Nonequilibrium dissociation mechanisms in low temperature nitrogen and carbon monoxide plasmas

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A B S T R A C T

The role of vibrational excitation in affecting the dissociation under discharge conditions characterized by reduced electric field $E/N \leqslant 80$ Td has been investigated in N_2. The kinetic calculations have been performed using a self-consistent approach, solving at the same time the master equation for the composition and the distribution of internal states (vibrational and electronic) and the Boltzmann equation for the electron energy distribution function. The results show that vibrational mechanisms involving heavy particle excited states dominate electron impact dissociation mechanisms involving the whole vibrational ladder for $E/N < 50$ Td, the two mechanisms being competitive for $E/N > 50$ Td.

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1. Introduction

A continuous interest is devoted to understand the role of vibrational energy in affecting chemical processes involving molecules (N_2, CO, CO_2) under discharge and post-discharge conditions [1–4].

Despite its apparent simplicity, the experimental determination of dissociation rates is very difficult, while theoretical calculations considering only electron-molecule dissociation processes fail in reproducing experimental dissociation rates even for simple molecules. This point was first emphasized by the Polak group [5] in the 70s, who showed that the experimental dissociation rate of nitrogen in glow discharges at low E/N cannot be predicted by the direct electron impact dissociation from the ground vibrational level of nitrogen (see also Ref. [6]). These experimental findings induced the plasma community to develop sophisticated theoretical models to explain the dissociation rate of diatomic molecules under electrical discharges beyond the direct impact dissociation. In particular a pure vibrational mechanism (PVM) [7–9] was developed, based on a three step mechanism: (i) introduction of vibrational quanta by resonant electron vibration excitation process (e-V); (i) redistribution of the quanta by vibration–vibration (V–V) and vibration–translation (V–T) energy exchange processes; (iii) overcoming by the same processes of the last vibrational level linked to a pseudo-level located in the continuum, *i.e.* miming the

dissociation process. The corresponding PVM rates were found orders of magnitude higher than the corresponding rates by direct electron-impact from the ground vibrational level $\upsilon = 0$. Some of the hypotheses contained in these results *i.e.* Maxwell distribution function for electrons and direct electron dissociation from $\upsilon = 0$ were eliminated and a direct dissociation mechanism from all vibrational levels was considered [10]. In any case the vibrational distribution of nitrogen was presenting a long *plateau* such as to promote dissociation directly from PVM and indirectly by a direct electronic mechanism (DEM) including transitions from all vibrational levels.

These results however were based on the knowledge, poor at that time, of the relevant cross sections. In particular the V–T_a rates involving nitrogen atoms were considered equal to the corresponding ones induced by nitrogen molecules which neglect multi-quantum transitions. Moreover, the e-V rates were estimated, by crude scaling law from the known e-V rates linking the first 8 levels. It should be noted that these results have been obtained considering 45 vibrational levels in nitrogen, a problem solved in the recently calculated rates and cross sections.

Inclusion of more realistic V–T_a rates from atomic nitrogen (considering also vibrational multi-quantum transitions) was attempted many years ago by Armenise et al. [11]. The main result of this study was the practical disappearance of PVM in dissociating nitrogen mainly due a new set of V–T_a. These rates are continuously updated especially for the processes involving low-lying vibrational levels important for the definition of a vibrational

temperature [12,13]. Insertion of these V–T$_a$ rates in the kinetic model confirmed the impossibility of PVM mechanisms based on the last vibrational level of the molecule [14].

The aim of the present paper is to reconsider the role of vibrational excitation in affecting the dissociation rates of simple molecules in plasmas sustained by low reduced electric fields E/N. Under these conditions the energy gained by electrons is mainly lost in pumping vibrational energy in the molecule through resonant e-V processes promoting chemical reactions activated by the vibrational energy. Under these conditions e-V cross sections and rates take an important role which justifies the enormous effort made by Laporta et al. to compute complete sets of e-V cross sections for the N$_2$ and CO systems [15,16].

Moreover in the nitrogen case we are considering a resonant dissociation mechanism i.e.

$$e^- + N_2(X^1\Sigma_g^+, \upsilon) \rightarrow N_2^-(^2\Pi_g) \rightarrow e^- + 2N(^4S), \qquad (1)$$
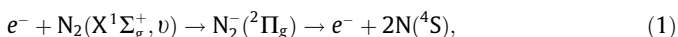
the cross sections of which have recently been calculated by extending the theory of e-V cross sections to the continuum [15,16] (Laporta et al. [17]).

2. Model

A zero dimensional code coupling the vibrational kinetics of N$_2$ with the electron energy distribution function (eedf) and with plasma-chemistry (dissociation, ionization, electronic excitation) has been developed in our laboratory to shed light on the different couplings existing in the non-equilibrium plasma [14,18]. In implicit form we write the vibrational kinetics as

$$\left(\frac{dN_\upsilon}{dt}\right) = \left(\frac{dN_\upsilon}{dt}\right)_{e-V} + \left(\frac{dN_\upsilon}{dt}\right)_{V-V} + \left(\frac{dN_\upsilon}{dt}\right)_{V-T_a} + \left(\frac{dN_\upsilon}{dt}\right)_{V-T_m}$$
$$+ \left(\frac{dN_\upsilon}{dt}\right)_{e-D} + \left(\frac{dN_\upsilon}{dt}\right)_{e-I} + \left(\frac{dN_\upsilon}{dt}\right)_{e-E} + \left(\frac{dN_\upsilon}{dt}\right)_{chem}$$
$$+ \left(\frac{dN_\upsilon}{dt}\right)_{rec}, \qquad (2)$$

where the different terms represent excitation and deexcitation processes involving the υth vibrational level due to e-V, V–V, V–T$_a$ and V–T$_m$ (vibration–translation energy exchange by molecule impact) processes. In addition e-D, e-I and e-E represent the loss of vibrational energy due to electron impact dissociation, ionization and excitation events starting from the υth level, while the last two terms represent the influence of plasmachemistry and recombination processes on the concentration of υth level. The system of vibrational master equations and the corresponding plasmachemistry equations are then coupled to the Boltzmann equation for the eedf written in compact form as

$$\frac{\partial n(\varepsilon, t)}{\partial t} = -\frac{\partial J_E}{\partial \varepsilon} - \frac{\partial J_{el}}{\partial \varepsilon} - \frac{\partial J_{ee}}{\partial \varepsilon} + S_{in} + S_{sup}, \qquad (3)$$

where $n(\varepsilon, t)$ is the number of electrons in the energy range $(\varepsilon, \varepsilon + d\varepsilon)$ at time t. The different terms on the right hand side of Eq. 3 describe the flux of electrons in the energy space due to (i) the electric field E ($\frac{\partial J_E}{\partial \varepsilon}$); (ii) the elastic collisions ($\frac{\partial J_{el}}{\partial \varepsilon}$); (iii) the electron–electron collisions ($\frac{\partial J_{ee}}{\partial \varepsilon}$); (iv) the inelastic collisions (S_{in}); (υ) the superelastic (second kind) collisions (S_{sup}). Details of the model can be found in [18] where one can also find the detailed list of elementary processes inserted in the kinetics as well as the corresponding sources of the different cross sections and rates. The present model considers 67 vibrational levels [15,14] for nitrogen implying a rescaling of the old rates based on 45 vibrational levels. Electron impact excitation, dissociation and ionization transitions involve all the vibrational ladder while the same processes are

promoted by bi-molecular collisions involving vibrationally and electronically excited states.

3. Results

3.1. Nitrogen

Before examining the model results we want to compare old results obtained (i) by PVM [7–9]; (ii) by the direct electron-impact dissociation obtained by using the experimental Cosby cross sections [19]; (iii) by multiplying the experimental electron-impact rates by a factor 70 to take into account the role of vibrational excited molecules (Park's model) [20] and (iv) by an upper limit of pure vibrational mechanism (ulPVM) [3,6]. In this last case we get the rate as a balance between the vibrational quanta introduced by e-V processes and the loss of vibrational quanta by the dissociation process i.e.

$$K_d^{(ulPVM)} = \sum_{\upsilon=1}^{\upsilon_{max}} \frac{\upsilon \, k_{e-V}(0 \rightarrow \upsilon)}{\upsilon_{max}}, \qquad (4)$$

where $k_{e-V}(0 \rightarrow \upsilon)$ is the rate coefficient of electron impact excitation process,

$$e^- + N_2(X^1\Sigma_g^+, \upsilon = 0) \rightarrow N_2^-(^2\Pi_g) \rightarrow e^- + N_2(X^1\Sigma_g^+, \upsilon). \qquad (5)$$
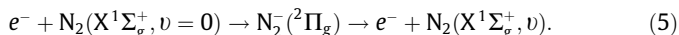
$\upsilon_{max} = 67$ is the number of vibrational states supported by the potential well of the N$_2$ ground state. Eq. (4) is derived from the balance of the input of vibrational quanta by e-V processes and the corresponding loss by dissociation (every dissociation event needs 67 vibrational quanta), i.e. no loss of vibrational quanta occur through V–T relaxation. All the rates reported in Fig. 1 have been obtained by considering a Maxwell distribution function for electrons and the complete set of e-V cross sections recently calculated by Laporta et al. [15]. Inspection of Fig. 1 shows that $K_d^{(ulPVM)}$ is orders of magnitude higher than the experimental rate, K_d^{Cosby} [19], in the electron temperature range $7500 < T_e < 30,000$ K, while for higher temperatures the curves get closer, crossing at about $T_e \sim 40,000$ K. In this temperature range $K_d^{(ulPVM)}$ is larger than the rate from the pure vibrational mechanism, which considers a non-equilibrium vibrational kinetics including V–V, V–T and e-V processes and a ladder climbing model for the dissociation process. $K_d^{(ulPVM)}$ is also larger than the corrected rates estimated by Park, K_d^{Park} [20], by increasing the rate obtained from recommended cross section by Cosby contribution by a factor 70.

Let us now consider the results obtained by our time dependent model. Contrary to the results reported in [21] we have run our time dependent equations at fixed electron density (molar fraction
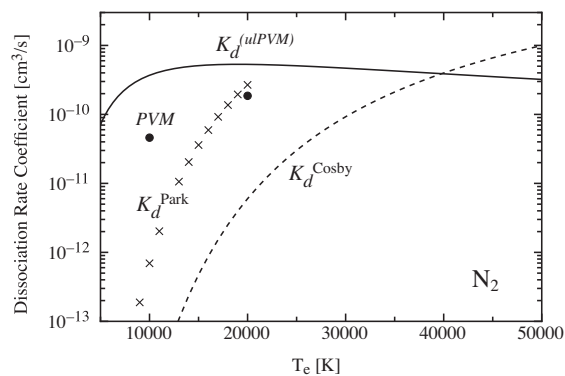

Fig. 1. Nitrogen dissociation rate as a function of T_e calculated according to different models. (*solid line*) $K_d^{(ulPVM)}$ from accurate e-V rates by Laporta et al. [15], (*dashed line*) dissociation rate from recommended cross section by Cosby [19], K_d^{Cosby}, (*crosses*) global dissociation rate from Park [20], K_d^{Park}, (*close circles*) pure vibrational mechanism PVM [7–9].