Quenching of \( \text{N}_2(\text{C}^3\Pi_u) \) in nanosecond discharge with high specific energy deposition

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Abstract: The depopulation mechanisms of the \( \text{N}_2(\text{C}^3\Pi_u) \) are investigated in a nanosecond discharge in a capillary tube. It is found that an additional collisional mechanism appears and dominates at high specific deposited energy. It is shown that the anomalously high deactivation of the \( \text{N}_2(\text{C}^3\Pi_u) \) can be explained by the quenching by electrons, and that the high electron densities can be sustained by reaction of associative ionization.

Keywords: nanosecond capillary discharge, high deposed energy

1. Introduction

Electronically excited species can be considered as highly reactive components produced by plasma. In air, for example, the collisional energy transfer from the excited \( \text{B}^3\Pi_g \), \( \text{C}^3\Pi_u \) states of molecular nitrogen to oxygen molecules, followed by \( \text{O}_2 \) dissociation, is a major reaction channel leading to fast gas heating [1] and the formation of \( \text{O} \) atoms [2].

It results from this observation that the knowledge of quenching reaction pathways and their associated rate constants is necessary in order to predict accurately the behavior of a highly reactive plasma in a given environment, and the efficiency of the plasma for a given application. In addition to this fact, the emission from radiative excited states is extensively used in plasma diagnostics, both for the quantitative detection of active species [2] and the measurement of plasma parameters [3]. Taking into account quenching effects properly is a requirement in order to perform such diagnostics successfully.

This study is dedicated to the measurement and modeling of the collisional deactivation rate of the \( \text{N}_2(\text{C}^3\Pi_u, v = 0) \) state at the conditions of high specific energy deposition, in a nanosecond discharge in pure nitrogen. The effect of a varying energy deposition on the quenching rate will be analyzed, and results will be compared to 0D detailed kinetic modeling to determine the possible nature of the quenching processes involved in such conditions.

2. Experimental setup

To get different values of deposited energy, the discharge was initiated in different volumes and with different end loads. Three experimental configurations were considered: (1) quartz capillary tube 1.5 mm in inner diameter and 68 mm of inner electrode distance with a 50 Ohm cable load; (2) quartz capillary tube 4 mm in inner diameter and 50 mm of interelectrode distance with a 50 Ohm cable load; (3) the same tube with \( R = \infty \) load (see Fig. 1).

The applied voltage pulses with 20 ns FWHM, 13 kV amplitude and 2 ns rise time (negative polarity) or 30 ns FWHM, 10 kV and 4 ns rise time (positive polarity) are used. Three pulses separated by 250 ns arrive to the HV electrode due to successive reflections between the generator and the discharge assembly. A fourth pulse at 670 ns is caused by an additional 3.8 kV pulse produced by the generator. Incident, reflected and transmitted currents are measured by two back current shunts, BCS1 and BCS2, mounted into the shield of the HV and LV cables, respectively, at 12.5 m distance from the discharge cell.

The pressure of the \( \text{N}_2 \), flowing at a 10 - 50 sccm rate, is varied from 4 to 50 mbar. Nitrogen (Air Liquide) with stated total impurities below 10 ppm is used in the experiment.

The (0-0) transition of the second positive system is observed, with band head at 337.1 nm [4]. The optical emission from the discharge is collected directly by the
entrance slit of an Andor SR500 Czerny-Turner monochromator with 500 mm focal length, through a 1 cm orifice in the grounded screen, without any focusing lens. A 1200 1/mm grating is used, resulting in a reciprocal dispersion of 1.7 nm/mm. The light is detected by a Hamamatsu H6610 photomultiplier tube (PMT), with typical rise time of 0.7 ns and transit time spread of 0.16 ns. Both slits are 100 µm wide; as a result, the optical resolution of this system is 0.4 nm FWHM, as checked with a mercury lamp.

3. Results
To check reliability of the measurements, the N₂(C₃Πᵥ, v = 0) emission decay at 337.1 nm was measured for different deposited energies. For the discharge tube 4 mm in diameter and $R = \infty$ load, the energy was the smallest between the experimental cases. These experimental conditions will further be referred to as “no transmitted current” case. The measurements show that in this case the decay of the light pulse is single-exponential, see dashed line in Fig. 2, and the measured lifetime is slightly faster than the predicted one, caused by quenching by ground state of N₂ and radiative decay [5], see dash-dot line in Fig. 2. This disagreement is more pronounced at higher specific deposited energies, for example, in case of 1.5 mm capillary at the presence of transmitted current (50 Ohm cable load) to the LV electrode. Increase of specific deposited energy also leads to the fact that the depopulation of the N₂(C₃Πᵥ, v = 0) state is not described by a single exponent anymore. At 27 mbar the decay rate is twice higher at the beginning of the pulse, than at the end, see the solid line in Fig. 2.

Further measurements show that the decay rate of the N₂(C₃Πᵥ, v = 0) emission is the highest for the first pulse, and so, corresponds to the highest energy release. Fig. 3 presents the decay rate for different pressures and different discharge configurations. The decrease of the decay rate for the following pulses (pulses with smaller energy) is clearly seen. It is also seen that the presence of transmitted current (increase of deposited energy) clearly increases the decay rate for all pulses, compared to the case when there is no transmitted current.

Fig. 3. Decay rates with and without (denoted by "nt") transmitted current, in the 4 mm capillary, for negative polarity pulses, in pure N₂ for different pressures. The error bars caused by the fitting procedure are always smaller than the symbols. Solid straight line (“theor.”) stands for the sum of radiative decay and quenching of N₂(C₃Πᵥ, v = 0) by N₂ in the ground state [5].

4. Discussion
The fact that the observed emission is not affected by absorption or stimulated emission was proved in [6], where five wavelengths from 337.2 to 335.6 nm in steps of 0.4 nm were used and the corresponding emission profiles were monitored. In [6] it was suggested that the anomalously high deactivation of the N₂(C₃Πᵥ, v = 0) state is caused by collisions with another species. This species can be electrons, or vibrationally or electronically excited N₂. Indeed, the N₂ dissociation degree is expected to be small, because of the high energetic cost [7] of production of N atoms at reduced electric fields of 100 - 300 Td typical for this discharge [8]. As a result, quenching on N atoms, whether in their ground or excited state, is unlikely to be the main cause of the observed high decay rate in the first pulse.

The possibility of the quenching of the N₂(C₃Πᵥ, v = 0) state by electrons in the FIW, mostly to the N₂(B¹Π₅) state, was first proposed in [5], to explain the complex behavior of the observed decay rate with gas pressure, that was obtained for pressures below 4 Torr. An order of magnitude of the quenching rate constant of about

Fig. 2. PMT signal for pure N₂ at 20.5 mbar in 4 mm tube without transmitted current at low deposited energy (dashed line) and for 27 mbar in 1.5 mm tube with transmitted current, at high deposited energy (solid line). Both are for 13 kV negative polarity pulses. Dash-dot line corresponds to quenching by ground state of N₂ and radiative decay [5] for pure N₂ at 20.5 mbar.
\[ k_{ec} = (5 - 10) \cdot 10^{-8} \text{cm}^3\text{s}^{-1} \] was estimated for this process, for a 1 eV electron temperature:

\[ e + N_2(C^3Π_u^-) \rightarrow k_{ec} \rightarrow e + N_2. \] (1)

In our paper, to check the reliability of the quenching by electrons, a numerical modeling has been performed. Kinetics of charged, electronically exited and neutral species was taken into account similar to [9]. The model is described in detail in [10]. Experimentally obtained dependence of electrical current vs time was taken as the initial date. The interpolated current is presented in Fig. 4.

The densities of main exited species and the electron density as a function of time are given by Fig. 5. At the conditions of high specific energy, the densities of the exited nitrogen species are high (see Fig. 5), and so, the reacting of associative ionization with \( N_2(A^3Σ^+u^-) \) and \( N_2(a'^1Σ^-u^-) \) molecules become important:

\[ N_2(A^3Σ^+u^-) + N_2(a'^1Σ^-u^-) \rightarrow N_4^+ + e, \] (2)

\[ N_2(a'^1Σ^-u^-) + N_2(a'^1Σ^-u^-) \rightarrow N_4^+ + e. \] (3)

High electron densities after the discharge are explained by production of charged species in the reactions (2), (3).

As far as the rate constant of the reaction (1) is not well-known, the calculations were made for \( k_{ec} = 9 \cdot 10^{-8} \text{cm}^3\text{s}^{-1} \) (curve (2) in the Fig. 6) and \( 5 \cdot 10^{-8} \text{cm}^3\text{s}^{-1} \) (curve (3)). In addition, the results of \( N_2(C^3Π_u^-) \) quenching without taking into account the reaction (1) are given in Fig. 6 (curve (4)).

The modelled emission profiles are in good agreement with PMT signal obtained at similar conditions in the experiment only if the quenching by electrons is taken into account. Thus, we can state that the anomalously high deactivation of the \( N_2(C^3Π_u^-) \) at conditions of high specific energy deposition is most likely connected to collisions with the electrons.

**Fig. 4.** The approximation of the transmitted current measured at 27 mbar in pure \( N_2 \).

**Fig. 5.** Temporal dynamics of electronically excited states of nitrogen at 27 mbar in pure \( N_2 \) with the transmitted current pulse presented in Fig. 4.

**Fig. 6.** Temporal dynamics of \( N_2(C^3Π_u^-) \) at 27 mbar in pure \( N_2 \) with the transmitted current pulse presented in Fig. 4. Curve (1) corresponds to PMT signal in arbitrary units, curves (2) - (4) correspond to numerical calculations with the quenching rate constant \( k_{ec} \) equal to \( 9 \cdot 10^{-8} \text{cm}^3\text{s}^{-1} \), \( 5 \cdot 10^{-8} \text{cm}^3\text{s}^{-1} \) and 0, respectively.

**5. Conclusions**

The decay rate of the \( N_2(C^3Π_u^-) \) state was measured for different total gas densities and different specific deposited energies, initiated in discharge tubes of different diameters. It was shown that in conditions when the specific deposited energy is high, the observed decay rate is significantly higher than predicted value, based on radiative decay and quenching by ground state \( N_2 \). Moreover, the high specific energy deposition can cause the fact that the deactivation of the \( N_2(C^3Π_u^-) \) state is not described by a single exponential decay.
Using 0D numerical modelling and experimentally measured dependence of electrical current upon time, it was shown that the observed emission decay can be explained by the quenching by electrons with the rate constant \( k_C = (6-7) \times 10^{-8} \text{ cm}^3\text{s}^{-1} \). High electron density in the early afterglow is sustained by reactions of associative ionization.

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7. References