RELAXATION KINETICS OF $N_2(B^3\Pi_g, v)$ IN PULSED RF DISCHARGES: EXPERIMENTAL RESULTS AND MECHANISMS

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Abstract

The relaxation of $N_2(B^3\Pi_g, v)$ states in a He-N_2 mixture has been studied in a pulsed rf post-discharge in the range 0.1 - 1.5 Torr. Time resolved spectra of various sequences of the ($B^3\Pi_g$ - $A^3\Sigma_u^+$) emission system and the decay of the (2,0) band have been measured. The structures in the (B,v') distribution have been analysed taking into account excitation by electrons and heavy particles collisions.

Introduction

$B^3\Pi_g$ state, because of its particular position in the N_2 electronic manifold, is involved in many energy transfer processes with the neighbouring states. The formation of B state by recombination of N atoms /1/, by pooling reaction of A metastables and by electronic energy transfer of A metastable to (X,v) molecules /2/ or by intersystem collisional transfer with neighbouring $A^3\Sigma_u^+$, $W^3\Delta_u$, $B'^3\Sigma_u^-$ states /3/ has clearly been recognised in environments free from electrons. The common feature of all these processes is the state to state nature of the rate coefficients appearing in the structures of the (B,v) distribution.

In electrical discharges, where the electron impact processes produce the excitation of the whole electronic manifold, the kinetics of B state is rather complex. Therefore a multi-diagnostic /4/ approach allowing the measure of short and long lived species as well as of electrons, is advisable, and a kinetic modelling is needed in order to rationalise the experimental results. To this concern, the analysis of the relaxation in pulsed a post-discharge, being complementary to that of the discharge, helps to guess the importance of the various processes /4/, /5/.

Here we present the results of the relaxation of $N_2(B,v)$ state carried out by time resolved emission spectroscopy and the comparison with the results obtained by a steady state model taking into account the excitation of B state by electron impact from X and A state, by heavy particles collisions (X+A, A+A, N+N), and radiative decay from C state as well as loss by collisions and First Positive System emission (FPS).

Experimental

The experimental set-up has been described elsewhere /4/, /5/, /6/. It essentially consists of a stainless steel chamber with 10 cm diameter disk electrodes at 5 cm separation, equipped with various optical ports and feedtroughs. The emission from the centre of the discharge gap (2mm height 0.2 mm width sampled region), is focused by a couple of lenses on a 1 m monochromator equipped of a 570 nm cut-off filter and 750 nm blaze grating, and measured by a photon counter. The photon counting detection is more advantageous than that by boxcar previously employed for FPS emission detection /7/, since the spectrum has a more stable baseline. This is particularly necessary in post discharge at low N_2 partial pressure when the signal is particularly weak. For most experiments, a 500 Hz 1/2 duty cycle pulsing has been used. The discharge power is 60 W as measured under cw operation.

Results and discussion

a) decay analysis

The decay of (2,0) peak intensity recorded at 0.1 torr 5% N_2-He and 0.1, 0.5 and 1.5 Torr at 100% N_2 discharges is shown in fig. 1. The fits by a three exponential law are also shown in the figure. The results indicate that for 5% N_2 case the fast component corresponds to the radiative decay time of the (B,v=2) level, that is 8.48 μsec, while for 100% N_2 case it is about 2 times faster. The amplitudes of the decay components, which are about 65%, 33% and 2% respectively at 0.1 Torr 5%

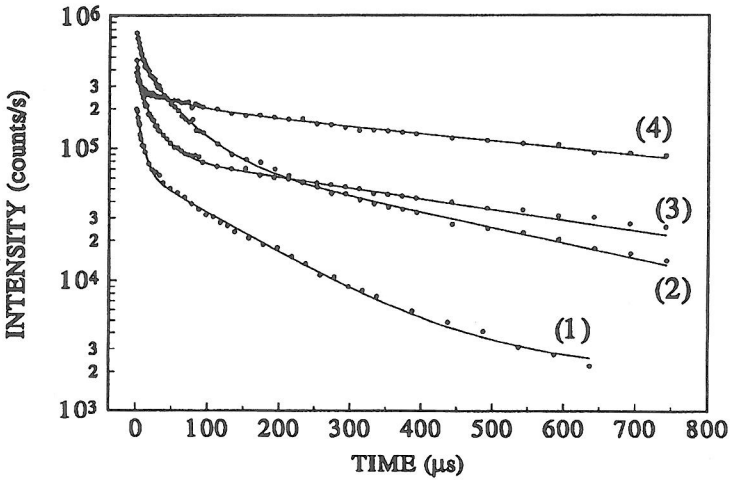

Fig.1 Decay of (B,2) level at 5% N_2 0.1 Torr 1) and at 100% N_2 0.1 Torr 2), 0.5 Torr 3), 1.5 Torr 4). Points: experiment, solid line: fit by three exponential law.

N_2,changes to about 20%, 20% and 60% respectively at 1.5 Torr 100% N_2. Such a behaviour indicates that the excitation by electron impact from the low vibrational levels ($v < 6$) of X state, taking place in the discharge, drops by switching-off the discharge because of the fast relaxation of the high energy electrons ($\varepsilon > 6$ eV) /6/. The slow components, instead, correspond to the excitation processes involving long lived species /5/ whose role increases as lower is the electron mean energy of the discharge. Such occurrence takes place as the partial pressure of N_2 increases /6/. It should be underlined that at $P_{N_2} = 5$ mTorr the quenching by N_2 /2/ of (B, 2) level is negligible with respect to the radiative loss. This is not the case at 1.5 Torr 100% N_2 for which the collisional loss should be about 2 or 5 times larger than the radiative one, depending on the quenching rate coefficient used that varies from 0.8 to 2.1 10^{-11} cm^3sec^{-1} /2/. The value of the fast component measured at 1.5 Torr 100% N_2 agrees better with the lower value of the quenching rate coefficient. However, the sensitivity of the three exponential fitting in inferring the decay time constants is not so strict, so that a variation of about 50% in the first component value could be rearranged by varying the other two components, still reproducing the experimental decay.

b) Vibrational analysis

The vibrational analysis has been carried out on the spectra of the sequences Δv= +2, +3, +4 after correction with the responsivity of the apparatus. In the present data handling the relative vibrational populations have been inferred from the first peak intensity of the vibronic bands, that is mainly formed by the contribution of P_{11} branch. We showed in /8/ that, under the present experimental conditions, the use of a more accurate method based on the fitting of the rovibronic bands of the FPS spectra, gives results in fairly good agreement with the peak method. This latter of course allows a quicker vibrational analysis.

The distributions obtained for the various sequences are attached each other to achieve the distribution for v=2-12 levels. Since the sensitivity of the photomultiplier does not allow the measure of sequences Δv= 0, 1 appearing in the near infrared region, the population of levels v=0, 1 has not been investigated. The distribution recorded at 0.1 torr 5% N_2 mixture and those in pure N_2 at 0.1 at 1.5 Torr measured at the end of 1 msec discharge and in post discharge at 750 μsec are shown in fig. 2. It can be seen that the relaxation in post discharge is more pronounced at low N_2 pressure.

c) Kinetic model

The main processes involved in the B state kinetics are the following:

$$N_2(X,v) + e \rightarrow N_2(B,v') + e \quad 1)$$
$$N_2(A,w) + e \rightarrow N_2(B,v') + e \quad 2)$$
$$N_2(X,v) + N_2(A,w) \rightarrow N_2(B,v') + N_2(X,w') \quad 3)$$
$$N_2(A,w) + N_2(A,w') \rightarrow N_2(B,v') + N_2(X,v) \quad 4)$$
$$N + N + M \rightarrow N_2(B,v') + M \quad 5)$$
$$N_2(C,v'') \rightarrow N_2(B,v) + h\nu \quad 6)$$
$$N_2(B,v') \rightarrow N_2(A,w) + h\nu \quad 7)$$
$$N_2(B,v') + N_2 \rightarrow N_2(W, B', X.....) \text{ or products} \quad 8)$$

A full undestanding of B relaxation would require the self consistent solution of these complex kinetics pattern, taking into account the coupling of the electron and molecular kinetics. This has been attempted in /9/, but with little comparison with experimental data. In most papers comparing the experiments a restricted number of the above processes has been considered. Here the fitting of the (B,v) distribution has been attempted by decoupling the individual excitations taking advantage of the partial knowledge of steady state (X,v), (A,v) and (C,v) vibrational distributions for selected times in discharge or post discharge, obtained on the basis of previous experimental analysis /4/, /5/, as well as of the knowledge of the excitation rate estimated on the basis of experimentally measured electron energy distribution function. We have used : for process 1) the state to state cross sections in /10/ ; for process 2) Frank-Condon scaling of the calculated total cross section in /11/; for process 3), the state to state rate coefficients calculated by Franck-Condon factor energy gap scaling law (FCFEGL), and normalizing the total rate coefficient to that measured by Piper /2/, after fitting his experimental distributions with FCFEGL rate coefficients; for process 4), experimental state to state rate coefficients of Piper for levels w=0,1 /12/; for process 5) state to state rate coefficients in /1/.
For process 8) we have considered that the experimental quenching rate coefficients of

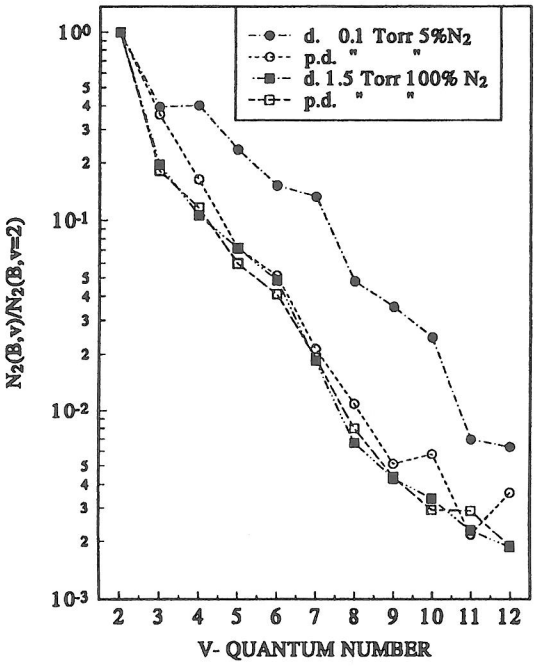

Fig.2 Experimental (B,v) distributions in discharge and post-discharge

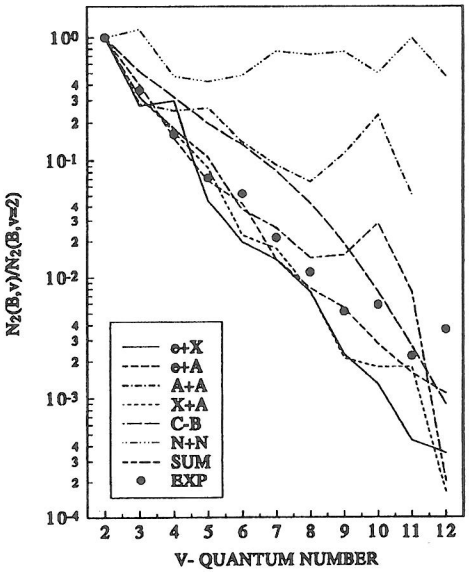

Fig. 3
Comparison between (B,V) distributions measured at 0.1 Torr 5% N_2 post-discharge with simulations by the kinetic model for: Boltzmann (X,v) and (A,v) distributions at Tv = 4000 K, $N_2(A)$ = 4×10^{10} cm^{-3}, N = 1% Tgas = 350 K. Te = 0.3 eV Ne = 1×10^{10}. The excitation rates ($cm^{-3}sec^{-1}$) are : R_{eX} = 2.4×10^{6}, R_{eA} = 2×10^{13}, R_{XA} = 5×10^{13}, R_{AA} = 5×10^{11}, R_{NN} = 10^{6}

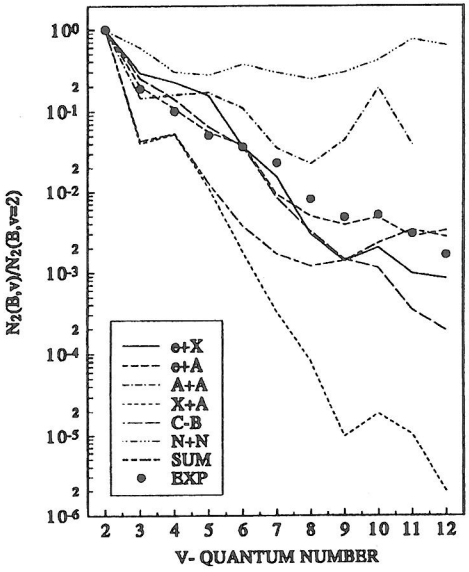

Fig.4
Comparison between (B,V) distributions measured at .5 Torr 100% N_2 post-discharge with simulations by the kinetic model for: Boltzmann (X,v) and (A,v) distributions at Tv = 2000 K, and 4000 K $N_2(A)$ = 1×10^{10}, N=1% Tgas =400 K. Te = 0.4 eV Ne = 1×10^{10} cm^{-3}. The excitation rates ($cm^{-3}sec^{-1}$) are : R_{eX} = 5×10^{9} R_{eA}= 7×10^{12}, R_{XA} = 2×10^{15}, R_{AA} = 5×10^{11}, R_{NN} = 2×10^{12} Tgas = 400 K

the B,v states measured by Piper represent the exit towards the whole manifold of neighbouring states /2/, /12/. The reverse processes that can also be effective have not been considered.

In fig. 3 and 4 we have shown the simulation of (B,v) distribution obtained in post-discharge (800 μsec) at 0.1 Torr 5% N_2 and 1.5 Torr pure nitrogen for the various processes above considered. We have used (X,v) and (A,v) inferred from papers /4/, /5/ that are almost Boltzmann like, while the electron temperature and density are inferred from /6/. In the figures it has also been shown the distribution obtained as the sum of the (B,v) distributions of each excitation process weighted by the corresponding rates. The agreement is rather poor. However we can see that the structures given by processes 2), 7), 8) follow very closely the experimental one. Such a situation is verified for all the post discharge conditions. The rate of process 2) is anyway 10 - 100 times lower that by process 3), which in turn fails in reproducing the experimental distribution. On the other hand processes 4) and 5) can compete in affecting the shape of (B,v) for the level 7-12 even thought the total rate is much lower than for 3).

In conclusion, the kinetic analysis here considered presents some discrepancies in reproducing correctly the real excitation of N_2(B, v) states, because the estimated rates of the various excitation processes disagree with the values necessary to reproduce the experiments. Such difficulty probably arises from both the poor knowledge of the state to state rate coefficient and the neglect of the processes pumping B state from (A $^3\Sigma_u^+$ v>7), W $^3\Delta_u$, B' $^3\Sigma_u^-$ neighbouring states. Work is still in progress.

Acknowledgements

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