

New accurate data for the spectrum of neutral silver

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Abstract. High resolution spectra of neutral silver have been recorded by Fourier Transform Spectrometry in the region 2000–8280 Å (50 000–12 000 cm⁻¹) with silver-neon and silver-argon hollow cathode lamps as sources. This work represents order-of-magnitude improvements, compared to previous work on Ag I, in accuracy of transition wavelengths and wavenumbers, and energy level values. 35 classified Ag I transitions are given, and the wavenumber uncertainty for the strongest lines is less than 0.002 cm⁻¹. Improved values for 28 energy levels are presented.

PACS. 32.30.-r Atomic spectra – 95.30.Ky Atomic and molecular data, spectra, and spectral parameters (opacities, rotation constants, line identification, oscillator strengths, gf values, transition probabilities, etc.)

1 Introduction

New measurements of the neutral silver spectrum are relevant both to astrophysics and atomic physics. In order to correctly interpret high resolution astrophysical spectra recorded with the new generation of astronomical telescopes improvements in the accuracy of the laboratory atomic data are required [1–3]. The accuracy of the laboratory atomic data is required to match, or ideally surpass, the capabilities of new spectrographs on both ground and space-based telescopes. In particular, the accuracy of the technique of using synthetic spectra to interpret high resolution stellar spectra depends on the quality of the atomic database used in creating the synthetic spectra.

In atomic physics interest in Ag I has recently focused on a two-photon transition at 661.2 nm between the ground state $5s^2S_{1/2}$ and the metastable level $4d^95s^2^2D_{5/2}$ [4] which decays by electric quadrupole radiation at 330.6 nm with a very small natural linewidth (approx. 0.8 Hz). When driven by the 661.2 nm Doppler-free two-photon transition in a beam or atomic fountain of laser-cooled silver atoms, it is an excellent candidate for an optical frequency standard [4]. The absolute value of the metastable $4d^95s^2^2D_{5/2}$ energy level found at high accuracy in this work has already been used to detect the very narrow two photon resonance [5] at 661.2 nm (see Fig. 1).

The most recent comprehensive measurements of the Ag I spectrum are those of Shenstone [6] and Rasmussen [7] both in 1940. Using as sources both an arc and a hollow cathode lamp Shenstone [6] greatly improved the

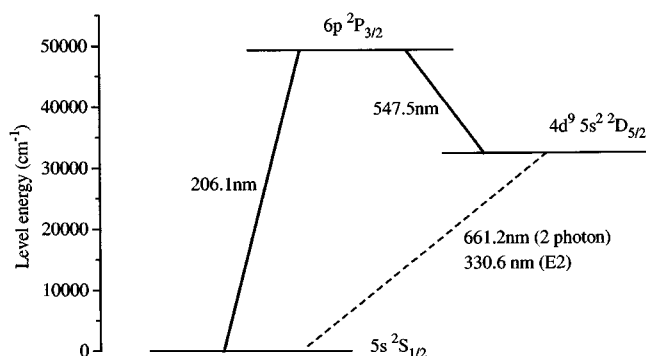


Fig. 1. Partial energy level diagram for Ag I indicating the transitions used to determine the energy of the metastable level $4d^95s^2^2D_{5/2}$.

knowledge of the Ag I energy level system. He listed 243 lines between 2500 and 66341 cm⁻¹ of which 148 were new. Shenstone also included lines unobserved by himself, but recorded in previous work by Paschen [9], Randall [10], Hetzler, Bouman and Burns [11], Walters [12] and Blair [13]. Rasmussen [7] presented measurements of 25 newly identified weak transitions and stated that for the stronger transitions his work was in agreement with that of Shenstone. In 1994 Larkins and Hannaford [4] reported new measurements of two transitions to determine the $4d^95s^2^2D_{5/2}$ energy level value with an uncertainty of 0.007 cm⁻¹.

In this paper we present accurate measurements of wavelengths and wavenumbers of 35 Ag I transitions, and 28 energy levels, including the $4d^95s^2^2D_{5/2}$ energy level. These transitions correspond to the majority of

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transitions observed by Shenstone using a hollow cathode lamp source, and are the strongest observed Ag I transitions. Weaker lines that were observed by Shenstone in his arc source only were not observed in this work.

The technique of Fourier Transform (FT) spectrometry, with its high spectral resolution and broad spectral range [3], is ideal for improving the accuracy of atomic data. The wavelength measurements for Ag I are an order of magnitude more accurate than previous work, and have been used to derive revised values for 28 Ag I energy levels.

2 Experimental details

The laboratory spectra used in this analysis were recorded using the the f/25 UV FT spectrometer at Imperial College, (ICFTS), London [14].

A water-cooled dc hollow cathode lamp was used as a light source, run in either neon or argon as carrier gas. This source gives spectra of Ag I and Ag II as well as the neutral and singly-ionized spectra of the particular carrier gas. The metal case of the lamp formed the anode, and the cathode was an open-ended cylinder of pure silver, 30 mm long and 5 mm in bore. The optimum running pressures were found to be 2 mbar in Ne, and 0.9 mbar in Ar. Spectra covering the 12 000–50 000 cm^{-1} wavenumber range were recorded, with the following photomultiplier tube detectors (PMT), filters and currents:

wavenumber range (cm^{-1})	PMT detector	filter	current (mA)
12 000–19 000	R928	LP540	450, 300, 75
15 000–28 000	IP28	WG295	300, 15
16 000–26 000	IP28	LP390	450
26 000–32 000	IP28	BP350	500
28 000–45 000	IP28	-	300
31 600–50 000	R166	-	300
24 000–31 000	IP28	UG1	450

Different currents were used: (l) low current runs (15–75 mA) to avoid self-absorption effects in the strongest lines, (m) medium current runs (300 mA) for the majority of lines, and (h) high current runs (450–500 mA) to bring up the weakest lines. The resolution of the spectra ranged from 0.045 cm^{-1} in the UV spectral region, to 0.035 cm^{-1} in the visible spectral region.

The wavenumber, wavelength, line width FWHM (full width at half maximum), equivalent width line intensity and signal-to-noise ratio (SNR) of the observed spectral lines were determined using the DECOMP and GREMLIN programs developed by Brault [15]. Natural silver consists of two isotopes, ^{107}Ag (51.84%) and ^{109}Ag (48.16%), each with nuclear spin 1/2. In this work the widths of the lines are determined by Doppler broadening

in the hollow cathode lamp, and since the nuclear magnetic moments for the Ag isotopes are small the hyperfine structure components of the silver lines are not observed as resolved components. However, although isotope and hyperfine structure are not resolved in the spectra, they do contribute to the observed line widths, as these would otherwise be proportional to wavenumber. A least-squares fit of a Voigt profile to each line was made, giving the wavenumber, wavelength, equivalent width line intensity, SNR and FWHM. It has been shown [16] that the uncertainty in the position of the centre of a properly resolved line is given by the full width at half maximum of the line divided by twice the SNR.

However the uncertainty in the absolute wavenumber of an observed spectral line depends not only on the precision with which its centre can be measured but also on the uncertainty in the absolute calibration. The starting point for the latter is the fact that the wavenumber scale of FT spectra is linear, and in principle to establish an absolute wavenumber scale only one standard line is required. However, the procedure used in practice at Imperial College is to carry out the calibration using 26 Ar II standard lines in the blue region measured interferometrically by Norlén [17], and then to carry this calibration into the UV and through the visible into the IR using overlapping spectra [18].

The combined uncertainty of the wavenumber calibration and line position determination is estimated to be approximately 1 mK (0.001 cm^{-1}) in the visible and near UV for strong isolated spectral lines. Further into the UV and IR this uncertainty is higher (2 mK) because of cumulative errors in calibrating overlapping spectra. A full discussion of the contributions to these uncertainties is given by Learner and Thorne [18].

Initially, at the time when the silver spectra of this work were recorded, no intensity calibration was carried out. However, an approximate intensity calibration was made at a later date using two standard lamps, tungsten and deuterium, for the visible and UV spectral regions respectively. Both standard lamps had been calibrated at the NPL (National Physical Laboratory UK). Individual intensity calibration runs were made and subsequently the instrument response curves determined, for each filter/detector combination used. The instrument response curves were then applied to the equivalent width line intensities found from the line fitting of each silver line in each individual spectrum. Since ten spectra were used in this work, the relative line intensities were then all placed on the same scale by using suitable silver lines as transfer lines between the spectra. Our usual intensity calibration procedure is described more fully in [19], and the resulting relative line intensities would have been of good accuracy if the tungsten and deuterium intensity calibration spectra had been recorded immediately before or after each silver spectrum. However, in this case, because of the delay of several weeks between the recording of the silver spectra and the intensity calibration spectra, we estimate the uncertainty in the relative intensities to be approximately 25% for lines of good SNR, and they should only

be used as a guide to the line intensities. In addition to the measured relative line intensities, the calculated $\log gf$ values of Kurucz [20] may also serve as a guide to the line intensities. Further details of these calculations may be found at the web site: <http://cfaku5.harvard.edu/>.

3 The spectrum of Ag I

Table 1 gives the classified lines of Ag I observed in this work. In the first and second columns the relative line intensity and the observed SNR of the line are given. The third column gives $\log gf$ values calculated by Kurucz [20] and these may also be used as a guide to the line intensities. The fourth column indicates the lamp current used for the spectrum in which the transition is observed: low (l), medium (m) or high (h) current (see Sect. 2). The fifth column gives the full width at half maximum (FWHM) of the line. It should be noted that the FWHM for lines of poor SNR (SNR < 10) is extremely unreliable. Air wavelengths, determined using the observed wavenumbers in column 7, are given in the sixth column, the conversion being carried out using the formula of Edlén [21] for the dispersion of air:

$$\lambda(\text{air}) = \frac{10^8}{\sigma} \left(1 + 8342.13 \times 10^{-8} + \frac{15997}{3.89 \times 10^9 - \sigma^2} + \frac{2406030}{1.3 \times 10^{10} - \sigma^2} \right)^{-1}$$

where σ is the vacuum wavenumber and $\lambda(\text{air})$ the air wavelength in Å.

The observed wavenumbers are shown in the seventh column, and the uncertainty in the wavenumber is given in the eighth column. The differences (O–C) between the observed wavenumbers and the wavenumbers derived from the energy levels (see Sect. 4) are given in the ninth column. Where one of the energy levels involved in a transition is determined from just one line a – replaces O–C as it is by necessity zero. The next column contains the configuration, term designation and J value of each energy level involved in the transition. The line identifications of Shenstone [6] have been used. The table contains 35 classified Ag I lines, with wavelengths at least an order of magnitude more accurate than in previous work.

4 The identification of lines and improvements to the energy levels

Wavenumbers of observed lines were compared with wavenumbers derived from measured energy levels (known as Ritz wavenumbers). Initially for this purpose the energy levels listed in Shenstone [6] were used. Following initial line identification a revision of the energy levels was carried out using the observed transitions in FTS spectra and a least-squares fitting program, ELCALC [22]. In this

calculation each line is given a weighting inversely proportional to the square of the uncertainty in the wavenumber. The revised energy level values have an order of magnitude higher accuracy than those of Shenstone [6]. The level-value uncertainties are calculated [23] from:

$$\Delta\bar{L} = \left[\sum_i (W_i \Delta L'_i)^2 \right]^{\frac{1}{2}} / \sum_i W_i$$

where

$$\Delta L'_i = [(\Delta\sigma_{ij}^2 + \Delta L_j^2) + (\bar{L} - L_i)^2]^{\frac{1}{2}},$$

$$W_i = (\Delta\sigma_{ij})^{-2}.$$

$\Delta\sigma_{ij}$ is the wavenumber uncertainty; ΔL_j is the uncertainty of the combining level; \bar{L} is the average level value, and L_i is the i th value of the level. However, because of the $(\Delta\sigma_{ij})^{-2}$ weighting this expression does not give realistic uncertainties in the case of an upper level which combines through a transition of high weight with a lower level that is tied into the array through transitions of low weight. For these cases physically reasonable uncertainties were assigned to the levels based on the uncertainties of the lines involved and the combining energy levels.

The optimized energy level values were then used to calculate the Ritz wavenumbers. The discrepancies between these calculated wavenumbers and observed wavenumbers are shown in the ninth column of Table 1.

The revised energy levels found in this work are listed in Table 2. The appropriate configuration, term designation and J value is given together with the relative uncertainty of each energy level value, which ranges from 0.001 cm^{-1} to as much as 0.038 cm^{-1} for a couple of levels with weak transitions. The uncertainty is also higher where a level is determined by just one transition, as is the case for many of the levels. However, the majority of the levels have an uncertainty of less than 0.004 cm^{-1} .

5 Summary

New accurate measurements of the Ag I spectrum using the technique of Fourier Transform Spectroscopy are reported. Order-of-magnitude improvements in accuracy of line wavenumbers and energy level values are presented.

We are very grateful to Bob Kurucz (Harvard Smithsonian Center for Astrophysics) for his advice and theoretical calculations of the Ag I spectrum and energy levels. We thank Anne Thorne for her help during the experimental aspects of this work. J.C. Pickering thanks The Royal Society (UK) for their support. PPARC of the UK also provided financial support for this work. V. Zilio acknowledges and wishes to thank the IAESTE organisation for funding his exchange visit to Imperial College.

Table 1. Ag I linelist.

intensity	SNR	Log gf (calc.)	I	width (mK)	λ (Å)	σ (cm^{-1})	σ uncer. (cm^{-1})	O-C (cm^{-1})	lower level	upper level
330 000	167	-0.209	m	50	8 273.5090	12 083.449	0.002	0.000	$4d^{10} ({}^1S) 5p$ $2P_{\frac{3}{2}}$	$4d^{10} ({}^1S) 6s$ $2S_{\frac{1}{2}}$
220 000	415	-0.474	m	51	7 687.7720	13 004.091	0.002	0.000	$4d^{10} ({}^1S) 5p$ $2P_{\frac{1}{2}}$	$4d^{10} ({}^1S) 6s$ $2S_{\frac{1}{2}}$
800	45	-2.630	h	85	5 475.3760	18 258.514	0.002	0.000	$4d^9 5s^2$ $2D_{\frac{5}{2}}$	$4d^{10} ({}^1S) 6p$ $2P_{\frac{3}{2}}$
35 000	231	-0.575	m	62	5 471.5550	18 271.264	0.001	-0.001	$4d^{10} ({}^1S) 5p$ $2P_{\frac{3}{2}}$	$4d^{10} ({}^1S) 5d$ $2D_{\frac{3}{2}}$
180 000	1014	0.379	m	70	5 465.4970	18 291.516	0.001	-	$4d^{10} ({}^1S) 5p$ $2P_{\frac{3}{2}}$	$4d^{10} ({}^1S) 5d$ $2D_{\frac{5}{2}}$
195 000	569	0.147	m	72	5 209.0780	19 191.910	0.001	0.002	$4d^{10} ({}^1S) 5p$ $2P_{\frac{1}{2}}$	$4d^{10} ({}^1S) 5d$ $2D_{\frac{3}{2}}$
500	12	-3.872	h	90	5 151.3920	19 406.824	0.004	0.000	$4d^9 5s^2$ $2D_{\frac{3}{2}}$	$4d^{10} ({}^1S) 7p$ $2P_{\frac{3}{2}}$
6 000	113	-2.824	m	69	4 668.4770	21 414.268	0.001	0.000	$4d^{10} ({}^1S) 5p$ $2P_{\frac{3}{2}}$	$4d^{10} ({}^1S) 7s$ $2S_{\frac{1}{2}}$
2 700	346	-3.148	h	69	4 476.0400	22 334.909	0.001	-0.001	$4d^{10} ({}^1S) 5p$ $2P_{\frac{1}{2}}$	$4d^{10} ({}^1S) 7s$ $2S_{\frac{1}{2}}$
1 400	152	-2.308	h	78	4 212.8140	23 730.416	0.001	0.000	$4d^{10} ({}^1S) 5p$ $2P_{\frac{3}{2}}$	$4d^{10} ({}^1S) 6d$ $2D_{\frac{3}{2}}$
15 000	289	-1.354	m	84	4 210.9600	23 740.867	0.001	-	$4d^{10} ({}^1S) 5p$ $2P_{\frac{3}{2}}$	$4d^{10} ({}^1S) 6d$ $2D_{\frac{5}{2}}$
170	13	-2.690	h	68	4 186.6290	23 878.838	0.003	0.000	$4d^9 5s^2$ $2D_{\frac{5}{2}}$	$4d^{10} ({}^1S) 7p$ $2P_{\frac{3}{2}}$
7 300	138	-1.575	m	90	4 055.4760	24 651.057	0.001	-0.001	$4d^{10} ({}^1S) 5p$ $2P_{\frac{1}{2}}$	$4d^{10} ({}^1S) 6d$ $2D_{\frac{3}{2}}$
380	42	-1.382	h	70	3 981.5800	25 108.555	0.001	0.000	$4d^{10} ({}^1S) 5p$ $2P_{\frac{3}{2}}$	$4d^{10} ({}^1S) 8s$ $2S_{\frac{1}{2}}$
1 500	123	-2.769	h	87	3 847.8460	25 981.198	0.001	-	$4d^9 5s^2$ $2D_{\frac{5}{2}}$	$4d^9 5s ({}^3D) 5p$ $4P_{\frac{3}{2}}$
250	12	-1.665	h	77	3 840.7500	26 029.195	0.003	-0.002	$4d^{10} ({}^1S) 5p$ $2P_{\frac{1}{2}}$	$4d^{10} ({}^1S) 8s$ $2S_{\frac{1}{2}}$
90	14	-1.322	h	86	3 811.7730	26 227.064	0.003	-0.001	$4d^{10} ({}^1S) 5p$ $2P_{\frac{3}{2}}$	$4d^{10} ({}^1S) 7d$ $2D_{\frac{3}{2}}$
1 460	90	-0.368	h	95	3 810.9410	26 232.795	0.001	-	$4d^{10} ({}^1S) 5p$ $2P_{\frac{3}{2}}$	$4d^{10} ({}^1S) 7d$ $2D_{\frac{5}{2}}$
70	3	-2.686	h	95	3 784.1850	26 418.268	0.016	-	$4d^9 5s^2$ $2D_{\frac{5}{2}}$	$4d^{10} ({}^1S) 8p$ $2P_{\frac{3}{2}}$
75	8	-3.109	h	90	3 709.1920	26 952.378	0.006	0.003	$4d^{10} ({}^1S) 5p$ $2P_{\frac{3}{2}}$	$4d^{10} ({}^1S) 9s$ $2S_{\frac{1}{2}}$
1 000	63	-0.607	h	100	3 682.5040	27 147.707	0.001	0.000	$4d^{10} ({}^1S) 5p$ $2P_{\frac{1}{2}}$	$4d^{10} ({}^1S) 7d$ $2D_{\frac{3}{2}}$
50	11	-2.134	h	97	3 625.1420	27 577.265	0.005	-0.005	$4d^{10} ({}^1S) 5p$ $2P_{\frac{3}{2}}$	$4d^{10} ({}^1S) 8d$ $2D_{\frac{3}{2}}$
400	24	-1.180	h	105	3 624.6900	27 580.701	0.002	-	$4d^{10} ({}^1S) 5p$ $2P_{\frac{3}{2}}$	$4d^{10} ({}^1S) 8d$ $2D_{\frac{5}{2}}$
50	4	-3.406	h	144	3 586.6790	27 872.988	0.020	-0.029	$4d^{10} ({}^1S) 5p$ $2P_{\frac{1}{2}}$	$4d^{10} ({}^1S) 9s$ $2S_{\frac{1}{2}}$
35	2	-1.871	h	152	3 569.7280	28 005.344	0.038	-	$4d^{10} ({}^1S) 5p$ $2P_{\frac{3}{2}}$	$4d^{10} ({}^1S) 10s$ $2S_{\frac{1}{2}}$
60	14	-2.459	h	79	3 537.2720	28 262.295	0.003	-	$4d^9 5s^2$ $2D_{\frac{5}{2}}$	$4d^9 5s ({}^3D) 5p$ $4P_{\frac{3}{2}}$
20	2	-2.867	h	150	3 521.3900	28 389.760	0.038	-	$4d^{10} ({}^1S) 5p$ $2P_{\frac{3}{2}}$	$4d^{10} ({}^1S) 9d$ $2D_{\frac{3}{2}}$
120	4	-1.913	h	150	3 521.1230	28 391.911	0.019	-	$4d^{10} ({}^1S) 5p$ $2P_{\frac{3}{2}}$	$4d^{10} ({}^1S) 9d$ $2D_{\frac{5}{2}}$
130	12	-1.419	h	95	3 508.0250	28 497.915	0.004	0.003	$4d^{10} ({}^1S) 5p$ $2P_{\frac{1}{2}}$	$4d^{10} ({}^1S) 8d$ $2D_{\frac{3}{2}}$
100	13	-1.634	h	90	3 501.9210	28 547.588	0.004	-	$4d^9 5s^2$ $2D_{\frac{5}{2}}$	$4d^9 5s ({}^3D) 5p$ $4F_{\frac{7}{2}}$
40	3	-1.359	h	103	3 457.0770	28 917.884	0.018	-	$4d^{10} ({}^1S) 5p$ $2P_{\frac{3}{2}}$	$4d^{10} ({}^1S) 10d$ $2D_{\frac{5}{2}}$
410 000	72	-0.299	l	100	3 382.8870	29 552.063	0.002	0.002	$4d^{10} ({}^1S) 5s$ $2S_{\frac{1}{2}}$	$4d^{10} ({}^1S) 5p$ $2P_{\frac{1}{2}}$
542 000	71	0.013	l	101	3 280.6800	30 472.701	0.002	-0.002	$4d^{10} ({}^1S) 5s$ $2S_{\frac{1}{2}}$	$4d^{10} ({}^1S) 5p$ $2P_{\frac{3}{2}}$
460	43	-1.347	m	175	2 069.8440	48 297.402	0.002	-	$4d^{10} ({}^1S) 5s$ $2S_{\frac{1}{2}}$	$4d^{10} ({}^1S) 6p$ $2P_{\frac{1}{2}}$
1 500	112	-1.031	m	211	2 061.1620	48 500.805	0.002	0.000	$4d^{10} ({}^1S) 5s$ $2S_{\frac{1}{2}}$	$4d^{10} ({}^1S) 6p$ $2P_{\frac{3}{2}}$

Note: Columns are as follows: intensity, the relative intensity of the transition; SNR, the observed signal-to-noise ratio of the transition; Log gf , the log gf value for the transition as calculated by Kurucz [20]; I, the spectrum current (h) high, (m) medium, (l) low current (see Sect. 2); width, a guide to the line pattern width in mK (1 mK = 0.001 cm^{-1}); λ , wavelength in air; σ , vacuum wavenumber of the transition; uncer. σ , the vacuum wavenumber uncertainty; O-C, the difference between the observed wavenumber and the wavenumber calculated from the energy levels in this work, a - indicates that one of the levels involved in the transition has been determined by only this transition; and lower level and upper level, the levels involved in the transition.

Table 2. Ag I Energy levels.

configuration	term	J	energy (cm^{-1})	uncertainty (cm^{-1})
$4d^{10} ({}^1S) 5s$	2S	0.5	0.000	0.002
$4d^{10} ({}^1S) 5p$	2P	0.5	29 552.061	0.001
$4d^{10} ({}^1S) 5p$	2P	1.5	30 472.703	0.001
$4d^9 5s^2$	2D	2.5	30 242.291	0.004
$4d^9 5s^2$	2D	1.5	34 714.305	0.007
$4d^{10} ({}^1S) 6s$	2S	0.5	42 556.152	0.002
$4d^{10} ({}^1S) 6p$	2P	0.5	48 297.402	0.003
$4d^{10} ({}^1S) 6p$	2P	1.5	48 500.805	0.002
$4d^{10} ({}^1S) 5d$	2D	1.5	48 743.969	0.002
$4d^{10} ({}^1S) 5d$	2D	2.5	48 764.219	0.002
$4d^{10} ({}^1S) 7s$	2S	0.5	51 886.971	0.002
$4d^{10} ({}^1S) 7p$	2P	1.5	54 121.129	0.005
$4d^{10} ({}^1S) 6d$	2D	1.5	54 203.119	0.002
$4d^{10} ({}^1S) 6d$	2D	2.5	54 213.570	0.003
$4d^{10} ({}^1S) 8s$	2S	0.5	55 581.258	0.003
$4d^9 5s ({}^3D) 5p$	4P	2.5	56 223.489	0.004
$4d^9 5s ({}^3D) 5p$	4P	1.5	58 504.586	0.005
$4d^{10} ({}^1S) 8p$	2P	1.5	56 660.559	0.017
$4d^{10} ({}^1S) 7d$	2D	1.5	56 699.768	0.003
$4d^{10} ({}^1S) 7d$	2D	2.5	56 705.498	0.003
$4d^{10} ({}^1S) 9s$	2S	0.5	57 425.078	0.008
$4d^{10} ({}^1S) 8d$	2D	1.5	58 049.973	0.007
$4d^{10} ({}^1S) 8d$	2D	2.5	58 053.404	0.004
$4d^{10} ({}^1S) 10s$	2S	0.5	58 478.047	0.038
$4d^9 5s ({}^3D) 5p$	4F	3.5	58 789.879	0.005
$4d^{10} ({}^1S) 9d$	2D	1.5	58 862.463	0.038
$4d^{10} ({}^1S) 9d$	2D	2.5	58 864.614	0.019
$4d^{10} ({}^1S) 10d$	2D	2.5	59 390.587	0.018

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