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Radiative Decay Rates for Electric Dipole, Magnetic Dipole and Electric Quadrupole Transitions in Triply Ionized Thulium (Tm IV)

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Abstract: A new set of radiative decay parameters (oscillator strengths, transition probabilities) for spectral lines in triply ionized thulium (Tm IV) has been obtained within the framework of the pseudo-relativistic Hartree-Fock (HFR) approach. The effects of configuration interaction and core-polarization have been investigated in detail and the quality of the results has been assessed through a comparison between different HFR physical models. The spectroscopic data listed in the present paper cover electric dipole as well as magnetic dipole and electric quadrupole transitions in a wide range of wavelengths from extreme ultraviolet to near infrared.

Keywords: atomic structure; oscillator strengths; transition probabilities; Tm IV spectrum

1. Introduction

Because of their unusual luminescent properties, triply charged lanthanide ions find many applications in different scientific and technological fields such as the lighting industry, photonics, laser physics and biotechnology, see e.g., [1–6]. If we except La^{3+}, all these ions are characterized by a ground electronic configuration of the type [Xe]4f^k with k varying from 1 (Ce^{3+}) to 14 (Lu^{3+}), which is mainly responsible for their interesting photophysical properties such as long-lived luminescence and sharp absorption and emission lines.

Until recently, their radiative properties were essentially investigated from spectroscopy experiments on ions embedded in compounds or crystal lattices. Among those ions, Tm^{3+} can be considered as being of moderate complexity with 4f^{12} as ground state configuration. Its emission spectrum has been studied in various compounds such as, for example, in thulium ethylsulphate [7,8], in CaF_2 [9], in $CaWO_4$ [10,11], in YVO_4 [12], or in $LiYF_4$ [13]. With regard to the free Tm^{3+} ion, the first spectrum analysis was published just a few years ago by Meftah et al. [14] who gave a selection of some prominent observed lines together with the corresponding transition probabilities estimated using a rather simple theoretical approach.

Let us also mention that triply ionized thulium has been proposed as being suitable for ultraprecise atomic optical clocks with naturally suppressed blackbody-radiation shift of clock transition frequency [15]. This ion has ground and long-living first excited states belonging to the 4f^{12} configuration, giving rise to electric quadrupole transitions within the optical or infrared wavelength range. Moreover, the width of the first excited state of two-hole nf^{12} configuration was estimated to be an order of magnitude smaller than that of the two-electron nf^2 first excited state with the same transition frequency making ions with nf^{12} as ground configuration, such as Tm^{3+} (n = 4), interesting candidates for providing clock transitions that have quality factors that are many orders of magnitude larger than the ones used in current atomic clocks [16].

In the present work, the radiative parameters corresponding to electric dipole, magnetic dipole and electric quadrupole transitions in Tm IV were computed using the relativistic Hartree-Fock (HFR) method including configuration interaction and core-polarization effects in different levels of approximation. These calculations are an extension of our previous investigations of triply ionized lanthanides La IV [17], Ce IV [18], Pr IV [19], Nd IV [20], and Yb IV [21].

2. Classified Lines and Term Analysis in Tm IV

Recently, the emission spectrum of thulium was observed in the spectral region 700–2320 Å and the first classification of the most important transitions of Tm IV was reported by Meftah et al. [14]. More precisely, using the 10.7 m normal-incidence vacuum ultraviolet spectrograph installed in Paris-Meudon Observatory, these authors were able to identify more than 760 lines as transitions between 157 levels of $4f^{11}5d$, 33 levels of $4f^{11}6p$, 9 levels of $4f^{11}6s$ and 10 levels of the $4f^{12}$ ground configuration in Tm IV. A parametric interpretation of the levels was carried out using the Cowan codes [22] by including $4f^{12}$, $4f^{11}6p$, $5p^54f^{13}$ and $4f^{11}5d$, $4f^{11}6s$, $5p^54f^{12}5d$ as interacting configurations in the even and odd parities, respectively. In their paper, Meftah et al. [14] mentioned that additional work on Tm IV was foreseen, notably to determine more levels with J = 2 and J = 1, as well as the lowest levels of $4f^{11}6d$ and $4f^{11}7s$ but, to our knowledge, no further investigation has been published so far.

3. Available Transition Rates

The only set of radiative data for electric dipole transitions available in the literature for Tm IV was published by Meftah et al. [14], who used the semi-empirical relativistic Hartree-Fock approach of Cowan [22] as described in the previous section. They only reported oscillator strengths for 59 transitions involving the $4f^{12}$ $^3H_6$ ground level and transition probabilities for 46 lines having $4f^{11}(^4I_{15/2})6p$ as upper configuration. Moreover, in this study, configuration interaction effects were discussed, in particular with core-excited configurations $5p^54f^{13}$ and $5p^54f^{12}5d$ which were shown to significantly reduce the oscillator strengths corresponding to $4f^{12}$–$4f^{11}5d$ transitions.

Using a detailed free ion Hamiltonian, including electrostatic and spin-orbit terms, as well as two-body, three-body, spin-spin, spin-other-orbit, and electrostatically correlated spin-orbit interactions, Dodson and Zia [23] calculated magnetic dipole and electric quadrupole lines and corresponding oscillator strengths within the ground configurations $4f^k$ throughout the full trivalent lanthanide series, including Tm IV.

4. Computational Method Used

The computational procedure used in the present work for modelling the atomic structure and calculating the radiative parameters in Tm IV is the pseudo-relativistic Hartree-Fock (HFR) method, originally introduced by Cowan [22]. In this approach, a set of orbitals are obtained for each electronic configuration included in the model by solving the Hartree-Fock equations for the spherically averaged atom. The equations are the result of the application of the variational principle to the configuration average energies. Two different physical models were employed in the calculations.

In the first model (A), we used the same approach as the one considered previously for the analysis of the isoelectronic ion Er III [24]. More precisely, the configuration sets explicitly retained for the computations were $4f^{12}$, $4f^{11}6p$, $4f^{11}7p$, $4f^{11}5f$, $4f^{11}6f$ for the even parity, and $4f^{11}6s$, $4f^{11}7s$, $4f^{11}5d$, $4f^{11}6d$, $4f^{11}7d$ for the odd parity. The core-valence interactions were included by means of a core-polarization pseudo-potential and a correction to the dipole operator according to the procedure described in many of our previous papers (see e.g., [25–27]). As a reminder, for atomic systems with n valence electrons, this core-polarization potential gives rise to the following one-particle, V_{P1}, and two-particle, V_{P2}, contributions:

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

$$V_{P2} = -\alpha_d \sum_{i>j} \frac{\vec{r}_i \cdot \vec{r}_j}{[(r_i^2 + r_c^2)(r_j^2 + r_c^2)]^{3/2}} \tag{2}$$

In addition, the usual dipole radial integral

$$\int_0^\infty P_{nl}(r)\, r\, P_{n'l'}(r)\, dr \tag{3}$$

has to be replaced by

$$\int_0^\infty P_{nl}(r)\, r \left[1 - \frac{\alpha_d}{(r^2 + r_c^2)^{3/2}}\right] P_{n'l'}(r)\, dr - \frac{\alpha_d}{r_c^3} \int_0^{r_c} P_{nl}(r)\, r\, P_{n'l'}(r)\, dr \tag{4}$$

The core-polarization parameters used in this approach were the dipole polarizability of the Tm^{4+} ionic core as reported by Fraga et al. [28], i.e., α_d = 4.32 a_0^3, and the cut-off radius corresponding to the HFR expectation value of r for the outermost core orbital (5p), i.e., r_c = 1.37 a_0, a_0 being the Bohr radius. However, as in the case of our previous analysis related to Er III, such core-polarization corrections were not considered in the atomic orbital calculation of the ground configuration $4f^{12}$. The 4f electrons being indeed located deep inside the Xe-like $5s^25p^6$ ionic core, the analytical polarization corrections to the dipole operator as introduced in our model [25–27] are no longer valid for transitions involving these electrons. As an alternative, the uncorrected <4f | r | 5d> radial matrix element corresponding to the $4f^{12}$–$4f^{11}5d$ transitions was scaled down by a factor 0.81, as we proceeded for Er III [24]. As a reminder, this technique was found to give a good agreement between the calculated radiative lifetimes and the accurate experimental values measured for $4f^{13}5d$ levels in Yb III [29] and $4f^{12}5d$ levels in Tm III [30], which can only decay by 4f–5d transitions to the $4f^{14}$ and $4f^{13}$ ground configurations, respectively.

In their observation and interpretation of the Tm IV spectrum, Meftah et al. [14] noticed a significant reduction of the resonance transition probabilities 4f–5d when the interaction $5p^64f^{11}5d$–$5p^54f^{12}5d$ was treated explicitly, this reduction appearing comparable in size to the core-polarization effects included in the close spectrum of Yb IV [21]. In order to confirm this assertion and verify it for all the transition arrays considered in the present work, i.e., $4f^{12}$–$4f^{11}5d$, $4f^{11}5d$–$4f^{11}6p$ and $4f^{11}6s$–$4f^{11}6p$, we built a second HFR physical model (B) in which the $5p^54f^{13}$, $5p^54f^{12}6p$ even-parity, and the $5p^54f^{12}5d$, $5p^54f^{12}6s$ odd-parity configurations were explicitly added to the set of interacting configurations included in model A. In this case, no additional core-polarization corrections were included.

In both models A and B, the radial energy parameters were adjusted using a well-established semi-empirical least-squares fitting procedure [22] in order to minimize the differences between computed and available experimental energy levels. More precisely, the average energies (E_{av}), the Slater integrals for direct (F^k) and exchange (G^k) electrostatic interactions, the spin-orbit integrals (ζ_{nl}), and the two-body second-order effective interaction parameters (α, β, γ) corresponding to the $4f^{12}$, $4f^{11}6p$ even- and the $4f^{11}5d$, $4f^{11}6s$ odd-parity configurations, together with the $4f^{11}5d$–$4f^{11}6s$ configuration interaction integrals (R^k), were adjusted using all the measured level energies listed in [14]. For the configurations that are not experimentally known, Slater integrals were multiplied by a scaling factor (0.85), as suggested by Cowan [22], while the spin-orbit integrals were kept at their ab initio values. The final results of the fits were found to be almost independent of the model used, the average energy deviations being very close to each other, i.e., 30 cm^{-1} (model A) and 25 cm^{-1} (model B) for the even parity, and 117 cm^{-1} (A) and 105 cm^{-1} (B) for the odd parity. We note that these values are comparable to the root mean-square deviations of 38 cm^{-1} (even levels) and 54 cm^{-1}

(odd levels) obtained by Meftah et al. [14] using a more restricted set of interacting configurations than those considered in our calculations. The differences in standard deviations, in particular in the odd parity, can be explained by the consideration of more extended multiconfiguration expansions in our models that introduce more uncertainties in our fits due to the unknown positions of additional configurations. However, the use of these more elaborate models are necessary to obtain reliable radiative transition rates, which was not the main goal of the work published by Meftah et al. [14], who were rather focused on the interpretation of the Tm IV energy level structure.

5. Electric Dipole Transitions

The oscillator strengths (log *gf*) computed in the present work using our two physical models, A and B, are compared to those reported by Meftah et al. [14] in Tables 1 and 2 for transitions involving the ground level $4f^{12}\,^3H_6$ and the $4f^{11}(^4I_{15/2})6p$ subconfiguration, respectively. In their investigation, the latter authors evaluated the importance of opening the $5p^6$ subshell on the oscillator strengths by comparing HFR calculations with and without $5p^54f^{13}$ and $5p^54f^{12}5d$ configurations. In fact, when adding these two configurations to a rather simple model including $4f^{12}$, $4f^{11}6p$ and $4f^{11}5d$, $4f^{11}6s$ in the even and odd parities, respectively, they found that the log *gf*-values corresponding to the $4f^{12}$–$4f^{11}5d$ resonance transitions were reduced by an average value of 0.18 while the $4f^{11}6s$–$4f^{11}6p$ and $4f^{11}5d$–$4f^{11}6p$ transition rates were almost unaffected. When looking at Table 1, we note that, for $4f^{12}$–$4f^{11}5d$ resonance transitions, the results obtained with our model A are in very good agreement with the oscillator strengths computed by Meftah et al. [14]; using their model including the $5p^54f^{13}$ and $5p^54f^{12}5d$ configurations, the mean deviation in log *gf* being found to be equal to 0.02. In other words, for the 4f–5d transitions, the core-polarization corrections considered in our model A lead to results comparable to those obtained by Meftah et al. [14] when opening the $5p^6$ subshell. However, this is no more the case when looking at the 5d–6p and 6s–6p transitions listed in Table 2. Indeed, for these transitions, the oscillator strengths calculated with our Model A appear systematically smaller than the values obtained by Meftah et al. [14] or by using our Model B, the mean ratios being found to be equal to $gf(A)/gf$ [14] = 0.77 ± 0.07 and $gf(A)/gf(B) = 0.79 \pm 0.03$. This implies that the core-excited configurations considered in these two latter approaches (by promoting one electron from the 5p core orbital only) are not sufficient to entirely take the core-valence electron correlations into account while the core-polarization corrections used in our calculation A are expected to model not only single excitations from 5p but also from other core subshells such as 5s and 4f, for example.

As there are no experimental radiative data available in the literature for Tm IV, a possible way of assessing the reliability of the results obtained in the present work lies in isoelectronic comparisons, particularly with the study performed in Er III a few years ago [24]. In this work, radiative lifetimes of seven excited states belonging to the $4f^{11}6p$ configuration, in the energy range from 55,547 to 81,838 cm^{-1}, have been measured using the time-resolved laser-induced fluorescence technique. The comparison of these accurate experimental data with core-polarization corrected HFR calculations, using the same physical model as the one considered in model A of the present work, has shown that the computed values were in excellent agreement (within 8%) with the measurements. An identical agreement (within 10%) was also found when comparing a similar theoretical model with experimental radiative lifetimes for $4f^{12}6p$ levels between 76,721 and 82,573 cm^{-1} in Tm III [30]. An accuracy of the same order of magnitude can therefore also be expected for the radiative decay rates computed in the present work for transitions depopulating the $4f^{11}6p$ levels in Tm IV, at least for the most intense lines.

Table 1. Calculated oscillator strengths (log *gf*) for transitions involving the lower $4f^{12}\,{}^3H_6$ ground level to upper $4f^{11}5d$ levels in Tm IV.

λ (Å) [1]	Transition		log *gf* (This Work)		log *gf* [14]	
	Lower Level [2]	Upper Level [2]	A [3]	B [4]	no CI [5]	CI [6]
748.928	0.00 (6)	133524.48 (5)	−2.21	−2.35	−1.83	−2.00
781.617	0.00 (6)	127939.33 (6)	−2.05	−2.04	−1.89	−2.00
787.460	0.00 (6)	126990.55 (5)	−1.12	−1.43	−1.01	−1.27
792.742	0.00 (6)	126144.12 (6)	−1.83	−1.86	−1.58	−1.73
793.374	0.00 (6)	126043.76 (7)	−1.95	−1.98	−1.96	−2.02
802.337	0.00 (6)	124636.37 (5)	−1.43	−2.41	−1.38	−1.83
804.050	0.00 (6)	124370.09 (6)	−1.25	−1.33	−1.18	−1.32
811.339	0.00 (6)	123253.77 (6)	−2.26	−2.56	−1.99	−2.23
812.435	0.00 (6)	123086.74 (5)	−0.61	−0.79	−0.48	−0.69
827.296	0.00 (6)	120875.97 (5)	−0.69	−0.85	−0.51	−0.73
829.041	0.00 (6)	120621.39 (6)	−1.81	−2.03	−1.73	−1.92
831.785	0.00 (6)	120223.30 (7)	−0.96	−1.28	−0.88	−1.14
839.626	0.00 (6)	119100.52 (7)	−0.91	−1.02	−0.72	−0.92
839.927	0.00 (6)	119057.80 (5)	−2.88	−3.08	−2.34	−2.54
850.291	0.00 (6)	117607.00 (6)	−1.77	−1.88	−1.65	−1.81
850.838	0.00 (6)	117531.05 (7)	−0.21	−0.38	−0.08	−0.29
863.720	0.00 (6)	115778.36 (5)	−2.00	−2.19	−1.72	−1.95
875.898	0.00 (6)	114168.84 (5)	−2.33	−2.65	−2.79	−2.92
888.951	0.00 (6)	112491.99 (5)	−0.61	−0.86	−0.38	−0.60
890.547	0.00 (6)	112290.52 (7)	−1.18	−1.32	−1.05	−1.24
893.806	0.00 (6)	111881.49 (5)	−0.91	−0.91	−1.22	−1.31
897.819	0.00 (6)	111381.45 (6)	−1.02	−1.23	−0.81	−1.14
898.984	0.00 (6)	111236.63 (5)	−2.11	−2.43	−1.29	−1.28
903.148	0.00 (6)	110723.68 (5)	−0.87	−1.00	−0.74	−0.92
908.328	0.00 (6)	110092.40 (6)	−1.69	−1.77	−1.31	−1.53
913.550	0.00 (6)	109463.34 (5)	−1.26	−1.33	−1.26	−1.41
916.354	0.00 (6)	109128.14 (6)	−1.37	−1.44	−1.23	−1.39
926.904	0.00 (6)	107885.74 (7)	−1.00	−1.10	−0.87	−1.08
929.338	0.00 (6)	107603.36 (6)	−1.47	−1.63	−0.31	−0.91
932.017	0.00 (6)	107294.13 (6)	−0.34	−0.45	−0.94	−0.55
935.493	0.00 (6)	106895.45 (7)	−1.30	−1.46	−1.40	−1.51
942.489	0.00 (6)	106101.98 (6)	−1.20	−1.24	−1.26	−1.39
944.471	0.00 (6)	105879.41 (6)	−0.87	−1.03	−0.68	−0.88
950.964	0.00 (6)	105156.00 (5)	−0.98	−1.09	−0.91	−1.09
963.402	0.00 (6)	103799.19 (6)	−0.87	−1.02	−0.84	−1.03
980.201	0.00 (6)	102020.08 (6)	−1.82	−1.95	−1.61	−1.81
981.108	0.00 (6)	101925.68 (5)	−1.32	−1.46	−1.46	−1.70
999.724	0.00 (6)	100027.46 (5)	−1.58	−1.66	−1.48	−1.65
1024.207	0.00 (6)	97637.17 (5)	−1.96	−2.34	−1.90	−2.04
1031.126	0.00 (6)	96982.12 (6)	−2.14	−2.09	−2.04	−2.16
1045.098	0.00 (6)	95685.30 (6)	−2.04	−2.20	−2.06	−2.24
1048.446	0.00 (6)	95379.52 (5)	−1.66	−1.76	−1.48	−1.65
1054.249	0.00 (6)	94854.50 (5)	−1.40	−1.52	−1.34	−1.54
1062.470	0.00 (6)	94119.93 (6)	−0.90	−1.01	−0.87	−1.05
1080.102	0.00 (6)	92583.34 (6)	−1.08	−1.10	−0.88	−1.03
1098.150	0.00 (6)	91061.55 (7)	−1.50	−1.66	−1.41	−1.63
1133.437	0.00 (6)	88226.85 (6)	−1.92	−1.92	−1.60	−1.75
1138.014	0.00 (6)	87872.31 (7)	−1.61	−1.72	−1.67	−1.84
1148.226	0.00 (6)	87090.72 (5)	−2.94	−2.91	−2.47	−2.67
1153.166	0.00 (6)	86717.61 (6)	−0.81	−0.88	−0.80	−0.95
1160.827	0.00 (6)	86145.56 (7)	−1.26	−1.37	−1.30	−1.47
1169.015	0.00 (6)	85542.07 (5)	−1.45	−1.57	−1.46	−1.64
1183.627	0.00 (6)	84485.81 (6)	−1.02	−1.10	−0.86	−1.04
1197.175	0.00 (6)	83530.02 (7)	−1.15	−1.21	−1.04	−1.21
1200.580	0.00 (6)	83293.13 (5)	−1.57	−1.66	−1.42	−1.60
1245.880	0.00 (6)	80264.65 (7)	−1.26	−1.34	−1.08	−1.26
1262.212	0.00 (6)	79225.87 (6)	−1.56	−1.64	−1.42	−1.59
1275.288	0.00 (6)	78413.63 (5)	−2.50	−2.60	−2.33	−2.53

Notes: [1] Experimental wavelengths from [14]; [2] Experimental energy levels in cm^{-1} from [14]. *J*-values are given between parentheses; [3] Model A used in the present work (see text); [4] Model B used in the present work (see text); [5] Calculations reported in [14] not including $5p^54f^{13}$ and $5p^54f^{12}5d$; [6] Calculations reported in [14] including $5p^54f^{13}$ and $5p^54f^{12}5d$.

Table 2. Calculated oscillator strengths (log *gf*) for transitions involving lower $4f^{11}5d$ and $4f^{11}6s$ levels to the upper $4f^{11}(^4I_{15/2})6p$ subconfiguration in Tm IV.

λ (Å) [1]	Transition		log *gf* (This Work)		log *gf* [14]	
	Lower Level [2]	Upper Level [2]	A [3]	B [4]	no CI [5]	CI [6]
1212.409	72011.02 (6)	154491.66 (6)	−1.30	−1.22	−1.20	−1.21
1212.792	72011.02 (6)	154466.21 (7)	−0.67	−0.57	−0.56	−0.55
1226.090	72931.67 (7)	154491.66 (6)	−1.47	−1.37	−1.36	−1.36
1226.478	72931.67 (7)	154466.21 (7)	−1.16	−1.07	−1.05	−1.05
1234.245	72931.67 (7)	153952.89 (8)	−0.29	−0.19	−0.16	−0.16
1258.711	74506.41 (9)	153952.89 (8)	−1.07	−1.00	−0.87	−0.88
1267.731	75585.02 (8)	154466.21 (7)	−0.97	−0.87	−0.79	−0.81
1270.461	74506.41 (9)	153217.84 (9)	−0.30	−0.20	−0.23	−0.22
1276.030	75585.02 (8)	153952.89 (8)	−0.65	−0.55	−0.58	−0.58
1288.111	75585.02 (8)	153217.84 (9)	−0.64	−0.54	−0.56	−0.55
1314.439	78413.63 (5)	154491.66 (6)	−0.58	−0.51	−0.51	−0.50
1328.460	78677.88 (9)	153952.89 (8)	0.35	0.44	0.45	0.45
1329.077	79225.87 (6)	154466.21 (7)	−0.50	−0.42	−0.39	−0.39
1341.565	78677.88 (9)	153217.84 (9)	−0.05	0.05	0.09	0.08
1345.118	80122.71 (8)	154466.21 (7)	−0.20	−0.09	−0.07	−0.07
1347.219	80264.65 (7)	154491.66 (6)	−0.79	−0.69	−0.63	−0.63
1347.679	80264.65 (7)	154466.21 (7)	−0.17	−0.07	−0.02	−0.02
1354.448	80122.71 (8)	153952.89 (8)	0.09	0.19	0.22	0.21
1357.073	80264.65 (7)	153952.89 (8)	−0.77	−0.67	−0.63	−0.63
1368.085	80122.71 (8)	153217.84 (9)	−0.96	−0.86	−0.81	−0.82
1370.232	72011.02 (6)	144991.40 (7)	0.24	0.33	0.36	0.36
1376.791	72931.67 (7)	145564.25 (8)	−0.31	−0.21	−0.20	−0.20
1384.904	82258.89 (8)	154466.21 (7)	−0.13	−0.03	−0.06	−0.06
1387.735	72931.67 (7)	144991.40 (7)	0.08	0.18	0.20	0.20
1394.817	82258.89 (8)	153952.89 (8)	−0.82	−0.76	−0.89	−0.86
1404.524	83293.13 (5)	154491.66 (6)	−0.01	0.09	0.12	0.11
1407.305	74506.41 (9)	145564.25 (8)	0.38	0.48	0.50	0.50
1409.212	83530.02 (7)	154491.66 (6)	−0.40	−0.29	−0.30	−0.30
1409.721	83530.02 (7)	154466.21 (7)	−0.27	−0.16	−0.19	−0.19
1420.008	83530.02 (7)	153952.89 (8)	−1.26	−1.15	−1.22	−1.21
1428.465	84485.81 (6)	154491.66 (6)	−0.27	−0.17	−0.13	−0.14
1429.001	75585.02 (8)	145564.25 (8)	0.13	0.23	0.23	0.23
1440.801	75585.02 (8)	144991.40 (7)	−0.15	−0.05	−0.04	−0.04
1531.399	80264.65 (7)	145564.25 (8)	−1.17	−1.07	−1.06	−1.07
1544.960	80264.65 (7)	144991.40 (7)	−1.00	−0.91	−0.93	−0.93
1615.952	92583.34 (6)	154466.21 (7)	−1.50	−1.36	−1.37	−1.36
1802.012	98972.81 (8)	154466.21 (7)	0.01	0.15	0.13	0.13
1818.839	98972.81 (8)	153952.89 (8)	0.55	0.69	0.71	0.71
1840.039	100145.04 (7)	154491.66 (6)	0.57	0.69	0.68	0.68
1840.910	100145.04 (7)	154466.21 (7)	0.59	0.71	0.71	0.71
1843.486	98972.81 (8)	153217.84 (9)	0.83	0.97	0.97	0.97
1858.450	100145.04 (7)	153952.89 (8)	0.37	0.49	0.48	0.48
2145.639	98972.81 (8)	145564.25 (8)	0.28	0.42	0.42	0.42
2172.361	98972.81 (8)	144991.40 (7)	0.55	0.69	0.69	0.69
2201.026	100145.04 (7)	145564.25 (8)	0.50	0.62	0.63	0.63
2229.134	100145.04 (7)	144991.40 (7)	−0.03	0.10	0.09	0.09

Notes: [1] Experimental wavelengths from [14]; [2] Experimental energy levels in cm^{-1} from [14]. *J*-values are given between parentheses; [3] Model A used in the present work (see text); [4] Model B used in the present work (see text); [5] Calculations reported in [14] not including $5p^54f^{13}$ and $5p^54f^{12}5d$; [6] Calculations reported in [14] including $5p^54f^{13}$ and $5p^54f^{12}5d$.

For all of these reasons, the model A used in the present work is expected to be the most reliable and, as a consequence, oscillator strengths (log *gf*) and transition probabilities (*gA*) computed with this model are reported as supplementary material in Table S1. In the latter, all Tm IV lines involving experimentally known levels for which the log *gf* values are greater than −4 are listed. This corresponds to 2913 spectral lines covering a wide wavelength range, from extreme ultraviolet to visible, or, more precisely, from 719 to 5325 Å.

6. Magnetic Dipole and Electric Quadrupole Transitions

It is well known that triply charged lanthanide ions exhibit very characteristic emission lines in the visible and near infrared regions due to 4f → 4f transitions. These transitions, forbidden by the electric dipole selection rules, are characterized by long lifetimes which facilitate 'time gated' emission experiments leading to significant improvement of signal-to-noise ratios in comparison to more traditional steady-state measurements. Therefore, radiative decay rates of such forbidden lines within the $4f^{12}$ ground configuration of Tm IV were also computed in the present work. Transition probabilities obtained using our physical model A for the most intense magnetic dipole (M1) and electric quadrupole (E2) lines are reported in Table 3. They are compared with the results recently published by Dodson and Zia [23] who calculated radiative transition probabilities for some M1 and E2 Tm IV lines using a detailed free ion Hamiltonian including electrostatic and spin-orbit terms as well as two-body, three-body, spin-spin, spin-other-orbit and electrostatically correlated spin-orbit interactions. When looking at Table 3, we can note that their results are generally in good agreement (within a few percent) with our transition probabilities, if we except some E2 transitions located at 3038.774, 3847.249, 4264.491, 4437.432, 4721.408, 5759.349, 6401.911 and 7967.695 Å for which larger discrepancies are observed. However, we note that, for these particular transitions, the cancellation factor as defined by Cowan [22] is very small (<0.05), indicating that the corresponding decay rates might be affected by larger uncertainties in our calculations. For all of the other forbidden lines reported in Table 3, an accuracy of about 10% can reasonably be estimated for our computed *gA*-values in view of their excellent agreement with the results obtained using a completely independent theoretical method [23].

Table 3. Transition probabilities for forbidden lines within the $4f^{12}$ ground-state configuration of Tm IV. Only transitions with *gA*-values greater than 0.01 s^{-1} (according to our model A) are listed.

λ (Å) [1]	Transition			*gA* (s^{-1})	
	Lower Level [2]	Upper Level [2]	Type [3]	This Work [4]	Other [5]
2829.678	0 (6)	35329 (6)	M1	1.52E+02	
3038.774	5634 (4)	38532 (2)	E2	7.51E−01	7.50E−02
3366.570	5634 (4)	35329 (6)	E2	1.83E−01	2.00E−01
3687.275	8217 (5)	35329 (6)	M1	4.94E+01	4.56E+01
3847.249	12547 (4)	38532 (2)	E2	4.47E−01	5.95E−02
4144.416	14410 (3)	38532 (2)	M1+E2	9.10E+01	1.15E+02
4264.491	15090 (2)	38532 (2)	M1+E2	1.32E−01	1.79E+00
4388.182	12547 (4)	35329 (6)	E2	5.05E−02	5.99E−02
4437.432	5634 (4)	28163 (2)	E2	4.24E−01	7.50E−02
4721.408	0 (6)	21174 (4)	E2	2.94E−02	6.93E−03
5759.349	21174 (4)	38532 (2)	E2	1.22E−01	1.81E−02
6401.911	12547 (4)	28163 (2)	E2	1.45E−02	2.40E−03
6433.154	5634 (4)	21174 (4)	M1	1.59E+01	1.72E+01
7062.639	21174 (4)	35329 (6)	E2	1.55E−02	1.46E−02
7269.222	14410 (3)	28163 (2)	M1	8.99E+01	7.00E+01
7646.868	15090 (2)	28163 (2)	M1	5.26E+01	4.65E+01
7715.433	8217 (5)	21174 (4)	M1	2.08E+02	2.03E+02
7967.695	0 (6)	12547 (4)	E2	1.05E−02	1.73E−04
9641.292	28163 (2)	38532 (2)	M1	6.33E+01	6.50E+01
11391.088	5634 (4)	14410 (3)	M1	7.68E+01	7.63E+01
11588.383	12547 (4)	21174 (4)	M1	5.26E+01	5.04E+01
12166.962	0 (6)	8217 (5)	M1	1.61E+02	1.60E+02
14461.107	5634 (4)	12547 (4)	M1	3.56E+01	3.56E+01
14780.571	14410 (3)	21174 (4)	M1	5.64E+00	5.84E+00
23085.722	8217 (5)	12547 (4)	M1	1.43E+01	
38708.464	5634 (4)	8217 (5)	M1	4.09E−01	
53657.049	12547 (4)	14410 (3)	M1	3.42E−01	

Notes: [1] Wavelengths in air deduced from the experimental energy levels taken from [14]; [2] Experimental energy levels in cm^{-1} from [14]. *J*-values are given between parentheses; [3] M1: magnetic dipole; E2: electric quadrupole; [4] Model A used in the present work (see text); [5] Dodson and Zia [23].

7. Conclusions

Oscillator strengths and transition probabilities for allowed and forbidden lines in triply ionized thulium have been obtained using a pseudo-relativistic Hartree–Fock model including core-polarization effects. Due to the lack of experimental data in this ion, the reliability of the new radiative parameters for electric dipole lines has been discussed and assessed through detailed comparisons with different calculations, explicitly including some configurations with an open $5p^6$ subshell, on the one hand, and through the excellent agreement observed between similar calculations and accurate laser lifetime measurements performed in the isoelectronic Er III and isonuclear Tm III ions, on the other hand. The new data concern about 3000 Tm IV spectral lines involving all the experimentally known energy levels in the $4f^{12}$, $4f^{11}5d$, $4f^{11}6s$ and $4f^{11}6p$ configurations. In the case of forbidden lines within the $4f^{12}$ ground configuration, our results have been found to be in good agreement with theoretical data recently published, if we except a few electric quadrupole transitions.

Supplementary Materials: The following table is available online at www.mdpi.com/2218-2004/5/3/28/s1, Table S1: Calculated oscillator strengths (log *gf*) and transition probabilities (*gA*) for Tm IV spectral lines. Wavelengths in vacuum (air) below (above) 2000 Å are deduced from the experimental energy levels reported in [14]. These levels are given with their rounded energies, parities and *J*-values in the present table (see [14] for more complete spectroscopic designations and accurate energies).

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References

1. Hemmilä, I. Luminescent lanthanide chelates-a way to diagnostic methods. *J. Alloys Compd.* **1995**, *225*, 480–485. [CrossRef]
2. Wybourne, B.G. The fascination of the rare earths—Then, now and in the future. *J. Alloys Compd.* **2004**, *380*, 96–100. [CrossRef]
3. Hasegawa, Y.; Wada, Y.; Yanagida, S. Strategies for the design of luminescent lanthanide(III) complexes and their photonic applications. *J. Photochem. Photobiol. C* **2004**, *5*, 183–202. [CrossRef]
4. Walsh, B.M.; Barnes, N.P.; Petros, M.; Yu, J.; Singh, U.N. Spectroscopy and modeling of solid state lanthanide lasers: Application to trivalent Tm^{3+} and Ho^{3+} in $YLiF_4$ and $LuLiF_4$. *J. Appl. Phys.* **2004**, *95*, 3255–3271. [CrossRef]
5. Dossing, A. Luminescence from lanthanide(3+) ions in solution. *Eur. J. Inorg. Chem.* **2005**, *2005*, 1425–1434. [CrossRef]
6. Suyver, J.F.; Aebischer, A.; Biner, D.; Gerner, P.; Grimm, J.; Heer, S.; Krämer, K.W.; Reinhard, C.; Güdel, H.U. Novel materials doped with trivalent lanthanides and transition metal ions showing near-infrared to visible photon upconversion. *Opt. Mater.* **2005**, *27*, 1111–1130. [CrossRef]
7. Wong, E.Y.; Richman, I. Analysis of the absorption spectrum and Zeeman effect of thulium ethylsulphate. *J. Chem. Phys.* **1961**, *34*, 1182–1185. [CrossRef]
8. Krupke, W.F.; Gruber, J.B. Optical-absorption intensities of rare-earth ions in crystals: The absorption spectrum of thulium ethyl sulfate. *Phys. Rev. A* **1965**, *139*, A2008. [CrossRef]
9. Muto, K. Absorption spectra and Zeeman effects of Tm^{3+} in CaF_2. *J. Phys. Chem. Solids* **1973**, *34*, 2029–2035. [CrossRef]
10. Wotman, D.E.; Morrison, C.A.; Leavitt, R.P. *Analysis of the Ground Configuration of* Tm^{3+} *in* $CaWO_4$; Harry Diamond Laboratories Report HDL-TR-1663: Washington, DC, USA, 1974.
11. Wotman, D.E.; Morrison, C.A.; Leavitt, R.P. Analysis of the ground configuration of Tm^{3+} in $CaWO_4$. *Phys. Rev. B* **1975**, *12*, 4780. [CrossRef]
12. Wotman, D.E.; Leavitt, R.P.; Morrison, C.A. Analysis of the ground configuration of Tm^{3+} in YVO_4. *J. Phys. Chem. Solids* **1974**, *35*, 591–593. [CrossRef]

13. Jenssen, H.P.; Linz, A.; Leavitt, R.P.; Morrison, C.A.; Wotman, D.E. Analysis of the optical spectrum of Tm^{3+} in $LiYF_4$. *Phys. Rev. B* **1975**, *11*, 92–101. [CrossRef]
14. Meftah, A.; Wyart, J.-F.; Champion, N.; Tchang-Brillet, W.-Ü.L. Observation and interpretation of the Tm^{3+} free ion spectrum. *Eur. Phys. J. D* **2007**, *44*, 35–45. [CrossRef]
15. Kozlov, A.; Dzuba, V.A.; Flambaum, V.V. Optical atomic clocks with suppressed blackbody-radiation shift. *Phys. Rev. A* **2014**, *90*, 042505. [CrossRef]
16. Derevianko, A.; Dzuba, V.A.; Flambaum, V.V. Highly charged ions as a basis of optical atomic clockwork of exceptional accuracy. *Phys. Rev. Lett.* **2012**, *109*, 180801. [CrossRef] [PubMed]
17. Biémont, E.; Clar, M.; Enzonga Yoca, S.; Fivet, V.; Quinet, P.; Träbert, E.; Garnir, H.-P. Atomic structure calculations and beam-foil observations of La IV. *Can. J. Phys.* **2009**, *87*, 1275–1282. [CrossRef]
18. Zhang, Z.G.; Svanberg, S.; Quinet, P.; Palmeri, P.; Biémont, E. Time-resolved laser spectroscopy of multiply ionized atoms—Natural radiative lifetimes in Ce IV. *Phys. Rev. Lett.* **2001**, *87*, 273001. [CrossRef] [PubMed]
19. Enzonga Yoca, S.; Quinet, P. Decay rates for radiative transitions in the Pr IV spectrum. *J. Phys. B At. Mol. Opt. Phys.* **2013**, *46*, 145003. [CrossRef]
20. Enzonga Yoca, S.; Quinet, P. Relativistic Hartree-Fock calculations of transition rates for allowed and forbidden lines in Nd IV. *J. Phys. B At. Mol. Opt. Phys.* **2014**, *47*, 035002. [CrossRef]
21. Wyart, J.-F.; Tchang-Brillet, W-Ü.L.; Spector, N.; Palmeri, P.; Quinet, P.; Biémont, E. Extended analysis of the spectrum of triply-ionized ytterbium (Yb IV) and transition probabilities. *Phys. Scr.* **2001**, *63*, 113. [CrossRef]
22. Cowan, R.D. *The Theory of Atomic Structure and Spectra*; University of California Press: Berkeley, CA, USA, 1981.
23. Dodson, C.M.; Zia, R. Magnetic dipole and electric quadrupole transitions in the trivalent lanthanide series: Calculated emission rates and oscillator strengths. *Phys. Rev. A* **2012**, *86*, 125102. [CrossRef]
24. Biémont, E.; Garnir, H.-P.; Bastin, T.; Palmeri, P.; Quinet, P.; Li, Z.S.; Zhang, Z.G.; Lokhnygin, V.; Svanberg, S. Radiative lifetime measurements and transition probabilities of astrophysical interest in Er III. *Mon. Not. R. Astron. Soc.* **2001**, *321*, 481–486. [CrossRef]
25. Quinet, P.; Palmeri, P.; Biémont, E.; McCurdy, M.M.; Rieger, G.; Pinnington, E.H.; Wickliffe, M.E.; Lawler, J.E. Experimental and theoretical lifetimes, branching fractions and oscillator strengths in Lu II. *Mon. Not. R. Astron. Soc.* **1999**, *307*, 934–940. [CrossRef]
26. Quinet, P.; Palmeri, P.; Biémont, E.; Li, Z.S.; Zhang, Z.G.; Svanberg, S. Radiative lifetime measurements and transition probability calculations in lanthanide ions. *J. Alloys Comp.* **2002**, *344*, 255–259. [CrossRef]
27. Quinet, P. An overview of the recent advances performed in the study of atomic structures and radiative processes in the lowest ionization stages of heavy elements. *Can. J. Phys.* **2017**, in press. [CrossRef]
28. Fraga, S.; Karwowski, J.; Saxena, K.M.S. *Handbook of Atomic Data*; Elsevier: Amsterdam, The Netherland, 1976.
29. Zhang, Z.G.; Li, Z.S.; Svanberg, S.; Palmeri, P.; Quinet, P.; Biémont, E. Experimental and theoretical lifetimes in Yb III. *Eur. Phys. J. D* **2001**, *15*, 301–305. [CrossRef]
30. Li, Z.S.; Zhang, Z.G.; Lokhnygin, V.; Svanberg, S.; Bastin, T.; Biémont, E.; Garnir, H.-P.; Palmeri, P.; Quinet, P. Radiative lifetime measurements in Tm III with time-resolved laser spectroscopy and comparosons with HFR calculations. *J. Phys. B At. Mol. Opt. Phys.* **2001**, *34*, 1349–1359. [CrossRef]