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Resonance Ionization Mass Spectroscopy with a Pulsed Thermal Atomic Beam

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Abstract

Resonance ionization mass spectroscopy (RIMS) and pulsed-laser induced desorption (PLID) have been combined for ultrasensitive detection and spectroscopy of very small samples of refractive elements. The method has been tested and applied to laser spectroscopy of 5×10^9 atoms (1.5 pg) of ^{195}Au ($T_{1/2} = 183 \text{ d}$) implanted at the ISOLDE on-line mass separator with 60 keV into graphite. A pulsed thermal atomic beam was formed by laser desorption with a 10 ns Nd:Yag laser pulse. Subsequently the atoms were photoionized in a three-colour, three-step resonant excitation to an autoionizing state. The selectivity was enhanced by a time-of-flight measurement of the photo ions. In resonance, one ion was detected per 10^5 atoms implanted resulting in a gain in detection efficiency by three orders of magnitude in comparison to the use of a continuous atomic beam. In the course of the experiments several unknown autoionizing states were found, and the lifetime of the $6d \text{ } ^2D_{3/2}$ state of gold was determined to be $\tau = 10.7(6) \text{ ns}$.

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1 Introduction

Resonance ionization mass spectroscopy (RIMS) has been proved to be a powerful tool for optical spectroscopy and in detecting trace amounts of almost any element [1]. The main features of RIMS are, (i) high sensitivity due to efficient ionization and detection of the photo ions produced, (ii) efficient reduction of interfering events due to the requirement of multiple, resonant transitions and mass-selective detection of the photo ions and, (iii) isotope selectivity by means of mass determination and use of the isotope shifts (IS) and hyperfine structure splittings (HFS) varying from isotope to isotope.

There is, however, an important drawback of this technique: In order to achieve an efficient ionization of the atoms under investigation, high-power lasers are required. Generally, the last excitation step leading to photo ionization represents the bottleneck of the excitation path. The effective cross sections for these transitions (into the continuum, to an autoionizing state or a Rydberg state) are generally several orders of magnitude lower than those for resonance transitions. Hence, in almost all cases, pulsed-laser systems have to be used. Furthermore, a high repetition rate is needed except for the few inert elements like noble gases which can be kept in a finite volume without losses due to wall absorption. For all other cases continuous atomic beams have to be used with the disadvantage of large losses due to the generally low duty cycle of high-power, pulsed laser systems. Taking typical values for an atomic beam ($T = 1000\text{ K}$, mass number $A = 100$) one obtains a mean velocity of $5 \times 10^4\text{ cm/sec}$ and hence a duty cycle of only 2×10^{-4} for a laser system with a repetition rate $\nu_{rep} = 10\text{ Hz}$ and a diameter of the laser beams $d = 1\text{ cm}$. This was exactly the main loss in our RIMS experiments on short-lived Au isotopes [2] where a Nd:Yag/dye laser system was used. An overall efficiency of one detected ion per 10^8 Au atoms in the sample has been determined in this experiment.

In case of elements with low ionization energy a copper-vapour/dye laser system represents an elegant way out. Overall efficiencies of up to 10^{-5} have been determined for Gd, Pu, and Tc [3,4] due to its high repetition rate of the order of 10 kHz . However, the use of such a laser system is limited (i) by the low pulse power

available and (ii) because the copper-vapour laser emits only two wavelengths in the yellow/green spectral region.

In case of elements with high ionization energy (and therefore resonance lines in the ultraviolet) one has to go back to the use of low-repetition, high-power pump lasers such as Nd:Yag or excimer lasers. Then the only possibility to beat the low duty cycle is to produce a pulsed beam of thermal atoms showing a time structure adequate for efficient ionization by the pulsed lasers used for RIMS [5]. Such a pulsed beam can be produced by pulsed-laser induced desorption (PLID) [6].

This publication reports on the combination of PLID with RIMS and its application for the investigation of Au isotopes. Similiar work is performed by Lee et al. [7]. In addition, we report on further studies in order to optimize the RIMS scheme for a future experiment on very neutron-deficient Au isotopes.

2 Principle of the experiment

The experimental set-up (Fig. 1) consists of a target with the implanted sample, a desorption laser, dye lasers used for resonance ionization spectroscopy (RIS), a time-of-flight (TOF) spectrometer and an ion detector. The desorption laser is focussed onto the target. When the desorbed atoms reach the interaction region, the atoms are stepwise excited and finally ionized via intermediate atomic levels by the RIS lasers. In order to increase the signal-to-background ratio the ions are detected by a time-focussing TOF spectrometer. This spectrometer consists of a two-stage acceleration region, a field-free drift tube, a 40° ion reflector and a microchannel plate (MCP) detector. Background ions created by the desorption laser are suppressed by pulsing the voltage of a deflector in the drift tube.

3 Experimental Set-up and Measurements

Table 1 indicates the excitation scheme and the properties of the lasers used for the present Au experiment. The set-up is the very same as used in the previous work [2], except for a third tunable dye laser necessary to search for autoionizing states, and a second Nd:Yag laser for pulsed desorption. As before, the mass resolution of the TOF spectrometer is $M/\Delta M \lesssim 300$. Ionized ^{197}Au has a time of flight of

$\simeq 43.7 \mu s$ and shows up in a time window of about $70 ns$.

3.1 Pulsed atomic beam

PLID provides an atomic beam with a temporal profile. This is due to the short duration of sample heating by the laser. Rises of the local temperature by $3000 K$ or more can easily be obtained while the average heating power is less than one *Watt*.

Tantalum, tungsten and graphite (all amorphous) were tested as substrate materials for desorption of implanted gold. Due to the higher reflectivity of Ta and W higher desorption power is required to deposit the energy into these substrates in comparison to graphite. This leads to more background ions and even to the creation of a laser-generated plasma. Graphite (Ringsdorff EK 986) was found to be the most reliable substrate material due to its high pureness, temperature resistance and absorption coefficient.

Velocity distributions of the desorbed atoms were measured to optimize the temporal overlap between atomic and RIS lasers beams. Figure 2 shows as an example the velocity distribution obtained by delaying the RIS lasers with respect to the desorption laser. The solid curve represents a fit by a Maxwellian distribution [9] corresponding to a temperature of $1200 K$ and a hydrodynamic velocity of $6 \times 10^4 cm/s$, which is given by

$$N(t) \sim \int_{X-r_L}^{X+r_L} x^2/t^3 e^{-(x/t-u)^2 M/2kT} dx . \quad (1)$$

Here, t is the drift time, X the driftlength given by the distance between the target and the center of the laser beams, r_L the radius of the laser beams, u the hydrodynamic velocity, M the mass of the atom and T the temperature.

3.2 Lifetime of the $6d^2D_{3/2}$ State

The delays between the three lasers used for RIS have to be adjusted properly in order to obtain maximum ionization efficiency. The delay times depend on the lifetime of the levels involved. Whereas $\tau(6p^2P_{1/2}) = 6.0(1) ns$ is known [10], no information exists on $\tau(6d^2D_{3/2})$.

Two different methods were used to determine this lifetime. The first one was to excite the $^2D_{3/2}$ state by a short laser pulse and to observe its decay by recording the fluorescence photons by a fast multiscaler device. The second was to determine the population of the $^2D_{3/2}$ state as a function of time by probing it by a short laser pulse which leads to photoionization.

Observation of the decay: The $6d\ ^2D_{3/2}$ state was excited by stepwise excitation via the intermediate $6p\ ^2P_{1/2}$ state. The laser pulse started a fast multiscaling device [11] with a dwell time of 2 ns and 2000 channels with 1 bit resolution. The single-photon pulses of a photomultiplier which was appropriately blocked to observe only the $^2D_{3/2} \rightarrow ^2P_{3/2}$, $\lambda = 481\text{ nm}$ transition, were stored in the registers of the multiscaler module. Its content was transferred after each laser shot into a LSI 11/23 computer and summed up. Typically 10^4 laser shots were used for a decay curve. For this measurement the laser intensity was kept low in order to have an average event rate of $\ll 1$ per laser shot.

Observation of the population: In this case, two Nd:Yag lasers were used. The first one pumped the dye lasers for the first and second transition, the second served to pump the dye laser for the transition from the $^2D_{3/2}$ state into the continuum. The population of the $^2D_{3/2}$ state was probed by recording the photo ion signal by an analog-to-digital converter (ADC) as a function of the delay between the two Nd:Yag lasers. Fig. 3 shows this signal. Thirty laser shots were used for each data point.

3.3 Search for autoionizing states

As briefly discussed before, the last excitation leading to photoionization represents the bottleneck of the RIS path. A transition into the continuum was induced in the previous experiment [2] by use of the 40 mJ output of a frequency doubled Nd:Yag laser. The estimated transition probability was $W(^2D_{3/2} \rightarrow \text{continuum}) \simeq 0.1$ [2]. This estimate has been confirmed experimentally in the meantime. The transition probability and hence the overall efficiency can be increased by resonant transitions to autoionizing states. Only little information on such states can be found in the literature [12]. Hence we searched for such states in the wavelength range $490\text{ nm} \leq \lambda_3 \leq 650\text{ nm}$ by using a third dye laser with a bandwidth of

6 GHz. Table 2 gives a compilation of the states found. The most intense resonance observed is shown in Fig. 4.

3.4 Determination of the Detection Efficiency

The detection efficiency is defined as the ratio of Au ions counted by the MCP detector in the appropriate time-of-flight window to the number of atoms implanted into the target. Having a very low detection limit we have found stable ^{197}Au in any type of material investigated. Hence radioactive samples were prepared by implanting mass-separated ^{195}Au ($T_{1/2} = 183\text{ d}$) ions at the ISOLDE on-line mass separator at CERN [13], differing in target material (C, Ta, W), implantation energy (6 keV - 60 keV) and number of atoms implanted ($5 \times 10^9 - 5 \times 10^{12}$ ^{195}Au atoms, spot size $d = 3\text{ mm}$). The actual number of ^{195}Au atoms was checked by γ -spectroscopy.

The samples were mounted in the RIMS/PLID apparatus. After a vacuum pressure of better than 10^{-7} mbar was reached, the beam of the desorption laser (Table 1, spot size of about 1 mm^2) was tuned over the target. Subsequent to each desorption pulse the bunch of desorbed atoms was probed by the RIS laser beams with a delay of $10\text{ }\mu\text{s}$ (Fig.2). During the course of the experiment the laser for the D_1 transition was continuously tuned over the resonance, whereas the other dye lasers were fixed in frequency.

Several signals were recorded simultaneously: (i) The ion signal of ^{195}Au in an analog mode digitized by an ADC, (ii) the same signal but in a single-event mode by use of a fast discriminator, (iii) the analog RIMS signal of desorbed stable ^{197}Au , (iv) the background ions in a time-of-flight window covering a mass range $180 \leq A \leq 190$, (v) the TOF signal recorded by a transient recorder (Le Croy TR 8818) and (vi), the fluorescence signal of stable ^{197}Au in an atomic beam. Fig.5 shows a typical RIMS signal of ^{195}Au and the fluorescence signal of ^{197}Au used for wavelength calibration. The number of ^{195}Au ions and background events obtained for each sample were stored and summed up in the computer in order to allow a calculation of the detection efficiency and the signal-to-background ratio.

Fig. 6 shows part of the TOF spectrum obtained with 300 laser shots from a sample containing 5×10^9 ^{195}Au atoms. A strong contamination by stable ^{197}Au

was observed which was obviously present in the target as impurity. Below the $A = 195$ mass peak some few background events are showing up which are due to the desorption process. A small mass peak at $41.3 \mu s$ corresponds to $A = 181$. These ions are correlated with the RIS laser pulse and disappeared when blocking the 592 nm laser light. Since this mass peak was much larger in case of a Ta target, we attribute it to ^{181}Ta .

4 Results and Discussion

Pulsed atomic beam: As stated before, graphite turned out to be the optimum material for desorbing implanted Au. Hence, the following discussion is restricted to the results obtained with graphite as target. No significant difference was noticed for the various implantation energies. About 60 % of the implanted radioactivity could be released by PLID which took about 200-300 laser shots at a pulse power density of about 10 MW/cm^2 . At these power densities Maxwellian velocity distributions were obtained with temperatures about 1200 K comparable to those for continuous evaporation of Au out of graphite [2].

Lifetime of the $6d \ ^2D_{3/2}$ state of Au: A lifetime of $\tau = 11.2(3) \text{ ns}$ was measured by counting time-differentially the fluorescence photons. The alternative technique of probing the population yielded $\tau = 10.2(2) \text{ ns}$ which disagrees with the other value. Both techniques have their advantages and drawbacks. While the first one is insensitive to intensity fluctuations of the lasers but lacks from pile-up, it is just the other way round for the second method. Hence we give as final result $\tau = 10.7(6) \text{ ns}$ where the error bar includes both experimental results. A Hartree-Fock calculation of the lifetime is in progress [14].

Autoionizing states of Au: Several transitions from the $^2D_{3/2}$ state to autoionizing states were found (Table 2). The resonances are fitted by a Shore-Fano profile with

$$\sigma_{tot} = \left\{ \left[(\Gamma/2)B + A(E - E_0) \right] / \left[(\Gamma/2)^2 + (E - E_0)^2 \right] \right\} + \sigma_{nr} \quad (2)$$

where σ_{tot} represents the total and σ_{nr} the nonresonant crosssection for photoionization. $\Gamma = \hbar/\tau$ is the linewidth with the lifetime τ of the autoionizing state, E_0 the transition energy and A, B the Shore-Fano parameters. The resulting parameters

E_0 , Γ and A/B are given in Table 2. The strongest resonance is found at 592.045(2) nm, 4433.3 cm^{-1} above the first ionization limit. If this transition is used instead of the non-resonant transition into the continuum induced by the frequency-doubled output of the Nd:Yag laser ($\lambda = 532 \text{ nm}$), one gains a factor of 20 as shown experimentally. The saturation pulse energy for the 592 nm transition was found to be about 20 mJ for a beam diameter of 1 cm. On the other hand one loses by the conversion of the Nd:Yag laser light into tunable dye laser output. With a typical pulse energy of 2 mJ of the dye laser at $\lambda = 592 \text{ nm}$ and a beam diameter of 1 cm the ionization efficiency is limited to 10 %, the same as it was in case of using the available 40 mJ at $\lambda = 532 \text{ nm}$. Hence, the remaining, still very important advantage of the use of a transition to an autoionizing state is the lower laser light intensity brought into the RIMS spectrometer. This results in a smaller number of non-resonantly ionized molecules (rest gas or desorbed) and hence in a reduction of the background events.

Detection efficiency and background: The detection efficiency is calculated from the total number of ^{195}Au ions detected in resonance in the appropriate TOF window and the known number of atoms implanted. Since the laser was continuously scanned over the D_1 resonance (Fig.5), a correction factor has to be applied accounting for the fraction of the time while the laser is in and off resonance. An overall efficiency of $\epsilon = 10^{-5}$ was repeatedly found. Thus a detection limit of 10^6 Au atoms is obtained defined by the requirement of 10 events for a statistically significant evidence. The background rate was determined to be 1 event per 1000 laser shots in a 100 ns time window. Since 200-300 laser shots are necessary to reach a desorption yield of 60 %, a signal-to-background ratio of 30 – 50 is obtained at the detection limit of 10^6 Au atoms.

The detection limit of $\epsilon = 10^{-5}$ can be calculated and estimated to have the following contributions: The probability to excite an atom from the 6s groundstate via the 6p intermediate state to the 6d state is $\epsilon_1 = 0.25$. Higher (available) laser intensity leads to power broadening of the resonances. The ionization efficiency of the third step is measured to be only $\epsilon_2 = 0.1$. Spatial and temporal overlap of the pulsed atomic and laser beams is estimated to be of the order of $\epsilon_3 = 0.2$ and inhomogenities of the RIS laser beams might lead to an additional reduction

of the efficiency by $\epsilon_4 = 0.2$. Three grids were used in the TOF spectrometer which reduce the transmission by $\epsilon_5 = 0.7$. The transmission of the ion optics and the secondary-electron efficiency of the MCP is estimated to be $\epsilon_6 = 0.2$. Only 50% of the atoms are in one of the two HFS levels ($\epsilon_7 = 0.5$). The maximum desorption yield was determined to be $\epsilon_8 = 0.6$. Hence the calculated efficiency is $\epsilon_{calc} = 4 \times 10^{-5}$ in satisfactory agreement with the experimental number.

5 Conclusion

The combination of RIMS with PLID enhanced considerably the applicability of the resonance ionization technique. Spectroscopy and trace analysis of refractive elements are now within reach. The apparative expenditure is high but has to be accepted if ultrasensitive detection is required. A continuation of the measurements of the HFS and IS of neutron-deficient Au isotopes [2] will be the first application. Similiar experiments on platin isotopes are in progress.

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Table 1: Excitation scheme of Au and properties of the lasers used for RIMS/PLID. The repetition rate of all lasers is fixed to 10 Hz. The dye laser used for spectroscopy in the D_1 line is described in detail in [8].

Purpose	Wavelength [nm]	Light source	Pulse energy [mJ]	Beam size [cm ²]	Pulse duration [ns]	Band width [GHz]
Desorption	532	Nd:Yag laser (home made)	2	0.02	10	15
Pump laser	532 355	Nd:Yag laser (Molelectron MY32)	30 30		15	15
Excitation $6s^2S_{1/2} \longrightarrow 6p^2P_{1/2}$	268 frequency doubled	Dye laser (modified Molelectron DL 16 P)	0.01	1	6	0.5
Excitation $6p^2P_{1/2} \longrightarrow 6d^2D_{3/2}$	406	Dye laser (Lambda FL 2001)	0.05	1	10	6
Excitation $6d^2D_{3/2} \longrightarrow$ autoionizing state	592	Dye laser (Lambda FL 2001)	2	1	10	6

Table 2: Autoionizing states of Au found by excitation of the $6d^2D_{3/2}$ state with tunable laser light in the wavelength range from 490 to 650 nm. E_0 indicates the position of the autoionizing state relative to the ground state. Γ , A and B are defined in (2).

E_0 [cm ⁻¹]		Wavelength [nm] from $6d^2D_{3/2}$	Γ [cm ⁻¹]	A/B
This work	Ref. [12]			
81268.1(1)	-	517.69(1)	2.6(2)	3.5(1.0)
80160.5(1)	-	549.18(1)	0.74(4)	0.0(3)
80012.1(5)	80011.5	553.69(16)	7.5(7)	-0.3(1)
78842.08(1)	-	592.045(2)	1.61(1)	-0.82(2)
78596.5(2)	78594.5	600.78(1)	5.4(3)	0.19(3)
77856(4)	77859.8	628.7(1)	19(5)	-0.5(2)
77544(4)	-	641.3(1)	6.0(5)	2.0(4)

Figure captions:

Figure 1: Experimental setup for pulsed laser induced desorption and resonance-ionization-mass spectroscopy. The potentials are $U_0 = 0\text{ V}$, $U_1 = 2.6\text{ kV}$, $U_2 = 2.4\text{ kV}$ and $U_3 = -2\text{ kV}$.

Figure 2: Velocity distribution of Au atoms desorbed by a 10 ns , 100 mJ/cm^2 pulse of a frequency-doubled Nd:Yag laser. The solid curve represents a fit by a Maxwellian distribution for $T = 1200\text{ K}$. The RIS lasers were focussed to $d = 3\text{ mm}$ at a distance from the target of $l = 8\text{ mm}$. In order to achieve highest detection efficiency, $d = 10\text{ mm}$ and $l = 6\text{ mm}$ were chosen resulting in a maximum of the velocity distribution at $t \simeq 10\text{ }\mu\text{s}$.

Figure 3: Photo ion signal as a function of the delay between the laser shots populating and, respectively, depopulating the $6d^2D_{3/2}$ State (crosses: linear scale, full dots: logarithmic scale, $t = 0$: all pulsed laser beams coincident). The maximum of the signal indicates the optimum delay between the two laser shots. The lifetime of the $^2D_{3/2}$ is given by the slope for $\Delta t > 10\text{ ns}$.

Figure 4: Resonance in the third excitation step of Au leading from the $6d^2D_{3/2}$ state to an autoionizing state with $\lambda = 592\text{ nm}$. The solid curve represents a fit by a Shore-Fano profile.

Figure 5: Resonances of ^{195}Au and ^{197}Au in the D_1 line. Top: Resonance-ionization-mass spectroscopy signal of laser-desorbed ^{195}Au ($T_{1/2} = 183\text{ d}$) implanted into graphite at 60 keV . Bottom: Simultaneously measured fluorescence signal of stable ^{197}Au in a thermal atomic beam. The RIMS signal is considerably power broadened due to exceeding laser intensity in the second excitation step ($\lambda = 406\text{ nm}$).

Figure 6: Part of the time-of-flight signal in case of resonance-ionization-mass spectroscopy of 5×10^9 atoms of ^{195}Au ($T_{1/2} = 183\text{ d}$) implanted at 60 keV into graphite. $T = 0$ is defined by the laser pulses used for resonant ionization. The large peak at mass $A = 197$ is due to stable ^{197}Au which was present as impurity in the graphite target. Since the ^{197}Au ion intensity is about 100 times larger than that of ^{195}Au , a strong signal by afterpulses of the MCP is observed at $T \geq 43.8\text{ }\mu\text{s}$.

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Fig. 1

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Fig. 6