J. Phys. D: Appl. Phys. **39** (2006) 2636–2639 doi:10.1088/0022-3727/39/12/N01

REPLY

Reply to comments on 'Intensity ratio of spectral bands of nitrogen as a measure of electric field strength in plasmas'

P Paris[1], M Aints[1], F Valk[1], T Plank[1], A Haljaste[1], K V Kozlov[2] and H-E Wagner[3]

[1] Institute of Experimental Physics and Technology, University of Tartu, Tähe 4, 51010 Tartu, Estonia

[2] Department of Chemistry, Moscow State University, 119899 Moscow, Russia

[3] Institute of Physics, Ernst Moritz Arndt University of Greifswald, Domstrasse 10A, D-17489 Greifswald, Germany

Received 21 March 2006, in final form 28 April 2006
Published 2 June 2006
Online at stacks.iop.org/JPhysD/39/2636

Abstract
It is argued that the experimental results presented by Paris *et al* in *J. Phys. D: Appl. Phys.* (2005) **38** 3894 are correct. It is shown that there is no evidence of filamentation or local electric field reinforcement in discharge. It is discussed that reaction scheme and rate constants for deactivation of excited nitrogen ion N_2^+ proposed by Pancheshnyi in his Comment must be specified for conditions corresponding to the experiment carried out by Paris *et al* .

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In his comments [1] Pancheshnyi points out that in our paper [2] the three-body collision process N_2^++N_2+M→N_4^++M is not taken into account as a deactivation process of excited N_2^+. Pancheshnyi presents a modified formula (equation (9) in [1]) for the deactivation mechanism, where three-body collisions are also considered. However, if this new formula is used for reduction of intensity ratios to the standard conditions, then the values of intensity ratio R, measured by Paris *et al* at different pressures, do no longer lie on a single curve $R_{\text{reduced}} = f(E/N)$ in contrast to the case of using reduction formula (1) in the paper [2]. Pancheshnyi suggests that the authors of the paper [2] have determined the intensity ratios of spectral bands as a function of the field strength incorrectly: the actual values of the field strength may deviate significantly from those presented in the paper [2]. '*It could be a partial filamentation of the discharge or local electric field reinforcement near the imperfections of the electrode surfaces that becomes apparent at very low-distance measurements*', claims Pancheshnyi.

In this reply we argue for the correctness of our experiment; we add some details to the description of the experimental set-up and briefly discuss the role of the three-body collisions in quenching excited states of nitrogen ions.

2. Absence of filamentation

The anode was polished with an abrasive (grain size 0.2 μm) to mirror quality. The local unevenness of the finished surface should be less than the grain size. The enhanced electric field near the protrusions of 0.2 μm in size could stretch into the inter-electrode space up to about 1 μm from the electrode surface. The mean free path of an electron in air at atmospheric pressure is about 0.5 μm and it increases with a decrease in pressure [3]. Thus, on average, an electron can undergo two or less collisions in the enhanced field near the anode. The electron energy distribution function remains invariable at such a short distance in this region and retains the shape obtained in the uniform field between the electrodes. As a result, the spectral distribution of the radiation from this near-anode region should be the same as that generated

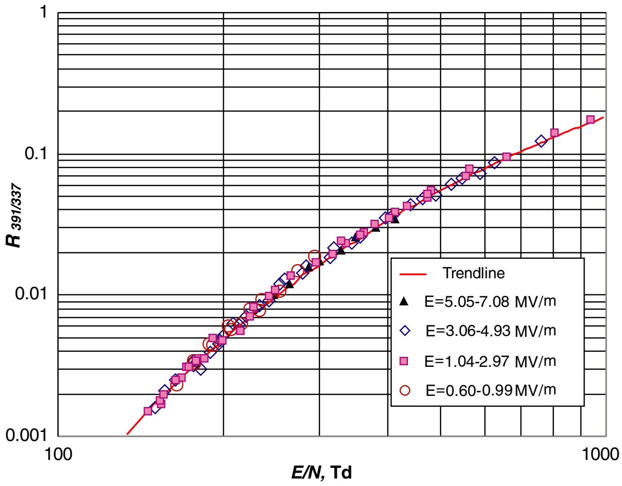

Figure 1. The intensity ratio $R_{391/337}$ as a function of E/N in the pressure range 13–99 kPa. The trendline is calculated according to formula (4) in [2].

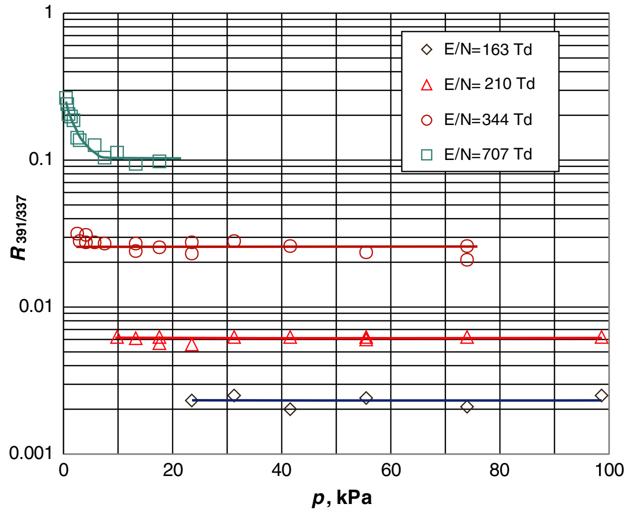

Figure 2. The ratio $R_{391/337}$ as a function of pressure p.

in the undisturbed field region. Moreover, as the region of the enhanced field forms a small part of the discharge gap with the undisturbed homogeneous field, the radiation from this region constitutes only a small fraction of the total radiation.

We have examined the discharge visually and photographically. The discharge was uniform in the plane parallel to the electrodes. No filamentation was found. The intensity distribution was determined by photos for the inter-electrode distances 1, 2 and 4 mm. The radiation intensity increased exponentially towards the anode. In the case of filamentation, the exponential intensity distribution should be distorted.

The cathode was a semi-transparent aluminium film evaporated on a quartz plate of optical quality. Imperfections on the cathode could also cause discharge filamentation due to the increased electron emission in the enhanced electric field. If the macroscopic electric field exceeds the value of about 10^7 V m^{-1}, a considerable field emission of electrons from the cathode would occur [4]. In our experiment, the electric field strength never exceeded the value of 7.8×10^6 V m^{-1}.

In figure 1, the intensity ratio $R_{391/337}$ is plotted as a function of E/N. The experimental points in figure 1 are obtained at different values of E. The local increase in E may lead to filamentation if field emission takes place. In the case of filamentation the electric field between electrodes as well as gas density and temperature should become non-uniform and changes in R should appear. The absence of deviation of R with the variation of E at $E/N =$ const is also an indirect indication of the absence of filamentation in our discharge cell.

Pancheshnyi suspects that our evaluation of the field strength is incorrect at short inter-electrode distances, where the role of the field enhancement might be more pronounced. To demonstrate the absence of that kind of shortcoming, we selected the intensity ratios for the inter-electrode distances greater than 1 mm. These ratios do not differ from those obtained at the shorter distances.

We also varied the discharge current within the limits of 0.5–16 μA. The radiation intensity was proportional to the current. The intensity ratio of the spectral bands was independent of the discharge current. The values of R obtained at different current strengths were within the limits of measurement uncertainty, the same as presented in paper [2]. The last result demonstrates the absence of a field distortion caused by current carriers in the gap.

3. Rate constant of the quenching reaction

According to the model proposed by Pancheshnyi, the intensity ratio R must depend quite strongly on pressure. In figure 2, we present the measured ratio R at fixed fields as a function of pressure. The absence of pressure-dependence of R in the pressure range 10–100 kPa shows that the three-body processes proposed by Pancheshnyi should have a minor effect on the quenching. In our opinion, the reasons for the discrepancy between our results and Pancheshnyi's model may be an unsuitable reaction scheme and inappropriate values of rate constants of reactions considered by Pancheshnyi.

Pancheshnyi used the value of rate constant $k_{\mathrm{conv}} = 5.0 \cdot 10^{-29}$ cm^6 s^{-1} with reference to Kossyi *et al* [5]. Kossyi refers to the handbook [6], which in its turn refers to different papers. We have selected some original papers dealing with the ion conversion reaction under consideration. The values of k_{conv} from these papers are presented in the table 1.

All these values of k_{conv} are obtained under low pressure conditions with pressure $p < 13$ Torr. Warneck [7] is of the opinion that the conversion reaction under discussion can change into a two-body reaction under high enough pressure: '*In view of the attachment nature of this reaction, the participation of a third body is required to stabilize the resultant N_4^+ ion. However, at sufficiently high pressures, the reaction can become effectively bimolecular if the lifetime of the N_4^+ complex is longer than the mean free flight time of the ions between collisions so that stabilization is always effective*' [7]. Thus, the use of those k_{conv} for higher pressures must be justified.

It is evident from papers [8–10] that k_{conv} depends on the reduced field strength E/N. The value $k_{\mathrm{conv}} = 5.0 \cdot 10^{-29}$ cm^6 s^{-1} used by Pancheshnyi is likely determined for

Table 1. Rate constant of the ion conversion reaction $N_2^+ + 2N_2 \rightarrow N_4^+ + N_2$.

No	k_{conv}, 10^{-29} cm^6 s^{-1}	Ref.	Comments
1	8.5	[7]	$T = 300$ K, $p = 0.09$–0.2 Torr, E–undetermined but probably low, mass-spectrometry
2	8	[8]	$T = 300$ K, $p = 0.5$–3.5 Torr, $E = 0$
3	7.0 ($E/N = 50$ Td) 5.5 ($E/N = 80$ Td) 4.0 ($E/N = 110$ Td) 2.0 ($E/N = 180$ Td)	[9]	$T = 300$ K, $p = 0.5$–1 Torr, $E/N = 15$–200 Td, drift tube
4	$5.0 \rightarrow 2.0$ ($E/N = 0 \rightarrow 90$ Td)	[10]	$T = 300$ K, $p = 0.1$–0.4 Torr, $E/N = 0$–90 Td, drift tube, mass-spectrometry
5	$6.8 \cdot (300/T)^{1.64}$	[11]	$T = 45$–400 K, $p = 0.2$–3 Torr, $E/N = 0$–75 Td, increase in E/N is accounted as temperature increase
6	5.83	[12]	$p = 1$–13 Torr, $E/N = 0$, laser-induced fluorescence

zero field. The value of k_{conv} decreases with the increase in E/N and reaches the value of $2 \cdot 10^{-29}$ cm^6 s^{-1} for E/N = 90 Td (row 4 in table 1) or for 180 Td (row 3 in table 1). In our experiments, the reduced field strength E/N had values in the range 150–5000 Td. Thus, in our conditions, the value of k_{conv} should be lower than that used by Pancheshnyi and it probably changes with E/N.

It follows from the experimental conditions described in papers [6–10] that k_{conv} presented in these papers is related to the ground electronic state of N_2^+. In the opinion of Pancheshnyi, the conversion rate of ions in the $N_2^+(B^2\Sigma_u^+, v = 0)$ state should differ insignificantly from that of the ions in the ground state [13]. However, an experimental justification of this opinion is absent up to now.

The use of the value of k_{conv} proposed by Pancheshnyi for the three-body quenching seems to be unjustified for our experimental conditions. Instead of the conversion we have to consider the collisional deactivation of $N_2^+(B^2\Sigma_u^+, v = 0)$ that also takes into account the three-body collisions. The collisional deactivation rate for $N_2^+(B^2\Sigma_u^+, v = 0)$ for higher pressures (in the range 1–600 Torr) was determined experimentally in paper [14]. It turned out that the quenching of the $N_2^+(B^2\Sigma_u^+, v = 0)$ state in pure nitrogen follows the Stern–Volmer relationship for the two-body processes. Significant deviation from a straight line appeared on the Stern–Volmer plot in air at pressures above 100 Torr, which indicates the presence of the three-body processes. It was ascertained that in the three-body process, leading to the quenching of excited nitrogen ions, at least one of the colliding molecules must be O_2. The authors of the paper [14] proposed an equation for the fraction of excited ions that radiate. Using the same notation as Pancheshnyi, this equation takes the following form:

$$g_{391} = (1 + \tau_0(n_{N2}k_{q,N2} + n_{O2}k_{q,O2})N + k_{q,3}n_{O2}N^2)^{-1}. \quad (1)$$

Here, n_{N2} and n_{O2} are the relative number densities of nitrogen and oxygen ($n_{N2} = 0.78$ and $n_{O2} = 0.21$ for air), τ_0 is the radiative lifetime of a nitrogen ion in the state $(B^2\Sigma_u^+, v = 0)$, N is the gas number density, $k_{q,N2}$ and $k_{q,O2}$ are the rate constants of quenching by nitrogen and oxygen molecules in two-body collisions and $k_{q,3}$ is the rate constant for a three-body collisional quenching, where an oxygen molecule participates as one of colliding particles. The value of this rate constant is $k_{q,3} = 3.1 \cdot 10^{-29}$ cm^6 s^{-1}, determined for zero field ($E/N = 0$) [14]. Note that the last term in formula (1) includes the factor n_{O2} instead of n_{N2} in formula (9) of the comments. If we use the formula presented above with the values of the rate constants and lifetimes presented in [14] (they differ from those used by Pancheshnyi) for reduction of our measured values of $R_{391/337}$ to standard conditions, then all points obtained at different pressures will lie on a single curve. This curve coincides with our previous curve presented in the paper [2] within limits of measurement uncertainties.

The discrepancy between our measurements and theoretical calculations (the numerical solution of the Boltzmann equation) is limited by the accuracy of the cross-sections used. Scattering of the results of different authors presented in figure 6 of our original paper [2] is a good demonstration of this limitation. Some problems arising with the calculations and with the comparison of results of different authors are described in our previous paper [15].

4. Conclusions

Our present conclusion is that the deactivation mechanism of $N_2^+(B^2\Sigma_u^+)$ in air is not clear enough and the values of the rate constants are not known sufficiently well for different experimental conditions. The E/N dependence of the rate constants is especially poorly investigated.

We are of the opinion that our experimental results presented in the paper [2] are correct. The discrepancy between our results and model proposed by Pancheshnyi is caused by uncertainties in reaction schemes and rates.

The discrepancy between our measurements and the theoretical values of other authors is also due to the limited accuracy of the cross-sections used.

We are convinced that our formula (4) in [2] is correct and valid for the standard conditions. However, the g-factor for the $N_2^+(B^2\Sigma_u^+)$ state must be specified more precisely.

Acknowledgments

We are grateful to Professor S Pancheshnyi for drawing attention to the absence of the three-body reaction in our treatment of the quenching process.

The results presented in this reply are based on research that has been supported by the Estonian Science Foundation (Grant No 5675).

References

[1] Pancheshnyi S 2006 Comments on 'Intensity ratio of spectral bands of nitrogen as a measure of electric field strength in plasmas' *J. Phys. D: Appl. Phys.* **39** 1708–10

[2] Paris P, Aints M, Valk F, Plank T, Haljaste A, Kozlov K V and Wagner H-E 2005 Intensity ratio of spectral bands of nitrogen as a measure of electric field strength in plasmas *J. Phys. D: Appl. Phys.* **38** 3894–9

[3] Badaloni S and Gallimberti I 1972 Basic data of air discharges *Universita di Padova Report* Upee-72/05

[4] Dutton J 1978 Spark breakdown in uniform fields *Electrical Breakdown of Gases* ed J M Meek and J D Craggs (Chichester: Wiley)

[5] Kossyi I A, Kostinsky A Yu, Matveyev A A and Silakov V P 1992 Kinetic scheme of the non-equilibrium discharge in nitrogen-oxygen mixtures *Plasma Sources Sci. Technol.* **1** 207–20

[6] Bortner M A and Bauer T (eds) 1978 *Defence Nuclear Agency Reaction Rate Handbook, 2nd edn* 1948H (General Electric, TEMPO) ch 24

[7] Warneck P 1967 Studies of ion-neutral reactions by a photoionization mass-spectrometer technique *J. Chem. Phys.* **46** 502–12

[8] Good A, Durden D A and Kebarle P 1970 Ion-molecule reactions in pure nitrogen and nitrogen containing traces of water at total pressure 0.5-4 torr. Kinetics of clustering reactions forming $H^+(H_2O)_n$ *J. Chem. Phys.* **52** 212–20

[9] McKnight L G, McAfee K B and Sipler D P 1967 Low-field drift velocities and reactions of nitrogen ions in nitrogen *Phys. Rev*. **164** 62–70

[10] Moseley J T, Snuggs R M, Martin D W and McDaniel E W 1969 Mobilities, diffusion coefficients, and reaction rates of mass-identified nitrogen ions in nitrogen *Phys. Rev.* **178** 240–8

[11] Böhringer H and Arnold F 1982 Temperature dependence of three-body association reactions from 45 to 400 K. The reactions $N_2^+ + 2N_2 \rightarrow N_4^+ + N_2$ and $O_2^+ + 2O_2 \rightarrow O_4^+ + O_2$ *J. Chem. Phys.* **77** 5534–41

[12] Frost M J and Sharp C R J 2001 Time-resolved kinetic studies of the $N_2^+ + N_2$ association reaction *Phys. Chem. Chem. Phys.* **3** 4536–41

[13] Pancheshnyi S V, Sobakin S V, Starikovskaya S M and Starikovskii A Yu 2000 Discharge dynamics and the production of active particles in a cathode-directed streamer *Plasma Phys. Rep.* **26** 1054–65

[14] Mitchell K B 1970 Fluorescence efficiencies and collisional deactivation rates for N_2 and N_2^+ bands excited by soft X rays *J. Chem. Phys.* **53** 1795–802

[15] Paris P, Aints M, Laan M and Valk F 2004 Measurement of intensity ratio of nitrogen bands as a function of field strength *J. Phys. D: Appl. Phys.* **37** 1179–84