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Decay rates for radiative transitions in the Pr IV spectrum

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Abstract
Transition probabilities and oscillator strengths for electric dipole radiation in triply ionized praseodymium are reported for the first time in this paper. They were computed using a semi-empirical relativistic Hartree–Fock approach including core-polarization effects. Due to the lack of experimental data in the Pr IV spectrum, the accuracy of our results is estimated and discussed on the basis of comparisons between calculations performed with a similar physical model and laboratory measurements previously published for the isoelectronic ion Ce^{2+}. In view of their great interest in optical materials and nanophotonics, radiative rates for forbidden lines within the $4f^2$ ground-state configuration of Pr^{3+} were also calculated in our work.

1. Introduction

Because of their unique photophysical properties, in particular with respect to the generation and amplification of light, triply ionized lanthanide elements hold a special place in photonics. The luminescence of these ions in compounds has been widely studied and has found applications in many scientific domains such as the lighting industry, laser physics, optical telecommunications, molecular biology, medical diagnostics, etc (see e.g. Hemmilä 1995, Wybourne 2004, Hasegawa *et al* 2004, Dossing 2005).

This luminescence is the result of the competition of radiative and non-radiative relaxation processes of electronically excited states in lanthanide ions that are characterized by a multitude of energy levels particularly because of the unfilled 4f orbital. Understanding the light emission from triply ionized lanthanides therefore requires reliable information about their atomic structure and radiative parameters. However, our knowledge of the spectra corresponding to these ions is still very fragmentary, most of the experimentally identified energy levels being listed in the tables of the National Institute of Standards and Technology (NIST, see Kramida *et al* 2012) which are entirely based on the compilation due to Martin *et al* (1978). Recently, there has been a revival of the interest in triply ionized lanthanides, and several spectral analyses based on high-resolution vacuum ultraviolet observations have been completed. Among the spectra considered, let us mention, e.g. Nd IV (Wyart *et al* 2006, Wyart *et al* 2007), Tm IV (Meftah *et al* 2007) and Yb IV (Wyart *et al* 2001). Theoretical investigations of $4f^k$ ground-state configurations in Pr IV ($k = 2$) and Nd IV ($k = 3$) have also been carried out by Wyart *et al* (2008).

Concerning the radiative properties of triply ionized lanthanides, the investigations performed so far were focused on a rather limited number of electric dipole transitions in La IV (Biémont *et al* 2009), Ce IV (Migdalek and Baylis 1979, Migdalek and Wyrozumska 1987, Glushkov 1992, Zhang *et al* 2001c, Savukov *et al* 2003), Pr IV (Sen and Puri 1989, Stanek and Migdalek 2004, Wyart *et al* 2005), Nd IV, Pm IV, Sm IV, Eu IV, Gd IV (Dzuba *et al* 2003), Yb IV (Wyart *et al* 2001) and Lu IV (Loginov and Tuchkin 2001, Anisimova *et al* 2001). Very recently, theoretical emission rates and oscillator strengths were published by Dodson and Zia (2012) for some magnetic dipole and electric quadrupole transitions within the $4f^k$ ($k =$ 1–13) configurations along the triply ionized lanthanide series from Ce IV to Yb IV.

In this work, the relativistic Hartree–Fock (HFR) approach, including core-polarization (CPOL) effects, has been used to estimate the radiative decay rates in Pr IV. The excellent agreement between experimental lifetime measurements and theoretical results obtained for the isoelectronic ion Ce^{2+} (see Biémont *et al* 2002) when using a similar HFR model allowed us to assess the reliability of the new set of transition probabilities. These calculations in Pr IV are an extension of our previous investigations of the triply charged lanthanide ions La IV (Biémont *et al* 2009), Ce IV (Zhang *et al* 2001c) and Yb IV (Wyart *et al* 2001). Due to their particular interest in optical physics and nanophotonics, the radiative parameters corresponding to forbidden transitions within the $4f^2$ ground-state configuration of Pr IV were also computed in our work and compared to available theoretical data.

2. Level structure of Pr IV

The ground state of Pr IV is [Xe]$4f^2$ $^3H_4$. All of the term energies experimentally deduced so far are listed in the NIST compilation (Martin *et al* 1978) which contains 88 levels identified as belonging to the $4f^2$, 4f5f, 4f6p, $5d^2$ even configurations and to the 4f5d, 4f6d, 4f6s, 4f7s, 5d6p odd configurations. This critical compilation was essentially based on the works of Sugar (1965, 1971a) and Crosswhite *et al* (1965) who observed the Pr IV spectrum emitted by sliding-spark discharges and reported line lists covering the wavelength region from 69.1 to 302.1 nm. The level compositions in the $4f^2$ configuration were taken from the theoretical analysis of Goldschmidt (1968) later refined to include additional magnetic interactions by Goldschmidt *et al* (1968) and Pasternak (1970). Theoretical percentages for levels of the 4f6s, 4f5d, 4f6d, 4f6p and 4f5f configurations were taken from Sugar (1965, 1971a) supplemented by some of his unpublished results (Sugar 1971b).

More recently, a theoretical study of the $4f^2$ ground-state configuration in Pr IV was published by Wyart *et al* (2008) who performed a parametric fit of level energies, taking into account the Coulomb and spin-dependent interactions beyond the first order of perturbation. In this study, an excellent agreement between theoretical and experimental energies was observed, the root-mean square deviation being found equal to only 1.29 cm^{-1} for the 12 known levels within the $4f^2$ configuration. This excellent agreement allowed the authors to predict an energy value of 48 044.66 cm^{-1} with a good accuracy for the one remaining unknown level in $4f^2$, i.e. $^1S_0$.

3. Radiative parameter calculations

Pr^{3+} ion is a Ba-like atomic system with two valence electrons surrounding a Xe-like core. As a consequence, intravalence and core-valence interactions should be both taken into account for calculating the atomic structure. In addition, relativistic effects must normally play an important role. A method which has appeared as a suitable compromise between a gratifying accuracy of the results (tested by comparison with accurate laser lifetime measurements), the moderate complexity of the codes used and the ability to obtain many new results in a limited CPU time, is the pseudo-relativistic Hartree–Fock (HFR) technique as described by Cowan (1981), but modified by us for the inclusion of CPOL effects. In this approach (HFR + CPOL), most of the intravalence correlation is represented within a configuration interaction scheme, while the core-valence correlation is described by a CPOL model potential and a correction to the dipole operator depending upon two parameters, i.e. the dipole polarizability of the ionic core, α_d, and the cut-off radius, r_c (for details see e.g. Quinet *et al* 1999). Although based on the Schrödinger equation, this method takes the most important relativistic effects, such as the mass–velocity contribution and the Darwin term, into account.

The physical HFR + CPOL model used for Pr IV was exactly the same as the one described in our previous paper related to the isoelectronic ion Ce III (Biémont *et al* 2002). In this model, the intravalence correlation was explicitly retained among the following configurations : $4f^2$ + 4fnp (n = 6–7) + $5d^2$ + 5dns (n = 6–7) + $6s^2$ + 5d6d + 4fnf (n = 5–7) + $6p^2$ for the even parity and 4fnd (n = 5–7) + 4fns (n = 6–8) + 5d6p + 4fng (n = 5–6) + 6s6p for the odd parity. CPOL effects were included using the dipole polarizability, α_d, equal to 5.40 a_0^3, as tabulated by Fraga *et al* (1976) for the Xe-like ionic core Pr^{5+}, while the cut-off radius, r_c, was chosen to be equal to 1.60 a_0 which corresponds to the expected value of r for the outermost core orbital ($5p^6$) as computed with Cowan's codes. However, as already mentioned in many previous papers on lowly ionized lanthanides (see e.g. Biémont *et al* 2001a, Li *et al* 2001), the inadequacy of the analytical polarization corrections to the dipole operator as introduced in the HFR + CPOL model for transitions involving the 4f electrons imposes the consideration of a scaling factor to the $\langle 4f|r|nd\rangle$ and $\langle 4f|r|ng\rangle$ dipole operators in order to compensate for the sudden collapse of the 4f orbital inside the Xe-like core. In this work, those operators were scaled down by the same factor as the one used in the case of Ce III, i.e. 0.80 (Biémont *et al* 2002). A similar approach was already successfully considered in many different ions of the lanthanide series, an excellent agreement (within a few per cent) between theoretical and experimental lifetimes having been found in Ce II (Zhang *et al* 2001b), Pr III (Biémont *et al* 2001a), Tm III (Li *et al* 2001), Er III (Biémont *et al* 2001b), Yb III (Zhang *et al* 2001a) and Yb IV (Wyart *et al* 2001).

Using a least-squares fitting procedure (Cowan 1981), average energies, Slater integrals, spin–orbit and effective interaction parameters were adjusted to obtain the best agreement between the calculated and the experimental energy levels taken from the NIST tables (Martin *et al* 1978). All the values listed in this compilation were used in the fit process if we except the two 5d6p levels at 195 917.0 and 202 487.0 cm^{-1}. Note that the accurate predicted value obtained by Wyart *et al* (2008) for the $^1S_0$ level of $4f^2$ (E = 48 044.66 cm^{-1}) was also used to obtain a complete set of parameters in this configuration. The radial parameters adopted in this work are given in table 1 (even parity) and table 2 (odd parity), while the energy levels computed with those parameters are compared with available experimental values in tables 3 and 4, respectively. As seen from these tables, the average deviations were found to be equal to 34 cm^{-1} for even-parity levels and to 95 cm^{-1} for odd-parity levels (which means 1/6000 and 1/2100 of the energy ranges, respectively). We also note that, for the 4f6p configuration, our parameters G^2(4f,6p) and G^4(4f,6p) differ by 20% from those deduced

Table 1. Adopted radial parameters (in cm^{-1}) for even-parity configurations of Pr IV.

Configuration	Parameter	HFR	Fitted	Fitted/HFR	Note
$4f^2$	E_{av}	11 981.0	10 400.3		
	$F^2(4f,4f)$	98 646.2	73 738.1	0.75	
	$F^4(4f,4f)$	61 885.0	54 930.9	0.89	
	$F^6(4f,4f)$	44 517.7	36 754.6	0.83	
	α	0.0	12.5		
	β	0.0	−293.7		
	γ	0.0	514.1		
	ζ_{4f}	826.8	757.6	0.92	
4f6p	E_{av}	138 401.5	142 460.0		
	ζ_{4f}	919.6	856.1	0.93	
	ζ_{6p}	2792.8	3221.7	1.15	
	$F^2(4f,6p)$	10 058.8	8469.4	0.84	
	$G^2(4f,6p)$	2542.6	3352.5	1.32	
	$G^4(4f,6p)$	2340.0	3037.5	1.30	
$5d^2$	E_{av}	162 046.9	148 622.1		
	$F^2(5d,5d)$	49 823.4	44 841.1	0.90	Fixed[a]
	$F^4(5d,5d)$	33 495.6	30 146.0	0.90	Fixed[a]
	α	0.0	0.0		
	β	0.0	0.0		
	ζ_{5d}	1220.9	1471.7	1.16	
4f5f	E_{av}	199 462.9	203 100.4		
	ζ_{4f}	920.9	864.9	0.94	
	ζ_{5f}	40.4	40.7	1.01	
	$F^2(4f,5f)$	7603.8	5960.0	0.78	
	$F^4(4f,5f)$	3137.6	4081.3	1.30	
	$F^6(4f,5f)$	1996.3	3270.0	1.63	
	$G^0(4f,5f)$	4509.7	1837.2	0.41	
	$G^2(4f,5f)$	3352.1	3236.3	0.97	
	$G^4(4f,5f)$	2326.4	3191.4	1.37	
	$G^6(4f,5f)$	1734.6	1747.2	1.01	

[a] Fixed parameter value in the fitting process.

Table 2. Adopted radial parameters (in cm^{-1}) for odd-parity configurations of Pr IV.

Configuration	Parameter	HFR	Fitted	Fitted/HFR	Note
4f5d	E_{av}	63 250.0	67 309.7		
	ζ_{4f}	911.6	922.1	1.01	
	ζ_{5d}	1074.1	1012.2	0.94	
	$F^2(4f,5d)$	30 877.1	22 249.0	0.72	
	$F^4(4f,5d)$	15 423.3	17 126.6	1.11	
	$G^1(4f,5d)$	13 563.4	10 483.3	0.77	
	$G^3(4f,5d)$	11 498.8	12 503.4	1.09	
	$G^5(4f,5d)$	8912.6	9067.9	1.02	
4f6d	E_{av}	191 463.7	196 063.7		
	ζ_{4f}	920.6	880.8	0.96	
	ζ_{6d}	253.5	238.8	0.94	
	$F^2(4f,6d)$	7001.3	4817.9	0.69	r1[a]
	$F^4(4f,6d)$	3080.6	2119.9	0.69	r1[a]
	$G^1(4f,6d)$	2247.3	2173.3	0.97	r2[b]
	$G^3(4f,6d)$	2147.1	2076.4	0.97	r2[b]
	$G^5(4f,6d)$	1733.8	1676.6	0.97	r2[b]
4f6s	E_{av}	99 087.4	102 304.9		
	ζ_{4f}	918.8	860.3	0.94	
	$G^3(4f,6s)$	3396.2	2827.1	0.83	
4f7s	E_{av}	196 972.3	201 525.9		
	ζ_{4f}	921.6	921.6	1.00	Fixed[c]
	$G^3(4f,7s)$	1186.9	1068.2	0.90	Fixed[c]

[a] Fixed ratio between these parameters in the fitting process.
[b] Fixed ratio between these parameters in the fitting process.
[c] Fixed parameter value in the fitting process.

Table 3. Experimental and calculated even-parity energy levels in Pr IV.

E_{exp}[a](cm^{-1})	$E_{calc}(cm^{-1})$	$\Delta E(cm^{-1})$	J	*LS* composition[b]
0.00	24	−24	4	97% $4f^2\ ^3H$
2152.09	2147	5	5	100% $4f^2\ ^3H$
4389.09	4371	18	6	100% $4f^2\ ^3H$
4996.61	4990	7	2	98% $4f^2\ ^3F$
6415.24	6405	10	3	100% $4f^2\ ^3F$
6854.75	6890	−35	4	65% $4f^2\ ^3F$ + 33% $4f^2\ ^1G$
9921.24	9902	19	4	64% $4f^2\ ^1G$ + 34% $4f^2\ ^3F$
17 334.39	17 329	5	2	90% $4f^2\ ^1D$ + 8% $4f^2\ ^3P$
21 389.81	21 352	38	0	99% $4f^2\ ^3P$
22 007.46	21 991	16	1	100% $4f^2\ ^3P$
22 211.54	22 212	0	6	100% $4f^2\ ^1I$
23 160.61	23 220	−59	2	92% $4f^2\ ^3P$ + 8% $4f^2\ ^1d$
	48 045	0	0	97% $4f^2\ ^1S$
136 850.85	136 941	−90	3	61% 4f6p ^3G + 28% 4f6p ^1F + 10% 4f6p ^3F
137 175.04	137 104	71	2	65% 4f6p ^3F + 15% 4f6p ^1D + 11% 4f6p ^3D
139 711.8	139 706	6	2	84% $5d^2\ ^3F$ + 5% 4f6p ^3D
139 875.31	139 803	72	3	54% 4f6p ^3F + 26% 4f6p ^3D + 13% 4f6p ^1F
140 225.92	140 270	−44	4	43% 4f6p ^3G + 40% 4f6p ^3F + 15% 4f6p ^1G
141 254.01	141 221	33	3	35% 4f6p ^3G + 31% 4f6p ^1F + 14% 4f6p ^3F
142 331.59	142 438	−107	2	53% 4f6p ^3D + 30% 4f6p ^3F + 15% 4f6p ^1D
142 565.94	142 507	59	4	56% 4f6p ^3G + 21% 4f6p ^3F + 19%
	142 609		3	81% $5d^2\ ^3F$ + 11% 4f6p ^3F
142 997.32	142 963	34	1	99% 4f6p ^3D
144 925.33	144 818	107	4	48% 4f6p ^1G + 41% $5d^2\ ^3F$ + 10% 4f6p ^3F
144 943.27	144 984	−41	3	61% 4f6p ^3D + 25% 4f6p ^1F + 12% 4f6p ^3F
145 281.20	145 214	67	5	100% 4f6p ^3G
145 362.7	145 505	−143	4	50% $5d^2\ ^3F$ + 28% 4f6p ^3F + 16% 4f6p ^1G
146 577.13	146 604	−27	2	65% 4f6p ^1D + 31% 4f6p ^3D
	149 145		2	65% $5d^2\ ^1D$ + 30% $5d^2\ ^3P$
	149 505		0	97% $5d^2\ ^3P$
	150 806		1	99% $5d^2\ ^3P$
	153 641		2	69% $5d^2\ ^3P$ + 29% $5d^2\ ^1D$
	155 161		4	95% $5d^2\ ^1G$
	172 271		0	93% $5d^2\ ^1S$
199 191.0	199 185	6	3	69% 4f5f ^3G + 27% 4f5f ^1F
199 595.8	199 635	−40	5	53% 4f5f ^3I + 38% 4f5f ^1H + 6% 4f5f ^3G
199 815.5	199 729	86	1	57% 4f5f ^3D + 36% 4f5f ^1P
200 202.6	200 191	11	4	87% 4f5f ^3G + 5% 4f5f ^3H
200 235.1	200 245	−10	5	42% 4f5f ^3I + 27% 4f5f ^1H + 17% 4f5f ^3G
200 417.0	200 409	8	3	33% 4f5f ^3D + 31% 4f5f ^1F + 21% 4f5f ^3G
200 697.1	200 722	−25	2	85% 4f5f ^3D + 6% 4f5f ^3F
200 893.8	200 936	−42	6	89% 4f5f ^3I + 7% 4f5f ^1I
201 365.2	201 358	7	1	43% 4f5f ^3S + 22% 4f5f ^3D + 21% 4f5f ^1P
201 985.3	202 024	−39	4	82% 4f5f ^3H + 15% 4f5f ^1G
202 327.9	202 311	17	5	72% 4f5f ^3G + 25% 4f5f ^1H
	202 441		1	83% 5d6s ^3D + 8% 4f5f ^3S
202 614.7	202 593	21	3	54% 4f5f ^3D + 38% 4f5f ^1F + 6% 4f5f ^3G
202 819.0	202 775	44	2	63% 4f5f ^3F + 20% 4f5f ^1D + 11% 5d6s ^3D
202 948.9	202 997	−48	7	100% 4f5f ^3I
203 265.4	203 254	11	1	40% 4f5f ^1P + 38% 4f5f ^3S + 16% 4f5f ^3D
	203 394		2	74% 5d6s ^3D + 9% 4f5f ^3F + 5% 4f5f ^3D
204 032.1	204 054	−22	5	84% 4f5f ^3H + 9% 4f5f ^1H
204 557.0	204 554	3	3	85% 4f5f ^3F + 7% 4f5f ^3D
204 541.7	204 565	−23	4	41% 4f5f ^3F + 36% 4f5f ^1G + 12% 4f5f ^3G
204 815.6	204 801	15	6	90% 4f5f ^3H + 5% 4f5f ^3I
	205 173		0	88% 4f5f ^3P + 9% 4f5f ^1S
205 541.6	205 535	6	2	48% 4f5f ^1D + 20% 4f5f ^3P + 20% 4f5f ^3F
	205 634		3	91% 5d6s ^3D
205 748.3	205 700	48	4	51% 4f5f ^3F + 45% 4f5f ^1G
206 299.4	206 319	−20	6	87% 4f5f ^1I + 7% 4f5f ^3H + 5% 4f5f ^3I
206 369.4	206 376	−7	1	89% 4f5f ^3P + 7% 4f5f ^3S
207 046.3	207 044	2	2	70% 4f5f ^3P + 22% 4f5f ^1D

[a] From Martin *et al* (1978).

[b] Composition in %. Only the first three main components larger than 5% are given.

Table 4. Experimental and calculated odd-parity energy levels in Pr IV.

E_{exp}[a] (cm^{-1})	E_{calc} (cm^{-1})	ΔE (cm^{-1})	J	LS composition[b]
61 170.95	61 324	−153	4	51% 4f5d ^{1}G + 43% 4f5d ^{3}H
61 457.48	61 662	−204	2	76% 4f5d ^{3}F + 23% 4f5d ^{1}D
63 355.94	63 187	169	3	87% 4f5d ^{3}G + 7% 4f5d ^{3}F + 6% 4f5d ^{1}F
63 580.59	63 515	65	4	56% 4f5d ^{3}H + 33% 4f5d ^{1}G + 10% 4f5d ^{3}F
64 123.54	64 086	38	3	92% 4f5d ^{3}F + 8% 4f5d ^{3}G
65 239.39	64 987	252	5	100% 4f5d ^{3}H
65 639.95	65 535	105	4	91% 4f5d ^{3}G + 9% 4f5d ^{3}F
65 321.67	65 701	−379	2	61% 4f5d ^{1}D + 24% 4f5d ^{3}F + 12% 4f5d ^{3}D
66 518.01	66 644	−126	4	77% 4f5d ^{3}F + 16% 4f5d ^{1}G + 6% 4f5d ^{3}G
66 967.72	66 819	148	1	95% 4f5d ^{3}D
67 899.32	67 763	136	5	98% 4f5d ^{3}G
68 077.83	67 878	200	6	100% 4f5d ^{3}H
68 411.51	68 487	−76	2	87% 4f5d ^{3}D + 10% 4f5d ^{1}D
68 495.57	68 513	−18	3	69% 4f5d ^{3}D + 28% 4f5d ^{1}F
70 755.33	70 710	45	1	93% 4f5d ^{3}P + 5% 4f5d ^{1}P
70 842.93	70 771	72	0	100% 4f5d ^{3}P
71 724.77	71 785	−61	3	66% 4f5d ^{1}F + 31% 4f5d ^{3}D
72 185.10	72 385	−200	2	94% 4f5d ^{3}P + 5% 4f5d ^{1}D
75 265.66	75 315	−49	5	98% 4f5d ^{1}H
78 776.38	78 743	33	1	91% 4f5d ^{1}P + 6% 4f5d ^{3}P
100 258.48	100 258	0	2	100% 4f6s ^{3}F
100 543.85	100 545	−1	3	69% 4f6s ^{3}F + 31% 4f6s ^{1}F
103 271.38	103 272	−1	4	100% 4f6s ^{3}F
103 753.75	103 753	1	3	69% 4f6s ^{1}F + 31% 4f6s ^{3}F
193 330.5	193 403	−73	2	80% 4f6d ^{3}F + 19% 4f6d ^{1}D
193 601.8	193 457	145	4	63% 4f6d ^{3}H + 30% 4f6d ^{1}G
193 805.1	193 853	−48	3	84% 4f6d ^{3}G + 14% 4f6d ^{1}F
194 022.2	194 056	−34	4	36% 4f6d ^{3}G + 24% 4f6d ^{1}G + 31% 4f6d ^{3}H
	194 166		3	71% 4f6d ^{3}F + 16% 4f6d ^{1}F + 8% 4f6d ^{3}D
	194 617		2	50% 4f6d ^{3}D + 30% 4f6d ^{1}D + 11% 4f6d ^{3}F
	194 683		1	88% 4f6d ^{3}D + 11% 4f6d ^{1}P
194 777.2	194 757	20	5	78% 4f6d ^{3}H + 16% 4f6d ^{1}H + 6% 4f6d ^{3}G
	195 303		0	100% 4f6d ^{3}P
	195 336		1	80% 4f6d ^{3}P + 16% 4f6d ^{1}P
196 584.7	196 539	45	4	58% 4f6d ^{3}G + 20% 4f6d ^{3}F + 18% 4f6d ^{1}G
196 800.0	196 856	−56	4	68% 4f6d ^{3}F + 28% 4f6d ^{1}G
	196 942		3	32% 4f6d ^{3}D + 31% 4f6d ^{1}F + 29% 4f6d ^{3}F
197 103.7	197 161	−57	5	82% 4f6d ^{3}G + 12% 4f6d ^{3}H + 5% 4f6d ^{1}H
197 196.9	197 266	−69	6	100% 4f6d ^{3}H
	197 275		2	50% 4f6d ^{3}D + 34% 4f6d ^{1}D + 8% 4f6d ^{3}F
198 155.4	197 921	234	3	59% 4f6d ^{3}D + 37% 4f6d ^{1}F
	197 989		2	82% 4f6d ^{3}P + 16% 4f6d ^{1}D
198 304.7	198 411	−106	5	79% 4f6d ^{1}H + 12% 4f6d ^{3}G + 9% 4f6d ^{3}H
	199 103		1	72% 4f6d ^{1}P + 19% 4f6d ^{3}P + 8% 4f6d ^{3}D
	199 597		2	100% 4f7s ^{3}F
199 727.7	199 729	−1	3	62% 4f7s ^{3}F + 38% 4f7s ^{1}F

[a] From Martin *et al* (1978).
[b] *LS* composition in %. Only the first three main components larger than 5% are given.

in the semi-empirical parametric fit performed by Wyart *et al* (2005). This is essentially due to the fact that the latter authors considered a much more limited set of configurations ($4f^2$ + 4f6p + $5p^54f^3$) in their physical model.

4. Electric dipole transitions

Oscillator strengths (log gf) and transition probabilities (gA) computed in this work are reported in table 5 for a sample of Pr IV lines between 118 and 302 nm. This sample is limited to transitions involving the levels below 150 000 cm^{-1} for which log gf is greater than −2.0.

An argument for assessing the reliability of the present results can be obtained from isoelectronic comparisons, particularly from results obtained recently in Ce III (Biémont *et al* 2002), the HFR + CPOL model adopted in this work being the same as that chosen for this isoelectronic ion. More precisely, radiative lifetimes of nine states in Ce III, in the energy range from 48 267 to 54 550 cm^{-1}, have been measured by Li *et al* (2000) using the time-resolved laser-induced fluorescence (LIF) technique. The comparison

Table 5. Computed oscillator strengths and transition probabilities in Pr IV.

Wavelength[a] (nm)	Lower level[b] E (cm^{-1})	Parity	J	Upper level[b] E (cm^{-1})	Parity	J	log gf[c]	gA[c] (s^{-1})	gA[d] (s^{-1})
118.7761	61 171	(Odd)	4	145 363	(Even)	4	−1.37	2.04E + 08	
119.3707	61 171	(Odd)	4	144 943	(Even)	3	−1.88	6.15E + 07	
119.3964	61 171	(Odd)	4	144 925	(Even)	4	−1.05	4.15E + 08	7.6E + 08
120.1619	63 356	(Odd)	3	146 577	(Even)	2	−1.90	5.91E + 07	
121.2802	64 124	(Odd)	3	146 577	(Even)	2	−1.36	1.99E + 08	
122.2764	63 581	(Odd)	4	145 363	(Even)	4	−1.55	1.26E + 08	
122.3983	63 581	(Odd)	4	145 281	(Even)	5	−1.86	6.09E + 07	
122.5687	63 356	(Odd)	3	144 943	(Even)	3	−1.76	7.69E + 07	
122.6397	61 457	(Odd)	2	142 997	(Even)	1	−0.81	6.84E + 08	
122.8586	61 171	(Odd)	4	142 566	(Even)	4	−0.42	1.69E + 09	
122.9067	63 581	(Odd)	4	144 943	(Even)	3	−1.63	1.04E + 08	
122.9336*	63 581	(Odd)	4	144 925	(Even)	4	−1.59	1.13E + 08	1.4E + 08
123.0691	65 322	(Odd)	2	146 577	(Even)	2	−0.60	1.09E + 09	
123.7600	64 124	(Odd)	3	144 925	(Even)	4	−1.68	9.20E + 07	1.0E + 08
124.8081	65 239	(Odd)	5	145 363	(Even)	4	−1.63	1.02E + 08	
124.9353	65 239	(Odd)	5	145 281	(Even)	5	−1.01	4.15E + 08	
125.3191	61 457	(Odd)	2	141 254	(Even)	3	−1.66	9.16E + 07	
125.4347*	65 640	(Odd)	4	145 363	(Even)	4	−1.24	2.45E + 08	
125.5637	65 640	(Odd)	4	145 281	(Even)	5	−1.07	3.59E + 08	
125.5943	65 322	(Odd)	2	144 943	(Even)	3	−1.62	1.02E + 08	
125.6136	66 968	(Odd)	1	146 577	(Even)	2	−1.52	1.28E + 08	
126.0981*	65 640	(Odd)	4	144 943	(Even)	3	−1.26	2.31E + 08	
126.2471	63 356	(Odd)	3	142 566	(Even)	4	−1.38	1.76E + 08	
126.4936	61 171	(Odd)	4	140 226	(Even)	4	−1.45	1.49E + 08	3.4E + 08
126.6062	63 581	(Odd)	4	142 566	(Even)	4	−1.00	4.18E + 08	
126.6218	63 356	(Odd)	3	142 332	(Even)	2	−0.96	4.62E + 08	
126.8319	66 518	(Odd)	4	145 363	(Even)	4	−0.77	7.07E + 08	
126.9633	66 518	(Odd)	4	145 281	(Even)	5	−1.15	2.95E + 08	
127.0584	61 171	(Odd)	4	139 875	(Even)	3	−1.18	2.71E + 08	4.1E + 08
127.5103	66 518	(Odd)	4	144 943	(Even)	3	−0.10	3.26E + 09	
127.5223	61 457	(Odd)	2	139 875	(Even)	3	−1.80	6.44E + 07	4.0E + 07
127.5395	66 518	(Odd)	4	144 925	(Even)	4	−0.26	2.27E + 09	3.0E + 09
127.8646	64 124	(Odd)	3	142 332	(Even)	2	−0.28	2.13E + 09	
127.9337	68 412	(Odd)	2	146 577	(Even)	2	−0.52	1.23E + 09	
128.0714	68 496	(Odd)	3	146 577	(Even)	2	−1.46	1.41E + 08	
128.7405*	65 322	(Odd)	2	142 997	(Even)	1	−0.87	5.42E + 08	
128.7442	63 581	(Odd)	4	141 254	(Even)	3	0.07	4.70E + 09	
129.0933	67 899	(Odd)	5	145 363	(Even)	4	0.08	4.85E + 09	
129.2295	67 899	(Odd)	5	145 281	(Even)	5	−0.07	3.40E + 09	
129.3220	65 239	(Odd)	5	142 566	(Even)	4	0.10	5.09E + 09	
129.5282	68 078	(Odd)	6	145 281	(Even)	5	0.43	1.07E + 10	
129.6504	64 124	(Odd)	3	141 254	(Even)	3	−0.57	1.06E + 09	
129.8264	67 899	(Odd)	5	144 925	(Even)	4	−1.29	2.05E + 08	1.3E + 09
129.8535	65 322	(Odd)	2	142 332	(Even)	2	−0.38	1.65E + 09	
129.9950	65 640	(Odd)	4	142 566	(Even)	4	−1.06	3.48E + 08	
130.0899	63 356	(Odd)	3	140 226	(Even)	4	−1.50	1.25E + 08	2.2E + 08
130.0946*	68 496	(Odd)	3	145 363	(Even)	4	−1.13	2.90E + 08	
130.4712	63 581	(Odd)	4	140 226	(Even)	4	−0.67	8.51E + 08	1.1E + 09
130.6860	63 356	(Odd)	3	139 875	(Even)	3	−1.20	2.47E + 08	6.8E + 08
130.8085	68 496	(Odd)	3	144 943	(Even)	3	−0.82	5.85E + 08	
130.9657*	63 356	(Odd)	3	139 712	(Even)	2	−0.30	1.95E + 09	
131.0708	63 581	(Odd)	4	139 875	(Even)	3	−1.53	1.16E + 08	2.7E + 08
131.4021	64 124	(Odd)	3	140 226	(Even)	4	−0.97	4.20E + 08	4.1E + 08
131.4961	66 518	(Odd)	4	142 566	(Even)	4	−0.54	1.11E + 09	
131.5279	66 968	(Odd)	1	142 997	(Even)	1	−0.57	1.04E + 09	
131.6961	65 322	(Odd)	2	141 254	(Even)	3	−0.90	4.78E + 08	
131.8879	70 755	(Odd)	1	146 577	(Even)	2	−1.47	1.30E + 08	
132.0101	64 124	(Odd)	3	139 875	(Even)	3	−0.26	2.09E + 09	1.8E + 09
132.0699	61 457	(Odd)	2	137 175	(Even)	2	−0.15	2.68E + 09	
132.1355	61 171	(Odd)	4	136 851	(Even)	3	0.10	4.76E + 09	
132.2506	65 640	(Odd)	4	141 254	(Even)	3	−1.65	8.65E + 07	
132.6376	61 457	(Odd)	2	136 851	(Even)	3	−0.74	6.88E + 08	
133.3573	65 239	(Odd)	5	140 226	(Even)	4	−0.06	3.29E + 09	3.8E + 09

Table 5. (Continued.)

Wavelength[a]	Lower level[b]			Upper level[b]				gA[c]	gA[d]
(nm)	E (cm^{-1})	Parity	J	E (cm^{-1})	Parity	J	log gf[c]	(s^{-1})	(s^{-1})
133.5963	71 725	(Odd)	3	146 577	(Even)	2	−0.45	1.32E + 09	
133.9288	67 899	(Odd)	5	142 566	(Even)	4	−0.41	1.44E + 09	
134.0738	65 640	(Odd)	4	140 226	(Even)	4	−0.14	2.69E + 09	2.9E + 09
134.0738	68 412	(Odd)	2	142 997	(Even)	1	−1.22	2.24E + 08	
134.1315	65 322	(Odd)	2	139 875	(Even)	3	−1.53	1.08E + 08	2.5E + 08
134.4229	72 185	(Odd)	2	146 577	(Even)	2	−0.77	6.27E + 08	
134.4264*	65 322	(Odd)	2	139 712	(Even)	2	−1.55	1.03E + 08	
134.7066	65 640	(Odd)	4	139 875	(Even)	3	−0.41	1.43E + 09	2.2E + 09
135.0068*	68 496	(Odd)	3	142 566	(Even)	4	−1.06	3.15E + 08	
135.2811	68 412	(Odd)	2	142 332	(Even)	2	−0.78	6.01E + 08	
135.4350	68 496	(Odd)	3	142 332	(Even)	2	−0.81	5.64E + 08	
135.4663	63 356	(Odd)	3	137 175	(Even)	2	−0.47	1.24E + 09	
135.6705	66 518	(Odd)	4	140 226	(Even)	4	−1.18	2.38E + 08	1.2E + 08
135.7989	71 725	(Odd)	3	145 363	(Even)	4	−0.94	4.17E + 08	
136.0639	63 356	(Odd)	3	136 851	(Even)	3	−0.22	2.19E + 09	
136.3190	66 518	(Odd)	4	139 875	(Even)	3	−1.50	1.14E + 08	3.0E + 08
136.4811	63 581	(Odd)	4	136 851	(Even)	3	−0.85	5.10E + 08	
136.5773	71 725	(Odd)	3	144 943	(Even)	3	−0.13	2.65E + 09	
136.6107	71 725	(Odd)	3	144 925	(Even)	4	−1.07	3.04E + 08	8.0E + 08
136.8895	64 124	(Odd)	3	137 175	(Even)	2	−1.40	1.41E + 08	
137.4414	68 496	(Odd)	3	141 254	(Even)	3	−0.43	1.31E + 09	
137.4414	72 185	(Odd)	2	144 943	(Even)	3	−0.22	2.13E + 09	
137.4682*	66 968	(Odd)	1	139 712	(Even)	2	−1.26	1.94E + 08	
138.2617	67 899	(Odd)	5	140 226	(Even)	4	−0.44	1.28E + 09	1.7E + 09
138.4234	70 755	(Odd)	1	142 997	(Even)	1	−0.67	7.46E + 08	
138.5914	70 843	(Odd)	0	142 997	(Even)	1	−0.68	7.30E + 08	
139.4106	68 496	(Odd)	3	140 226	(Even)	4	−0.68	7.21E + 08	8.1E + 08
139.7110	70 755	(Odd)	1	142 332	(Even)	2	−0.52	1.05E + 09	
139.8029	65 322	(Odd)	2	136 851	(Even)	3	−1.63	7.88E + 07	
139.9313	68 412	(Odd)	2	139 875	(Even)	3	−0.36	1.50E + 09	1.8E + 09
140.0961	68 496	(Odd)	3	139 875	(Even)	3	−0.54	9.77E + 08	1.2E + 09
141.2182	72 185	(Odd)	2	142 997	(Even)	1	−1.97	3.58E + 07	
142.4357	66 968	(Odd)	1	137 175	(Even)	2	−0.57	8.76E + 08	
142.5587	72 185	(Odd)	2	142 332	(Even)	2	−1.23	1.92E + 08	
142.6594	75 266	(Odd)	5	145 363	(Even)	4	−0.39	1.35E + 09	
142.8253	75 266	(Odd)	5	145 281	(Even)	5	−1.89	4.22E + 07	
143.5555	75 266	(Odd)	5	144 925	(Even)	4	0.03	3.45E + 09	5.6E + 09
143.8244	71 725	(Odd)	3	141 254	(Even)	3	−1.24	1.87E + 08	
144.7829	72 185	(Odd)	2	141 254	(Even)	3	−1.33	1.49E + 08	
145.0190*	70 755	(Odd)	1	139 712	(Even)	2	−1.57	8.53E + 07	
146.2942	68 496	(Odd)	3	136 851	(Even)	3	−1.18	2.04E + 08	
146.7342	71 725	(Odd)	3	139 875	(Even)	3	−1.52	9.28E + 07	1.2E + 08
147.4913	78 776	(Odd)	1	146 577	(Even)	2	−0.25	1.75E + 09	
147.7321	72 185	(Odd)	2	139 875	(Even)	3	−0.92	3.66E + 08	4.1E + 08
148.5880	75 266	(Odd)	5	142 566	(Even)	4	−0.64	6.83E + 08	
150.5578	70 755	(Odd)	1	137 175	(Even)	2	−1.33	1.38E + 08	
152.0977	2152	(Even)	5	67 899	(Odd)	5	−1.64	6.61E + 07	
152.3462	0	(Even)	4	65 640	(Odd)	4	−1.72	5.44E + 07	
153.0352	9921	(Even)	4	75 266	(Odd)	5	−1.99	2.96E + 07	
153.5483*	71 725	(Odd)	3	136 851	(Even)	3	−1.47	9.70E + 07	
153.9404	75 266	(Odd)	5	140 226	(Even)	4	−0.62	6.73E + 08	8.1E + 08
155.3617	2152	(Even)	5	66 518	(Odd)	4	−1.51	8.60E + 07	
155.9489	0	(Even)	4	64 124	(Odd)	3	−1.50	8.64E + 07	
157.0133	4389	(Even)	6	68 078	(Odd)	6	−0.79	4.36E + 08	
157.2804	0	(Even)	4	63 581	(Oodd)	4	−1.49	8.63E + 07	
157.3435*	78 776	(Odd)	1	142 332	(Even)	2	−1.56	7.45E + 07	
157.4547	4389	(Even)	6	67 899	(Odd)	5	−0.18	1.77E + 09	
157.5101	2152	(Even)	5	65 640	(Odd)	4	−0.31	1.32E + 09	
157.6911	4997	(Even)	2	68 412	(Odd)	2	−1.65	5.98E + 07	
157.8381	0	(Even)	4	63 356	(Odd)	3	−0.40	1.06E + 09	
158.5100	2152	(Even)	5	65 239	(Odd)	5	−0.88	3.45E + 08	
161.0816	6415	(Even)	3	68 496	(Odd)	3	−1.68	5.40E + 07	
161.3002	6415	(Even)	3	68 412	(Odd)	2	−0.86	3.59E + 08	

Table 5. (Continued.)

Wavelength[a] (nm)	Lower level[b] E (cm^{-1})	Parity	J	Upper level[b] E (cm^{-1})	Parity	J	log gf[c]	gA[c] (s^{-1})	gA[d] (s^{-1})
161.3654	4997	(Even)	2	66 968	(Odd)	1	−0.95	2.87E + 08	
161.8032	9921	(Even)	4	71 725	(Odd)	3	−0.49	8.23E + 08	
162.2305	6855	(Even)	4	68 496	(Odd)	3	−0.57	6.84E + 08	
162.7552	17 334	(Even)	2	78 776	(Odd)	1	−1.20	1.60E + 08	
162.7911	2152	(Even)	5	63 581	(Odd)	4	−1.70	4.99E + 07	
163.4770	0	(Even)	4	61 171	(Odd)	4	−1.10	1.99E + 08	
163.8151	6855	(Even)	4	67 899	(Odd)	5	−1.61	6.11E + 07	
164.1082*	78 776	(Odd)	1	139 712	(Even)	2	−1.98	2.60E + 07	
167.6084	6855	(Even)	4	66 518	(Odd)	4	−1.20	1.51E + 08	
168.8489	6415	(Even)	3	65 640	(Odd)	4	−1.45	8.27E + 07	
169.7611	6415	(Even)	3	65 322	(Odd)	2	−1.39	9.46E + 07	
170.1112	6855	(Even)	4	65 640	(Odd)	4	−1.90	2.88E + 07	
171.2368*	78 776	(Odd)	1	137 175	(Even)	2	−1.60	5.76E + 07	
171.3526	4997	(Even)	2	63 356	(Odd)	3	−1.56	6.17E + 07	
173.2859	6415	(Even)	3	64 124	(Odd)	3	−0.79	3.57E + 08	
174.6158	6855	(Even)	4	64 124	(Odd)	3	−1.75	3.88E + 07	
176.2861	6855	(Even)	4	63 581	(Odd)	4	−1.06	1.85E + 08	
176.6883	9921	(Even)	4	66 518	(Odd)	4	−0.80	3.40E + 08	
177.1137	4997	(Even)	2	61 457	(Odd)	2	−0.93	2.53E + 08	
179.8058	23 161	(Even)	2	78 776	(Odd)	1	−1.82	3.14E + 07	
183.8573	17 334	(Even)	2	71 725	(Odd)	3	−1.87	2.65E + 07	
184.1082	6855	(Even)	4	61 171	(Odd)	4	−1.27	1.05E + 08	
186.3615	9921	(Even)	4	63 581	(Odd)	4	−1.82	2.90E + 07	
187.1931	17 334	(Even)	2	70 755	(Odd)	1	−1.81	2.97E + 07	
188.4870	22 212	(Even)	6	75 266	(Odd)	5	−0.12	1.43E + 09	
195.1234	9921	(Even)	4	61 171	(Odd)	4	−1.66	3.90E + 07	
195.4609	17 334	(Even)	2	68 496	(Odd)	3	−1.56	4.81E + 07	
195.7825	17 334	(Even)	2	68 412	(Odd)	2	−1.79	2.82E + 07	
199.2924	22 007	(Even)	1	72 185	(Odd)	2	−1.45	5.95E + 07	
202.5062	21 390	(Even)	0	70 755	(Odd)	1	−1.57	4.40E + 07	
203.9150	23 161	(Even)	2	72 185	(Odd)	2	−0.87	2.17E + 08	
204.7047	22 007	(Even)	1	70 843	(Odd)	0	−1.47	5.40E + 07	
205.0726	22 007	(Even)	1	70 755	(Odd)	1	−1.54	4.53E + 07	
205.8485	23 161	(Even)	2	71 725	(Odd)	3	−1.49	5.10E + 07	
208.3228	17 334	(Even)	2	65 322	(Odd)	2	−0.97	1.66E + 08	
210.0418	23 161	(Even)	2	70 755	(Odd)	1	−1.52	4.55E + 07	
215.4313	22 007	(Even)	1	68 412	(Odd)	2	−1.39	5.87E + 07	
219.3370	21 390	(Even)	0	66 968	(Odd)	1	−1.71	2.67E + 07	
220.5131	23 161	(Even)	2	68 496	(Odd)	3	−1.55	3.85E + 07	
225.1584*	100 544	(Odd)	3	144 943	(Even)	3	−1.06	1.14E + 08	
225.250	100 544	(Odd)	3	144 925	(Even)	4	−0.52	3.91E + 08	2.7E + 08
226.5696	17 334	(Even)	2	61 457	(Odd)	2	−1.75	2.34E + 07	
233.446	103 754	(Odd)	3	146 577	(Even)	2	0.26	2.23E + 09	
233.908	100 258	(Odd)	2	142 997	(Even)	1	0.04	1.34E + 09	
237.505	103 271	(Odd)	4	145 363	(Even)	4	−0.10	9.55E + 08	
237.609	100 258	(Odd)	2	142 332	(Even)	2	0.03	1.28E + 09	
237.898	100 544	(Odd)	3	142 566	(Even)	4	0.47	3.47E + 09	
237.966	103 271	(Odd)	4	145 281	(Even)	5	0.61	4.81E + 09	
239.232	100 544	(Odd)	3	142 332	(Even)	2	−0.15	8.30E + 08	
239.897	103 271	(Odd)	4	144 943	(Even)	3	0.02	1.23E + 09	
240.000	103 271	(Odd)	4	144 925	(Even)	4	−0.49	3.72E + 08	1.6E + 09
240.259	103 754	(Odd)	3	145 363	(Even)	4	−0.12	8.76E + 08	
242.707	103 754	(Odd)	3	144 943	(Even)	3	0.15	1.60E + 09	
242.813	103 754	(Odd)	3	144 925	(Even)	4	0.13	1.51E + 09	3.1E + 09
243.857	100 258	(Odd)	2	141 254	(Even)	3	0.08	1.35E + 09	
245.564	100 544	(Odd)	3	141 254	(Even)	3	−0.12	8.29E + 08	
251.9272*	100 544	(Odd)	3	140 226	(Even)	4	−1.01	1.03E + 08	1.0E + 08
252.344	100 258	(Odd)	2	139 875	(Even)	3	−1.01	1.01E + 08	9.0E + 07
254.1731*	100 544	(Odd)	3	139 875	(Even)	3	−0.86	1.43E + 08	1.8E + 08
254.411	103 271	(Odd)	4	142 566	(Even)	4	−0.66	2.25E + 08	
255.2342*	100 544	(Odd)	3	139 712	(Even)	2	−0.75	1.82E + 08	
257.5739*	103 754	(Odd)	3	142 566	(Even)	4	−1.42	3.77E + 07	
263.197	103 271	(Odd)	4	141 254	(Even)	3	−0.96	1.06E + 08	

Table 5. (Continued.)

Wavelength[a] (nm)	Lower level[b] E (cm^{-1})	Parity	J	Upper level[b] E (cm^{-1})	Parity	J	log gf[c]	gA[c] (s^{-1})	gA[d] (s^{-1})
266.585	103 754	(Odd)	3	141 254	(Even)	3	−0.60	2.35E + 08	
270.519	103 271	(Odd)	4	140 226	(Even)	4	0.27	1.68E + 09	2.2E + 09
270.801	100 258	(Odd)	2	137 175	(Even)	2	−0.14	6.61E + 08	
272.911	100 544	(Odd)	3	137 175	(Even)	2	−0.11	7.01E + 08	
273.112	103 271	(Odd)	4	139 875	(Even)	3	0.03	9.63E + 08	1.3E + 09
273.201	100 258	(Odd)	2	136 851	(Even)	3	−0.01	8.68E + 08	
274.100	103 754	(Odd)	3	140 226	(Even)	4	0.00	8.81E + 08	1.2E + 09
275.347	100 544	(Odd)	3	136 851	(Even)	3	0.11	1.15E + 09	
276.760	103 754	(Odd)	3	139 875	(Even)	3	−0.07	7.32E + 08	1.1E + 09
302.052	103 754	(Odd)	3	136 851	(Even)	3	−1.37	3.15E + 07	

[a] Air (above 200 nm) and vacuum (below 200 nm) wavelengths observed by Sugar (1965). Starred values were deduced from experimental energy levels compiled by Martin *et al* (1978).
[b] From Martin *et al* (1978).
[c] This work.
[d] From Wyart *et al* (2005).

Table 6. Transition probabilities for forbidden lines within the 4f^2 ground-state configuration of Pr IV.

Air wavelength[a] (nm)	Transition	Type[b]	gA (This work) (s^{-1})	gA (Other)[c](s^{-1})
450.0902	$^3H_4 - {}^1I_6$	E2	1.63E-02	2.11E-02
498.3791	$^3H_5 - {}^1I_6$	M1	6.42E + 00	6.29E + 00
550.3866	$^3F_2 - {}^3P_2$	M1 + E2	6.84E-02	6.49E-02
560.9344	$^3H_6 - {}^1I_6$	M1	6.31E + 00	6.14E + 00
587.6972	$^3F_2 - {}^3P_1$	M1 + E2	1.82E-01	9.11E-02
597.0146	$^3F_2 - {}^3P_2$	M1 + E2	8.31E-01	8.00E-01
609.8402	$^3F_2 - {}^3P_0$	E2	1.10E-01	2.78E-03
613.1068	$^3F_4 - {}^3P_2$	E2	1.61E-01	3.06E-02
641.1683	$^3F_3 - {}^3P_1$	E2	1.67E-01	1.94E-02
650.9979	$^3F_4 - {}^1I_6$	E2	2.50E-02	2.87E-02
755.1150	$^1G_4 - {}^3P_2$	E2	8.68E-02	1.67E-02
810.2958	$^3F_2 - {}^1D_2$	M1	3.82E + 00	3.69E + 00
813.4261	$^1G_4 - {}^1I_6$	E2	2.28E-02	2.57E-02
915.5709	$^3F_3 - {}^1D_2$	M1	5.01E + 00	4.77E + 00
953.9696	$^3F_4 - {}^1D_2$	E2	2.31E-02	4.73E-03
1007.6623	$^3H_4 - {}^1G_4$	M1	1.56E + 00	1.51E + 00
1286.7901	$^3H_5 - {}^1G_4$	M1	1.80E + 00	1.76E + 00
1458.4438	$^3H_4 - {}^3F_4$	M1	1.39E + 00	1.37E + 00
1558.3623	$^3H_4 - {}^3F_3$	M1	4.27E-02	4.39E-02
1715.9100	$^1D_2 - {}^3P_2$	M1	3.09E + 00	
2125.8758	$^3H_5 - {}^3F_4$	M1	4.49E-01	
2139.3369	$^1D_2 - {}^3P_1$	M1	5.43E-01	
2851.4754	$^3F_3 - {}^1G_4$	M1	2.70E + 00	
3260.1682	$^3F_4 - {}^1G_4$	M1	1.97E + 00	
4469.0540	$^3H_5 - {}^3H_6$	M1	3.22E + 00	
4645.3791	$^3H_4 - {}^3H_5$	M1	2.72E + 00	2.60E + 00
7047.1330	$^3F_2 - {}^3F_3$	M1	2.72E +00	
8669.5351	$^3P_1 - {}^3P_2$	M1	1.16E-01	
16 185.9865	$^3P_0 - {}^3P_1$	M1	1.40E-02	
22 746.4098	$^3F_3 - {}^3F_4$	M1	1.36E-02	

[a] Deduced from experimental levels (Martin *et al* 1978).
[b] Contributions larger than 1%.
[c] Dodson and Zia (2012).

of these accurate laboratory measurements with the HFR + CPOL calculations of Biémont *et al* (2002) has shown that the computed values were in excellent agreement (in all cases within the experimental error bars, i.e. 5%) with the experimental results. Consequently, a similar accuracy can also be expected for the radiative parameters obtained in Pr IV, at least for the most intense transitions.

On the theoretical side, some data for electric dipole radiation in Pr IV were published by Sen and Puri (1989) and Stanek and Migdalek (2004) who limited their investigations to the $6s^2\ {}^1S_0$–$6s6p\ {}^{1,3}P_1$ transitions (not yet observed experimentally). When comparing our results for ${}^1S_0$–${}^1P_1$ (log gf = 0.30) and ${}^1S_0$–${}^3P_1$ (log gf = −2.21), we found a rather good agreement with those obtained by Stanek and Migdalek (2004) using a relativistic multiconfiguration Dirac–Fock with the CPOL model (log gf = 0.36 and −2.38, respectively), a larger discrepancy being observed with the local spin density result of Sen and Puri (1989) for the ${}^1S_0$–${}^1P_1$ transition (log gf = 0.42). However, it is worth noting that the results presented by those authors were more of qualitative than quantitative character due to the very limited treatment of intravalence and core-valence correlations. Transition probabilities for some 4f5d–4f6p and 4f6s—4f6p lines in the Pr IV spectrum were also computed by Wyart *et al* (2005) using a semi-empirical HFR approach. Their values are reported in table 5 for comparison. We can see that our results agree with those from Wyart *et al* within a factor of 2 on average. The main reason for this discrepancy is of course related to the different physical models used, the one considered in our work (including a large set of interacting configurations plus CPOL effects) is much more extended than the calculation of Wyart *et al* carried out with a very limited number of configurations.

5. Forbidden transitions

Part of the unusual spectroscopic properties of triply ionized lanthanides results from the shielding of the 4f orbitals by the filled $5s^2$ and $5p^6$ sub-shells. Each of these elements has very characteristic emission lines in the visible and near infrared range due to 4f → 4f transitions. These transitions, forbidden by the electric dipole selection rules, result in very long lived excited states, with typical luminescence lifetimes on the micro- to millisecond timescale. These long lifetimes facilitate 'time-gated' emission experiments which lead to drastic improvement of signal-to-noise ratios compared with more traditional steady-state measurements by removing short lived emission and scattered excitation. For this reason, transition probabilities for magnetic dipole (M1) and electric quadrupole (E2) lines within the $4f^2$ configuration of Pr IV were also calculated in this work.

Our results are presented in table 6 for lines with gA-values greater than 0.01 s^{-1}. They are also compared, in the same table, with the data recently published by Dodson and Zia (2012). These latter authors obtained emission rates for some M1 and E2 transitions in all triply ionized lanthanides 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. As observed in table 6, their results are generally in very good agreement (within a few per cent) with our transition probabilities if we except the ${}^3P$–${}^3F$, ${}^1G$–${}^3P$ and ${}^1D$–${}^3F$ electric quadrupole lines for which larger discrepancies are observed.

6. Conclusion

Oscillator strengths and transition probabilities for allowed and forbidden lines in triply ionized praseodymium 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 the excellent agreement observed between similar calculations and accurate laser lifetime measurements performed in the isoelectronic ion Ce III. In the case of forbidden lines, our results have been found to be in good agreement with theoretical data recently published if we except a few electric quadrupole transitions.

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