Radiative decay data for highly excited Zr I levels

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ABSTRACT

Radiative lifetimes of 17 excited levels in Zr I, in the energy interval 29000–40 974 cm−1, have been investigated using the time-resolved laser-induced fluorescence method. The levels belong to the 4d5s5p, 4d5p and 4d5s5p electronic configurations and were excited in a single-step process from either the ground term, 4d5s2 1D2, or from the low-lying 4d5s2 3P and 3F terms. For three levels, we confirm previous measurements while for 14 of the levels the lifetimes have been measured for the first time. The experimental results are compared to theoretical calculations performed with a multiconfiguration relativistic Hartree–Fock method including core-polarization effects. Theoretical transition probabilities of astrophysical interest, scaled by the experimental lifetimes, for the depopulating channels of the investigated levels are also presented.

Key words: atomic data – atomic processes – methods: laboratory.

1 INTRODUCTION

Accurate values of oscillator strengths for spectral lines of neutral zirconium are of great interest in astrophysics for the determination of the chemical composition of stellar atmospheres. Recent examples include the determination of the zirconium abundance in the metal-poor red giant star HD 221170 (Yushchenko et al. 2005; Ivans et al. 2006) and in the CH star CS 31062-050 (Johnson & Bolte 2004). Measurements of radiative lifetimes of excited states in Zr I are necessary to determine the needed transition probabilities and to assess the accuracy of the theoretical data in this complex system.

The low-lying levels of Zr I have been investigated using different experimental approaches in a series of previously published papers. The radiative lifetimes of the z 3G, y 4G and y 5G levels were measured using beam-sputtering excitation by a fast Ar+ beam (Ramanujam 1977; Andersen, Ramanujam & Bahr 1978). Collinear fast-beam laser modulation spectroscopy was used to determine radiative lifetimes of the z 3G and y 4G, 3,4,5 levels in Zr I (Poulsen et al. 1981, 1982). Hannaford & Lowe (1981) applied the time-resolved laser-induced fluorescence (TR-LIF) method and sputtering from a hollow cathode discharge to measure the radiative lifetimes of all levels in the z 3G, y 3G and y 5G terms. Biémont et al. (1981) also used the TR-LIF method to obtain lifetime values for 34 levels in Zr I. The oscillator strengths of the transitions depopulating these levels were determined by the same authors from a combination of the lifetimes with measured branching fractions (BFs). Lifetimes of 11 levels belonging to the z 3G and y 3G and y 5G terms have been investigated with TR-LIF applied to a Zr atomic beam, produced by a sputtering process in a hollow cathode discharge (Duquette, Salih & Lawler 1982). Rudolph & Helbig (1982) measured lifetimes of 15 Zr I levels in the energy interval 25 630–29 002 cm−1, using the delayed coincidence method with pulsed laser excitation. Lifetimes of the levels y 4G, x 3G, z 1G and x 3D were measured using picosecond LIF by Langhans, Schade & Helbig (1995).

When reviewing the published results, it appears that the lifetimes for most of the measured levels are consistent when selective laser excitation was applied. When this is not the case (Ramanujam 1977; Andersen et al. 1978), the lifetimes obtained by beam-foil spectroscopy are generally longer, which may be due to cascading effects resulting from the non-selective excitation which is typical of this method.

Despite all these efforts, there is still a need for radiative data for many transitions of astrophysical interest, particularly for transitions from highly excited levels which are weak and, consequently, less dependent upon damping parameters in astrophysical analyses.

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This has led some groups to deduce ‘astrophysical’ (mostly solar) gf values for transitions of Zr I for which data were not available (see e.g. Thevenin 1989, 1990; Meylan et al. 1993). As is well known, however, this process is somewhat hazardous and sensitive to possible blending problems which might affect the absorption or emission features. When experimental transition probabilities are missing, theoretical approaches can provide the relevant information (i.e. A values) but the precision could be lower particularly for the weakest lines. However, not much theoretical data are available in Zr I. The only published work to our knowledge is that of Bogdanovich et al. (1995, 1996) who investigated transitions arising from the 4d^2s5p and 4d^1s5p configurations with a superposition of configuration approach based on radial orbitals obtained by the Hartree–Fock method. This scarcity of theoretical results is easily explained by the complexity of the calculations in neutral heavy elements. It is therefore necessary to assess the reliability of the calculations by comparisons with experiment whenever possible.

In this paper, we report transition probabilities of high-excitation transitions in Zr I (emitted from levels in the range 29 000 to 40 973 cm\(^{-1}\)) obtained from a combination of TR-LIF lifetime measurements and BF calculated using a partly relativistic model including extensive configuration interaction effects.

## 2 LIFETIME MEASUREMENTS

A partial energy level diagram of Zr I is presented in Fig. 1. The energies of the excited levels as well as their designations are taken from Moore’s (1958, 1971) tables.

![Figure 1. A partial energy level diagram of Zr I. Some of the excitation transitions and decay channels are shown. Energy levels and designations are from Moore’s (1958, 1971) tables.](image)

The TR-LIF method was used in this work for the lifetime measurements in Zr I. The experimental setup, shown in Fig. 2, is part of the Lund Laser Centre (LLC) in Sweden and has been described in detail previously (Bergström et al. 1988; Xu et al. 2004).

Free atoms and ions, in different ionization stages, were produced by laser ablation, using the second harmonic of a Nd:YAG laser (532 nm). The sample, in our case a Zr foil, was placed in a vacuum chamber with a pressure of about 10\(^{-5}\) mbar. The excitation of the Zr atoms was performed using a pulsed, tunable dye laser that crossed the laser ablation beam at 90° angle about 10 mm above the Zr target surface. The dye laser operated using a DCM dye and was pumped by a second Nd:YAG laser. The repetition rate of the lasers was 10 Hz. The excitation pulses were compressed by stimulated Brillouin scattering (SBS) to approximately 1 ns. To expand the wavelength range, Stokes and anti-Stokes Raman components could be produced in a tube filled with hydrogen at a pressure of about 10 bar (Fig. 2). In all measurements reported here, the second harmonic of the dye laser pulse was used with or without the Raman components. The LIF was measured in a

![Figure 2. TR-LIF setup at the LLC.](image)
Radiative decay data for excited Zr I levels

Table 1. Odd levels measured in Zr I and the corresponding excitation schemes. $E$ is the energy of the level and $\lambda_{\text{air}}$ is the air wavelength.

<table>
<thead>
<tr>
<th>Level</th>
<th>$E^a$ (cm$^{-1}$)</th>
<th>Excitation $\lambda_{\text{air}}$ (nm)</th>
<th>Scheme$^b$</th>
<th>Detection $\lambda_{\text{air}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x $^3G_4$</td>
<td>29 001.65</td>
<td>360.12</td>
<td>$2\omega+S$</td>
<td>432.54</td>
</tr>
<tr>
<td>w $^3G_3$</td>
<td>31 326.81</td>
<td>319.12</td>
<td>$2\omega$</td>
<td>507.83</td>
</tr>
<tr>
<td>w $^3G_4$</td>
<td>31 694.52</td>
<td>321.20</td>
<td>$2\omega$</td>
<td>506.49</td>
</tr>
<tr>
<td>y $^3S_1$</td>
<td>31 850.77</td>
<td>313.87/375.37</td>
<td>$2\omega+S$</td>
<td>365.51/373.74</td>
</tr>
<tr>
<td>w $^3G_5$</td>
<td>32 152.16</td>
<td>323.41</td>
<td>$2\omega$</td>
<td>515.87</td>
</tr>
<tr>
<td>u $^3F_4$</td>
<td>33 163.98</td>
<td>301.44</td>
<td>$2\omega$</td>
<td>464.48</td>
</tr>
<tr>
<td>u $^3F_3$</td>
<td>33 420.47</td>
<td>304.32</td>
<td>$2\omega$</td>
<td>465.76/483.90</td>
</tr>
<tr>
<td>u $^3F_4$</td>
<td>33 559.34</td>
<td>309.35</td>
<td>$2\omega$</td>
<td>471.19/480.95</td>
</tr>
<tr>
<td>t $^3D_1$</td>
<td>36 125.16</td>
<td>313.11</td>
<td>$2\omega$</td>
<td>408.31</td>
</tr>
<tr>
<td>t $^3D_2$</td>
<td>36 294.87</td>
<td>312.07</td>
<td>$2\omega$</td>
<td>354.97</td>
</tr>
<tr>
<td>v $^3P_1$</td>
<td>36 489.10</td>
<td>309.58</td>
<td>$2\omega$</td>
<td>410.76</td>
</tr>
<tr>
<td>u $^3P_0$</td>
<td>36 538.27</td>
<td>310.84</td>
<td>$2\omega$</td>
<td>446.00/485.16</td>
</tr>
<tr>
<td>t $^3P_1$</td>
<td>36 970.65</td>
<td>313.69</td>
<td>$2\omega$</td>
<td>305.03</td>
</tr>
<tr>
<td>v $^3P_2$</td>
<td>37 008.40</td>
<td>313.32</td>
<td>$2\omega$</td>
<td>448.08</td>
</tr>
<tr>
<td>u $^3P_2$</td>
<td>37 450.23</td>
<td>308.30</td>
<td>$2\omega$</td>
<td>300.54</td>
</tr>
<tr>
<td>t $^3P_1$</td>
<td>40 973.94</td>
<td>278.68</td>
<td>$2\omega+AS$</td>
<td>271.75/375.48</td>
</tr>
</tbody>
</table>

$^a$Moore (1958, 1971).

$^b$2$\omega$ means the second harmonic, S and AS indicates the first Stokes and anti-Stokes components, respectively.

direction perpendicular to the ablation and excitation beams by a grating monochromator and a fast photomultiplier (Hamamatsu R1564U). In between the LIF measurements, the ablation laser was turned off and the temporal shape of the excitation laser pulse was registered using the same setup. The excitation and observation wavelengths as well as the excitation schemes are presented in Table 1.

The TR-LIF signal was digitized by a fast oscilloscope (Tektronix DSA 602), averaged over 1000 laser pulses and stored in a computer. The two Nd:YAG lasers were synchronized by a pulse generator which determined the delay between the ablation and the excitation pulses. To avoid effects such as radiation trapping and collisional quenching, delays between 2.4 and 7.4 $\mu$s were used. The LIF decay curves were analysed using the computer program DECIFF (Palmeri et al. 2008) by fitting a single exponential decay convoluted by the measured excitation laser pulse and a background function to the decay data. Fig. 3 shows the data and the fitted function for the $^3D_2$ level. At least 10 decay curves, recorded under different experimental conditions, were registered for each level. Our experimental results are given in Table 2 where the quoted uncertainties include both statistical errors and possible systematic effects. For more details, see e.g. Xu et al. (2004).

3 THEORETICAL APPROACH

The experimental measurements were compared to theoretical lifetimes obtained by a Relativistic Hartree–Fock method (Cowen 1981), taking configuration interaction and core-polarization effects into account (HFR + CP method). The relativistic corrections were the Blume–Watson spin-orbit, the mass-velocity and the one-body Darwin term. The correlation effects were introduced in different ways according to the type of interactions, i.e. valence–valence or core–valence.

Valence–valence correlation was taken into account by explicitly including the most strongly interacting configurations involving the four electrons outside the 3d$^{10}$4s$^2$4p$^5$ ionic core. These configurations were 4d$^2$5s$^2$, 4d$^3$5s, 4d$^3$6s, 4d$^4$5p$^2$, 4d$^5$5s6s, 4d$^5$5s5d, 4d$^5$5s6d, 4d$^5$5d$^2$, 4d$^5$5d, 4d$^6$6s$^2$, 4d$^4$4f$^2$, 4d$^5$s$^2$6s, 4d$^5$s$^2$5d, 4d$^5$s$^2$6d, 4d$^5$s$^2$5p$^2$, 4d$^5$s$^2$5d$^2$ for the even parity and 4d$^5$5s5p, 4d$^5$5p$^2$, 4d$^5$5s4f, 4d$^5$5s5f, 4d$^5$5s6f, 4d$^5$5p5d, 4d$^5$5p6d, 4d$^5$5p$^2$, 4d$^5$6p, 4d$^5$4f, 4d$^5$5f, 4d$^6$6f, 4d$^5$s$^2$5p, 4d$^5$s$^2$6p, 4d$^5$p$^2$ for the odd parity. Core–valence interactions were considered through a polarization model potential and a correction to the dipole operator, according to a procedure described previously (Quinet et al. 1999; Moore (1958, 1971)).

Figure 3. Decay of the level $^3D_2$ level at 36 294 cm$^{-1}$, with an evaluated lifetime of 4.0 ± 0.3 ns. Background subtracted data points with typical error bars are plotted together with the fitted single exponential convoluted by the measured laser pulse (solid line). The dashed curve shows the recorded laser pulse.
Table 2. Experimental and calculated lifetimes (in ns) and Landé factors (g) for odd parity levels in Zr I. $E$ is the energy of the level (in cm$^{-1}$).

<table>
<thead>
<tr>
<th>Level$^a$</th>
<th>$E_{\text{exp}}$ (cm$^{-1}$)</th>
<th>$g_{\text{exp}}^c$</th>
<th>$E_{\text{calc}}$ (cm$^{-1}$)</th>
<th>$g_{\text{calc}}^c$</th>
<th>$\tau_{\text{exp}}$ (ns)</th>
<th>$\tau_{\text{calc}}$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x^3\text{G}_3$</td>
<td>29 001.65</td>
<td>1.21</td>
<td>28 880</td>
<td>1.20</td>
<td>6.9 $\pm$ 0.3</td>
<td>6.6 $\pm$ 0.2$^d$</td>
</tr>
<tr>
<td>$y^3\text{S}_1$</td>
<td>31 386.81</td>
<td>0.75</td>
<td>31 388</td>
<td>0.76</td>
<td>8.2 $\pm$ 0.5</td>
<td>8.2</td>
</tr>
<tr>
<td>$\text{u}^1\text{F}_2$</td>
<td>33 163.98</td>
<td>0.70</td>
<td>33 253</td>
<td>0.85</td>
<td>10.1 $\pm$ 0.6</td>
<td>10.9</td>
</tr>
<tr>
<td>$\text{t}^3\text{P}_1$</td>
<td>36 970.65</td>
<td>1.22</td>
<td>36 375</td>
<td>1.20</td>
<td>10.2 $\pm$ 0.5</td>
<td>9.8</td>
</tr>
</tbody>
</table>

$^a$From Moore (1958, 1971). $^b$This work: TR-LIF measurements. $^c$This work: HFR + CP calculations. $^d$Level untraceable in the HFR calculations.

4 DISCUSSION

Zirconium belongs to the palladium group elements (4d elements).

The two lowest even configurations are 4d$^5$5s$^2$ and 4d$^5$5s. The lowest terms in these configurations, including the ground state 4d$^5$5s$^2$ $^3\text{F}_2$, are plotted in Fig. 1. In the same figure, some of the excitation and decay channels of the investigated odd levels are shown.

In Table 2, we compare the experimental and theoretical radiative lifetimes. For three of the levels, there exist previous experimental lifetimes and this work confirms all except the $x^3\text{G}_3$ lifetime obtained by Rudolph & Helbig (1982) which seems to be somewhat longer but there is no clear explanation for this difference. The experimental and theoretical data are in reasonable agreement for most of the levels. However, for three levels (at 31 850.77, 36 538.27 and 37 008.40 cm$^{-1}$) discrepancies exist. The largest difference is observed for the $y^3\text{S}_1$ level (18.2 $\pm$ 0.9 compared to 4.1 ns). On the experimental side, it is interesting to note that the laser wavelength used to excite this level i.e. 313.87 nm (4d$^5$5s$^2$ $^3\text{F}_2$–4d$^5$5s5p $^3\text{S}_1$) is very close to the excitation wavelength of the 4d$^5$5p $^3\text{D}_2$ level in Zr II. Although this coincidence should offer no real complication in the present experiment, we also tested using the 361.37 nm excitation channel combined with two different fluorescence channels (Table 1) with consistent results. The Zr II level has been studied previously by Biémont et al. (1981) and Langhans et al. (1995) and has a radiative lifetime of $\sim$7 ns. Using the excitation channel at 313.87 nm and a decay channel at 438 nm, we obtain the

A semi-empirical adjustment of the radial parameters was carried out where the average energies, the Slater and spin–orbit integrals together with the effective interaction parameters ($\alpha$, $\beta$) belonging to the 4d$^5$5s$^2$, 4d$^5$5s, 4d$^5$, 4d$^5$5p and 4d$^5$5p configurations were adjusted to obtain the best agreement between the calculated and the experimental energy levels taken from the NIST compilation (Moore 1958, 1971). Only the experimental levels below 40 000 cm$^{-1}$ were included in the semi-empirical process because, according to our calculations, above that limit there are several dozens of unknown energy levels belonging to higher configurations such as 4d$^5$5s5d, 4d$^5$5s6s, 4d$^5$6s, 4d$^5$5p$^2$, 4d$^5$5s6p and 4d$^5$5s$^2$5p. In the 4d$^5$5s configuration, we were unable to reproduce the experimental levels at 15 146.48, 15 457.40 and 15 699.86 cm$^{-1}$ for the 4d$^5$(4f$^2$)5s$^2$ $^3\text{F}$ term indicating that the assignments or that the term values could be incorrect. These levels were instead predicted to fall around 20 300 cm$^{-1}$ in the HFR calculation. Moreover, for the odd-parity levels at 36 070.65 ($J = 1$), 37 450.23 ($J = 2$), 38 270.81 ($J = 1$), 38 326.72 ($J = 2$), 38 566.00 ($J = 2$), 38 881.80 ($J = 3$), 39 174.44 ($J = 4$), 39 704.10 ($J = 1$), 39 803.73 ($J = 3$) and 39 766.47 ($J = 2$) cm$^{-1}$, it was impossible to establish an unambiguous correspondence between the $ab$ initio calculated and the experimentally determined energies due to the large number of predicted levels appearing closely at these energies. Consequently, we excluded those levels from the fitting procedure. The mean deviations of the fits were 96 cm$^{-1}$ (46 levels and 17 parameters) for the even parity and 139 cm$^{-1}$ (157 levels and 23 parameters) for the odd parity.

The calculated lifetimes (HFR + CP) are presented in the last column of Table 2. The transition probabilities of the depopulation channels of the levels for which the lifetimes have been measured in this work are given in Table 3. The HFR transition probabilities have been scaled using the measured lifetimes. This table is restricted to the most intense transitions for which the calculated BFs are expected to be the most accurate.
Radiative decay data for excited Zr\textsuperscript{1} levels

<table>
<thead>
<tr>
<th>$E_{\text{up}}$ (cm\textsuperscript{-1})</th>
<th>$J_{\text{up}}$</th>
<th>$E_{\text{low}}$ (cm\textsuperscript{-1})</th>
<th>$J_{\text{low}}$</th>
<th>$\gamma_{\text{up}}$ (Å)</th>
<th>BF\textsubscript{HFR}</th>
<th>gA\textsuperscript{*} (s\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>29001.65</td>
<td>5</td>
<td>1240.84</td>
<td>4</td>
<td>3601.17</td>
<td>0.968</td>
<td>1.54(9)</td>
</tr>
<tr>
<td>31326.81</td>
<td>3</td>
<td>0.00</td>
<td>2</td>
<td>3191.23</td>
<td>0.257</td>
<td>2.19(8)</td>
</tr>
<tr>
<td>31694.52</td>
<td>4</td>
<td>570.41</td>
<td>3</td>
<td>3250.42</td>
<td>0.033</td>
<td>2.84(7)</td>
</tr>
<tr>
<td>32152.16</td>
<td>5</td>
<td>1240.84</td>
<td>4</td>
<td>3234.13</td>
<td>0.333</td>
<td>4.75(8)</td>
</tr>
<tr>
<td>33163.98</td>
<td>3</td>
<td>540.41</td>
<td>3</td>
<td>3064.38</td>
<td>0.025</td>
<td>1.54(7)</td>
</tr>
<tr>
<td>33420.47</td>
<td>3</td>
<td>510.68</td>
<td>2</td>
<td>3526.48</td>
<td>0.048</td>
<td>2.35(7)</td>
</tr>
<tr>
<td>33559.34</td>
<td>4</td>
<td>5087.30</td>
<td>3</td>
<td>3792.14</td>
<td>0.019</td>
<td>1.48(7)</td>
</tr>
<tr>
<td>36125.16</td>
<td>1</td>
<td>4186.11</td>
<td>2</td>
<td>3130.06</td>
<td>0.013</td>
<td>9.38(6)</td>
</tr>
<tr>
<td>36220.45</td>
<td>3</td>
<td>510.68</td>
<td>2</td>
<td>3122.57</td>
<td>0.112</td>
<td>1.88(7)</td>
</tr>
<tr>
<td>36294.87</td>
<td>2</td>
<td>4186.11</td>
<td>2</td>
<td>3130.06</td>
<td>0.581</td>
<td>7.26(8)</td>
</tr>
</tbody>
</table>

$\tau$ = 6.9 ± 0.3 ns

$\tau$ = 8.2 ± 0.5 ns

$\tau$ = 7.7 ± 0.4 ns

$\tau$ = 10.1 ± 0.6 ns

$\tau$ = 10.2 ± 0.5 ns

$\tau$ = 4.0 ± 0.3 ns

$\tau$ = 4.2 ± 0.3 ns

$\tau$ = 4.0 ± 0.3 ns

Zr\textsuperscript{1} lifetime of 7.0 ns in perfect agreement with the previous measurements.

5 CONCLUSIONS

In this work, radiative lifetimes are reported for 17 levels belonging to the odd 4d\textsuperscript{5}s\textsuperscript{5}p, 4d\textsuperscript{5}s\textsuperscript{5}p and 4d\textsuperscript{5}p electronic configurations in Zr\textsuperscript{1}. For the three levels measured before, we obtain consistent results whereas for 14 of the investigated levels the results are obtained for the first time. The new measurements have been compared with (HFR + CP) calculations. For most of the levels, there is good agreement between theory and experiment. The uncertainties in the experimental lifetimes are between 4 and 10 per cent.

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