Intensity ratio of nitrogen bands as a function of field strength
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The ratio of intensities of the first negative and the second positive system of the emission spectrum of molecular nitrogen as a function of the applied electric field strength was measured experimentally for air in the pressure range from 2 to 760 Torr. The non-selfsustained dc discharge in a parallel-plane gap was used for gas excitation. The field strength was varied in the range of 150 – 5000 Td. The results are compared with the theoretical estimates made by other authors.

1. Introduction

In plasma applications and research, an estimation of the electrical field strength in the plasma is a frequent task. Spectroscopic method based on the measurement of the intensity ratio of nitrogen bands can be used for this purpose when the excitation of molecules from the ground state by electron impact is the dominant process in plasma. Usually, the intensity of the most intensive spectral band of the second positive system (SPS) of the nitrogen molecule \( \text{N}_2 \), and the intensity of the most intensive band of the first negative system (FNS) of the ionized molecule \( \text{N}_2^+ \), are compared [1–4]. These bands correspond to transitions \( \text{N}_2 (C_3 \Pi_u, v=0) \rightarrow \text{N}_2 (B_3 \Pi_g, v=0) \) and \( \text{N}_2^+ (B_2 \Sigma^+_g, v=0) \rightarrow \text{N}_2^+ (X_2 \Sigma^+_g, v=0) \). Wavelengths of these bandheads are 337.1 nm and 391.4 nm, respectively. We denote below the ratio of the intensities of those bands by \( R_{391/337} \).

For determination of the field strength, the ratio of those intensities must be known as a function of the electric field strength. Results of theoretical calculation of \( R_{391/337} \) as a function of reduced field strength \( E/N \), where \( E \) is electric field strength and \( N \) is gas number density, are presented in publications [2, 4, 5]. The calculated ratios \( R_{391/337} \) in these publications differ from each other remarkably, as it is exposed in Figure 5 and pointed out in papers [3, 6]. An experimental determination of \( R_{391/337} \) as a function of \( E/N \) in air is performed and the results are presented in our previous paper [6]. The shape of the experimental curve follows the theoretical predictions but experimentally determined values are about 3 to 6 times higher than the theoretical ones.

There are some reasons for continuing experimental investigations of behavior of relative intensities of the bands of the nitrogen spectrum depending on the field strength:

- Our previous measurements of \( R_{391/337} \) were carried out in the \( E/N \) range of 135 – 285 Td. There is a need to extend the range of the investigated field strength.
- The \( R_{391/337} (E/N) \) curve presented in paper [6] was measured in air at the atmospheric pressure. It is not obvious that this dependence is valid for lower or higher pressures. Thus, measurements at different pressures should be carried out.

In this report, the intensity ratio of rotational bands of 0–0 vibrational transition of FNS and 0–0 vibrational transition of SPS of nitrogen as a function of the reduced field strength is recorded experimentally. The steady state discharge is applied in contrast to the pulsed discharge used in our previous work [6]. The aim of the study is to find the relationships that could be used for field strength estimations in air at atmospheric and lower pressures.

2. Experimental set-up and measuring procedure

The sketch of the experimental set-up is presented in Figure 1. The gas was excited between parallel plate electrodes. The electrodes were installed in a vacuum chamber equipped with quartz windows. Ambient air was dried with silica gel, filtered out of the dust and directed into the chamber. The airflow rate through the chamber was maintained about 1 l/min during all the measurements. The pressure in the chamber was controlled by valves. It was measured with the help of piezo transducer.
The uncertainty of measurement results was less than 2%. The distance between electrodes was adjustable with an accuracy of 0.01 mm. The anode was made of brass. A thin semitransparent aluminum coating evaporated on a quartz plate served as a cathode. The cathode was stressed via a current limiting resistor $R = 100 \text{ M} \Omega$. The anode was grounded via a digital ammeter that could provide the current resolution of 0.1 nA. The initial electrons were liberated from the cathode by the UV radiation of the low-pressure mercury lamp. An interference filter in front of the lamp transmitted only the mercury line $\lambda = 253 \text{ nm}$.

The diameter of the illuminated area of the cathode was 18 mm. The electric field strength was set by adjusting the distance between electrodes and/or the applied voltage. The radiation from the discharge gap was focused on the input slit of a monochromator. We used an achromatic quartz lens of 75 mm focal length, which gave the magnification of 0.5 times. The linear dispersion of the monochromator MDR-23 was 1.3 nm/mm. The 0.15 mm wide slits were used. A photomultiplier PM (PMH-100-4, Hamamatsu) in the photon counting mode was used for detection of the radiation. The photocathode of the PM was cooled down to -20°C. As a result, the dark count rate was reduced to about 40 s$^{-1}$. The counting time was set equal to 1 s. A computer stored the values of the counting rate.

The relative spectral sensitivity of the entire optical system was determined using a tungsten lamp and a deuterium lamp, whose spectral characteristic was known.

The instrumental function of the system was determined for every distance $d$ between the electrodes. For that purpose the discharge gap was illuminated with a mercury lamp and the spectral response of the recording system, $F(\lambda)$, was registered for mercury line $\lambda_{M} = 404.7 \text{ nm}$.

Values of pressure, discharge current, and counting rate of PM were measured simultaneously for each recorded wavelength, $\lambda$.

3. Experimental conditions

The distance between electrodes was varied from 0.15 to 5.0 mm. Pressure was varied over the region of 2 – 740 Torr. The air temperature in the discharge chamber was between 18 and 26°C. In order to avoid distortions of the homogeneous electric field by the space charge, the discharge current was kept in the limits 1 – 2 $\mu$A. The value of the current strength was set by adjusting applied voltage $U$. The voltage was always kept some percent below the breakdown voltage for given $d$ and $p$. Figure 2 represents the values of $U$ and $Nd$ that correspond to the recorded spectra. The spectrum was recorded in the wavelength intervals of 335.5 – 338.0 nm and 390.5 – 395.0 nm with the scanning step 0.04 nm. An example of the recorded bands of the nitrogen spectrum is presented in Figure 3. The band of the 0-0 transition of SPS is in the wavelength interval of 335 – 338 nm. The 0-0 transition band of FNS (small peak at 391.4 nm) together with the 2-5 transition band of SPS (high peak at 394.3 nm) appears in the interval from 390 to 395 nm. If a value of the applied voltage was fixed, the current and the radiation intensity of the discharge changed slowly in time. It was likely caused by reduction of the cathode emissivity and long-duration fluctuations in the intensity of the Hg lamp. These changes per day were always less than 10% and they were taken into account by scaling the recorded radiation intensity with the current. The radiation intensity of the discharge in the investigated spectral bands was proportional to the discharge current.

![Figure 2](image1.png)  
**Figure 2.** $U-Nd$ region, where the spectrum was recorded.

![Figure 3](image2.png)  
**Figure 3.** Spectrum of non-self-sustained discharge in dry air. $p = 740 \text{ Torr}$, $d = 0.65 \text{ mm}$, $U = 3058 \text{ V}$, $E/N = 210 \text{ Td}$, $T = 301 \text{ K}$, $I = 1.8 \mu\text{A}$. Points – measurements, red curve – calculated spectrum, blue line – background.
4. Data processing

In order to compare the intensities of the selected bands, we first calculated the intensity distribution in bands, $S_i(\lambda)$. Indices $i = 0, 1, 2$ correspond to 0–0 and 2–5 bands of SPS and 0–0 band of FNS, respectively. Formulae for these calculations and values of the transition probabilities and molecular constants are taken from the paper [7]. The intensities of the rotational lines were normalized so that the sum of the intensities in a certain band is equal to one.

The next step was the calculation of normalized convolution integrals:

$$\Phi_i(\lambda) = \frac{\lambda_i}{\lambda} \int S_i(\lambda - x) F_i(x) dx,$$

where $F_i(\lambda)$ is the instrumental function with unit amplitude. To match the calculated dependencies $\Phi_i(\lambda)$ with the experimental points, coefficients $\alpha_i$ were introduced to denote the amplitude of $i$-th band and $\beta_i$ to denote that of the background. Using the least-square method, the values of $\alpha_0$ and $\beta_0$ were found such that the curve $\alpha_0 \Phi_0(\lambda) + \beta_0$ was the best fit of experimental points of the 0–0 band of SPS. In the wavelength region 390–395 nm, where the overlapping of bands 2–5 of SPS and 0–0 of FNS takes place, the sum $\alpha_1 \Phi_1(\lambda) + \alpha_2 \Phi_2(\lambda) + \beta_{12}$ was fitted to the experimental points choosing appropriate values for $\alpha_1$ and $\alpha_2$ and $\beta_{12}$. Curves $\alpha_0 \Phi_0(\lambda) + \beta_0$ and $\alpha_1 \Phi_1(\lambda) + \alpha_2 \Phi_2(\lambda) + \beta_{12}$ are presented in figure 3 (red curves) together with experimental points. Blue line indicate value of $\beta_0$ and $\beta_{12}$. Finally, the intensity ratio $R_{391/337}$ was calculated as $R_{391/337} = \frac{\alpha_2}{\alpha_0} K$. Here, $K = 1.8$ takes into account the difference in sensitivity of our light detection system at wavelengths 337 and 391 nm. The changes in the sensitivity within the bands were neglected.

5. Results and discussion

The intensity ratio $R_{391/337}$ is presented in Figure 4 as a function of the reduced field strength $E/N$ for different pressures. The common tendency is that $R_{391/337}$ increases with $E/N$ rapidly. In the pressure range of approximately 100–760 Torr, the ratio $R$ as a function of the reduced field strength does not depend on pressure. At lower pressures at a fixed value of the reduced field, a decrease of the pressure leads to an increase of the ratio $R$. One can see that the points lay on a single trendline in pressure region from about 100 to 760 Torr. Points obtained at different lower pressures lay on different trendlines, which are parallel to each other in log-log scale. The dependence of the intensity ratio on pressure is, in our opinion, caused by the difference in values of the collisional deactivation coefficients of the state $N_2(C^3Π_u, v = 0)$ and those of the state $N_2^*(B^2Σ_u^+, v = 0)$ (see Table I). Therefore, the radiation intensities of the bands change differently with the pressure and, as a consequence, the intensity ratio of the bands changes with pressure.

![Figure 4: Intensity ratio of nitrogen bands as a function of reduced field strength measured at different pressures](image)

<table>
<thead>
<tr>
<th>States</th>
<th>Radiative lifetime $\tau_0$ (in $10^9$ s)</th>
<th>Deactivation rate constants (in $10^{10}$ cm$^3$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k_{N_2}$ for $N_2$ molecule</td>
</tr>
<tr>
<td>$N_2^*(B^2Σ_u^+, v=0)$</td>
<td>62</td>
<td>2.1</td>
</tr>
<tr>
<td>$N_2(C^3Π_u, v=0)$</td>
<td>42</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Data in the Table are from [8, 9].

If spontaneous emission and collisional quenching are the only processes of depopulation of a certain excited state, then the fraction of molecules that radiates is a function of gas number density $N$:

$$g(N) = \frac{1}{1 + \tau_0 N (n_{N_2} k_{g N_2} + n_{O_2} k_{g O_2})}.$$

Here $n_{N_2}$ and $n_{O_2}$ are the relative densities of nitrogen and oxygen. $n_{N_2} = 0.78$ and $n_{O_2} = 0.21$ in air. The intensity ratio $R_{391/337}$, measured at gas density $N$, can be reduced to normal density $N_0$ as follows:
\[ R_{391/337}(E_0 / N_0) = R_{391/337}(E / N) \frac{g(N_s)}{n_s} \frac{g(N)}{n_c}, \quad (1) \]

where \( E_0 / N_0 = E / N \) and subscripts \( N_2^+ B \) and \( N_2 C \) indicate states \( N_2^+(B^2\Sigma_u^+, \nu=0) \) and \( N_2 (C^3\Pi_u, \nu=0) \), respectively. Results of this reduction to normal conditions are presented in Figure 5. One can see that the points obtained in the pressure range of 2-760 Torr lay well on a single trendline. The empirical formula derived for this trendline is

\[ R_{391/337}(E_0 / N_0) = A e^{-\frac{B}{E/N}} \quad (2) \]

where \( A = 3.33, B = 90.4 \) and the unit of \( E/N \) is Td. Trendlines in Figure 4 are drawn using equations (1) and (2). Points with uncertainty bars in Figure 5 are taken from our previous paper [6], where we measured the same dependence of the intensity ratio at atmospheric pressure, but the pulsed \( KrF^* \) excimer laser was used instead of mercury lamp to liberate initial electrons from the cathode. In that case, the excitation of nitrogen occurred during time interval of about 30 ns. Pauses between pulses were about 0.1 s. One can see that points obtained under the pulsed excitation lay on the same curve as points obtained in the steady state excitation conditions.

6. Conclusions

According to our knowledge, it is the first time when in air the dependence of the intensity ratio of nitrogen bands on the field strength is determined experimentally in a wide range of \( E/N \) values.

- The experimental setup is straightforward and causes no interpretation difficulties.
- The results of the study allow the estimation of the reliability of theoretical calculations.
- The relationship (2) could be used for \( E/N \) estimation in low-temperature plasma studies in air if the excitation of molecules from the ground state by electron impact is the dominant process.

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References