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Hyperfine-structure measurements and new levels evaluation in singly ionized praseodymium

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Abstract. Results of systematic studies of the hyperfine structure of singly ionized praseodymium are presented. For many of the known energy levels the hyperfine constants A and B have been measured more precisely and found consistent with previous literature data. Identification of some new energy levels has also been performed. The hyperfine structure of some unclassified lines has been recorded by the method of laser induced fluorescence in a hollow cathode discharge. J quantum numbers and A-values for upper and lower levels have been determined. Identification has been achieved through comparison of the obtained results with those for known levels. Three new low-lying levels in singly ionized praseodymium have been discovered. Some of the recorded unclassified lines involve two new levels and their identification requires further investigations.

PACS. 39.30.+w Spectroscopic techniques

1 Introduction

Praseodymium is an element belonging to the rare earths group (open $4f$ shell). Its only stable isotope ^{141}Pr has the nuclear spin value $I = 5/2$, and its nuclear electromagnetic moments, relevant for the observed hyperfine structure, are as follows: the magnetic dipole moment $\mu_I = 4.2754(5)\mu_n$ [1], the electric quadrupole moment $Q = -0.066$ b [2]. The latter has a particularly small value, which is reflected in the values of B hyperfine structure constants.

As all the other elements of this group it has a very complex spectrum, resulting from a complicated energy levels scheme. This concerns the element in all ionization stages; the subject of the present work is singly ionized praseodymium. The energy levels system of the odd configurations of the singly ionized praseodymium, known hitherto, was established in the years seventies and eighties. The review of the state of knowledge in this subject is presented in the work of Ginibre [3]. That work contains the energy values of 45 low-lying and 60 high-lying ($E > 30\,000$ cm^{-1}) *odd* levels, as well as the constants of the hyperfine magnetic dipole interactions for those levels, determined with the method of Fourier spectroscopy. The work [3] contains besides 187 experimentally studied *even* levels; another work by the same author [4] is essentially devoted only to the interpretation of the hyperfine structure of the *even* levels.

A large number of the unclassified spectral lines in praseodymium, part of which are certainly lines of singly ionized praseodymium, shows, that the actual number of electronic levels of PrII must be much larger than known until now. The main aim of the present work is to prepare a possibly extensive basis of experimental data for the further theoretical description of the fine and the hyperfine structure of the levels belonging to *odd* configurations of PrII, through a more precise measurement of hyperfine constants of known levels, as well as the completion of the energy level scheme with new levels, which would allow the identification of the remaining unclassified spectral lines.

The experimental access to the presently unknown levels of PrII has become rather limited – observation of any optical transitions involving a known and a hitherto unknown level proves to be hardly possible; on the contrary, observation of transitions involving *two* unknown levels does not encounter any severe difficulties and it is their classification that constitutes a problem. The method of classification of the spectral lines on the basis of the *hfs* measurements seems to be the most efficient method for seeking new levels, provided the *hfs* A- and B-constants of the levels (both known and unknown) have been determined with an accuracy sufficient to prevent partial overlapping of the error intervals for various levels. Since the results presented in Ginibre's work [3] do not fulfill this requirement, in the present work a number of the known levels have been remeasured with the use of laser induced fluorescence (LIF) in a hollow cathode. This method does not assure as high a precision of the measurements as the collinear spectroscopy on a fast ion beam [5], but it is

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still considerably higher than in the case of Fourier spectroscopy [3].

The application of the LIF method in a hollow cathode for the identification of new electronic levels offers a great advantage: the fluorescence light is being recorded by a monochromator in selected channels, thus apart from the information on the *hfs* of the spectral line under investigation we obtain information on the fluorescence wavelength, which is found very useful for choice of the proper level in the case of more then one-identification possibility. The method of LIF in the hollow cathode proves to be particularly efficient in the studies of praseodymium due to the fact, that this element has only one stable isotope, therefore the *hfs* spectra are quite legible, even with a respectively large Doppler broadening.

This work presents the results of the measurements of the hyperfine constants of the known levels, which could be identified uniquely on the basis of the investigations performed on the lines in the spectral region 562–602 nm. The new electronic levels found constitute in the LS-coupling a term ^3G, which completes the level system with the core $4f^3(^4I)$ of the configurations $6s$ and $5d$. Until now no other theoretically predicted low-lying odd levels could be observed; most likely transitions between the known and the unknown levels are very weak. The remaining unclassified lines, which have been investigated, proved to be transitions between two (both the lower and the upper) new electronic levels. In this situation, in order to determine the energies of those levels, the hyperfine structure of the lines, previously observed as fluorescence channels (in the spectral region 415–465 nm), has been investigated whenever possible (*i.e.* within the limits of operation of the accessible experimental setup). The results of these investigations are inconclusive yet and further studies, involving an extension and improvement of the present experimental setup, are in progress.

2 Experimental setup

As already mentioned, the experimental method applied has been laser induced fluorescence in a hollow cathode. The principle of the method is as follows. The laser beam passes through the hollow cathode discharge (the cathode being made of praseodymium). The laser frequency is scanned very slowly over the spectral region under investigation. When the frequency of the light is in resonance with a transition between certain hyperfine structure components of the upper and the lower levels respectively (within the Doppler broadening), the light is absorbed and the excitation is followed by fluorescence. Since the fluorescence signal from a single fluorescence channel only is recorded at a time (the fluorescence light is observed through a monochromator), it is possible to separate the hyperfine spectra of all the lines appearing in the investigated region.

As source of the exciting radiation a cw single-mode tunable dye laser operating on rhodamine 6G and optically pumped by an argon ion laser has been used. Both the laser and the stabilization system have been described in the previous paper [6]. However, some parameters important for the present experiment are quoted below.

The value of the output power of the laser varied over a rather broad range. As it is commonly known, the laser power used in measurements depends on two factors: on one hand it is determined by the position of the transition's wavelength with respect to the gain curve of the dye (accessible output power), on the other hand it depends on the optimum value of the power for the measurements on the individual transitions (this might be rather low for strong lines in order to avoid power saturation effects). The laser power applied varied – according to the factors mentioned – from *ca.* 10 mW to *ca.* 300 mW.

The linewidth and frequency stability of the laser are typical for the laser system used and conform with the specifications. The precise numbers for neither the short-term nor the long-term linewidth of the laser radiation have been determined, but the accuracy obtained in the measurements on an atomic beam [6] with the use of the same laser suggests, that the linewidth be less than 1 MHz.

The laser beam, formed by a telescope system and intensity-modulated by a mechanical chopper (controlled by a lock-in amplifier), passes through the hollow cathode discharge twice: directly and after being reflected from a mirror placed behind the device.

We have observed simultaneously the optogalvanic signal and the fluorescence light from the hollow cathode discharge. The whole setup is presented in Figure 1. The optogalvanic signal from the discharge is passed directly to the computer, while the fluorescence light passes through the monochromator (always only one fluorescence wavelength is selected) to the photomultiplier and then the signal, amplified by the lock-in amplifier, is also directed to the computer.

The hollow cathode lamp consists of a copper cylinder with a rather wide axial hole. Praseodymium is placed inside the cathode in the form of a well-fitting axially hollowed cylinder (thus it covers the inner walls of the cathode with a kind of thick layer).

The hollow cathode, prepared in this way, is then screwed in the middle of the metal tube. On both sides of the cathode two, also axially hollowed, aluminium anodes are placed; they are electrically insulated from the metal tube (and thus from the cathode) *via* ceramics pieces and are provided with wires, led to the outside of the device through a feedthrough. On both sides of the metal tube glass tubes are sealed, which are closed with glass windows.

The whole device is evacuated by a rotational vacuum pump and then filled with argon (the pressure amounts to 0.55 mbar) as a buffer gas. The discharge current used in experiments with praseodymium has been typically 30–40 mA.

Simultaneously with the induced fluorescence, a marker signal from a stable Fabry-Perot interferometer and the absorption spectrum of molecular iodine have been recorded. The *FSR* of the marker amounts to 149.98(4) MHz; because of the poor resolution no correction of the FSR of the marker has been attempted and the

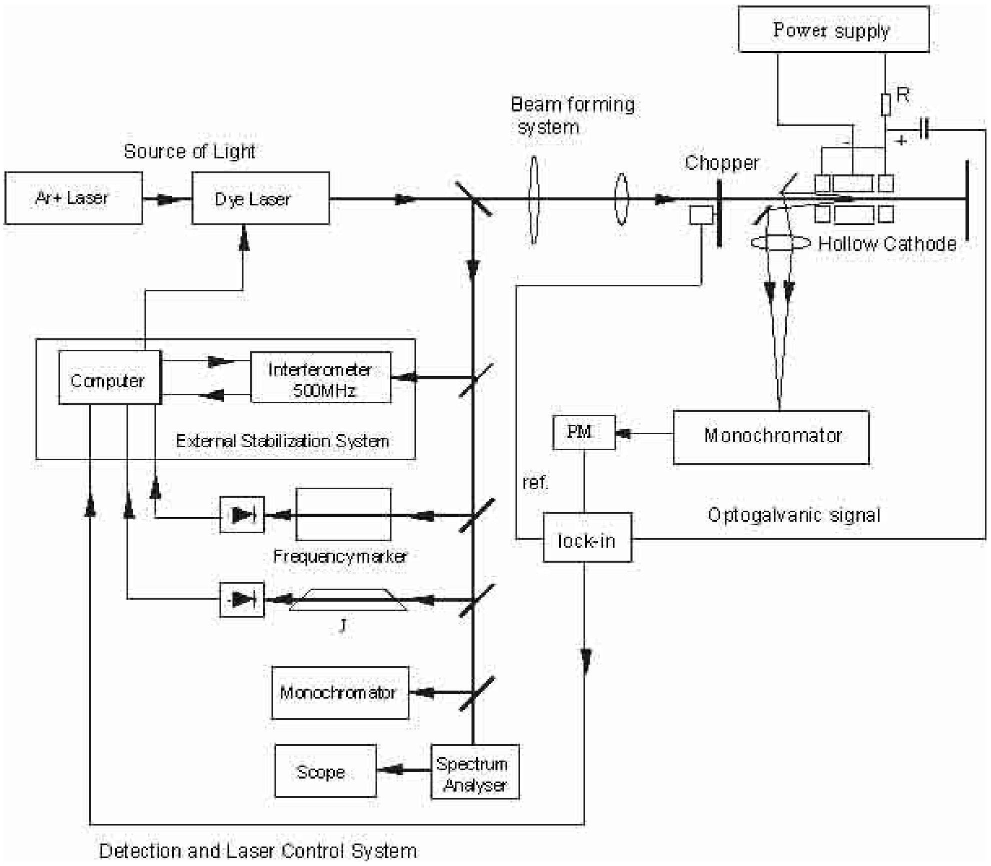

Fig. 1. Experimental setup for registration of the hyperfine spectra of praseodymium by the method of laser induced fluorescence (LIF).

value from the previous paper [6] (quoted in the caption under Fig. 2) has been directly adopted.

As in [6], in the present work a number of scans for each individual line has been recorded. In Figure 2 we present an exemplary recorded spectrum of the hyperfine structure in the praseodymium ion together with the curve representing the obtained optimum *hfs* fit.

3 Determination of the hfs constants of the “known” electronic levels

The calibration of the recorded LIF spectra and calculation of the hyperfine constants was performed using the methods described in the previous paper [6].

As in [6], the A- and B-constants have been determined in two ways:

(a) independent determination of the positions of individual components and calculation of A and B from a redundant set of equations,
(b) direct least-squares-fit of A and B values to the entire recorded spectrum.

In order to evaluate the positions of the individual hyperfine structure components a curve composed of a number of Voigt profiles is least-squares-fitted to the experimentally recorded spectrum. A more detailed description of both methods applied follows.

(a) Position of each *hfs* component has been determined *via* least-squares-fit of a curve, composed of a specified number of Voigt profiles. In the procedure commercial program packages Peak-Fit (SPSS) and Origin (Microcal) have been applied. The fit parameters (for each individual *hfs* component) have been: intensity, center position, halfwidth, proportions of the Gauss and Lorentz components. The numerical calculations have been performed with no constraints on the parameters for the individual components; in particular no relationships between the parameters concerning different components have been assumed. In further evaluation (solving a redundant set of equations) each component has been represented by its center position.

(b) Also in this case each component has been represented by a Voigt profile, and a theoretical curve, composed of a specified number of Voigt profiles, has been least-squares-fitted to the experimentally recorded spectrum. In the fit procedure a program “Fitter”, created at the Universität der Bundeswehr in Hamburg, has been applied. The fit parameters have been: intensity, center position, halfwidth, proportions of the Gauss and Lorentz components. However, in contrast to method (a), *common* halfwidths and proportions of the Gauss and Lorentz components have been applied for all the *hfs* components in a spectrum. Moreover, the center positions of the *hfs* components have been no more independent but related to one another *via* Casimir relations, and in each iteration the values of A- and B-constants have been varied, which has

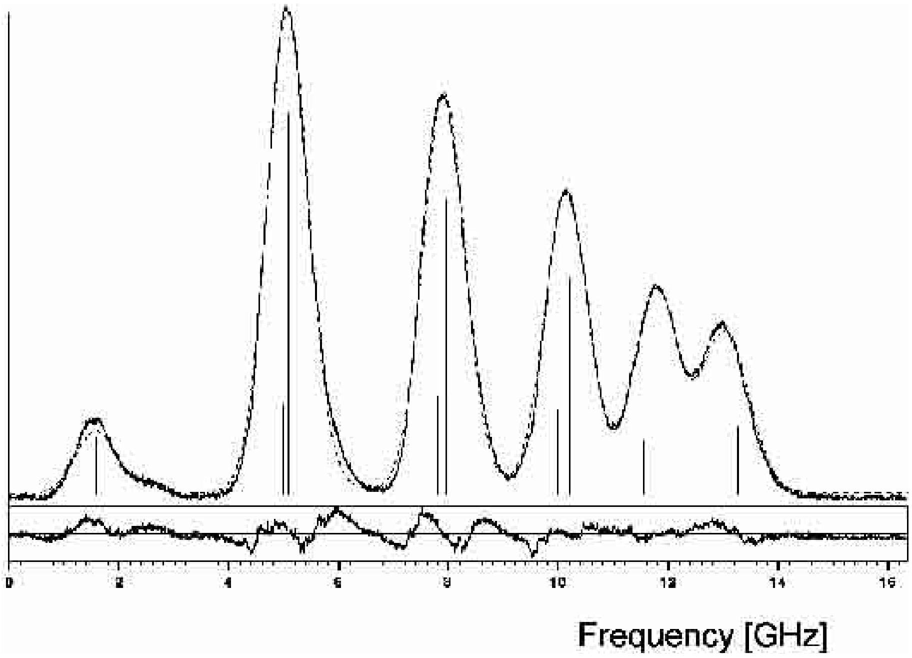

Fig. 2. Hyperfine structure of the line $\lambda = 585.609$ nm in singly ionized praseodymium observed by the method of the laser induced fluorescence on the hollow cathode discharge – experimental spectrum and theoretical curve, representing the least-squares-fit of a composition of Voigt profiles to the spectrum. The lower trace depicts the fit errors in intensity, magnified with respect to the ordinate scale applied for the spectrum itself.

led to a consequent variation of the positions of individual *hfs* components. Also the intensities of the components could be "bound" *via* known theoretical relations [7]. This procedure allowed better resolved components to be taken into account with higher statistical weights.

Method (a) yields slightly better results in the case of well-resolved lines, while method (b) proves to perform better in the case of poorly resolved lines. Generally, because of a larger linewidth in a hollow cathode than on an atomic beam, resulting from Doppler broadening, the results obtained in the present work with method (b) proved to be better than those obtained with method (a).

In order to find a reliable estimate for the experimental errors of the A- and B-constants determined in this work, some lines in Pr atom, previously measured by Childs and Goodman by ABMR-LIRF method [8], have now been studied in a hollow cathod by LIF method. Statistical errors (mean standard deviations) have been calculated and the results compared with those of Childs and Goodman. Since for all the investigated lines our results were consistent with [8] within the mean standard deviations, we considered it an adequate error estimate for the measurements in a hollow cathod with LIF method in general. All the errors quoted in tables contained in this work have been determined in this way.

All the spectral lines investigated and the results of their classification are listed in Table 1. The lines observed for the first time and classified within this work have been marked with an asterisk; these lines involve new odd (lower) levels, also marked with an asterisk. The remaining lines have been studied in order to determine the *hfs* constants of the known levels, belonging to odd configurations of PrII, and the results obtained are given in Table 2 (this table includes also the results for the new odd levels). For comparison, the literature data for these constants, determined with other methods [3, 5], are presented. All the relevant data concerning the even (upper) levels, involved in the transitions classified within this work, are contained in Table 3 (since all of them are already known levels, they bear no special marks in the table).

As clearly visible, the present results for the A-constants are in good agreement with those obtained with the LIF method on the fast ion beam [5] for most of the levels investigated with this method. The errors of the obtained B-constants reach 100% of the values themselves, since the values are very small and cause the shifts of only a few MHz in the *hfs* pattern of the spectral lines.

4 New electronic levels

The essential part of the experiment consisted in the identification and spectroscopic classification of the energy levels. The important aspects, taken into account in the selection of the lines to be measured, were: on the one side – a convenient spectral range for the laser generation (possibly rhodamine 6G), and on the other side – the expected intensities (the tabelarized intensities in arc and spark discharges were considered the initial qualitative estimate). At the first step, we have investigated the unclassified lines, presented in the paper of Ginibre [3]. According to NBS tables [9], those lines seem to be the strongest among all the unclassified ones in praseodymium ion. As already mentioned, the lines, which were successfully classified within this work, the designation of both the levels involved, and the wavelengths of the strongest fluorescence channels, are presented in Table 1 among all the other investigated lines and marked with an asterisk. The A- and B-values for the new odd (lower) levels are given in Table 2 among the data for all the other investigated odd levels and marked with an asterisk.

Table 1. Classification of the investigated transitions in praseodymium ion.

λ[nm]	Energy [cm^{-1}] [10]		Transition classification		Fluorescence [nm]
	odd level	even level	odd level	even level	
601.780	8965.63	25578.49	$4f^3(^4I)\ 5d\ ^5G^o_2$	$4f^3(^4I)\ 6p\ ^5H_3$	
600.633	13373.61	30018.10	$4f^3(^4I)\ 5d\ ^3K^o_8$	$4f^3(^4I)\ 6p\ ^3I_7$	
594.072	11749.49	28577.79	$4f^3(^4I)\ 5d\ ^3H^o_6$	$4f^3(^4I)\ 6p\ ^5H_7$	
593.990	10030.32	26860.95	$4f^3(^4I)\ 5d\ ^3I^o_7$	$4f^3(^4I)\ 6p\ ^5I_7$	
593.066	10116.63	26973.49	$4f^3(^4I)\ 5d\ ^5G^o_4$	$4f^2\ 5d^2\ ^3G_5$	
590.867*	12431.39*	29350.98	$4f^3(^4I)\ 5d\ ^3G^o_4$	$4f^3(^4I)\ 6p\ ^3H_5$	385.280
590.311*	10769.48*	27705.01	$4f^3(^4I)\ 5d\ ^3G^o_3$	$4f^2\ 5d6s\ ^3F_4$	385.080
588.848	8489.87	25467.47	$4f^3(^4I)\ 5d\ ^5I^o_5$	$4f^2\ 5d^2\ ^3F_4$	
588.452	13029.09	30018.10	$4f^3(^4I)\ 5d\ ^3L^o_8$	$4f^3(^4I)\ 6p\ ^3I_7$	
587.473	9128.67	26146.01	$4f^3(^4I)\ 5d\ ^3H^o_4$	$4f^3(^4I)\ 6p\ ^3I_5$	
587.383	9378.63	26398.52	$4f^3(^4I)\ 5d\ ^5H^o_5$	$4f^3(^4I)\ 6p\ ^3K_6$	
585.968	11447.73	28508.79	$4f^3(^4I)\ 5d\ ^5G^o_5$	$4f^3(^4I)\ 6p\ ^5H_6$	
585.609*	10769.48*	27841.06	$4f^3(^4I)\ 5d\ ^3G^o_3$	$4f^3(^4I)\ 6p\ ^3H_4$	383.072
585.263	10116.63	27198.24	$4f^3(^4I)\ 5d\ ^5G^o_4$	$4f^3(^4I)\ 6p\ ^5H_5$	
584.713	9128.66	26226.56	$4f^3(^4I)\ 5d\ ^3H^o_4$	$4f^3(^4I)\ 6p\ ^5H_4$	
584.705	10030.31	27128.00	$4f^3(^4I)\ 5d\ ^3I^o_7$	$4f^3(^4I)\ 6p\ ^5K_8$	
584.499*	14157.81*	31261.68	$4f^3(^4I)\ 5d\ ^3G^o_5$	$4f^3(^4I)\ 6p\ ^3H_6$	381.829
582.259*	12431.39*	29601.05	$4f^3(^4I)\ 5d\ ^3G^o_4$	$4f^3(^4I)\ 6p\ ^3H_5$	381.602
581.856	9044.95	26226.56	$4f^3(^4I)\ 5d\ ^5G^o_3$	$4f^3(^4I)\ 6p\ ^5H_4$	
581.533	12826.94	30018.10	$4f^3(^4I)\ 5d\ ^5G^o_6$	$4f^3(^4I)\ 6p\ ^3I_7$	
581.515	8465.04	25656.69	$4f^3(^4I)\ 5d\ ^3I^o_6$	$4f^3(^4I)\ 6p\ ^5I_6$	
581.355	11005.57	28201.95	$4f^3(^4I)\ 5d\ ^5I^o_7$	$4f^2\ 5d^2\ ^1L_8$	
581.058	11611.05	28816.25	$4f^3(^4I)\ 5d\ ^5I^o_8$	$4f^3(^4I)\ 6p\ ^5K_9$	
578.891	7446.43	24716.04	$4f^3(^4I)\ 5d\ ^5I^o_4$	$4f^3(^4I)\ 6p\ ^5I_5$	
578.528*	10769.48*	28049.92	$4f^3(^4I)\ 5d\ ^3G^o_3$	$4f^2\ 5d^2\ ^3G_4$	380.031
577.590	7446.43	24754.95	$4f^3(^4I)\ 5d\ ^5I^o_4$	$4f^2\ 5d^2\ ^3G_4$	
577.312	7438.23	24754.95	$4f^3(^4I)\ 5d\ ^3I^o_5$	$4f^2\ 5d^2\ ^3G_4$	
576.979	9646.67	26973.48	$4f^3(^4I)\ 5d\ ^5I^o_6$	$4f^2\ 5d^2\ ^3G_5$	
571.963	8099.72	25578.49	$4f^3(^4I)\ 5d\ ^5H^o_4$	$4f^3(^4I)\ 6p\ ^5H_3$	
571.909	12243.49	29723.97	$4f^3(^4I)\ 5d\ ^5H^o_7$	$4f^3(^4I)\ 6p\ ^3K_8$	
571.382*	14157.81*	31654.31	$4f^3(^4I)\ 5d\ ^3G^o_5$	$4f^2\ 5d^2\ ^3K_6$	376.187
569.592	9646.67	27198.24	$4f^3(^4I)\ 5d\ ^5I^o_6$	$4f^3(^4I)\ 6p\ ^5H_5$	
568.395	10116.63	27705.01	$4f^3(^4I)\ 5d\ ^5G^o_4$	$4f^2\ 5d6s\ ^3F_4$	
566.219	8489.87	26146.01	$4f^3(^4I)\ 5d\ ^5I^o_5$	$4f^3(^4I)\ 6p\ ^3I_5$	
565.992	8099.72	25762.81	$4f^3(^4I)\ 5d\ ^5H^o_4$	$4f^2\ 5d^2\ ^3G_3$	
564.036	10116.63	27841.06	$4f^3(^4I)\ 5d\ ^5G^o_4$	$4f^3(^4I)\ 6p\ ^3H_4$	
562.305	10729.75	28508.79	$4f^3(^4I)\ 5d\ ^5H^o_6$	$4f^3(^4I)\ 6p\ ^5H_6$	

* new transition (new level) – classified for the first time.

Because in the present situation, when not only A and B *hfs* constants but also J quantum numbers are unknown, it is sometimes possible to obtain several fits which describe the hyperfine structure equally well (within the experimental error); thus in order to determine the *correct* value of J quantum number, as well as the values of A- and B-constants of an unknown level involved in a transition in *each specific case*, the following procedure has been applied.

First, in the fit procedure a number of *trial* J values have been applied in turn and the fit results have been compared with one another. In many cases incorrectly assumed J values have not led to satisfactory results, thus the choice of the unique correct value was rather straightforward. The number of trial values applied (from which only one value was correct) was in most cases less than ten, and depended on the final result. For the levels with low J quantum numbers usually incorrect trial assignments, where the assumed J value differed from the correct one by more than ±1, resulted in theoretical curves totally inconsistent with the originally recorded spectrum, irrespective of the A- and B-values (*e.g.* missing or superfluous components, distinctly different intensities of the components), and thus no explicit fit was required to reject such assignments.

In some cases, however, assignment of the correct J value exclusively on the basis of the hyperfine structure has not been possible for the reasons described above. Then a combined analysis has been performed. On the basis of the obtained properties of the investigated lines

Table 2. Comparison of the *hfs* constants for the investigated odd levels in praseodymium ion, obtained within this work, with available literature data.

Designation [3]	Energy [cm^{-1}]	A [MHz]	B [MHz]	Source
$4f^3(^4I)\,5d\ ^3\mathrm{I}^o_5$	7438.23	709.5 (1.5)	8 (5)	
		709.3 (1.2)	19.5 (6.0)	[5]
	7438.23	714 (6)		[3]
	7438.23			[10]
$4f^3(^4I)\,5d\ ^5I^o_4$	7446.43	1069.3 (3.0)	−7 (4)	averaged over 2 lines
	7446.43	1062 (7)		[3]
	7446.43			[10]
$4f^3(^4I)\,5d\ ^5H^o_4$	8099.66	769.7 (2.5)	44 (12)	averaged over 2 lines
		770.8 (0.8)	34.7 (4.6)	[5]
	8099.62	768 (14)		[3]
	8099.72			[10]
$4f^3(^4I)\,5d\ ^3I^o_6$	8465.04	573.7 (1.5)	−6 (5)	
		573.9 (0.7)	−5.1 (5.4)	[5]
	8465.04	576 (5)		[3]
	8465.04			[10]
$4f^3(^4I)\,5d\ ^5I^o_5$	8489.87	793.5 (2.5)	43 (20)	averaged over 2 lines
	8489.87	795 (6)		[3]
	8489.87			[10]
$4f^3(^4I)\,5d\ ^5G^o_2$	8965.63	1705.1 (5.3)	23 (9)	
	8965.57	1614 (120)		[3]
	8965.63			[10]
$4f^3(^4I)\,5d\ ^5G^o_3$	9044.95	940.0 (5.5)	7 (10)	
	9044.94	943 (17)		[3]
	9045.00			[10]
$4f^3(^4I)\,5d\ ^3H^o_4$	9128.67	840.5 (3.5)	−37 (20)	averaged over 2 lines
	9128.66	834 (7)		[3]
	9128.67			[10]
$4f^3(^4I)\,5d\ ^5H^o_5$	9378.55	613.9 (2.0)	−1 (1)	
		613.8 (0.8)	9.1 (5.4)	[5]
	9378.55	612 (11)		[3]
	9378.63			[10]
$4f^3(^4I)\,5d\ ^5I^o_6$	9646.62	626.9 (2.0)	20 (5)	averaged over 2 lines
	9646.62	618 (10)		[3]
	9646.67			[10]
$4f^3(^4I)\,5d\ ^3I^o_7$	10030.32	462.3 (3.0)	29 (10)	averaged over 2 lines
	10030.32	471 (8)		[3]
	10030.31			[10]
$4f^3(^4I)\,5d\ ^5G^o_4$	10116.63	653.9 (2.5)	0 (10)	averaged over 4 lines
	10116.63	666 (27)		[3]
	10116.63			[10]
$4f^3(^4I)\,5d\ ^5H^o_6$	10729.75	529.1 (3.5)	4 (3)	
	10729.72	516 (46)		[3]
	10729.75			[10]
$4f^3(^4I)\,5d\ ^5I^o_7$ *	10769.48	1161.7 (2.5)	−72 (30)	
$4f^3(^4I)\,5d\ ^3G^o_7$	11005.52	546.6 (2.0)	8 (7)	
		546.7 (1.0)	9.7 (7.0)	[5]
	11005.52	558 (40)		[3]
	11005.57			[10]

Table 2. *Continued.*

Designation [3]	Energy [cm^{-1}]	A [MHz]	B [MHz]	Source
$4f^3(^4I)\ 5d\ ^5G^o_5$	11447.73	566.8 (4.5)	−21 (10)	
	11447.73	600 (110)		[3]
	11447.73			[10]
$4f^3(^4I)\ 5d\ ^5I^o_8$	11611.03	419.9 (3.0)	33 (15)	
	11611.01	423 (14)		[3]
	11611.05			[10]
$4f^3(^4I)\ 5d\ ^3H^o_6$	11749.49	556.3 (5.0)	27 (10)	
	11749.49	546 (92)		[3]
	11749.49			[10]
$4f^3(^4I)\ 5d\ ^5H^o_7$	12243.51	493.1 (5.0)	−16 (10)	
	12243.51	480 (40)		[3]
	12243.49			[10]
$4f^3(^4I)\ 5d\ ^3G^o_4$ *	12431.39	855.2 (1.5)	−49 (30)	
$4f^3(^4I)\ 5d\ ^5G^o_6$	12826.94	487.5 (2.5)	−23 (10)	
		487.3 (1.0)	−17.4 (5.6)	[5]
	12826.94	489 (46)		[3]
	12826.94			[10]
$4f^3(^4I)\ 5d\ ^3L^o_8$	13029.09	574.2 (5.5)	−17 (12)	
	13029.09	588 (14)		[3]
	13029.09			[10]
$4f^3(^4I)\ 5d\ ^3K^o_8$	13373.61	498.5 (3.0)	−30 (15)	
	13373.61	507 (46)		[3]
	13373.61			[10]
$4f^3(^4I)\ 5d\ ^3G^o_5$ *	14157.81	688.0 (3.0)	−66 (35)	

* new level – classified for the first time.

(particularly assumed J and A for upper and lower level), and the fluorescence wavelengths, through comparison with properties for known or theoretically predicted levels, identification of new levels has been performed. The features important for the identification process are compiled in Table 4.

The result was the level scheme depicted graphically in Figure 3. While all the upper levels in the investigated transitions are the already known levels belonging to even configurations of PrII, the lower levels are new ones. An attempt at the identification of the new lower levels has been performed on the basis of three lines: 578.528 nm, 590.867 nm and 571.382 nm. The remaining lines have been applied to prove the classification. The new energy levels have been classified as follows:

$$E = 10769.48\ \text{cm}^{-1} \quad - \quad 4f^3(^4I)5d \quad ^3G^o_3,$$

$$E = 12431.39\ \text{cm}^{-1} \quad - \quad 4f^3(^4I)5d \quad ^3G^o_4,$$

$$E = 14157.81\ \text{cm}^{-1} \quad - \quad 4f^3(^4I)5d \quad ^3G^o_5.$$

Since each of the three new levels has been observed in more than one spectral line, their actual existence seems very probable.

5 Discussion

5.1 Energy values

An average linewidth of the spectral lines in praseodymium, resulting from the hyperfine splitting, amounts to about 0.3 cm^{-1}. Transition wavelength, understood as the position of the center of gravity of the line, may thus be determined precisely provided the hyperfine constants are known. It is probably the reason, why the energy values determined taking into consideration the presence of the *hfs* [3] in some cases differ slightly from those listed in NIST tables, which were based on earlier measurements [10]. Therefore an attempt to determine the energy values of the levels has been made within this work. The precise wavelengths have been evaluated from the positions of the centers of gravity of the *hfs* of the lines with respect to the molecular iodine spectrum. Since the positions of the iodine lines are known with an accuracy of 0.0001 cm^{-1} [11], the experimental uncertainty of the energy differences between the upper and the lower levels of the transitions, measured in this way, is mainly due to the pressure

Table 3. Comparison of the *hfs* constants for the investigated even levels in praseodymium ion, obtained within this work, with available literature data.

Designation [3,4]	Energy [cm^{-1}] [10]	A [MHz]	B [MHz]	Source
$4f^3(^4I)\ 6p\ ^5I_5$	24716.04	734.9 (2.0)	18 (10)	
		735.0 (1.1)	15.9 (3.5)	[5]
		731 (15)		[3]
$4f^2\ 5d^2\ ^3G_4$	24754.95	604.1 (2.0)	5 (5)	averaged over 2 lines
		560 (15)		[3]
$4f^2\ 5d^2\ ^3F_4$	25467.47	735.4 (2.5)	23 (10)	
		736.2 (1.5)	16.2 (6.6)	[5]
		733 (15)		[3]
$4f^3(^4I)\ 6p\ ^5H_3$	25578.49	1030.9 (1.8)	14 (10)	averaged over 2 lines
		1031.6 (2.2)	12.2 (6.6)	[5]
		891 (17)		[3]
$4f^3(^4I)\ 6p\ ^5I_6$	25656.69	654.3 (1.5)	−3 (5)	
		655 (5)		[3]
$4f^2\ 5d^2\ ^3G_3$	25762.81	854.7 (3.0)	−42 (15)	
		857 (27)		[3]
$4f^3(^4I)\ 6p\ ^3I_5$	26146.01	632.7 (3.0)	−28 (15)	averaged over 2 lines
		616 (30)		[3]
$4f^3(^4I)\ 6p\ ^5H_4$	26226.56	678.1 (6.0)	−2 (8)	averaged over 2 lines
		620 (15)		[3]
$4f^3(^4I)\ 6p\ ^3K_6$	26398.52	659.7 (2.0)	−9 (3)	
		660 (10)		[3]
$4f^3(^4I)\ 6p\ ^5I_7$	26860.95	595.1 (3.0)	3 (5)	
		588 (15)		[3]
$4f^2\ 5d^2\ ^3G_5$	26973.49	601.3 (1.0)	−3 3	
		601.7 (1.2)	−1.6 (3.7)	[5]
		611 (7)		[3]
$4f^3(^4I)\ 6p\ ^5K_8$	27128.00	598.6 (3.0)		
		600 (10)		[3]
$4f^3(^4I)\ 6p\ ^5H_5$	27198.24	582.9 (2.0)	−10 (10)	averaged over 2 lines
		583.3 (1.1)	−4.6 (4.3)	[5]
		600 (15)		[3]
$4f^2\ 5d6s\ ^3F_4$	27705.01	643.5 (5.5)	12 (10)	averaged over 2 lines
		640 (15)		[3]
$4f^3(^4I)\ 6p\ ^3H_4$	27841.06	542.7 (3.5)		averaged over 2 lines
		627(130)		[3]
$4f^2\ 5d^2\ ^3G_4$	28049.92	621.4 (3.5)		
		612 (27)	−70 (35)	[3]
$4f^2\ 5d^2\ ^1L_8$	28201.95	538.8 (2.0)	4 (5)	
		544 (10)		[3]
$4f^3(^4I)\ 6p\ ^5H_6$	28508.79	619.5 (3.5)	−29 (10)	
		637 (20)		[3]
$4f^3(^4I)\ 6p\ ^5H_7$	28577.79	531.1 (3.0)	−12 (10)	
		536 (5)		[3]

Table 3. *Continued.*

Designation [3,4]	Energy [cm^{-1}] [10]	A [MHz]	B [MHz]	Source
$4f^3(^4I)\ 6p\ ^5K_9$	28816.25	504.1(5.0)	−3 (5)	averaged over 2 lines
		505 (13)		[3]
$4f^3(^4I)\ 6p\ ^3H_5$	29350.98	487.2(3.5)		
		480 (55)	15 (25)	[3]
$4f^3(^4I)\ 6p\ ^3H_5$	29601.05	510.9(3.5)		
		522 (55)	50 (40)	[3]
$4f^3(^4I)\ 6p\ ^3K_8$	29723.97	529.4(4.0)	−12 (10)	
		529 (10)		[3]
$4f^3(^4I)\ 6p\ ^3I_7$	30018.10	528.6(3.0)	5 (3)	averaged over 3 lines
		525.9(1.1)	4.0 (3.7)	[5]
		495 (40)		[3]
$4f^3(^4I)\ 6p\ ^3H_6$	31261.68	730.2(3.0)		
		729 (47)	15 (25)	[3]
$4f^3(^4I)\ 6p\ ^3K_6$	31654.31	531.6(3.5)		
		505 (47)	15 (25)	[3]

Table 4. The lines in singly ionized praseodymium, involving new lower levels $4f^3(^4I)\ 5d\ ^3G^{\text{o}}_{3,4,5}$, which have been investigated and classified for the first time within this work, together with the features important for the classification process (the *hfs* constants for both the levels involved and the fluorescence channels).

No.	Transition		Lower level			Upper level			Fluorescence
	λ [nm]	k [cm^{-1}]	J	A [MHz]	B [MHz]	J	A [MHz]	B [MHz]	λ[nm]
1	578.528	17280.44	3	1164.1(3.5)	−87 (45)	4	621.4(3.5)	−70 (35)	380.031
2	585.609	17071.58	3	1159.2(2.5)	−60 (30)	4	539.7(3.5)	30 (20)	383.072
3	590.311	16935.53	3	1161.0(3.0)	−68 (25)	4	647.5(5.5)	40 (40)	385.080
4	582.259	17169.66	4	854.7(1.5)	−72 (35)	5	510.9(1.5)	50 (40)	381.602
5	590.867	16919.59	4	855.7(1.5)	−25 (30)	5	487.2(1.5)	15 (25)	385.280
6	571.382	17496.50	5	690.1(4.0)	−75 (50)	6	531.6(3.5)	15 (25)	376.187
7	584.499	17103.87	5	685.8(3.5)	−57 (35)	6	730.2(3.0)	15 (25)	381.829

broadening and saturation of the iodine lines and does not exceed 0.005 $^{-1}$. It is, however, impossible to determine the energy values of *each* of the levels *separately* on the basis of the analysis of a single transition. Therefore in the calculations the literature energy values of the upper levels [3, 10], which are equal with an accuracy of 0.01 cm^{-1} except for two levels: 25578.49 cm^{-1} and 28816.25 cm^{-1}, have been adopted as correct and the energies of the lower levels have been determined. Transitions involving the two upper levels, whose energy values given by the two sources slightly differ, were not taken into account at the first approach.

The results are presented in Table 2, where the subsequent positions in the column "energy" denote: the value obtained in the present experiment, the value by Ginibre [3] and the one from NIST tables [10], respectively. In most cases the energy values obtained within this work are closer to those by Ginibre [3] (it concerns the levels: 9045.00 cm^{-1}, 9378.63 cm^{-1}, 9646.67 cm^{-1}, 10030.3 cm^{-1}, 11005.57 cm^{-1} and 12243.49 cm^{-1}). For three levels (8965.63 cm^{-1}, 9128.67 cm^{-1} and 10729.75 cm^{-1}) the results obtained are consistent with NIST values [10]; for two levels (8099.72 cm^{-1} and 11611.05 cm^{-1}) the values obtained are the "means" of the Ginibre's and NIST results.

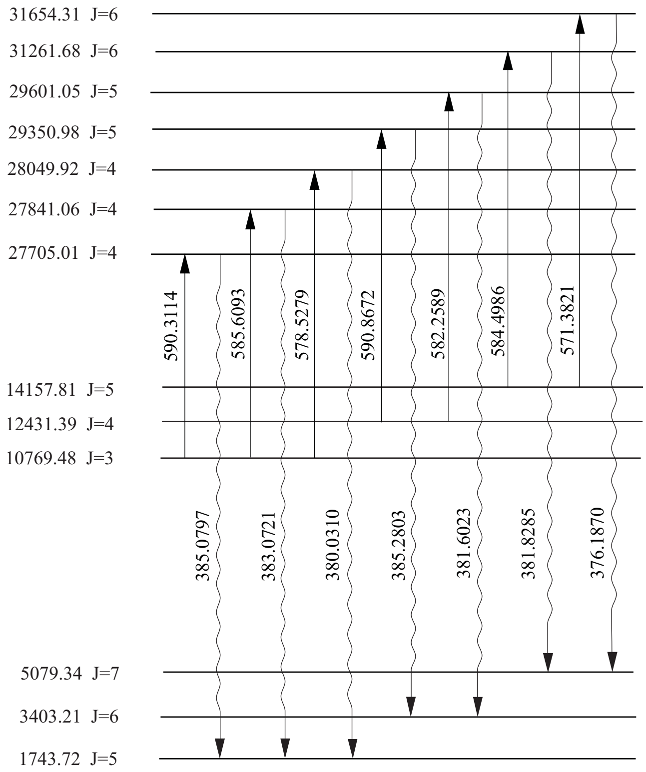

Fig. 3. Diagram of the levels in investigated transitions, obtained as a result of the identification procedure.

The energy values 8099.72 cm^{-1} and 8965.63 cm^{-1}, combined with precise values of the transition wavelengths 571.963 nm and 601.780 nm, suggest that the energy of the upper level 25578.49 cm^{-1} [10] is more reliable than the value given by Ginibre [3].

As already stressed, the energy values of the odd lower levels, obtained within this work, are accurate, provided the energy values for the even upper levels, adopted from the literature [3, 10], can be considered reliable. The new levels deserve particular caution in this respect, since for obvious reasons their energy values cannot be compared with any literature data.

5.2 Hyperfine constants A and B

The obtained values of the *hfs* constants A and B for the levels belonging to the *odd* configurations of PrII (the lower levels of the transitions) are presented in Table 2, while those concerning the levels belonging to the *even* configurations (the upper levels) – in Table 3.

Despite the general consistency of the results for the A constants of the lower levels with the values given by Ginibre [3], in some particular cases the discrepancies are substantial. It concerns *e.g.* the level 8965.63 cm^{-1}, for which the value obtained (1705.1 MHz) is 91 MHz larger than the available literature value by Ginibre [3], and the level 11447.73 cm^{-1} (the respective difference between the two A values amounts to 33 MHz). More serious dicrepancies are found for the upper levels (levels 24754.95 cm^{-1}, 26226.56 cm^{-1}, 27841.06 cm^{-1} and 30018.10 cm^{-1} in Tab. 3) – in some cases the differences exceed the error limits quoted by Ginibre. However, throughout both Tables 2 and 3 no discrepancies between our A values and those obtained with the more precise collinear ionic beam method [5], whenever available, can be found.

6 Conclusions

The results obtained fully prove the usefulness of the analysis of the *hfs* measured with the LIF method in a hollow cathode for the identification of the new electronic levels in PrII.

The *hfs* constants of 21 known, low-lying odd and 26 high-lying even levels have been measured. Three new electronic levels have been found.

As already mentioned, the analysis of the remaining strong unclassified lines of PrII indicates, that both the upper and the lower levels are new, hitherto unknown electronic levels. In many cases these levels have low J quantum numbers, thus their identification should improve the accuracy of the theoretical description of *hfs* and *fs* in singly ionized praseodymium. The identification of those levels requires further investigation.

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