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Radiative lifetimes in Ce I and Ce II

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Abstract. New radiative lifetime measurements based on time-resolved laser-induced fluorescence techniques are reported for 18 even-parity levels belonging to the $4f5d^26p$ and $4f^25d^2$ configurations of Ce I and 6 even-parity levels belonging to the $5d^26s$, $4f5d6p$, and $4f6s6p$ configurations of Ce II. Free neutral and singly ionized cerium atoms were produced by laser ablation. The Ce I and Ce II levels range in energy from 26 545 to 29 102 cm^{-1}, and 42 573 to 48 152 cm^{-1}, respectively.

PACS. 32.70.Cs Oscillator strengths, lifetimes, transition moments – 42.62.Fi Laser spectroscopy

1 Introduction

Accurate determinations of radiative lifetimes for rare-earth (RE) elements are of great importance in analysis of solar and stellar spectra, and with application to theoretical calculations [1–3]. In astrophysics, there is a need for radiative lifetimes of RE elements, which show large abundance in stellar objects particularly in chemically peculiar (CP) stars, in connection with the determination of elemental abundances. From a theoretical point of view, experimental values are very useful for comparison with theoretical model predictions. In addition, the radiative lifetimes of RE atoms and ions are also of interest in plasma physics, high intensity discharge lamp technology, and laser chemistry.

A large variety of methods for determining lifetimes of excited atomic/ionic levels have been developed. The different techniques have been reviewed, *e.g.* in reference [4]. Among the methods available, the technique employing a selective excitation of the investigated levels, for example using a tunable laser, has turned out to be a reliable one. In recent years, the development of laser spectroscopic techniques has made the measurements of radiative lifetimes in the ultraviolet and vacuum-ultraviolet spectral ranges feasible and a large number of lifetime measurements have been performed using such techniques on atom/ion sources like hollow cathodes, thermal ovens or laser-induced plasmas [5–8]. In the present work, we performed lifetime measurements in neutral and singly ionized cerium atoms using time-resolved laser-induced fluorescence (LIF) techniques combined with the methods of laser-pulse compression by stimulated Brillouin scattering (SBS) in water, and laser-wavelength extension by stimulated Stokes Raman scattering (SSRS) in hydrogen gas.

Cerium ($Z = 58$), one of RE elements, has been observed in the spectra of various stars [9–12]. Radiative lifetimes of Ce I, and Ce II have previously been studied experimentally, but especially for even-parity high-lying excited levels of Ce I and Ce II data are lacking. Lifetime measurement results on 26 even-parity levels (between 12 114 and 22 971 cm^{-1}) and 6 odd-parity levels (between 26 868 and 30 543 cm^{-1}) of Ce I were reported by Bisson *et al.* using a multistep laser excitation technique [13]. Li *et al.* published 2 even-parity lifetimes (22 600.48 and 22 970.28 cm^{-1}) of Ce I and 5 even-parity and 3 odd-parity lifetimes (between 24 663 and 39 395 cm^{-1}) of Ce II using time-resolved laser-induced fluorescence techniques [14]. Andersen *et al.* measured 1 even-parity level (24 663.05 cm^{-1}) and 3 odd-parity level of Ce II in the wavelength range from 25 776 to 31 341 cm^{-1} in 1975 using the beam-foil method [15]. In 1995, Langhans *et al.* reported 7 even-parity lifetimes (24 663–27 813 cm^{-1}) and 4 odd-parity lifetimes (26 268–29 751 cm^{-1}) of Ce II measured by the time-resolved LIF technique applied to a hollow-cathode discharge [16]. Radiative lifetimes of 18 even-parity levels in Ce II have been presented by Zhang *et al.* in 2001 using the time-resolved LIF technique applied to a laser-induced plasma [17].

In the present paper, lifetime results on 18 even-parity levels in the wavenumber range from 26 545 to 29 102 cm^{-1} of Ce I, and 6 even-parity levels from 42 573 to 48 152 cm^{-1} of Ce II are reported using time-resolved LIF spectroscopy. In the measurements, free cerium atoms and singly ionized ions were obtained in a laser-induced cerium plasma. Stimulated Stokes Raman Scattering techniques were used to extend the tunable range of the exciting dye laser source.

2 Experimental methods

The measurements were undertaken with the method of selective excitation of an atomic or ionic level by tunable

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laser radiation and time-resolved detection of the fluorescence from the decaying investigated levels. The experimental setup used for the lifetime measurements is previously described [8,17]. Free neutral and singly ionized cerium atoms were obtained by focusing a pulsed 532 nm Nd:YAG laser (Continuum Surelite) beam onto a pure cerium foil, which was placed as a rotating target in a vacuum chamber with about 10^{-6}–10^{-5} mbar background pressure. The pulse of the ablation laser has a duration of 10 ns and a repetition rate of 10 Hz. The pulse energy normally was in the range of 2–10 mJ. After the impinging of the laser pulse on the cerium foil, a small plasma containing electrons, atoms and ions of various ionization stages was produced and expanded from the foil. The laser-induced plasma source has the advantage of high atomic and ionic populations in ground as well as metastable states, which can be used as a starting point for laser excitation. In addition, the plasma density and temperature can be adjusted by changing the pulse energy and beam size on the foil, and the time delay between the ablation and the excitation pulses.

The excitation radiation originated from a pulsed dye laser. The methods of laser-pulse compression by stimulated Brillouin scattering (SBS) in water [18], and frequency up-conversion using a KDP crystal and a BBO crystal were employed. The pulses from a 532 nm Nd:YAG pumping laser (Continuum NY-82) with an 8-ns pulse duration and a single pulse energy of 400 mJ were shortened by SBS in water. This results in a compression of the pulse to about 1 ns and a remaining single-pulse energy of about 120 mJ. The compressed laser pulse was employed to pump a dye laser (Continuum Nd-60), in which DCM dye was utilized. In order to obtain the required excitation, the radiation from the dye laser could be frequency doubled in a KDP crystal, and then mixed with the fundamental frequency in a BBO crystal in order to produce the third harmonic of the dye laser frequency. A retarding plate was placed between the KDP and the BBO crystals for phase matching. A SSRS cell with hydrogen at about 10 bars was used in this experiment to extend the tunable range of the dye laser source. The Stokes component (S) of Raman shifting was produced by means of focusing the second harmonic (2ω), or the third harmonic (3ω) of the dye laser radiation into the SSRS cell. The excitation radiation from the SSRS cell was selected using a CaF_2 Pellin-Broca prism, and was then horizontally sent into the vacuum chamber. The Nd:YAG laser was externally triggered from a delay generator (Stanford Research Systems Model 535), which also controlled the plasma-generating laser.

The excitation beam interacted with the neutral or singly ionized cerium atoms about 1 cm above the foil. The fluorescence, released at the decay from the excited levels, was collected by a fused-silica lens and focused to the entrance slit of a 1/8 m monochromator. A Hamamatsu 1564U micro-channel-plate (MCP) photomultiplier tube with a risetime of 0.2 ns was placed at the output of the monochromator, and was connected to a transient recorder (Tektronix Model DSA 602), which has a 1 GHz bandwidth and a 2 G samples/s real-time sampling rate. The temporal shape of the excitation pulses was also recorded for short-lived states of Ce II with the same detection system by inserting a metal rod into the interaction zone of the excitation laser and the plasma while the ablation beam was blocked.

3 Measurements and results

The ground electronic configurations of the Ce I and Ce II are $4f5d6s^2$ and $4f5d^2$, respectively. In the measurements the energy levels were taken from the NIST atomic spectra database. The excitation was performed by a single-photon process from the ground state or appropriate metastable states of Ce I and Ce II, and the excitation lines for the studied states are in the region 207–377 nm. The region can be covered by different non-linear processes ($2\omega+S$, $3\omega+S$ and 3ω) using the DCM dye operated in the wavelength region 622–652 nm. The radiative lifetimes of 18 even-parity levels belonging to the $4f5d^26p$ and $4f^25d^2$ configurations of Ce I and 6 even-parity levels belonging to the $5d^26s$, $4f5d6p$ and $4f6s6p$ configurations of Ce II were measured. The levels measured are summarized in Table 1.

In the measurements, fluorescence signals in the different decay channels from the excited upper levels to possible lower levels were checked and the strongest one was normally utilized for the decay recordings. All possible systematic errors, which can influence lifetime values, were carefully investigated. Attempts to observe lifetime variations were made by changing various experimental parameters.

Collisional quenching and radiation trapping effects are considered negligible since the background pressure in the vacuum chamber was very low, and since consistent lifetime values were obtained when the detected fluorescence intensity was varied by a factor of 10 by changing the delay time between the ablation and the excitation pulses. The delay times between the ablation and the excitation pulses for the Ce I measurements was between 2 and 15 μs and for Ce II between 0.7 and 2.5 μs, with a sufficient signal-to-noise ratio for evaluating the lifetime also for the longest delays. The difference in delay times between Ce I and Ce II is due to the lower speeds of atoms compared to ions.

It is well known that Zeeman quantum beats can distort decay curves if the sublevels of the excited level are coherently excited, and polarized detection is used. Therefore, a static magnetic field of about 100 G, provided by a pair of Helmholtz coils, was added or removed over the plasma in this experiment for each measured level to look for possible influences. No effect was observed. Flight-out-of-view effects for long-lived states were carefully avoided by adjusting the position and width of the entrance slit of the monochromator and the delay times between the ablation and the excitation pulses. No observable effects were found for measurements under different conditions.

The Ce I and Ce II lifetimes reported here fall in the range 10–30 ns, and 2–7 ns, respectively. Therefore,

Table 1. Radiative lifetimes measured for Ce I and Ce II.

Configuration	E (cm^{-1})	Origin	Excitation λ(nm)$_{\rm vac.}$	Observed λ(nm)$_{\rm vac.}$	Lifetime (ns) This work
Ce I					
$4f(^2\mathrm{F^o})5d^2(^3\mathrm{F})(^4\mathrm{I^o})6p$					
	26 545.399	0.0	376.713	398	11.9(1.0)
	26 589.936	0.0	376.082	376, 395	14.3(1.2)
$4f^2(^3\mathrm{H})5d^2(^3\mathrm{F})$	26 742.956	0.0	373.930	393	13.9(1.4)
	26 913.605	228.849	374.745	465	21.7(2.0)
	27 091.644	0.0	369.117	387	12.5(1.1)
$4f(^2\mathrm{F^o})5d^2(^3\mathrm{F})(^4\mathrm{G^o})6p$	27 323.740	228.849	369.073	369, 386	15.6(1.4)
	27 483.038	0.0	363.860	383	26(2)
	27 488.295	228.849	366.845	383	21.6(2.0)
$4f^2(^3\mathrm{H})5d^2(^3\mathrm{F})$	27 539.493	0.0	363.114	395	26(2)
	27 541.881	0.0	363.083	381	14.0(1.1)
	27 575.557	0.0	362.640	363, 397	15.4(1.2)
	27 594.029	0.0	362.397	380	12.6(1.0)
	27 682.976	228.849	361.232	454	14.7(1.5)
	27 722.717	0.0	360.715	408	13.5(1.4)
	27 754.738	228.849	363.294	383	16.3(1.5)
$4f^2(^3\mathrm{H})5d^2(^3\mathrm{P})$	28 885.245	1 279.424	362.242	389	18.7(1.5)
	29 066.231	1 279.424	359.883	387	18.8(1.6)
$4f(^2\mathrm{F^o})5d^2(^1\mathrm{G})(^2\mathrm{K^o})6p$	29 102.000	1 388.941	360.840	346	16.7(1.4)
Ce II					
$5d^2(^3\mathrm{F})6s$	42 573.191	0.0	234.889	283	6.3(0.5)
$4f5d(^1\mathrm{P^o})6p$	43 460.533	0.0	230.093	284	3.3(0.4)
$5d^2(^1\mathrm{D})6s$	47 466.445	0.0	210.675	319, 269	6.2(0.5)
$5d^2(^1\mathrm{G})6s$	47 489.280	0.0	210.573	265	2.3(0.2)
$4f6s(^3\mathrm{F^o})6p$	48 024.675	0.0	208.226	278, 298	2.0(0.2)
$5d2(^1\mathrm{G})6s$	48 151.739	0.0	207.676	279	3.3(0.3)

we adopted different fitting processes for the evaluation of lifetimes. For the lifetimes longer than 10 ns, occurring for Ce I, a least-squares exponential fitting procedure was applied to the decay at times when the excitation pulse had vanished. On the other hand, for lifetimes shorter than 10 ns occurring in Ce II, the evaluation process was performed by fitting the experimental fluorescence decay curve to a convolution of the detected excitation pulse and a pure exponential function. The effects of the finite duration of the excitation pulse and the limited response time of the detection system were taken into account in the deconvolution fitting process because the recorded excitation curve includes the real laser pulse and the time-response function of the detection system. Typical experimental curves of Ce I and Ce II (27 549.029 cm^{-1} and 47 489.28 cm^{-1}, respectively) for the exponential and the deconvolution fitting procedures are shown in Figure 1.

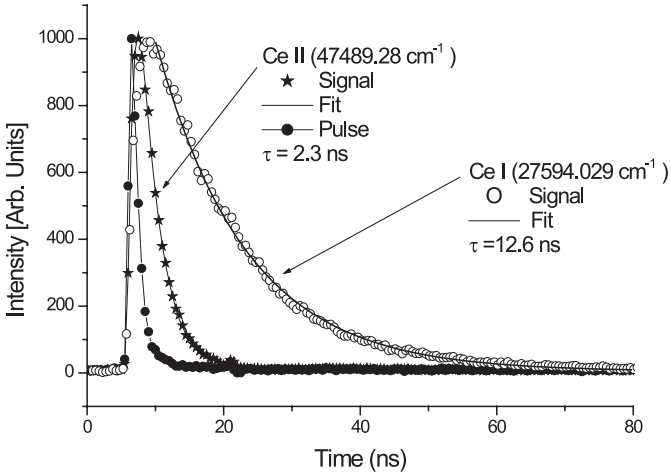

Fig. 1. Typical experimental curves for Ce I and Ce II (27 549.029 cm^{-1} and 47 489.28 cm^{-1}, respectively). For the 47 489.28 cm^{-1} level of Ce II, a recorded excitation pulse curve is also shown. Fits are included.

In order to obtain a sufficiently smooth curve for evaluating the radiative lifetime, each decay curve was obtained by averaging fluorescence photons from 1 000 pulses. To ensure that saturation effects in the excitation were eliminated, the fluorescence signals were recorded with different neutral density filters inserted in the exciting laser light path. For each level measured, the final lifetime value was obtained from at least 9 separate measurements under different experimental conditions. The experimental lifetime results are included in Table 1. The uncertainties reported in Table 1 contain the statistical uncertainties, but also include possible remaining systematic errors. As a test, we also remeasured the level (22 970.784 cm^{-1}) of Ce I,

and the value obtained, 21(2) ns, agrees well with the results by Bisson *et al.* [13] and Li *et al.* [14].

In summary, radiative lifetimes of 18 even-parity levels in Ce I and 6 even-parity levels in Ce II have been measured for the first time. Stimulated Brillouin scattering (SBS) in water, stimulated Stokes Raman scattering (SSRS) in hydrogen gas, and frequency upconversion in KDP and BBO crystals were employed in this experiment. The new data are expected to be helpful for astrophysical analyses.

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