

Transition probabilities in singly ionized promethium and the identification of Pm II lines in Przybylski's star and HR 465[★]

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ABSTRACT

The first theoretical transition probabilities are obtained for a set of 46 Pm II transitions of astrophysical interest. These data fill in a gap in astrophysics and will allow to establish, on a firmer basis, the presence of some lines of this radioactive element in the spectra of chemically peculiar stars and, consequently, a quantitative investigation of the stellar Pm abundance. A search for Pm II lines in Przybylski's star (HD 101065) and in HR 465 is reported and discussed, supporting the detection of this ion. A more detailed quantitative analysis is awaiting the availability of dedicated model atmospheres for these stars.

Key words: atomic data – line: identification – stars: chemically peculiar.

1 INTRODUCTION

Promethium ($Z = 61$), which belongs to the lanthanide group, was first identified in laboratory by Marinsky, Glendenin & Coryell (1947). Presently, 24 unstable isotopes and isomers are known (Lide 1996). The two longest lived isotopes, ¹⁴⁵Pm and ¹⁴⁷Pm, have half-lives of 17.7 and 2.6 yr, respectively, implying that, if they are found in cosmic sources, then they have been made *in situ*.

The controversy about the possible presence of Pm in Przybylski's star (HD 101065) and in HR 465 (HD 9996) – which are two chemically peculiar (CP) stars – started with the paper by Aller & Cowley (1970), these authors suggesting the 'possible presence of promethium' in HR 465. The Pm II identification could neither be confirmed nor refuted on the basis of the subsequent analysis of Wolff & Morrison (1972). The identification of Pm in HR 465 was rediscussed by Havnes & van den Heuvel (1972) who showed that the identification might be due to chance, a point of view contradicted by Aller & Cowley (1972).

The surveys performed by Cowley (1976, 1984), on the basis of a computer-automated method of wavelength coincidence statistics, found no convincing evidence for Pm II identification in HR 465. However, recently, Cowley et al. (2004) reported the possible identification of Pm in the spectra of HD 101065 and HD 965, an identification based on traditional and statistical line-identification

methods. They also discuss the possibility that the wavelength coincidences are due to chance or to contamination of the laboratory light sources. At present, a firm conclusion about the presence of Pm in these CP stars remains an open issue that can have important implications for our understanding of the composition of CP stars.

The revived Pm identification raises important questions about the origin of the short-lived radioactive elements, but also of the remaining stable elements which almost all present significant abundance peculiarities in these stars. Conventional nucleosynthesis processes like the s- or r-processes cannot be expected to take place in cold envelopes of unevolved stars, so that only spallation reactions (operating directly at the stellar surface) can be imagined at the present time as a possible explanation for generating this short-lived element. Cowley & Bord (2004) have suggested that the acceleration of protons and α -particles to high energies by the strong magnetic fields of CP stars may be responsible for nuclear spallation reactions leading to the production of radioactive elements like Pm. The magnetic fields required to accelerate the bombarding particles must be at least 1000 times stronger than those in solar flares to lead to measurable quantities of Pm through neutron captures by Nd isotopes. They concluded that 'the validity of the [spallation] mechanism (...) remains in question'. In a very recent paper, Goriely (2007) re-examined the spallation process and showed that nuclear reactions can explain the *full* pattern of peculiar abundances for all the 55 elements between Li and U observed at the surface of HD 101065, including the presence of radioelements like Pm. More generally, Goriely (2007) and Yushchenko et al. (2007) have stressed the importance of spallation nucleosynthesis as opposed to the diffusion process as a possible explanation for the abundance

[★]Based on spectra obtained on the VLT (ESO, Paranal, Chile) and retrieved from the ESO archives.

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peculiarities of CP stars. As emphasized by Goriely (2007), the role of nuclear processes in the formation of these chemical peculiarities would be clearly demonstrated if the presence of short-lived radioelements at the surface of CP stars could be confirmed spectroscopically.

Recently, Gopka et al. (2004) claimed that they have identified some lines of radioactive (mostly neutral) elements with $Z = 84-99$ [with the exception of At ($Z = 85$) and Fr ($Z = 87$)] in the spectrum of Przybylski's star (see also Yushchenko et al. 2007 who added lines from the second spectrum of the above-mentioned elements). The detection of such actinides and subactinides would strongly favour the spallation mechanism with respect to the diffusive process (Goriely 2007), but still need to be further confirmed, just like the Pm case.

The analysis of the available observations however is hindered by the large uncertainties resulting from the lack of transition probabilities for Pm II. In this perspective, a detailed investigation of the atomic transitions of this radioelement is strongly needed and particularly interesting not only for confirming the presence of this element in some stars but also for a quantitative reliable determination of its abundance.

For the above-stated reasons, we have decided to perform a first investigation of the transition probabilities in Pm II having in mind that reliable atomic data are key parameters for the line identification and abundance determination of promethium in CP stars. The present paper will focus on the Pm case.

2 ENERGY LEVELS

The ground state of Pm II is $[\text{Xe}] 4f^5 6s^2 7H^\circ_2$ and its ionization energy is $87\,900\text{ cm}^{-1}$ (10.90 eV) according to a spectroscopic determination by Sugar & Reader (1965), stepwise laser excitation methods being unable to provide a value for the ionization limit (Worden et al. 1978).

The spectrum of Pm II is not well known. Between 220.0 and 690.0 nm, the wavelengths and relative intensities of about 2200 lines were determined by Meggers, Scribner & Bozman (1951) but it was not possible to differentiate Pm I and Pm II lines with the arc and spark light sources employed. Davis & Reader (1972a) have re-observed the Pm spectrum and have prepared a line list with 17 500 entries between 310.0 and 1000.0 nm including lines from both the neutral and the singly ionized element but many of them were not separated according to ionization state.

The levels listed by Martin, Zalubas & Hagan (1978) are taken from these investigations and from unpublished material of Davis & Reader (1972b). 169 level values of Pm II are quoted by Martin et al. (1978) but identifications are proposed for only 19 of them, which belong to the $4f^5 ({}^6H^\circ) 6s {}^7H^\circ$, ${}^5H^\circ$, $4f^5 ({}^6F^\circ) 6s {}^7F^\circ$, ${}^5F^\circ$ and $4f^5 ({}^6H^\circ) 5d {}^7K^\circ$ terms.

Additional values of levels were proposed by Otto et al. (1995) who classified four levels of the low-lying $4f^5 ({}^6H^\circ) 5d {}^7K^\circ$ odd multiplet and also five levels of the upper $4f^5 ({}^6H^\circ) 6p {}^7I$ even term. The identified levels used in the present investigation (23 odd and five even levels) were taken from Martin et al. (1978), from the online NIST compilation (NIST 2006) and from Otto et al. (1995). The density of the levels did prevent identification of additional levels on the basis of the calculations of the present work and of the available Landé factors. For the configurations unknown experimentally, the energies of the lowest spectroscopic levels were adopted from Brewer (1971b).

3 THE HYPERFINE STRUCTURE

The Pm spectrum is affected by hyperfine structure. In an early work, Reader & Davis (1963) measured the hyperfine splitting of 450 lines produced in a hollow cathode discharge and used two lines to determine the magnetic dipole and electric quadrupole moments of ${}^{147}\text{Pm}$. Hyperfine structure and isotope shifts of the two transitions at 557.6 and 542.5 nm of the isotopes ${}^{145}\text{Pm}$ and ${}^{147}\text{Pm}$ were investigated by Alkhazov et al. (1992) using collinear laser ion beam spectroscopy. The values obtained for the nuclear spins confirmed values due to Reader (1966) from earlier hollow cathode experiments, Budick & Marrus (1963) from atomic beam magnetic resonance measurements, Stapleton, Jeffries & Shirley (1961) from paramagnetic resonance observations and Straume, Gloevhoeiden & Burke (1980) from an ion beam device. Extensive data about hyperfine structure (75 lines of ${}^{147}\text{Pm}$) are due to Otto et al. (1995) who used a hollow cathode discharge and a Fabry-Perot interferometer. As a consequence of these investigations, the nuclear spins of Pm isotopes are $5/2$ (${}^{145}\text{Pm}$, ${}^{151}\text{Pm}$), 3 (${}^{146}\text{Pm}$) and $7/2$ (${}^{147}\text{Pm}$, ${}^{149}\text{Pm}$), and Pm II is obviously affected by hyperfine structure.

The broadening effects on the line profiles must normally be taken into account for reliable and accurate abundance determinations of this element in stellar atmospheres. They are not, however, of crucial importance for the present investigation which is focussed only on line identification.

4 THE CALCULATION OF RADIATIVE PARAMETERS IN Pm II

The calculations of atomic structures in the case of lanthanide ions, particularly for singly ionized promethium, are extremely complex and, to our knowledge, have never been attempted. This complexity results from the fact that configuration interaction and relativistic effects must be considered simultaneously in the calculations. The ground state of Pm II is $[\text{Xe}] 4f^5 6s$ and the opening of the 4f shell gives rise to a huge number of energy levels. In addition, there is a marked overlap of the different low-lying configurations leading to strong configuration interactions. The energy matrices are very large and these dimensions quickly impose severe limitations to the calculations even with powerful computers.

In the present work, the calculations were performed using a version of Cowan's code (HFR approach: Cowan, 1981) with increased matrix dimensions up to 5000. The configurations explicitly introduced in the model were $4f^4 5d^2$, $4f^4 5d 6s$, $4f^4 6s^2$, $4f^5 6p$, $4f^6$ and $4f^4 6p^2$ for the even parity and $4f^5 6s$, $4f^5 5d$, $4f^4 5d 6p$ and $4f^4 6s 6p$ for the odd parity. Among these configurations, only a few experimental energy levels are available for the configurations $4f^5 6p$, $4f^5 6s$ and $4f^5 5d$. The HFR method has appeared particularly efficient and flexible for extensive calculations of radiative properties in lanthanide ions [see e.g. Biémont & Quinet 2003; Biémont 2005; see also the data base DREAM (Biémont & Quinet 2005) and the references therein at the web site <http://www.umh.ac.be/astro/dream.shtml>] and also in ions of the sixth row period (see e.g. Quinet et al. 2006; Fivet et al. 2006a,b; Palmeri et al. 2006).

When using Cowan's code, it is usual to combine *ab initio* calculations with least-squares fit of the calculated eigenvalues to the observed energy levels. However, in Pm II, in view of the dimensions of the matrices involved and of the lack of experimental energy levels, this approach was not possible. We adjusted only the average energies of the different configurations in order to better reproduce the lowest energy level in each configuration. The scaling factor of the Slater integrals was then chosen for a best fit of the observations,

Table 1. Values of the average energies and of the Slater parameters used in the calculations for the odd and even parities. All the numbers are expressed in cm^{-1} .

Configuration	Parameter	<i>Ab initio</i> value ^a	Fitted	Ratio
4f ⁵ 6s	E_{av}	37 787	39 489	1.045
	$F^2(4f,4f)$	67 559	70 570	1.045
	$F^4(4f,4f)$	42 087	43 962	1.045
	$F^6(4f,4f)$	30 194	31 539	1.045
	ζ_{4f}	984	890	0.904
4f ⁵ 5d	E_{av}	47 063	47 470	1.001
	ζ_{4f}	978	909	0.929
	ζ_{5d}	531	494	0.930
4f ⁴ 5d6p	E_{av}	78 068	–	–
4f ⁴ 6s6p	E_{av}	84 446	–	–
4f ⁵ 6p	E_{av}	60 039	60 853	1.014
	ζ_{4f}	984	881	0.895
	ζ_{6p}	1170	1200	1.026
4f ⁴ 5d ²	E_{av}	55 770	–	–
4f ⁴ 5d6s	E_{av}	51 332	–	–
4f ⁴ 6s ²	E_{av}	56 833	–	–
4f ⁶	E_{av}	73 866	–	–
4f ⁴ 6p ²	E_{av}	11 0843	–	–

Ratio = fitted/*ab initio*.

^aThe average energies have been modified in order to better reproduce the lowest level of each configuration.

the optimal value being 0.70 in agreement with the suggestions of Cowan (1981) regarding the rare earths. In fact, when varying the scaling factor between 0.85 and 0.70, it was observed that the mean deviation between the observed and calculated levels was decreasing from 772 to 227 cm^{-1} . The spin–orbit integrals were kept at their *ab initio* values with the exception of the configurations for which experimental levels are available.

Some parameters were optimized, in a smaller calculation including only three of the 10 configurations, in order to better reproduce the observed levels. For the odd parity, the 18 levels of the 4f⁵6s configuration and the five levels of the 4f⁵5d configuration were fitted by adjusting the parameters which are listed in Table 1. For 4f⁵6s, the ratios of the $F^k(4f,4f)$ ($k = 2, 4, 6$) Slater integrals were kept fixed. The average energies of the configurations unknown experimentally were chosen to better reproduce the lowest levels as taken from Brewer (1971b). The standard deviation was 51 cm^{-1} . For the even parity, five experimental levels were considered and the average energy as well as the spin–orbit parameters were adjusted. They appeared however more sensitive to the addition of higher energy configurations whose values were also adopted from Brewer (1971b). The mean deviation was 102 cm^{-1} . The values of the parameters adopted in the final calculation are quoted in Table 1. The comparison of the experimental and theoretical energy levels is shown in Table 2. The composition of the levels is reported in Tables 3 and 4 for the even and odd parity, respectively, where we give only the three largest components. It appears obvious that the even levels are more strongly perturbed than the odd ones.

The calculated Landé factors listed in Table 2 agree quite well with the measurements except for two even levels at 23 261 and 25 016 cm^{-1} for which somewhat larger, but still reasonable, discrepancies are observed.

Core–valence interactions were taken into account through a polarization model potential and a correction to the dipole operator according to a well-established procedure (see e.g. Quinet et al. 1999) giving rise to the HFR + CPOL method. CPOL effects were

Table 2. Calculated (Calc.) and experimental (Exp.) energy levels, experimental and theoretical Landé g-factors in Pm II. The values are quoted in cm^{-1} .

Configuration	Term	J	$E_{\text{Exp.}}^a$ (cm^{-1})	$E_{\text{Calc.}}^b$ (cm^{-1})	Δ^c (cm^{-1})	$g_{\text{Exp.}}^d$	$g_{\text{Calc.}}^e$
4f ⁵ (⁶ F ^o)6s	⁷ F ^o	0	5281	5273	8	–	–
		1	5391	5366	25	1.493	1.478
		2	5631	5575	56	1.481	1.478
		3	6049	5955	94	1.482	1.481
		4	6705	6585	120	1.500	1.488
4f ⁵ (⁶ F ^o)6s	⁵ F ^o	1	6629	6550	79	0.000	0.019
		2	7013	6886	127	1.010	1.001
		3	7701	7543	158	1.230	1.251
4f ⁵ (⁶ H ^o)6s	⁷ H ^o	2	0	–10	10	0.000	0.012
		3	446	426	20	0.728	0.727
		4	1133	1106	27	1.038	1.036
		5	1984	1943	41	1.190	1.192
		6	2950	2888	62	1.290	1.280
4f ⁵ (⁶ H ^o)6s	⁵ H ^o	3	1603	1547	56	0.531	0.537
		4	2667	2600	67	0.920	0.918
		5	3812	3723	89	1.100	1.107
4f ⁵ (⁶ H ^o)5d	⁷ K ^o	6	5018	4894	124	1.200	1.214
		4	5332	5332	0	0.412	0.410
		5	6131	6144	–13		0.772
		6	7041	7059	–18		0.978
		7	8042	8058	–16		1.107
		8	9119	9121	–2		1.193
		3	23 261	23 452	–191	0.617	0.429
		4	24 157	24 291	–134	0.855	0.836
4f ⁵ (⁶ H)6p	⁷ I	5	25 016	24 942	74	1.110	0.991
		6	26 028	26 084	–56	1.160	1.120
		7	27 110	27 055	55		1.161

^aFrom Martin et al. (1978), NIST (2006) or Otto et al. (1995). ^bThis work: HFR + CPOL values. ^c $\Delta = E_{\text{Exp.}} - E_{\text{Calc.}}$. ^dFrom Martin et al. (1978). ^eThis work: HFR + CPOL results.

included in the calculations by considering, for the 4f⁴ core, the values of the dipole polarizability $\alpha_d = 5.89$ au (Fraga, Karwowski & Saxena 1976) and the cut-off radius $r_c = 1.67$ au corresponding to the HFR mean radius of the 5p orbital.

The transition probabilities are reported in Table 5. We give both the HFR and HFR + CPOL results for the 46 transitions connecting the 23 experimental levels which have been identified. It is observed that the polarization effects generally decrease the oscillator strengths and that their effect must be taken into account in order to obtain a reliable scale of f -values in this ion. We give also in the table, for information, the intensities of some lines as they have been observed in the laboratory [see Reader et al. 1980 and the NIST compilation (NIST 2006)].

As this is the first set of transition probabilities obtained, there are no other experimental or theoretical results available for comparison.

5 THE PARTITION FUNCTIONS OF Pm I, Pm II AND Pm III

In order to estimate the detrimental effect of missing experimental levels on the partition functions of Pm I and Pm II, two calculations were performed, the first one using only the available experimental levels and the second one based on the experimental levels completed with calculated values. For Pm I, we used the experimental

Table 3. Percentage composition of the even levels of Pm II. Only the three largest components are listed.

Configuration	Level	$E^a_{\text{Exp.}} \text{ (cm}^{-1}\text{)}$			Composition (per cent)						
$4f^5(^6H)6p$	7I_3	23 261.30	58	$4f^5(^6H)6p$	7I_3	5	$4f^4(^5I)5d^2$	5H_3	3	$4f^4(^5I)5d^2$	5H_3
$4f^5(^6H)6p$	7I_4	24 157.20	40	$4f^5(^6H)6p$	7I_4	6	$4f^4(^5I)5d^2$	7H_4	6	$4f^4(^5I)5d^2$	5G_4
$4f^5(^6H)6p$	7I_5	25 015.69	58	$4f^5(^6H)6p$	7I_5	6	$4f^5(^6H)6p$	5I_5	3	$4f^4(^5I)5d^2$	3I_5
$4f^5(^6H)6p$	7I_6	26 027.56	51	$4f^5(^6H)6p$	7I_6	12	$4f^4(^5I)5d^2$	5I_6	6	$4f^4(^5F)5d^2$	7I_6
$4f^5(^6H)6p$	7I_7	27 110.08	45	$4f^5(^6H)6p$	7I_7	10	$4f^4(^5F)5d^2$	7I_7	4	$4f^4(^5I)5d^2$	5K_7

^aFrom Otto et al. (1995).**Table 4.** Percentage composition of the odd levels of Pm II. Only the three largest components are listed.

Configuration	Level	$E^a_{\text{Exp.}} \text{ (cm}^{-1}\text{)}$			Composition (per cent)						
$4f^5(^6F^o)6s$	$^7F_0^o$	5280.88	95	$4f^5(^6F^o)6s$	$^7F_0^o$	1	$4f^5(^4D^o)6s$	$^5D_0^o$	1	$4f^5(^4D^o)6s$	$^5D_0^o$
$4f^5(^6F^o)6s$	$^7F_1^o$	5391.46	93	$4f^5(^6F^o)6s$	$^7F_1^o$	1	$4f^5(^4D^o)6s$	$^5D_1^o$	1	$4f^5(^4D^o)6s$	$^5D_1^o$
$4f^5(^6F^o)6s$	$^5F_1^o$	6629.40	93	$4f^5(^6F^o)6s$	$^5F_1^o$	1	$4f^5(^4D^o)6s$	$^3D_1^o$	1	$4f^5(^4D^o)6s$	$^3D_1^o$
$4f^5(^6H^o)6s$	$^7H_2^o$	0.00	94	$4f^5(^6H^o)6s$	$^7H_2^o$	2	$4f^5(^4G^o)6s$	$^5G_2^o$	1	$4f^5(^4G^o)6s$	$^5G_2^o$
$4f^5(^6F^o)6s$	$^7F_2^o$	5632.40	91	$4f^5(^6F^o)6s$	$^7F_2^o$	2	$4f^5(^6F^o)6s$	$^5F_2^o$	2	$4f^5(^4F^o)6s$	$^5F_2^o$
$4f^5(^6F^o)6s$	$^5F_2^o$	7012.87	90	$4f^5(^6F^o)6s$	$^5F_2^o$	2	$4f^5(^4F^o)6s$	$^3F_2^o$	2	$4f^5(^6F^o)6s$	$^7F_2^o$
$4f^5(^6H^o)6s$	$^7H_3^o$	446.45	83	$4f^5(^6H^o)6s$	$^7H_3^o$	11	$4f^5(^6H^o)6s$	$^5H_3^o$	2	$4f^5(^4G^o)6s$	$^5G_3^o$
$4f^5(^6H^o)6s$	$^5H_3^o$	1602.97	83	$4f^5(^6H^o)6s$	$^5H_3^o$	11	$4f^5(^6H^o)6s$	$^7H_3^o$	2	$4f^5(^4G^o)6s$	$^3G_3^o$
$4f^5(^6F^o)6s$	$^7F_3^o$	6048.50	89	$4f^5(^6F^o)6s$	$^7F_3^o$	3	$4f^5(^6F^o)6s$	$^5F_3^o$	2	$4f^5(^4F^o)6s$	$^5F_3^o$
$4f^5(^6F^o)6s$	$^5F_3^o$	7701.09	88	$4f^5(^6F^o)6s$	$^5F_3^o$	3	$4f^5(^6F^o)6s$	$^7F_3^o$	3	$4f^5(^4F^o)6s$	$^3F_3^o$
$4f^5(^6H^o)6s$	$^7H_4^o$	1133.45	85	$4f^5(^6H^o)6s$	$^7H_4^o$	10	$4f^5(^6H^o)6s$	$^5H_4^o$	1	$4f^5(^4G^o)6s$	$^5G_4^o$
$4f^5(^6H^o)6s$	$^5H_4^o$	2666.76	85	$4f^5(^6H^o)6s$	$^5H_4^o$	11	$4f^5(^6H^o)6s$	$^7H_4^o$	1	$4f^5(^4G^o)6s$	$^3G_4^o$
$4f^5(^6H^o)5d$	$^7K_4^o$	5332.36	94	$4f^5(^6H^o)5d$	$^7K_4^o$	2	$4f^5(^4G^o)5d$	$^5I_4^o$	2	$4f^5(^4G^o)5d$	$^5I_4^o$
$4f^5(^6F^o)6s$	$^7F_4^o$	6705.18	89	$4f^5(^6F^o)6s$	$^7F_4^o$	3	$4f^5(^6F^o)6s$	$^5F_4^o$	2	$4f^5(^4F^o)6s$	$^5F_4^o$
$4f^5(^6H^o)6s$	$^7H_5^o$	1983.52	88	$4f^5(^6H^o)6s$	$^7H_5^o$	8	$4f^5(^6H^o)6s$	$^5H_5^o$			
$4f^5(^6H^o)6s$	$^5H_5^o$	3812.31	88	$4f^5(^6H^o)6s$	$^5H_5^o$	8	$4f^5(^6H^o)6s$	$^7H_5^o$			
$4f^5(^6H^o)5d$	$^7K_5^o$	6131.47	95	$4f^5(^6H^o)5d$	$^7K_5^o$	2	$4f^5(^4G^o)5d$	$^5I_5^o$	1	$4f^5(^4G^o)5d$	$^5I_5^o$
$4f^5(^6H^o)6s$	$^7H_6^o$	2950.31	91	$4f^5(^6H^o)6s$	$^7H_6^o$	5	$4f^5(^6H^o)6s$	$^5H_6^o$			
$4f^5(^6H^o)6s$	$^5H_6^o$	5017.77	90	$4f^5(^6H^o)6s$	$^5H_6^o$	5	$4f^5(^6H^o)6s$	$^7H_6^o$			
$4f^5(^6H^o)5d$	$^7K_6^o$	7040.66	96	$4f^5(^6H^o)5d$	$^7K_6^o$	1	$4f^5(^4G^o)5d$	$^5I_6^o$			
$4f^5(^6H^o)6s$	$^7H_7^o$	4000.15	93	$4f^5(^6H^o)6s$	$^7H_7^o$	3	$4f^5(^6H^o)6s$	$^5H_7^o$	2	$4f^5(^4I^o)6s$	$^5I_7^o$
$4f^5(^6H^o)5d$	$^7K_7^o$	8041.72	97	$4f^5(^6H^o)5d$	$^7K_7^o$						
$4f^5(^6H^o)5d$	$^7K_8^o$	9119.34	97	$4f^5(^6H^o)5d$	$^7K_8^o$	1	$4f^5(^4I^o)5d$	$^5L_8^o$			

^aFrom Martin et al. (1978) and from NIST (2006).

energies compiled by Martin et al. (1978) and the calculated values obtained using an HFR model including the five lowest configurations, that is, $4f^5 6s^2$, $4f^4 5d 6s^2$, $4f^5 5d 6s$, $4f^4 5d^2 6s$ and $4f^5 6s 6p$. All the Slater integrals (F^k , G^k and R^k) were scaled down by a factor of 0.70 and the average energies were adjusted to reproduce the lowest level predicted by Brewer (1971a) for each configuration. Among the huge number (several thousands) of calculated energies obtained using the set of five configurations mentioned above, only 304 values below $20\,000 \text{ cm}^{-1}$ were considered in the partition function calculations. It is worth noting that, for the same energy range, experimental values are available for only 13 levels in the NIST tables (Martin et al. 1978). In the case of Pm II, the 173 experimental levels reported in Martin et al. (1978) and Otto et al. (1995) were completed by the HFR calculations performed in the present work and described in Section 4. In fact, 1623 computed levels between 0 and $35\,000 \text{ cm}^{-1}$ were included in the partition function calculations.

For Pm III, for which no experimental level values are available in the literature, the partition functions could only be estimated

using theoretically predicted energies. These were obtained using the Cowan's code including the $4f^5$, $4f^4 6p$, $4f^3 5d^2$, $4f^3 5d 6s$, $4f^3 6s^2$, $4f^4 5d$, $4f^4 6s$ and $4f^3 5d 6p$ configurations from which the 523 levels situated below $50\,000 \text{ cm}^{-1}$ were retained in the partition function calculations. All the Slater integrals were scaled down by 0.75 and the average energies were adjusted to reproduce the energy of the lowest level of each configuration as predicted by Brewer (1971b).

The partition functions calculated in the present work are given in Table 6 for temperatures ranging from 3000 to $14\,000 \text{ K}$.

6 TENTATIVE DETECTION OF Pm II LINES IN PRZYBYLSKI'S STAR SPECTRUM

As pointed out in Section 1, Cowley et al. (2004) have reported Pm I and Pm II detection in Przybylski's star (HD 101065). The detection of Pm I lines is actually quite surprising, since an ionization equilibrium calculation based on the Saha formula shows that Pm II is by far the dominant species. A rough ionization equilibrium

Table 5. Calculated oscillator strengths (log gf) for the transitions connecting the identified levels for which experimental energies are available. We give both the HFR and HFR + CPOL values. The laboratory intensities are also reported for some transitions.

$\lambda_{\text{Exp.}}$ (nm) ^a	E_{low} ^b (cm ⁻¹)	Designation ^b	E_{upp} ^c (cm ⁻¹)	Designation ^c	$I_{\text{Exp.}}$ ^d	log gf ^e	log gf ^f
413.795	2950.31	6s ⁷ H ^o ₆	27 110.08	6p ⁷ I ₇		0.39	0.30
415.786	1983.52	6s ⁷ H ^o ₅	26 027.56	6p ⁷ I ₆		0.44	0.36
418.603	1133.45	6s ⁷ H ^o ₄	25 015.69	6p ⁷ I ₅		0.41	0.32
429.778	0.00	6s ⁷ H ^o ₂	23 261.30	6p ⁷ I ₃	600	0.17	0.08
432.592	4000.15	6s ⁷ H ^o ₇	27 110.08	6p ⁷ I ₇	250	-0.41	-0.54
433.205	2950.31	6s ⁷ H ^o ₆	26 027.56	6p ⁷ I ₆	200	-0.46	-0.58
434.053	1983.52	6s ⁷ H ^o ₅	25 015.69	6p ⁷ I ₅		-0.26	-0.37
434.212	1133.45	6s ⁷ H ^o ₄	24 157.20	6p ⁷ I ₄	300	-0.78	-0.90
438.188	446.45	6s ⁷ H ^o ₃	23 261.30	6p ⁷ I ₃	200	-0.61	-0.71
443.251	1602.97	6s ⁵ H ^o ₃	24 157.20	6p ⁷ I ₄	400	-0.62	-0.70
447.323	2666.76	6s ⁵ H ^o ₄	25 015.69	6p ⁷ I ₅	300	-2.13*	-2.44*
450.015	3812.31	6s ⁵ H ^o ₅	26 027.56	6p ⁷ I ₆	600	-1.67	-1.89
450.859	1983.52	6s ⁷ H ^o ₅	24 157.20	6p ⁷ I ₄		-2.13	-2.33
451.792	1133.45	6s ⁷ H ^o ₄	23 261.30	6p ⁷ I ₃		-2.19	-2.68
452.520	5017.77	6s ⁵ H ^o ₆	27 110.08	6p ⁷ I ₇	600	-0.63	-0.73
453.072	2950.31	6s ⁷ H ^o ₆	25 015.69	6p ⁷ I ₅		-1.38	-1.45
453.853	4000.15	6s ⁷ H ^o ₇	26 027.56	6p ⁷ I ₆		-1.62	-1.67
461.587	1602.97	6s ⁵ H ^o ₃	23 261.30	6p ⁷ I ₃	100	-0.75	-0.76
465.193	2666.76	6s ⁵ H ^o ₄	24 157.20	6p ⁷ I ₄		-0.67	-0.67
471.491	3812.31	6s ⁵ H ^o ₅	25 015.69	6p ⁷ I ₅		-1.62	-1.76
475.836	5017.77	6s ⁵ H ^o ₆	26 027.56	6p ⁷ I ₆		-2.33	-2.37
485.430	2666.76	6s ⁵ H ^o ₄	23 261.30	6p ⁷ I ₃		-1.93	-1.92
491.387	3812.31	6s ⁵ H ^o ₅	24 157.20	6p ⁷ I ₄		-1.15	-1.15
498.132	7040.66	5d ⁷ K ^o ₆	27 110.08	6p ⁷ I ₇		-2.53	-2.61
499.913	5017.77	6s ⁵ H ^o ₆	25 015.69	6p ⁷ I ₅		-3.71*	-3.88*
502.471	6131.47	5d ⁷ K ^o ₅	26 027.56	6p ⁷ I ₆		-2.09	-2.10
507.903	5332.36	5d ⁷ K ^o ₄	25 015.69	6p ⁷ I ₅		-2.66	-2.69
524.283	8041.72	5d ⁷ K ^o ₇	27 110.08	6p ⁷ I ₇		-0.97	-1.04
526.532	7040.66	5d ⁷ K ^o ₆	26 027.56	6p ⁷ I ₆		-2.46	-2.54
529.392	6131.47	5d ⁷ K ^o ₅	25 015.69	6p ⁷ I ₅	200	-0.91	-0.97
531.065	5332.36	5d ⁷ K ^o ₄	24 157.20	6p ⁷ I ₄		-1.34	-1.41
545.983	6705.18	6s ⁷ F ^o ₄	25 015.69	6p ⁷ I ₅		-4.11*	-4.40*
552.067	6048.50	6s ⁷ F ^o ₃	24 157.20	6p ⁷ I ₄		-3.75	-3.58
554.608	6131.47	5d ⁷ K ^o ₅	24 157.20	6p ⁷ I ₄	800	-0.18	-0.26
555.688	9119.34	5d ⁷ K ^o ₈	27 110.08	6p ⁷ I ₇	120	0.02	-0.03
555.839	8041.72	5d ⁷ K ^o ₇	26 027.56	6p ⁷ I ₆	150	-0.83	-0.94
556.173	7040.66	5d ⁷ K ^o ₆	25 015.69	6p ⁷ I ₅	200	0.03	-0.04
557.602	5332.36	5d ⁷ K ^o ₄	23 261.30	6p ⁷ I ₃	800	-0.09	-0.17
567.061	5632.40	6s ⁷ F ^o ₂	23 261.30	6p ⁷ I ₃		-3.51	-3.08
572.841	6705.18	6s ⁷ F ^o ₄	24 157.20	6p ⁷ I ₄		-4.81*	-4.41*
580.802	6048.50	6s ⁷ F ^o ₃	23 261.30	6p ⁷ I ₃		-3.77*	-3.26
603.839	6705.18	6s ⁷ F ^o ₄	23 261.30	6p ⁷ I ₃		-4.33*	-5.08*
607.509	7701.09	6s ⁵ F ^o ₃	24 157.20	6p ⁷ I ₄		-3.06	-3.28
615.274	7012.87	6s ⁵ F ^o ₂	23 261.30	6p ⁷ I ₃		-3.16	-3.18
642.487	7701.09	6s ⁵ F ^o ₃	23 261.30	6p ⁷ I ₃		-2.98	-3.16

^aFrom Reader et al. (1980) or otherwise calculated from the experimental levels of Martin et al. (1978) and Otto et al. (1995). ^bFrom Martin et al. (1978) or from the NIST compilation (NIST 2006). ^cFrom Otto et al. (1995). ^dFrom Reader et al. (1980). ^eThis work: HFR results. ^fThis work: HFR + CPOL results. *Cancellation effects present (cancellation factor <0.01; see Cowan 1981).

calculation, using the partition functions listed in Table 6, shows indeed that the relative fractions of Pm I, Pm II and Pm III are, respectively, 1.120, 98.877 and 0.003 per cent for a temperature of 6500 K and an electronic pressure of $P_e = 40$ (CGS units) close to the values encountered in the atmosphere of Przybylski's star.

Cowley et al. (2004) claim is based on the so-called wavelength coincidence statistics (WCS) technique. This technique counts the number of line coincidences between a laboratory line list and the measured lines or blends in an observed spectrum. Comparing this number of 'hits' with the ones obtained when shifting the labora-

tory line list by random wavelength increments leads to a number directly related to the probability that lines of the considered element are indeed present in the star. Quite interestingly, when applied to an element like Pm whose isotopes are all short lived, the mere detection of Pm lines must be a signature of ongoing nucleosynthesis in the considered star. Of course the WCS probability depends on the tolerance allowed for the line coincidences. Cowley et al. (2004) allow tolerances of 0.01, 0.02, 0.04 or 0.06 Å. All the lines are equally considered, whatever their atomic parameters can be (they were unknown until now in the case of Pm II). It is expected,

Table 6. Partition functions in Pm I, Pm II and Pm III.

T (K)	Pm I		Pm II		Pm III
	Exp. levels only ^a	Exp. + Calc. levels ^b	Exp. levels only ^c	Exp. + Calc. levels ^d	Calc. levels ^e
3000	24.08	26.55	38.33	45.14	22.24
3500	27.83	33.89	45.23	58.44	25.95
4000	31.56	43.81	52.04	74.99	29.79
4500	35.38	56.87	58.76	95.51	33.84
5000	39.40	73.48	65.44	120.70	38.21
5500	43.77	93.80	72.13	151.16	43.00
6000	48.64	117.85	78.91	187.42	48.34
6500	54.10	145.49	85.85	229.85	54.31
7000	60.27	176.51	92.99	278.69	61.02
7500	67.18	210.61	100.40	334.04	68.54
8000	74.88	247.49	108.09	395.87	76.94
8500	83.38	286.82	116.08	464.06	86.25
9000	92.65	328.27	124.37	538.38	96.53
9500	102.67	371.53	132.97	618.53	107.80
10 000	113.40	416.32	141.86	704.18	120.07
10 500	124.79	462.36	151.03	794.94	133.34
11 000	136.79	509.40	160.45	890.41	147.60
11 500	149.35	557.22	170.11	990.18	162.84
12 000	162.41	605.62	179.98	1093.83	179.04
12 500	175.91	654.42	190.03	1200.97	196.17
13 000	189.79	703.47	200.24	1311.21	214.19
13 500	204.02	752.62	210.59	1424.15	233.06
14 000	218.54	801.75	221.06	1539.46	252.75

^aCalculated using the experimental energy levels compiled by Martin et al. (1978) (223 levels). ^bCalculated using the experimental energy levels compiled by Martin et al. (1978) completed with those obtained by HFR calculations performed in the present work (see text) (514 levels). ^cCalculated using the experimental energy levels reported in Martin et al. (1978) and Otto et al. (1995) (173 levels). ^dCalculated using the experimental energy levels reported in Martin et al. (1978) and Otto et al. (1995) completed with those obtained by HFR calculations performed in the present work (see text) (1623 levels). ^eCalculated using the HFR energy levels predicted in the present work (see text) (523 levels).

however, that lines with high-lying lower levels and/or low oscillator strengths must be quite weak.

An approach different from the WCS one has been adopted in the present study, since the atomic parameters of many Pm II lines are now available. The Pm II lines are thus analysed individually, taking into account their inferred equivalent width, which can now be estimated from the $\log gf$ and excitation potential listed in Table 5. This equivalent width has been roughly estimated as $\log gf - \theta \chi_{\text{exc}}$, where χ_{exc} is the excitation potential and θ is the reduced temperature, estimated at 5040/6600 for Przybylski's star.

Of course the best way to test for the presence of a given chemical element in a star consists of using an appropriate model atmosphere. However, all 'classical' models (e.g. Kurucz 1995; Castelli & Kurucz 2003) grossly fail to reproduce most spectral regions of Przybylski's star, while more reliable models, taking into account in particular the stratification of its atmosphere, are not yet available (see however Shavrina et al. 2006).

Lines falling in the vicinity of Pm II lines have been identified using the lists of Moore (1953), VALD (Kupka et al. 1999, and references therein), DREAM (see above), as well as the line lists posted on Cowley's web site (<http://www.astro.lsa.umich.edu/~cowley/prznew2.html>). The depth of the various blending contributions has been evaluated by searching, for each species contributing to the blend, for lines with the same excitation potential and of similar oscillator strength, present in other (cleaner) regions of the spectrum.

In order to estimate the probability of a blend with an unclassified line from the second or the third spectrum of a lanthanide element, one can evaluate the line density of such species in the

investigated spectral region. To give an idea, we have calculated the line densities for two particular ions, that is, Ce II and Pr III, for which a large number of energy levels have been established experimentally. When considering all the lines with the intensity factor $\log gf - \theta \chi_{\text{exc}} > -2$ listed in the DREAM data base for these ions in the spectral region 400–600 nm, we found average line densities of the order of 4.5 and 0.05 lines nm^{-1} for Ce II and Pr III, respectively. For linewidths of 0.01 nm, this corresponds approximately to probabilities of blending with a Ce II or a Pr III line equal to 4.5 and 0.05 per cent. These values can be considered as gross approximations of probabilities of blending with a line from the second or the third spectrum of a lanthanide element in the region 400–600 nm since they depend on the element and on the intensity of the radiative transitions chosen to calculate the line densities.

In fact, the main source of error in the following discussion does not reside in the uncertainties on the line position, oscillator strengths or excitation potentials, but rather on the missing (or incomplete) second and third spectra of many atoms. Hence many lines in the spectrum of Przybylski's star simply cannot be identified because they very likely belong to an ion whose transitions are not (yet) tabulated. In the very unfortunate circumstance where such a transition coincides with the position of a Pm II line, then we will erroneously conclude that the Pm II line has indeed been detected. However, given the relatively large number of Pm II lines discussed below, it must be hoped that such unfortunate line coincidences do not happen often enough as to invalidate our analysis.

The eight first strongest Pm II lines, ordered by decreasing (estimated) equivalent width, are discussed below and displayed in Fig. 1. The VLT/UVES spectrum, retrieved from the ESO archives

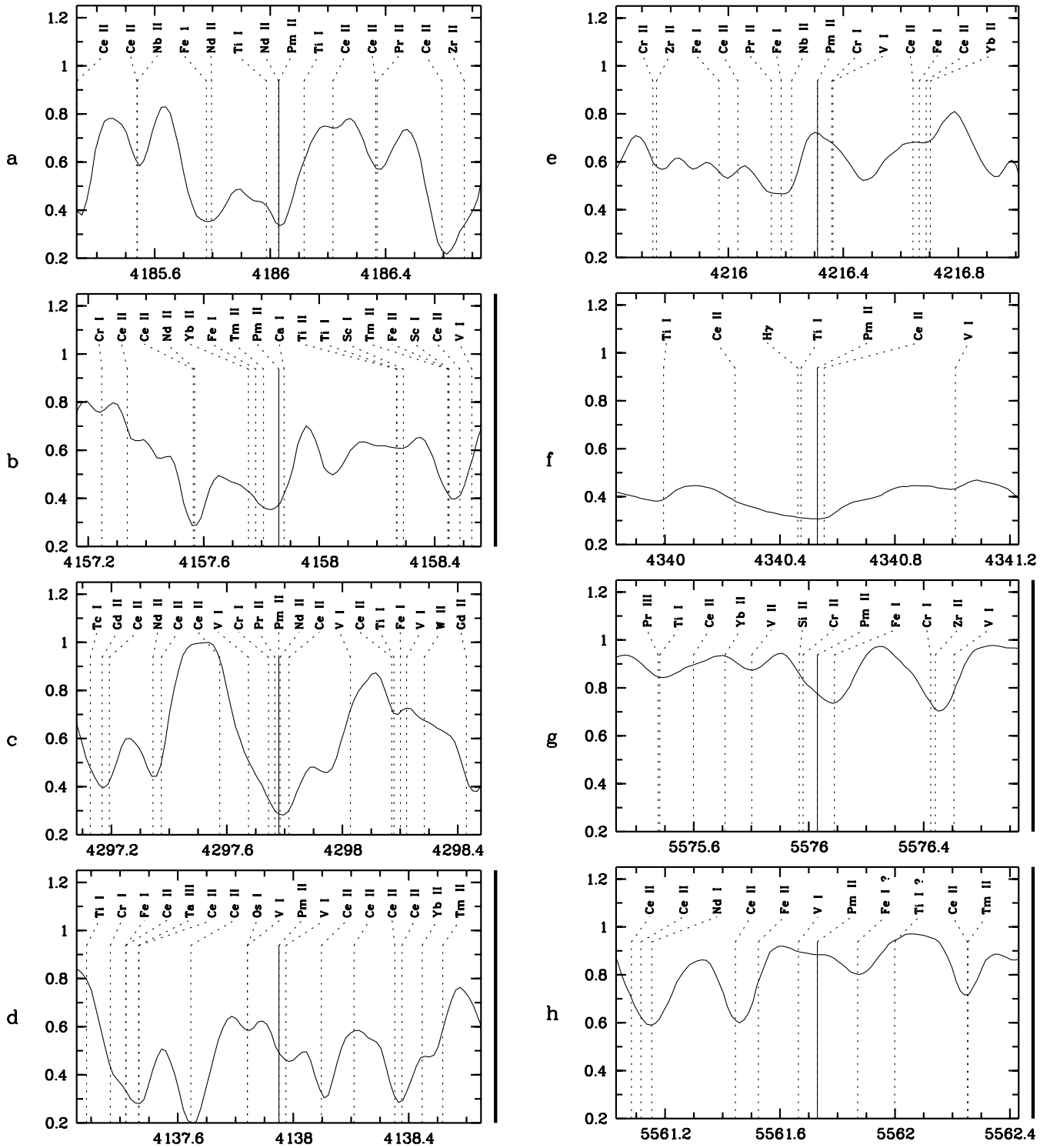


Figure 1 – continued

Figure 1. The eight (expected) strongest Pm II lines in the spectrum of Przybylski's star are plotted, ordered by decreasing equivalent width (as estimated in Section 5). Tentative identifications have been attempted as well for neighbouring lines, but they are in some cases very uncertain. The cases where Pm II is the main identified contributor to the spectral feature are indicated with a bold vertical bar on the right-hand side of the panel (i.e. in the other cases, blends with identified species hinder the detection of the possible contribution of Pm II to the central feature).

(Bagnulo et al. 2002), has been corrected for the Doppler shift by cross-correlating the few (Fe and Ti) lines in common between the Sun and Przybylski's star. The spectral resolution is $R = 80\,000$, the signal-to-noise ratio (S/N) is nearly 300 in the red spectral region. The spectra have been normalized to a nearby continuum point. To allow an easy comparison between the strength of the various spectral features, all spectra are plotted on the same scale in Fig. 1. The following considerations apply.

(a) 418.603 nm: The strongest Pm II line is unfortunately not observable because of the coinciding strong Nd II 418.6029 nm line.

(b) 415.786 nm: The nearby Ca I 415.7878 nm line is not supposed to go deeper than 90 per cent of the continuum, based on another clean Ca I line (601.5923 nm) of similar parameters (same excitation potential, similar log gf). Similarly, the Fe I 415.7780 nm line depth should be around 75 per cent of the continuum, and the 415.7807 nm Tm II line should not go deeper than 85 per cent. This leaves room for a major contribution of Pm II 415.786 nm to the blend. If this should be the case, then the wavelength of the observed Pm II line should rather be 415.783 nm instead of 415.786 nm.

(c) 429.778 nm: This line is unfortunately blended by the strong Pr II λ 429.7766 nm, Nd II λ 429.7784 nm and Ce II λ 429.7815 nm lines, and is not observable.

(d) 413.795 nm: The nearby V I 413.7974 nm falls near the core of the blend. However, clean V I lines with similar excitation potential and log gf (354.0535, 418.6767 nm) are not as deep (depth: 80 per cent of the continuum). With similar arguments, the nearby (fainter) Fe I 413.7967 nm and Ti I 413.7985 nm lines were discarded. Hence the absence of other identified contributor to the blend is an argument in favour of a Pm II contribution, provided that its wavelength is 413.799 nm instead of 413.795 nm.

(e) 421.631 nm: Line identification is a challenge in this region. No feature is observed in the vicinity of this Pm II line so that the expectedly fainter Pm II lines in subframes (f), (g) and (h) should not go deeper than 75 per cent of the continuum.

(f) 434.053 nm: If present, this line is not observable because of the blend with H γ .

(g) 557.603 nm: This line provides strong support for the presence of Pm II. The Fe I 557.6089 nm line is clearly blended on its blue wing. Despite the fact that weaker blending lines have been searched for (given the proximity to the continuum), no other contributor than Pm II could be identified. The line depth can be estimated at about 85 per cent, which is well in line with the expected Pm II 557.603 nm line strength.

(h) 556.173 nm: The nearby V I 556.1664 nm line is detected, but it may leave room for a faint Pm II line before the stronger line around 556.187 nm. Note that the identification of this line as Fe I is quite uncertain.

All weaker Pm II lines are not observed because of blends. Indeed, they are not expected to be easily detected, since they should be weaker than the Pm II 556.173 nm line, which has only a depth of 5 per cent.

The above discussion shows that for each spectral region where the spectrum is sufficiently clean, a line is indeed observed at the precise location of a laboratory Pm II line. Moreover, the depth of these lines are ordered as expected, based on their atomic parameters. It can thus be concluded that the atomic parameters computed in the present paper support the detection of Pm II in Przybylski's star. Nevertheless, a definitive claim for detection should await the availability of dedicated model atmospheres.

7 Pm II LINES IN THE HR 465 SPECTRUM

Cowley et al. (2004) have reviewed previous searches for Pm lines in the spectrum of HR 465 (HD 9996). It was pointed out that there is very weak support to the original identification of Pm lines in HR 465, but the problem has not been revisited since the 1970s. HR 465 shows spectrum variability with a period nearly 22–24 yr (Preston & Wolf 1970). The spectrum used in the present work has

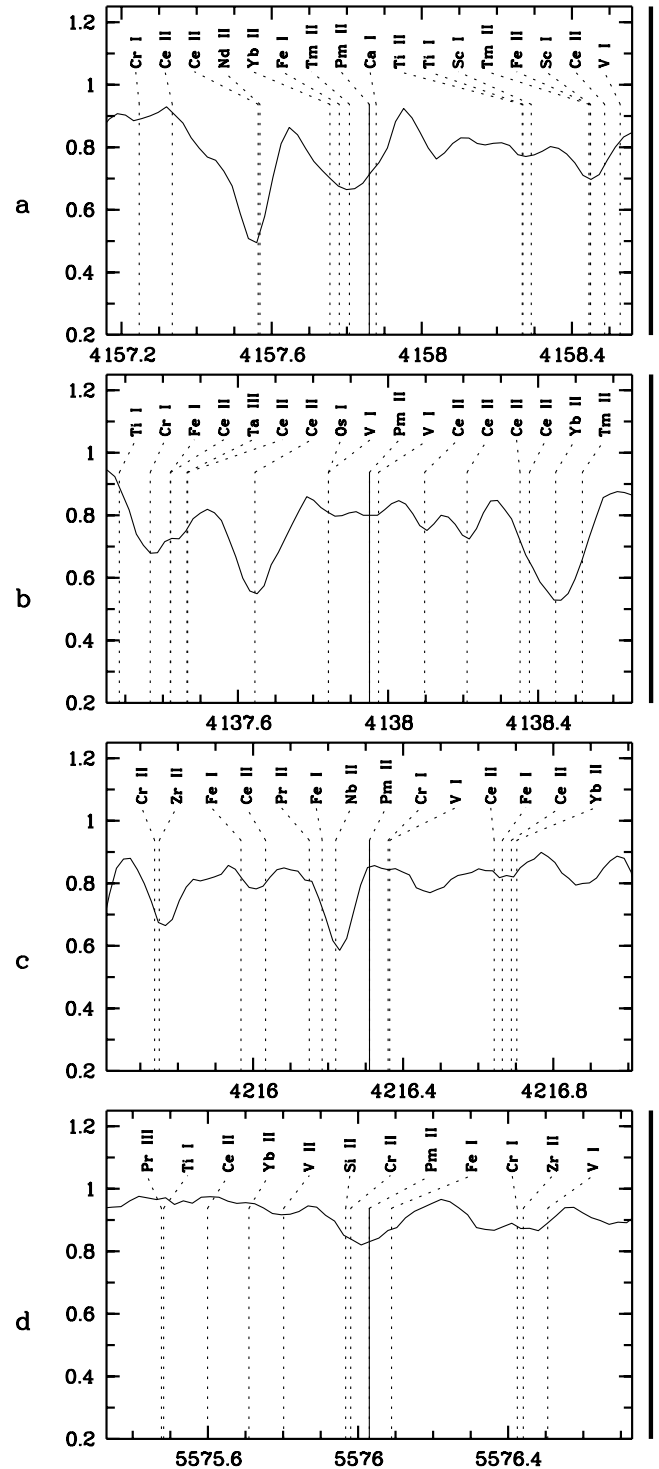


Figure 2. The five (expected) strongest Pm II lines in the 2004 spectrum of HR 465. Identifications of the strongest neighbouring lines are also shown.

been obtained in 2004, when lanthanides were strong and Cr weak, with the 1.8-m telescope of Bohuynsan Observatory (Korea). The spectral resolution is $R = 80\,000$ and S/N larger than 100.

Making use of the detectability diagnostics presented in Section 5 for Przybylski's star, we only show in Fig. 2 the five strongest detectable Pm II lines, ordered by decreasing (estimated) equivalent width, and discuss them individually. As for Przybylski's star, the

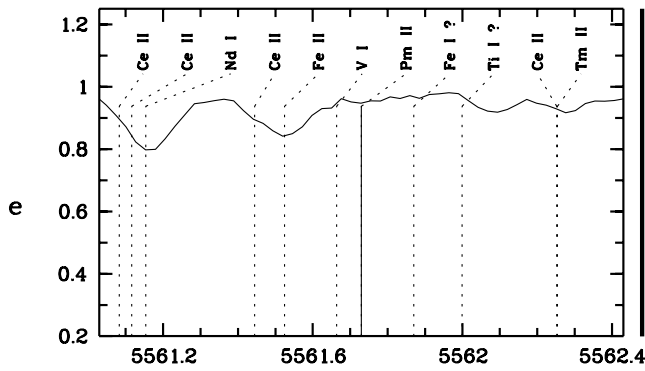


Figure 2 – continued

lines at 418.603, 429.778 and 434.053 nm are omitted from the discussion because of their strong blending by lines of other elements.

(a) 415.786 nm: the Fe I 415.7780 nm line (its depth should be around 15 per cent of the continuum), and the 415.775 nm Yb II line are the main contributors to the observed blend. The Pm II 415.786 nm line is clearly detected in the red wing of this blend.

(b) 413.795 nm: The lines of the first spectra are faint at the temperature of HR 465, so the Pm line is clean. The observed wavelength is 413.792 nm.

(c) 421.631 nm: As in Przybylski's star, no clear evidence for the Pm II line is seen at this wavelength. This line (and the following ones) should thus have a depth not larger than 10 per cent of the continuum.

(d) 557.602 nm: The Fe I 557.6089 nm line is faint, contrarily to the situation prevailing for the cooler Przybylski's star. There is room for a moderately strong contribution of the 557.602 nm Pm II line among the blend Fe I 557.608 nm, Cr II 557.598 nm and Si II 557.5967 nm.

(e) 556.173 nm: This Pm line seems clean albeit rather weak.

8 CONCLUSIONS

Transition probabilities are calculated for 46 Pm II transitions of astrophysical interest. The complexity of the spectrum of this element imposes severe constraints to the model used for the calculation of radiative parameters but nevertheless we believe that the oscillator strengths obtained are reliable and susceptible to provide accurate quantitative information about the abundance of promethium in some CP and other stars. The present analysis supports the detection of Pm II lines in the spectrum of Przybylski's star. The identification of Pm II lines in HR 465 also seems secure. A more detailed quantitative analysis is awaiting the availability of accurate models for the outer layers of these strange and fascinating astrophysical objects.

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