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Revised interpretation of the Na I EUV absorption spectrum

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Abstract

Spectral data for neutral sodium were recently compiled by Sansonetti (2008 *J. Phys. Chem. Ref. Data* **37** 1659). In that compilation, some of the energy levels of the $2p^5 3snl$ configurations were quoted from the studies of the absorption spectrum in the extreme ultraviolet (EUV) region, while others were quoted from beam-foil and laser-spectroscopy studies of emission in the visible region. These two sets of data partially overlap. However, in Sansonetti (2008) the energy levels observed in both types of studies were not recognized as being the same entities and were listed as different quantum states, interpreted in different coupling schemes. In addition, the analysis of the absorption spectrum was based on an oversimplified theoretical model and is incomplete. The present work identifies the energy levels commonly observed in absorption and emission studies and provides a consistent description of the $2p^5 3snl$ energy levels. As a result, about a hundred energy levels are revised. In particular, the connection of the quartet level system with the ground state is firmly established based on absorption studies.

 Online supplementary data available from stacks.iop.org/JPhysB/43/205001/mmedia

1. Introduction

In the compilation by Sansonetti [1], the core-excited energy levels of the $2p^5 3snl$ configurations were largely based on absorption spectra analysed by Baig *et al* [2, 3]. A significant part of this level system was also based on observations of Holmgren *et al* [4] using the laser spectroscopy of a pulsed hollow-cathode discharge and on the beam-foil study of Gaardsted and Andersen [5]. In the studies of emission spectra [4, 5], the energy levels were interpreted in terms of the LS coupling scheme, while the absorption spectra were interpreted in the JK (J_1l) coupling scheme. As a result, it is difficult to put together the results of these two types of studies.

The interpretation of the level system in the work of Baig *et al* [2] was largely based on the analysis of Rydberg series converging to several ionization limits. Certainly, this analysis is easier to make if the levels are interpreted in the LSJ_1l coupling scheme, in which the orbital momentum l of the outer electron is combined with the LSJ_1 level of the atomic core. Such interpretation makes it easy to identify the highly excited level series converging to the various LSJ_1 states of the core. However, the coupling scheme is in fact intermediate. Our

calculations (see below) show that even the highest $2p^5 3sns,nd$ configurations with $n \geq 9$ are only 80 to 90% pure in the LSJ_1l coupling scheme. For lower configurations, the LSJ_1l purity decreases and is only 60% for $2p^5 3s3d$ and 67% for $2p^5 3s4s$. The compositions of the $2p^5 3snd$ levels have very small contributions of $2p^5 3sns$ states. This means that the $2p^5 3snd$ series based on different LSJ_1 states of the core strongly interact with each other. In addition, several members of the $2p^5 3sns,nd$ series have large admixtures of the $2p^5 3p^2$ configuration. Therefore, the interpretation of Baig *et al* [2], which took into account only interactions between the $2p^5 3sns$ and $2p^5 3snd$ configurations, is inadequate. Two prominent broad features at 320.32 Å and 321.57 Å were assigned by Baig *et al* [2] to the $2p^5 4s^2$ configuration, while in an earlier study, Connerade *et al* [6] correctly identified them as belonging to the $2p^5 3p^2$ configuration. The latter authors did not specify the LS terms responsible for these features.

In the compilation [1], a number of weak absorption lines were quoted from Wolff *et al* [7] without identification. A close examination of possible absorption transitions shows that most of these lines are spurious (i.e. do not belong to Na I), while a few of them are also present on the spectrograms

of Baig *et al* [2, 3], which allows us to determine the wavelengths more precisely and ascertains that they indeed are due to Na I.

In this study, we re-interpret the entire set of observed data on the $2p^53sns$ and $2p^53snd$ levels, including the results of the laser-spectroscopy and beam-foil studies [4, 5], and construct a consistent level scheme based on a least-squares fitting of the energy levels with Cowan's codes [8, 9]. As a result, many of the identifications of Baig *et al* [2] are revised, and several new ones are proposed.

2. Experimental data

The absorption spectrum of neutral sodium in the EUV region was observed by Baig *et al* [2, 3] using a synchrotron radiation source and a 3 m normal incidence vacuum spectrograph with a 5000 lines mm^{-1} gold-coated holographic grating and photographic registration. The spectra were calibrated in wavelength by superposing the known absorption spectra of neon and helium. The uncertainty of the calibration was ± 0.002 Å. This provided for the measurement of absorption peak positions with a total uncertainty of ± 0.008 Å for sharp lines.

The measurement results presented by Baig *et al* [2] include only wavelengths of the peaks but not their intensities. However, a set of figures included in the paper, which reproduce tracings of photographic plates in various regions of the spectrum, provide sufficient detail to identify the peaks and estimate their observed intensities. Since the analysis of the line series is to a large extent based on observed relative intensities, we needed to extract these intensities from the spectrogram figures. With this purpose in mind, we digitized these figures and identified the observed absorption peaks with the wavelengths given in the tables of Baig *et al* [2]. Then the rough wavelengths determined by the wavelength-scale markers on the figures were corrected by building calibration curves for each figure separately. The calibration curves were second or third degree polynomials that fitted the rough wavelengths of the peaks to their exact positions given by Baig *et al* [2]. The accuracy of well-resolved peak wavelengths determined in this way varied depending on the quality of the figure from ± 0.010 Å for figure 4 (range 322.7–330 Å) to ± 0.08 Å for figure 1 (range 318–402.9 Å). This accuracy was sufficient to identify all the peaks. The relative intensities of commonly present lines measured on different figures were used to bring all intensities to a common arbitrary scale. Baig *et al* [2] mentioned that the blackening of the photographic plates was nonlinear versus the incident light intensity. We did not try to correct this nonlinearity. The intensity values have only qualitative meaning, distinguishing strong lines from weak ones. The quality of the figures in Baig *et al* [2] is insufficient to determine the peak widths, except for the very broad features at 321.57 Å and 320.32 Å whose full width at half maximum (FWHM) is approximately 0.5 Å. For this reason, our relative intensity values correspond to peak heights at the maximum and do not account for the differences in line widths. From figure 4 of Baig *et al* [2], widths of some of the strongest isolated peaks could be approximately estimated.

The sharpest peaks corresponding to the $2p^53s(^1P^\circ)ns$ $^2P^\circ$ series have widths ≈ 0.03 Å, while the broader peaks of the $2p^53s(^1P^\circ)nd$ $^2P^\circ$ series have widths decreasing with n , between 0.09 Å ($n = 6$, 325.840 Å) and 0.03 Å ($n = 12$, 323.203 Å).

An unexpected outcome of this procedure was that we found a few cases in which the wavelength given by Baig *et al* [2] was clearly a mistake (a rather different value was determined from the figures). For example, the wavelength 324.823 Å corresponds to a wing of a strong asymmetric line having a peak wavelength 324.884(8) Å. In addition, there are some moderately intense lines not included in the tables of Baig *et al* [2]. Some of these lines were previously reported by Wolff *et al* [8] (without identification).

Part of figure 4 of Baig *et al* [2] was reproduced with much better quality in figure 2 of Baig and Bhatti [3]. We determined the wavelengths of peaks in this range that were missing in the tables of Baig *et al* [2] from this figure with an uncertainty of ± 0.008 Å for strong lines and ± 0.010 Å for weak lines.

The list of lines from Baig *et al* [2] between 320 and 403 Å with relative intensities and new level assignments is given in table 1. The level assignments are discussed in section 5.

3. Theory

Energies and oscillator strengths of Na I were calculated in the present work with the suite of Cowan's programs RCN, RCN2, RCG and RCE [8, 9]. In this calculation, the following sets of configurations were included: (1) $2p^6ns,nd$ ($n = 3-9$), $2p^53snp,nf$ ($n = 3-9$), $2p^53p4s$, $2p^53pnd$ ($n = 3, 4$), $2p^53d4p$, $2p^53d4f$ (even parity); (2) $2p^63p$, $2p^6np,nf$ ($n = 4-9$), $2p^53d^2$, $2p^53sns,nd$ ($n = 3-20$), $2p^53pnp$ ($n = 3-15$), $2p^53p4f$, $2p^53dns,nd$ ($n = 4-7$) (odd parity). The total number of included configurations was 32 for even parity and 72 for odd parity. In the RCN/RCN2 calculations, we used the HFR option (approximate Hartree–Fock with some relativistic corrections) described in Cowan's book [8].

In the initial calculation, the radial parameters were scaled from their *ab initio* HFR values using the scaling factors empirically determined by Holmgren *et al* [4] (listed in their table V), and the average energies of all configurations were shifted from their Hartree–Fock values according to the values listed in table IV of Holmgren *et al* [4]. This allowed us to identify most of the experimentally known energy levels with the levels from our calculations, and confirm some of the previous level assignments. In particular, the identifications [2] of the higher members of the $2p^53sns,nd$ series above the $2p^53s$ $^3P^\circ_0$ limit with the $2p^53s(^1P^\circ)ns,nd$ $^2[1]^\circ_{1/2,3/2}$ states were confirmed. The *LS* designations of these levels are $2p^53s(^1P^\circ)ns,nd$ $^2P^\circ_{1/2,3/2}$. The identifications of the higher members of the series converging to the $2p^53s$ $^3P^\circ_0$ limit were confirmed as well. Then some of the radial parameters were allowed to vary in order to fit the observed energy levels, which produced the improved sets of predicted energy levels and oscillator strengths. This allowed us to identify more energy levels with the features observed in the absorption

Table 1. Absorption lines of Na I between 320 and 403 Å from Baig *et al* [2].

λ_{obs} (Å)	Rel. intens.	σ_{obs} (cm ⁻¹)	Level ^a (cm ⁻¹)	Level unc. (cm ⁻¹)	Configuration	Term ^b	J^c	JK term ^b	Comments ^d
320.32(2)	23	312 188	312 356	5	2p ⁵ (² P°)3p ² (¹ S)	2P°	1/2		C, W, r
321.57(2)	70	310 974	310 981	2	2p ⁵ (² P°)3p ² (¹ S)	2P°	3/2		C, W, r
322.67(2)	9	309 914		19	2p ⁵ 3s(¹ P°)20d	2P°	1/2,3/2	(¹ P° ₁) ² [1]	
322.70(2)	10	309 885		19	2p ⁵ 3s(¹ P°)19d	2P°	1/2,3/2	(¹ P° ₁) ² [1]	W
322.75(2)	12	309 837		19	2p ⁵ 3s(¹ P°)18d	2P°	1/2,3/2	(¹ P° ₁) ² [1]	W
322.79(2)	16	309 799		19	2p ⁵ 3s(¹ P°)17d	2P°	1/2,3/2	(¹ P° ₁) ² [1]	W
322.84(2)	22	309 751		19	2p ⁵ 3s(¹ P°)16d	2P°	1/2,3/2	(¹ P° ₁) ² [1]	W
322.90(2)	31	309 693		19	2p ⁵ 3s(¹ P°)15d	2P°	1/2,3/2	(¹ P° ₁) ² [1]	W
322.984(8)	41	309 613		8	2p ⁵ 3s(¹ P°)14d	2P°	1/2,3/2	(¹ P° ₁) ² [1]	W
323.01(2)	14	309 588		19	2p ⁵ 3s(¹ P°)15s	2P°	1/2,3/2	(¹ P° ₁) ² [1]	W
323.077(8)	51	309 524		8	2p ⁵ 3s(¹ P°)13d	2P°	1/2,3/2	(¹ P° ₁) ² [1]	W
323.13(2)	14	309 473		19	2p ⁵ 3s(¹ P°)14s	2P°	1/2,3/2	(¹ P° ₁) ² [1]	
323.203(8)	60	309 403		8	2p ⁵ 3s(¹ P°)12d	2P°	1/2,3/2	(¹ P° ₁) ² [1]	C, W
323.263(8)	14	309 346		8	2p ⁵ 3s(¹ P°)13s	2P°	1/2,3/2	(¹ P° ₁) ² [1]	
323.366(8)	73	309 247		8	2p ⁵ 3s(¹ P°)11d	2P°	1/2,3/2	(¹ P° ₁) ² [1]	C, W
323.443(8)	21	309 173		8	2p ⁵ 3s(¹ P°)12s	2P°	1/2,3/2	(¹ P° ₁) ² [1]	W
323.579(8)	84	309 044		8	2p ⁵ 3s(¹ P°)10d	2P°	1/2,3/2	(¹ P° ₁) ² [1]	C, W
323.679(8)	27	308 948		8	2p ⁵ 3s(¹ P°)11s	2P°	1/2,3/2	(¹ P° ₁) ² [1]	W
323.862(8)	88	308 773		8	2p ⁵ 3s(¹ P°)9d	2P°	1/2,3/2	(¹ P° ₁) ² [1]	C, W
324.001(8)	47	308 641		8	2p ⁵ 3s(¹ P°)10s	2P°	1/2,3/2	(¹ P° ₁) ² [1]	W
324.277(8)	97	308 378		8	2p ⁵ 3s(¹ P°)8d	2P°	1/2,3/2	(¹ P° ₁) ² [1]	C, W
324.470(8)	82	308 195		8	2p ⁵ 3s(¹ P°)9s	2P°	1/2,3/2	(¹ P° ₁) ² [1]	C, W
324.884(8)	107	307 802		8	2p ⁵ 3s(¹ P°)7d	2P°	1/2,3/2	(¹ P° ₁) ² [1]	C, W, n
325.178(8)	158	307 524		8	2p ⁵ 3s(¹ P°)8s	2P°	1/2,3/2	(¹ P° ₁) ² [1]	C, W
325.306(10)	9	307 403		9	2p ⁵ 3s(³ P°)20s	4P°	1/2	(³ P° ₀) ² [0]	n, n1
325.360(10)	10	307 352		9	2p ⁵ 3s(³ P°)19s	4P°	1/2	(³ P° ₀) ² [0]	n, n1
325.403(10)	12	307 312		9	2p ⁵ 3s(³ P°)18s	4P°	1/2	(³ P° ₀) ² [0]	r
325.450(10)	15	307 267		9	2p ⁵ 3s(³ P°)17s	4P°	1/2	(³ P° ₀) ² [0]	n
325.517(8)	18	307 204		8	2p ⁵ 3s(³ P°)16s	4P°	1/2	(³ P° ₀) ² [0]	
325.614(8)	21	307 112		8	2p ⁵ 3s(³ P°)15s	4P°	1/2	(³ P° ₀) ² [0]	
325.700(8)	29	307 031		8	2p ⁵ 3s(³ P°)14s	4P°	1/2	(³ P° ₀) ² [0]	
325.840(8)	114	306 899		8	2p ⁵ 3s(¹ P°)6d	2P°	1/2,3/2	(¹ P° ₁) ² [1]	C, W, r
326.039(8)	5	306 712		8	2p ⁵ 3s(³ P°)12s	4P°	1/2	(³ P° ₀) ² [0]	
326.239(8)	27	306 524		8	2p ⁵ 3s(³ P°)11s	4P°	1/2	(³ P° ₀) ² [0]	W
326.325(8)	214	306 443		8	2p ⁵ 3s(¹ P°)7s	2P°	1/2,3/2	(¹ P° ₁) ² [1]	C, W
326.45(2)	10	306 326		19	2p ⁵ 3s(³ P°)9d	4F°	3/2	(³ P° ₀) ² [2]	
326.51(2)	24	306 269		19	2p ⁵ 3s(³ P°)13s	2P°	1/2,3/2	(³ P° ₁) ² [1]	W
326.618(8)	31	306 168		7	2p ⁵ 3s(³ P°)10s	4P°	1/2	(³ P° ₀) ² [0]	W
326.674(8)	13	306 116		7	2p ⁵ 3s(³ P°)12s	2P°	1/2,3/2	(³ P° ₁) ² [1]	
326.76(2)	8	306 035		19					W, n
326.837(8)	27	305 963		7	2p ⁵ 3s(³ P°)8d	4F°	3/2	(³ P° ₀) ² [2]	W
326.907(8)	23	305 897		7	2p ⁵ 3s(³ P°)11s	2P°, 4P°	1/2,3/2	(³ P° ₁) ² [1]	W
326.96(2)	11	305 848		19	2p ⁵ 3s(³ P°)16s	2P°	3/2	(³ P° ₂) ² [2]	W
327.05(2)	18	305 764		19	2p ⁵ 3s(³ P°)15s	2P°	3/2	(³ P° ₂) ² [2]	W
327.13(2)	39	305 689		19	2p ⁵ 3s(³ P°)9s	4P°	1/2	(³ P° ₀) ² [0]	C, W, t
327.175(8)	11	305 647		7	2p ⁵ 3s(³ P°)14s	2P°	3/2	(³ P° ₂) ² [2]	
327.266(8)	33	305 562		7	2p ⁵ 3s(³ P°)12d	4P°	1/2,3/2	(³ P° ₂) ² [0], ² [1]	W, t
327.326(8)	6	305 506		7	2p ⁵ 3s(³ P°)13s	2P°	3/2	(³ P° ₂) ² [2]	
327.432(8)	171	305 407		7	2p ⁵ 3s(¹ P°)5d	2P°	1/2,3/2	(¹ P° ₁) ² [1]	C, W, r
327.486(8)	25	305 357		7	2p ⁵ 3s(³ P°)12s	2P°	3/2	(³ P° ₂) ² [2]	
327.526(8)	20	305 319		7	2p ⁵ 3s(³ P°)7d	4F°	3/2	(³ P° ₀) ² [2]	W
327.62(2)	21	305 232		19	2p ⁵ 3s(³ P°)8d	4D°	1/2,3/2	(³ P° ₁) ² [1]	r
327.639(8)	27	305 214		7	2p ⁵ 3s(³ P°)10d	4P°	1/2,3/2	(³ P° ₂) ² [0], ² [1]	C, W
327.715(8)	18	305 143		7	2p ⁵ 3s(³ P°)9s	2P°, 4P°	1/2,3/2	(³ P° ₁) ² [1]	W, t
327.818(8)	8	305 047		7	2p ⁵ 3s(³ P°)8s	4P°	1/2	(³ P° ₀) ² [0]	W
327.931(8)	31	304 942		7	2p ⁵ 3s(³ P°)9d	4P°	1/2,3/2	(³ P° ₂) ² [0], ² [1]	W
327.990(8)	31	304 887		7					C, W, n
328.057(8)	18	304 825		7	2p ⁵ 3s(³ P°)10s	2P°	3/2	(³ P° ₂) ² [2]	
328.12(2)	51	304 767		19	2p ⁵ 3s(³ P°)7d	4D°	1/2,3/2	(³ P° ₁) ² [1]	C, W
328.217(8)	11	304 676		7					W, n
328.290(8)	12	304 609		7	2p ⁵ 3s(³ P°)8d	4P°	1/2,3/2	(³ P° ₂) ² [0], ² [1]	
328.357(8)	53	304 547		7	2p ⁵ 3s(³ P°)6d	4F°	3/2	(³ P° ₀) ² [2]	C, W, t

Table 1. (Continued.)

λ_{obs} (Å)	Rel. intens.	σ_{obs} (cm ⁻¹)	Level ^a (cm ⁻¹)	Level unc. (cm ⁻¹)	Configuration	Term ^b	J^c	JK term ^b	Comments ^d
328.460(8)	30	304 451		7	2p ⁵ 3s(1P°)6s	2P°	1/2,3/2	(1P° ₁) ² [1]	W
328.546(8)	14	304 371		7	2p ⁵ 3s(3P°)9s	2P°	3/2	(3P° ₂) ² [2]	W
328.64(2)	10	304 284		19					W, n
328.77(2)	5	304 164		19					n
328.85(2)	36	304 090		18	2p ⁵ 3s(3P°)7d	2P°	1/2	(3P° ₂) ² [0]	n, t
328.889(8)	50	304 054		7	2p ⁵ 3s(3P°)7d	4P°	3/2	(3P° ₂) ² [1]	C, W, t
328.975(8)	14	303 974		7	2p ⁵ 3s(3P°)7s	4P°	1/2	(3P° ₀) ² [0]	W
329.23(2)	17	303 739		18	2p ⁵ 3s(3P°)8s	2P°	3/2	(3P° ₂) ² [2]	C, W, t, r
329.291(8)	3	303 683		7	2p ⁵ 3s(3P°)6d	4D°	1/2	(3P° ₁) ² [1]	t, r
329.597(8)	7	303 401		7	2p ⁵ 3s(3P°)7s	2P°, 4P°	1/2,3/2	(3P° ₁) ² [1]	C, W
329.779(8)	8	303 233		7	2p ⁵ 3s(3P°)6d	4P°	1/2,3/2	(3P° ₂) ² [0], ² [1]	C, W, t
330.10(2)	7	302 939		18					n, W
330.218(8)	18	302 830		7	2p ⁵ 3s(3P°)6d	2P°	1/2	(3P° ₂) ² [1]	C, W, t, r
330.375(8)	15	302 686		7	2p ⁵ 3s(3P°)7s	2P°	3/2	(3P° ₂) ² [2]	W
330.624(8)	24	302 458		7	2p ⁵ 3s(3P°)5d	4D°	1/2	(3P° ₁) ² [1]	t, r
330.667(8)	63	302 419		7	2p ⁵ 3s(3P°)5d	4F°	3/2	(3P° ₁) ² [2]	C, W, t, r
330.97(2)	10	302 142		18	2p ⁵ 3s(3P°)6s	2P°	1/2	(3P° ₀) ² [0]	C, W, t, r
331.152(8)	61	301 976		7	2p ⁵ 3s(1P°)4d	2P°	1/2	(1P° ₁) ² [1]	C, W, t, r
331.578(8)	7	301 588		7	2p ⁵ 3s(1P°)4d	2P°	3/2	(1P° ₁) ² [1]	W, t, r
331.690(16)	21	301 486		15	2p ⁵ 3s(3P°)6s	4P°	1/2	(3P° ₁) ² [1]	n, W, t
331.760(8)	11	301 423		7	2p ⁵ 3s(3P°)6s	4P°	3/2	(3P° ₁) ² [1]	W, t
332.23(2)	6	300 996		18					n, W
332.472(8)	54	300 777		7	2p ⁵ 3s(3P°)6s	2P°	3/2	(3P° ₂) ² [2]	C, W
332.645(8)	77	300 621		7	2p ⁵ 3s(1P°)5s	2P°	3/2	(1P° ₁) ² [1]	C, W, t
333.07(2)	5	300 237		18					n
333.289(8)	7	300 040		7	2p ⁵ 3s(3P°)4d	4F°	3/2	(3P° ₀) ² [2]	
333.95(2)	6	299 446		18					W
333.99(2)	14	299 410		18					W
334.464(16)	99	298 986		14	2p ⁵ 3s(3P°)4d	2D°	3/2	(3P° ₁) ² [2]	n, n1, W
335.177(8)	19	298 350		7	2p ⁵ 3s(3P°)5s	2P°	1/2	(3P° ₀) ² [0]	W, r
335.742(8)	386	297 848		7	2p ⁵ 3s(3P°)4d	2P°	3/2	(3P° ₂) ² [2]	C, W, r
335.881(8)	39	297 724		7	2p ⁵ 3s(3P°)4d	2P°	1/2	(3P° ₂) ² [1]	r
335.971(8)	446	297 645		7	2p ⁵ 3s(3P°)5s	2P°	3/2	(3P° ₁) ² [1]	C, W
336.616(8)	20	297 074		7	2p ⁵ 3s(3P°)5s	4P°	3/2	(3P° ₂) ² [2]	W
338.124(16)	14	295 749		14	2p ⁵ 3s(1P°)3d	2D°	3/2	(1P° ₁) ² [2]	n, n1, W
338.380(8)	23	295 526		7	2p ⁵ 3s(1P°)3d	2P°	1/2	(1P° ₁) ² [1]	C, W, r
338.646(8)	39	295 294		7	2p ⁵ 3s(1P°)3d	2P°	3/2	(1P° ₁) ² [1]	C, W, r
338.96(2)	12	295 020		17					n
340.679(8)	11	293 531	293 528	4	2p ⁵ 3s(3P°)3d	4F°	3/2	(3P° ₀) ² [2]	W
341.157(16)	9	293 120	293 133.1	4	2p ⁵ 3s(3P°)3d	4D°	1/2	(3P° ₁) ² [1]	n, W, r
341.290(16)	9	293 006	293 010.3	4	2p ⁵ 3s(3P°)3d	4D°	3/2	(3P° ₁) ² [2]	n, W
342.36(2)	291	292 090		17	2p ⁵ 3s(3P°)3d	2D°	3/2	(3P° ₁) ² [1]	C, W, r
343.194(8)	154	291 380		7	2p ⁵ 3s(1P°)4s	2P°	1/2	(1P° ₁) ² [1]	C, W, r
343.895(8)	395	290 786		7	2p ⁵ 3s(1P°)4s	2P°	3/2	(1P° ₁) ² [1]	C, W, r
344.247(8)	34	290 489		7	2p ⁵ 3s(3P°)3d	2P°	3/2	(3P° ₂) ² [2]	C, W, r
344.550(8)	534	290 234		7	2p ⁵ 3s(3P°)3d	2P°	1/2	(3P° ₂) ² [1]	C, W, r
346.45(2)	27	288 642		17	2p ⁵ 3s(3P°)4s	2P°	1/2	(3P° ₀) ² [0]	n, C, W
346.678(8)	323	288 452		7	2p ⁵ 3s(3P°)4s	2P°	3/2	(3P° ₂) ² [2]	C, W, r
347.983(8)	13	287 370	287 374.8	4	2p ⁵ 3s(3P°)4s	4P°	1/2	(3P° ₁) ² [1]	W
348.624(8)	13	286 842	286 849.5	4	2p ⁵ 3s(3P°)4s	4P°	3/2	(3P° ₁) ² [1]	W, r
400.82(2)	513	249 489		12	2p ⁵ 3s ²	2P°	1/2		C, W
402.949(8)	477	248 170		5	2p ⁵ 3s ²	2P°	3/2		C, W

^a The level values are shown only if they are different from the wavenumber in the previous column.

^b If two LS or JK terms are given for the level classification, and two J values are given in the J column, it means that the line is doubly classified. In all such cases, the first term designation refers to the first given J value, and the second term refers to the second J value. For example, the line at 329.597 Å is a blend of the 2p⁵3s(3P°)7s 2P°_{1/2} and 4P°_{3/2} transitions.

^c If two J values are given, it means that the line is a blend of two transitions.

^d Comments key: n—the wavelength was determined in the present work from the spectrograms given in [2,3]; n1—new energy level; C—this line was also observed by Connerade *et al* [6]; W—this line was also observed by Wolff *et al* [7]; r—identification suggested by Baig *et al* [2] is revised in the present work; t—tentative identification.

spectrum [2]. The procedure was iteratively repeated with progressive introduction of new identified levels and free parameters, until most of the strong and moderately intense lines in the observed spectrum were identified.

As a result, for even parity, all 24 known energy levels of the $2p^53s3p$ and $2p^53s4p$ configurations were fitted with a standard deviation of 150 cm^{-1} by seven free parameters. For odd parity, 83 known and newly identified energy levels of the $2p^53sns,nd$ ($n \leq 9$) and $2p^53p^2$ configurations were fitted with a standard deviation of 84 cm^{-1} by eight free parameters. The results of the fitting, such as the values of the average configuration energies and scaling factors relative to the *ab initio* HFR calculation, are given in the online supplementary appendix A (available at stacks.iop.org/JPhysB/43/205001/mmedia).

The most successful previous theoretical interpretation of the $(2p^53s)3p$, $3d$ and $4s$ configurations was made by Froese Fischer [10] using a multiconfiguration Hartree–Fock (MCHF) approach. Her calculations produced energy levels that agreed with experimental ones to about 240 cm^{-1} on average, while the standard deviations of her calculated fine-structure intervals from experiment were 11 cm^{-1} for quartet levels and 38 cm^{-1} for doublets. In table 2 we compare the experimental energy levels of the $(2p^53s)3p$, $3d$ and $4s$ configurations with the calculations of Froese Fischer [10] and with the results of our parametric fitting. In this table, the experimental energies of the quartet levels were derived from the observations of Holmgren *et al* [4], and Gaardsted and Andersen [5], while energies of the even-parity doublet levels were derived from lines observed by Sugar *et al* [11]. The energies of the odd-parity doublet levels were determined in this work based on the observations of Baig *et al* [2], except for the $2p^53s(1P^\circ)3d\ ^2D^\circ_{5/2}$ level, which was determined from the transition to $2p^63d\ ^2D$ at $375.14(10)\text{ \AA}$ observed by Pedrotti *et al* [13]. The position of the quartet levels relative to the ground state (and hence relative to the doublet levels) was established in the present work (see below) with an uncertainty of $\pm 3.9\text{ cm}^{-1}$.

Table 2 shows that the results of our parametric fitting agree well with the calculations of Froese Fischer [10], which confirms our identifications of the odd-parity doublet levels.

Out of the 23 total energy levels of the $2p^53s3d$ configuration, 16 are now experimentally known.

As one can see in table 2, the average term energies predicted by our parametric fitting with Cowan’s codes are more accurate than *ab initio* calculations of Froese Fischer [10]. However, as explained earlier (see Kramida *et al* [12] and references therein), the fine-structure splittings calculated with Cowan’s codes are less accurate than those calculated with the MCHF method. This is due to the omission of spin–spin and spin–other–orbit interactions in the approximation used in Cowan’s codes. Therefore, to predict previously unobserved energy levels with the highest accuracy, we use a combination of results of the two calculations. Namely, we combine the average term energies resulting from our parametric fitting with the fine-structure splittings calculated by Froese Fischer [10]. In a few cases when one of the fine-structure components of the term is experimentally known, the

fine-structure intervals calculated by Froese Fischer [10] are sufficient to predict the excitation energies of the unobserved fine-structure components. In this way the energies of the seven unknown levels can be predicted with reasonably small uncertainties. These predicted values are given in table 3.

4. Connection of the quartet levels with the ground state

The energy of the lowest quartet level, $2p^5(2P^\circ)3s3p(3P^\circ)\ ^4S_{3/2}$, was given by Sansonetti [1] as $263\,773(15)\text{ cm}^{-1}$ with a reference to Pedrotti *et al* [13]. However, the wavelength of the $2p^63p\ ^2P^\circ_{3/2,1/2}-2p^5(2P^\circ)3s3p(3P^\circ)\ ^4S_{3/2}$ transition observed by Pedrotti *et al* [13] was $405.26(10)\text{ \AA}$, which corresponds to the upper level value of $263\,730(60)\text{ cm}^{-1}$. Thus, the reference to Pedrotti *et al* [13] in [1] was inappropriate. The value $263\,773(15)\text{ cm}^{-1}$ was actually given by Gaardsted and Andersen [5] in the header of their table III with a reference to Froese Fischer [10]. Earlier, Holmgren *et al* [4] gave the same value with a reference to experimental data from Sugar *et al* [11]. Examination of the list of observed transitions reveals that there are 14 observed intercombination transitions connecting the quartet levels of the $2p^53s3p$, $2p^53s3d$ and $2p^53s4s$ configurations with the ground state either directly or via the precisely known $2p^63p\ ^2P^\circ_{1/2,3/2}$ levels. Six of these transitions correspond to doubly classified lines in which the lower $2p^63p\ ^2P^\circ_{1/2,3/2}$ levels were unresolved. The list of observed intercombination transitions is given in table 4.

Holmgren *et al* [4] and Gaardsted and Andersen [5] in their determination of relative positions of quartet levels did not account for these intercombination transitions. Since these transitions connect different parts of the quartet level system to the ground state with different uncertainties, a least-squares optimization is required in order to determine the quartet levels more accurately. To make this level optimization, we used the computer code LOPT [14]. In the list of transitions defining the level optimization problem, we assigned to each observed spectral line its measurement uncertainty quoted from the original data source [2, 4, 5, 11, 13]. For the wavelengths determined from the figures of Baig *et al* [2, 3], the assigned uncertainty was a combination of the standard deviation of wavelengths given by Baig *et al* [2], which we used as reference lines, from fitted correction curves, and the measurement uncertainty specified by Baig *et al* for these wavelengths ($\pm 0.008\text{ \AA}$). The unresolved components of doubly classified absorption lines from Sugar *et al* [11] were given weights proportional to the calculated relative intensities of the corresponding transitions. In the calculation of these intensities, we assumed that the lower levels of these transitions were populated according to their statistical weights.

As a result of the least-squares optimization, the energy of the lowest quartet level, $2p^5(2P^\circ)3s3p(3P^\circ)\ ^4S_{3/2}$, was determined to be $263\,745.3 \pm 3.9\text{ cm}^{-1}$. The specified total uncertainty accounts for the systematic uncertainty of the measurements of Baig *et al* [2], $\pm 1.7\text{ cm}^{-1}$, which follows from their specification of the wavelength calibration

Table 2. Energy levels (in cm^{-1}) for $(2p^5 3s)3p$, $3d$ and $4s$ configurations of Na I relative to $2p^5(^2P^\circ)3s3p(^3P^\circ) ^4S_{3/2}$ ($E_{\text{exp}} = (263\,745.3 \pm 3.9) \text{ cm}^{-1}$).

Configuration	Term	J	E_{exp}	Unc. exp.	E_{th} [10]	$E_{\text{exp}} - E_{\text{th}}$	E_{fit}	$E_{\text{exp}} - E_{\text{fit}}$	$E_{\text{fit}} - E_{\text{th}}$	
$2p^5(^2P^\circ)3s3p(^3P^\circ)$	4D	7/2	2841.4	0.9	2726	-115	2 824	18	98	
		5/2	3188.6	0.7	3084	-105	3 174	15	90	
		3/2	3537.0	0.7	3434	-103	3 523	14	89	
		1/2	3830.7	0.9	3726	-105	3 831	0	105	
	4P	5/2	4768.6	0.7	4795	26	4 911	-142	116	
		3/2	5152.1	0.7	5179	27	5 208	-56	29	
		1/2	5341.2	1.3	5381	40	5 568	-227	187	
	2D	3/2	5981	13	5932	-49	5 728	253	-204	
		5/2	6451	13	6389	-62	6 102	349	-287	
	2P	1/2	6837	13	6849	12	6 842	-5	-7	
		3/2	7132	13	7138	6	7 140	-8	2	
	2S	1/2	9491	14	9821	330	9 643	-152	-178	
		3/2	16 851	14	17 369	518	16 670	181	-699	
	$2p^5(^2P^\circ)3s3p(^1P^\circ)$	2S	1/2	17 033	14	17 459	426	16 952	81	-507
3/2			17 274	14	17 659	385	17 333	-59	-326	
$2p^5 3s(^3P^\circ)4s$	2D	3/2	18 331	14	18 780	449	18 344	-13	-436	
		1/2	18 587	15	18 953	366	18 779	-192	-174	
		5/2	22 555.1	0.6	22 611		22 515	40	-96	
	$^2P^\circ$	3/2	23 104.2	0.7	23 177	73	23 081	23	-96	
1/2		23 629.5	0.9	23 713	84	23 635	-5	-78		
$2p^5 3s(^3P^\circ)3d$	$^2P^\circ$	3/2	24 707	8	24 774	67	24 714	-7	-60	
		1/2	24 897	17	24 978	81	24 895	2	-83	
	$^2F^\circ$	1/2	26 489	8	26 179	-310	26 500	-11	321	
		7/2			26 317		26 412		95	
$2p^5 3s(^1P^\circ)4s$	$^2P^\circ$	3/2	26 744	8	26 492	-252	26 674	70	182	
		5/2			26 831	514	26 771		-60	
	$^2P^\circ$	3/2	27 041	8	27 197	156	27 041	0	-156	
		1/2	27 635	8	27 824	189	27 736	-101	-88	
$2p^5 3s(^3P^\circ)3d$	$^2D^\circ$	5/2			27 809		27 861		52	
		3/2	28 345	17	27 965	-380	28 020	325	55	
	$^4P^\circ$	1/2	28 474.3	0.8	28 262	-212	28 519	-45	257	
		3/2	28 543.9	0.8	28 331	-213	28 579	-35	248	
	$^4F^\circ$	9/2	28 595.3	1.6	28 386	-209	28 611	-16	225	
		5/2	28 654.1	0.8	28 450	-204	28 666	-12	216	
	$^4F^\circ$	7/2	28 704.4	1.0	28 498	-206	28 702	3	204	
		5/2	29 168.6	1.0	28 959	-210	29 201	-32	242	
	$^4D^\circ$	3/2	29 265.0	0.9	29 058	-207	29 278	-13	220	
		7/2			29 077		29 297		220	
		1/2	29 387.8	1.4	29 161	-227	29 364	24	203	
		5/2			29 556		29 829		273	
	$2p^5 3s(^1P^\circ)3d$	$^4F^\circ$	3/2	29 783	3	29 568	-215	29 836	-53	268
			5/2			31 458		31 531		73
$^2P^\circ$		3/2	31 549	7	31 510	-39	31 586	-37	76	
		7/2			31 739		31 892		153	
$^2P^\circ$		1/2	31 781	7	31 743	-38	31 906	-125	163	
		3/2	32 004	13	31 919	-85	32 004	0	85	
$^2D^\circ$		5/2	31 995	90	31 955	-40	32 037	-42	82	

uncertainty, $\pm 0.002 \text{ \AA}$. The uncertainties of the optimized energies of the quartet levels relative to $2p^5(^2P^\circ)3s3p(^3P^\circ) ^4S_{3/2}$ vary between $\pm 0.6 \text{ cm}^{-1}$ (for $2p^5 3s(^3P^\circ)4s ^4P^\circ_{5/2}$) and $\pm 3 \text{ cm}^{-1}$ (for $2p^5 3s(^3P^\circ)3d ^4F^\circ_{3/2}$). For the majority of the quartet levels, the uncertainties are in the range 0.7–1.3 cm^{-1} . This is a significant improvement over the level values determined in [4, 5], which had uncertainties between ± 2 and $\pm 5 \text{ cm}^{-1}$.

The complete list of experimentally determined energy levels of the $2p^5 3l3l'$ and $2p^5 3s4s$ configurations is given in table 5. The identification of the levels is discussed in the following section.

5. Discussion of level assignments

The $2p^5 3s4s$ and $2p^5 3s3d$ configurations give rise to the group of prominent absorption lines between 342 and 347 \AA and some weak lines in a wider range of 338–349 \AA . We identified these lines based on the energy levels calculated by Froese Fischer [10] and on the relative intensities predicted by our calculations. Our identifications are different from those of Baig *et al* [2]. In particular, Baig *et al* [2] assigned the $2p^5 3s(^3P^\circ_1)4s ^2[1]^\circ_{3/2}$ level to the weak line at 347.853 \AA (intensity 7 on the scale of table 1). This level, which in *LS* coupling has a dominant contribution of $2p^5 3s(^3P^\circ)4s ^4P^\circ_{3/2}$,

Table 3. Predicted energy levels (in cm^{-1}) of the $2p^5 3s 3d$ configuration of Na I relative to $2p^5(^2P^\circ)3s3p(^3P^\circ)^4S_{3/2}$ ($E_{\text{exp}} = 263\,745.3 \pm 3.9 \text{ cm}^{-1}$).

Configuration	Term	J	$E_{\text{predicted}}$	Splitting	Method ^a
$2p^5 3s(^3P^\circ)3d$	$^2F^\circ$	7/2	26 345(120)	514(40)	1
		5/2	26 859(120)		1
	$^2D^\circ$	5/2	28 189(40)		2
		$^4D^\circ$	7/2		29 284(12)
			5/2		29 763(12)
$2p^5 3s(^1P^\circ)3d$	$^2F^\circ$	5/2	31 577(120)	281(40)	1
		7/2	31 858(120)		1

^a Prediction method key: 1—based on the centre of gravity of the term calculated by the present parametric fitting and the fine-structure splitting calculated by Froese Fischer [10]; 2—based on the fine-structure splitting calculated by Froese Fischer [10].

was firmly established in the beam-foil study of Gaardsted *et al* [5] by two combinations with other quartet levels. This allowed us to unambiguously identify the line at 348.624 Å with this level. The line at 347.853 Å does not correspond to any possible energy level of Na I; hence we discarded it as spurious. The level $2p^5 3s(^3P^\circ_0)4s^2[0]^\circ_{1/2}$ was associated by Baig *et al* [2] with a prominent line at 346.678 Å. We reassigned this level to the moderately intense line at 346.45 Å that was not included in the tables of Baig *et al* [2], but is present on their spectrograms and was also reported by Connerade *et al* [6] and Wolff *et al* [7]. The strong line at 346.678 Å is now identified with the $2p^5 3s(^3P^\circ_2)4s^2[2]^\circ_{3/2}$ level. This identification is supported by the large calculated oscillator strength. The latter level in LS coupling has a dominant contribution of $2p^5 3s(^3P^\circ)4s^2 P^\circ_{3/2}$. It was previously assigned by Baig *et al* [2] to the above-mentioned weak line at 348.624 Å, now identified with the $2p^5 3s(^3P^\circ)4s^4 P^\circ_{3/2}$ level.

It should be noted that, as seen from figure 1 of Baig *et al* [2], their spectrum contained several weak lines between 349 and 399 Å. These lines do not correspond to any possible energy level in Na I. Wolff *et al* [7] also observed a number of

weak lines in this region. They attributed some of these lines to molecular absorption. None of these lines coincide with those observed by Baig *et al*. This means that Baig *et al* [2] and Wolff *et al* [7] probably had different impurities in their spectra.

The weak broad line at 353.44 Å observed by Wolff *et al* [7] was included in the compilation by Sansonetti [1] with an assignment to the $2p^6 4s-2p^5 3s(^1P^\circ)9d,10s$ transitions. Despite the good agreement of the observed wavenumber with the difference of the corresponding energy levels, this assignment can be ruled out, because Wolff *et al* [7] did not observe any of the known strong absorption lines having an excited lower energy level. Thus, we discarded this line.

Some of the weak lines from Baig *et al* [2] included in table 1 without identification may also be due to impurities. However, there are possible energy levels in Na I that can be associated with these lines. At the present state of understanding of the Na I spectrum, we did not find it possible to identify them.

Wolff *et al* [7] observed a sharp, very weak absorption line at 342.10 Å, which Sansonetti [1] included in the Na I line list without identification. This line is fairly close to the predicted wavelength of the transition from the ground state to the $2p^5 3s(^3P^\circ)3d^4 P^\circ_{3/2}$ level at $292\,289.2 \text{ cm}^{-1}$. However, there is no trace of this line on the spectrograms of Baig *et al* [2]. Thus, we conclude that the line observed by Wolff *et al* [7] was due to some impurity rather than to Na I.

As noted by Baig *et al* [2], the identification of the upper members of the $2p^5 3s(^1P^\circ)ns,nd^2 P^\circ$ series above the $2p^5 3s^3 P^\circ_0$ limit is fairly easy because there is very little mixing of configurations. Below the $2p^5 3s^3 P^\circ$ limits, configuration interactions mix the levels belonging to different series so strongly that the positions and intensities of the observed absorption lines no longer follow any traceable trend along the series, with only a few exceptions. One of these exceptions is the $2p^5 3s(^3P^\circ_0)ns^2[0]^\circ$ series. Above $n = 8$, this series exhibits a regular decline of intensities with increasing n , except for the $n = 13$ member, which is masked by a

Table 4. Observed intercombination transitions connecting doublet and quartet levels of Na I.

λ_{obs} (Å)	σ_{obs} (cm^{-1})	Rel. int. ^a	Lower level	Upper level	Reference
340.679(8)	293 531(7)	11a	$2p^6 3s^2 S_{1/2}$	$2p^5 3s(^3P^\circ)3d^4 F^\circ_{3/2}$	[2]
341.157(16)	293 120(14)	9a	$2p^6 3s^2 S_{1/2}$	$2p^5 3s(^3P^\circ)3d^4 D^\circ_{1/2}$	[2] ^b
341.290(16)	293 006(14)	9a	$2p^6 3s^2 S_{1/2}$	$2p^5 3s(^3P^\circ)3d^4 D^\circ_{3/2}$	[7], [2] ^b
347.983(8)	287 370(7)	13a	$2p^6 3s^2 S_{1/2}$	$2p^5 3s(^3P^\circ)4s^4 P^\circ_{1/2}$	[2]
348.624(8)	286 842(7)	13a	$2p^6 3s^2 S_{1/2}$	$2p^5 3s(^3P^\circ)4s^4 P^\circ_{3/2}$	[2]
396.88(2)	251 965(13)	a	$2p^6 3p^2 P^\circ_{1/2}$	$2p^5(^2P^\circ)3s3p(^3P^\circ)^4 P_{3/2}$	[11]
			$2p^6 3p^2 P^\circ_{3/2}$	$2p^5(^2P^\circ)3s3p(^3P^\circ)^4 P_{3/2}$	[11]
397.52(2)	251 560(13)	282	$2p^6 3p^2 P^\circ_{3/2}$	$2p^5(^2P^\circ)3s3p(^3P^\circ)^4 P_{5/2}$	[11], [13]
398.98(10)	250 640(60)	338	$2p^6 3p^2 P^\circ_{3/2}$	$2p^5(^2P^\circ)3s3p(^3P^\circ)^4 D_{1/2}$	[13]
			$2p^6 3p^2 P^\circ_{1/2}$	$2p^5(^2P^\circ)3s3p(^3P^\circ)^4 D_{1/2}$	[13]
399.42(10)	250 360(60)	152	$2p^6 3p^2 P^\circ_{1/2}$	$2p^5(^2P^\circ)3s3p(^3P^\circ)^4 D_{3/2}$	[13]
400.14(10)	249 910(60)	64	$2p^6 3p^2 P^\circ_{3/2}$	$2p^5(^2P^\circ)3s3p(^3P^\circ)^4 D_{5/2}$	[13]
405.26(10)	246 760(60)	190	$2p^6 3p^2 P^\circ_{3/2}$	$2p^5(^2P^\circ)3s3p(^3P^\circ)^4 S_{3/2}$	[13]
			$2p^6 3p^2 P^\circ_{1/2}$	$2p^5(^2P^\circ)3s3p(^3P^\circ)^4 S_{3/2}$	[13]

^a Symbol ‘a’ after the intensity value means ‘observed in absorption’. Relative intensities of absorption lines were determined in the present work from the spectrograms given by Baig *et al* [2].

^b The wavelength was determined in the present work from figure 3 of Baig *et al* [2].

Table 5. Optimized energy levels of the $2p^5 3l3l'$ and $2p^5 3s4s$ configurations of Na I.

Configuration	Term	J	Level (cm^{-1})	Unc. ^a	N_{lines}^b	Leading percentages ^c			
$2p^5 3s^2$	$2P^\circ$	3/2	248 170	3.9	1	93	6	$2p^5(^2P^\circ)3p^2(^1S)$	$2P^\circ$
$2p^5 3s^2$	$2P^\circ$	1/2	249 489	3.9	1	93	6	$2p^5(^2P^\circ)3p^2(^1S)$	$2P^\circ$
$2p^5(^2P^\circ)3s3p(^3P^\circ)$	$4S$	3/2	263 745.3	3.9	8	97			
$2p^5(^2P^\circ)3s3p(^3P^\circ)$	$4D$	7/2	266 586.7	3.9(0.9)	3	98			
$2p^5(^2P^\circ)3s3p(^3P^\circ)$	$4D$	5/2	266 933.9	3.8(0.7)	8	93			
$2p^5(^2P^\circ)3s3p(^3P^\circ)$	$4D$	3/2	267 282.3	3.8(0.7)	9	90	5	$2p^5(^2P^\circ)3s3p(^3P^\circ)$	$2D$
$2p^5(^2P^\circ)3s3p(^3P^\circ)$	$4D$	1/2	267 576.0	3.8(0.9)	6	94			
$2p^5(^2P^\circ)3s3p(^3P^\circ)$	$4P$	5/2	268 513.9	3.8(0.7)	6	82	17	$2p^5(^2P^\circ)3s3p(^3P^\circ)$	$2D$
$2p^5(^2P^\circ)3s3p(^3P^\circ)$	$4P$	3/2	268 897.4	3.8(0.7)	8	49	45	$2p^5(^2P^\circ)3s3p(^3P^\circ)$	$2D$
$2p^5(^2P^\circ)3s3p(^3P^\circ)$	$4P$	1/2	269 086.5	3.9(1.3)	3	94			
$2p^5(^2P^\circ)3s3p(^3P^\circ)$	$2D$	3/2	269 726	13	1	48	43	$2p^5(^2P^\circ)3s3p(^3P^\circ)$	$4P$
$2p^5(^2P^\circ)3s3p(^3P^\circ)$	$2D$	5/2	270 196	13	1	78	15	$2p^5(^2P^\circ)3s3p(^3P^\circ)$	$4P$
$2p^5(^2P^\circ)3s3p(^3P^\circ)$	$2P$	1/2	270 582	13	1	94			
$2p^5(^2P^\circ)3s3p(^3P^\circ)$	$2P$	3/2	270 877	13	1	92			
$2p^5(^2P^\circ)3s3p(^3P^\circ)$	$2S$	1/2	273 236	13	1	82	12	$2p^5(^2P^\circ)3s3p(^1P^\circ)$	$2S$
$2p^5(^2P^\circ)3s3p(^1P^\circ)$	$2D$	5/2	280 596	14	1	86	5	$2p^5 3s(^3P^\circ)4p$	$2D$
$2p^5(^2P^\circ)3s3p(^1P^\circ)$	$2S$	1/2	280 778	14	1	62	10	$2p^5 3s(^3P^\circ)4p$	$2S$
$2p^5(^2P^\circ)3s3p(^1P^\circ)$	$2P$	3/2	281 019	14	1	38	47	$2p^5(^2P^\circ)3s3p(^1P^\circ)$	$2D$
$2p^5(^2P^\circ)3s3p(^1P^\circ)$	$2D$	3/2	282 076	14	1	39	45	$2p^5(^2P^\circ)3s3p(^1P^\circ)$	$2P$
$2p^5(^2P^\circ)3s3p(^1P^\circ)$	$2P$	1/2	282 332	14	1	73	9	$2p^5(^2P^\circ)3s3p(^1P^\circ)$	$2S$
$2p^5 3s(^3P^\circ)4s$	$4P^\circ$	5/2	286 300.4	3.8(0.6)	6	99			
$2p^5 3s(^3P^\circ)4s$	$4P^\circ$	3/2	286 849.5	3.8(0.7)	7	87	or 55	$2p^5 3s(^3P^\circ)4s$	$2[1]^\circ$
$2p^5 3s(^3P^\circ)4s$	$4P^\circ$	1/2	287 374.8	3.8(0.9)	5	87	or 56	$2p^5 3s(^3P^\circ)4s$	$2[1]^\circ$
$2p^5 3s(^3P^\circ)4s$	$2P^\circ$	3/2	288 452	7	1	86	or 52	$2p^5 3s(^3P^\circ)4s$	$2[2]^\circ$
$2p^5 3s(^3P^\circ)4s$	$2P^\circ$	1/2	288 642	17	1	62	or 53	$2p^5 3s(^3P^\circ)4s$	$2[0]^\circ$
$2p^5 3s(^3P^\circ)3d$	$2P^\circ$	1/2	290 234	7	1	67	or 35	$2p^5 3s(^3P^\circ)3d$	$2[1]^\circ$
$2p^5 3s(^3P^\circ)3d$	$2P^\circ$	3/2	290 489	7	1	44	or 40	$2p^5 3s(^3P^\circ)3d$	$2[2]^\circ$
$2p^5 3s(^1P^\circ)4s$	$2P^\circ$	3/2	290 786	7	1	89	or 89	$2p^5 3s(^1P^\circ)4s$	$2[1]^\circ$
$2p^5 3s(^1P^\circ)4s$	$2P^\circ$	1/2	291 380	7	1	68	or 68	$2p^5 3s(^1P^\circ)4s$	$2[1]^\circ$
$2p^5 3s(^3P^\circ)3d$	$2D^\circ$	3/2	292 090	17	1	51	or 29	$2p^5 3s(^3P^\circ)3d$	$2[1]^\circ$
$2p^5 3s(^3P^\circ)3d$	$4P^\circ$	1/2	292 219.6	3.9(0.8)	4	94	or 62	$2p^5 3s(^3P^\circ)3d$	$2[0]^\circ$
$2p^5 3s(^3P^\circ)3d$	$4P^\circ$	3/2	292 289.2	3.9(0.8)	5	77	or 73	$2p^5 3s(^3P^\circ)3d$	$2[1]^\circ$
$2p^5 3s(^3P^\circ)3d$	$4F^\circ$	9/2	292 340.6	4.1(1.6)	1	99	or 99	$2p^5 3s(^3P^\circ)3d$	$2[4]^\circ$
$2p^5 3s(^3P^\circ)3d$	$4D^\circ$	5/2	292 399.4	3.9(0.8)	6	48	or 81	$2p^5 3s(^3P^\circ)3d$	$2[2]^\circ$
$2p^5 3s(^3P^\circ)3d$	$4F^\circ$	7/2	292 449.7	3.9(1.0)	3	53	or 84	$2p^5 3s(^3P^\circ)3d$	$2[3]^\circ$
$2p^5 3s(^3P^\circ)3d$	$4F^\circ$	5/2	292 913.9	3.9(1.0)	3	56	or 57	$2p^5 3s(^3P^\circ)3d$	$2[2]^\circ$
$2p^5 3s(^3P^\circ)3d$	$4D^\circ$	3/2	293 010.3	3.9(0.9)	6	43	or 37	$2p^5 3s(^3P^\circ)3d$	$2[2]^\circ$
$2p^5 3s(^3P^\circ)3d$	$4D^\circ$	1/2	293 133.1	4(1.4)	3	87	or 71	$2p^5 3s(^3P^\circ)3d$	$2[1]^\circ$
$2p^5 3s(^3P^\circ)3d$	$4F^\circ$	3/2	293 528	4.3(3.2)	2	58	or 61	$2p^5 3s(^3P^\circ)3d$	$2[2]^\circ$
$2p^5 3s(^1P^\circ)3d$	$2P^\circ$	3/2	295 294	7	1	54	or 54	$2p^5 3s(^1P^\circ)3d$	$2[1]^\circ$
$2p^5 3s(^1P^\circ)3d$	$2P^\circ$	1/2	295 526	7	1	70	or 70	$2p^5 3s(^1P^\circ)3d$	$2[1]^\circ$
$2p^5 3s(^1P^\circ)3d$	$2D^\circ$	5/2	295 740	90	1	67	or 67	$2p^5 3s(^1P^\circ)3d$	$2[2]^\circ$
$2p^5 3s(^1P^\circ)3d$	$2D^\circ$	3/2	295 749	14	2	54	or 54	$2p^5 3s(^1P^\circ)3d$	$2[2]^\circ$
$2p^5(^2P^\circ)3p^2(^1S)$	$2P^\circ$	3/2	310 981	2	1	79	6	$2p^5(^2P^\circ)3d^2(^1S)$	$2P^\circ$
$2p^5(^2P^\circ)3p^2(^1S)$	$2P^\circ$	1/2	312 356	5	1	56	19	$2p^5(^2P^\circ)3d^2(^1S)$	$2P^\circ$

^a The second value of uncertainty given in parentheses for the quartet levels is the uncertainty of the separation from the lowest quartet level, $2p^5(^2P^\circ)3s3p(^3P^\circ)4S_{3/2}$.

^b Number of spectral lines determining the level.

^c The percentage composition of the levels was determined in the present work by a parametric fitting using Cowan's codes [8, 9]. The first percentage value refers to the configuration and term given in the first two columns of the table. For levels with $J = 1/2, 3/2$, the leading percentage in the JK coupling scheme is given in order to facilitate a comparison with level assignments previously given by Baig *et al* [2].

much more intense line from the $2p^5 3s(^1P^\circ)6d^2[1]^\circ$ term at 325.840 Å. This series, converging on the $2p^5 3s^3P^\circ_0$ limit at 307 731.07 cm^{-1} (324.959 Å), is easily identified in figure 2 of Baig and Bhatti [3]. This series was listed up to $n = 17$ in table 1(e) of Baig *et al* [2]. However, consideration of the quantum defects shows that their $n = 17$ assignment is incorrect. The wavenumber 307 314 cm^{-1} , given for the line at 325.4 Å, corresponds to an effective quantum number of

16.2 rather than the listed value of 15.2. The line clearly belongs to the $2p^5 3s(^3P^\circ_0)18s^2[0]^\circ_{1/2}$ level, while the $n = 17$ line, which we measured at 325.460(8) Å, was omitted by Baig *et al* [2]. We also measured the wavelengths of the $n = 19$ and 20 members of this series at 325.356(8) Å and 325.31(2) Å, respectively.

In the region of strong configuration interactions between 300 000 and 305 700 cm^{-1} (333 and 327 Å, respectively),

it is difficult to unambiguously identify all of the observed lines. Here, oscillator strengths calculated with Cowan's codes are of little help because of very strong cancellations in the calculation. Thus, many of our level assignments in this region are only tentative.

The $2p^53s4s$ configuration is best described in the LS coupling scheme in which its purity is 83%. For the $2p^53s3d$ configuration, the purity is almost the same, about 61%, in the LS and JK coupling schemes. For the higher odd-parity configurations, the JK coupling scheme becomes increasingly purer with an increasing principal quantum number.

For the even-parity $2p^53s3p$ configuration, the best coupling scheme is the version of LS coupling suggested by Sugar *et al* [11], in which the outer 3s and 3p electrons are first combined with each other to produce an intermediate $L_{n=3}S_{n=3}$ term. Then this term is combined with the $L_{n=2}S_{n=2}$ term of the $2p^5$ shell and with the total J to produce the final LSJ term. In this coupling scheme, the purity of the $2p^53s3p$ configuration is 78%, while in the usual LS coupling with sequential summations of electronic shells, used by Froese Fischer [10], the purity is 70%. However, even in the best coupling scheme the $2p^5(2P^\circ)3s3p(1P^\circ)2D_{3/2}$ and $2P_{3/2}$ levels are strongly mixed with each other. Our parametric fitting yields somewhat higher percentage of the $2D_{3/2}$ character for the lower of these two levels at $281\,032\text{ cm}^{-1}$, and a higher percentage of $2P_{3/2}$ for the higher level at $282\,063\text{ cm}^{-1}$. This indicates that, in both calculations of Froese Fischer [10] and Sugar *et al* [11], designations of these two levels may be interchanged. In order to avoid confusion in the comparisons of results of different authors, we retained the designations of Sugar *et al* [11].

6. Conclusion

As a result of this work, all energy levels of the $2p^53s^2$, $2p^53s3p$ and $2p^53s4s$ configurations, most of the $2p^53s3d$ levels, and two of the $2p^53p^2$ levels of Na I are firmly established. Many of the levels belonging to the $2p^53s4p$, $2p^53sns$ ($n = 5-20$) and

$2p^53snd$ ($n = 4-20$) configurations are also firmly established, while several of them are tentatively identified. All prominent absorption lines and most of the moderately intense and weak ones observed by Baig *et al* [2] are explained in a classification scheme consistent with the results of other absorption and emission spectroscopy experiments. The connection of the quartet level system of Na I with the ground state is determined with a greatly improved precision based on a least-squares optimization of all observed transitions. Level compositions of the $2p^53s^2$, $2p^53s3p$, $2p^53s4s$ and $2p^53s3d$ configurations are determined by parametric fitting.

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