient ionization of neptunium atoms were subsequently accessed spectroscopically. Altogether five resonance ionization schemes were investigated and characterized concerning their saturation behavior and relative efficiency. Applying a calibrated sample, an overall efficiency of 0.3% was determined.

1. Introduction

After the decay of the fission products, the radiotoxicity of spent nuclear fuel is predominantly determined by long-lived isotopes of plutonium, neptunium, americium, and curium. Among these isotopes, ^{237}Np ($T_{1/2} = 2.14 \times 10^6$ a) is considered as a major long-term hazard since neptunium is easily soluble under natural groundwater conditions and has a high radiotoxicity [1,2]. Hence, extensive research is carried out on the geochemical properties of neptunium and its migration behavior in different host materials. Most of these experiments use the isotope ^{237}Np, which is detected by α-particle spectroscopy or inductively coupled plasma mass spectrometry (ICP-MS) [3]. Unfortunately, the determination of neptunium ultratrace amounts in environmental samples is unsatisfactory with both techniques. The radiometric method is limited in sensitivity due to the long half-life of ^{237}Np, while ICP-MS is hampered by isobaric interferences and peak tailing, in particular from the prominent isotope ^{238}U, normally present in high abundances in environmental samples [4]. Alternative sensitive mass spectrometric methods like thermal ionization mass spectrometry (TIMS) or accelerator mass spectrometry (AMS) require either extensive sample preparation or access to accelerator facilities. Until now, many experiments on neptunium migration have been carried out with concentrations of ^{237}Np significantly exceeding 10^{-10} mol/L as expected in the aquifer in case of a leakage in a nuclear waste repository. However, a direct extrapolation of results obtained in such experiments to the ultratrace level may lead to incorrect results, as speciation and migration of neptunium may be affected by its concentration [5]. In certain cases, ^{239}Np ($T_{1/2} = 2.36$ d) can be used to circumvent this problem. Due to its high specific activity this isotope can be detected at lowest levels by γ-ray spectroscopy. Unfortunately, its short half-life precludes long-term experiments, like diffusion experiments on different clays [6]. As a consequence, an alternative, highly sensitive method for ultratrace determination of neptunium isotopes is highly desirable.

RIMS uses laser light of different, well-tuned wavelengths to excite and ionize atoms in several subsequent resonant steps. The laser ions are separated from any thermally produced ions of different mass by a mass spectrometer and detected by ion counting. Because of the uniqueness of atomic transitions, resonant ionization schemes are element specific. Thus, RIMS mass spectra are free of isobaric interferences, which is a precondition for ultratrace determination. Furthermore, valuable information on the isotopic pattern is obtained. A detection limit of less than 10^6 atoms (1 fg) per sample has been demonstrated for plutonium isotopes, regardless of their half-life [7]. RIMS is used on a routine basis for the determination of ultratrace amounts of plutonium in various environmental samples.

Early laser spectroscopic investigations on Np were focussed on the term analysis of low lying energy levels [8] and the determination of the ionization potential [9]. Previous RIMS experiments on

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neptunium at Mainz University were carried out using a laser system of three dye lasers pumped by two copper vapor lasers [10,11]. Primary objective of these experiments was an accurate redetermination of the ionization potential of neptunium, while no direct application for ultratrace analysis was envisaged. Meanwhile, the dye laser setup was replaced by a solid state laser system consisting of three titanium:sapphire (Ti:sa) lasers pumped by a frequency doubled neodymium:YAG (Nd:YAG) laser at 532 nm [7]. The novel laser system has also been used at on-line facilities for selective ionization of short-lived radionuclides [12,13] and proved to be much more reliable and easier to operate than the dye laser setup.

Since Ti:sa lasers work in a different wavelength range compared to the dye lasers used previously, alternative schemes for excitation and ionization of neptunium must be identified. Ti:sa lasers are tunable from $10500-14\ 500\mathrm{cm}^{-1}$. Correspondingly, the light of at least one of the lasers has to be frequency doubled to exceed the ionization potential of neptunium at $50\ 535\mathrm{cm}^{-1}$ (6.2655 eV) in a three-step resonance excitation scheme. Numerous odd parity energy levels around $25\ 000\mathrm{cm}^{-1}$, tabulated in the literature [14], are accessible from the ground state by blue laser radiation and can be used as first excitation steps. However, little information can be found on levels suitable for the second excitation step towards states of even parity. Especially, the knowledge on even parity energy levels above $35\ 000\mathrm{cm}^{-1}$ is scarce. Therefore, this work focusses on resonance ionization spectroscopy (RIS) of ^{237}Np for the identification and characterization of high-lying states and autoionizing states suitable for ultratrace analysis.

2. Experimental setup

The search for suitable excitation/ionization schemes for Ti:sa laser resonance ionization of neptunium was performed by in-source spectroscopy at the MABU (Mainz Atomic Beam Unit) setup, as shown in Fig. 1. Atomic vapor of neptunium formed inside a graphite furnace, which is resistively heated to temperatures up to 1700 K, is irradiated by laser radiation for resonant excitation and ionization. The furnace has an inner diameter of 2.2 mm and a length of 40 mm. Due to the electric field produced by the potential difference of the resistive heating, ions are pulled towards the extraction hole for further acceleration and guidance by an ion optical lens system. A 90° quadrupole deflector ensures the separation of the ions from any effusing neutral atoms and allows for a simple entrance of the laser radiation into the oven, anticollinear to the escaping atom beam. A subsequent quadrupole mass filter suppresses contaminating ions, which are predominantly produced by surface ionization in the hot furnace. As those arise primarily from alkaline and alkaline earth elements, masses of the majority of these background ions are rather low and thus sufficiently far off from those of neptunium isotopes. Therefore, the mass filter can be used at a low mass resolution of $\Delta m/m \approx 150$, ensuring high transmission. The mass separated ions are detected by a channeltron detector operated in single ion counting mode.

The laser system consists of a set of three tunable nanosecond Ti:sa lasers simultaneously pumped by a frequency doubled Nd:YAG laser with a repetition rate of 7 kHz (Fig. 1). Each Ti:sa laser is pumped by $15-17$ W of 532 nm light and delivers output powers of up to 3 W with a typical laser pulse duration of 50 ns. Frequency selection for two of the lasers is obtained by a combination of a birefringent filter and an etalon, resulting in a spectral bandwidth of about 5 GHz. This design has the advantage of high output power and longterm stability. The third laser is equipped with a motorized grating in Littrow configuration as frequency selective element. This allows for a broad continuous tuning range of more than $2\ 000\mathrm{cm}^{-1}$ at a spectral bandwidth of ~7 GHz, suitable for spectral search on atomic transitions. Pulses of individual lasers are temporally synchronized using fast switching of intra-cavity Pockels cells. The wavelengths of the lasers are monitored with commercial wavemeters (High Finesse-WS6, ATOS-LM007). The blue laser radiation necessary for the first excitation step is produced by second harmonic generation (SHG) on the fundamental radiation of one Ti:sa laser with a BBO ($\beta-\mathrm{BaB_2O_4}$) crystal. The radiation of all three lasers is focussed with telescopes and overlapped using dichroic mirrors and polarizing optics. Finally, the overlapped laser beams are directed into the graphite oven of the MABU setup as indicated in Fig. 1. Output powers of ~2 W for fundamental wavelengths of the conventional Ti:sa lasers, ~1.2 W for the grating-assisted Ti:sa laser, and about 300 mW for the second harmonic are available. About two thirds of the power reaches the MABU setup after optical beam transport.

The sample material, neptunium oxide, was dissolved in nitric acid and dried on zirconium foils, which served as reducing agent, before insertion into the graphite furnace. All spectroscopic results were obtained with a total neptunium amount of less than 10^{15} atoms (1 μg) of ^{237}Np, subdivided into a number of refills of the oven.

3. Measurements and results

3.1. High-lying excited states

The scheme used for excitation of atomic neptunium and identification of high-lying excited states is shown in Fig. 2(A). Starting from the even parity $[\mathrm{Rn}]5f^46d7s^{2}\,{}^6L_{11/2}$ ground state (GS) of atomic neptunium, one of six selected first excited states (FES) of odd

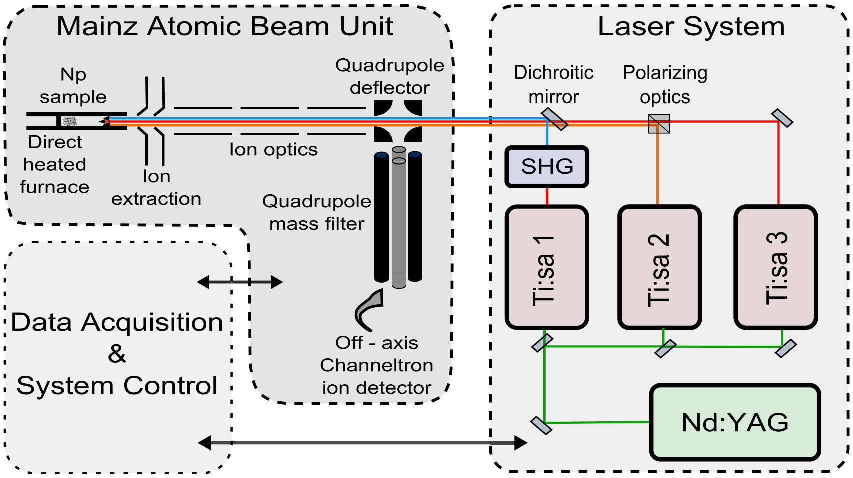

Fig. 1. Scheme of the experimental setup with Ti:sa laser system, MABU vacuum unit, data acquisition, and system control. For details see text.