

# Deactivation dynamics of vibrationally excited nitrogen molecules by nitrogen atoms.

## Effects on non-equilibrium vibrational distribution and dissociation rates of nitrogen under electrical discharges

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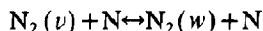
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The non-equilibrium vibrational distribution and the dissociation kinetics of N<sub>2</sub> in electrical discharges has been calculated by solving an appropriate vibrational master equation. Attention has been devoted to the role of nitrogen atoms in deactivation the vibrational distribution. To this end, a complete set of V-T (vibration-translation) deactivation rates of vibrationally excited molecules by nitrogen atoms has been calculated using a quasiclassical trajectory technique. The results show that nitrogen atoms formed by electron impact are able to deactivate the high vibrational levels ( $v > 25$ ) of N<sub>2</sub> strongly affecting the heavy particle dissociation kinetics of N<sub>2</sub>.

### 1. Introduction

Non-equilibrium vibrational kinetics of N<sub>2</sub> plays an important role in determining the properties of N<sub>2</sub> containing plasmas [1,2]. The lowest vibrational levels, in fact, strongly affect the electron energy distribution function through second kind collisions [2], while the long plateau in the vibrational distribution promotes vibrational mechanisms for dissociating and ionizing N<sub>2</sub> [2]. The long plateau is the result of the interplay between V-V (vibration-vibration) and V-T (vibration-translation) energy exchange processes, the former being predominant when assuming the rate coefficients of vibrational deactivation by nitrogen atoms to be essentially the same as those by N<sub>2</sub> molecules [3]. This assumption is the main weakness of the approach as pointed out in different papers [1-3]. Recently detailed state ( $v$ ) to state ( $w$ ) rate coefficients of the process



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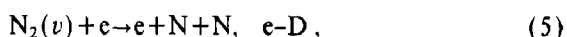
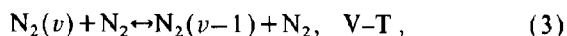
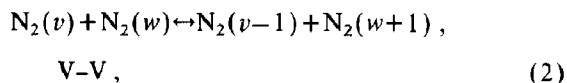
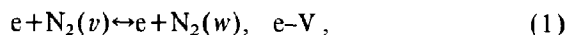
have been calculated [4,5]. The values of these rate coefficient single out the increasing importance of the  $\text{N} + \text{N}_2(v)$  processes when  $v$  increases. Unfortunately, these calculations were confined to low  $v$  ( $v < 15$ ) values (i.e. to a vibrational range dominated by V-V processes).

In this Letter, we report the extension of the calculations over the entire range of  $v$  values. Using a simplified model, we analyze the impact of these states on state vibrational deexcitation rate coefficients on the role played by nitrogen atoms in determining the vibrational distribution of N<sub>2</sub> as well as the dissociation kinetics of N<sub>2</sub> under non-equilibrium conditions.

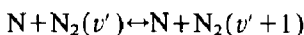
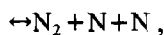
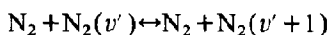
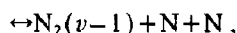
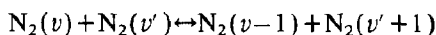
### 2. The vibrational kinetics and deactivation dynamics

A refined model has been developed in our laboratory to understand the vibrational kinetics of N<sub>2</sub> in electrical discharges. The model is based on the coupling between the vibrational master equation for

the vibrational distribution ( $N_v$ ), the dissociation kinetics and the Boltzmann equation for the electron energy distribution function [1-3]. This last equation gives the rate coefficients for vibrational excitation and for dissociation by electron impact to be utilized in the vibrational master equation. In this Letter, however, to better characterize the role played by nitrogen atoms in determining  $N_v$ , we make use of a simplified model confined to the following elementary processes



Process (1) represents the introduction of vibrational quanta by electron impact collisions, while processes (2)-(4) represent heavy particle collisions leading to a redistribution (V-V) and the loss (V-T) of the introduced vibrational quanta. Finally, process (5) represents the dissociation of the molecule by electron impact. Dissociation can occur also through heavy particle collisions involving vibrationally excited molecules and the last bound vibrational  $v'$  level of the molecule, i.e. through the processes



the reverse of these reactions representing recombination processes [1]. The vibrational master equation is then written as shown in refs. [1-3].

To solve the master equation we need all the relevant rate coefficients. As already mentioned, to obtain the rate coefficients involving electrons we must solve the Boltzmann equation for the electron energy distribution coupled to the non-equilibrium vibra-

tional and the dissociation kinetics. We simplify this procedure by taking the e-V and e-D rates corresponding to a given  $E/N$  (reduced electric field) value and to a given vibrational temperature ( $T_v = 5000$  K). These values, which are illustrated in fig. 1, will be considered constant during the time evolution of  $N_v$  under fixed conditions of  $E/N$  ( $E/N = 3 \times 10^{-16}$  V cm<sup>2</sup>), electron density ( $n_e = 10^{11}$  cm<sup>-3</sup>), pressure and gas temperature ( $p = 5$  Torr;  $T = 500$  K). In turn, these values have been obtained by solving the Boltzmann equation with appropriate cross sections (see ref. [3] for details).

V-V and V-T rates involving  $N_2$  molecules are those discussed in our previous works [1-3].

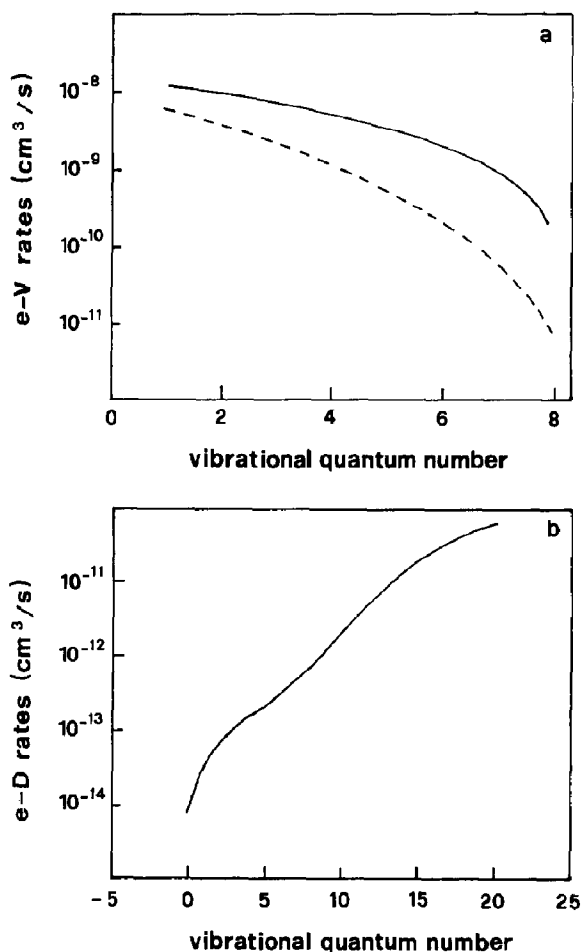


Fig. 1. e-V (a) and e-D (b) rates as a function of vibrational quantum number ( $E/N = 3 \times 10^{-16}$  V cm<sup>2</sup>,  $p = 5$  Torr,  $T_g = 500$  K,  $T_v = 4000$  K,  $n_e = 10^{11}$  cm<sup>-3</sup>). For the e-V rates we report both direct (dashed line) and reverse (full line) rates.

The calculation of the  $N+N_2(v)$  state selected rate constants has been carried out using a quasiclassical trajectory technique. To this end, for each given initial vibrational energy a batch of  $M$  classical trajectories was calculated. For each trajectory the collision and rotational energies, though randomly generated, were weighted to mimic the distribution associated with the chosen rotational ( $T_{\text{rot}}$ ) and translational ( $T_{\text{tr}}$ ) temperature. The integral defining, at fixed  $T_{\text{rot}}$  and  $T_{\text{tr}}$  values, the vibrational state ( $v$ ) to state ( $w$ ) rate constant is evaluated using a Monte Carlo technique [6]. In this approach the integral is approximated by the sum of  $M$  boolean functions valued one only when the vibrational energy of the products is closer to that of the  $w$  state than to that of any other state.

Critical parameters of the calculation are the maximum value of the impact parameter  $b_{\text{max}}$  and the number of integrated trajectories  $M$ . The value of  $b_{\text{max}}$ , in fact, was chosen to be large enough not to exclude any reactive trajectory but at the same time small enough to avoid unnecessary calculations. The value of  $M$  was varied with the initial vibrational number  $v$  to allow an approximately constant density of trajectories with  $b$  when increasing  $v$  (an increase of  $v$  implies an increase in  $b_{\text{max}}$  as a result of the larger stretching of the vibrationally excited molecule).

Ab initio calculations of the potential energy of  $N-N_2$  are reported in ref. [7]. As already mentioned, previous trajectory calculations at low vibrational energy have been reported in refs. [4,5] using the LEPS potential surface based on empirical arguments [4]. The surface has a collinear barrier of 36 kcal/mol. As usual for LEPS surfaces, the parameters were derived from spectroscopic data except for the Sato parameters which were optimized to reproduce the collinear barrier. The results for  $T_{\text{rot}}=T_{\text{tr}}=500$  K are reported in tables 1 and 2. Actually, the dynamical calculations were performed in steps of five vibrational levels starting from the first one.

To get a complete table of rate coefficients for  $N+N_2(v)$  processes we performed a fitting of calculated data by taking into account the following considerations:

(a) VT rate coefficients obtained by molecular dynamics are affected by statistical error which may

become large when there are only a few reactive trajectories (as is the case of low initial vibrational levels).

(b) A set of continuous curves derived from the fitting of the coefficients as a function of only one variable shows strong discontinuities when plotted as a function of the other variable.

To overcome the first difficulty, a least-squares interpolation is needed, while the second difficulty can be overcome by performing a two-dimensional interpolation: a first examination of the behaviour of the known rates has shown that linear two-dimensional interpolations are unsatisfactory. Thus the problem requires the generation of a non-linear two-dimensional least-squares interpolation with a minimum number of ad hoc assumptions and possibly no spurious extrema as a function of  $v$  and  $w$  (a usual problem with high-degree polynomial interpolations).

Due to these considerations, we used a layered neural network to fit the data. Neural networks [8] are computer-simulated nets of non-linear processing units whose input is an adjustable weight linear combination of outputs from other units. In a layered neural network each unit considers only the output from units of the preceding "layer".

We have used a two-layer neural network with a single hidden layer to fit the logarithms of the data as a function of  $v$  and  $w$ . The hidden layer was made up by 25 biased units with a sigmoidal output function and the output layer by a single linear unit. Accordingly, the net had one hundred adjustable weights. The calculation step was slowly linearly reduced in order to help the relaxation of the net dynamics to the minimum error.

The resulting behaviour is quite satisfactory. It lacks spurious extrema and is intrinsically smooth when plotted as a function of both  $v$  and  $w$ , as illustrated by the sample of typical results shown in fig. 2.

From calculated and interpolated values listed in tables 1 and 2 it can be easily seen that the reactive deactivation channel is more efficient than the non-reactive one. Moreover, one has to consider that deactivation occurs also through multiquantum transitions.

Table 1

Reactive rate coefficients ( $\text{cm}^3 \text{s}^{-1}$ ) for the process  $\text{N}_2(\nu) + \text{N} \rightarrow \text{N}_2(w) + \text{N}$  ( $T_{\text{tr}} = T_{\text{rot}} = 500 \text{ K}$ )

$w$	$\nu=10$	$\nu=15$	$\nu=20$	$\nu=25$	$\nu=30$	$\nu=35$	$\nu=40$	$\nu=45$
0		$0.1 \times 10^{-14}$	$0.1 \times 10^{-13}$	$0.2 \times 10^{-13}$	$0.5 \times 10^{-13}$	$0.6 \times 10^{-13}$	$0.1 \times 10^{-13}$	$0.1 \times 10^{-12}$
1			$0.4 \times 10^{-14}$	$0.2 \times 10^{-13}$	$0.6 \times 10^{-13}$	$0.8 \times 10^{-13}$	$0.9 \times 10^{-13}$	$0.1 \times 10^{-12}$
2			$0.7 \times 10^{-14}$	$0.3 \times 10^{-13}$	$0.5 \times 10^{-13}$	$0.5 \times 10^{-13}$	$0.9 \times 10^{-13}$	$0.7 \times 10^{-13}$
3	$0.3 \times 10^{-14}$	$0.2 \times 10^{-14}$	$0.7 \times 10^{-14}$	$0.2 \times 10^{-14}$	$0.2 \times 10^{-13}$	$0.6 \times 10^{-13}$	$0.8 \times 10^{-13}$	$0.8 \times 10^{-13}$
4		$0.2 \times 10^{-14}$	$0.3 \times 10^{-14}$	$0.3 \times 10^{-13}$	$0.2 \times 10^{-13}$	$0.4 \times 10^{-13}$	$0.7 \times 10^{-13}$	$0.5 \times 10^{-13}$
5			$0.1 \times 10^{-13}$	$0.2 \times 10^{-13}$	$0.5 \times 10^{-13}$	$0.7 \times 10^{-13}$	$0.8 \times 10^{-13}$	$0.8 \times 10^{-13}$
6			$0.7 \times 10^{-14}$	$0.2 \times 10^{-13}$	$0.7 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.1 \times 10^{-12}$	$0.1 \times 10^{-12}$
7		$0.1 \times 10^{-14}$	$0.1 \times 10^{-13}$	$0.2 \times 10^{-13}$	$0.7 \times 10^{-13}$	$0.7 \times 10^{-13}$	$0.7 \times 10^{-13}$	$0.2 \times 10^{-12}$
8		$0.5 \times 10^{-14}$	$0.7 \times 10^{-14}$	$0.3 \times 10^{-13}$	$0.6 \times 10^{-13}$	$0.6 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.8 \times 10^{-13}$
9		$0.2 \times 10^{-14}$	$0.7 \times 10^{-14}$	$0.3 \times 10^{-13}$	$0.6 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.1 \times 10^{-12}$	$0.1 \times 10^{-12}$
10		$0.1 \times 10^{-14}$	$0.2 \times 10^{-13}$	$0.4 \times 10^{-13}$	$0.6 \times 10^{-13}$	$0.2 \times 10^{-12}$	$0.1 \times 10^{-12}$	$0.2 \times 10^{-12}$
11		$0.3 \times 10^{-14}$	$0.2 \times 10^{-13}$	$0.6 \times 10^{-13}$	$0.9 \times 10^{-13}$	$0.8 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.1 \times 10^{-12}$
12		$0.2 \times 10^{-14}$	$0.3 \times 10^{-13}$	$0.6 \times 10^{-13}$	$0.9 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.1 \times 10^{-12}$	$0.1 \times 10^{-12}$
13		$0.5 \times 10^{-14}$	$0.2 \times 10^{-13}$	$0.4 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.1 \times 10^{-12}$	$0.1 \times 10^{-12}$	$0.1 \times 10^{-12}$
14		$0.6 \times 10^{-14}$	$0.2 \times 10^{-13}$	$0.3 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.2 \times 10^{-12}$	$0.1 \times 10^{-12}$	$0.3 \times 10^{-12}$
15		$0.5 \times 10^{-14}$	$0.3 \times 10^{-13}$	$0.3 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.2 \times 10^{-12}$	$0.2 \times 10^{-12}$	$0.2 \times 10^{-12}$
16			$0.3 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.2 \times 10^{-12}$	$0.2 \times 10^{-12}$	$0.2 \times 10^{-12}$	$0.2 \times 10^{-12}$
17			$0.4 \times 10^{-13}$	$0.7 \times 10^{-13}$	$0.2 \times 10^{-12}$	$0.3 \times 10^{-12}$	$0.2 \times 10^{-12}$	$0.2 \times 10^{-12}$
18			$0.4 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.2 \times 10^{-12}$	$0.2 \times 10^{-12}$	$0.3 \times 10^{-12}$	$0.3 \times 10^{-12}$
19			$0.8 \times 10^{-13}$	$0.2 \times 10^{-12}$	$0.3 \times 10^{-12}$	$0.4 \times 10^{-12}$	$0.3 \times 10^{-12}$	$0.4 \times 10^{-12}$
20			$0.5 \times 10^{-13}$	$0.2 \times 10^{-12}$	$0.3 \times 10^{-12}$	$0.3 \times 10^{-12}$	$0.4 \times 10^{-12}$	$0.3 \times 10^{-12}$
21				$0.2 \times 10^{-12}$	$0.3 \times 10^{-12}$	$0.4 \times 10^{-12}$	$0.4 \times 10^{-12}$	$0.4 \times 10^{-12}$
22				$0.2 \times 10^{-12}$	$0.3 \times 10^{-12}$	$0.4 \times 10^{-12}$	$0.4 \times 10^{-12}$	$0.5 \times 10^{-12}$
23				$0.4 \times 10^{-12}$	$0.4 \times 10^{-12}$	$0.6 \times 10^{-12}$	$0.5 \times 10^{-12}$	$0.5 \times 10^{-12}$
24				$0.3 \times 10^{-12}$	$0.5 \times 10^{-12}$	$0.6 \times 10^{-12}$	$0.6 \times 10^{-12}$	$0.4 \times 10^{-12}$
25				$0.3 \times 10^{-12}$	$0.5 \times 10^{-12}$	$0.6 \times 10^{-12}$	$0.7 \times 10^{-12}$	$0.7 \times 10^{-12}$
26					$0.6 \times 10^{-12}$	$0.6 \times 10^{-12}$	$0.8 \times 10^{-12}$	$0.6 \times 10^{-12}$
27					$0.8 \times 10^{-12}$	$0.9 \times 10^{-12}$	$0.9 \times 10^{-12}$	$0.8 \times 10^{-12}$
28					$0.1 \times 10^{-11}$	$0.1 \times 10^{-11}$	$0.1 \times 10^{-11}$	$0.1 \times 10^{-11}$
29					$0.1 \times 10^{-11}$	$0.1 \times 10^{-11}$	$0.1 \times 10^{-11}$	$0.8 \times 10^{-12}$
30					$0.1 \times 10^{-11}$	$0.1 \times 10^{-11}$	$0.1 \times 10^{-11}$	$0.1 \times 10^{-11}$
31						$0.2 \times 10^{-11}$	$0.1 \times 10^{-11}$	$0.1 \times 10^{-11}$
32						$0.2 \times 10^{-11}$	$0.2 \times 10^{-11}$	$0.1 \times 10^{-11}$
33						$0.2 \times 10^{-11}$	$0.2 \times 10^{-11}$	$0.2 \times 10^{-11}$
34						$0.4 \times 10^{-11}$	$0.2 \times 10^{-11}$	$0.2 \times 10^{-11}$
35						$0.3 \times 10^{-11}$	$0.3 \times 10^{-11}$	$0.2 \times 10^{-11}$
36							$0.3 \times 10^{-11}$	$0.3 \times 10^{-11}$
37							$0.5 \times 10^{-11}$	$0.3 \times 10^{-11}$
38							$0.6 \times 10^{-11}$	$0.4 \times 10^{-11}$
39							$0.8 \times 10^{-11}$	$0.5 \times 10^{-11}$
40							$0.7 \times 10^{-11}$	$0.5 \times 10^{-11}$
41								$0.7 \times 10^{-11}$
42								$0.9 \times 10^{-11}$
43								$0.1 \times 10^{-10}$
44								$0.1 \times 10^{-10}$
45								$0.1 \times 10^{-10}$

### 3. Results

Fig. 3a shows the time evolution of non-equilibrium vibrational distributions obtained from our

calculations. For comparison, in fig. 3b those obtained, as in our previous works, by using as deactivation rates from nitrogen atoms the ones of nitrogen molecules are also shown. In the last case the

Table 2

Inelastic rate coefficients ( $\text{cm}^3 \text{s}^{-1}$ ) for the process  $\text{N}_2(\nu) + \text{N} \rightarrow \text{N}_2(w) + \text{N}$  ( $T_{\text{tr}} = T_{\text{rot}} = 500 \text{ K}$ )

$w$	$\nu=10$	$\nu=15$	$\nu=20$	$\nu=25$	$\nu=30$	$\nu=35$	$\nu=40$	$\nu=45$
0		$0.3 \times 10^{-14}$	$0.2 \times 10^{-13}$	$0.1 \times 10^{-13}$	$0.5 \times 10^{-13}$	$0.7 \times 10^{-13}$	$0.7 \times 10^{-13}$	$0.1 \times 10^{-12}$
1			$0.4 \times 10^{-14}$	$0.3 \times 10^{-13}$	$0.3 \times 10^{-13}$	$0.8 \times 10^{-13}$	$0.7 \times 10^{-13}$	$0.7 \times 10^{-13}$
2			$0.2 \times 10^{-13}$	$0.1 \times 10^{-13}$	$0.4 \times 10^{-13}$	$0.9 \times 10^{-13}$	$0.7 \times 10^{-13}$	$0.1 \times 10^{-12}$
3			$0.8 \times 10^{-14}$	$0.2 \times 10^{-13}$	$0.5 \times 10^{-13}$	$0.4 \times 10^{-13}$	$0.7 \times 10^{-13}$	$0.1 \times 10^{-12}$
4				$0.2 \times 10^{-13}$	$0.2 \times 10^{-13}$	$0.4 \times 10^{-13}$	$0.9 \times 10^{-13}$	$0.9 \times 10^{-13}$
5		$0.2 \times 10^{-14}$		$0.2 \times 10^{-13}$	$0.2 \times 10^{-13}$	$0.5 \times 10^{-13}$	$0.8 \times 10^{-13}$	$0.1 \times 10^{-12}$
6		$0.2 \times 10^{-14}$	$0.6 \times 10^{-14}$	$0.3 \times 10^{-13}$	$0.5 \times 10^{-13}$	$0.5 \times 10^{-13}$	$0.9 \times 10^{-13}$	$0.1 \times 10^{-12}$
7			$0.1 \times 10^{-13}$	$0.3 \times 10^{-13}$	$0.4 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.1 \times 10^{-12}$	$0.1 \times 10^{-12}$
8			$0.3 \times 10^{-14}$	$0.2 \times 10^{-13}$	$0.5 \times 10^{-13}$	$0.8 \times 10^{-13}$	$0.7 \times 10^{-13}$	$0.2 \times 10^{-12}$
9			$0.2 \times 10^{-13}$	$0.2 \times 10^{-13}$	$0.5 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.7 \times 10^{-13}$	$0.9 \times 10^{-13}$
10	$0.2 \times 10^{-9}$		$0.9 \times 10^{-14}$	$0.4 \times 10^{-13}$	$0.8 \times 10^{-13}$	$0.6 \times 10^{-13}$	$0.2 \times 10^{-12}$	$0.2 \times 10^{-12}$
11			$0.8 \times 10^{-14}$	$0.4 \times 10^{-13}$	$0.9 \times 10^{-13}$	$0.9 \times 10^{-13}$	$0.9 \times 10^{-13}$	$0.1 \times 10^{-12}$
12		$0.2 \times 10^{-14}$	$0.4 \times 10^{-14}$	$0.3 \times 10^{-13}$	$0.7 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.1 \times 10^{-12}$	$0.1 \times 10^{-12}$
13			$0.1 \times 10^{-13}$	$0.2 \times 10^{-13}$	$0.7 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.1 \times 10^{-12}$	$0.3 \times 10^{-12}$
14			$0.1 \times 10^{-13}$	$0.3 \times 10^{-13}$	$0.9 \times 10^{-13}$	$0.8 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.1 \times 10^{-12}$
15		$0.2 \times 10^{-9}$		$0.4 \times 10^{-13}$	$0.7 \times 10^{-13}$	$0.7 \times 10^{-13}$	$0.2 \times 10^{-12}$	$0.1 \times 10^{-12}$
16			$0.1 \times 10^{-13}$	$0.4 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.2 \times 10^{-12}$	$0.1 \times 10^{-12}$	$0.2 \times 10^{-12}$
17			$0.4 \times 10^{-14}$	$0.4 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.2 \times 10^{-12}$	$0.2 \times 10^{-12}$	$0.9 \times 10^{-13}$
18			$0.1 \times 10^{-13}$	$0.4 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.2 \times 10^{-12}$	$0.2 \times 10^{-12}$	$0.1 \times 10^{-12}$
19			$0.1 \times 10^{-13}$	$0.5 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.2 \times 10^{-12}$	$0.1 \times 10^{-12}$	$0.2 \times 10^{-12}$
20			$0.2 \times 10^{-9}$	$0.6 \times 10^{-13}$	$0.6 \times 10^{-13}$	$0.2 \times 10^{-12}$	$0.2 \times 10^{-12}$	$0.2 \times 10^{-12}$
21				$0.8 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.2 \times 10^{-12}$	$0.4 \times 10^{-12}$	$0.3 \times 10^{-12}$
22				$0.7 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.2 \times 10^{-12}$	$0.3 \times 10^{-12}$	$0.4 \times 10^{-12}$
23				$0.6 \times 10^{-13}$	$0.1 \times 10^{-12}$	$0.3 \times 10^{-12}$	$0.4 \times 10^{-12}$	$0.5 \times 10^{-12}$
24				$0.8 \times 10^{-13}$	$0.2 \times 10^{-12}$	$0.4 \times 10^{-12}$	$0.3 \times 10^{-12}$	$0.3 \times 10^{-12}$
25				$0.2 \times 10^{-9}$	$0.2 \times 10^{-12}$	$0.4 \times 10^{-12}$	$0.3 \times 10^{-12}$	$0.3 \times 10^{-12}$
26					$0.2 \times 10^{-12}$	$0.3 \times 10^{-12}$	$0.5 \times 10^{-12}$	$0.6 \times 10^{-12}$
27					$0.2 \times 10^{-12}$	$0.4 \times 10^{-12}$	$0.5 \times 10^{-12}$	$0.5 \times 10^{-12}$
28					$0.2 \times 10^{-12}$	$0.5 \times 10^{-12}$	$0.7 \times 10^{-12}$	$0.6 \times 10^{-12}$
29					$0.4 \times 10^{-12}$	$0.3 \times 10^{-12}$	$0.7 \times 10^{-12}$	$0.6 \times 10^{-12}$
30					$0.3 \times 10^{-9}$	$0.5 \times 10^{-12}$	$0.7 \times 10^{-12}$	$0.6 \times 10^{-12}$
31						$0.5 \times 10^{-12}$	$0.1 \times 10^{-11}$	$0.8 \times 10^{-12}$
32						$0.5 \times 10^{-12}$	$0.1 \times 10^{-11}$	$0.9 \times 10^{-12}$
33						$0.6 \times 10^{-12}$	$0.1 \times 10^{-11}$	$0.1 \times 10^{-11}$
34						$0.7 \times 10^{-12}$	$0.1 \times 10^{-11}$	$0.1 \times 10^{-11}$
35						$0.3 \times 10^{-9}$	$0.1 \times 10^{-11}$	$0.1 \times 10^{-11}$
36							$0.1 \times 10^{-11}$	$0.1 \times 10^{-11}$
37							$0.1 \times 10^{-11}$	$0.2 \times 10^{-11}$
38							$0.1 \times 10^{-11}$	$0.2 \times 10^{-11}$
39							$0.1 \times 10^{-11}$	$0.1 \times 10^{-11}$
40							$0.3 \times 10^{-9}$	$0.2 \times 10^{-11}$
41								$0.2 \times 10^{-11}$
42								$0.2 \times 10^{-11}$
43								$0.2 \times 10^{-11}$
44								$0.3 \times 10^{-11}$
45								$0.3 \times 10^{-9}$

vibrational distribution and the production of nitrogen atoms ( $N_{\nu=46}$ ) monotonically increase as a function of time, reflecting the prevalence of V-V rates over V-T ones. On the other hand, fig. 3a shows that

the increased importance of nitrogen atoms V-T rates prevents the growth of  $N_{\nu}$  starting from  $t = 7.8 \times 10^{-3}$  s onward (i.e. from the time at which the nitrogen atom concentration and, therefore, the related V-T

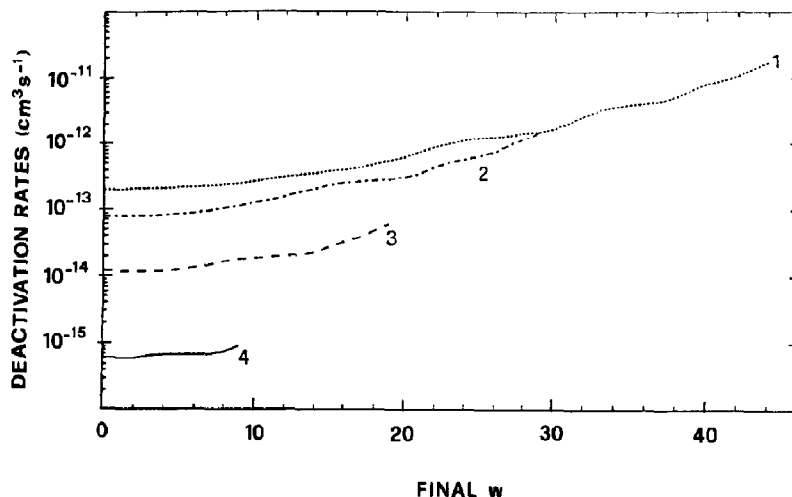


Fig. 2. Deactivation rate coefficients (reactive + inelastic) for the process  $N + N_2(v) \rightarrow N + N_2(w)$ ,  $v > w$ , as a function of final vibrational quantum number  $w$  for different initial  $v$  ( $T_{tr} = T_{rot} = 500$  K) (curve (1):  $v = 45$ ; curve (2):  $v = 30$ ; curve (3):  $v = 20$ ; curve (4):  $v = 10$ ).

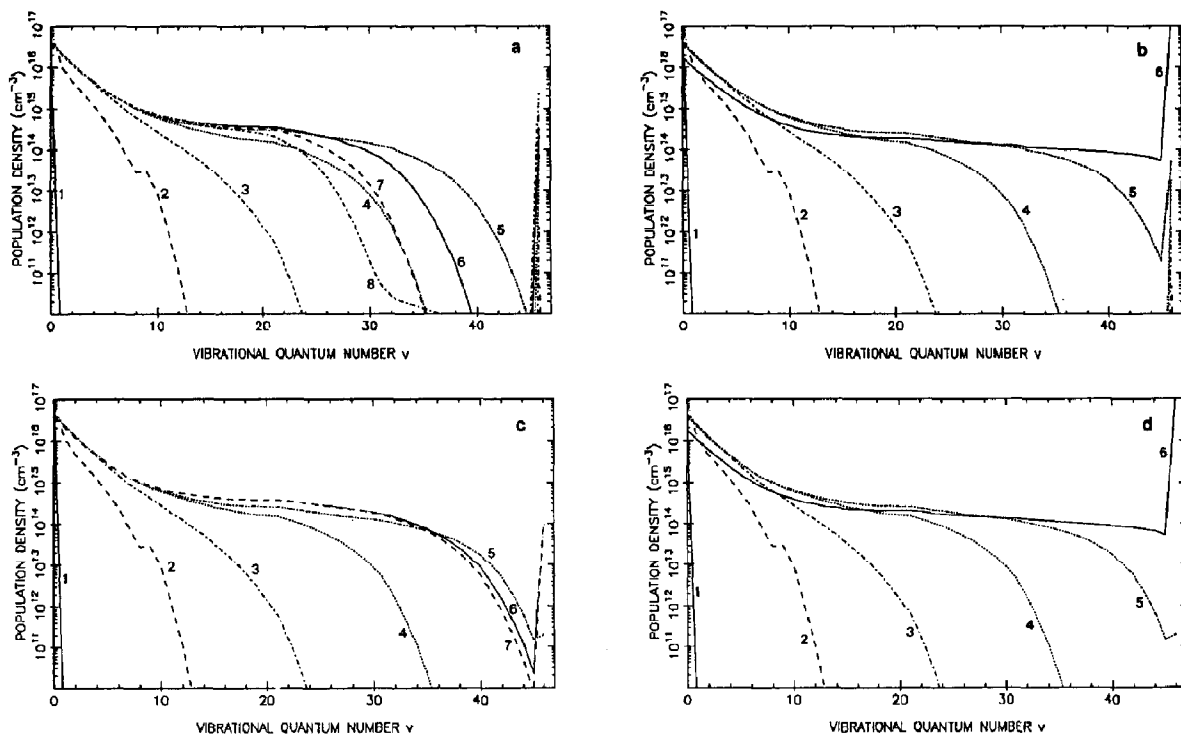


Fig. 3. Time dependent non-equilibrium vibrational distributions of  $N_2$  calculated by inserting (a) and by neglecting (b) atomic nitrogen deactivation. Curves (c) and (d) are the same as (a) and (b) but neglecting the electron impact dissociation (e-D) processes. The different curves refer to different relaxation times: (a) (1)  $10^{-11}$  s, (2)  $1.8 \times 10^{-4}$  s, (3)  $1.5 \times 10^{-3}$  s, (4)  $3.8 \times 10^{-3}$  s, (5)  $7.8 \times 10^{-3}$  s, (6)  $1.9 \times 10^{-2}$  s, (7)  $4.4 \times 10^{-2}$  s, (8) 9.2 s; (b) curves (1)–(4) as in (a) but (5)  $6.4 \times 10^{-3}$  and (6) 0.28 s; (c) curves (1)–(5) as in (b) but (6)  $6.1 \times 10^{-2}$  s, (7) 0.27 s; (d) curves (1)–(6) as in (b).

deactivation rates prevail on the V-V rates for the high-lying vibrational levels). The long plateau of fig. 3b extending up to the dissociation limit ends earlier when, as in the case of fig. 3a, more appropriate V-T rates from nitrogen atoms are inserted in the model. It should be noted, however, that in both cases the concentration of vibrational levels is practically the same up to approximately  $v=25$ . This means that only upper levels, whose concentration can differ up to two orders of magnitude depending on the different estimates on V-T rate coefficients, can be affected by the presence of nitrogen atoms. This scenario, of course, modifies the role of "pure" vibrational mechanisms in dissociating and ionizing  $N_2$  under non-equilibrium conditions. In order to rationalize how the vibrational distribution  $N_v$  is modified when neglecting the formation of nitrogen atoms in the electronic channel (i.e. by neglecting process (5)) we show in figs. 3c and 3d the related population densities for the same cases illustrated in figs. 3a and 3b. One can see that under the assumption of low V-T rates from nitrogen atoms (fig. 3d) both the vibrational distribution and the concentration of nitrogen atoms do not depend on the presence of the electronic channel (compare figs. 3d and 3b). This means that in this case  $N_2$  dissociation is dominated by a pure vibrational mechanism (see ref. [3]). On the contrary, by taking into account the present  $N+N_2$  V-T rates, the situation with and without e-D rates changes strongly. In particular, use of the present V-T rates for nitrogen atoms together with the disregard of e-D ones strongly affects the results as can be appreciated by comparing figs. 3c and 3a. In this case, in fact, the absence of the electronic channel in the dissociation of  $N_2$  was the effect of increasing the importance of the pure vibrational dissociation mechanism. The formed nitrogen atoms do, however, deactivate the high vibrational levels of  $N_2$  thereby decreasing the dissociation rate by means of a pure vibrational mechanism (i.e. the presence of nitrogen atoms is self-limiting). This means that in the more realistic case reported in fig. 3a the dissociation of  $N_2$  preferentially occurs through channel (5) and the formed nitrogen atoms are able to decrease the concentration of high-lying vibrational levels as reported previously. This point can be better understood by looking at fig. 4 where we have reported the dissociation constants (units of

$s^{-1}$ ) obtained according to:

- (1) the e-D mechanism from  $v=0$ ,
- (2) the e-D mechanism involving all vibrational levels,
- (3) the pure vibrational mechanism.

Fig. 4 shows that the dissociation constant associated with the pure vibrational mechanism is smaller than the one calculated according to the e-D mechanism involving all vibrational levels (actually the first 25 ones [3]), a result strongly differing from the conclusions reported in our previous papers. It should be noted that the time evolution of the different global rate coefficients reported in fig. 4 is linked to the time evolution of the vibrational distribution since we are considering constant the rate coefficient for all elementary processes. Therefore, the decrease in the e-D rate from  $v=0$  is due to the depletion of the concentration of this level as a function of time, while the increase of e-D rate involving all vibrational levels is due to the increase of the elementary rate coefficient of channel (5) as a function of vibrational quantum number. Also interesting is the time dependence of the global dissociation constant associated with the pure vibrational mechanism. This shows two maxima. The first of them is linked to the

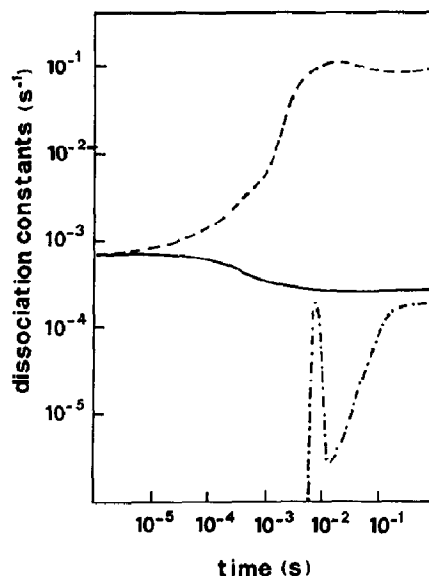


Fig. 4. Dissociation constants for the different mechanisms as a function of time (dashed line: e-D mechanism from all vibrational levels; full line: e-D from  $v=0$ ; dashed-dot line: pure vibrational mechanism).

evolution of vibrational distributions (in particular of the last vibrational level), while the second one, coming into play at later times, is the result of a "recombination assisted dissociation mechanism" (see ref. [1]). The last mechanism relies on the fact that the recombination of nitrogen atoms, produced by the e-D process, preferentially pumps the last vibrational level of the molecule, which can either decay to the low-lying levels or redissociate through heavy particle collisions.

#### 4. Conclusions

In this work we show the importance of  $N+N_2$  collisions in deactivating the  $N_2$  vibrational distribution in electrical discharges. We find that the introduction of accurate estimates of rate coefficients for this process dramatically alters the vibrational distribution.

As for the pure vibrational mechanisms discussed in recent year by our group, we can say that it appears that they seem to lose ground at least when the dissociation process relies mainly on the last vibrational level of the molecule. The e-D mechanism involving all the vibrational levels of the molecule seems to dominate the dissociation process when using the data of fig. 1 for the e-D rate coefficients as a function of vibrational quantum number. On the other hand if we neglect the contribution of vibrational states to the e-D mechanism again the pure vibrational mechanism can become the main channel for the dissociation process.

The present results represent a further improvement in the modeling of the dissociation kinetics of  $N_2$  under non-equilibrium conditions.

They also suggest that the characterization of the process is still far from being fully understood in spite of the efforts performed in the present and other recent investigations [9,10] reported in the literature. Therefore, we are planning to go beyond the simple model examined here and investigate the effect of the new set of V-T deactivating rates on the whole

kinetics of  $N_2$  under discharge conditions. In particular the conversion of electronic into vibrational energies could modify the relative importance of the different dissociation channels also in the presence of deactivating species [9-11].

Further work [12] is also being made along the line of testing semiclassical estimates of  $N+N_2$  rate coefficients against reduced dimensionality quantum calculations. Improvements are also needed on the side of the potential energy surface presently based on an empirical correction to ab initio results. A different energy or location of the main surface features can in fact alter the picture presented here because of the high sensitivity of calculated rate coefficients to the potential energy surface shape.

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