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LIF measurement of the collision quenching of $N_2^+(B^2\Sigma_u^+, v=0)$ by N_2 and O_2 in a short-pulse discharge

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The determination of the electric field strength in a discharge by spectroscopic methods is an old issue that is nowadays receiving renewed attention, in both low and high pressure discharges. In air or, more generally, in nitrogen containing discharges, this is achieved by looking at emissions belonging to the Second Positive System (SPS) of N_2: $C^3\Pi_u \rightarrow B^3\Pi_g$ and to the First Negative System (FNS) of N_2^+: $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$. The intensity ratio of these two emissions is very sensitive to the mean electron energy, and then to the reduced electric field E/N, due to the large difference of excitation thresholds of the two excited states, 11.03 eV for $N_2(C^3\Pi_u, v=0)$ and 18.7 eV for $N_2^+(B^2\Sigma_u^+, v=0)$. The emission ratio is proportional to the ratio of the populations of the emitting states. Populations are calculated at the stationary state as the ratio of excitation and quenching rates. Excitation rates are calculated by solving the Boltzmann equation with the proper cross sections, with the reduced electric field - E/N - as a parameter, in the hypothesis of local field approximation. A working hypothesis is that both $N_2(C^3\Pi_u)$ and $N_2^+(B^2\Sigma_u^+)$ are excited by electron impact with ground state nitrogen molecules. E/N is deduced from the best match of calculated and measured SPS and FNS emission ratio. As pressure increases the collision quenching overcomes the radiative quenching and becomes dominant at atmospheric pressure for both emitting states. The accurate knowledge of collision quenching rate constants is then of fundamental importance. In [1] the data of [2] and [3] were adopted for the collision quenching of $N_2(C^3\Pi_u)$ and $N_2^+(B^2\Sigma_u^+)$ respectively. Later in [4] it was pointed out that the associative ion conversion, $N_2^+(B^2\Sigma_u^+, v=0) + N_2 + M \rightarrow N_4^+ + M$, with its $5\times10^{-29} cm^6 s^{-1}$ rate constant, becomes dominant at high pressure, and has to be taken into account in the calculation of the total quenching of the FNS emitter. The choice of collision quenching rate constants relies on a large amount of literature. A good convergence of data is found about the quenching of $N_2(C^3\Pi_u, v=0,1)$ by N_2 (see [5]), and the data of [2] are a good choice. Large discrepancies exist, instead, between the many measurements of rate constants for $N_2^+(B^2\Sigma_u^+, v=0)$ by N_2 and O_2. We have reported in table I these literature data: rate constant values differ by about a factor four for nitrogen quencher and by about a factor two for oxygen quencher. The data are listed according to the method used for the excitation of the electronic state of the nitrogen ion, and to the method being selective or non-selective. It is clearly seen that selective excitation methods, i.e. those based on the absorption of resonant radiation, give the largest values. Among the non selective methods, i.e. those that excite the whole manifold of electronic states, pulsed discharge based methods give the lowest values, while continuous electron/proton beam and soft X-ray methods give intermediate values. It is quite evident that the rate constants values are dependent on the measurement method, and that the choice of the right value is a matter that deserves a thorough discussion. For instance at 1 atm of nitrogen the calculation of the SPS and FNS emission ratio can then be affected by a factor 1.43 variation according to the choice of quenching rate constants.

In the pulsed discharge method of [3], [2] a fast rise and fall time voltage pulse, with duration of few tens of ns, was applied to produce a discharge with the fast ionization wave (FIW) mechanism. After discharge-off, the decay of the emission intensity was measured and fitted by a single exponential function to get the quenching rate. A weak point of this method is that in the FIW, as pointed out by the same authors in [2], the relaxation of the EEDF in the energy range for inelastic processes proceeds for a time comparable to that of depopulation of the investigated levels. A strong point of the FIW excitation method was that, due to the short duration and low

Table 1: $N_2^+(B^2\Sigma_u^+, v=0)$ quenching rate constants $(10^{-10} cm^3 s^{-1})$ by N_2 and O_2.

quencher		*ref.*	excitation	sel./non sel.
N_2	O_2		method	
8.84 ± 0.37	10.45 ± 0.45	this work	resonant laser (LIF)	sel.
8.2 ± 1.2		[6]	resonant laser (LIF)	
7.5	11	[7]	resonant radiation	
5.4 ± 1.0		[8]	resonant radiation	
3.9 ± 1.4		[9]	electron beam	non sel.
4.3 ± 0.27	7.2 ± 3	[10]	electron beam	
$(6.0-7.7) \pm 1.5$		[11]	electron beam	
3.66 (at 300 K)		[12]	electron beam	
4.15		[13]	pulsed proton beam	
4.53	7.36	[14]	soft X-ray	
$(1.37-2.17)$		[15]	pulsed discharge (invertron)	
2.1 ± 0.2	5.1 ± 0.5	[3]	pulsed discharge (FIW)	

repetition rate of the discharge, the dissociation degree and the concentration of excited species is very low, so that it is possible to consider for the quenching the species and concentrations that constitute the initial gas feed only. Resonant excitation methods are the most direct and less affected by spurious effects, since they are based on the measurement of the quenching rate of an excess population of the single vibronic state that is selectively excited by absorption of resonant radiation. In [6], laser radiation was used to excite $N_2^+(B^2\Sigma_u^+, v=0)$ from the ion ground state and the fluorescence pulse decay provided the quenching rate. A sufficient population of ions was produced in a continuous d.c. discharge. This is a possible weak point, since the exact gas composition in presence of gases that can be easily dissociated might not be neatly known. In this contribution we revisit this subject by combining the cleaniness of laser induced fluorescence measurements with the advantage of production of ground state ions by means of a short duration, low repetition rate discharge, that are the same advantages as those described for the FIW excitation method. New data on $N_2^+(B^2\Sigma_u^+, v=0)$ quenching by N_2 and O_2 are provided that can help in the decision of which values to adopt in the application of spectroscopic methods to the E/N determination.

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