Revised interpretation of the Na I EUV absorption spectrum

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Abstract
Spectral data for neutral sodium were recently compiled by Sansonetti [1]. In that compilation, some of the energy levels of the $2p^5 3s nl$ configurations were quoted from 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 [1] 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 a 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 $2p^5 3s nl$ 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.

1. Introduction

In the compilation by Sansonetti [1], the core-excited energy levels of the $2p^5 3s nl$ configurations were largely based on absorption spectra analyzed by Baig et al. [2,3]. A significant part of this level system was also based on observations of Holmgren et al. [4] using 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* ($J_1 l$) 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 $LSJ_1 l$ 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 $2p^5 3s n$s,nd configurations with $n \geq 9$ are only 80 to 90% pure in the $LSJ_1 l$ coupling scheme. For lower configurations the $LSJ_1 l$ purity decreases and is only 60% for $2p^5 3s3d$ and 67% for $2p^5 3s4s$. The compositions of the $2p^5 3s n$d levels have very small contributions of $2p^5 3s n$s states. This means that the $2p^5 3s n$d series based on different LSJ_1 states of the core

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strongly interact with each other. In addition, several members of the $2p^53s\mathit{n}s,\mathit{n}d$ series have large admixtures of the $2p^53p^2$ configuration. Therefore, the interpretation of Baig et al. [2], which took into account only interactions between the $2p^53s\mathit{n}s$ and $2p^53s\mathit{n}d$ configurations, is inadequate. Two prominent broad features at 320.32 Å and 321.57 Å were assigned by Baig et al. [2] to the $2p^54s^2$ configuration, while in an earlier study Connerade et al. [6] correctly identified them as belonging to the $2p^53p^2$ 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 $2p^53s\mathit{n}s$ and $2p^53s\mathit{n}d$ 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 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 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 Fig. 4 (range 322.7 to 330 Å) to ±0.08 Å for Fig. 1 (range 318 to 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 non-linear vs the incident light intensity. We did not try to correct this non-linearity. The intensity values have only qualitative meaning, distinguishing strong lines from weak ones. The quality of 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 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 Fig. 4 of Baig et al. [2], widths of some of the strongest isolated peaks could be approximately estimated. The sharpest peaks corresponding to the $2p^53s(^1P°)ns$ $^2P°$ series have widths ≈0.03 Å, while the broader peaks of the $2p^53s(^1P°)nd$ $^2P°$ 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 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 Fig. 4 of Baig et al. [2] was reproduced with much better quality in Fig. 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.

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	312188	312356	5	$2p^5(^2P°)3p^2(^1S)$	$^2P°$	1/2		C, W, r
321.57(2)	70	310974	310981	2	$2p^5(^2P°)3p^2(^1S)$	$^2P°$	3/2		C, W, r
322.67(2)	9	309914		19	$2p^53s(^1P°)20d$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	
322.70(2)	10	309885		19	$2p^53s(^1P°)19d$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	W
322.75(2)	12	309837		19	$2p^53s(^1P°)18d$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	W
322.79(2)	16	309799		19	$2p^53s(^1P°)17d$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	W
322.84(2)	22	309751		19	$2p^53s(^1P°)16d$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	W
322.90(2)	31	309693		19	$2p^53s(^1P°)15d$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	W
322.984(8)	41	309613		8	$2p^53s(^1P°)14d$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	W
323.01(2)	14	309588		19	$2p^53s(^1P°)15s$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	W
323.077(8)	51	309524		8	$2p^53s(^1P°)13d$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	W
323.13(2)	14	309473		19	$2p^53s(^1P°)14s$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	
323.203(8)	60	309403		8	$2p^53s(^1P°)12d$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	C, W
323.263(8)	14	309346		8	$2p^53s(^1P°)13s$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	
323.366(8)	73	309247		8	$2p^53s(^1P°)11d$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	C, W

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]
323.443(8)	21	309173		8	$2p^53s(^1P°)12s$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	W
323.579(8)	84	309044		8	$2p^53s(^1P°)10d$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	C, W
323.679(8)	27	308948		8	$2p^53s(^1P°)11s$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	W
323.862(8)	88	308773		8	$2p^53s(^1P°)9d$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	C, W
324.001(8)	47	308641		8	$2p^53s(^1P°)10s$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	W
324.277(8)	97	308378		8	$2p^53s(^1P°)8d$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	C, W
324.470(8)	82	308195		8	$2p^53s(^1P°)9s$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	C, W
324.884(8)	107	307802		8	$2p^53s(^1P°)7d$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	C, W, n
325.178(8)	158	307524		8	$2p^53s(^1P°)8s$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	C, W
325.306(10)	9	307403		9	$2p^53s(^3P°)20s$	$^4P°$	1/2	$(^3P°_0)^2[0]$	n
325.360(10)	10	307352		9	$2p^53s(^3P°)19s$	$^4P°$	1/2	$(^3P°_0)^2[0]$	n
325.403(10)	12	307312		9	$2p^53s(^3P°)18s$	$^4P°$	1/2	$(^3P°_0)^2[0]$	r
325.450(10)	15	307267		9	$2p^53s(^3P°)17s$	$^4P°$	1/2	$(^3P°_0)^2[0]$	n
325.517(8)	18	307204		8	$2p^53s(^3P°)16s$	$^4P°$	1/2	$(^3P°_0)^2[0]$	
325.614(8)	21	307112		8	$2p^53s(^3P°)15s$	$^4P°$	1/2	$(^3P°_0)^2[0]$	
325.700(8)	29	307031		8	$2p^53s(^3P°)14s$	$^4P°$	1/2	$(^3P°_0)^2[0]$	
325.840(8)	114	306899		8	$2p^53s(^1P°)6d$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	C, W, r
326.039(8)	5	306712		8	$2p^53s(^3P°)12s$	$^4P°$	1/2	$(^3P°_0)^2[0]$	
326.239(8)	27	306524		8	$2p^53s(^3P°)11s$	$^4P°$	1/2	$(^3P°_0)^2[0]$	W
326.325(8)	214	306443		8	$2p^53s(^1P°)7s$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	C, W
326.45(2)	10	306326		19	$2p^53s(^3P°)9d$	$^4F°$	3/2	$(^3P°_0)^2[2]$	
326.51(2)	24	306269		19	$2p^53s(^3P°)13s$	$^2P°$	1/2,3/2	$(^3P°_1)^2[1]$	W
326.618(8)	31	306168		7	$2p^53s(^3P°)10s$	$^4P°$	1/2	$(^3P°_0)^2[0]$	W
326.674(8)	13	306116		7	$2p^53s(^3P°)12s$	$^2P°$	1/2,3/2	$(^3P°_1)^2[1]$	
326.76(2)	8	306035		19					W, n
326.837(8)	27	305963		7	$2p^53s(^3P°)8d$	$^4F°$	3/2	$(^3P°_0)^2[2]$	W
326.907(8)	23	305897		7	$2p^53s(^3P°)11s$	$^2P°$	1/2,3/2	$(^3P°_1)^2[1]$	W
326.96(2)	11	305848		19	$2p^53s(^3P°)16s$	$^2P°$	3/2	$(^3P°_2)^2[2]$	W
327.05(2)	18	305764		19	$2p^53s(^3P°)15s$	$^2P°$	3/2	$(^3P°_2)^2[2]$	W
327.13(2)	39	305689		19	$2p^53s(^3P°)9s$	$^4P°$	1/2	$(^3P°_0)^2[0]$	C, W, t
327.175(8)	11	305647		7	$2p^53s(^3P°)14s$	$^2P°$	3/2	$(^3P°_2)^2[2]$	
327.266(8)	33	305562		7	$2p^53s(^3P°)12d$	$^4P°$	1/2,3/2	$(^3P°_2)^2[0],^2[1]$	W, t
327.326(8)	6	305506		7	$2p^53s(^3P°)13s$	$^2P°$	3/2	$(^3P°_2)^2[2]$	
327.432(8)	171	305407		7	$2p^53s(^1P°)5d$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	C, W, r
327.486(8)	25	305357		7	$2p^53s(^3P°)12s$	$^2P°$	3/2	$(^3P°_2)^2[2]$	
327.526(8)	20	305319		7	$2p^53s(^3P°)7d$	$^4F°$	3/2	$(^3P°_0)^2[2]$	W
327.62(2)	21	305232		19	$2p^53s(^3P°)8d$	$^4D°$	1/2,3/2	$(^3P°_1)^2[1]$	r
327.639(8)	27	305214		7	$2p^53s(^3P°)10d$	$^4P°$	1/2,3/2	$(^3P°_2)^2[0],^2[1]$	C, W
327.715(8)	18	305143		7	$2p^53s(^3P°)9s$	$^2P°,^4P°$	1/2,3/2	$(^3P°_1)^2[1]$	W, t
327.818(8)	8	305047		7	$2p^53s(^3P°)8s$	$^4P°$	1/2	$(^3P°_0)^2[0]$	W
327.931(8)	31	304942		7	$2p^53s(^3P°)9d$	$^4P°$	1/2,3/2	$(^3P°_2)^2[0],^2[1]$	W
327.990(8)	31	304887		7					C, W, n
328.057(8)	18	304825		7	$2p^53s(^3P°)10s$	$^2P°$	3/2	$(^3P°_2)^2[2]$	
328.12(2)	51	304767		19	$2p^53s(^3P°)7d$	$^4D°$	1/2,3/2	$(^3P°_1)^2[1]$	C, W
328.217(8)	11	304676		7					W, n
328.290(8)	12	304609		7	$2p^53s(^3P°)8d$	$^4P°$	1/2,3/2	$(^3P°_2)^2[0],^2[1]$	

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]
328.357(8)	53	304547		7	$2p^53s(^3P°)6d$	$^4F°$	3/2	$(^3P°_0)^2[2]$	C, W, t
328.460(8)	30	304451		7	$2p^53s(^1P°)6s$	$^2P°$	1/2,3/2	$(^1P°_1)^2[1]$	W
328.546(8)	14	304371		7	$2p^53s(^3P°)9s$	$^2P°$	3/2	$(^3P°_2)^2[2]$	W
328.64(2)	10	304284		19					W, n
328.77(2)	5	304164		19					n
328.85(2)	36	304090		18	$2p^53s(^3P°)7d$	$^2P°$	1/2	$(^3P°_2)^2[0]$	n, t
328.889(8)	50	304054		7	$2p^53s(^3P°)7d$	$^4P°$	3/2	$(^3P°_2)^2[1]$	C, W, t
328.975(8)	14	303974		7	$2p^53s(^3P°)7s$	$^4P°$	1/2	$(^3P°_0)^2[0]$	W
329.23(2)	17	303739		18	$2p^53s(^3P°)8s$	$^2P°$	3/2	$(^3P°_2)^2[2]$	C, W, t, r
329.291(8)	3	303683		7	$2p^53s(^3P°)6d$	$^4D°$	1/2	$(^3P°_1)^2[1]$	t, r
329.597(8)	7	303401		7	$2p^53s(^3P°)7s$	$^2P°, ^4P°$	1/2,3/2	$(^3P°_1)^2[1]$	C, W
329.779(8)	8	303233		7	$2p^53s(^3P°)6d$	$^4P°$	1/2,3/2	$(^3P°_2)^2[0],^2[1]$	C, W, t
330.10(2)	7	302939		18					n, W
330.218(8)	18	302830		7	$2p^53s(^3P°)6d$	$^2P°$	1/2	$(^3P°_2)^2[1]$	C, W, t, r
330.375(8)	15	302686		7	$2p^53s(^3P°)7s$	$^2P°$	3/2	$(^3P°_2)^2[2]$	W
330.624(8)	24	302458		7	$2p^53s(^3P°)5d$	$^4D°$	1/2	$(^3P°_1)^2[1]$	t, r
330.667(8)	63	302419		7	$2p^53s(^3P°)5d$	$^4F°$	3/2	$(^3P°_1)^2[2]$	C, W, t, r
330.97(2)	10	302142		18	$2p^53s(^3P°)6s$	$^2P°$	1/2	$(^3P°_0)^2[0]$	C, W, t, r
331.152(8)	61	301976		7	$2p^53s(^1P°)4d$	$^2P°$	1/2	$(^1P°_1)^2[1]$	C, W, t, r
331.578(8)	7	301588		7	$2p^53s(^1P°)4d$	$^2P°$	3/2	$(^1P°_1)^2[1]$	W, t, r
331.690(16)	21	301486		15	$2p^53s(^3P°)6s$	$^4P°$	1/2	$(^3P°_1)^2[1]$	n, W, t
331.760(8)	11	301423		7	$2p^53s(^3P°)6s$	$^4P°$	3/2	$(^3P°_1)^2[1]$	W, t
332.23(2)	6	300996		18					n, W
332.472(8)	54	300777		7	$2p^53s(^3P°)6s$	$^2P°$	3/2	$(^3P°_2)^2[2]$	C, W
332.645(8)	77	300621		7	$2p^53s(^1P°)5s$	$^2P°$	3/2	$(^1P°_1)^2[1]$	C, W, t
333.07(2)	5	300237		18					n
333.289(8)	7	300040		7	$2p^53s(^3P°)4d$	$^4F°$	3/2	$(^3P°_0)^2[2]$	
333.95(2)	6	299446		18					
333.99(2)	14	299410		18					W
334.464(16)	99	298986		14	$2p^53s(^3P°)4d$	$^2D°$	3/2	$(^3P°_1)^2[2]$	n, W
335.177(8)	19	298350		7	$2p^53s(^3P°)5s$	$^2P°$	1/2	$(^3P°_0)^2[0]$	W, r
335.742(8)	386	297848		7	$2p^53s(^3P°)4d$	$^2P°$	3/2	$(^3P°_2)^2[2]$	C, W, r
335.881(8)	39	297724		7	$2p^53s(^3P°)4d$	$^2P°$	1/2	$(^3P°_2)^2[1]$	
335.971(8)	446	297645		7	$2p^53s(^3P°)5s$	$^2P°$	3/2	$(^3P°_1)^2[1]$	C, W
336.616(8)	20	297074		7	$2p^53s(^3P°)5s$	$^4P°$	3/2	$(^3P°_2)^2[2]$	W
338.124(16)	14	295749		14	$2p^53s(^1P°)3d$	$^2D°$	3/2	$(^1P°_1)^2[2]$	n, W
338.380(8)	23	295526		7	$2p^53s(^1P°)3d$	$^2P°$	1/2	$(^1P°_1)^2[1]$	C, W, r
338.646(8)	39	295294		7	$2p^53s(^1P°)3d$	$^2P°$	3/2	$(^1P°_1)^2[1]$	C, W, r
338.96(2)	12	295020		17					n
340.679(8)	11	293531	293528	4	$2p^53s(^3P°)3d$	^4F	3/2	$(^3P°_0)^2[2]$	W
341.157(16)	9	293120	293133.1	4	$2p^53s(^3P°)3d$	^4D	1/2	$(^3P°_1)^2[1]$	n, W, r
341.290(16)	9	293006	293010.3	4	$2p^53s(^3P°)3d$	^4D	3/2	$(^3P°_1)^2[2]$	n, W
342.36(2)	291	292090		17	$2p^53s(^3P°)3d$	$^2D°$	3/2	$(^3P°_1)^2[1]$	C, W, r
343.194(8)	154	291380		7	$2p^53s(^1P°)4s$	$^2P°$	1/2	$(^1P°_1)^2[1]$	C, W, r
343.895(8)	395	290786		7	$2p^53s(^1P°)4s$	$^2P°$	3/2	$(^1P°_1)^2[1]$	C, W, r
344.247(8)	34	290489		7	$2p^53s(^3P°)3d$	$^2P°$	3/2	$(^3P°_2)^2[2]$	C, W, r

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]
344.550(8)	534	290234		7	$2p^53s(^3P°)3d$	$^2P°$	1/2	$(^3P°_2)^2[1]$	C, W, r
346.45(2)	27	288642		17	$2p^53s(^3P°)4s$	$^2P°$	1/2	$(^3P°_0)^2[0]$	n, C, W
346.678(8)	323	288452		7	$2p^53s(^3P°)4s$	$^2P°$	3/2	$(^3P°_2)^2[2]$	C, W, r
347.983(8)	13	287370	287374.8	4	$2p^53s(^3P°)4s$	$^4P°$	1/2	$(^3P°_1)^2[1]$	W
348.624(8)	13	286842	286849.5	4	$2p^53s(^3P°)4s$	$^4P°$	3/2	$(^3P°_1)^2[1]$	W, r
400.82(2)	513	249489		12	$2p^53s^2$	$^2P°$	1/2		C, W
402.949(8)	477	248170		5	$2p^53s^2$	$^2P°$	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 $2p^53s(^3P°)7s\ ^2P°_{1/2}$ 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 Baig et al. [2,3]; 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.

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 (Hartree-Fock with 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 $2p^53s\ ^3P°_0$ limit with the $2p^53s(^1P°)ns,nd\ ^2[1]°_{1/2,3/2}$ states, were confirmed. The *LS* designations of these levels are $2p^53s(^1P°)ns,nd\ ^2P°_{1/2,3/2}$. The identifications of the higher members of the series converging to the $2p^53s\ ^3P°_0$ 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 improved sets of predicted energy levels and oscillator strengths. This allowed us to identify more energy levels with the features observed in the absorption 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 7 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 8 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 Appendix A.

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 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 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 & 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 $2p^53s(^1P°)3d\ ^2D°_{5/2}$ level, which was determined from the transition to $2p^63d\ ^2D$ at 375.14(10) Å observed by Pedrotti et al. [12]. 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 ±3.9 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.

Table 2. Energy levels (in cm^{-1}) for $(2p^53s)3p$, 3d, and 4s configurations of Na I relative to $2p^5(^2P°)3s3p(^3P°)\ ^4S_{3/2}$ (E_{exp} = 263745.3±3.9) cm^{-1}).

Configuration	Term	J	E_{exp}	Unc. exp.	E_{th} [10]	E_{exp}–E_{th}	E_{fit}	E_{exp}–E_{fit}	E_{fit}–E_{th}
$2p^5(^2P°)3s3p(^3P°)$	^4D	7/2	2841.4	0.9	2726	–115	2824	18	98
		5/2	3188.6	0.7	3084	–105	3174	15	90
		3/2	3537.0	0.7	3434	–103	3523	14	89
		1/2	3830.7	0.9	3726	–105	3831	0	105
	^4P	5/2	4768.6	0.7	4795	26	4911	–142	116
		3/2	5152.1	0.7	5179	27	5208	–56	29
		1/2	5341.2	1.3	5381	40	5568	–227	187
	^2D	3/2	5981	13	5932	–49	5728	253	–204
		5/2	6451	13	6389	–62	6102	349	–287
	^2P	1/2	6837	13	6849	12	6842	–5	–7

Configuration	Term	J	E_{exp}	Unc. exp.	E_{th} [10]	E_{exp}–E_{th}	E_{fit}	E_{exp}–E_{fit}	E_{fit}–E_{th}
		3/2	7132	13	7138	6	7140	–8	2
	^{2}S	1/2	9491	14	9821	330	9643	–152	–178
$2p^5(^2P°)3s3p(^1P°)$	^{2}D	5/2	16851	14	17369	518	16670	181	–699
	^{2}S	1/2	17033	14	17459	426	16952	81	–507
	^{2}P	3/2	17274	14	17659	385	17333	–59	–326
	^{2}D	3/2	18331	14	18780	449	18344	–13	–436
	^{2}P	1/2	18587	15	18953	366	18779	–192	–174
$2p^53s(^3P°)4s$	^{4}P°	5/2	22555.1	0.6	22611		22515	40	–96
		3/2	23104.2	0.7	23177	73	23081	23	–96
		1/2	23629.5	0.9	23713	84	23635	–5	–78
	^{2}P°	3/2	24707	8	24774	67	24714	–7	–60
		1/2	24897	17	24978	81	24895	2	–83
$2p^53s(^3P°)3d$	^{2}P°	1/2	26489	8	26179	–310	26500	–11	321
	^{2}F°	7/2			26317		26412		95
	^{2}P°	3/2	26744	8	26492	–252	26674	70	182
	^{2}F°	5/2			26831	514	26771		–60
$2p^53s(^1P°)4s$	^{2}P°	3/2	27041	8	27197	156	27041	0	–156
		1/2	27635	8	27824	189	27736	–101	–88
$2p^53s(^3P°)3d$	^{2}D°	5/2			27809		27861		52
		3/2	28345	17	27965	–380	28020	325	55
	^{4}P°	1/2	28474.3	0.8	28262	–212	28519	–45	257
		3/2	28543.9	0.8	28331	–213	28579	–35	248
	^{4}F°	9/2	28595.3	1.6	28386	–209	28611	–16	225
	^{4}P°	5/2	28654.1	0.8	28450	–204	28666	–12	216
	^{4}F°	7/2	28704.4	1.0	28498	–206	28702	3	204
		5/2	29168.6	1.0	28959	–210	29201	–32	242
	^{4}D°	3/2	29265.0	0.9	29058	–207	29278	–13	220
		7/2			29077		29297		220

Configuration	Term	J	E_{exp}	Unc. exp.	E_{th} [10]	E_{exp}–E_{th}	E_{fit}	E_{exp}–E_{fit}	E_{fit}–E_{th}
		1/2	29387.8	1.4	29161	–227	29364	24	203
		5/2			29556		29829		273
	^{4}F°	3/2	29783	3	29568	–215	29836	–53	268
$2p^5 3s(^1P°)3d$	^{2}F°	5/2			31458		31531		73
	^{2}P°	3/2	31549	7	31510	–39	31586	–37	76
	^{2}F°	7/2			31739		31892		153
	^{2}P°	1/2	31781	7	31743	–38	31906	–125	163
	^{2}D°	3/2	32004	13	31919	–85	32004	0	85
		5/2	31995	90	31955	–40	32037	–42	82

Out of the 23 total energy levels of the $2p^5 3s3d$ configuration, 16 are now experimentally known. Based on a combination of our parametric fitting and the term splittings calculated by Froese Fischer [10], the energies of the seven unknown levels can be predicted with reasonably small uncertainties. These predicted values are given in Table 3.

Table 3. Predicted energy levels (in cm^{-1}) of the $2p^5 3s3d$ configuration of Na I relative to $2p^5(^2P°)3s3p(^3P°)\ ^4S_{3/2}$ (E_{exp} = 263745.3±3.9) cm^{-1}).

Configuration	Term	J	$E_{predicted}$	Splitting	Method [a]
$2p^5 3s(^3P°)3d$	^{2}F°	7/2	26345(120)		1
		5/2	26859(120)	514(40)	1
	^{2}D°	5/2	28189(40)		2
	^{4}D°	7/2	29284(12)		2
		5/2	29763(12)		2
$2p^5 3s(^1P°)3d$	^{2}F°	5/2	31577(120)		1
		7/2	31858(120)	281(40)	1

[a] Prediction method key: 1 – based on the center 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].

4. Connection of the quartet levels with the ground state

The energy of the lowest quartet level, $2p^5(^2P°)3s3p(^3P°)\ ^4S_{3/2}$, was given by Sansonetti [1] as 263773(15) cm^{-1} with a reference to Pedrotti et al. [12]. However, the wavelength of the $2p^6 3p\ ^2P°_{3/2,1/2} - 2p^5(^2P°)3s3p(^3P°)\ ^4S_{3/2}$ transition observed by Pedrotti et al. [12] was 405.26(10) Å, which corresponds to the upper level value of 263730(60) cm^{-1}. Thus, the reference to Pedrotti et al. [12] in Ref. [1] was inappropriate. The value 263773(15) 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 $2p^63p$ $^2P°_{1/2,3/2}$ levels. Six of these transitions correspond to doubly classified lines in which the lower $2p^63p$ $^2P°_{1/2,3/2}$ levels were unresolved. The list of observed intercombination transitions is given in Table 4.

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)	293531(7)	11*a*	$2p^63s$	$^2S_{1/2}$	–	$2p^53s(^3P°)3d$	$^4F°_{3/2}$	[2]
341.157(16)	293120(14)	9*a*	$2p^63s$	$^2S_{1/2}$	–	$2p^53s(^3P°)3d$	$^4D°_{1/2}$	[2][b]
341.290(16)	293006(14)	9*a*	$2p^63s$	$^2S_{1/2}$	–	$2p^53s(^3P°)3d$	$^4D°_{3/2}$	[7], [2][b]
347.983(8)	287370(7)	13*a*	$2p^63s$	$^2S_{1/2}$	–	$2p^53s(^3P°)4s$	$^4P°_{1/2}$	[2]
348.624(8)	286842(7)	13*a*	$2p^63s$	$^2S_{1/2}$	–	$2p^53s(^3P°)4s$	$^4P°_{3/2}$	[2]
396.88(2)	251965(13)	*a*	$2p^63p$	$^2P°_{1/2}$	–	$2p^5(^2P°)3s3p(^3P°)$	$^4P_{3/2}$	[11]
			$2p^63p$	$^2P°_{3/2}$	–	$2p^5(^2P°)3s3p(^3P°)$	$^4P_{3/2}$	[11]
397.52(2)	251560(13)	282	$2p^63p$	$^2P°_{3/2}$	–	$2p^5(^2P°)3s3p(^3P°)$	$^4P_{5/2}$	[11], [12]
398.98(10)	250640(60)	338	$2p^63p$	$^2P°_{3/2}$	–	$2p^5(^2P°)3s3p(^3P°)$	$^4D_{1/2}$	[12]
			$2p^63p$	$^2P°_{1/2}$	–	$2p^5(^2P°)3s3p(^3P°)$	$^4D_{1/2}$	[12]
399.42(10)	250360(60)	152	$2p^63p$	$^2P°_{1/2}$	–	$2p^5(^2P°)3s3p(^3P°)$	$^4D_{3/2}$	[12]
400.14(10)	249910(60)	64	$2p^63p$	$^2P°_{3/2}$	–	$2p^5(^2P°)3s3p(^3P°)$	$^4D_{5/2}$	[12]
405.26(10)	246760(60)	190	$2p^63p$	$^2P°_{3/2}$	–	$2p^5(^2P°)3s3p(^3P°)$	$^4S_{3/2}$	[12]
			$2p^63p$	$^2P°_{1/2}$	–	$2p^5(^2P°)3s3p(^3P°)$	$^4S_{3/2}$	[12]

[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].

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 [13]. In the transitions input file for the level optimization procedure, we assigned each observed spectral line its measurement uncertainty according to the published data [2,4,5,11,12]. 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 (±0.008 Å). 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, $2p^5(^2P°)3s3p(^3P°)$ $^4S_{3/2}$, was determined to be 263745.3±3.9 cm^{-1}. The specified total uncertainty accounts for the systematic uncertainty of the measurements of Baig et al. [2], ±1.7 cm^{-1}, which follows from their specification of the wavelength calibration uncertainty, ±0.002 Å. The uncertainties of the optimized energies of the quartet levels relative to $2p^5(^2P°)3s3p(^3P°)$ $^4S_{3/2}$ vary between ±0.6 cm^{-1} (for $2p^53s(^3P°)4s$ $^4P°_{5/2}$) and ±3 cm^{-1} (for $2p^53s(^3P°)3d$ $^4F°_{3/2}$). 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 Refs. [4,5], which had uncertainties between ±2 cm^{-1} and ±5 cm^{-1}.

The complete list of experimentally determined energy levels of the $2p^53l3l'$ and $2p^53s4s$ configurations is given in Table 5. The identification of the levels is discussed in the following section.

Table 5. Optimized energy levels of the $2p^53l3l'$ and $2p^53s4s$ configurations of Na I.

Configuration	Term	J	Level, cm^{-1}	Unc. [a]	N_{lines} [b]	Leading percentages [c]			
$2p^53s^2$	$^2P°$	3/2	248170	3.9	1	93	6	$2p^5(^2P°)3p^2(^1S)$	$^2P°$
$2p^53s^2$	$^2P°$	1/2	249489	3.9	1	93	6	$2p^5(^2P°)3p^2(^1S)$	$^2P°$
$2p^5(^2P°)3s3p(^3P°)$	^4S	3/2	263745.3	3.9	8	97			
$2p^5(^2P°)3s3p(^3P°)$	^4D	7/2	266586.7	3.9(0.9)	3	98			
$2p^5(^2P°)3s3p(^3P°)$	^4D	5/2	266933.9	3.8(0.7)	8	93			
$2p^5(^2P°)3s3p(^3P°)$	^4D	3/2	267282.3	3.8(0.7)	9	90	5	$2p^5(^2P°)3s3p(^3P°)$	^2D
$2p^5(^2P°)3s3p(^3P°)$	^4D	1/2	267576.0	3.8(0.9)	6	94			
$2p^5(^2P°)3s3p(^3P°)$	^4P	5/2	268513.9	3.8(0.7)	6	82	17	$2p^5(^2P°)3s3p(^3P°)$	^2D
$2p^5(^2P°)3s3p(^3P°)$	^4P	3/2	268897.4	3.8(0.7)	8	49	45	$2p^5(^2P°)3s3p(^3P°)$	^2D
$2p^5(^2P°)3s3p(^3P°)$	^4P	1/2	269086.5	3.9(1.3)	3	94			
$2p^5(^2P°)3s3p(^3P°)$	^2D	3/2	269726	13	1	48	43	$2p^5(^2P°)3s3p(^3P°)$	^4P
$2p^5(^2P°)3s3p(^3P°)$	^2D	5/2	270196	13	1	78	15	$2p^5(^2P°)3s3p(^3P°)$	^4P
$2p^5(^2P°)3s3p(^3P°)$	^2P	1/2	270582	13	1	94			
$2p^5(^2P°)3s3p(^3P°)$	^2P	3/2	270877	13	1	92			
$2p^5(^2P°)3s3p(^3P°)$	^2S	1/2	273236	13	1	82	12	$2p^5(^2P°)3s3p(^1P°)$	^2S
$2p^5(^2P°)3s3p(^1P°)$	^2D	5/2	280596	14	1	86	5	$2p^53s(^3P°)4p$	^2D
$2p^5(^2P°)3s3p(^1P°)$	^2S	1/2	280778	14	1	62	10	$2p^53s(^3P°)4p$	^2S
$2p^5(^2P°)3s3p(^1P°)$	^2P	3/2	281019	14	1	38	47	$2p^5(^2P°)3s3p(^1P°)$	^2D
$2p^5(^2P°)3s3p(^1P°)$	^2D	3/2	282076	14	1	39	45	$2p^5(^2P°)3s3p(^1P°)$	^2P
$2p^5(^2P°)3s3p(^1P°)$	^2P	1/2	282332	14	1	73	9	$2p^5(^2P°)3s3p(^1P°)$	^2S
$2p^53s(^3P°)4s$	$^4P°$	5/2	286300.4	3.8(0.6)	6	99			
$2p^53s(^3P°)4s$	$^4P°$	3/2	286849.5	3.8(0.7)	7	87	or 55	$2p^53s(^3P°_1)4s$	$^2[1]°$
$2p^53s(^3P°)4s$	$^4P°$	1/2	287374.8	3.8(0.9)	5	87	or 56	$2p^53s(^3P°_1)4s$	$^2[1]°$
$2p^53s(^3P°)4s$	$^2P°$	3/2	288452	7	1	86	or 52	$2p^53s(^3P°_2)4s$	$^2[2]°$
$2p^53s(^3P°)4s$	$^2P°$	1/2	288642	17	1	62	or 53	$2p^53s(^3P°_0)4s$	$^2[0]°$
$2p^53s(^3P°)3d$	$^2P°$	1/2	290234	7	1	67	or 35	$2p^53s(^3P°_2)3d$	$^2[1]°$
$2p^53s(^3P°)3d$	$^2P°$	3/2	290489	7	1	44	or 40	$2p^53s(^3P°_2)3d$	$^2[2]°$
$2p^53s(^1P°)4s$	$^2P°$	3/2	290786	7	1	89	or 89	$2p^53s(^1P°_1)4s$	$^2[1]°$
$2p^53s(^1P°)4s$	$^2P°$	1/2	291380	7	1	68	or 68	$2p^53s(^1P°_1)4s$	$^2[1]°$
$2p^53s(^3P°)3d$	$^2D°$	3/2	292090	17	1	51	or 29	$2p^53s(^3P°_1)3d$	$^2[1]°$
$2p^53s(^3P°)3d$	$^4P°$	1/2	292219.6	3.9(0.8)	4	94	or 62	$2p^53s(^3P°_2)3d$	$^2[0]°$
$2p^53s(^3P°)3d$	$^4P°$	3/2	292289.2	3.9(0.8)	5	77	or 73	$2p^53s(^3P°_2)3d$	$^2[1]°$

Configuration	Term	J	Level, cm^{-1}	Unc. [a]	N_{lines} [b]	Leading percentages [c]				
$2p^53s(^3P°)3d$	$^4F°$	9/2	292340.6	4.1(1.6)	1	99	or 99	$2p^53s(^3P°_2)3d$	$^2[4]°$
$2p^53s(^3P°)3d$	$^4D°$	5/2	292399.4	3.9(0.8)	6	48	or 81	$2p^53s(^3P°_2)3d$	$^2[2]°$
$2p^53s(^3P°)3d$	$^4F°$	7/2	292449.7	3.9(1.0)	3	53	or 84	$2p^53s(^3P°_2)3d$	$^2[3]°$
$2p^53s(^3P°)3d$	$^4F°$	5/2	292913.9	3.9(1.0)	3	56	or 57	$2p^53s(^3P°_1)3d$	$^2[2]°$
$2p^53s(^3P°)3d$	$^4D°$	3/2	293010.3	3.9(0.9)	6	43	or 37	$2p^53s(^3P°_1)3d$	$^2[2]°$
$2p^53s(^3P°)3d$	$^4D°$	1/2	293133.1	4(1.4)	3	87	or 71	$2p^53s(^3P°_1)3d$	$^2[1]°$
$2p^53s(^3P°)3d$	$^4F°$	3/2	293528	4.3(3.2)	2	58	or 61	$2p^53s(^3P°_0)3d$	$^2[2]°$
$2p^53s(^1P°)3d$	$^2P°$	3/2	295294	7	1	54	or 54	$2p^53s(^1P°_1)3d$	$^2[1]°$
$2p^53s(^1P°)3d$	$^2P°$	1/2	295526	7	1	70	or 70	$2p^53s(^1P°_1)3d$	$^2[1]°$
$2p^53s(^1P°)3d$	$^2D°$	5/2	295740	90	1	67	or 67	$2p^53s(^1P°_1)3d$	$^2[2]°$
$2p^53s(^1P°)3d$	$^2D°$	3/2	295749	14	2	54	or 54	$2p^53s(^1P°_1)3d$	$^2[2]°$
$2p^5(^2P°)3p^2(^1S)$	$^2P°$	3/2	310981	2	1	79	6	$2p^5(^2P°)3d^2(^1S)$	$^2P°$
$2p^5(^2P°)3p^2(^1S)$	$^2P°$	1/2	312356	5	1	56	19	$2p^5(^2P°)3d^2(^1S)$	$^2P°$

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

5. Discussion of level assignments

The $2p^53s4s$ and $2p^53s3d$ configurations give rise to the group of prominent absorption lines between 342 and 347 Å and some weak lines in a wider range of 338–349 Å. 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 $2p^53s(^3P°_1)4s\ ^2[1]°_{3/2}$ level to the weak line at 347.853 Å (intensity 7 on the scale of Table 1). This level, which in LS coupling has a dominant contribution of $2p^53s(^3P°)4s\ ^4P°_{3/2}$, 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 $2p^53s(^3P°_0)4s\ ^2[0]°_{1/2}$ was associated by Baig et al. [2] with a prominent line at 346.678 Å. We re-assigned 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 $2p^53s(^3P°_2)4s\ ^2[2]°_{3/2}$ level. This identification is supported by the large calculated oscillator strength. The latter level in LS coupling has a dominant contribution of $2p^53s(^3P°)4s\ ^2P°_{3/2}$. It was previously assigned by Baig et al. [2] to the above-mentioned weak line at 348.624 Å, now identified with the $2p^53s(^3P°)4s\ ^4P°_{3/2}$ 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 $2p^64s$ – $2p^53s(^1P°)9d,10s$ 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 $2p^53s(^3P°)3d$ $^4P°_{3/2}$ level at 292289.2 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], identification of the upper members of the $2p^53s(^1P°)ns,nd$ $^2P°$ series above the $2p^53s$ $^3P°_0$ limit is fairly easy because there is very little mixing of configurations. Below the $2p^53s$ $^3P°$ 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 $2p^53s(^3P°_0)ns$ $^2[0]°$ 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 much more intense line from the $2p^53s(^1P°)6d$ $^2[1]°$ term at 325.840 Å. This series, converging on the $2p^53s$ $^3P°_0$ limit at 307731.07 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 1e of Baig et al. [2]. However, consideration of the quantum defects shows that their n = 17 assignment is incorrect. The wavenumber 307314 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 $2p^53s(^3P°_0)18s$ $^2[0]°_{1/2}$ 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 300000 and 305700 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 $2p^5 3s4s$ configuration is best described in the *LS* coupling scheme in which its purity is 83%. For the $2p^5 3s3d$ 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 $2p^5 3s3p$ 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 $2p^5 3s3p$ 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 $2p^5(^2P°)3s3p(^1P°)$ $^2D_{3/2}$ 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 281032 cm^{-1}, and a higher percentage of $^2P_{3/2}$ for the higher level at 282063 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 comparisons of results of different authors, we retained the designations of Sugar et al. [11].

Conclusion

As a result of the present work, all energy levels of the $2p^5 3s^2$, $2p^5 3s3p$, and $2p^5 3s4s$ configurations, most of the $2p^5 3s3d$ levels, and two of the $2p^5 3p^2$ levels of Na I are firmly established. Many of the levels belonging $2p^5 3s4p$, $2p^5 3sns$ (n = 5–20), and $2p^5 3snd$ (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. 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 $2p^5 3s^2$, $2p^5 3s3p$, $2p^5 3s4s$, and $2p^5 3s3d$ configurations are determined by parametric fitting.

Acknowledgments

The author is grateful to J. Sansonetti, Yu. Ralchenko, J. Reader, and C. Froese Fischer for helpful discussions.

APPENDIX A. Parametric fitting of the $2p^5 3nl'$ configurations of Na I

The general procedure of the parametric fitting was described in section 3. The RCN calculations were made with inclusion of the Breit energies in the calculations (see Cowan [8]). The average configuration energies were computed in the following way.

First, a series of RCN/RCN2/RCG/RCE calculations was used to produce a set of theoretical energy levels with scaling of all electrostatic parameters $F^k(i, j)$ by a factor of 0.75 and no scaling for the spin-orbit parameters ζ. Such calculation always produces a negative energy for the lowest (ground) energy level (in this case, $2p^63s\ ^2S_{1/2}$), because the average energy of the ground configuration is assumed by RCN/RCN2 to be zero, and configuration interactions repel the ground-state level toward negative energies. Then all average configuration energies in the input file for RCG were shifted upwards and the RCG/RCE calculations were repeated to produce a set of theoretical levels with the ground state energy equal to zero. Thus adjusted values of the average energies were adopted as the Hartree-Fock values. Then, in the vector input file RCEINP [9], the theoretical energy levels were replaced with known experimental values, some parameters were defined as variable, and the least squares fitting was made with the RCE program. The resulting scaling factors for the average configuration energies are defined as the ratios of the fitted average energies to the Hartree-Fock values defined as described above.

Holmgren et al. [4] found that fitted configuration average energies of the $2p^53lnl'$ configurations were shifted relative to the Hartree-Fock values by about 6000 cm^{-1}. This shift was found to be almost constant along series of increasing n. Instead of introducing a constant shift of average energies of unknown configurations, we linked these average energies to the average energy of the highest firmly known configuration at a fixed ratio. With such scaling, all experimentally identified levels of odd-parity configurations with principal quantum number $n \leq 20$ were fitted with reasonably small deviations of the order of 100 cm^{-1}. The fitted average configuration energies, as well as their Hartree-Fock values and scaling factors, are listed in Table 6.

Table 6. Fitted and Hartree-Fock average configuration average energies of the $2p^53lnl'$ configurations of Na I.

Configuration	Fitted value, cm^{-1}	Rms unc., cm^{-1}	Linked group No.	HF, cm^{-1}	Fit/HF	Fit – HF, cm^{-1}
Even parity						
$2p^53s3p$	273535.3	38		265134	1.032	8401
$2p^53s4p$	294625.4	91	1	288484	1.021	6142
$2p^53s4f$	301132.1	93	1	294878	1.021	6254
$2p^53s5p$	300882.4	93	1	294632	1.021	6250
$2p^53s5f$	303704.2	93	1	297405	1.021	6299
$2p^53s6p$	303611.9	93	1	297315	1.021	6297
$2p^53s6f$	305105.2	94	1	298782	1.021	6323
$2p^53s7p$	305060.7	94	1	298738	1.021	6322
$2p^53s7f$	305948.1	94	1	299611	1.021	6338
$2p^53s8p$	305922.9	94	1	299586	1.021	6337
$2p^53s8f$	306493.9	94	1	300147	1.021	6347
$2p^53s9p$	306478.2	94	1	300131	1.021	6347
$2p^53s9f$	306867.3	94	1	300514	1.021	6354
$2p^53p3d$	324555.0	fixed		318507	1.019	6048
$2p^53p4s$	320218.3	fixed		314170	1.019	6048
$2p^53p4d$	332590.7	fixed		326542	1.019	6048
$2p^53d4p$	357620.7	fixed		351572	1.017	6048

Configuration	Fitted value, cm^{-1}	Rms unc., cm^{-1}	Linked group No.	HF, cm^{-1}	Fit/HF	Fit – HF, cm^{-1}
$2p^53d4f$	366095.8	fixed		360048	1.017	6048
Odd parity						
$2p^53s^2$	253607.9	62		246009	1.031	7599
$2p^53s4s$	288732.2	31		282289	1.023	6444
$2p^53s3d$	294251.1	23		287598	1.023	6654
$2p^53s5s$	298052.0	13	1	292435	1.019	5617
$2p^53s4d$	300057.4	45		294321	1.019	5737
$2p^53s6s$	301944.9	13	1	296268	1.019	5677
$2p^53p^2$	304161.6	62		296565	1.026	7597
$2p^53s5d$	302843.0	13	1	297152	1.019	5691
$2p^53s7s$	303864.4	13	1	298158	1.019	5707
$2p^53s6d$	304357.9	13	1	298644	1.019	5714
$2p^53s8s$	304953.5	13	1	299231	1.019	5723
$2p^53s7d$	305254.1	13	1	299526	1.019	5728
$2p^53s9s$	305631.9	13	1	299899	1.019	5733
$2p^53s8d$	305828.4	13	1	300092	1.019	5737
$2p^53s9d$	306218.3	13	1	300476	1.019	5742
$2p^53p4p$	326203.9	fixed		320156	1.019	6048
$2p^53p4f$	333379.2	fixed		327331	1.018	6048
$2p^53d4s$	350494.3	fixed		344446	1.018	6048
$2p^53d^2$	357478.8	fixed		348431	1.026	9048
$2p^53d4d$	364912.4	fixed		358864	1.017	6048

In the even parity, the radial parameters ζ_{2p}, $F^2(2p, np)$, $G^1(2p, 3s)$, $G^{0,2}(2p, 3p)$, and $G^1(3s, np)$ of all configurations were linked together in five groups. The ratios of parameters within each group were fixed at the Hartree-Fock values. Similarly, in the odd parity, the parameters ζ_{2p}, and the $G^1(2p, ns)$ of all configurations were linked in two groups with ratios fixed at the Hartree-Fock value. Each of such linked groups of parameters introduced one free parameter in the fitting. The rest of the single-configuration radial parameters were fixed at 75% of the Hartree-Fock values. No effective parameters, such as α or illegal-rank parameters were introduced. The fitted and Hartree-Fock values of all single-configuration radial parameters of the $2p^53s3p$, $2p^53s4p$, $2p^53s^2$, $2p^53p^2$, $2p^53s3d$, and $2p^53s4s$ configurations are listed in Table 7. Since the Hartree-Fock values of the parameters of all other configurations can be easily calculated, the scaling factors given in tables 6 and 7 provide sufficient data to calculate all parameters for higher-*n* configurations.

Table 7. Fitted and Hartree-Fock values of single-configuration radial parameters of the $2p^53lnl'$ configurations of Na I.

Configuration	Parameter	Fitted value, cm^{-1}	Rms unc., cm^{-1}	Linked group No.	HF, cm^{-1}	Fit/HF
Even parity						
$2p^53s3p$	ζ_{2p}	908.7	79	2	898.1	1.01
	ζ_{3p}	23.2	fixed		23.2	1.00
	$F^2(2p,3p)$	7669.2	269	3	6286.7	1.22

Configuration	Parameter	Fitted value, cm^{-1}	Rms unc., cm^{-1}	Linked group No.	HF, cm^{-1}	Fit/HF
	$G^1(2p,3s)$	3506.6	178	5	4075.2	0.86
	$G^0(2p,3p)$	1820.3	66	6	2258.5	0.81
	$G^2(2p,3p)$	1646.6	60	6	2043.1	0.81
	$G^1(3s,3p)$	26213	145	4	32005.6	0.82
$2p^5 3s4p$	ζ_{2p}	909.2	79	2	898.6	1.01
	ζ_{4p}	4.7	fixed		4.7	1.00
	$F^2(2p,4p)$	1444.4	51	3	1184	1.22
	$G^1(2p,3s)$	4204.4	214	5	4886	0.86
	$G^0(2p,4p)$	334.4	fixed		445.9	0.75
	$G^2(2p,4p)$	306	fixed		408	0.75
	$G^1(3s,4p)$	2879.5	16	4	3515.7	0.82
Odd parity $2p^5 3s^2$	ζ_{2p}	954.4	22	2	896.2	1.06
$2p^5 3p^2$	$F^2(3p,3p)$	18079.7	fixed		24106.3	0.75
	ζ_{2p}	959.4	22	2	900.7	1.07
	ζ_{3p}	25.6	fixed		25.6	1.00
	$F^2(2p,3p)$	5050.5	fixed		6734	0.75
	$G^0(2p,3p)$	1818.7	fixed		2424.9	0.75
	$G^2(2p,3p)$	1657.7	fixed		2210.3	0.75
$2p^5 3s3d$	ζ_{2p}	957.5	22	2	899	1.07
	$F^2(2p,3d)$	638.7	fixed		851.6	0.75
	$G^1(2p,3s)$	4619.6	38	3	4792.8	0.96
	$G^1(2p,3d)$	90.5	fixed		120.7	0.75
	G3(2p,3d)	50	fixed		66.7	0.75
	$G^2(3s,3d)$	3424.4	fixed		4565.9	0.75
$2p^5 3s4s$	ζ_{2p}	956.6	22	2	898.2	1.07
	$G^1(2p,3s)$	4814.8	40	3	4995.5	0.96
	$G^1(2p,4s)$	513.2	4	3	532.5	0.96
	$G^0(3s,4s)$	1334.5	fixed		1779.3	0.75

For each parity separately, the configuration-interaction (CI) parameters were scaled by a common factor chosen by trial and error so that the standard deviation of the fitting of known levels was minimized. For even parity, the optimal ratio of the CI parameters to their Hartree-Fock values was found to be 0.92, while for odd parity it was 0.87.

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