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Measurements of selected NI multiplet strength ratios and comparison with recent calculations

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Abstract. Results of recent calculations of multiplet strengths of atomic nitrogen (NI) are compared with arc emission measurements. Intensities of eleven infrared multiplets are measured and transformed into multiplet strength values applying the determined arc temperature values. Properly defined seven multiplet strength ratios are selected for comparison with results of calculations and previously obtained experimental data. Our measured multiplet strength ratios are in a very good agreement with the recent Breit-Pauli results of Tachiev and Froese Fischer.

PACS. 32.70.Cs Oscillator strengths, lifetimes, transition moments – 32.70.Fw Absolute and relative intensities – 52.70.Kz Optical (ultraviolet, visible, infrared) measurements

1 Introduction

During the last 20 years numerous theoretical [1–15] as well as experimental [16–21] papers have been published containing line strength data for atomic nitrogen. Accurate knowledge of these atomic constants is of considerable interest e.g. for studies of astrophysical objects and for diagnostics of laboratory plasmas. Comprehensive results of calculations of NI line strengths are reported by the Opacity Project team [1,6] (multiplet data) and by Kurucz and Bell [4] (fine structure results — semiempirial data). Less comprehensive calculations, going down to the fine structure level, have been performed by the Hibbert group applying the CIV3 configuration interaction code [2,3,7]. A limited number of NI line strengths (fine structure components) for some quartet transitions in NI are reported also by Tong et al. [5]. Results of a critical analysis of all theoretical as well as experimental data reported up to 1995 could be found in the monograph by Wiese et al. [22]. Results of new approaches have been recently reported by Zheng et al. [9,10] and by Çelik et al. [15] (weakest bound electron potential model (WBEPM) theory), by Tachiev and Froese Fischer [11,12] (Breit-Pauli data) and by the Tayal group [8,13,14] (B-spline R-matrix approach).

Experimental data on NI line strengths available in literature are based on arc emission measurements of total line intensities. From these directly measured data relative or absolute line strengths (fine structure components) are determined. The absolute scales are then obtained by normalizing relative data to lifetime values or arbitrary taken reference data. Generally, emission experiments provide reliable relative line strength values, especially when the studied transitions originate from the same upper level or from levels only slightly separated in energy and in addition when the lines are not too far in wavelength. Therefore, in order to test recent calculations, we decided to measure relative multiplet strengths and compare them with the corresponding data taken from theoretical approaches. Similarly as in our previous papers [18–21] we used the standard emission spectroscopy technique applying the most suitable source for thermal excitation of the NI spectrum — the wall-stabilized high-current arc.

In our former paper [20] we focused our attention on accurate determination of relative line strengths (fine structure components) within selected multiplets. Since the NI multiplet strengths and consequently the multiplet intensities differ from each other significantly, the small amount of the nitrogen admixture in the excitation source was adjusted for each multiplet separately, in order to achieve optimal conditions for determination of total line intensities (large line to continuum (line to noise) ratios, negligible self absorption). Therefore determinations of multiplet strength ratios are not possible on the basis of our previous measurements.

In the present paper we focus our attention on high quality measurements of some selected NI multiplet multiplet strength ratios. In Section 3 we describe the selection of NI multiplet pairs in detail. The operation conditions of the excitation source (the admixture of nitrogen) were optimally adjusted for each multiplet pair.

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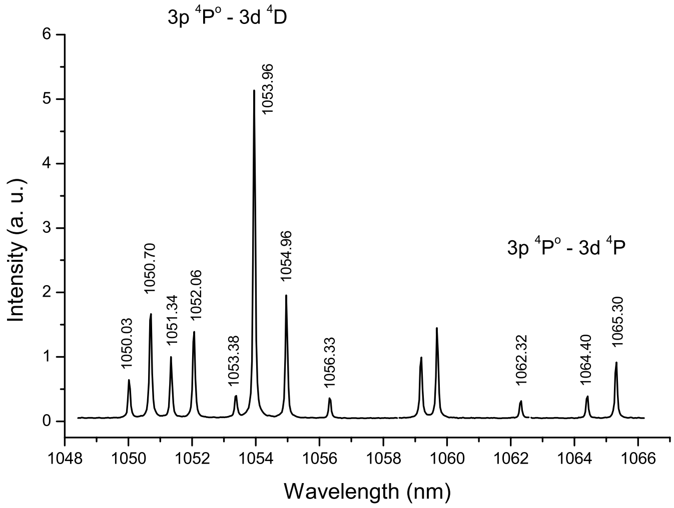

Fig. 1. The measured spectrum (after radiance calibration) in the wavelength range 1048–1066 nm is shown. All fine structure components of the $3p\ ^4\mathrm{P}^o - 3d\ ^4\mathrm{D}$ and three components of the $3p\ ^4\mathrm{P}^o - 3d\ ^4\mathrm{P}$ multiplet are visible. The not marked spectral feature in between (near 1059–1060 nm) are the NI double excited transition $3p'\ ^2\mathrm{F}^o - 3d'\ ^2\mathrm{G}$, consisting of three fine structure components (two of them are very close in wavelength).

2 Detection of spectra and plasma diagnostics

The wall-stabilized arc was operated at atmospheric pressure and a current of 40 amps. Helium was applied as the working gas, while nitrogen was added only in small amounts. At such operating conditions the plasma fills up the arc discharge channel and produces uniform plasma layers along the arc axis. Close to the arc axis the gradients of the plasma parameters are very weak. Moreover, because of the small admixture of nitrogen, self-absorption processes in NI spectral transitions are negligible along the line of sight. Therefore, for the purpose of this study, we selected and measured only the radiation emitted from this particular homogeneous plasma layer in vicinity of the arc axis. This was accomplished by applying an optical imaging system, which is described in detail e.g. in [18,20]. The optical system allows also checking if the studied spectral lines are optically thin — details are also outlined in [18,20]. At these plasma and imaging conditions the observed NI infrared spectra are very intense at rather weak background (continuum) radiation. The spectra were recorded with a grating spectrometer equipped with a CCD detector sensitive up to 1700 nm. With our spectrometer and this detector the radiation in a wavelength interval of 17 nm could be simultaneously recorded. The wavelength dependence of the efficiency of the detector was calibrated against signals measured from a tungsten strip radiation standard. In Figure 1, as an example, the measured spectrum (after radiance calibration) in the wavelength range from 1048 to 1066 nm is shown. In this figure all eight fine structure components of the $3p\ ^4\mathrm{P}^o - 3d\ ^4\mathrm{D}$ and three components of the $3p\ ^4\mathrm{P}^o - 3d\ ^4\mathrm{P}$ transition are visible, including the second strongest line of the last mentioned multiplet at 1065.30 nm. The spectral feature between the two marked multiplets are the transition $3p'\ ^2\mathrm{F}^o - 3d'\ ^2\mathrm{G}$, consisting of three fine structure components (two of them are very close in wavelength).

The advantage of our excitation source is — that at fixed arc currents — very small variations in the (small) nitrogen admixture changes significantly the population of exited nitrogen atoms (measured line intensities), but does not influence substantially the electron density and the plasma temperature.

The temperature of the plasma (excitation temperature, characterizing the population of excited NI levels) was determined from measured intensity ratio of two NI multiplets: $3p\ ^2\mathrm{S}^o - 3d\ ^2\mathrm{P}$ and $3s'\ ^2\mathrm{D} - 3p'\ ^2\mathrm{D}^o$, applying the Boltzmann plot method. These two multiplets are close in wavelength and their upper terms are spaced in energy by 0.73 eV. The respective transition probabilities have been taken from Wiese et al. [22]. For the plasma layer close to the arc axis we determined a temperature of 14000 ± 1400 K.

The electron density of the plasma was deduced from measured full width at half maximum (FWHM) of the HeI spectral line ($2p\ ^3\mathrm{P}^o - 5d\ ^3\mathrm{D}$, $\lambda = 402.636$ nm), which is — at our plasma conditions — predominantly broadened by the quadratic Stark effect. Applying the respective broadening parameters (electron impact width and asymmetry parameter) reported by Griem [23] an electron density of $(3.0 \pm 0.6) \times 10^{15}$ cm^{-3} was determined.

3 Selection of multiplet pairs

For our investigation we have selected multiplet pairs fulfilling two requirements:

(i) the excitation energy gap between the upper terms is very small compared to the plasma temperature value expressed in energy units, and
(ii) all fine structure components (or at least their majority) appear in a wavelength interval, which may by registered in a single exposition of our CCD detector.

The spectrometer's dispersion and the dimension of the CCD detector determine the above-mentioned spectral interval. In cases if both (complete) multiplets could not be detected simultaneously, the missing part was measured in the subsequent exposition of the CCD detector together with a part of the spectrum measured in the preceding exposition. In this way uncertainties in measurements of line (multiplet) intensity ratios, originating from possible small plasma parameter drifts, are significantly reduced.

Figure 2 shows the partial Grotrian diagram of NI with our selected multiplets arranged in seven pairs. The transitions involve five lower terms belonging to the $(^3\mathrm{P}^o)3p$ configuration. The respective six upper terms belong to the $3d$ and $4s$ configurations (at the same core configuration as the lower terms).

In Table 1 the selected transition pairs are listed, together with multiplet strength data taken from literature.

Table 1. Comparison of recently calculated multiplet strengths (quoted in atomic units) classified into seven transition pairs (ratios). In the third column the wavelengths (centers of gravity) of the multiplets are listed while in the fourth the excitation energy gaps between the respective upper terms in cm^{-1}.

Pair	Multiplet	λ_{mult} (nm)	$\Delta E_{a,b}$ (cm^{-1})	S_{ki} (atomic units) Ref. [1] (1987)	Ref. [2] (1991)	Ref. [5] (1994)	Ref. [8] (1999)	Ref. [11] (2002)
(1a)	$3p\ ^4D^o - 3d\ ^4P$	998.82	−160.50	12.7	19.0	10.7	10.9	14.7
(1b)	$3p\ ^4D^o - 3d\ ^4D$	983.06		91.5	84.5	88.3	89.3	95.2
			Ratio:	*0.14*	*0.22*	*0.12*	*0.12*	*0.15*
(2a)	$3p\ ^4S^o - 4s\ ^4P$	1439.9	−934.42	22.5	22.3	—	23.1	19.9
(2b)	$3p\ ^2P^o - 3d\ ^2P$	1462.8		34.1	25.7	—	24.9	21.6
			Ratio:	*0.66*	*0.87*	—	*0.93*	*0.92*
(3a)	$3p\ ^2D^o - 3d\ ^2D$	1204.4	287.38	56.1	51.5	—	52.2	53.6
(3b)	$3p\ ^4S^o - 3d\ ^4P$	1234.8		172	133	—	152	135
			Ratio:	*0.33*	*0.39*	—	*0.34*	*0.40*
(4a)	$3p\ ^2D^o - 3d\ ^2D$	1204.4	1440.28	56.1	51.5	—	52.2	53.6
(4b)	$3p\ ^4P^o - 4s\ ^4P$	1221.6		106	100	—	92	108
			Ratio:	*0.53*	*0.51*	—	*0.57*	*0.50*
(5a)	$3p\ ^2D^o - 4s\ ^2P$	1357.9	−938.15	69.0	63.0	—	64.8	54.2
(5b)	$3p\ ^2P^o - 3d\ ^2D$	1362.0		197	178	—	184	167
			Ratio:	*0.35*	*0.35*	—	*0.35*	*0.32*
(6a)	$3p\ ^4P^o - 3d\ ^4P$	1070.7	−160.50	85.1	95.3	86.1	79.2	85.7
(6b)	$3p\ ^4P^o - 3d\ ^4D$	1052.6		303	284	292	301	296
			Ratio:	*0.28*	*0.34*	*0.29*	*0.26*	*0.29*
(7a)	$3p\ ^4P^o - 4s\ ^4P$	1221.6	−1152.90	106	100	100	92	108
(7b)	$3p\ ^4S^o - 3d\ ^4P$	1234.8		172	133	165	152	135
			Ratio:	*0.62*	*0.75*	*0.61*	*0.61*	*0.80*

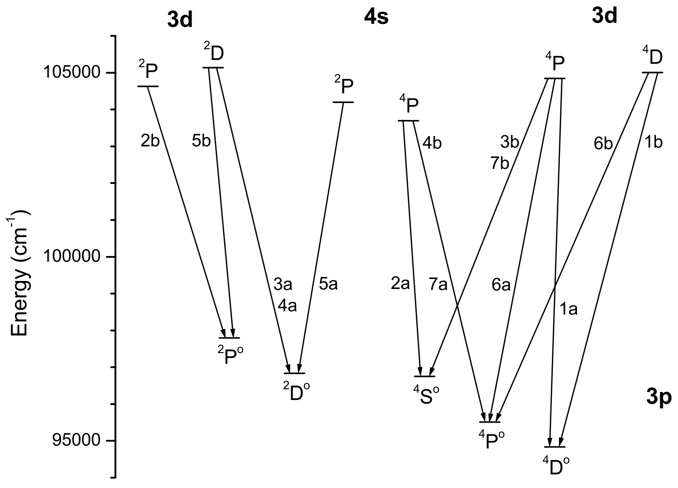

Fig. 2. Partial Grotrian diagram of excited NI terms showing the studied transitions grouped into multiplet pairs. All upper terms (doublets and quartets) belonging to transition arrays 3*p*-3*d*, and 3*p*-4*s* are within an energy interval of only 1440 cm^{-1}.

In column 3 the wavelengths of the center of gravity of the corresponding multiplets are given, while in column 4 the excitation energy gaps (in cm^{-1}) between the respective upper terms. In columns 5–9 theoretical multiplet strength data (in atomic units), which have been calculated in the last 20 years, are listed together with their ratios. In the case of two pairs (#4 and #5) the discrepancies between calculated strengths (and their ratios) determined in different papers are small and also within the expected uncertainty limits of our experiment. On the other hand in all other cases the scatter of theoretical data is significantly larger — the line strength ratios disagree by more than 20%, and in the case of pair #1 even exceeds the factor of 1.8. In all these cases our measured line strength ratios may provide reliable results indicating which theoretical data set is trustworthier.

4 Determination of multiplet intensities and evaluation of multiplet strength ratios

Our line (multiplet) intensity measurements are based on at least 15 independently registered spectra. Individual fine structure components were fitted with Voigt profiles. The shapes (the Gaussian and Lorentzian parts) were kept fixed within each multiplet. The Gaussian part originates mainly from Doppler and instrumental broadening. The Doppler width was calculated from the known plasma temperature value, while the apparatus width

Table 2. Comparison of measured multiplet strength ratios with data taken from literature.

Pair number	Multiplets	S^a_{ki}/S^b_{ki}							
		This work	[1]	[2]	[5]	[8]	[11]	[18]	[22]
(1)	$(3p\ ^4\mathrm{D}^o - 3d\ ^4\mathrm{P})$ / $(3p\ ^4\mathrm{D}^o - 3d\ ^4\mathrm{D})$	0.15 ± 0.02	0.14	0.23	0.12	0.12	0.15	0.31	0.29
(2)	$(3p\ ^4\mathrm{S}^o - 4s\ ^4\mathrm{P})$ / $(3p\ ^2\mathrm{P}^o - 3d\ ^2\mathrm{P})$	0.74 ± 0.09	0.66	0.87	—	0.93	0.92	—	0.85
(3)	$(3p\ ^2\mathrm{D}^o - 3d\ ^2\mathrm{D})$ / $(3p\ ^4\mathrm{S}^o - 3d\ ^4\mathrm{P})$	0.41 ± 0.06	0.33	0.39	—	0.34	0.40	—	0.36
(4)	$(3p\ ^2\mathrm{D}^o - 3d\ ^2\mathrm{D})$ / $(3p\ ^4\mathrm{P}^o - 4s\ ^4\mathrm{P})$	0.53 ± 0.06	0.53	0.51	—	0.57	0.50	—	0.50
(5)	$(3p\ ^2\mathrm{D}^o - 4s\ ^2P)$ / $(3p\ ^2\mathrm{P}^o - 3d\ ^2\mathrm{D})$	0.37 ± 0.05	0.35	0.35	—	0.35	0.32	—	0.26
(6)	$(3p\ ^4\mathrm{P}^o - 3d\ ^4\mathrm{P})$ / $(3p\ ^4\mathrm{P}^o - 3d\ ^4\mathrm{D})$	0.30 ± 0.03	0.28	0.34	0.30	0.26	0.29	0.19	0.19
(7)	$(3p\ ^4\mathrm{P}^o - 4s\ ^4\mathrm{P})$ / $(3p\ ^4\mathrm{S}^o - 3d\ ^4\mathrm{P})$	0.78 ± 0.09	0.62	0.75	0.61	0.60	0.80	—	0.72

was determined from spectra taken from a low pressure Plücker — type discharge. The Lorentzian width (for each multiplet separately) was determined by accurate fitting of a selected strong and well-isolated line belonging to the analyzed multiplet. The shape (Voigt function) obtained in this way were then applied for fitting all fine structure components belonging to a given multiplet and then integrated in order to obtain total line and multiplet intensities.

The multiplet strength ratios (S_a/S_b) were calculated from corresponding measured intensity ratios (I_a/I_b) according to the formula:

$$S_a/S_b = (\lambda_a/\lambda_b)^4 \, (I_a/I_b) \exp\left(\left(E_a - E_b\right)/kT\right), \qquad (1)$$

where: λ_a and λ_b are the wavelengths of the multiplets (centers of gravity) and $E_a - E_b = \Delta E_{a,b}$ are the excitation energy gaps listed in Table 1.

The electron density of our plasma $(3.0 \pm 0.6) \times 10^{15}$ cm^{-3} is — according to LTE criteria (see for example Drawin [24]) — high enough for establishing Boltzmann population between NI excited levels with principal quantum numbers $n \geq 3$.

5 Results and discussion

In Table 2 our measured multiplet strength ratios are compared with results of calculations presented in Table 1, with experimental data of [18] and with ratios based on data recommended by NIST [22]. The uncertainty limits quoted in column 3 include: (i) the standard deviations of measured intensity ratios I_a/I_b; (ii) the uncertainties of the line profile fitting procedure; (iii) the possible (very small) departures from optically thin conditions and (iv) the error in the determination of the plasma temperature

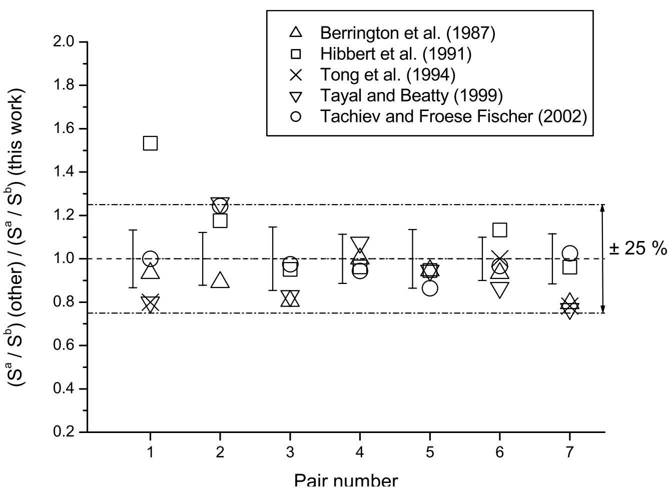

Fig. 3. Comparison of multiplet strength ratios evaluated on the basis of data obtained within various theoretical approaches with those determined in this work. For each measured ratio the corresponding error bar is shown on the left side of the evaluated ratios based on theoretical multiplet strengths.

($\Delta T = \pm 1400$ K). Since the $\Delta E_{a,b}$ — values are small (see Tab. 1), the contribution originating from the last mentioned agent does not exceed 3% even in the case of pair #4 (the largest $\Delta E_{a,b}$ value). The total measuring error was calculated by taking a square root over the sum of all above mentioned uncertainty sources.

Since the main goal of this paper was to verify experimentally various theoretical approaches on line strength calculations, in Figure 3 results of these calculations are compared with our measurements.

All ratios evaluated from literature data (multiplet strength ratios) are compared with our results by dividing them by our measured ratios. Nearly all evaluated ratios agree with our measurements within a satisfying uncertainty limit of ±25%. As can be seen from this figure and from Table 2, all measured ratios (with one exception — pair #2) are in an excellent agreement (within our experimental uncertainty limits) with the recent Breit-Pauli data of Tachiev and Froese-Fischer [11,12]. In the case of five studied multiplet pairs (## 1, 3, 4, 6 and 7) the discrepancy does not exceed 6%, while in the case of the result #5 amounts 14%. Very good agreement between our measurements and the calculations of Tachiev and Froese-Fischer we found also comparing strengths of individual fine structure components including intersystem transitions (see [21]). Therefore we may state that the results of our measurements and the detailed analysis of theoretical data justify the conclusion, that within the last 20 years a significant improvement in the quality of theoretical data on multiplet strengths has been achieved, including calculations of the fine structure.

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