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Abstract
Radiative lifetime measurements have been performed, with a time-resolved laser-induced fluorescence technique, for 18 even-parity levels of Pr I and 15 odd-parity levels of Nd I. The new results are compared with the few experimental data available in the literature and good agreement is found. However, fragmentary knowledge of the spectra prevents reliable calculation of branching fractions and calls for additional laboratory efforts in order to provide the astrophysicists with reliable transition probabilities needed for investigating the magnetic fields in chemically peculiar stars.

1. Introduction

Radiative parameters of spectral lines (i.e. oscillator strengths or transition probabilities), particularly of rare-earth ions, are needed in astrophysics for investigating the composition of chemically peculiar (CP) stars which are characterized by strong overabundances of the lanthanides when compared to the solar system values. Obtaining significant maps of magnetic fields and abundance inhomogeneities in such stars requires simultaneous observation of stellar spectra in different spectral ranges. Infrared and visible observations of CP stars are, in that respect, complementary in relation to the fact that the spectral lines in these different wavelength ranges allow us to probe different depths in stellar atmospheres and to shed some light on the relations between inhomogeneities and abundance anomalies. When strong magnetic fields are present, high resolution observations in the near infrared region allow us to resolve many Zeeman splittings and to impose some additional constraints on the modelling of the magnetic field topology. In this way, they appear complementary to magnetic field observations with spectro-polarimetric techniques carried out in the visible region. For such purposes, the lanthanide atoms and ions are particularly suited for visible and infrared studies of stellar spectra but the relevant atomic data (wavelengths or energy levels, transition

probabilities, oscillator strengths, lifetime values, etc) are frequently missing. Keeping this lack of data in mind, it is obvious that additional laboratory effort for such atoms and ions is needed and timely. The forthcoming VLT/VLTI (very large telescope interferometer) instruments AMBER and CRIRES will indeed open new and unprecedented prospects for the investigation of magnetic fields in CP stars and will provide useful information about the role of magnetism regarding ion migration across the stellar surface and regarding the chemical stratification.

In that context, the purpose of the present work is to contribute to this effort and to provide new information regarding the radiative properties of two neutral lanthanides (praseodymium and neodymium) for which the available information is still very limited in the literature (see, e.g., Biémont and Quinet 2003). Obtaining radiative data of astrophysical interest for infrared or visible transitions (i.e. transition probabilities or oscillator strengths) is naturally dependent upon the combination of lifetime measurements and branching fraction determinations (either by considering experimental approaches or theoretical calculations). The second approach has failed in the present work (see below) and, consequently, it calls for further laboratory measurements regarding both term analysis and branching fraction measurements. However, as outlined in the following sections, laboratory analyses have to face many 'technical' difficulties in view of the complexity of the spectra involved.

Pr I has one isotope, ^{141}Pr, but it shows hyperfine structure ($I = 5/2$). Nd I has seven stable isotopes: ^{142}Nd (27.2%), ^{143}Nd (12.2%), ^{144}Nd (23.8%), ^{145}Nd (8.3%), ^{146}Nd (17.2), ^{148}Nd (5.7%) and ^{150}Nd (5.6%). The nuclear spin of the isotopes 143 and 145 is 7/2, these two odd-mass stable isotopes being consequently affected by hyperfine structure (Lu *et al* 1991, Ma *et al* 1997, Li *et al* 2000).

The ground-state level of Pr I is $4f^3 6s^2$ $^4I_{9/2}$ and that of Nd I is $4f^4 6s^2$ $^5I_4$. The energy levels of Pr I, as compiled by NIST (Martin *et al* 1978; http://physics.nist.gov/cgi-bin/ AtData/main_asd), belong to the configurations $4f^3 6s^2$, $4f^2 5d 6s^2$, $4f^2 5d^2 6s$, $4f^3 5d 6s$, $4f^3 6s 6p$, $4f^2 5d 6s 6p$, $4f^2 6s^2 6p$, $4f^2 5d^2 6p$ and $4f^3 5d 6p$ but many of the suggested assignments are dubious. Fifteen additional levels, most of them strongly perturbed, have been assigned by Ginibre (1981) to the configurations $4f^2 5d 6s^2$ and $4f^2 5d^2 6s$. Recently, new levels of Pr I (with no labels) have been proposed in the literature (Ruczkowski *et al* 2003) but in the framework of a hyperfine structure analysis; consequently, further progress in the analysis of the spectrum of this element is expected in the near future. The experimentally determined energy levels of Nd I, taken from the NIST compilation, belong to the configurations $4f^4 6s^2$, $4f^3 5d 6s^2$, $4f^4 5d 6s$, $4f^3 5d^2 6s$, $4f^4 6s 6p$, $4f^3 5d 6s 6p$, $4f^4 5d^2$, $4f^4 5d 6p$, $4f^3 5d^2 6p$ and $4f^4 6s 7s$. It should also be emphasized that the designation of many levels is still uncertain and that most of them show strong configuration interaction mixings. Seven assigned even levels and five unassigned odd levels have been determined by Aufmuth *et al* (1992). We are not aware of a more recent term analysis in Nd I. In addition, it must be emphasized that a large number of levels in both atoms (Pr I and Nd I) are not yet assigned.

The Pr I and Nd I transition probabilities or radiative lifetimes published so far are still very sparse and call also for many additional efforts.

In Pr I, 14 lifetime values for even-parity levels, between 19 123 and 24 195 cm^{-1}, have been reported by Gorshkov and Komarovskii (1985) using a multichannel delayed-coincidence method. These results are quoted in the compilation of Blagoev and Komarovskii (1994). More recently, Song *et al* (1998) have measured 14 additional long-lived levels between 16 887 and 28 501 cm^{-1} using thermal atomic beam with single-step pulsed laser excitation. Transition probabilities or oscillator strengths have been reviewed by Komarovskii (1991) and the resonance transitions have been considered by Doidge (1995a, 1995b, 1996) in his compilation.

Table 1. Levels measured in Pr I and the corresponding excitation schemes.

						Lifetime (ns)	
E (cm^{-1})[a]	J	Origin	Excitation λ (nm)$_{vac}$	Observed λ (nm)$_{vac}$	Laser mode[b]	This work	Previous[c]
19 474.75	11/2	0.0	513.485	513	$2\omega + 3S$	26(2)	26(0.6)
19 820.69	11/2	0.0	504.523	505	$2\omega + 3S$	58(4)	57(3)
19 861.89	11/2	0.0	503.476	503	$\omega + A$	83(7)	82(4)
20 089.26	11/2	0.0	497.778	498	$\omega + A$	76(7)	
20 154.60	9/2	0.0	496.164	496	$\omega + A$	104(9)	
20 171.75	11/2	0.0	495.742	496	$\omega + A$	232(25)	
20 190.85	9/2	1376.6	531.512	495	$2\omega + 3S$	12.2(0.7)	12(1.2)
20 344.28	9/2	0.0	491.538	492	$\omega + A$	34(2)	34(3)
20 827.15	13/2	1376.6	514.124	514	$2\omega + 3S$	69(5)	
22 272.48	7/2	0.0	448.984	449	$2\omega + 2S$	303(35)	
22 509.40	9/2	0.0	444.259	473	$2\omega + 2S$	30(2)	29(2.5)
22 566.39	7/2	0.0	443.136	443	$2\omega + 2S$	353(40)	
22 694.60	9/2	0.0	440.633	469	$2\omega + 2S$	168(18)	
22 761.90	9/2	0.0	439.331	468	$2\omega + 2S$	55(5)	
22 921.34	9/2	0.0	436.274	464	$2\omega + 2S$	71(6)	
22 924.39	9/2	0.0	436.217	464	$2\omega + 2S$	29(2)	
23 242.13	9/2	0.0	430.253	457	$2\omega + 2S$	146(16)	
24 136.57	11/2	1376.6	439.368	470	$2\omega + 2S$	17.7(1.0)	

[a] From the NIST compilation (http://physics.nist.gov/cgi-bin/AtData/main_asd).
[b] ω and 2ω designate the fundamental frequency and the second harmonic of the dye laser; A, $2S$ and $3S$ represent the first-order anti-Stokes, the second- and the third-order Stokes components.
[c] Gorshkov and Komarovskii (1985): pulsed-electron delayed coincidence.

In Nd I, according to the compilation of Blagoev and Komarovskii (1994), 18 lifetimes have been measured by Marek and Stahnke (1980) in the energy range 16 979–24 121 cm^{-1}, using the delayed-coincidence method. Additional results for 38 levels, in the 17 787–25 662 cm^{-1} energy range, were obtained by Gorshkov *et al* (1982) using the same technique but with a different excitation mode. Although the agreement between the two sets of results is generally within the error bars, there are a few notable discrepancies. Transition probabilities have been determined by Corliss and Bozman (1962) (arc measurements), Penkin and Komarovskii (1973) (relative values), Penkin and Komarovskii (1976) and Komarovskii (1991) (review) and a critical review of the resonance lines is given by Doidge (1995a, 1995b, 1996).

In the present work, as a further contribution to our knowledge of the radiative properties of these two atoms, new lifetimes have been measured by the time-resolved laser-induced fluorescence technique using an experimental setup at the Lund Laser Centre in Sweden. They concern 18 even-parity levels of Pr I and 15 odd-parity levels of Nd I. For most of them, there were no data previously available.

2. Experimental lifetime measurements

In the present experiment, 33 radiative lifetimes of Pr I and Nd I levels, in the energy ranges 19 474–24 136 cm^{-1} and 18 741–27 130 cm^{-1}, respectively, have been measured with the method of selective single-step excitation using a tunable pulsed laser radiation and a time-resolved detection of the emitted fluorescence by a fast detection system. The levels under investigation were obtained from the NIST atomic spectra database available on the web at http://www.physics.nist.gov/cgi-bin/AtData/levels_form. They are reported in tables 1 and 2 with the relevant excitation schemes.

Table 2. Levels measured in Nd I and the corresponding excitation schemes.

			Excitation	Observed	Laser[b]	Lifetime (ns)	
E (cm^{-1})[a]	J	Origin	λ (nm)$_{vac}$	λ (nm)$_{vac}$	mode	This work	Previous[c,d]
18 741.337	4	0.0	533.579	568	$2\omega + 3S$	83(5)	77.4(5.4)[c], 85(7)[d]
20 300.875	5	0.0	492.590	493	$\omega + AS$	12.7(1.0)	11.8(0.8)[c] 11(1)[d]
		1128.056	521.572		$2\omega + 3S$		
22 367.268	5	0.0	447.081	471	$2\omega + 2S$	46(3)	45(3)[d]
22 490.970	3	0.0	444.622	445	$2\omega + 2S$	84(6)	84(7)[d]
22 530.372	5	0.0	443.845	467	$2\omega + 2S$	114(10)	
22 677.810	4	0.0	440.959	464	$2\omega + 2S$	64(5)	
22 736.693	5	0.0	439.817	463	$2\omega + 2S$	82(8)	
23 433.840	5	1128.056	448.314	448	$2\omega + 2S$	73(6)	
23 438.440	4	1128.056	448.222	448	$2\omega + 2S$	45(4)	
23 968.310	5	1128.056	437.824	463	$2\omega + 2S$	64(6)	
24 291.930	5	1128.056	431.707	456	$2\omega + 2S$	45(4)	
24 702.585	6	2366.597	447.708	476	$2\omega + 2S$	56(5)	
25 609.372	6	2366.597	430.241	430	$2\omega + 2S$	72(7)	
26 763.662	8	3681.696	433.239	461	$2\omega + 2S$	53(4)	
27 130.927	8	5048.602	452.851	453	$2\omega + 2S$	51(4)	

[a] From the NIST compilation (http://physics.nist.gov/cgi-bin/AtData/main_asd).

[b] ω and 2ω designate the fundamental frequency and the second harmonic of the dye laser; A, S, $2S$ and $3S$ represent the first-, the second-, the third-order Stokes and the first-order anti-Stokes components.

[c] Marek and Stahnke (1980): delayed coincidence with laser excitation.

[d] Gorshkov *et al* (1982): pulsed-electron delayed coincidence.

The experimental setup used in the measurements is schematically shown in figure 1. Free praseodymium or neodymium atoms were produced by laser ablation. A pure praseodymium or neodymium foil, rotating in a vacuum chamber with 10^{-6}–10^{-5} mbar pressure, was irradiated perpendicularly by a 532 nm laser pulse, emitted from a Nd:YAG laser (Continuum Surelite) with 10 ns pulse duration. The pulse energy was normally in the range of 2–10 mJ and produced a plasma containing neutral as well as ionized atoms expanding into the interaction zone about 10 mm above the foil, where the centre of the vacuum chamber is located. In this technique, the metastable states of the atoms and ions could be populated and served as starting points for subsequent laser excitation. Since the ions move much faster than the neutral atoms (500–1000 m^{-1} s), some time after the ions have left the interaction zone, the plasma contains essentially the Pr or Nd atoms.

In order to excite these atoms to the required levels, a primary pumping laser pulse, emitted from a seeder injected Nd:YAG laser (Continuum NY-82) with 8 ns pulse duration and 400 mJ pulse energy at 532 nm was sent to a temporal compressor, based on a technique of stimulated Brillouin scattering (SBS) in water. The design and construction of the SBS compressor include a SBS phase-conjugated reflector, a polarization beam isolator and a beam expander. A 150 cm and a 30 cm glass tube, filled with pure water and sealed with anti-reflection coated windows, serve as an amplifier and a generator, respectively. The pulse duration of the output from the SBS temporal compressor was about 1 ns and the loss in pulse energy was about 50%. The dye laser was operated with DCM dye and a pulse energy of 10 mJ could be produced, which is powerful enough for performing the subsequent nonlinear processes in order to obtain the required short wavelength radiation. A nonlinear potassium dihydrogen phosphate (KDP) crystal was utilized for frequency doubling of the dye laser radiation.
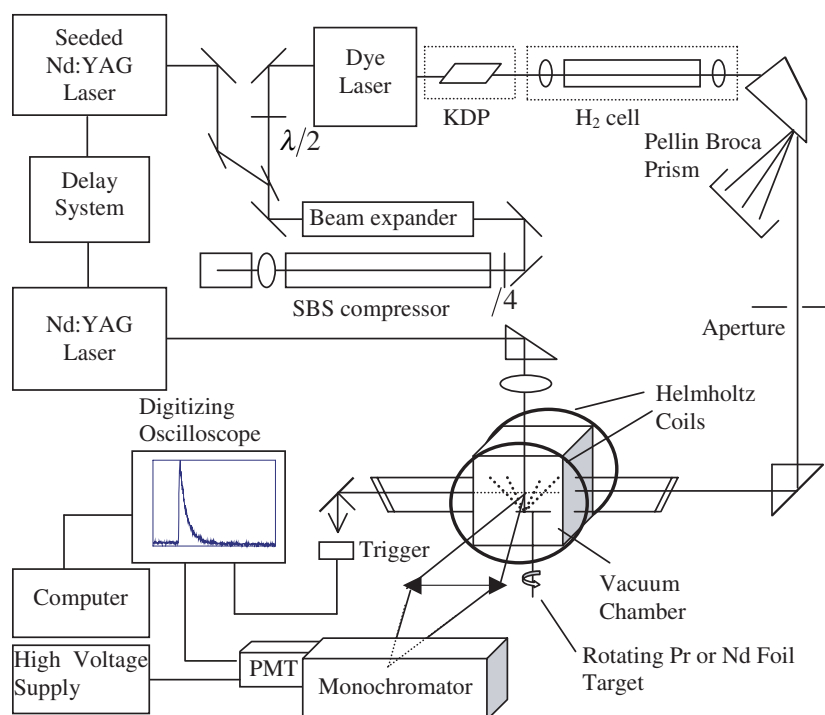
Figure 1. General scheme of the experimental device used for the lifetime measurements.

The fundamental frequency, or the second harmonic of the dye laser beam was focused into a stimulated Stokes Raman scattering (SSRS) cell to generate the required excitation in the range from 430.2 to 534.6 nm. H_2 was chosen as a fill gas in the SSRS cell due to its large shift of 4155 cm^{-1}, wide transparency range and easy handling to reach reasonably high pressure. In our case, the gas pressure was about 10 bar. Different Raman shifted components were used in our experiment as summarized in tables 1 and 2.

The irradiation from the SSRS cell was first isolated with a Pellin–Broca prism, and then the appropriate excitation light passed through two apertures and was sent horizontally into a vacuum chamber.

The two Nd:YAG lasers were controlled externally by a digital delay generator (Stanford Research Systems Model 535), which was used to adjust the delay time between the excitation and ablation lasers. When the atoms moved into the centre of the vacuum chamber, the excitation beam interacted with the Pr or Nd atoms. Fluorescence released at decay was captured using a 1/8 m monochromator and a Hamamatsu 1564U photomultiplier with a rise time of 0.2 ns. The photomultiplier was connected to a digital transient oscilloscope (Tektronix Model DSA 602 for Pr I or Tektronix Model TDS 684B for Nd I), in which the signals were averaged and then transferred to a computer for lifetime evaluation using the method of least-squares exponential curve fitting. A smooth fluorescence decay curve can be obtained for lifetime evaluation by averaging fluorescence photons from 1000 pulses. Typical experimental (open circles) and fitted (solid line) curves are shown in figure 2, where the inset shows the same data but in a semi-logarithmic representation.

Several processes, such as collisions and flight-out-of-view effects, can cause errors in experimental lifetimes. In the measurements, attempts were made to eliminate these effects by adjusting the different experimental parameters. Long delay times (15–35 μs for Pr I and
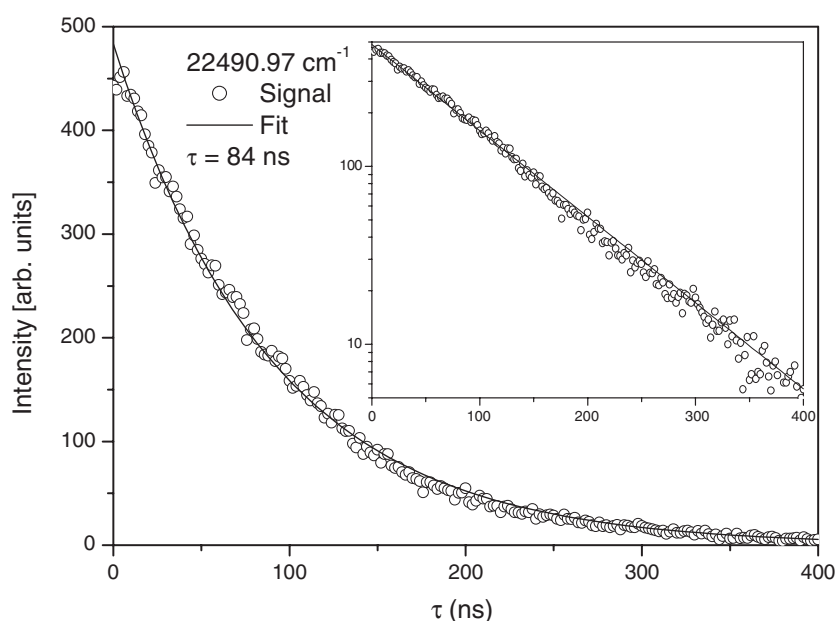
Figure 2. A typical Nd I experimental decay curve with an exponential fit. The lifetime for this level, situated at $22\,490.970$ cm^{-1}, is 84(6) ns.

7–15 μs for Nd I) between the ablation and excitation pulses were adopted to minimize the possible flight-out-of-view effects. The long delay time can also be helpful in identifying the Nd I and Pr I lines because the delay time is about 2–6 μs for Nd II, 1–2 μs for Nd III and 3–8 μs for Pr II. A static magnetic field of about 100 Gauss, provided by a pair of Helmholtz coils, was employed to eliminate potential Zeeman quantum beats effects. In the inset of figure 2, a very slight oscillation can be observed, which is due to quantum beats appearing without the presence of a strong magnetic field. To make sure that the experimental lifetimes were not affected by collisions and radiative trapping, the intensity of the ablation pulse and the delay time were changed, i.e. the atomic density and temperature were changed. The signal intensities were varied by a factor of 8, but the lifetime values were found to be nearly constant, which implied that the collisional quenching and radiation trapping effects were negligible. Different neutral density filters, inserted in the exciting light path, were used to avoid the saturation effect. The final lifetime of each level was obtained by averaging a number of recordings (about nine) under different experimental conditions. The lifetimes measured are reported in tables 1 and 2. The error bars quoted in the tables include the statistical scattering between the different recordings and also the possibilities of remaining systematic effects.

The new Nd I experimental values agree well (within the error bars) with the previous measurements (for four levels) by Gorshkov *et al* (1982) who used a pulsed-electron delayed-coincidence method and Marek and Stahnke (1980) who used a laser excitation delayed-coincidence technique.

Similar considerations apply in the case of Pr I when comparing our new results with those obtained by Gorshkov and Komarovskii (1985) using a pulsed-electron delayed-coincidence method.
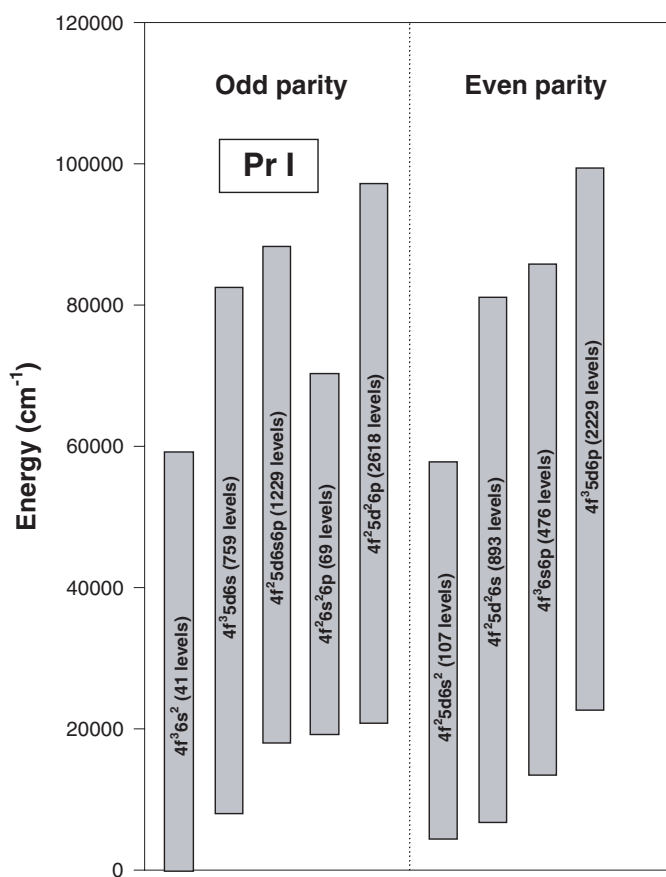
Figure 3. Predicted energies and theoretical numbers of levels for the low-lying configurations of Pr I. The energy ranges have been obtained through monoconfigurational HFR calculations.

3. Calculations in Pr I and Nd I

In Pr I, according to the NIST compilation (**Martin** *et al* 1978), the low-lying levels, belonging to the odd-parity configurations $4f^36s^2$, $4f^35d6s$, $4f^25d6s6p$, $4f^26s^26p$ and $4f^25d^26p$ and to the even-parity configurations $4f^25d6s^2$, $4f^25d^26s$, $4f^36s6p$ and $4f^35d6p$, exhibit a large number of possible levels, i.e. 4716 and 3705, respectively. Simple monoconfigurational calculations performed with the HFR approach (**Cowan** 1981) show that these configurations overlap in a wide range of energy and, consequently, highly mixed eigenfunctions may be expected. This is illustrated in figure 3 where the predicted energy ranges of the configurations mentioned above are shown. Among these 4716 and 3705 possible levels, only 126 and 284 have been determined experimentally, with unambiguous labelling, up to 32 704 and 31 172 cm^{-1}, respectively (**Martin** *et al* 1978). This small number of available level assignments renders entirely unreliable a least-squares fitting procedure of the calculated eigenvalues of the Hamiltonian to the observed energy levels in order to deduce more realistic Slater or configuration interaction parameters than the values calculated in an *ab initio* way. In addition, due to the large number of calculated levels appearing in the same energy ranges (about 1000 for both parities) and to the important mixing between these states, it was impossible to establish an unambiguous correspondence between the *ab initio* calculated and the experimentally

determined levels. The use of the existing Landé factors was not even of great help for making the identification more reliable.

The situation is still worse in Nd I for which the low-lying configurations $4f^4 6s^2$, $4f^4 5d6s$, $4f^3 5d6s6p$, $4f^4 5d^2$, $4f^4 6s7s$ (even parity) and $4f^3 5d6s^2$, $4f^3 5d^2 6s$, $4f^4 6s6p$, $4f^4 5d6p$ (odd parity) are so complex (11 158 and 10 618 levels, respectively) that their full consideration was prevented, in the present work, by the computer limitations (too large matrix dimensions). A physical model in which the sizes of the energy matrices were reduced by including only a limited number of terms of the subshell $f^w (w = 3, 4)$ in setting up the quantum states for the complete configurations (i.e. ^{5}I, ^{5}G, ^{5}F, ^{5}S, ^{3}L, ^{3}K1, ^{3}H1, ^{3}G1, ^{3}D1, ^{3}P1 and ^{1}L1 terms of $4f^4$ in the calculation of $4f^4 6s^2$, $4f^4 5d6s$, $4f^4 5d^2$, $4f^4 6s7s$, $4f^4 6s6p$, $4f^4 5d6p$ configurations and ^{4}I, ^{4}F, ^{4}S, ^{2}K, ^{2}H1, ^{2}G1, ^{2}D1 and ^{2}P terms of $4f^3$ in the calculation of $4f^3 5d6s6p$, $4f^3 5d6s^2$, $4f^3 5d^2 6s$, allowing us to reduce the total number of energy levels from 11 158 to 4264 and from 10 618 to 3986 for the even and odd parities, respectively) was not even very successful in view of some convergence problems occurring in the self-consistent-field approach for some configurations when building the HFR wavefunctions. These convergence problems and the necessity to consider, for computational reasons, an oversimplified theoretical model has prevented reliable calculations of transition rates in Nd I.

4. Conclusions

New reliable radiative lifetime measurements have been performed with time-resolved laser-induced fluorescence techniques for 18 even-parity levels of Pr I and 15 odd-parity levels of Nd I. Unsuccessful calculations aimed at providing the necessary branching fractions in order to deduce the corresponding transition probabilities have highlighted the need for further laboratory analyses in these two atoms regarding both the term analyses and the branching fraction determination which are still extremely fragmentary. The new results presented here constitute a first contribution towards providing the astrophysicists with reliable transition probabilities needed for investigating the chemical composition and magnetic fields in chemically peculiar stars.

Acknowledgments

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