# Analysis of Line Strength Data for the Spectra of C(I), N(II), N(I) and O(II)

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Recently determined experimental and theoretical data on line strengths within 3s-3p and 3p-3d multiplets for C(I), N(II), N(I) and O(II) are analyzed. An overall satisfactory agreement between experimental data and results of recent sophisticated calculations is found with exception of only some weaker transitions. However, the measured and calculated relative line strengths disagree significantly with data resulting from the LS coupling scheme, particularly for 3p-3d transitions. In numerous cases these differences are — to a considerable degree — "regular" along the isoelectronic sequences C(I)–N(II) and N(I)–O(II). For some multiplets these discrepancies also correlate with departures from the Landé interval rule for terms involved in the corresponding transitions.

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#### 1. Introduction

Experience shows that in atoms and ions of light elements such as carbon, nitrogen and oxygen the spinorbit interaction is small compared with the dominating Coulomb interaction. In this approximation (Russell– Saunders coupling scheme) the energy levels belonging to a given term are expected to obey the Landé interval rule [1]. On the other hand, within this coupling scheme the relative line strengths of fine structure components for a given multiplet can be easily calculated from the Wigner's 6-j symbols [2].

However, line strength studies based on arc emission measurements and theoretical calculations performed in the last 15 years for the above mentioned emitters show a rather differentiated picture. For quite a large number of multiplets significant deviations from the LS coupling scheme have been found, especially for 3p-3d transitions.

Recent advanced calculations of line strengths [3–15] provide data for fine structure components which are for some multiplets in good agreement with measured ones, but for other transitions significant departures from LS coupling results as well as from measurements are encountered [16–27]. Departures of line strengths from values predicted by the LS coupling scheme are often caused by strong mixing of energy levels belonging to terms with different multiplicity. Such level mixing manifests itself by the appearance of LS-forbidden intersystem transitions (see for example Refs. [16–18, 23]).

In this paper we report an analysis of recently deter-

mined line strength data for the first two members of the carbon (C(I), N(II)) and nitrogen (N(I), O(II)) isoelectronic sequence, devoted to the search of possible correlations between departures from the Landé interval rule and departures of line strengths of fine structure components from the LS coupling scheme.

## 2. Observed departures of term splitting from the Landé interval rule

Table I contains the list of C(I), N(II) and N(I), O(II)multiplets being studied. For each multiplet the departures from the Landé interval rule (in percent) for the lower and upper terms for the respective emitters are listed. The departures are defined as:

$$D = \frac{\left|R^{\text{obs.}} - R^{\text{Land}}\right|}{R^{\text{Land}}} \times 100\%,\tag{1}$$

where  $R^{\text{obs.}}$  and  $R^{\text{Land}}$  are the observed ratios and those resulting from the LS coupling scheme, respectively. The corresponding observed energy values have been taken from [28].

Large departures are encountered: for the term  $3d \ ^4D$ , in the case of both members of the isoelectronic sequence (N(I) and O(II)); for the term  $3d \ ^3D^{\circ}$ , in the case of C(I); and for the term  $3s \ ^3P^{\circ}$  of ionized nitrogen. In the last case, the observed interval ratio for N(II) exceeds those resulting from the Landé interval rule by factor of 2.16, while for the corresponding term in C(I) the splitting agrees very well with the LS coupling scheme (the corresponding ratio is 1.06). As can be seen from Table I, the departures from Landé interval rule show no clear regular behavior along the members of the isoelectronic sequence, with exception of the following terms: (i) in

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TABLE I

Observed departures from the Landé interval rule (defined by Eq. (1)) for the lower (L) and upper (U) terms of selected transitions in C(I), N(II), N(I), O(II) are quoted. In the case of quartet terms D, F the first values correspond to the interval between level pairs with larger J values.

Term		C(I)	N(II)			
	L	U	L	U		
$3s \ ^{3}P^{o}-3p \ ^{3}S$	5.5		116			
$3s\ ^3P^{\mathrm{o}}{-}3p\ ^3P$	5.5	17.4	116	17.3		
$3s\ ^3P^{\mathrm{o}}{-}3p\ ^3D$	5.5	5.0	116	5.5		
$3p$ $^3\!S extrm{}3d$ $^3\!P^{\mathrm{o}}$		9.5	—	7.7		
$3p$ $^{3}P$ – $3d$ $^{3}P^{\rm o}$	17.4	9.5	17.3	7.7		
$3p~^3\!P{-}3d~^3\!D^{\rm o}$	17.4	49.9	17.3	15.7		
$3p~^3\!D3d~^3\!D^{\rm o}$	5.0	49.9	5.5	15.7		
$3p~^3\!D3d~^3\!F^{\rm o}$	5.0	57.1	5.5	2.9		
	Ν	N(I)		O(II)		
	L	U	L	U		
$3s$ $^4P$ – $3p$ $^4S^{\rm o}$	16.8		9.7	—		
$3s~^4\!P3p~^4\!P^{\rm o}$	16.8	25.5	9.7	19.5		
$3s~^4\!P{-}3p~^4\!D^{\rm o}$	16.8	2.7; 0.8	9.7	2.8; 1.0		
$3p~^4\!P^{ m o} \!-\! 3d~^4\!P$	25.5	21.1	19.5	34.0		
$3p\ ^4\!P^{\rm o}{-}3d\ ^4\!D$	25.5	47.4; 38.1	19.5	183; 97.2		
$3p\ ^4D^{\rm o}{\rm -}3d\ ^4D$	2.7; 0.8	47.4; 38.1	2.8; 1.0	183;97.2		
$3p$ $^4D^{\rm o}-3d$ $^4F$	2.7; 0.8	12.0; 27.9	2.8; 1.0	2.1; 3.1		

N(I) and O(II) —  $3d \ ^4D$  (large and increasing departures),  $3p \ ^4P^{\rm o}$  (medium and slightly decreasing departures),  $3d \ ^4P$  (medium and increasing departures), and (ii) in C(I) and N(II) —  $3p \ ^3P$  (similar departure around 17%). In the case of terms  $3p \ ^4D^{\rm o}$  in N(I) and O(II), and the term  $3d \ ^4F$  in O(II), the observed intervals are in very good agreement with the LS coupling scheme the discrepancies do not exceed 3.1%.

#### 3. Selection of experimental line strength data

As mentioned in Sect. 1, accurate relative line strengths (within given multiplets) have been recently obtained by applying arc plasmas as excitation sources. The relative strengths of fine structure components  $(S_{ki})$ are directly derived from intensity measurements  $(I_{ki})$  of fine structure components belonging to the selected multiplet, according to the relation

$$S_{ki} = I_{ki} \left(\frac{\lambda_{ki}}{\lambda_0}\right)^4 \exp\left(-\frac{E_k - E_0}{kT}\right),\tag{2}$$

where  $I_{ki}$  is the total line intensity of the selected fine structure component,  $\lambda_{ki}$  and  $\lambda_0$  are the wavelengths of the fine structure component and the multiplet as a whole, respectively,  $E_k$  and  $E_0$  are respectively: the excitation energy of the upper level "k" of the selected transition and the "center of gravity" of all energy levels belonging to the considered upper term, kT is the plasma temperature expressed in energy units.

Due to the small fine structure splitting of the terms, the individual spectral lines (fine structure components) are usually very close in wavelength and thus possible errors arising from intensity calibration procedures are small.

The exponential factor in Eq. (2) is usually very small compared to typical temperatures of arc plasmas ( $kT \approx$ 1.0 to 1.5 eV). Thus the accurate knowledge of the temperature is not very crucial. In the case of upper terms originating from configuration 3p these exponential corrections do not exceed 0.3%, while for terms arising from the configuration 3d they are negligible. However, in the papers taken for our analysis all these corrections have been taken into account.

In order to obtain reliable line strength data two essential conditions are required to be fulfilled: (i) the population of energy levels within the upper term should be statistical, i.e. according to the Boltzmann law, and (ii) the self-absorption of radiation within the studied spectral lines should be negligible. For search of possible correlations between departures from the Landé interval rule and the departures of line strengths from the LS coupling scheme, the following experimental line strength data have been taken: for the C(I) spectrum from Refs. [20, 21], for N(II) from Ref. [17], for N(I) from Refs. [22, 27], and for O(II) from Ref. [19]. In all above mentioned experiments the requirements concerning statistical population of excited levels and optical thin conditions of the plasma have been carefully checked.

### 4. Relative line strengths within multiplets of C(I) and N(II)

In Table II the relative line strengths within multiplets (normalized to the sum of 100) for three 3s-3p and five 3p-3d transitions are listed. The LS data are compared: for C(I) with experimental data taken from Ref. [20] (transitions 3s-3p) and Ref. [21] (transitions 3p-3d) and with calculations of Hibbert et al. [4], while for N(II) with measured data taken from Ref. [17] and the calculations of Froese Fischer and Tachiev [12]. The C(IV)3intermediate coupling calculations of Hibbert et al. [4] are the most recent comprehensive data set available for the C(I) spectrum and the results are in good agreement with recent measured data. For the N(II) spectrum two recent sets of data are available: the data of Bell et al. [6] and the above mentioned set of Froese Fischer and Tachiev [12]. Since both calculations yield data which are in very good mutual agreement, we decided to quote only the results of the more recent paper. In columns 7 and 10 of Table II, the relative discrepancies between experimental results and the LS data, defined as D = 100% ·  $(S^{\text{expt}} - S^{\text{LS}})/S^{\text{LS}}$ , are listed.

# TABLE II

Comparison of experimental and theoretical relative line strengths for selected multiplets of C(I) and N(II). Individual sets of line strength data are normalized to the sum of 100. In columns 7 and 10 the relative discrepancies defined as  $D = 100\% \cdot (S^{\text{expt}} - S^{\text{LS}})/S^{\text{LS}}$ , between experimental results and the LS data are listed. Experimental data on neutral carbon are taken: for 3s-3p transitions from Ref. [20], while for 3p-3d transitions from Ref. [21].

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	D [%]
${}^{3}P^{o} - {}^{3}S$ 2 1 55.6 51.7 52.4 -5.8 54.0 52.2	-6.1
1 1 33.3 35.7 34.8 4.5 33.0 34.3	3.0
0 1 11.1 12.7 12.8 15.3 13.0 13.4	20.7
${}^{3}P^{\circ}{}^{-3}P$ 2 2 41.7 42.2 40.6 -2.6 43.4 42.7	2.4
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	-7.9
2 1 13.9 14.9 15.1 8.6 15.4 14.8	6.5
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	-3.6
1 2 13.9 13.4 14.0 0.7 12.7 13.0	-6.5
$ \begin{vmatrix} 0 & 1 & 11.1 & 10.5 & 10.9 & -1.8 & 10.8 & 11.2 \end{vmatrix} $	0.9
${}^{3}P^{\circ}-{}^{3}D$ 2 3 46.7 46.7 46.3 -0.9 48.3 48.5	3.9
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	-6.4
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	3.6
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	-0.1
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	-7.8
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	13.3
${}^{3}S{-}{}^{3}P^{\circ}$   1   2   55.6   57.0   59.0   6.1   57.0   56.3	1.3
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	-0.9
	-3.6
$^{3}P^{-3}P^{0}$ 2 2 41.7 43.1 43.5 4.3 44.4 44.8	7.4
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	33.3
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	-2.9
	7.2
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	-33.2
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	-15.8
P - D 2 3 40.7 40.0 45.5 -2.0 40.0 47.2	1.1
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2.4
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	9.0 12.8
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	-12.0 -13.4
2 1 0556 046 < 05 - 048 055	-10.4
$^{3}D^{-3}D^{\circ}$ 3 3 41 5 49.6 50.0 20.5 44.9 45.7	10.1
2 2 2 231 255 254 100 251 242	4.8
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	-12.0
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.6
2 1 5.00 4.6 4.7 -6.0 4.66 4.79	-4.2
$\begin{vmatrix} 2 & 3 & 5.19 \\ 2 & 3 & 5.19 \\ 0.15 \\ \end{vmatrix}$ $\begin{vmatrix} 0.15 \\ 0.6 \\ - \\ 0.6 \\ \end{vmatrix}$ $\begin{vmatrix} 0.05 \\ - \\ 2.68 \\ 3.27 \\ \end{vmatrix}$	-37.0
1 2 5.00 0.33 < < 0.6 - 3.05 3.63	-27.4
$^{3}D^{-3}F^{\circ}$ 3 4 42.9 43.5 44.9 4.7 43.0 43.3	0.9
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	1.0
$ \begin{vmatrix} 1 & 2 & 20.0 \\ 21.0 & 20.4 \\ 20.0 & 20.1 \\ 20.0 & 20.0 \\ 20.0 & 20.$	0.0
$\begin{vmatrix} 3 & 3 & 3.70 \end{vmatrix}$ 1.8 $\begin{vmatrix} 1.9 & -48.6 & 3.10 & 3.09 \end{vmatrix}$	-16.5
$\begin{vmatrix} 2 & 2 & 3.70 \\ 2.8 & 2.7 & -27.0 \\ 3.34 & 3.48 \end{vmatrix}$	-5.9
$\begin{vmatrix} 3 & 2 & 0.106 & 0.00650 \end{vmatrix}$ <0.1 $-$ 0.078 <0.2	

In the case of 3s-3p transitions, the LS data are in good agreement with measurements as well as with calculations. Exceptions are the data for the multiplet  ${}^{3}P^{\circ}-{}^{3}S$ , where significant departures are encountered, especially for the N(II) spectrum. As mentioned in Sect. 1, this significant discrepancy is caused by strong level mixing between terms  $3s {}^{3}P^{\circ}$  and  $3s {}^{1}P^{\circ}$ . In the case of the N(II) energy level system, the energy gap between these terms is of the order of the fine structure splitting of the triplet term, and thus leading to the appearance of strong intersystem transitions (for details see [17, 18]). The large departure of measured line strengths from results obtained from 6-j symbols reflects the violation of the Landé interval rule for the term  $3s {}^{3}P^{\circ}$  in N(II).

In the case of 3p-3d transitions large discrepancies are usually found for weaker fine structure components. For both emitters a clear behavior is found in the case of two multiplets:  ${}^{3}P{-}{}^{3}P^{\circ}$ ,  ${}^{3}D{-}{}^{3}D^{\circ}$ , and to some extent in the multiplet  ${}^{3}D - {}^{3}F^{\circ}$ . For the multiplet  ${}^{3}P - {}^{3}P^{\circ}$ both measured line strengths, originating from transitions with  $\Delta J = 0$ , are larger than those predicted by the LS coupling scheme. On the other hand, the measured  $S_{ki}$  values with  $\Delta J = -1$  (in emission), are significantly weaker than the LS data. Also in the case of the multiplet  ${}^{3}D{-}{}^{3}D^{\circ}$  the experimental line strengths with  $\Delta J = 0$  are larger than the LS data, however only for the transitions 3–3, and 2–2. In the case of the transitions 1–1 the measured line strengths for both emitters (C(I) and N(II)) are smaller than the LS data. For both transitions with  $\Delta J = -1$  (in emission) again the LS coupling scheme provides significantly larger  $S_{ki}$  values than observed. The observations are in agreement with results of both (C(I) and N(II)) recent advanced calculations. Figure 1 presents the C(I) spectrum from the wavelength interval 1159–1168 nm measured in [21], showing the fine structure components of the multiplet 3p  $^{3}D-3d$   $^{3}D^{\circ}$ . The numbers above individual components are the measured total line intensities (integrated over the whole line profile) and the intensities computed from the data of Hibbert et al. [4]. and from the LS data, for the temperature T = 11000 K corresponding to the experiment [21]. The intensities are normalized to the value of 100 for the strongest line within the multiplet.

The measured spectrum unambiguously proves the results of Hibbert et al. [4] showing that the components  ${}^{3}D_{1}-{}^{3}D_{2}^{\circ}$  and  ${}^{3}D_{2}-{}^{3}D_{3}^{\circ}$  are significantly weaker than expected from the LS coupling scheme. In the case of the N(II) spectrum, these discrepancies are much smaller the observed line intensities differ from the LS data by only 37% and 27%, for the two above mentioned transitions, respectively. For these fine structure components, the discrepancies between measured and calculated data are somewhat larger than the uncertainty limits of the experiment. The smaller discrepancies observed in N(II) are in accordance with the smaller departure from the Landé interval rule for the term  $3d \, {}^{3}D^{\circ}$ .

In the case of the strong multiplet  ${}^{3}D{-}{}^{3}F^{\circ}$  the measured line strengths for all transitions agree well with



Fig. 1. The measured C(I) spectrum in the wavelength range 1159–1168 nm is shown. The fine structure components of the multiplet 3p  $^{3}D-3d$   $^{3}D^{\circ}$  are marked with the corresponding J values. The numbers above individual fine structure components are the line intensities (normalized to the value of 100 for the strongest component 3–3): measured in [21] and computed on the basis of LS data and the results of Hibbert et al. [4] for the temperature of experiment [21]. In this wavelength interval also one Ar(I) line and the lines belonging to the C(I) multiplet 3p  $^{3}S-3d$   $^{3}P^{\circ}$  appear.

recent calculations. For transitions with  $\Delta J = 0$  the experimental data are significantly weaker than the LS data. The departures from the Landé interval rule in the case of the lower term 3p  $^{3}D$  are nearly the same for both emitters (about 5%), but for the upper term 3d  $^{3}F^{\circ}$  the departure for N(II) is significantly smaller. The observed departures of line strengths from LS results are indeed smaller in the case of N(II).

Concluding this part of the analysis, the following "regularities" are observed: (i) for transitions with  $\Delta L = 0$ , the fine structure components with  $\Delta J = 0$  are usually stronger than those predicted by the LS coupling scheme, with the exception of the transition  $3p \ ^3D_1 - 3d \ ^3D_1^{\circ}$  and (ii) for transitions with  $\Delta L = -1$  (in emission) the observed fine structure components with  $\Delta J = 0$  are usually significantly weaker. The conclusion concerning the  $3p \ ^3D_1 - 3d \ ^3D_1^{\circ}$  component is confirmed by recent calculations only in the case of the C(I) spectrum. For N(II) the theoretical result is in good agreement with the result obtained from the LS coupling scheme. The recent experiment of Mar et al. [29], however, supports the experimental data of [17] for this particular transition.

## 5. Relative line strengths within multiplets of N(I) and O(II)

Data on measured and calculated line strengths for the spectra of N(I) and O(II) are presented in Tables III–V. In Tables III and V, similarly as in Table II, relative line strengths normalized (each multiplet) to the sum of 100 are shown. Because for some 3p-3d transitions reliable experimental data for complete sets of O(II) are

not available, in Table IV line strengths for some N(I) and O(II) multiplets (normalized to the strongest mea-

sured fine structure component within given multiplet) are compared.

#### TABLE III

Comparison of experimental and theoretical relative line strengths for selected multiplets of N(I) and O(II). Individual sets of line strength data are normalized to the sum of 100. In columns 8 and 12 the relative discrepancies defined as  $D = 100\% \cdot (S^{\text{expt}} - S^{\text{LS}})/S^{\text{LS}}$ , between experimental results and the LS data are listed.

Transition $J_i$ $J_k$ LS					N(I)			O(II)				
	- 0	- 10		Theory [3]	Theory [12]	Expt. [27]	$D \ [\%]$	Theory [5]	Theory [12]	Expt. [19]	D [%]	
3s - 3p												
${}^4P - {}^4S^{\mathrm{o}}$	5/2	3/2	50.0	52.9	53.0	53.4	6.8	52.0	52.2	52.4	4.8	
	3/2	3/2	33.3	32.1	32.0	31.9	-4.2	32.5	32.4	32.1	-3.6	
	1/2	3/2	16.7	15.1	15.0	14.7	-12.0	15.5	15.5	15.5	-7.1	
${}^4P - {}^4P^{\mathrm{o}}$	5/2	5/2	35.0	36.8	36.7	35.8	2.3	36.8	36.8	36.8	5.1	
	3/2	3/2	4.44	5.64	5.65	5.8	30.6	5.51	5.56	5.51	24.2	
	1/2	1/2	2.78	2.51	2.52	2.6	-6.5	2.52	2.50	2.56	-7.8	
	5/2	3/2	15.0	14.4	14.3	14.3	-4.7	14.6	14.5	14.3	-4.6	
	3/2	1/2	13.9	14.2	14.2	14.7	5.8	14.1	14.2	14.7	5.9	
	3/2	5/2	15.0	13.1	13.2	13.3	-11.3	13.2	13.2	13.3	-11.5	
	1/2	3/2	13.9	13.3	13.4	13.5	-2.9	13.3	13.3	12.8	-7.6	
${}^4P - {}^4D^{\mathrm{o}}$	5/2	7/2	40.0	39.8	39.8	39.8	-0.5	40.0	40.0	39.3	-1.7	
	3/2	5/2	21.0	22.2	22.2	21.9	4.3	22.0	22.1	22.2	5.7	
	1/2	3/2	8.33	9.05	9.08	9.3	11.6	8.94	8.96	9.25	11.0	
	5/2	5/2	9.00	7.87	7.82	8.0	-11.1	7.98	7.95	7.81	-13.2	
	3/2	3/2	10.7	10.3	10.2	10.1	-5.6	10.3	10.2	10.4	-3.0	
	1/2	1/2	8.33	8.55	8.56	8.5	2.0	8.49	8.49	8.51	2.2	
	5/2	3/2	1.00	0.79	0.78	0.8	-20.0	0.80	0.80	0.844	-15.6	
	3/2	1/2	1.67	1.51	1.50	1.6	-4.2	1.52	1.51	1.70	1.6	

## TABLE IV

Comparison of experimental and theoretical relative line strengths for selected multiplets of N(I) and O(II). Individual sets of line strength data are normalized to the strongest observed fine structure component  $(S_{ki} = 100)$  in each multiplet. In columns 8 and 12 the relative discrepancies defined as  $D = 100\% \cdot (S^{\text{expt}} - S^{\text{LS}})/S^{\text{LS}}$ , between experimental results and the LS data are listed.

Transition	$J_i$	$J_{h}$	LS	N(I)				O(II)			
		• <i>K</i>		Theory [3]	Theory [12]	Expt. [22]	$D \ [\%]$	Theory [5]	Theory [12]	Expt. [19]	D [%]
3p - 3d											
${}^{4}P^{o} - {}^{4}P$	5/2	5/2	233	29.7	55.5	52.5	-77.5	45.7	33.5	34.6	-85.2
	3/2	3/2	29.6	1.9	0.020		_	13.5	1.68	34.2	15.4
	1/2	1/2	18.5	30.8	24.5	27.8	49.8	27.5	36.5	—	
	5/2	3/2	100	17.7	35.0	35.5	-64.5	24.1	16.8	17.8	-82.2
	3/2	1/2	92.7	13.0	30.8	34.4	-62.8	19.6	9.6	7.44	-92.0
	3/2	5/2	100	100	100	100		100	100	100	
	1/2	3/2	92.7	71.8	82.7	84.3	-9.0	72.9	72.5	75.8	-18.2
${}^{4}P^{o} - {}^{4}D$	5/2	7/2	100	100	100	100		100	100	100	
	3/2	5/2	52.5	33.0	38.6	35.3	-32.8	25.1	18.7	17.6	-66.5
	1/2	3/2	20.8	8.53	12.7	11.8	-43.5	9.63	5.30	13.4	-35.5
	5/2	5/2	22.5	39.7	36.5	37.3	65.6	33.5	33.4	12.2	-45.9
	3/2	3/2	26.8	30.3	31.1	28.7	7.2	33.0	32.7	34.1	27.4
	1/2	1/2	20.8	14.4	18.6	18.1	-12.9	15.2	10.0	9.48	-54.5
	5/2	3/2	2.50	8.50	6.59	6.62	165	9.29	11.7		_
	3/2	1/2	4.18	9.85	7.41	7.35	76.1	10.7	14.4	14.4	245.4

# TABLE V

Comparison of experimental and theoretical relative line strengths for selected multiplets of N(I) and O(II). Individual sets of line strength data are normalized to the sum of 100. In columns 8 and 12 the relative discrepancies defined as  $D = 100\% \cdot (S^{\text{expt}} - S^{\text{LS}})/S^{\text{LS}}$ , between experimental results and the LS data are listed.

Transition	J	$J_{h}$	LS	N(I) O(II)							
	01	σĸ	10	Theory [3]	Theory [12]	Expt. [22]	D [%]	Theory [5]	Theory [12]	Expt. [19]	D [%]
3p-3d											
${}^{4}D^{o} - {}^{4}D$	7/2	7/2	34.3	42.3	40.9	39.7	15.7	42.6	46.5	47.1	37.3
	5/2	5/2	17.3	15.3	16.9	17.2	-0.6	13.1	12.1	13.6	-21.2
	3/2	3/2	8.00	4.90	6.50	7.0	-12.5	6.40	6.09	6.63	-17.1
	1/2	1/2	5.00	2.7	3.73	3.6	-28.0	3.94	3.27	4.06	-18.9
	7/2	5/2	5.71	10.3	8.87	8.7	52.4	6.85	6.30	7.27	27.3
	5/2	3/2	7.00	9.9	8.87	9.1	30.0	8.92	8.65	7.58	8.2
	3/2	1/2	5.00	5.8	5.30	5.8	16.0	5.69	5.19	4.79	-4.2
	5/2	7/2	5.71	3.1	2.74	2.9	-49.2	4.91	5.17	5.48	-4.1
	3/2	5/2	7.00	3.4	3.44	3.2	-54.3	3.80	3.25	0.375	-94.6
	1/2	3/2	5.00	2.3	2.72	2.7	-46.0	3.79	3.59	3.09	-38.2
${}^{4}D^{o} - {}^{4}F$	7/2	9/2	35.7	36.3	36.3	36.3	1.7	35.7	35.7	35.5	-0.7
	5/2	7/2	24.5	25.3	25.4	26.1	6.5	25.1	25.1	26.5	8.3
	3/2	5/2	16.0	16.7	16.8	15.9	-0.6	16.4	16.5	15.4	-3.8
	1/2	3/2	10.0	10.3	10.4	10.8	8.0	10.3	10.2	10.2	1.9
	7/2	7/2	4.08	3.0	2.90	3.0	-26.5	3.54	3.50	3.61	-11.5
	5/2	5/2	5.22	4.3	4.13	4.0	-23.4	4.77	4.75	4.61	-11.6
	3/2	3/2	4.00	3.7	3.68	3.5	-12.5	3.81	3.80	3.71	-7.1
	7/2	5/2	0.204	0.14	0.14	0.13	-36.3	0.16	0.16	0.175	-14.3
	5/2	3/2	0.286	0.22	0.21	0.21	-26.6	0.24	0.24	0.320	11.9
${}^{4}P^{o} - {}^{4}D$	5/2	7/2	40.0	40.9	39.8	40.8	2.0				
	3/2	5/2	21.0	13.5	15.3	14.4	-31.4				
	1/2	3/2	8.33	3.49	5.05	4.80	-42.4				
	5/2	5/2	9.00	16.2	14.5	15.2	68.9				
	3/2	3/2	10.7	12.4	12.4	11.7	9.4				
	1/2	1/2	8.33	5.90	7.41	7.40	-11.1				
	5/2	3/2	1.00	3.48	2.62	2.70	170				
	3/2	1/2	1.67	4.03	2.95	3.00	79.7				
${}^{4}P^{\mathrm{o}}-{}^{4}P$	5/2	5/2	35.0	11.2	16.9	15.7	-55.1				
	3/2	3/2	4.44	0.720	0.00621	_					
	1/2	1/2	2.78	11.6	7.46	8.30	199				
	5/2	3/2	15.0	6.67	10.7	10.6	-29.3				
	3/2	1/2	13.9	4.92	9.38	10.3	-25.9				
	3/2	5/2	15.0	37.7	30.4	29.9	99.4				
	1/2	3/2	13.9	27.1	25.2	25.2	81.3				
${}^{4}D^{o} - {}^{4}P$	7/2	5/2	40.0	10.1	16.9	15.7	-60.7				
	5/2	3/2	21.0	0.509	2.98	3.00	-85.7				
	3/2	1/2	8.33	0.0958	1.20	1.30	-84.4				
	5/2	5/2	9.00	36.5	28.2	25.0	178				
	3/2	3/2	10.7	26.9	26.6	28.4	166				
	1/2	1/2	8.33	14.2	11.9	12.3	47.9				
	3/2	5/2	1.00	4.86	6.96	8.11	711				
	1/2	3/2	1.67	6.77	5.33	6.11	266				
	7/2	5/2	40.0	10.1	16.9	15.7	-60.7				

For 3s-3p transitions in N(I) as well as in O(II) an overall good agreement between measured line strength data and results of recent calculations is found. Discrepancies between measured  $S_{ki}$ -values and the LS data show quite regular behavior along the two members of the N(I) isoelectronic sequence. The observed departures from LS coupling results are usually larger in the case of N(I). This can be explained by larger departures from the Landé interval rule for the terms 3s <sup>4</sup>P and 3p <sup>4</sup>P<sup>o</sup> in N(I) (compared to the respective terms in O(II)). The observed fine structure splitting of the term 3p <sup>4</sup>D<sup>o</sup> agrees well with the Landé interval rule in the case of both emitters.

The measured results (being in good agreement with recent calculations) for the multiplet  $3s \ ^4P - 3p \ ^4P^{\rm o}$  provide a very convincing example of such "regular" departure from LS data: the transitions between levels 3/2-3/2, 3/2-1/2 and 5/2-5/2 are stronger, while all other lines are weaker than predicted by LS coupling. The largest discrepancies are encountered for the transition 3/2-3/2: 30% in N(I) and 24% in O(II). Also the line strengths for the multiplet  $3s \ ^4P-3p \ ^4D^{\rm o}$  show similar "regular" behavior: two transitions: 5/2-5/2 and 5/2-3/2 are weaker, while the transition 1/2-3/2 is stronger than expected from LS coupling scheme.

More complex is the situation in the case of 3p-3d transitions. The measured line strengths are in rather good agreement with the very recent data of Froese Fischer and Tachiev [12]. The somewhat older C(IV)3 data of Hibbert et al. [3], often disagree with experimental data, particularly for multiplets with  $\Delta L = 0$ . The best agreement between measured line strengths and recent calculations is found in the case of the strongest multiplet among the 3p-3d transition array  $({}^{4}D^{\circ}-{}^{4}F)$ . However, "regular" departures (i.e. encountered in N(I) and O(II)) from LS results appear also within this multiplet — all fine structure components with  $\Delta J = 0$  are weaker than those obtained from LS coupling scheme. The discrepancies are larger in the case of the N(I) spectrum in accordance with the larger departure from the Landé interval rule for the upper term  ${}^{4}F$  in N(I) (the splitting of the lower term  $3p \ ^4D^{\circ}$  in the case of both emitters agree well with the Landé rule).

Similar regularities are also found in the case of the multiplet  $3p \ ^4D^{\circ}-3d \ ^4D$ . Fine structure components being stronger (compared to LS data) in N(I) are also usually stronger in O(II). On average the discrepancies between measured and LS data are considerably larger than in the case of the multiplet  $3p \ ^4D^{\circ}-3d \ ^4F$ . Despite the significantly larger departure from the Landé interval rule for the upper term  ${}^{4}D$  in the case of O(II), the observed discrepancies in line strengths (between observed and LS values) are nearly the same for both emitters. In Fig. 2 the N(I) spectrum obtained in [22], comprising all lines belonging to the multiplet  $3p \ ^4D^{\circ}-3d \ ^4D$  is shown. In order to compare the measured data with theoretical results, the intensities of individual fine structure components have been computed from respective line strengths (LS-data, Hibbert et al. [3] and Froese Fischer and Tachiev [12]) and normalized to the strongest component 7/2-7/2. Similarly as has been done in Fig. 1 for the analysis of the C(I) spectrum, these computed intensities are quoted in Fig. 2 above the corresponding pairs of *J*-values. Figure 2 clearly illustrates the improvement of the quality of theoretical data: the best overall agreement with experimental data is found in the case of Froese Fischer and Tachiev's calculations [12], slightly worser agreement is found if the experimental data are compared with the older C(IV)3 calculations [3], while the disagreement with the LS data is significant.



Fig. 2. The measured N(I) spectrum in the wavelength range 977–988 nm is shown. The fine structure components of the multiplet 3p  ${}^{4}D^{\circ}$ –3d  ${}^{4}D$  are marked with the corresponding J values. The numbers above individual fine structure components are the line intensities (normalized to the value of 100 for the strongest component 7/2–7/2): measured in [22] and computed on the basis of LS data, the results of Hibbert et al. [3] and the results of Froese Fischer and Tachiev [12] for the temperature of experiment [22].

In Fig. 3 the N(I) spectrum in the wavelength range 1049–1057 nm, obtained in our previous paper [22] is shown. The measured intensities of all fine structure components belonging to the multiplet  $3p \, {}^{4}P^{o}-3d \, {}^{4}D$  are again compared with results based on calculated line strength data taken from [3] and [12]. Similarly as in Fig. 2, the line intensities are normalized to the strongest component corresponding to the transition 5/2-7/2. Again the experimental data show very good agreement with calculations of Froese Fischer and Tachiev [12] and to some extent with those of Hibbert et al. [3]. Large discrepancies are encountered if the measured data are compared with those resulting from LS coupling. For the two weakest transitions (5/2-3/2 and 3/2-1/2), the measured line strengths are larger than predicted by the LS coupling by factors 2.7 and 1.8, respectively. Large discrepancies are encountered also for stronger components, e.g. the observed line strength for the transition 5/2-5/2 exceeds the LS result nearly by factor of 1.7, while for the transition 1/2-3/2 the measured value is nearly factor of 2 below the LS value.



Fig. 3. The measured spectrum in the wavelength range 1049–1057 nm obtained in [22] comprising all fine structure components of the N(I) multiplet  $3p \ ^4P^{\circ}-3d \ ^4D$  is shown. The individual components are marked with the corresponding J values. The numbers above individual spectral lines are the intensities (normalized to the value of 100 for the strongest component 5/2-7/2): measured in [22] and computed on the basis of LS data, the results of Hibbert et al. [3] and the results of Froese Fischer and Tachiev [12] for the temperature of experiment [22].

#### 6. Conclusions

The majority of experimental data on line strengths for C(I), N(II), N(I) and O(II) presented in Tables II–V, significantly disagree with line strengths obtained from the LS coupling scheme. In numerous cases these observed departures exhibit "regular" behavior along the isoelectronic sequences C(I)–N(II) and N(I)–O(II). On the other hand, very good agreement between experimental data and the results of recent advanced calculations is found. The progress in line strength calculations achieved in the last several years can be regarded as being satisfactory. Worthy to stress is the improvement of the quality of theoretical data for N(I) — from C(IV)3 calculations of Hibbert et al. [3] to the recent results of Froese Fischer and Tachiev [12].

The departures of measured line strengths from those resulting from the LS coupling scheme are on average significantly larger for the spectra N(I) and O(II) than for C(I) and N(II). Also the observed departures from the Landé interval rule are larger in the case of the terms of neutral nitrogen and singly ionized oxygen. However, a simple quantitative correlation between departures from the Landé interval rule and the observed departures of line strengths from the LS coupling scheme has not been found.

More important for predicting possible departures of line strengths from LS coupling scheme seems to be the analysis of the energy level system of the emitter for possible mixing of close lying energy levels belonging to terms with different multiplicities. In the case of all stud-

ied emitters, the terms belonging to the 3s and 3p configurations are rather well separated, with exception of the terms  $3s {}^{3}P^{\circ}$  and  $3s {}^{1}P^{\circ}$  in N(II). The terms originating from the configuration 3d are significantly closer in energies, particularly in the case of N(I) — the energy gaps between terms with different multiplicities are of the same order as the fine structure splitting of the respective terms. All these terms  $({}^{2}P, {}^{4}P, {}^{2}F, {}^{4}F, {}^{2}D$  and  $^{4}D$ ) are within an energy interval of about 550 cm<sup>-1</sup>. As a consequence of the level mixing, similarly as in the case of the N(II) spectrum [17], strong N(I) intersystem transitions are observed (see [16, 23]). In Fig. 4, the spectrum obtained in our previous work [22] is shown illustrating how strong are these forbidden lines, compared to the allowed transitions, causing obviously large departures of allowed line strengths from those expected from LS coupling scheme. In this figure the spectrum comprising the fine structure components belonging to the "weak" LS allowed multiplet  $3p \ ^4D^{\circ}-3d \ ^4P$  as well as four — rather strong — intersystem transitions, is shown. As can be seen, in the case of this multiplet even the recent data of Froese Fischer and Tachiev [12] do not agree well with measured data (see also the numerical data in Table IV).



Fig. 4. The measured spectrum in the wavelength range 988–1006 nm comprising all fine structure components of the N(I) multiplet 3p  ${}^{4}D^{\circ}-3d$   ${}^{4}P$  is shown. The individual components are marked with the corresponding J values. The numbers above individual spectral lines are the intensities (normalized to the value of 100 for the strongest component 3/2-3/2): measured in [22] and computed on the basis of LS data, the results of Hibbert et al. [3] and the results of Froese Fischer and Tachiev [12] for the temperature of experiment [22]. The lines marked with \* are transitions between terms of different multiplicities.

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