Eur. Phys. J. D **23**, 323–326 (2003)
DOI: 10.1140/epjd/e2003-00055-3

THE EUROPEAN PHYSICAL JOURNAL D

Lifetime measurements in Tm I, Tm II, and Tm III by time-resolved laser spectroscopy

H.-L. Xu[1,2,a], Z.-K. Jiang[1,2], and S. Svanberg[1]

[1] Department of Physics, Lund Institute of Technology, P.O. Box 118, 221 00 Lund, Sweden
[2] Department of Physics, Jilin University, Changchun 130023, P.R. China

Received 20 August 2002 / Received in final form 7 January 2003
Published online 4 March 2003 –

Abstract. Natural radiative lifetimes of eight levels in Tm I ($4f^{13}5d6p$ and $4f^{12}5d6s^2$ configurations), two levels in Tm II ($4f^{12}5d6s$ configuration) and three levels in Tm III ($4f^{12}5d$ configuration) have been measured by using time-resolved laser spectroscopy. Free thulium atoms, as well as singly and doubly ionized ions, were obtained in a laser-induced thulium plasma and the investigated states were selectively populated by a single-step excitation process with a tunable narrow-band laser pulse.

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

1 Introduction

The increasing interest in the study of the radiative properties of rare earth (RE) elements results mainly from their connection with solar and stellar spectra, in which a large number of rare earth atomic and ionic lines have been observed [1–4]. In astrophysics, accurate radiative parameters of RE elements are primarily used for the analysis of solar and stellar spectra with regard to the understanding of star chemical composition. On the other hand, the study of radiative parameters of RE elements is also of great interest in laser chemistry, in the diagnostics of impurities of fusion plasmas, and in laser applications. For example, the level structure of free RE ions is similar to that in the RE-doped crystals, and the comparison of the levels of the free ions with those in crystals could thus provide a help for the better understanding of the RE-doped crystalline structure. Such crystals have large utilization in solid state lasers and for information processing.

Radiative lifetimes, branching ratios and oscillator strengths are among the most fundamental spectroscopic characteristics of an atomic/ionic system. The determination of these properties of RE elements is required in performing studies of the quantitative elemental abundance from astrophysical spectra of stars, the free interstellar medium, nebulae etc., because they all depend heavily upon the accuracy of the experimental data. Thulium ($Z = 69$) is an odd-Z RE element and has a single stable isotope with mass number 169. Neutral thulium has been identified in the metal deficient G 6 star HD 18474 [5]. Tm II has been observed in the solar photospheric spectrum [6]. Besides in the Sun, Tm II has also been observed in the peculiar A star HD 110066 [7] and the CP star [8]. Doubly ionized thulium has been identified in the silicon Ap star HD 192913 [9].

The purpose of the present investigation is mainly to experimentally determine radiative lifetimes for thulium. Lifetime measurements of Tm I, Tm II and Tm III were thus performed using the time-resolved laser-induced fluorescence (LIF) technique, which has been proven to be a reliable method for determination of radiative lifetimes due to selective excitation of the investigated levels. Previously, a lot of work has been performed regarding lifetime measurements in thulium. A review by Blagoev and Komarovskii in 1994 collected all the lifetimes of neutral and singly ionized thulium atoms before 1993 [10]. Later on, Guo *et al.* presented 11 odd-parity lifetimes of Tm I in 1993 using time-resolved atomic-beam laser spectroscopy [11]. In 1996, Anderson *et al.* published large-scale lifetime data for odd-parity, as well as even-parity levels of Tm I and Tm II using time-resolved LIF techniques applied to a hollow-cathode discharge source [12]. For comparison with the time-resolved LIF method, Rieger *et al.* measured 16 lifetimes of Tm II using the fast-beam-laser technique in 16 levels which had previously been investigated [13]. Recently, radiative lifetimes of 8 levels in Tm III have been measured by Li *et al.* using time-resolved LIF techniques [14].

In this paper, we measured eight levels of Tm I, two levels of Tm II, and three levels of Tm III by using time-resolved laser spectroscopy. In the measurements, free Tm, Tm^+, and Tm^{++} particles were obtained in a laser-produced thulium plasma. The Stimulated Stokes Raman Scattering (SSRS) technique was used for extending the tunable range of the exciting dye laser source.

[a] e-mail: huailiang.xu@fysik.lth.se

Table 1. Levels measured and excitation schemes.

Configuration[a]	Term	J	E (cm^{-1})	Excitation λ (mn)$_{\rm vac.}$	Exc. laser conversion scheme[b]	Observed fluorescence λ(nm)$_{\rm vac.}$
Tm I						
$4f^{12}(^3\mathrm{F}_3)5d_{5/2}6s^2$	(4, 5/2)	7/2	31 510.24	317.357	2ω	317
$4f^{12}(^3\mathrm{F}_2)5d_{3/2}6s^2$	(7/2, 3)	7/2	45 018.23	222.132	3ω	406
		9/2	45 091.022	221.573	3ω	441
$4f^{13}(^2\mathrm{F}^{\rm o}_{7/2})5d6p(^3\mathrm{P}^{\rm o}_0)$	(7/2, 0)	7/2	45 131.67	221.573	3ω	459
		7/2	45 149.63	221.485	3ω	458
		5/2	45 908.35	217.825	3ω	443
		9/2	46 238.51	216.219	3ω	464
$4f^{13}(^2\mathrm{F}^{\rm o}_{7/2})5d6p(^3\mathrm{P}^{\rm o}_2)$	(7/2, 2)	7/2	46 500.09	215.053	3ω	433
Tm II						
$4f^{12}\ 5d6s$	(4, 2)	4	27 009.39	370.241	$2\omega + S$	374
		4	27 254.42	366.912	$2\omega + S$	370
Tm III						
$4f^{12}(^3\mathrm{H}_6)5d_{5/2}$	(6, 5/2)	9/2	30 535.69	327.485	2ω	327
$4f^{12}(^3\mathrm{F}_4)5d_{3/2}$	(4, 3/2)	7/2	32 262.88	309.953	2ω	310
$4f^{12}(^3\mathrm{H}_5)5d_{5/2}$	(4, 3/2)	5/2	39 278.57	254.591	$3\omega + 2S$	328

[a] From NIST Atomic Spectra Database. [b] 2ω means frequency doubling, 3ω means frequency tripling, S, $2S$ represent the first-, and the second-order stockes components.

2 Measurements and results

The ground configurations of Tm I, Tm II and Tm III are $4f^{13}6s^2$, $4f^{13}6s$, and $4f^{13}$, respectively. All the excitations in this present experiment are from the ground states. Radiative lifetimes of eight levels of Tm I belonging to the $4f^{13}5d6p$ and $4f^{12}5d6s^2$ configurations, two levels of Tm II belonging to the $4f^{12}5d6s$ configuration, and three levels of Tm III belonging to the $4f^{12}5d$ configuration were measured by single-step excitation. These levels, obtained from the NIST atomic spectra database, are presented in Table 1 with excitation schemes.

The details of our experimental apparatus have been described elsewhere (see *e.g.* [15]) and therefore only a brief description is given here. A laser-induced thulium plasma was used as the Tm, Tm^+, and Tm^{++} source. The plasma was produced by focusing 532 nm wavelength laser pulses, emitted from a 10 ns duration Nd:YAG laser (Continuum Surelite) with variable pulse energy in the range 2–10 mJ, on a rotating thulium foil, which are placed in a vacuum chamber with 10^{-6}–10^{-5} mbar background pressure. In order to generate the required excitation pulses, an injection seeded, Q-switched and frequency doubled Nd:YAG laser (Continuum NY-82), characterized by an 8 ns pulse duration and a 400 mJ pulse energy, was used to pump a dye laser (Continuum Nd-60). However, before entering the dye laser, the beam from the Nd:YAG laser was sent into a compressor, based on stimulated Brillouin scattering in water, to shorten the laser pulse to about 1 ns. The dye laser, operated with a DCM dye, was effectively frequency doubled in a KDP crystal, or frequency tripled in a BBO crystal by frequency mixing of the second harmonic with the fundamental frequency. A retarding plate was placed between the KDP and the BBO crystals to make the polarization direction of the second harmonic and of the fundamental frequency parallel for type-I phase matching [16]. According to the excitation requirements shown in Table 1, different orders of Stokes Raman scattering from the second- or the third-harmonic beam were obtained by focusing the beam into a cell with hydrogen at about 10 bars. Then the excitation light was isolated with a CaF_2 Pellin-Broca prism and sent into the vacuum chamber crossing the thulium plasma at a distance of about 10 mm above the foil. Both Nd:YAG lasers, operated in an external trigger mode, were controlled by a digital delay generator (Stanford Research Systems Model 535).

After ablation from the thulium foil, generated free Tm atoms, Tm^+, and Tm^{++} ions entered the interaction region. By properly choosing excitation wavelength and trigger parameters, Tm, Tm^+ and Tm^{++} were selectively excited, respectively. Fluorescence from the levels under study was collected by a fused-silica lens, and then appropriately filtered by a 1/8 m monochromator (resolution of 6.4 nm/mm), finally to be detected by a Hamamatsu 1564U microchannel-plate (MCP) photomultiplier tube (200 ps rise time). The time-resolved signal from the detector was captured by means of a digital oscilloscope (Tektronix Model DSA 602), where an average of 1000 pulses was performed for obtaining a sufficiently high signal-to-noise ratio. A Thorlabs SV2-FC photo diode (120 ps rise time), driven by the excitation beam, was employed to trigger the oscilloscope. Through a GPIB cable, the time-resolved fluorescence decay data were transferred to a personal computer and the lifetime evaluation was performed by an exponential fit.

Before the measurements, a careful check was made to verify that the selected Tm I, Tm II, and Tm III levels were indeed studied by observing most of the decay channels from the upper levels to possible lower levels. In the

Table 2. Observed radiative lifetimes and comparison with previous results.

		Lifetime (ns)				
Configuration	$E(\mathrm{cm}^{-1})$	This work	Previous			
Tm I						
$4f^{12}(^3\mathrm{F}_3)5d_{5/2}6s^2$	31 510.24	56(4)	55.1[a]			
$4f^{12}(^3\mathrm{F}_2)5d_{3/2}6s^2$	45 018.23	29(2)				
	45 091.022	35(2)				
$4f^{13}(^2\mathrm{F}^\mathrm{o}_{7/2})5d6p(3\mathrm{P}^\mathrm{o}_0)$	45 131.67	100(7)				
	45 149.63	167(12)				
	45 908.35	43(3)				
	46 238.51	39(3)				
$4f^{13}(^2\mathrm{F}^\mathrm{o}_{7/2})5d6p(3\mathrm{P}^\mathrm{o}_2)$	46 500.09	28(2)				
Tm II						
$4f^{12}\ 5d6s$	27 009.39	40(3)	38.2[a]	34[b]	32.1(1.3)[c]	28.9[d]
	27 254.42	41(3)	38.7[a]	34[b]	35.6(2.1)[c]	41.0[d]
Tm III						
$4f^{12}(^3\mathrm{H}_6)5d_{5/2}$	30 535.69	140(15)				
$4f^{12}(^3\mathrm{F}_4)5d_{3/2}$	32 262.88	62(2)				
$4f^{12}(^3\mathrm{H}_5)5d_{5/2}$	39 278.57	38(3)				

[a] Anderson *et al.* [12] (time-resolved LIF on a hollow-cathode lamp with ±5% uncertainly). [b] Curtis *et al.* [19] (beam foil spectroscopy). [c] Rieger *et al.* [13] (fast-beam-laser technique). [d] Quinet *et al.* [18] (HFR calculations).

measurements, possible systematic errors were considered. The plasma density and temperature in the interaction region can be adjusted by changing the delay time between the producing and interrogating laser pulses. With appropriately varied plasma conditions, the intensity of fluorescence signal was changed by a factor of 8, while the lifetimes remained constant within the experimental scattering. This confirmed that the collisional quenching and radiation trapping effects within the parameter range used were negligible. A magnetic field of about 100 gauss was added over the plasma zone by a pair of Helmholtz coils not only to wash out potential quantum beats effects on long lifetimes, but also to reduce the plasma background light associated with recombination between electrons and the ions [17]. The entrance slit of the monochromator was opened maximally in order to eliminate flight-out-of-view effects for longer lifetime measurements. Different neutral density filters were inserted in the exciting laser light path in order to avoid saturation effects. About 9 fluorescence decay curves for each studied level were recorded under different experimental conditions. All experimental lifetime results are listed in Table 2 with estimated error bars, which also allow for possible uncompensated effects.

3 Discussion

The experimental data from the present investigation are compared with previously published results in Table 2, including the theoretical values by Quinet *et al.* [18]. The lifetimes for one level in Tm I and two levels in Tm II agree well within the quoted uncertainties with those by Anderson *et al.* (1996) using the time-resolved laser-induced fluorescence technique on a hollow-cathode discharge source. For the 27 254 cm^{-1} level of Tm II, a rather good agreement is found with the Relativistic Hartree-Fock (HFR) calculations [18], however, the discrepancies between our value and those given by Rieger *et al.* (fast-beam-laser technique) and by Curtis *et al.* (beam foil spectroscopy) [19] are found to be about 11% and 15%, respectively. In particular, for the 27 009 cm^{-1} level of Tm II, for which Rieger *et al.* suggested to perform an independent measurement, our results is close to the one measured by Anderson *et al.* Disagreements with data obtained in early beam foil measurements are not uncommon. However, it is harder to understand the discrepancies with beam-laser measurements for the two levels of Tm II since the two methods yielded good agreement in other cases (see, *e.g.* Yb II [20,21] and Nd II [22,23]). The lifetimes obtained in the present work will, when they are combined with the intensity measurements (branching ratios), be helpful for astrophysicist for obtaining the elemental abundance in the stellar objects.

This work was financially supported by the Swedish Research Council and by the National Natural Science Foundation of China (No. 10274025).

References

1. C. Jaschek, M. Jaschek, *The Behaviour of Chemical Elements in Stars* (Cambridge University Press, Cambridge, 1995)
2. V.F. Gopka, A.V. Yushchenko, Astron. Rep. **39**, 662 (1995)
3. C.R. Cowley, G. Mathys, Astron. Astrophys. **339**, 165 (1998)
4. T. Ryabchikova, N. Piskunov, I. Savanov, F. Kupka, V. Malanushenko, Astron. Astrophys. **343**, 229 (1999)
5. M.J.F. Figueroa, M.R. Fernandez, Opt. Pura Apl. **10**, 265 (1977)

6. J.E. Ross, L.H. Aller, Solar Phys. **36**, 21 (1974)
7. S.J. Adelman, C.J. Adelman, Mon. Not. R. Astron. Soc. **235**, 1361 (1988)
8. C.R. Cowley, Phys. Scripta **T8**, 28 (1984)
9. T.A. Ryabchikova, E.S. Davidova, S.J. Adelman, Publ. Astron. Soc. Pac. **102**, 581 (1990)
10. K.B. Blagoev, V.A. Komarovskii, At. Data Nucl. Data Tables **56**, 1 (1994)
11. C. Guo, H. Yu, Y. Yu, W. Peng, Z. Jiang, Z. Phys. D **27**, 239 (1993)
12. H.M. Anderson, E.A. Den Hartog, J.E. Lawler, J. Opt. Soc. Am. B **13**, 2382 (1996)
13. G. Rieger, M.M. Mccurdy, E.H. Pinnington, Phys. Rev. A **60**, 4150 (1999)
14. Z.S. Li, Z.G. Zhang, V. Lokhnygin S. Svanberg, T. Bastin, E. Biémont, H.P. Garnir, P. Palmeri, P. Quinet, J. Phys. B **34**, 1349 (2001)
15. H. Xu, Z. Jiang, S. Svanberg, J. Phys. B **36**, 411 (2003)
16. W.L. Glab, J.P. Hessler, Appl. Opt. **26**, 3181 (1987)
17. Z.G. Zhang, S. Svanberg, P. Quinet, P. Palmeri, E. Biémont, Phys. Rev. Lett. **87**, 273001 (2001)
18. P. Quinet, P. Palmeri, E. Biémont, J. Quant. Spectrosc. Radiat. Transf. **62**, 625 (1999)
19. L.J. Curtis, I. Martinson, R. Buchta, Nucl. Instrum. Meth. **110**, 391 (1973)
20. Z.S. Li, S. Svanberg, P. Quinet, X. Tordoir, E. Biémont, J. Phys. B **32**, 1731 (1999)
21. R.W. Berends, E.H. Pinnington, B. Guo, Q. Ji, J. Phys. B **26**, L701 (1993)
22. C.M. Pinciuc, R.C. Rivest, M.R. Izawa, R.A. Holt, S.D. Rosner, T.J. Scholl, Can. J. Phys. **79**, 1159 (2001)
23. Unpublished data