

# Radiative lifetimes for the 4p excited states of phosphorus and the oscillator strengths of solar lines

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**Abstract.** Radiative lifetimes for the levels of the  $3s^23p^24p$  configuration in neutral phosphorus have been determined experimentally for the first time and also theoretically. Experiments were performed by using two-photon UV laser excitation and subsequent fluorescence detection in a laser-produced plasma. In relativistic Hartree-Fock calculations, the Cowan code extended to 42 configurations was used. Finally, the lifetimes for all the 13 excited states in the 4p configuration were calculated and for 6 of them the values were measured experimentally. Theoretical branching ratios were combined with experimental lifetimes, to deduce oscillator strengths and these were used for the evaluation of the phosphorus abundance in the sun. A value of 5.49 (0.04) was obtained in the usual logarithmic scale.

**Key words:** atomic data – Sun: atmosphere

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## 1. Introduction

A number of atomic phosphorus spectral lines have been observed in astrophysical objects, e.g. in interstellar clouds, in circumstellar shells and in the solar photosphere. Oscillator strengths of the astronomically observed phosphorus spectral lines are needed for the evaluation of phosphorus abundance in these objects. Presently such evaluations are based on theoretically obtained data, because of the lack of experimental results. Spectroscopic investigations of the phosphorus atom are difficult since the resonance spectral lines are situated in the VUV region and since the element evaporates as molecules. Furthermore, the commonly used thermal evaporation and dissociation methods are practically impossible to apply in a controlled way due to the transitions between different allotropic forms, and due to the direct transition from a solid to a gas without passing the liquid phase. As far as we know, only a few 3p-4s resonance transition upper-state lifetimes have been experimentally obtained

by using the electron excitation and phase shift techniques [Savage & Lawrence 1966] or the beam-foil method [Curtis et al. 1971; Livingston et al. 1975]. The transition probabilities of the 4s-4p lines observed in the spectrum of the solar photosphere have not been investigated experimentally so far.

Our experimental study was stimulated by the need of confirmed oscillator strengths for an accurate evaluation of the abundance of phosphorus in the sun, and for checking the results of theoretical calculations. At the same time we tried to see whether it was possible to improve upon the relativistic Hartree-Fock calculation by including a larger number of configurations than in an earlier calculation [Biémont et al. 1994].

The parity of the states in which we are interested is the same as that for the ground state, and therefore we need two photons for the excitation. In our earlier investigation on tellurium we used two-step laser excitation via the resonance states employing thermally heated cells [Zerne et al. 1994]. However, in the case of the phosphorus 4p states, one of the photons has to be in the VUV region and the other one in the IR region, with the consequence that the experiment is rather complex. It is easier to apply the direct two-photon excitation by UV photons. This technique has been applied earlier in lifetime measurements in oxygen [Kröll et al. 1984], in nitrogen [Bengtsson et al. 1991] and sulphur [Zerne et al. 1996]. In the latest experiments in sulphur [Zerne et al. 1996; Berzinsh et al. 1996] a laser produced plasma was successfully employed for atomisation and we used it in the present experiment, too.

## 2. Experimental setup

The experimental set-up is quite simple and it is described in detail elsewhere [Zerne et al. 1996]. The light from a Nd:YAG pumped dye laser operating on mixed Rhodamine 610 and Rhodamine 640 dyes was frequency-doubled in a KPD crystal and the laser beam in resonance with the two-photon transitions (299-306 nm) was focused about 1 cm above red phosphorus powder in a container inside a vacuum chamber. Laser-induced fluorescence light was collected by quartz lenses perpendicularly to the laser and atomic beams through a VUV monochromator (Acton Model VM 502), and detected by a photomulti-

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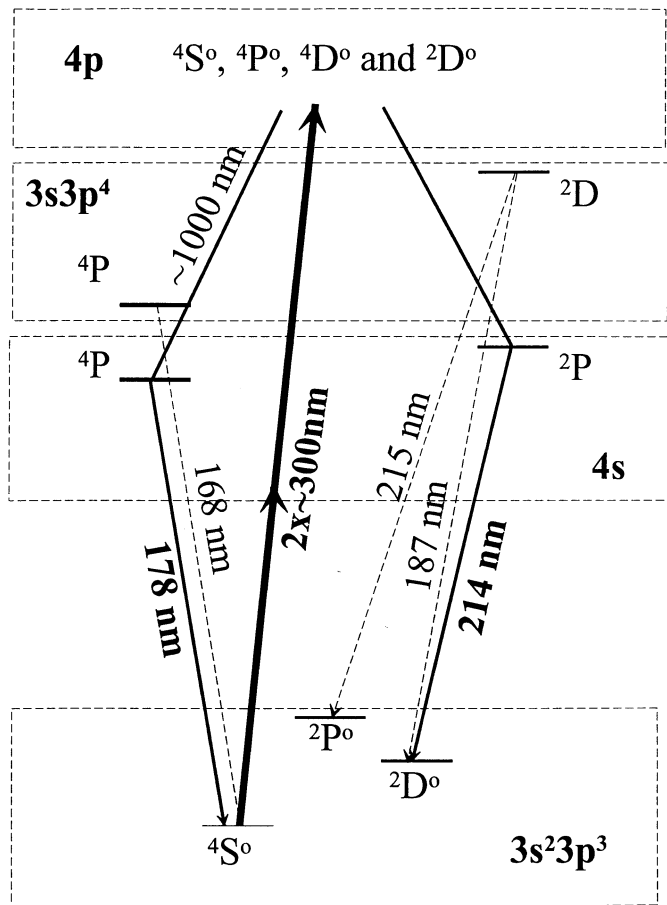


Fig. 1. Partial energy and transition diagram of neutral phosphorus.

plier tube (Hamamatsu R1220). The data acquisition and evaluation were performed by using a digital oscilloscope (Tektronix Model DSA 602) and a personal computer.

For the plasma generation, the doubled output at 532 nm of another Nd:YAG laser (Continuum Surelite) was used. The radiation from this laser was focused on the surface of the red phosphorus powder. A pulse energy of about 20 mJ was sufficient for the ablation of the powder. After each laser pulse a crater in the powder was generated and the surface was out of the laser focus. It was necessary to bring the powder back in focus for the next laser pulse. Therefore the container was shaken by an electromagnet at a frequency in resonance with the mechanical vibrations of the container/magnet arrangement.

### 3. Measurements and results

The lifetimes of the 4p  $4S^{\circ}$ ,  $4P^{\circ}$ ,  $4D^{\circ}$  states were measured by detection of 178 nm cascade light corresponding to  $4s\ 4P - 3p^3\ 4S_{1/2}^{\circ}$  transitions (See Fig. 1), since light detectors have a low efficiency for the direct emission at  $1\ \mu\text{m}$ . The lifetime of the 4p  $2D_{3/2}^{\circ}$  state was measured by detecting at 214 nm a wavelength corresponding to the  $4s\ 2P - 3p^3\ 2D^{\circ}$  transition. This detection scheme was possible since the lifetimes of the 4s states are about 15 times shorter than the lifetimes of the investigated

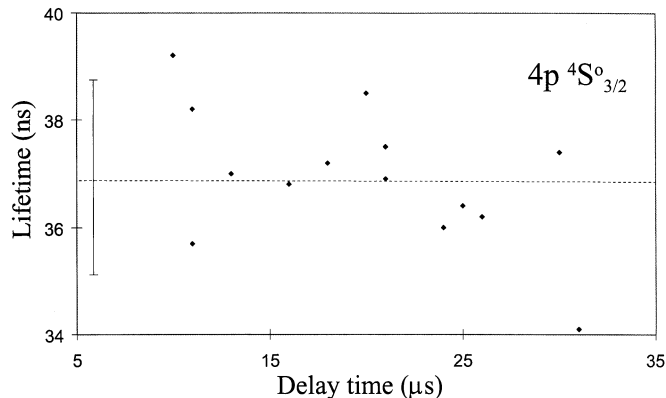


Fig. 2. Measured radiative lifetime of the  $4s\ 4S_{3/2}^{\circ}$  state as a function of the delay time for the UV laser pulse with respect to the ablation pulse.

4p states [Savage and Lawrence 1966]. We have to note that two states of the  $3s3p^4$  configuration have lower energies than the investigated states. By selecting 168 nm for the detection we checked for possible decay down to  $3s3p^4\ 4P$  states from excited quartet states, but we never observed fluorescence in this pathway. In the case of doublet states we could not observe the decay channels  $4s\ 2P - 3p^3\ 2D^{\circ}$  and  $3p^4\ 2D - 3p^3\ 2P^{\circ}$  separately, because of the unresolved 214 nm and 215 nm lines in detection. However, we assume that only the first decay channel through the  $4s\ 2P$  state is open, since we could not observe fluorescence at 187 nm, corresponding to transitions from  $3p^4\ 2D$  to the  $3p^3\ 2D^{\circ}$  state. Therefore, we conclude that in the branching fraction determination from the 4p states we can neglect transitions to the  $3s3p^4$  states.

A strong magnetic field was applied over the interaction region to wash out possible quantum beats due to level splitting in the laboratory magnetic field. For each of the investigated levels, fluorescence decay curves were measured by averaging a number of transients. The lifetime was evaluated by fitting decay curves to an exponential, for delays long enough to be outside of the duration of the laser pulse. For each excited state about 20 decay curves were sampled at different experimental conditions. We changed the delay time between an atomisation laser pulse and the excitation laser pulse in the 10–30  $\mu\text{s}$  range, which corresponds to a large parameter space regarding species concentration and intensity. No difference in lifetimes was observed (See Fig. 2.). An arithmetical mean value was calculated as the radiative lifetime for each state and the results are given in Table 1. Two standard deviations are taken as error bars.

### 4. Theory

Similarly to a previous analysis [Biémont et al. 1994], we have used for the present calculations the relativistic Hartree-Fock (HFR) method i.e. a Hartree-Fock method including relativistic corrections to the wavefunctions and energies. The HFR technique, described by Cowan (1981), was originally introduced by Cowan and Griffin (1976). The computational procedure, similar to that adopted in previous work (see e.g. [Biémont and

**Table 1.** Radiative lifetimes of the 4p states in phosphorus (all results in ns).

Level	Energy (cm <sup>-1</sup> )	This work		Previous		
		HFR	Experiment	SST <sup>*a</sup>	CA <sup>*b</sup>	STFD <sup>*c</sup>
<sup>2</sup> S <sub>1/2</sub> <sup>o</sup>	64239.59	79.9		99.1	150.2	140.2
<sup>2</sup> P <sub>1/2</sub> <sup>o</sup>	67971.07	36.2		44.9	39.0	36.6
<sup>2</sup> P <sub>3/2</sub> <sup>o</sup>	68088.08	36.4		44.7	39.1	37.2
<sup>2</sup> D <sub>3/2</sub> <sup>o</sup>	66813.04	41.0	41.6±4.8	68.7	51.4	48.2
<sup>2</sup> D <sub>5/2</sub> <sup>o</sup>	67113.87	40.7		51.4	50.3	46.9
<sup>4</sup> S <sub>3/2</sub> <sup>o</sup>	66834.65	22.0	36.9±1.8	42.5	35.0	33.0
<sup>4</sup> P <sub>1/2</sub> <sup>o</sup>	66343.44	37.7		36.8	38.4	36.5
<sup>4</sup> P <sub>3/2</sub> <sup>o</sup>	66360.28	37.3	38.9±6.2	35.9	38.9	36.4
<sup>4</sup> P <sub>5/2</sub> <sup>o</sup>	66544.24	37.7		37.9	38.2	35.9
<sup>4</sup> D <sub>1/2</sub> <sup>o</sup>	65373.56	41.3		43.7	49.0	45.8
<sup>4</sup> D <sub>3/2</sub> <sup>o</sup>	65450.13	41.1	48.1±8.2	43.7	48.8	45.6
<sup>4</sup> D <sub>5/2</sub> <sup>o</sup>	65585.13	41.0	48.4±5.5	43.6	48.0	44.8
<sup>4</sup> D <sub>7/2</sub> <sup>o</sup>	65788.46	41.0	48.3±4.4	43.5	47.7	44.5

\* These values must be considered as upper limits (see the text),

<sup>a</sup> Biémont et al. (1994), <sup>b</sup> Biémont and Grevesse (1973), <sup>c</sup> Kurucz and Peytremann (1975).

Hansen 1985,1986]) is only briefly summarised here. Slater integrals were first computed *ab initio*. Energies and spectra were computed in intermediate coupling with HFR basis functions using the Slater-Condon theory. This approach, based on the non-relativistic Schrödinger equation, does consider the most important relativistic effects i.e. the mass velocity terms and the Darwin correction.  $F^k$ ,  $G^k$  and  $R^k$  integrals were fixed at 80% of their initial values and the spin-orbit integrals ( $\zeta$ ), calculated by the Blume-Watson method, were not scaled down. The set of configurations used by Biémont et al. (1994) (21 configurations) was extended as much as possible within the computer limits. CI was finally retained among the following 42 configurations:  $3s^23p^3 + 3s^23p^2np$  ( $n=4-7$ ) +  $3s^23p^2nf$  ( $n=4-7$ ) +  $3p^4np$  ( $n=4-5$ ) +  $3p^4nf$  ( $n=4-5$ ) +  $3p^5 + 3s3p^3ns$  ( $n=4-5$ ) +  $3s3p^3nd$  ( $n=3-5$ ) +  $3s^23p4s^2 + 3s^23p4p^2 + 3s^23p3d4s + 3s^23p4s4d$  and  $3s3p^4 + 3s^23p^2ns$  ( $n=4-7$ ) +  $3s^23p^2nd$  ( $n=3-7$ ) +  $3p^4nd$  ( $n=3-5$ ) +  $3p^4ns$  ( $n=4-5$ ) +  $3s3p^3np$  ( $n=4-5$ ) +  $3s3p^3nf$  ( $n=4-5$ ) +  $3s^23p4s4p$  for the odd and even parities, respectively. When comparing with the configurations sets used by Biémont et al. (1994), it is seen that some additional configurations within the Layzer complexes  $n=4$  and  $n=5$  have been introduced in the calculations and that the Rydberg series  $3s^23p^2nl$  ( $l=s, p, d$  and  $f$ ) have been extended up to  $n=7$ . In that way, the largest part of the correlation effects is expected to be adequately incorporated into the model. No fitting of the calculated Hamiltonian eigenvalues was attempted but the average energies of the configurations were increased by about  $16085 \text{ cm}^{-1}$  in order to correctly adjust the ground state. It should be emphasised that this correction has no effect on the derived lifetimes or oscillator strengths.

Moreover, through separate calculations, the effect on the final results of the  $3s^23p4d^2$ ,  $3s^23p4f^2$ ,  $3p^34s^2$ ,  $3p^34p^2$ ,  $3p^33d^2$ ,  $3p^33d4s$  and  $3p^34s4d$  odd configurations was estimated and found negligible ( $< 1\%$ ). The same conclusions were reached for the  $3s^23p4s4f$ ,  $3p^34s4p$ ,  $3p^34s4f$  even configurations. It should also be emphasised that the choice of the scaling factor (0.80) was not dramatic: adopting 0.90 would modify the lifetime values of the levels belonging to the 4p configuration by less than 1% (except for the <sup>2</sup>S<sub>1/2</sub> state where the change is reaching a few %).

The set of calculated oscillator strengths for the 4s-4p transitions of P I resulting from the above mentioned configurations is given in Table 2. The  $f$  values are compared with the CA [Biémont and Grevesse 1973], the STFD [Kurucz and Peytremann 1975] and the SST (with TEC corrections) [Biémont et al. 1994] previous results. Though the present data are expected to be more accurate than the HFR results published by Biémont et al. (1994), they differ only by a few%, indicating that the most important correlation effects have probably been included in both calculations.

The HFR lifetime values are presented in Table 1, where they are compared with the experimental results obtained in the present work. The agreement between theory and experiment is good if we exclude the <sup>4</sup>S<sub>3/2</sub> level, for which the HFR result appears substantially smaller than the laser measurement. As this lifetime value is dominated by the  $4s^4P - 4p^4S^o$  decays, it is expected that the discrepancy results from an overestimation of the corresponding radial integral in the HFR approach. Lifetime values deduced from published oscillator strengths (see Table 2 in Biémont et al. (1994)) are also given for comparison in the same table: CA [Biémont and Grevesse 1973], SST [Biémont et al. 1994] and STFD [Kurucz and Peytremann 1975] results. It should be emphasised that the derived lifetimes in the last three columns of Table 1 must be considered as upper limits because the intercombination lines and possible de-excitation transitions to the ground state have not been considered for calculating the lifetimes. It is nevertheless remarkable that the Coulomb approximation, although being a monoconfigurational approach, leads generally to results in good agreement with experiment (except for the <sup>2</sup>D<sup>o</sup> levels)!

Adopting the theoretical branching fractions as obtained in the present calculation (warranted because of the good agreement found for lifetimes) and combining them with the laser lifetime values, we deduce the normalised oscillator strengths reported in column 3 of Table 2 under the label HFR(corr). We have assumed that the ratios of experimental to theoretical lifetimes are not  $J$ -dependent for the <sup>4</sup>D<sup>o</sup> and <sup>4</sup>P<sup>o</sup> terms and that the ratio for <sup>4</sup>D<sub>1/2</sub><sup>o</sup> is equal to the mean value of the results derived for the other  $J$ -values within the same term.

The astrophysical implications of the present results can easily be derived from the solar analysis carried out previously [Biémont et al. 1994]. Using the same equivalent widths measured on the Jungfraujoeh spectra [Delbouille et al. 1973, 1981], the corrected  $f$  values obtained in the present work and adopting the Holweger and Müller (1974) solar model with a depth-independent isotropic microturbulence of 0.85 km/s, the mean

**Table 2.** Oscillator strengths  $\lg(gf)$  for the 4s-4p transitions in phosphorus.

Transition	$\lambda$ (nm)	This work		Previous		
		HFR(a.i.) <sup>a</sup>	HFR(corr) <sup>b</sup>	SST <sup>c</sup>	CA <sup>d</sup>	STFD <sup>e</sup>
$^2P_{1/2} - ^2S_{1/2}^o$	1571.2	-0.51		-0.52	-0.75	-0.72
$^2P_{3/2} - ^2S_{1/2}^o$	1648.3	-0.29		-0.31	-0.46	0.43
$^2P_{1/2} - ^2P_{1/2}^o$	990.4	-0.30		-0.39	-0.29	-0.26
$^2P_{1/2} - ^2P_{3/2}^o$	979.0	-0.69		-0.69	-0.59	-0.56
$^2P_{3/2} - ^2P_{1/2}^o$	1020.5	-0.52		-0.58	-0.59	-0.57
$^2P_{3/2} - ^2P_{3/2}^o$	1008.4	0.14		0.06	0.11	0.13
$^2P_{1/2} - ^2D_{3/2}^o$	1118.7	0.17	0.16	-0.03	0.09	0.12
$^2P_{3/2} - ^2D_{3/2}^o$	1157.3	-0.66	-0.67	-0.77	-0.61	-0.59
$^2P_{3/2} - ^2D_{5/2}^o$	1118.3	0.41	0.40	0.34	0.35	0.38
$^4P_{1/2} - ^4S_{3/2}^o$	917.6	-0.59	-0.81	-1.27	-0.60	-0.57
$^4P_{3/2} - ^4S_{3/2}^o$	930.5	-0.20	-0.42	-0.63	-0.30	-0.27
$^4P_{5/2} - ^4S_{3/2}^o$	952.7*	0.12	-0.10	-0.01	-0.12	-0.10
$^4P_{1/2} - ^4P_{1/2}^o$	960.9	-1.03	-1.05	-1.02	-0.91	-0.88
$^4P_{1/2} - ^4P_{3/2}^o$	959.4	-0.22	-0.24	-0.14	-0.21	-0.18
$^4P_{3/2} - ^4P_{1/2}^o$	975.1*	-0.16	-0.18	-0.17	-0.21	-0.19
$^4P_{3/2} - ^4P_{3/2}^o$	973.5	-0.34	-0.36	-0.19	-0.71	-0.68
$^4P_{3/2} - ^4P_{5/2}^o$	956.3	-0.37	-0.39	-0.36	-0.17	-0.15
$^4P_{5/2} - ^4P_{3/2}^o$	997.7	-0.27	-0.29	-0.70	-0.18	-0.15
$^4P_{5/2} - ^4P_{5/2}^o$	979.7*	0.29	0.27	0.26	0.19	0.22
$^4P_{1/2} - ^4D_{1/2}^o$	1059.7*	-0.14	-0.21	-0.17	-0.24	-0.21
$^4P_{1/2} - ^4D_{3/2}^o$	1051.2*	-0.06	-0.13	-0.10	-0.24	-0.21
$^4P_{3/2} - ^4D_{1/2}^o$	1076.9*	-1.00	-1.07	-1.01	-0.94	-0.91
$^4P_{3/2} - ^4D_{3/2}^o$	1068.1*	-0.12	-0.19	-0.15	-0.13	-0.10
$^4P_{3/2} - ^4D_{5/2}^o$	1053.0*	0.31	0.24	0.27	0.17	0.20
$^4P_{5/2} - ^4D_{3/2}^o$	1097.3	-1.43	-1.50	-1.40	-1.16	-1.13
$^4P_{5/2} - ^4D_{5/2}^o$	1081.3*	-0.34	-0.41	-0.35	-0.20	-0.17
$^4P_{5/2} - ^4D_{7/2}^o$	1058.2*	0.52	0.45	0.49	0.45	0.48

<sup>a</sup> Ab initio, <sup>b</sup> Corrected (See text), <sup>c</sup> Biémont et al. (1994), <sup>d</sup> Biémont and Grevesse (1973), <sup>e</sup> Kurucz and Peytremann (1975). \* Solar lines used in the evaluation of the abundance.

photospheric abundance derived from a set of ten lines (marked with asterisks in Table 2) is now established at 5.49 (0.04) (in the usual logarithmic scale), where the quoted uncertainty represents twice the standard deviation of the mean. This result is not very different but is nevertheless slightly higher than the result reported by Biémont et al. (1994). The discrepancy previously observed with the meteoritic result reported by Anders and Grevesse (1989)  $AP = 5.57(0.04)$  is thus correspondingly decreased.

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## References

Anders E., Grevesse N., 1989, *Geochim. Cosmochim. Acta* 53, 197.

- Bengtsson G.J., Hansen K., Larsson J., Schade W., Svanberg S., 1991, *Z. Phys.* D22, 397
- Berzinsh U., Zerne R., Svanberg S., Biémont E., 1997, *Phys. Rev.* A55, 1836
- Biémont E., Grevesse N., 1973, *At. Data Nucl. Data Tables* 12, 217
- Biémont E., Hansen J.E., 1985, *Phys. Scr.* 31, 509; 1986, *ibid.* 33, 117; 1986, *ibid.* 34, 116
- Biémont E., Martin F., Quinet P., Zeippen C.J., 1994, *Astron. Astrophys.* 283, 339
- Cowan R.D., Griffin D.C., 1976, *J. Opt. Soc. Am.* 66, 1010
- Cowan R.D., 1981, *The Theory of Atomic Structure and Spectra*, Univ. of Colorado Press
- Curtis L.J., Martinson I., Buchta R., 1971, *Phys. Scr.* 3, 197
- Delbouille L., Neven N. and Roland G., 1973, *Photometric Atlas of the Solar Spectrum from  $\lambda 3000$  to  $\lambda 10000$* , Institut d'Astrophysique, Université de Liège
- Delbouille L., Roland G., Brault J.W., Testerman L., 1981, *Photometric Atlas of the Solar Spectrum from 1850 to 10000  $\text{cm}^{-1}$* , KPNO, Tucson, AZ, USA
- Holweger H., Müller E.A., 1974, *Solar Phys.* 39, 19

- Kröll S., Lundberg H., Persson A. and Svanberg S., 1984, Phys. Rev. Lett. 55, 284
- Kurucz R.L., Peytremann E., 1975, Smiths. Astron. Obs. Spec. Rep. 362
- Livingston A.E., Kernahan J.A., Irvin D.J., Pinnington E.H., 1975, Phys. Scr. 12, 223
- Savage B.D., Lawrence G.M., 1966, Astrophys. J. 146, 940
- Zerne R., Berzinsh U., Svanberg S., 1994, Z. Phys. D 32, 31
- Zerne R., Caiyan Luo, Berzinsh U., Svanberg S., 1997, Phys. Scr., in press