Chapter 1
Recent Investigations of Radiative Lifetimes and Transition Probabilities in Heavy Elements ($37 \le Z \le 92$)

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Abstract We present a review of the progress realized regarding the radiative properties (transition probabilities, lifetimes, branching fractions) of the heavy atoms and ions ($Z \ge 37$) of the fifth and sixth rows of the periodic table and of the lanthanides. In all cases, the discussion is limited to the first three ionization stages. The present review is motivated by the recent developments in astrophysics, laser physics or plasma physics. Further progress in the domain considered here is essentially hindered by the poor knowledge of the atomic spectra particularly concerning the energy levels.

1.1 Introduction

There is a growing interest in atomic data of heavy ions in different fields of physics including plasma diagnostics in fusion research, absorption spectroscopy in environmental studies, and investigations of the chemical composition of astrophysical objects. As part of an on-going effort to meet this demand, we report, in the present paper, on the progress realized during the past few years concerning the radiative parameters determination of three groups of heavy elements: the fifth and the sixth rows of the Mendeleev table and also the lanthanides ions (LI).

In order to clarify the relative importance of the **r**- and **s**-processes for the production of heavy elements in the Galaxy, the astrophysicists need accurate atomic data (transition probabilities, oscillator strengths, radiative lifetimes, branching fractions (BF), hyperfine structure constants, ...) particularly for the heavy elements belonging to the sixth row ($55 \le Z \le 86$) of the Mendeleev table. In astrophysics, radiative data are strongly needed for transitions originating from the ground level or from low-excitation levels which are predominantly populated in cold stars. There is also an increasing demand for weaker high-excitation lines currently identified on the high-resolution astrophysical spectra now available. In addition, opacity calculations require data for a huge number of lines emitted in all the spectral ranges.

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An element like tungsten, which is important for thermonuclear fusion research because it is used as a plasma facing material in Tokamak devices, belongs also to this group. Due to its high melting point and thermal conductivity, and its low tritium retention and erosion rate under plasma loading, tungsten is indeed a very attractive element for Tokamaks. The International Thermonuclear Experimental Reactor (ITER), which will be the next step toward the realization of fusion, will use tungsten, together with beryllium and carbon-fiber reinforced composites, as plasma facing materials. Atomic data for tungsten ions are therefore urgently needed.

The heavy refractory elements of the fifth row, frequently difficult to produce in the laboratory, require also further investigations, many gaps subsisting concerning the available atomic data. As an example, ruthenium plays an important role in stellar nucleosynthesis. When the stars are in the ‘asymptotic giant branch (AGB)’ phase, they experience thermal pulses, generating a rich nucleosynthesis by the **s**-process. The convective envelope of the star may penetrate the region where **s**-process elements have been produced, and may bring them to the stellar surface, where they become observable. A few **s**-process elements are particularly interesting with that respect because they provide information on the time-scales involved in the process and ruthenium is among these elements.

The investigation of the atomic structure of the lanthanide ions is often prevented by the complexity of the configurations concerned involving an open 4f-shell, by the high density of low-energy levels and, consequently, by the huge number of transitions generally appearing in the visible spectral range. Their knowledge however is vital and strongly needed in astrophysics in relation with the problematics of stellar abundance determination, cosmochronology and nucleosynthesis, these elements appearing generally overabundant in chemically peculiar (CP) stars. Outside astrophysics, the lighting-research community is interested in LI, the rare-earths salts being used in many commercial metal-halide high-intensity discharge lamps.

In astrophysics, strong magnetic fields have been detected in hot stars (e.g. O, A and B types). Detailed investigations of these fields require the knowledge of accurate Landé g-factors. Many of these g-factors are unknown or inadequately known, particularly for the heavy elements or ions of the periodic table. Available data for many levels (even of low excitation energy) are still lacking or, when they exist, their accuracy frequently suffers from the limitations of the “old” laboratory analyses.

Due to their complexity, but also to their low cosmic abundances, most of the heavy elements have generally attracted less interest of the spectroscopists during the last decades but the analysis of a large number of high-resolution astrophysical spectra, obtained in recent years from the ground or from space (e.g. with the Hubble Space Telescope), has modified somewhat the situation and has stimulated further theoretical and laboratory investigations of these ions.

For these reasons, we present here an update of the results obtained concerning the radiative properties (oscillator strengths, A-values, lifetimes, BFs, Landé factors, ...) of the three groups of elements just mentioned (more precisely, the first three ionization stages only have been considered). The present paper is an update of recent reviews on similar topics [5–7].

1.2 Experimental Techniques

1.2.1 Measurement of Lifetimes for Metastable States Using Heavy Ion Storage Rings

The optical observation, at a heavy-ion storage ring, of the light emitted from metastable levels of singly ionized elements allows atomic lifetime measurements in the millisecond up to the second range. We briefly consider here some lifetime measurements performed at the Stockholm heavy-ion storage ring (the CRYRING), a sophisticated experimental device which was operated by the Manne Siegbahn Laboratory (MSL) up to 2009 and which is updated by the DESIREE (Double ElectroStatic Ion Ring ExpEriment) device. This work has been done in collaboration with Prof. S. Mannervik and his team at Stockholm University. The measurements made at CRYRING have been extensively discussed in a review paper [63] and the details will not be repeated here. This technique was interesting because it did allow, with an accuracy reaching typically 1 % or so, the measurement of long lifetimes (up to several tens of seconds) of low-lying metastable states frequently important in astrophysics. In addition, these long lifetimes, very sensitive to small configuration interaction (CI) effects, provided the opportunity to test the theoretical models used in atomic structure calculations for heavy elements or ions.

Among the difficulties encountered when using this technique (for a discussion, see e.g. Refs. [54, 62]), let us mention, besides the technical difficulties associated with a very sophisticated experimental device, that only a limited number of levels were accessible through time-consuming measurements and also the fact that some corrections, like those associated with repopulation effects, needed to be carefully taken into account. During the measurements, there was a possibility of laser probing of the populations [64]. In this approach, an allowed transition was induced from the metastable level to an upper level. This upper level, whose lifetime reached generally a few ns, was decaying back to a metastable or another low-lying level, the intensity of the fluorescence decay being proportional to the population of the metastable state.

In the framework of a well-established collaboration between Stockholm, Liège and Mons universities, the CRYRING measurements have been applied with success to Sr II [12], Xe II [93] (fifth group), Ba II [43] (sixth group), La II [29] and Nd II [20] (LI). When the comparison was possible, an excellent agreement theory-experiment was observed.

The investigation of the radiative decay of the metastable level 5d $^4D_{7/2}$ in Xe^+ has appeared particularly interesting [93]. Lifetime measurements of this level in a storage ring are difficult since magnetic mixing of the metastable with a short-lived level quenches its population. Theoretically, we found that the decay is heavily dominated by an M2 transition and not by M1/E2 transitions (as usually expected). Decay rates were determined at different magnetic field strengths B in order to allow a nonlinear extrapolation to $B = 0$ and the experimental measurement ($\tau = 2.4 \pm 0.8$ s) was found in agreement with the calculated MCDF value (2.32 s), but much smaller than previous estimations.

A similar effect was found in Kr II [13] where the radiative lifetime of the metastable $4s^24p^4(^3P)4d\ ^4D_{7/2}$ level shows also an unusual situation regarding the importance of an M2 depopulation channel. While the first order M1 and E2 channels were expected to contribute in a dominant way to the decay, the experimental result ($\tau = 0.57\ \pm 0.03$ s) was far too short to be due to these channels and, only if second order contributions to the decay branches (including essentially the M2 contribution), were taken into account in the calculations, could the unexpected short lifetime be explained.

For the discussion, let us mention that in the lighter homologous Ar^+ (not belonging to the groups of elements considered in the present paper), a laser probing investigation of the $3s^23p^4(^1D)3d\ ^2G_{7/2,9/2}$ metastable doublet states [58, 92] has allowed us to establish the unexpected and extraordinary strong contribution of an electric octupole (E3) transition to the ground state, in addition to the M1 decay channels to the 3d $^{2,4}F$ states and the E2 contributions to the 4s ^2P, ^2D states. It is interesting to mention that a similar effect (unexpected importance of an E3 contribution) was neither found in Kr II nor in Xe II.

1.2.2 Allowed Transitions Investigated with Laser-Induced Fluorescence Spectroscopy

A second technique, widely used for lifetime measurements in heavy ions, is the time-resolved laser-induced fluorescence (TR-LIF) spectroscopy. For the description of the method, see e.g. the numerous references quoted in [5–7]. The lifetime of an excited atomic state i, τ_i, can be measured by observing the fluorescence decay from this level using the following formula:

$$I(t) = I(0)e^{-\frac{t}{\tau_i}} \tag{1.1}$$

where $I(0)$ is the initial intensity and $I(t)$ the intensity at time t.

A very direct way of investigating atomic lifetimes is to use short-pulse laser excitation and subsequent fast time-resolved detection of the fluorescence light emitted. This technique has been described in many papers (see e.g. [5, 7]) and, consequently, only the essential characteristics will be recalled here. Slight modifications and adaptation of the basic technique were needed for experiments according to the ions considered. The experimental results discussed in the present paper have been obtained at the Lund Laser Centre (LLC) in Sweden (in the framework of collaborations with Prof. S. Svanberg and his group) and at the Jilin University at Changchun (China) (in coll. with Prof. Z.K. Jiang and Prof. Z.W. Dai and their collaborators).

A laser-produced plasma is used as an ion source. This plasma is obtained by focusing, on a solid target placed in a vacuum chamber, the green beam of a Continuum Surelite Nd:YAG laser, which has a pulse duration of 10 ns and an energy of about 5–10 mJ. A small plume of plasma is produced after each pulse. The expanding plasma is crossed by an excitation beam at about 1–2 cm above the target.

The delay between the plasma production and the excitation pulse can be varied by externally triggering the lasers used in the experiment with a digital delay generator. The plasma density and temperature in the observed region can be adjusted by changing the plasma production laser pulse energy, the size of the focus point, the distance above the target surface, and the delay times between the ablation and excitation pulses. Three types of laser excitation have been considered in our work, i.e. one-step excitation, two-step excitation and two-photon excitation. A detailed description can be found, for example, in the papers quoted in Refs. [5–7] and in the Tables 1.1 and 1.3.

In relation with the main characteristics of the TR-LIF technique, the following points must be underlined:

- Many levels are accessible in a selective way by using different excitation schemes and different dye lasers.
- The method has appeared efficient and useful for investigating many neutral, singly ionized and doubly ionized heavy elements. We were able to produce also trebly ionized atoms but only in the case of cerium.
- The lifetimes accessible, with an accuracy of typically a few percent, are ranging roughly from 1 ns to several hundreds of nanoseconds.

In order to get the relevant transition probabilities or oscillator strengths, the experimental lifetimes, however, must be combined with BF measurements (using e.g. the FTS method) or calculations (adopting e.g. the HFR or MCDF approaches: see Sect. 1.3).

The TR-LIF method, combined with BF determination, has been extensively used in many atoms and ions of the fifth and sixth periods and of the lanthanide group. The results are discussed in the following sections.

1.2.3 Study of Intermediate Charges with the Beam-Foil Spectroscopy

The beam-foil spectroscopy (BFS) was one of the rare methods allowing the investigation of the atomic structure of moderately charged ions. The experimental device of Liège University was used for that purpose. The experimental details can be found in the relevant publications (see e.g. [21]) and, consequently, we just recall here the main characteristics of this method.

A beam of ions was produced by a Van de Graaff accelerator equipped with a conventional radio-frequency source. The beam was analyzed by a magnet and focused inside a target chamber. Beams with energies up to 2 MeV could be produced. Inside the chamber, the beam was excited and ionized by passing through a very thin (about 20 μg/cm^2) carbon foil. Just after the foil, the light, emitted by the excited ions, was observed at right angle by a Seya-Namioka-type spectrometer equipped with an $R = 1$ m concave 1 200 l/inch grating blazed for normal incidence at 110.0 nm. The entrance slit of the spectrometer had a width of 120 μm and was situated at 15 mm from the axis of the 10 mm diameter ion beam.

The light was detected by a thin, back-illuminated, liquid nitrogen cooled CCD detector specially developed for far UV measurements. The CCD worked under vacuum and was cooled down by liquid nitrogen to −90 °C for noise reduction. The CCD, which replaces the exit slit of the spectrometer, was tilted to an angle of 125° relatively to the spectrometer exit arm axis in order to be tangential to the Rowland circle. Under that geometry, it has a dispersion of 0.02 nm/pixel and detects light over a 20 nm wide region with a fairly constant resolution giving a line width (FWHM) of about 0.12 nm. The whole system was working under vacuum (10^{-5} Torr). The CCD images were transferred to a networked computer and analyzed by a specially written software.

A problem affecting the beam-foil spectra is the rather low spectral resolution just mentioned. At that resolution, we find many lines blended. In addition, beam-foil excitation is non-selective; this results in the production of a range of ion charge states (the spectra of neighboring ions often overlap each other) and in the excitation of a plethora of individually weak spectral lines that arise from the multitude of excited levels. The use of a CCD camera represents a major improvement over spectral scanning techniques and assures both better data accumulation (counting statistics) and constancy of conditions across a selected spectral range.

We have investigated with the BFS the spectrum emitted by the trebly ionized lanthanum (La^{3+}) [21]. This work has emphasized the difficulties inherent to the investigation of the fourth spectrum of the rare-earths which could eventually be observed in some hot stars. Some xenon ions (Xe V, VI, VII and VIII) have also been studied using the BFS technique combined with relevant calculations [15, 17, 19, 39, 40].

1.3 Theoretical Approaches

1.3.1 General Characteristics

In the lanthanides, strong configuration interactions are expected to occur between the low-lying configurations for the first ionization stages along the isoelectronic sequences. A second characteristic of the LI is the sudden collapse of the 4f orbital occurring at lanthanum. This collapse is enhanced when the number of 4f electrons is increasing. These considerations and the fact that a huge number of levels arise from the $4f^N$ configurations make the analysis of the lanthanide spectra extremely difficult and time consuming.

The radiative properties of the LI have been rather little investigated in the past in relation with these complex electronic structures (unfilled 4f shell) and the fact that the laboratory analyses are still extremely fragmentary or even missing for many ions. Low motivation resulted also from the rather small cosmic abundances of these elements in astrophysics compared, e.g., to the high abundances of the iron-group elements.

Theoretical investigations of the elements or ions of the fifth and six rows of the periodic table are also extremely demanding having in mind the strong constraint resulting from the simultaneous consideration, in the calculations, of both configuration interaction and relativistic effects.

1.3.2 The Relativistic Hartree-Fock Method

For heavy systems, accurate calculations of atomic structures require that both intravalence and core-valence correlation are considered in a detailed way. Simultaneous treatment of both types of effects, within a CI scheme, is very complex and reliable only if extensive configuration mixing is considered. However, in practice, the number of interacting configurations that can be introduced in Cowan's codes [27] is severely limited by the computer capabilities. In particular, the inclusion of core-polarization (CPOL) effects through the consideration of a huge number of configurations with open inner shells is essentially prevented by computational reasons. As the CPOL effects are expected to be important in lowly charged heavy atoms, an approach in which most of the intravalence correlation is represented within a CI scheme while core-valence correlation for systems with more than one valence electron is described by a CPOL model potential with a core penetration corrective term can be considered as an alternative. This approach was suggested by Migdalek and Baylis [66] and adopted in our calculations.

Cowan's suite of computer codes [27], based on the HFR approximation, was modified accordingly (see e.g. [5, 81]). This approach, although based on the Schrödinger equation, does include the most important relativistic effects such as the mass-velocity corrections and the Darwin contribution.

For an atom with n valence electrons, the one-particle operator of the potential can be expressed as:

$$V_{P1} = -\frac{1}{2}\alpha_d \sum_{i=1}^{n} \frac{r_i^2}{(r_i^2 + r_c^2)^3} \tag{1.2}$$

where α_d is the static dipole polarizability of the ionic core for which numerical values are available in the literature [38] and r_c a cut-off radius corresponding to the HFR expectation value of $\langle r \rangle$ for the outermost core orbital of a given ion. Additional corrections, which include the core-penetration effects [44, 45], were considered as described in Ref. [5].

The HFR + CPOL method has appeared successful and efficient for describing the atomic structure of many heavy atoms and ions. In particular, the theoretical lifetime values agree, in most cases, within a few (generally <20) percent with the experimental results as they were measured with the TR-LIF method. Larger discrepancies were observed however for a number of weak transitions (but in this case, the experimental results are also generally less accurate!). Some care must be exercised when the transitions are affected by substantial cancellation effects in the calculation of the line strengths [27]. As the experiment allows generally to obtain

BFs for a rather limited number of transitions, the above theoretical methodology has allowed to extend the BF determination to many transitions of astrophysical interest.

1.3.3 The Multiconfigurational Dirac-Fock Method

In some specific ions (for more details, see the publication lists given in the Tables 1.1 and 1.3), a fully relativistic technique i.e. the multiconfigurational Dirac-Fock (MCDF) method was used [42, 78]. This approach, which includes relativity in a more detailed way because it is based on a fully relativistic scheme, should a priori be more accurate than the HFR + CPOL approximation for heavy ions but this approach, however, was generally found less flexible. In addition, it consumes more computer time and its use is frequently hindered by difficult convergence problems. This is why, for most ions, the HFR + CPOL method was generally prioritized.

The list of specific ions, which were considered in the framework of the MCDF approach, includes Tc II [75], Sb I [47], Bi II [72], Pb II and Bi III [83]. Some lowly charged tungsten ions (i.e. W IV, V, VI) were also investigated with the MCDF approach.

1.4 The Results

1.4.1 The Fifth Row of the Periodic Table

The fifth row of the periodic table includes the elements Rb ($Z = 37$) up to Xe ($Z = 54$). We report, in Table 1.1, a summary of the results obtained so far along this group. 206 lifetimes have been measured by TR-LIF spectroscopy at the LLC (Sweden) or at the University of Jilin (China). For some ions (see the starred m-values in Table 1.1), only theoretical results (HFR + CPOL) have been obtained. The configurations involved are given in column 4 and the number of transitions (N), for which transition probabilities have been determined, appear in column 5. In most cases, only the strongest transitions, depopulating the levels for which the lifetimes have been measured, are given in the different publications where the details about the experiments and about the calculations can also be found (see the last column of Table 1.1).

Some short comments about the different ions are relevant here.

In Y II, the overall quality of the HFR + CPOL calculations has been assessed by comparisons with new and previous lifetime measurements. New measurements are concerning 5 levels of the lifetime 4d5p and 5s5p configurations in the energy range 32 048–44 569 cm^{-1}. A similar theoretical model applied to Y III leaded to results in good agreement with new laser measurements for two 5p levels [23].

Table 1.1 Fifth-row elements: number of measured lifetimes (m), configurations involved, number of depopulating transitions (N) and the corresponding references

Z	Ion	m	Conf.	N	Ref.
39	Y II	5	4d5p, 5s5p	84	[23]
	Y III	2	5p	182	[23]
40	Zr I	17	$4d^25s5p$, $4d^35p$, $4d5s^25p$	78	[61]
	Zr II	16	$4d^25p$	242	[59]
41	Nb II	17	$4d^35p$	107	[71]
	Nb III	20^*	$4d^25p$	76	[71]
42	Mo II	16	$4d^45p$	110	[57]
43	Tc II	6^*	$4d^55p$	20	[75]
44	Ru I	10	$4d^75p$, $4d^65s5p$, $4d^76p$	163	[37]
	Ru II	23	$4d^65p$	178	[77]
	Ru III	6^*	$4d^55p$	25	[77]
45	Rh II	17	$4d^75p$	113	[87]
46	Pd I	6	$4d^95p$	20	[100]
47	Ag II	–	$4d^95d$	7	[14]
		12^*	$4d^85s^2$, $4d^96s$, $4d^95d$	65	[25]
48	Cd I	11	5s5p, 5snd ($n=6$–9), 5sns ($n=7, 8$)	102	[99]
	Cd II	5	$4d^{10}5p$, $4d^{10}6s$, $4d^{10}5d$	10	[99]
50	Sn I	40	5pnp ($n=10$–13, 15–19, 27, 31, 32)		[107]
			5pnf ($n=4, 5, 9$–19, 22, 23), 5p8p		[107]
	Sn I	9	5p7p		[106]
51	Sb I	12	$5p^26s$, $5p^25d$	55	[47]
Total		$206+44^*$		1637	

In Zr I, for three levels, we confirm previous measurements while, for 14 other levels, the lifetimes have been measured for the first time [61]. In Zr II, for 12 levels, there were no previous results available [59].

We used the TR-LIF technique to measure 17 radiative lifetimes in Nb II [71] while BFs were measured from spectra recorded using FTS. In addition, transition probabilities (76 transitions in the range 143.0–314.0 nm) were calculated, for the first time, in Nb III using a HFR + CPOL method. The derived solar photospheric niobium abundance, $A_{\rm Nb} = 1.44 \pm 0.06$ (logarithmic scale), was found in agreement with the meteoritic value. The stellar Nb/Eu abundance ratio determined using synthetic spectra, including hyperfine broadening of the lines, for five metal-poor stars confirms that the **r**-process is a dominant production method for the n-capture elements in these stars.

The lifetimes measured by Hannaford and Lowe [46] in Mo II concern levels with energies in the range 45 800–50 700 cm^{-1}. Lifetimes for higher energy levels are missing although transitions from these levels are likely to be observed in astrophysics or in plasma physics. Consequently, we have reported lifetime measurements for levels with higher energies, i.e. in the range 48 000–61 000 cm^{-1} [57].

In astrophysics, technetium is an **s**-process element with no stable isotope. Consequently, no experimental transition probabilities or lifetimes are available for this atom. Using three independent theoretical approaches (CA, HFR + CPOL, AUTOSTRUCTURE), oscillator strengths have been calculated for a set of Tc II transitions of astrophysical interest and the reliability of their absolute scale has been assessed [75]. The examination of the spectra emitted by some Ap stars has allowed the identification of Tc II transitions in HD 125 248. This Tc II detection should however await confirmation from spectral synthesis relying on dedicated model atmospheres.

In 1984, the solar photospheric abundance of ruthenium was determined [9] from 9 lines of Ru I using a one-dimensional (1D) model [48]. The result, $A_{\mathrm{Ru}} = 1.84 \pm 0.10$, differed from the meteoritic result ($A_{\mathrm{Ru}} = 1.76 \pm 0.03$) by 0.08 dex. The BFs were derived from arc measurements [26] affected by large systematic errors. New f values have been obtained for Ru I from LLC measurements (10 new lifetimes) [37] in the range 225.0–471.0 nm. A recent 3D model proposed by Asplund *et al.* [3] was used for the calculations. The new abundance value is now: $A_{\mathrm{Ru}} = 1.72 \pm 0.12$ which is very close to the meteoritic result. The f values obtained for Ru II show that the lines of this ion are too weak to be observed in the photospheric spectrum [37, 77].

In singly ionized rhodium, no radiative data have been published so far in the literature despite the fact that several Rh II lines have been identified in different astrophysical spectra such as the solar spectrum [68] and the spectra of the HgMn type star χ Lupi [56], the super-rich mercury star HD 65 949, the HgMn star HD 175 640 and the peculiar Przybylski's star HD 101 065 [28]. For that reason, 17 radiative lifetimes of Rh II have been measured with the TR-LIF technique and combined with theoretical BFs (HFR + CPOL model) in order to deduce new oscillator strengths for a set of 113 Rh II transitions in the spectral range 153.0–417.6 nm [87].

Similar motivations, in particular the need of oscillator strengths for investigating the chemical composition of CP stars, for the modeling of stellar atmospheres and for the understanding of the buildup of the elements in nucleosynthesis, was a strong motivation to undertake new lifetime measurements and BF determination in Pd I [100], Sb I [47], Cd I and Cd II [99].

Radiative parameters have been obtained by laser-produced plasma and TR spectroscopy for transitions depopulating the levels belonging to the $4d^8 5s^2$, $4d^9 6s$ and $4d^9 5d$ configurations of Ag II [14, 25]. The light emitted by the plasma was analyzed by a grating monochromator coupled with a time-resolved optical multichannel analyzer system. Spectral response calibration of the experimental system was performed using a deuterium lamp in the wavelength range from 200 to 400 nm, and a standard tungsten lamp in the range from 350 to 600 nm. The transition probabilities were obtained from measured BFs and theoretical radiative lifetimes.

The interstellar gas-phase abundance of tin appears to be enriched with respect to that of the Sun [97]. In the stars, tin isotopes are produced by the p-, **s**- and **r**-processes and some transitions of Sn I have been identified in the photospheric solar

Table 1.2 Investigated xenon ions

Z	Ion	Conf.	Ref.
54	Xe II	5d	[29]
	Xe V	$5s5p^3$, $5s^25p5d$, $5s^25p6s$, $5s^25p^2$, $5s^25p6p$, $5s^25p4f$	[17]
	Xe VI	$5s^2nl$ (np, nf, nh, nk; $n \leq 8$), $5p^3$, $5s^2nl$ (ns, nd, ng, ni; $n \leq 8$), $5s5p^2$	[15]
	Xe VII	5s5p, $5p^2$, 5s5d, 5s6s, 5p5d, 4f5p, 5p5d, 5s5f	[19]
	Xe VIII	5p, 5d	[19]
	Xe IX	$4d^96p$, $4d^94f$, $4d^95f$	[39, 40]

spectrum and in the spectra of some CP hot stars [1]. In recent years, with the increasing demand for an experimental realization of quantum logic devices, potential interest for new or improved lasers and other optical devices, the interest in accurate information on high Rydberg states of Sn I has also rapidly increased [55, 91]. For these reasons, using the TR-LIF technique in a Sn atomic beam, 40 natural radiative lifetimes have been measured for even-parity 5pnp ($J = 1, 2$) and 5pnf levels along the Rydberg series and for all the 5p8p perturbing states with energies in the range 52 263.8–59 099.9 cm^{-1} [107]. A two-step laser excitation scheme was used in the experiment. Through an analysis of the energy levels structure by the multichannel quantum defect theory (MQDT), the channel admixture coefficients have been obtained and used to fit the theoretical lifetimes to the experimental ones in order to predict new values for the levels not measured. A generally good overall agreement between experimental and theoretical MQDT and HFR lifetimes has been achieved except for a few levels. Landé g-factors have been measured by the same method and also by the Zeeman quantum-beat technique for most of these even-parity levels [102]. Lifetimes for 9 levels and Landé g_J factors for eight levels of the 5p7p configuration have also been obtained by the same techniques. The results obtained were compared with HFR + CPOL results [106].

We summarize in Table 1.2 the results obtained so far for some xenon ions (Xe II, Xe V, Xe VI, Xe VII, Xe VIII and Xe IV).

1.4.2 The Sixth Row of the Periodic Table

The results obtained for the sixth row of the periodic table, i.e. for the elements Cs ($Z = 55$) up to Rn ($Z = 86$), are presented in Table 1.3. The presentation is similar to that of Table 1.1. Up to now, 167 lifetimes have been measured by TR-LIF spectroscopy for these atoms or ions. For the starred values in Table 1.3, only theoretical results (HFR + CPOL) have been obtained. In most cases, only the strongest transitions depopulating the levels for which the lifetimes have been measured are given in the different publications. The following comments are relevant here.

Hafnium ($Z = 72$) has been observed in the spectra of some stars like the barium star HD 202 109 [104], Sirius A [103] and the photosphere of δ Scuti [104]. Hafnium

Table 1.3 Sixth-row elements: number of measured lifetimes (m), configurations involved, number of the depopulating transitions (N) and the corresponding references

Z	Ion	m	Conf.	N	Ref.
72	Hf I	2	$5d6s^26p$	–	[60]
	Hf III	9	5d6p	55	[60]
73	Ta I	14	$5d^36s6p$, $5d^46p$	23	[32]
	Ta II	3	$5d^36p$	100	[85]
	Ta III	6	$5d^26p$	206	[36]
74	W I	141*		143	[76]
	W II	9	$5d^36s6p$, $5d^46p$	6 265	[70]
	W III	2	$5d^36p$	4 826	[88]
75	Re I	11	$5d^46s^26p$, $5d^56s6p$	81	[74]
	Re II	7	$(5d + 6s)^56p$	45	[73]
76	Os I	12	$5d^66s6p$, $5d^76p$	129	[82]
	Os II	9	$5d^56s6p$, $5d^66p$	137	[82]
77	Ir I	9	$5d^76s6p$	206	[101]
	Ir II	4	$5d^76p$	223	[101]
78	Pt II	8	$5d^86p$	164	[84]
79	Au I	3	$5d^96s6p$	6	[33]
	Au II	1	$5d^96p$	63	[33]
	Au II	22*	$5d^97s$, $5d^96d$	114	[18]
	Au III	60*	$5d^86p$, $5d^76s6p$	146	[30]
80	Hg I	10	$6sns$ ($n = 7$–10), $6snd$ ($n = 6$–11)	–	[24]
81	Tl I	15	$6s^2ns$ ($n = 7$–14), $6s^2nd$ ($n = 6$–12)	48	[16]
82	Pb I	29	$6pns$ ($n = 7$–13), $6pnd$ ($n = 6$–13)	–	[53]
	Pb I	3	6p7s	136	[11]
	Pb II	1	7s	2	[83]
83	Bi II	42*	$6pnp$ ($n = 7$–8), $6pnf$ ($n = 5, 6$), $6s6p^3$, $6pns$ ($n = 7$), $6pnd$ ($n = 6$)	43	[72]
	Bi III	–	7s	2	[83]
Total		167 + 265*		13 163	

is also a possible chronometer for stellar and galactic evolution [79]. In astrophysics, radiative data are needed for transitions originating from the ground term or from low excitation levels which are mostly populated in cold stars. This has motivated an investigation of hafnium atoms and ions [60]. Radiative lifetimes of nine odd levels in Hf III and of two odd levels in Hf I have been measured for the first time by laser spectroscopy and transition probabilities have been deduced for 55 transitions of Hf III.

During the past few years, there have been several analyses of the atomic structure of neutral tantalum (Ta I), an element with "moderate" complexity, the ground configuration being $5d^3 6s^2$, but little has been done concerning the transition probability determination while there is an obvious need in astrophysics [52, 95], the photospheric abundance of tantalum being still unknown [2]. Radiative lifetimes of 14 odd-parity Ta I levels, in the energy range 30 664–45 256 cm^{-1}, have been measured [32] and new transition probabilities deduced for a set of strong lines depopulating the levels investigated experimentally.

Singly ionized tantalum, Ta II, has been looked for but not detected in the χ Lupi CP star [31]. The richness and complexity of the Ta II spectrum impose severe limitations in the determination of absolute transition probabilities which is affected by the fragmentary knowledge of the atomic structure of this ion even for low-lying configurations. 3 new lifetimes have been obtained experimentally in Ta II and compared with the calculated results obtained for the low-lying levels ($E < 44\,000$ cm^{-1}) [85].

Ta III suffers from the lack of accurate theoretical and experimental f-values or lifetimes, the only set of transition probabilities available in this ion being that reported by Azarov *et al.* [4]. We have realized the first lifetime measurements for six odd-parity levels belonging to the $5d^2 6p$ configuration. Weighted transition probabilities (gA values) have also been obtained for the strong lines depopulating the investigated levels [36].

Radiative data of tungsten ions are important in plasma physics. With its low yield and high threshold for sputtering [69], tungsten is widely used in fusion reactors as a divertor target. Tungsten is also important in astrophysics, neutral tungsten being identified in Ap stars (see e.g. [51]). More recently, W I lines have been detected and investigated in the spectrum of HD 221 170 (see e.g. [105]). The dominant species, except in cool stars, is in fact expected to be W II, the line of singly ionized tungsten at 203 nm having been observed in the UV spectrum of one Am star [90]. Some lifetime measurements are available in W II but radiative data are still lacking for many transitions. Till now, doubly ionized tungsten (W III) has not been identified in hot stars. In W III, the only work available is that of Schultz-Johanning *et al.* [94]. In our work, an extensive set of oscillator strengths has been calculated for W II [70] and W III [88] which represents a considerable extension of the available data, the accuracy of the new results being assessed through comparisons with the TR-LIF measurements performed for 9 levels of W II and 2 levels of W III. The uncertainty in the new oscillator strengths, not affected by cancellation effects, should not exceed 15 %. Transition probabilities for allowed and forbidden lines in W I, II and III have been discussed in two recent papers [76, 86]. For the E1 transitions, recommended values are proposed from a critical evaluation of the data available in the literature. For the M1 and E2 transitions, for which no data had been published, a new set of radiative rates has been obtained using a HFR + CPOL approach. The tables summarizing the compiled data are expected to be useful for plasma modeling in fusion reactors. An extension of these calculations to higher ionization stages (W IV, W V, W VI, W VII and W VIII) is in progress.

An investigation of Re (I and II) [73, 74] and Os (I and II) [82] ions was also carried out. For ten of the 11 odd-parity levels measured in Re I, there were no previous results available. Reliable semi-empirical transition probabilities have been deduced for 81 Re I and 45 Re II lines. For 9 levels of Os I and 4 levels of Os II, the lifetimes were measured for the first time. It was possible to deduce oscillator strengths for 129 transitions of Os I and 137 transitions of Os II appearing in the wavelength range 180.0–870.0 nm. These results have allowed us to revise the abundance of osmium in the solar photosphere ($A_{\mathrm{Os}} = 1.25 \pm 0.11$). The newly derived oscillator strengths have been applied as well to derive the osmium abundance in the carbon-rich metal-poor star HD 187 861 [82].

Metal-poor halo stars with greatly enhanced abundances of the heavy neutron-capture elements have been identified and have stimulated much interest in recent years [96]. It has been emphasized recently [49, 50] that accurate abundance values of iridium in stars is of great significance not only in radioactive cosmochronology but also for putting constraints on the structure and nucleosynthetic evolution of supernovae originating from the first stellar generation. Our work in Ir I and Ir II [101] ions has led to the results summarized in Table 1.3.

Radiative lifetimes of eight odd-parity states of Pt II, in the energy range extending from 51 408 to 64 388 cm^{-1}, have been measured by means of the TR-LIF technique [84]. Free, singly ionized platinum ions were obtained in a laser-produced plasma and a tunable laser with 1.5 ns duration pulse was used to selectively excite the Pt^+ ions. The comparison of the experimental results with HFR calculations emphasizes the importance of valence-valence correlation and of CPOL effects in this complex ion. A new set (164 transitions) of calculated transition probabilities has been reported.

In plasma physics, gold is used as an active medium in metal vapor lasers. Numerous laser transitions, in the spectral range 253–763 nm, have been observed when exciting a helium discharge in a gold-plated hollow cathode by Reid *et al.* [89]. Consequently, the determination of accurate radiative parameters of Au II excited states, including transition probabilities, is of great interest. In astrophysics, neutral and singly ionized gold (Au I, Au II) have been identified in Ap and Bp stars but, up to now, doubly ionized gold (Au^{++}) has been much less investigated than Au^+ in both laboratory and stellar spectra. The only work concerning the observation of this ion in the CP HgMn-type stars κ Cancri and χ Lupi is due to Wahlgren *et al.* [98], and is related to the analysis of the spectra obtained with the Goddard High Resolution Spectrograph onboard the HST. Our contributions regarding gold ions concern the three species [18, 30, 33] and the results are summarized in Table 1.3.

The investigations of the heavy elements with $Z \geq 80$ include contributions to the determination of transition probabilities and lifetimes in Hg I [24], Tl I [16], Pb I and Pb II [11, 53, 83], Bi II [72] and Bi III [83] (see Table 1.3). More details can be found in the relevant publications.

1.4.3 The Lanthanide Ions

Extensive discussions about lifetime and transition probability determination in LI have been presented in our previous compilations on the subject [5, 7]. In particular, the difficulties associated with both the theoretical and the experimental investigations of the elements or ions of this group have been emphasized. We limit the present discussion to the results obtained since 2005.

Presently, a firm conclusion about the presence of radioactive elements, particularly Pm, in CP stars remains an open issue that can have important implications for our understanding of the composition of these stellar objects. In a recent paper, Goriely [41] has stressed the importance of spallation nucleosynthesis compared to diffusion processes as a possible explanation of the peculiar abundances spectroscopically determined at the surface of HD 101 065. Although it remains difficult to disentangle the effect of both processes theoretically, this conclusion does not necessarily reduce the role of the diffusion processes which have proven to be of first importance to understand the atmosphere of CP stars. In this context, the first theoretical transition probabilities have been obtained for a set of 46 Pm II transitions of astrophysical interest [34]. These data fill in a gap in astrophysics and should allow to establish, on a firmer basis, the presence of some lines of this radioactive element in the spectra of CP stars and, consequently, a quantitative investigation of the stellar Pm abundance. A search for Pm II lines in Przybylski's star (HD 101 065) and in HR 465 has been reported and discussed, supporting the detection of this ion.

The spectra of moderately ionized lanthanides are of considerable interest in several fields of physics including quantum information, lighting industry, laser materials, and stellar physics. Our knowledge of these spectra is still very fragmentary. Recently, there has been a revival in the interest in trebly ionized lanthanides, and several spectral analyses have been completed on the basis of VUV high resolution observations. For these reasons, HFR and MCDF calculations of atomic structure and transition rates have been carried out in trebly ionized lanthanum (La^{3+}, $Z = 57$) [21]. The calculations had to cope with CI effects but also with the very complex situation of the collapse of the 4f wave function. The results have been compared to experimental data obtained with BFS in the extreme ultraviolet, at ion energies that favor the production of the La IV spectrum. Besides transitions known from sliding spark discharges, many more lines were observed that have not yet been identified. TR measurements yielded 3 level lifetimes in La IV that agree roughly with the results of our own calculations. This work opens the way to additional investigations of the trebly ionized elements of the lanthanide group.

1.4.4 The DESIRE and DREAM Databases

About 700 lifetimes have been measured by time-resolved laser-induced fluorescence (TR-LIF) spectroscopy for the elements Rb to Xe, Cs to Rn and for the lanthanides and, in many cases, the corresponding BFs have been calculated using a HFR + CPOL approach [5, 7]. This combination of lifetime measurements with theoretical and, when possible, experimental e.g. obtained with the Fourier Transform Spectroscopy (FTS), BF determination has led to transition probabilities for about 64 000 (lanthanides) and about 15 000 transitions (fifth and sixth rows of the periodic table). All these results are stored in two databases i.e. the DREAM database: **D**atabase on **R**are **E**arths **A**t **M**ons University [10] and the **DESIRE database**: **D**atabas**E** for the **SI**xth **R**ow **E**lements [8, 35], respectively.

The main aim of these databases is to provide the scientific community with updated spectroscopic information and radiative parameters. The database contains information about the wavelengths, oscillator strengths, transition probabilities and radiative lifetimes of neutral, singly or doubly ionized elements.

In the database, for each line in a specific spectrum, the tables show, respectively:

- The wavelength (in Å) deduced from the experimental energy levels. These wavelengths are given in air above 2 000 Å and in vacuum below that limit.
- The lower level of the transition represented by its experimental value (in cm^{-1}), its parity [(e) for even and (o) for odd] and its J-value. Level energies are taken from the NIST compilations (http://www.nist.gov/physlab/data/asd.cfm) and, when needed, from subsequent publications.
- The upper level of the transition presented in the same way as the lower level.
- The calculated oscillator strength, $\log gf$, where $g = 2J + 1$ is the statistical weight of the lower level of the transition. More details about the computational procedure are given in the different publications listed in the database.
- The calculated transition probability, gA, in s^{-1}, where $g = 2J + 1$ is the statistical weight of the upper level of the transition.
- The cancellation factor, CF, as defined by Cowan [17]. Small values of this factor (typically $CF < 0.01$) indicate transitions possibly affected by severe cancellation effects in the calculation of the line strengths.

The tables are accessible directly on the web sites http://www.umh.ac.be/~astro/dream.shtml and http://www.umh.ac.be/~astro/desire.shtml. In our compilation, the spectra are classified in order of increasing Z-values and, for a given Z, according to the ionization degree. More details about the computational procedure are also given in the different publications listed in the compilation. Only transitions for which $\log gf > -4.0$ are reported in the tables. For some ions, experimental oscillator strengths or normalized f values obtained using measured lifetimes are given. In these cases, EXPT or NORM appears in the last column of the tables.

1.4.5 The Landé Factors

In astrophysics, strong magnetic fields have been detected in hot stars of the types O, B and A. Definite spectropolarimetric detections have been reported e.g. for Ap, Be or β Cephei stars, the field strength reaching in some cases several tens of kG [65].

Detailed investigations of these magnetic fields require the knowledge of accurate Landé g-factors. Many of these g-factors are unknown or poorly known, particularly for the heavy elements of the periodic table. In the past, some experimental data have been published in the successive NIST compilations (see e.g. [67]) but data for many levels, even in the case of low excitation energy, are still lacking or, when they exist, their accuracy is frequently suffering from the limitations inherent to "old" laboratory analyses.

For these reasons, Landé g-factors have been calculated, in intermediate coupling (HFR + CPOL approach), for 2 084 levels belonging to atoms or ions of the sixth row of the periodic table [22]. The results have been refined using least-squares fittings of the Hamiltonian eigenvalues to the observed energy levels (when available). The new results fill in some gaps in the existing data for a large number of levels belonging to ions of astrophysical interest and are expected to be useful for investigating magnetic fields in CP stars. This work extends the results reported for doubly ionized lanthanides [80]. In that paper, Landé g-factors have been calculated for over 1 500 energy levels ($57 \leq Z \leq 71$) using a similar approach.

Experimental methods have also been applied and Landé g-factors have been measured by TR-LIF and Zeeman quantum-beat techniques for the even-parity levels of the $J = 1$ 5pnp ($n = 11$–13, 15–19) and $J = 2$ 5pnp ($n = 11$–13, 15–19, 31, 32), 5pnf ($n = 4$, 5, 9–19, 22, 23) Rydberg series and for all the 5p7p and 5p8p perturbing levels of neutral tin [102, 106]. A two-color two-step excitation scheme was used in the experiment. The experimental results have been compared with theoretical g-values obtained by the multichannel quantum defect theory and the HFR model, respectively. In most cases, the theoretical values agree well with the experimental results.

Many additional Landé factors have been also obtained for a number of ions not mentioned in the present section. These values can be found in the relevant papers quoted in the last column of Tables 1.1 to 1.3.

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