

# *In situ* determination of absolute number densities of nitrogen molecule triplet states in an rf-plasma sheath

B. Krames<sup>a)</sup> and Th. Glenewinkel-Meyer<sup>b)</sup>

*Institut für Physik, Technische Universität Chemnitz, 09107 Chemnitz, Germany*

J. Meichsner

*Institut für Physik, Ernst-Moritz-Arndt-Universität Greifswald, 17487 Greifswald, Germany*

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A laser induced fluorescence technique (LIF) in combination with optical emission spectroscopy (OES) and Rayleigh scattering (RS) was applied to investigate absolute number densities of the population of the three nitrogen triplet states  $C^3\Pi_u$ ,  $B^3\Pi_g$ , and the metastable  $A^3\Sigma_u^+$  in an asymmetric low pressure rf discharge. Primary targets of this investigation were the three lowest vibrational levels ( $v=0,1,2$ ) of each triplet state and additionally  $v=8$  of  $A^3\Sigma_u^+$  which can be populated very efficiently in the plasma sheath. Calibration of LIF intensities to absolute densities of  $A^3\Sigma_u^+$  and  $B^3\Pi_g$  has been realized by comparison with the signal of the RS experiment done in pure nitrogen gas. Calibration of  $C^3\Pi_u$  which we could not detect by LIF but rather only by OES was achieved after comparing OES and LIF signals of the  $B^3\Pi_g$  state. Excitation energies of the analyzed states range from 6 up to 11.5 eV and the measured number densities differ by about seven orders of magnitude from as much as  $10^{12} \text{ cm}^{-3}$  down to almost  $10^5 \text{ cm}^{-3}$ . In addition to the interpretation of the results this article describes the used calibration methods which are partly based on a suggestion made by P. Bogen (Proceedings of the XVI International Conference on Phenomena in Ionized Gases, Invited Papers, edited by W. Böttcher, H. Wenk, and E. Schultz-Gulde, Düsseldorf, 1983, pp. 164–173). © 2001 American Institute of Physics.  
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## I. INTRODUCTION

*In situ* determination of absolute number densities is one of the more daunting tasks facing the experimentalist when trying to fully characterize a complicated reaction system. Attempts were made by careful evaluation of all absolute apparatus parameters used for species detection, such as, quantum efficiency of the detector, solid angle of the acceptance aperture, transmission efficiency of the system, possible geometric discrimination effects, and so on. One of the more successful approaches is a comparison of the signal of interest with a signal from a known reference source taken in the same experimental setup. Chemical titration is one of those, see, e.g., Ref. 1. Another approach, depending only on optical methods,<sup>2,3</sup> is where the absolute number density of one reaction partner is determined from simultaneous detection of its own optical emission which in turn has to be compared to the emission from the reaction products. Other methods make use of carefully calibrated optical absorption experiments.<sup>4</sup> A number of suggestions have been made for a convenient method employing laser induced fluorescence (LIF) techniques.<sup>5–8</sup> We will present here very successful LIF measurements of absolute number densities of transient species using a method suggested by P. Bogen a number of years ago.<sup>9</sup>

The reaction system of interest is an already rather complicated state-state regime of an rf-nitrogen plasma sheath where a whole plethora of reaction partners (electrons, ions, energetic neutrals, radicals, UV and VUV photons) influence particle density distributions as a function of process parameters. Particularly, the electron dynamics in front of the powered discharge electrode is affected by the strong sheath potential modulation in an asymmetric and capacitively coupled rf discharge.<sup>10</sup> The first step towards complete understanding of the reaction mechanisms at hand is a comparison of experimentally and theoretically determined absolute number densities for all species. We will present absolute number density data on the nitrogen metastable triplet state  $A^3\Sigma_u^+$  and the triplet states  $B^3\Pi_g$  and  $C^3\Pi_u$  as important carriers of internal energy in excess of several electron volts which are able to reach the electrode surface by penetrating the plasma sheath. Especially for the modeling and interpretation of the spatial behavior of the metastables it is important to determine the absolute number densities with the adequate accuracy, for which the used method is a good choice.

The article is organized as follows: we describe the experimental setup and our adaptation of Bogen's method using Rayleigh scattering as a reference source for LIF measurements, since a detailed description of the method has not been published yet. We will then present our experimental results, the absolute density data, and briefly discuss their behavior for different vibronic molecular states. We will conclude by asking for more theoretical support on this subject.

<sup>a)</sup>Present address: Institut für Physik, Ernst-Moritz-Arndt-Universität, 17487 Greifswald, Germany; electronic mail: krames@physik.tu-chemnitz.de

<sup>b)</sup>Present address: Robert-Bosch-GmbH, Dept. K5/ESM3, Steiermärker Str. 3-5, 70442 Stuttgart, Germany.

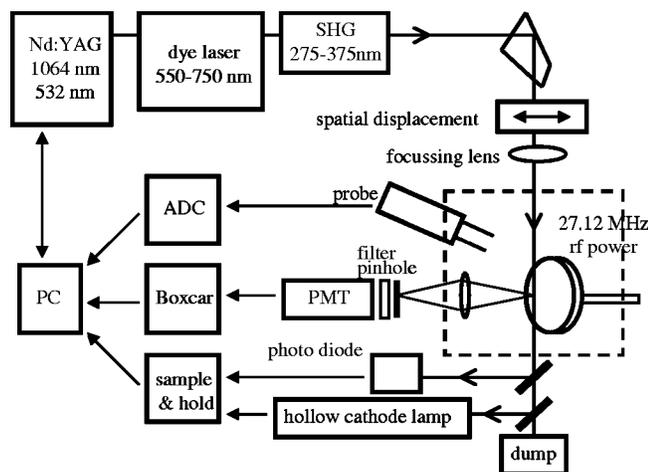


FIG. 1. Schematic view of the LIF apparatus. Shown are the laser system, the vacuum chamber with the driven rf-electrode, and the electronic equipment. The laser beam enters perpendicular to the axis of optical detection. Both pass parallel to the surface of the electrode.

## II. EXPERIMENT

### A. Apparatus

The results described below were determined in an apparatus developed and used for an *in situ* characterization of axial relative density profiles of triplet state nitrogen molecules in an rf-discharge plasma (Fig. 1). A capacitively coupled 27.12 MHz radio frequency power supply generates an asymmetric discharge between a 60 mm diameter driven electrode and the grounded walls of the vacuum chamber. A sustainable plasma ensues between 5 and 100 Pa of nitrogen gas pressure and power delivered up to 100 W.

A pulsed laser beam (8 ns pulse width, 30 Hz repetition rate) excites the plasma species of interest, a photomultiplier (PMT) combined with a boxcar averager detects the time-resolved laser induced fluorescence. Spectral filtering (edge and bandpass) as well as spatial filtering reduce scattered laser light and continuous emission from the plasma background. Spatial filtering is achieved as follows (see also Fig. 1). The laser beam enters the chamber perpendicular to the axis of rotational symmetry of the vessel and the driven electrode ( $z$  axis). It passes parallel to the surface of the electrode and defines the second,  $x$ , axis. Perpendicular to both axes mentioned before the optical detection system (fused silica window, lens, pinhole, and PMT) defines the third remaining,  $y$ , axis. By use of the pinhole in the detection system we define an active detection volume by the cross section of the laser excitation beam and light detection cone along their respective axis to be about  $2 \times 2 \times 1 \text{ mm}^3$ . This detection volume can be translated along the apparatus  $z$  axis for determination of  $z$ -dependent relative density profiles of plasma species.

Triplet states which are not amenable to LIF detection were quantified via optical emission spectroscopy (OES). Here the PMT is replaced by an optical fiber bundle which carries the emitted spontaneous fluorescence light to the entrance slit of a grating monochromator. A cooled charge-coupled device (CCD) camera serves as the detector. In this case the detection volume is not as well localized as in the

LIF experiment and the acceptance cone of this system precludes a direct signal comparison. However, several transitions have been measured using both methods and serve as a calibration for those bands that cannot be seen by LIF.

The molecular states of interest detected in this experiment comprise the metastable molecular nitrogen triplet state  $A^3\Sigma_u^+$  and the triplet states  $B^3\Pi_g$  and  $C^3\Pi_u$ . Due to missing convenient intermediates for LIF detection of the  $C^3\Pi_u$  state and its short radiative lifetime absolute calibration was performed solely by OES comparing simultaneous LIF and OES results on the  $B^3\Pi_g$  state with the signal intensities for the  $C^3\Pi_u$  state.

### B. Method

The experimental method for absolute number density calibration of LIF detected species follows a suggestion made by P. Bogen<sup>9</sup> in 1983. In brief, the unknown absolute number density is determined by comparison between the LIF signal and a Rayleigh scattering signal from excitation of a known density of scatterers with known Rayleigh scattering cross section. For the time integrated signal intensities  $\int \Phi dt$  one can derive the dependencies on apparatus determined and molecular quantities as follows

$$\int \Phi dt \propto \sigma n P F Q \quad (1)$$

for the Rayleigh scattering and

$$\int \Phi dt \propto \sigma n P F Q \frac{g A_{ij}}{\sum_j A_{ij}} \frac{1}{1+S} \quad (2)$$

for the LIF Signal. Here,  $\sigma$  are the cross sections,  $n$  is the number density of the scatterer,  $P$  the geometrical factors depending only on the light polarization,  $F$  the filter transmission factors,  $Q$  the relative quantum efficiencies of the light detection system,  $g$  the statistical weight of the LIF transition due to other fluorescence transitions and collisional decays, the  $A_{ij}$  Einstein coefficients, and  $S$  the saturation parameter for the LIF transition. All other possible apparatus dependent parameters will cancel out when determining the number density for the LIF case via the ratio  $\int \Phi_{\text{LIF}} dt / \int \Phi_{\text{Ray}} dt$ .

In our experiment we chose molecular nitrogen in its ground electronic state  $X^1\Sigma_g^+$  to be the Rayleigh scatterer, where the molecular number density is just determined by the gas pressure inside the vessel when the discharge is off. The Rayleigh scattering cross section can be expressed via

$$\sigma = \frac{8\pi^3}{3n^2\lambda^4} |\epsilon - 1|^2 \quad (3)$$

with

$$\epsilon = 1 + 4\pi\alpha n,$$

and therefore

$$\sigma = \frac{128\pi^5 \alpha^2}{3\lambda^4}, \quad (4)$$

where  $\alpha$  is the molecular polarizability and  $\lambda$  the scattered light wavelength. The polarizability contains an isotropic

part  $\alpha_0$  and an anisotropy factor  $\kappa$  that makes  $\alpha$  depend on the angle between the molecular frame of reference and the laser polarization. Both constants  $\alpha_0$  and  $\kappa$  are given by Bridge and Buckingham<sup>11</sup> to be  $\alpha_0=1.767 \text{ \AA}^3$  and  $|\kappa|=0.1313$ . In our experiment with the laser polarization fixed in the laboratory frame we need to average over the possible molecular orientations and we will get an apparent polarizability  $\alpha$  depending on the angle between laser polarization and the  $y$  axis of detection. These are  $\alpha_{\parallel}^2=0.03072\alpha_0^2$  for the laser polarized parallel with respect to the detection axis and  $\alpha_{\perp}^2=1.02413\alpha_0^2$  for the vertical case. This polarization dependence can be used to test whether the signal in the Rayleigh reference experiment is really due to Rayleigh scattering.

The LIF cross section, on the other hand, is derived via

$$\sigma(\omega) = \frac{1}{4} \frac{g_i}{g_j} \lambda_{ij}^2 A_{ij} f(\omega, \omega_{ij}), \quad (5)$$

where  $f(\omega, \omega_{ij})$  is a line shape function assumed to be normalized Gaussian. Accordingly

$$f(\omega, \omega_{ij}) = \sqrt{\frac{4 \ln 2}{\pi \Delta \omega_d^2}} \exp\left(-4 \ln 2 \left(\frac{\omega - \omega_{ij}}{\Delta \omega_d}\right)^2\right)$$

with

$$\Delta \omega_d = \omega_{ij} \sqrt{\frac{(8 \ln 2) k_B T}{m c^2}}, \quad (6)$$

$\Delta \omega_d$  being the Doppler width for nitrogen at temperature  $T$ ,  $A_{ij}$  is again the Einstein coefficient, and  $g_i, g_j$  the respective statistical weights of the lower and upper molecular state participating in the transition.<sup>12,13</sup> The cross section  $\sigma$  is then given via integration over the line shape function and we get

$$\sigma = \sqrt{\pi \ln 2} \frac{e^2}{\epsilon_0 m_e c} \frac{f_{ij}}{\Delta \omega}$$

with

$$\Delta \omega = \sqrt{\Delta \omega_l^2 + \Delta \omega_d^2}, \quad (7)$$

where now  $f_{ij}$  is the oscillator strength and  $\Delta \omega$  the combined width of the transition due to Doppler broadening and the laser line width  $\Delta \omega_l$ . Assuming the laser line shape to be Gaussian also, the specification of its width can be verified using narrow krypton lines.  $e, \epsilon_0, m_e,$  and  $c$  are the usual natural constants. Data for  $A_{ij}$  and  $f_{ij}$  can be taken from Laux and Kruger.<sup>14</sup>

With all these theoretical formulas at hand we are now left with the experimental determination of Rayleigh and LIF signal intensities, Rayleigh scatterer number density, and the LIF saturation parameter which will be described in the next section. Before we come to that discussion we will briefly address the factors entering into our signal and therefore number density determination via OES.

The calibration via OES simply requires that similar bands can be measured via LIF, via the PMT setup without a laser using a bandpass filter to select the vibrational band in question and via using the fiber bundle, monochromator, CCD setup. By accounting for the appropriate Einstein coef-

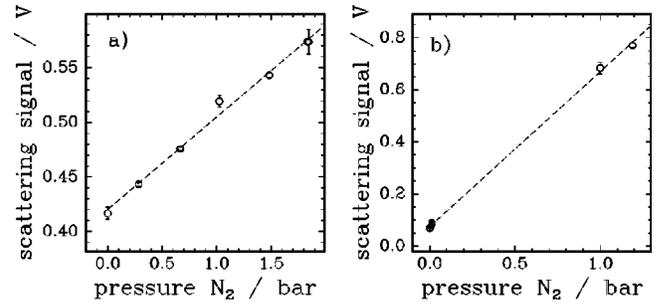


FIG. 2. Detector response of the optical system as a function of nitrogen pressure for the Rayleigh scattering experiment: (a) data taken at 686 nm for comparison with LIF for  $A^3\Sigma_u^+, v=0 \rightarrow B^3\Pi_g, v=3$ , (b) at 337 nm for comparison with  $B^3\Pi_g, v=0 \rightarrow C^3\Pi_u, v=0$ .

ficients and the fraction of fluorescence detected from the transition for each case the detector signals can easily be compared and referenced to the Rayleigh scattering measurement via the LIF experiment.

### III. RESULTS AND DISCUSSION

For the Rayleigh scattering experiment two different laser wavelengths were used. In the visible the scattering at 686 nm was measured for comparison with LIF studies on the  $A^3\Sigma_u^+, v=0 \rightarrow B^3\Pi_g, v=3$  vibrational band between 684 and 688 nm. In the UV we determined the signal at 337 nm to compare with the  $B^3\Pi_g, v=0 \rightarrow C^3\Pi_u, v=0$  vibrational band between 336 and 337.3 nm. In both cases the Rayleigh scattering was measured at different number densities corresponding to pressures of up to 5 bar and given as the detector response in volts per pressure unit [Figs. 2(a) and 2(b)].

For the LIF signal two other preparatory measurements have to be performed. A determination of relative signal yield versus incident laser power gives a saturation parameter of  $S=1.324$  for the  $A^3\Sigma_u^+ \rightarrow B^3\Pi_g$  transition and  $S=0$  for  $B^3\Pi_g \rightarrow C^3\Pi_u$  in the UV region [Figs. 3(a) and 3(b)]. Another important factor is the determination of the total population of a vibrational state in question by calculating and measuring the complete spectrum (Figs. 4 and 5) and extrapolating to this result from laser detection of a single rovibrational transition. Furthermore, for the  $A^3\Sigma_u^+ \rightarrow B^3\Pi_g$  transition excitation the radiative lifetime of the  $B^3\Pi_g$  state is long enough for quenching to compete with fluorescence decay. This has to be taken into account and we

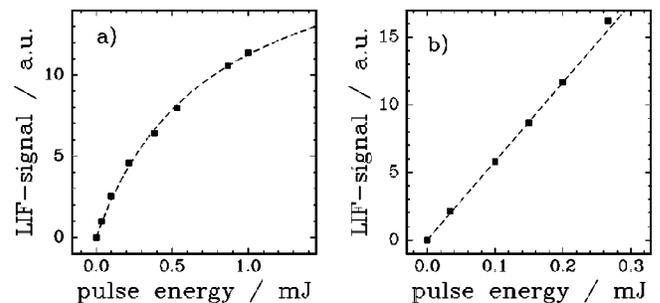


FIG. 3. Determination of the saturation parameter  $S$  for the LIF detection: (a)  $A^3\Sigma_u^+, v=0 \rightarrow B^3\Pi_g, v=3$ , (b)  $B^3\Pi_g, v=0 \rightarrow C^3\Pi_u, v=0$ .

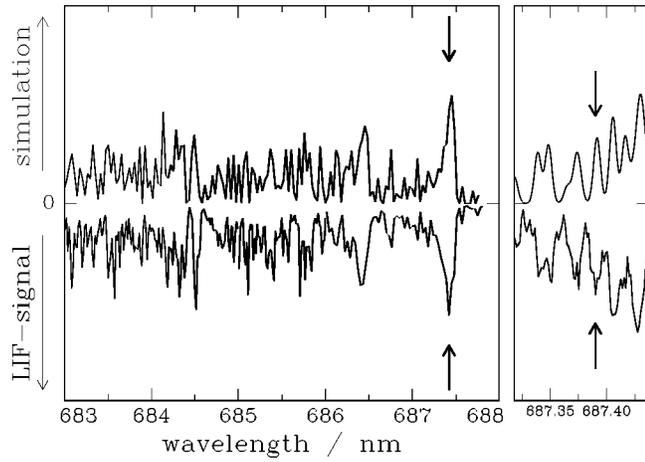


FIG. 4. Comparison of experimental (bottom) and theoretical (top) LIF spectra for  $A^3\Sigma_u^+, v=0 \rightarrow B^3\Pi_g, v=3$ . At a rotational temperature of  $340 \pm 20$  K the simulated spectra fit the observed spectra. The arrow indicates a transition used for calibration with the quantum numbers of the angular momentum  $J=7$  of  $Q_{12}$ ,  $J=9$  of  $R_{13}$ , and  $J=39$  of the  $P_{23}$  branch.

use a quenching rate constant in pure nitrogen of  $k_q = 2.54 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  (from Ref. 15) and a fluorescence rate of  $R_s = 1.208 \times 10^5 \text{ s}^{-1}$  derived from the known Einstein coefficients.

If we now measure the fluorescence signal for different vibrational bands at different positions  $z$  from the driven rf-electrode we arrive at a peak density of  $9 \times 10^{11} \text{ cm}^{-3}$  for the  $A^3\Sigma_u^+, v=0$  state at a gas pressure of 50 Pa and an effective discharge voltage around 100 V. Further results are depicted in Fig. 6 and given in Table I, the latter showing them in comparison with results by De Benedictis *et al.*<sup>16</sup> derived in a parallel-plate, pulsed discharge afterglow experiment. The order of magnitude and relative behavior agree well with their data taking into account their gas pressure being lower and the discharge setup being quite different.

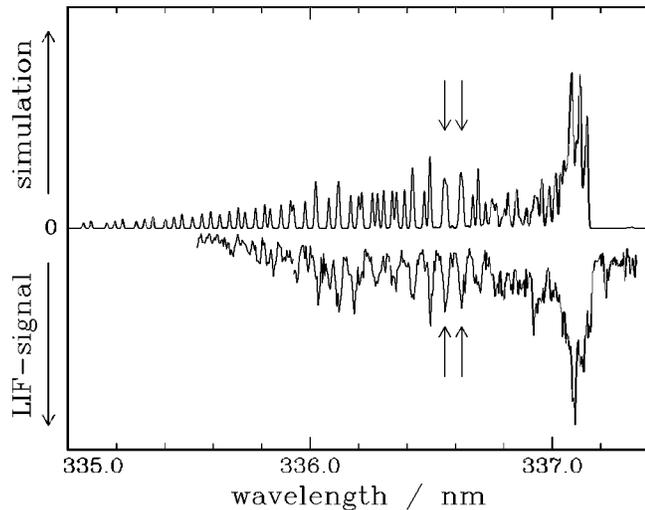


FIG. 5. Comparison of experimental (bottom) and theoretical (top) LIF spectra for  $B^3\Pi_g, v=0 \rightarrow C^3\Pi_u, v=0$ . At a rotational temperature of  $340 \pm 20$  K the simulated spectra fit the observed spectra. The arrows indicate transitions used for calibration with the quantum numbers of the angular momentum  $J=5$  and  $J=6$  of the  $R$  branch ( $R_1, R_2, R_3, f+e$ ).

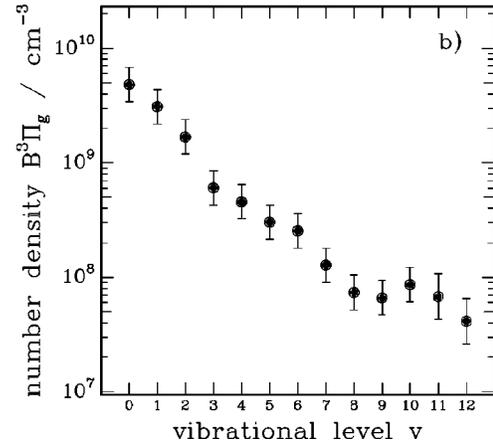
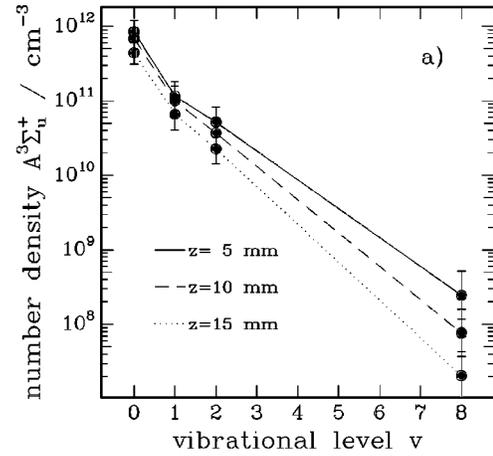


FIG. 6. Absolute density values for different vibrational states: (a) for the metastable  $A^3\Sigma_u^+$  and (b) for the  $B^3\Pi_g$  state of triplet nitrogen. The values for the  $A^3\Sigma_u^+$  state are indicated for different distances  $z$  from the driven rf-electrode.

TABLE I. Absolute number densities, given in  $\text{cm}^{-3}$ , of different vibronic states of triplet nitrogen molecules. The data are given for the maximum of the  $z$ -dependent distribution function, which for some states falls inside the sheath region, and are valid for a nitrogen pressure of 50 Pa and an effective discharge voltage of 100 V. Missing values were not determined, the error is estimated to be less than 20%. In comparison with results by De Benedictis *et al.* (Ref. 16).

Vibrational state	Number density $n$ in $\text{cm}^{-3}$			
	$A^3\Sigma_u^+$	$B^3\Pi_g$	$C^3\Pi_u$	$A^3\Sigma_u^+$
0	$9.2 \times 10^{11}$	$4.8 \times 10^9$	$1.5 \times 10^6$	$1 \times 10^{11}$
1	$1.3 \times 10^{11}$	$3.1 \times 10^9$	$8.7 \times 10^5$	$2.7 \times 10^{10}$
2	$5.3 \times 10^{10}$	$1.7 \times 10^9$	$3.0 \times 10^5$	$1.7 \times 10^{10}$
3		$6.0 \times 10^8$		$1.6 \times 10^{10}$
4		$4.5 \times 10^8$		$9 \times 10^9$
5		$3.0 \times 10^8$		$3 \times 10^9$
6		$2.5 \times 10^8$		$4 \times 10^9$
7		$1.3 \times 10^8$		$4 \times 10^8$
8	$2.7 \times 10^8$	$7.2 \times 10^7$		$6 \times 10^8$
9		$6.5 \times 10^7$		$3 \times 10^8$
10		$8.5 \times 10^7$		
11		$6.7 \times 10^7$		
12		$4.1 \times 10^7$		

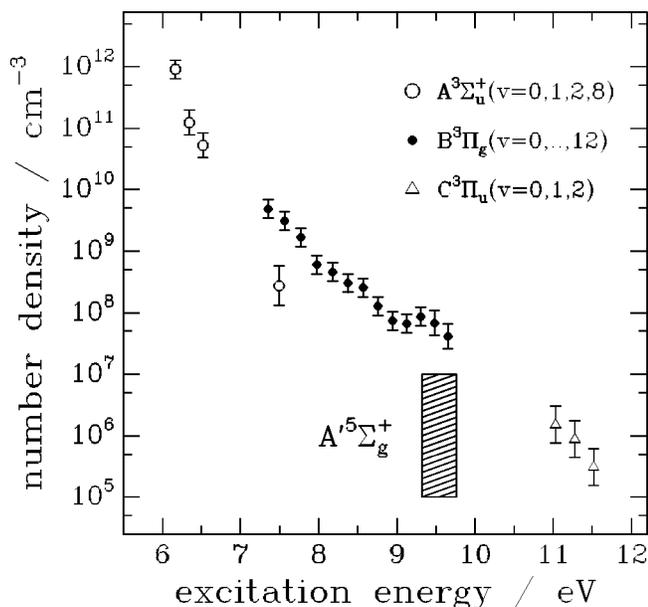


FIG. 7. Comparison of the density values of the  $A^3\Sigma_u^+$ ,  $B^3\Pi_g$ , and  $C^3\Pi_u$  state as a function of excitation energy above the nitrogen ground state. Note the overpopulation for  $A^3\Sigma_u^+, v=0,1$  and  $B^3\Pi_g, v=9\cdots 12$  and underpopulation for  $A^3\Sigma_u^+, v=8$ .

Number densities for the  $B^3\Pi_g, v=0$  state under our conditions are around  $5 \times 10^9 \text{ cm}^{-3}$  and for the  $C^3\Pi_u, v=0$  state derived from OES measurements are in the  $(1 \text{ to } 2) \times 10^6 \text{ cm}^{-3}$  range.

Apart from the determination of absolute number densities in this experiment other interesting results can be gleaned from the data. If we plot the number densities of all states measured as a function of their average excitation energy with respect to the nitrogen ground state, Fig. 7, we get an almost exponential falloff towards high energies. This behavior is due to an interplay between several different factors.

First, the apparent lifetimes of each state in the plasma, which depend on the different radiation lifetimes and quenching rates. The radiation lifetime decreases with increasing excitation energy from the  $A^3\Sigma_u^+$  to  $B^3\Pi_g$  to  $C^3\Pi_u$  state, just as the cross section for quenching increases along the same line.

Second, density piles up in states with small excitation energies due to radiation cascade processes. The dominant loss process for, i.e., the  $C^3\Pi_u$  state is radiation decay into the  $B^3\Pi_g$  state, for which this, in turn, is an important production process. We can expect a similar behavior between the  $B^3\Pi_g$  and  $A^3\Sigma_u^+$  state.

Lastly, cross sections for excitation by electron impact vary over several orders of magnitude for the three triplet states and depend on electron kinetic energy. This energy distribution itself varies strongly with spatial location in the discharge. We mapped out by measurements and qualitative modeling in our group the resulting effect on the spatial distributions of the triplet states.<sup>17</sup> The results of this aspect of our studies will be published later.

Another interesting result is the deviation from this exponential falloff behavior indicated by the apparent pileup of

intensity for  $A^3\Sigma_u^+, v=0$  and, less so, for  $A^3\Sigma_u^+, v=1$  but also in apparent overrepresentation of  $B^3\Pi_g, v=9\cdots 12$ . The former should be explained by the very long radiative lifetime of  $A^3\Sigma_u^+, v=0,1$  of about 2 s where it acts as a final pool for higher lying triplet states being deexcited in radiative cascades or collisions and to the inefficient conversion of  $A^3\Sigma_u^+, v=0,1$  into singlet ground state nitrogen via collisions. The latter deviation, surplus number density of  $B^3\Pi_g, v=9\cdots 12$ , can be attributed to, again, very inefficient quenching of these states compared to an extrapolation of the rates for the  $B^3\Pi_g, v=0\cdots 8$  states.<sup>15</sup> In addition, previous experiments have shown that  $B^3\Pi_g, v>9$  is coupled to a state of the quintet manifold,  $A'^5\Sigma_g^+$ , which is also metastable.<sup>18</sup> Population into this state is continuously refed via recombination of two ground state nitrogen atoms. The lowered density of  $A^3\Sigma_u^+, v=8$  compared to the  $B^3\Pi_g$  states of similar excitation energy is due to a more efficient quenching of  $A^3\Sigma_u^+, v=8$  by singlet ground state nitrogen. This process is very inefficient<sup>19,20</sup> for  $A^3\Sigma_u^+, v\leq 2$ .

#### IV. SUMMARY AND OUTLOOK

Absolute number densities of triplet nitrogen molecules were measured by calibration of LIF experiments with data from Rayleigh scattering on ground state nitrogen molecules using the same apparatus. Absolute values for the densities of different vibronic states show comparable magnitude and state dependence as previous data from a parallel-plate, pulsed discharge afterglow. In our case, however, data were accumulated *in situ* in an rf-driven low pressure plasma and can be viewed as online monitoring of the important sheath region close to the surface in an rf-process plasma. Relative density profiles as a function of distance  $z$  from the driven rf-electrode can already be explained using a simple excitation-quenching/reaction-diffusion model which is the topic of another, forthcoming publication. Modeling of absolute number densities should in principle be amenable to particle-in-cell Monte Carlo simulations which are at present outside our own capabilities, unfortunately. Further support by theory is dearly needed.

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