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# Electron and vibrational kinetics in an N<sub>2</sub>-H<sub>2</sub> glow discharge with application to surface processes

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**Abstract.** The electron and vibrational kinetics in an N<sub>2</sub>-H<sub>2</sub> glow discharge have been analysed using a self-consistent theoretical approach valid in the conditions of a low-pressure moderate current, positive column. This model is based on the solutions to the homogeneous Boltzmann equation and the two systems of rate balance equations for the vibrational levels N<sub>2</sub>(X<sup>1</sup> $\Sigma_{g}^{+}$ , v) and H<sub>2</sub>(X<sup>1</sup> $\Sigma_{g}^{+}$ , v'), which take into account e-V, V-V, and V-T processes for the N<sub>2</sub>-N<sub>2</sub> and H<sub>2</sub>-H<sub>2</sub> systems as well as those involving N<sub>2</sub>-H<sub>2</sub> collisions. This paper presents a large amount of calculated data on the vibrational distribution functions of N<sub>2</sub>(X, v) and H<sub>2</sub>(X, v') molecules, electron energy distribution function, rate of dissociation and electron rate coefficients for excitation. This formulation provides a relationship between the characteristic vibrational temperatures  $T_v(N_2)$  and  $T_v(H_2)$  and a dependence of  $T_v(N_2)$  on the fractional H<sub>2</sub> concentration, which are in satisfactory agreement with measurements by emission spectroscopy and by CARs. The model also predicts the strong decrease of the rate of dissociation of N<sub>2</sub> as it is observed in flowing discharges when a few per cent of H<sub>2</sub> is added to N<sub>2</sub>.

### 1. Introduction

The study of reactive plasmas in mixtures containing N<sub>2</sub> molecules currently motivates considerable attention as these mixtures are commonly employed for surface treatments (e.g. metal surface nitriding and coating). In particular, for steel surface nitriding in industrial reactors, the plasma is a N2-H2 glow discharge and the sample to be nitrided is usually connected as a cathode [1-5]. The production of nitrogen active species created in such applications (e.g. N,  $N_2(X, v)$ ,  $N_2^+$ ,  $N_2^*$ ) constitutes, therefore, an active field of research. In previous publications, the active species N,  $N_2^+$ ,  $N_2(B^3\Pi_g)$ and  $N_2(C^3\Pi_u)$  have been extensively studied by emission spectroscopy [2, 3], while the populations in the  $N_2(X^1\Sigma_g^+, v)$  levels have been determined either by using rare gas actinometry [2] or by the CARS method [4, 5]. However, in those previous works no theoretical studies of the electron and the vibrational kinetics have been attempted in a self-consistent manner.

It is the purpose of this paper to analyse the kinetics in an N<sub>2</sub>-H<sub>2</sub> homogeneous glow discharge (i.e. in a classical positive column) of both the electrons and the vibrationally excited molecules in the electronic ground states N<sub>2</sub>( $X^{1}\Sigma_{g}^{+}, v$ ) and H<sub>2</sub>( $X^{1}\Sigma_{g}^{+}, v'$ ). As a second aim, we pretend to analyse previously reported measurements in the negative glow near the cathode fall [1-5] where, as it is well known, there are quite different electric fields and a marked spatial inhomogeneity of the plasma. Although theory and experiment have not been performed for the same conditions, we will show that some of the characteristic features exhibited in the previous measurements, and not conveniently discussed in earlier papers, may be attributed to the coupling of the vibrational kinetics of  $N_2(X, v)$  and  $H_2(X, v')$ molecules each other and, therefore, they are satisfactorily explained by present theoretical predictions using an homogeneous model.

The self-consistent theoretical approach presented in this paper is based on simultaneous solutions to the homogeneous electron Boltzmann equation and the two systems of vibrational rate balance equations for the populations  $N_2(X, 0 \le v \le 45)$  and  $H_2(X, 0 \le v' \le 14)$ . Both systems take into account electron-vibration (e-V), vibration-vibration (V-V) and vibration-translation (V-T) energy exchange processes, as well as the processes of dissociation by the V-V and V-T exchanges and atomic reassociation. The V-V and V-T processes include both the exchanges between equal collision partners,  $N_2$ - $N_2$  and  $H_2-H_2$ , and those involving different partners  $N_2$  and  $H_2$ . Inelastic and superelastic collisions of the electrons with vibrationally excited molecules  $N_2(X, v > 0)$  and  $H_2(X, v' > 0)$  have been accounted for in the Boltzmann equation and in the systems for the vibrational levels owing to the relatively large fractional vibrational concentrations in these levels. Such processes are in the origin of a strong coupling between the electron energy distribution function (EDF) and both vibrational distribution functions (VDFs) of molecules  $N_2(X, v)$  and  $H_2(X, v')$ . The role of other species produced by reactive transfers in  $N_2$ -H<sub>2</sub> plasma such as NH radicals are briefly referred to in the conclusions of present paper.

The organization of this paper considers the discussion of the basic system of equations in section 2. In section 3 we present the collisional data used in this work. In particular, we will emphasize the analysis of the data for the V-V and V-T rate coefficients involving collisions between different collision partners. In section 4 we discuss the principal results derived from the present theoretical model. These include, among other data, the EDF and the VDFs for  $N_2(X, v)$  and  $H_2(X, v')$ , and the corresponding vibrational temperatures for both gases calculated in a fully self-consistent manner. Section 5 is concerned with the analysis and interpretation of experiments in an  $N_2$ -H<sub>2</sub> reactor for steel surface nitriding. Finally, in section 6 we present the principal conclusions of this work.

#### 2. Theoretical formulation

The theoretical approach used here is based on solutions to the coupled system formed by the electron Boltzmann equation and two systems of rate balance equations for the populations of the vibrational levels  $N_2(X^1\Sigma_g^+, v)$ and  $H_2(X^1\Sigma_g^+, v')$ . The Boltzmann equation is coupled to the systems for the vibrational populations through both inelastic and superelastic electron-vibration (e-V) collisions.

In this work we assume that the anisotropies resulting from the electric field are sufficiently small that we may use the steady-state homogeneous electron Boltzmann equation, as derived from the usual two-term expansion in spherical harmonics. This latter assumption is valid for the range of the values of the ratio of the electric field to the gas density used in this paper as has been clearly demonstrated [6] for N<sub>2</sub>. Higher order term approximations are, therefore, out of the scope of this work, for the sake of clearness of the main purpose of present paper, which is the analysis of the strong coupling of the kinetics of  $N_2(X, v)$  and  $H_2(X, v')$  molecules to each other and to that of the electrons. Under the present approximations the Boltzmann equation can be written for a  $N_2-H_2$  mixture as follows

$$-\frac{\mathrm{d}}{\mathrm{d}u}\left[\frac{1}{3}\left(\frac{E}{N}\right)^2\frac{u}{\left(\sum_{\mathrm{s}}\delta_{\mathrm{s}}\sigma_{\mathrm{cs}}\right)}\frac{\mathrm{d}f}{\mathrm{d}u}+\left(\sum_{\mathrm{s}}\delta_{\mathrm{s}}\frac{2m}{M_{\mathrm{s}}}\sigma_{\mathrm{cs}}\right)\right]$$

$$\times u^{2} \left( f + \frac{KT_{g}}{e} \frac{\mathrm{d}f}{\mathrm{d}u} \right) + 4 \left( \sum_{s} \delta_{s} B_{\mathrm{os}} \sigma_{\mathrm{os}} \right) uf \right]$$

$$= \sum_{s} \delta_{s} \left( \sum_{i,j} \delta_{\mathrm{si}} [(u + V_{\mathrm{si}}^{j}) \sigma_{\mathrm{si}}^{j} (u + V_{\mathrm{si}}^{j}) f(u + V_{\mathrm{si}}^{j}) - u \sigma_{\mathrm{si}}^{j} (u) f(u)] + \sum_{i,j} \delta_{\mathrm{sj}} [(u - V_{\mathrm{si}}^{j}) \sigma_{\mathrm{sj}}^{i} (u - V_{\mathrm{si}}^{j}) - u \sigma_{\mathrm{si}}^{j} (u) f(u)] \right) .$$

$$\times f(u - V_{\mathrm{si}}^{j}) - u \sigma_{\mathrm{sj}}^{i} (u) f(u)] \right).$$

$$(1)$$

Here f(u) is the electron energy distribution function (EDF), normalized such that  $\int_0^{\infty} f(u)\sqrt{u} \, du = 1$ , u is the electron energy expressed in eV, E/N is the ratio of the electric field to the total gas density, e and m are the absolute value of the electron charge and the electron mass, respectively,  $T_g$  is the gas temperature in Kelvin, and K is the Boltzmann constant. The subscript s is for N<sub>2</sub> or H<sub>2</sub>, so that  $\sigma_{cs}$  denotes the momentum transfer cross section for collisions of the electrons with molecules of type s,  $\delta_s$  is the fractional concentration of both gases in the mixture,  $\delta_s = [N_2]/N$ or =  $[H_2]/N$ ,  $M_s$  is the molecular mass,  $B_{os}$  is the rotational constant (=  $2.5 \times 10^{-4}$  and  $7.54 \times 10^{-3}$  eV for N<sub>2</sub> and H<sub>2</sub>, respectively), and  $\sigma_{\infty} = 8\pi q_s^2 a_0^2/15$ , where  $q_s$  is the electric quadrupole moment in units of  $ea_0^2(q_s = 1.01$  in N<sub>2</sub> and 0.62 in H<sub>2</sub>),  $a_0$  denoting the Bohr radius. The three terms on the left-hand side (LHS) of equation (1) represent, therefore, the energy gain by the electrons from the electric field, the energy loss due to the elastic collisions and the energy loss due to the excitation and de-excitation of rotational levels. The latter process has been treated here in the continuous approximation [7]. On the other hand, the terms on the right-hand side (RHS) of equation (1) represent the effects of inelastic collisions of electrons with heavy species s, in the case of the first two terms of (1), and of superelastic collisions, in the case of the last two terms.  $\sigma_{si}^{j}$  and  $\sigma_{si}^{i}$  are the inelastic and superelastic electron cross sections for a transition from the *i*th to the *j*th state of the species s, with i < j,  $V_{si}^{j}$  is the corresponding energy threshold, and  $\delta_{si}$  is the relative number density of molecules of type s in the *i*th state (e.g. in N<sub>2</sub>, we have  $\delta_{si} = N_i / [N_2]$ ).

The following simplifications have been introduced in solving equation (1), as we have discussed separately for both gases in previous works [8–10]: (i) the excitation of electronic states was treated as a single energy loss process assuming, in this case, that all the molecules of both species are in the ground vibrational level,  $N_2(X, v = 0)$  or  $H_2(X, v' = 0)$ ; (ii) the superelastic collisions of electrons with molecules in electronically excited states were neglected; (iii) the ionization process was treated similarly to an excitation with a single energy loss; (iv) the creation of secondary electrons by ionization was neglected.

Inelastic and superelastic collisions of the electrons with N<sub>2</sub>(X, v > 0) and H<sub>2</sub>(X, v' > 0) molecules have been taken into account in (1) owing to the large fractional populations,  $\delta_v = N_v / [N_2]$  and  $\delta_{v'} = N_{v'} / [H_2]$ , in excited vibrational levels usually present in an N<sub>2</sub>-H<sub>2</sub> glow discharge. Thus, equation (1) is coupled through the fractional vibrational populations  $\delta_v$  and  $\delta_{v'}$  to the systems of steady-state rate balance equations for these populations, which for a given vth level in N<sub>2</sub>, for instance, can be written in a symbolic form as follows:

$$\left(\frac{\mathrm{d}N_{v}}{\mathrm{d}t}\right)_{\mathrm{e-V}} + \left(\frac{\mathrm{d}N_{v}}{\mathrm{d}t}\right)_{\mathrm{V-V}}^{\mathrm{N_{2}-N_{2}}} + \left(\frac{\mathrm{d}N_{v}}{\mathrm{d}t}\right)_{\mathrm{V-T}}^{\mathrm{N_{2}-N_{2}}} + \left(\frac{\mathrm{d}N_{v}}{\mathrm{d}t}\right)_{\mathrm{V-T}}^{\mathrm{N_{2}-H_{2}}} + \left(\frac{\mathrm{d}N_{v}}{\mathrm{d}t}\right)_{\mathrm{V-T}}^{\mathrm{N_{2}-H_{2}}} + \left(\frac{\mathrm{d}N_{v}}{\mathrm{d}t}\right)_{\mathrm{R}} = 0.$$

$$(2)$$

The various terms in equation (2) account for the e-V, V-V and V-T energy exchange processes and for atomic reassociation according to the following reactions:

$$e-V(N_2): \qquad e+N_2(X,v) \leftrightarrows e+N_2(X,w) \qquad (3)$$

$$V-V(N_2-N_2): N_2(X, v) + N_2(X, w-1) \Leftrightarrow N_2(X, v-1) + N_2(X, w)$$
(4)

$$V-T(N_2-N_2): N_2 + N_2(X, v) \leftrightarrows N_2 + N_2(X, v - 1)$$
(5)

$$V-V(N_2-H_2):$$
  

$$N_2(X,v) + H_2(X,v'-1)$$
  

$$= N_2(X,v-1) + H_2(X,v')$$
(6)

$$V-T(N_2-H_2): H_2 + N_2(X, v) \leftrightarrows H_2 + N_2(X, v - 1)$$
(7)

$$R(N_2): N + N \to N_2(X, v = 0).$$
 (8)

The vibrational populations  $\delta_{v'}$  in H<sub>2</sub> are determined by an equation involving reactions physically identical to these for N<sub>2</sub>. Explicit expressions for the terms in both equations are given in [8] and [10] for N<sub>2</sub> and H<sub>2</sub> respectively.

The V-V and V-T reactions consider single quantum transitions only, which are the most likely ones. The transitions from the X, v and X, v' levels to excited electronic states by electron collisions were discarded in the model as the corresponding rate coefficients are much smaller than those for the e-V processes in the range of values for E/N considered here. The reactions (4) and (5), as well as the similar reactions for H<sub>2</sub>, also take into account dissociation by the V-V and V-T processes [8, 10], which is modelled, as suggested by Cacciatore *et al* [11], as a transition from the last bound level (v = 45 in N<sub>2</sub> and v' = 14 in H<sub>2</sub>) to a pseudolevel (46 or 15) in the continuum, being the corresponding rates (in cm<sup>-3</sup> s<sup>-1</sup>) given by

$$(v_{\rm diss}^{v})_{\rm N_2} = [N_2]^2 \left( \delta_{45} \sum_{v=1}^{45} \delta_v P_{45,46}^{v,v-1} + \delta_{45} P_{45,46} \right) \qquad (9)$$

and

$$(v_{\text{diss}}^{v})_{\text{H}_{2}} = [\text{H}_{2}]^{2} \left( \delta_{14} \sum_{v'=1}^{14} \delta_{v'} P_{14,15}^{v',v'-1} + \delta_{14} P_{14,15} \right) (10)$$

where the coefficients P denote the relevant V-V and V-T rate coefficients involving in vibrational dissociation.

The last term of equation (2) takes into account, in a symbolic form, the process of atomic reassociation, which is assumed to populate only the vibrational level v = 0 (or v' = 0 in the case of the analogous equation for H<sub>2</sub>). In a previous work [8] the effects of atomic reassociation populating other vth levels have been analysed in detail for N<sub>2</sub>. Here we do not assume any reassociation mechanism in particular, but just that the atomic reassociation rate into v = 0 must exactly equal the total dissociation rate by the V-V and V-T processes, by writing

$$\left(\frac{\mathrm{d}N_0}{\mathrm{d}t}\right)_{\mathrm{R}} = v_{\mathrm{diss}}^v \tag{11}$$

either in equation (2) for  $N_2$  or in the equation for  $H_2$ .

Finally, we note that we have discarded the effects of the V-T exchanges involving dissociated atoms, although previous calculations have shown that these reactions can be very important in H<sub>2</sub>, even for relative atom concentrations as small as  $10^{-2}$  [10]. This behaviour is a result of the existence of a reactive process in which atomic exchange occurs between the atom and the molecule. The V-T processes with H atoms in a pure  $H_2$  discharge originate a rapid fall-off in the VDF at  $v' \ge 3$ . However, in the present case of a N<sub>2</sub>-H<sub>2</sub> mixture, we will show that the VDF in H<sub>2</sub> always presents negligible populations at these v'th levels, even when we do not consider the V-T exchanges with H atoms, so that the neglect of such processes only introduces minor modifications in the results obtained with the present model.

For a given set of the independent parameters E/N, degree of ionization  $n_e/N$ , fractional composition of the mixture  $[N_2]/N$  and  $[H_2]/N$ , with  $N = [N_2]+[H_2]$ , and  $T_g$ , the Boltzmann equation and the systems of rate balance equations for the vibrational populations of both gases can be solved to yield the EDF, f(u), and the VDFs in  $N_2$ ,  $\delta_v = N_v / [N_2] (0 \le v \le 45)$ , and in H<sub>2</sub>,  $\delta_{v'} = N_{v'}/[H_2](0 \leq v' \leq 14)$ . Each VDF can be characterized by a vibrational temperature defined as the characteristic vibrational temperature of the Treanor-like distribution [12] that best fits to the calculated VDF for the lowest four levels. We have, therefore, two dependent parameters,  $T_v(N_2)$  and  $T_v(H_2)$ , giving a measure of the degree of vibrational excitation. However, in practice for the purposes of presentation of calculated data, it is useful to use one of these temperatures as an independent parameter instead of  $n_e/N$ .

#### 3. Collisional data

The electron cross sections used in this paper are exactly the same as in previous works in pure  $N_2$  [8] and pure

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Nitrogen	$e + N_2(X, v) \leftrightarrows e + N_2(X, w)$
	(v = 0,, 9; w = v + 1,, 10)
	$e + N_2(X, v = 0) \rightarrow e + N_2(Y)$
	$(Y=A^3\Sigma^+_{\mathfrak{u}},B^3\Pi_{\mathfrak{g}},W^3\Delta_{\mathfrak{u}},B'^3\Sigma^{\mathfrak{u}},a'^1\Sigma^{\mathfrak{u}},a^1\Pi_{\mathfrak{g}},$
	$\mathbf{w}^{1}\Delta_{\mathbf{u}}, \mathbf{C}^{3}\Pi_{\mathbf{u}}, \mathbf{E}^{3}\Sigma_{\mathbf{g}}^{+}, \mathbf{a}^{\prime\prime1}\Sigma_{\mathbf{g}}^{+}, \mathbf{c}^{\prime1}\Sigma_{\mathbf{u}}^{+}, \mathbf{c}^{1}\Pi_{\mathbf{u}},$
	$b^{1}\Pi_{u}, b^{\prime 1}\Sigma_{u}^{+})$
	$\mathbf{e} + \mathbf{N_2}(\mathbf{X}, \mathbf{v} = 0) \rightarrow \mathbf{e} + \mathbf{N_2^+} + \mathbf{e}$
Hydrogen	$e + H_2(X, v') = e + H_2(X, w')$
, iyorogon	(y' = 0,, 9; w' = y' + 1,, 10)
	$\mathbf{e} + \mathbf{H}_2(\mathbf{X}, \mathbf{v}' = 0) \rightarrow \mathbf{e} + \mathbf{H}_2(\mathbf{Y}')$
	$(\mathbf{Y}' = \mathbf{b}^3 \Sigma^{\ddagger}, \mathbf{c}^3 \Pi_{\nu}, \mathbf{a}^3 \Sigma^{\ddagger}, \mathbf{e}^3 \Sigma^{\ddagger}, \mathbf{B}^1 \Sigma^{\ddagger}, \mathbf{C}^1 \Pi_{\nu},$
	$\mathbf{E}^{1}\Sigma_{\tau}^{1}, \mathbf{E}^{1}\Sigma_{\tau}^{1}, \mathbf{B}^{\prime 1}\Sigma_{\tau}^{1}, \mathbf{D}^{1}\Pi_{u}, \mathbf{B}^{\prime \prime 1}\Sigma_{\tau}^{1}, \mathbf{D}^{\prime 1}\Pi_{u})$
	$e + H_2(X v' = 0) \rightarrow e + H(1s) + H(n = 2)$
	$a + H_2(X, Y = 0) \rightarrow a + H(1s) + H(n = 2)$
	$\mathbf{e} + \mathbf{n}_2(\mathbf{x}, \mathbf{v} = 0) \rightarrow \mathbf{e} + \mathbf{n}_1(\mathbf{x}) + \mathbf{n}_1(\mathbf{v} = 0)$
	$\mathbf{e} + \mathbf{H}_2(\mathbf{X}, \mathbf{V}' = 0) \rightarrow \mathbf{e} + \mathbf{H}_2^{\mathrm{T}} + \mathbf{e}$

Table 1. Inelastic and superelastic electron processes in the Boltzmann equation.

 $H_2$  [10]; the reader should refer to these papers for details. Table 1 shows a list of the various inelastic and superelastic processes included in equation (1).

In what concerns the V–V and V–T rate coefficients for both gases involving collisions between equal collision partners, i.e.  $N_2-N_2$  or  $H_2-H_2$ , the collisional data used for  $H_2$  are exactly the same as in [10], while for  $N_2$ we have replaced our previously reported data [8] with those obtained by Billing and co-workers [13, 14]. As we have discussed [15], the V–V and V–T rate coefficients used in [8] seem to overestimate the actual rates. The reader should refer to these references for details.

The rate coefficients for V-V energy exchanges between  $N_2$  and  $H_2$  have been calculated from the SSH (Schwartz, Slawsky, Herzfeld) formulation [16-23], which for the case of reaction (6) can be written as

$$P_{v,v-1}^{v'-1,v'} = Z_{N_2-H_2} \frac{U_{v,v-1}^2 U_{v',v'-1}^2}{\hbar^2} \times 8L^2 \mu KT_g F(Y_{v,v-1}^{v'-1,v'}) \qquad \Delta E_{v,v-1}^{v'-1,v'} < 0 (12)$$

and

$$P_{v,v-1}^{v'-1,v'} = [\text{RHS of (12)}] \exp\left(\frac{\Delta E_{v,v-1}^{v'-1,v'}}{KT_g}\right)$$
$$\Delta E_{v,v-1}^{v'-1,v'} > 0 \tag{13}$$

with  $Z_{N_2-H_2}$ ,  $U_{v,v-1}^2$ ,  $U_{v',v'-1}^2$  and  $\Delta E_{v,v-1}^{v'-1,v'}$  given by the expressions:

$$Z_{\rm N_2-H_2} = \pi d_{12}^2 \left(\frac{8KT_g}{\pi\mu}\right)^{1/2}$$
(14)

$$U_{v,v-1}^{2} = \frac{v}{1 - \chi_{e}(N_{2})v} \frac{\hbar}{8L^{2}\mu^{*}(N_{2})\omega(N_{2})}$$
(15)

$$U_{v',v'-1}^{2} = \frac{v'}{1 - \chi_{e}(H_{2})v'} \frac{\hbar}{8L^{2}\mu^{*}(H_{2})\omega(H_{2})}$$
(16)

$$\Delta E_{v,v-1}^{v'-1,v'} = \hbar \omega(N_2) [1 - 2\chi_e(N_2)v] - \hbar \omega(H_2) [1 - 2\chi_e(H_2)v'].$$
(17)

Here,  $d_{12} = [d(N_2) + d(H_2)]/2 = 3.34$  Å is the distance of closest approach,  $\mu$  is the reduced collisional mass N<sub>2</sub>-H<sub>2</sub>,  $\mu^*(N_2)$  and  $\mu^*(H_2)$  are the reduced mass of molecules, and L is a length characterizing the short range exponential of the intermolecular potential. The anharmonic Morse oscillator parameters are:  $\omega(N_2) = 4.44 \times 10^{14} \text{ s}^{-1}$ ;  $\omega(H_2) = 8.29 \times 10^{14} \text{ s}^{-1}$ ;  $\chi_e(N_2) = 6.073 \times 10^{-3}$ ;  $\chi_e(H_2) = 2.757 \times 10^{-2}$ . Finally, the adiabaticity factor,  $F(Y_{v,v-1}^{v'-1,v'})$ , is given by [18, 19]

$$F(y) = \begin{cases} \frac{1}{2}[3 - \exp(-2y/3)] \exp(-2y/3) \\ \text{for } y \leq 20 \\ 8(\pi/3)^{1/2} y^{7/3} \exp(-3y^{2/3}) \\ \text{for } y > 20 \end{cases}$$
(18)

where

$$Y_{v,v-1}^{v'-1,v'} = \frac{\pi L}{\hbar} \left( \frac{\mu}{2KT_g} \right)^{1/2} \left| \Delta E_{v,v-1}^{v'-1,v'} \right|.$$
(19)



**Figure 1.** Rate coefficients for the V–V exchanges  $N_2(v) + H_2(v'-1) \rightarrow N_2(v-1) + H_2(v')$  (full curves) and for the reverse exchanges (broken curves), as a function of the vth quantum number in  $N_2$  and for various v'th quantum numbers in  $H_2$ . These data have been calculated for  $T_9 = 400$  K and using an intermolecular potential length L = 0.3 Å.



**Figure 2.** As in figure 1 for the direct reaction  $(v, v' - 1) \rightarrow (v - 1, v')$  and for L = 0.3 Å (full curves) and 0.2 Å (broken curves).

In this paper we have assumed L = 0.3 Å for the following reasons: (a) our calculations for N<sub>2</sub> [8, 15] have shown that the SSH theory with L = 0.2 Å yields probabilities one order of magnitude larger than those calculated previously [13, 14] using a three-dimensional semi-classical collision model which includes an intermolecular potential with both long and short range interactions; (b) present calculated sSH probabilities with L = 0.3 Å are about one order of magnitude smaller than those calculated using this same theory with L = 0.2 Å (see figure 2); (c) the potential lengths used in the works of Billing and Fisher [13, 24] for both gases do not present large differences (0.25 Å in N<sub>2</sub> and 0.28 Å in H<sub>2</sub>).

Figure 1 shows the calculated rate coefficients  $P_{v,v-1}^{v'-1,v'}$  and  $P_{v-1,v}^{v',v'-1}$  of reaction (6) for L = 0.3 Å, as a function of the vibrational quantum number v in N<sub>2</sub> and for v' = 1, 6, and 11 in H<sub>2</sub>. We note that the reverse V-V coefficients are obtained by detailed balancing

$$P_{v-1,v}^{v',v'-1} = P_{v,v-1}^{v'-1,v'} \exp\left(-\frac{\Delta E_{v,v-1}^{v'-1,v'}}{KT_{g}}\right).$$
 (20)

Figure 2 shows a comparison between the rate coefficients  $P_{v,v-1}^{v'-1,v'}$  calculated for L = 0.3 Å and 0.2 Å, as a function of the vth level and for v' = 5, 8, 11 and 14. This figure shows that the probabilities of energy transfer in a V-V exchange are rapidly increasing with the coefficient  $\alpha = 1/L$  in the exponent of the repulsive intermolecular potential  $V(r) = V_0 \exp(-\alpha r)$ . Figures 1 and 2 are for a gas temperature  $T_g = 400$  K, which represents a typical average value under present conditions.

Owing to the larger energy difference in a single quantum transition in H<sub>2</sub> than in N<sub>2</sub>, the most effective V-V reactions in the N<sub>2</sub>-H<sub>2</sub> system correspond to a populating mechanism in N<sub>2</sub> and a depopulating one in H<sub>2</sub>, i.e.  $\Delta E_{v,v-1}^{v'-1,v'} < 0$  in equation (17). This is always true except at the highest v'th levels in H<sub>2</sub>( $\Delta E_{v,v-1}^{v'-1,v'} > 0$  only for  $v' \ge 9$ ). This fact enables us to explain figure 3, in which we represent the following sums of the V-V(H<sub>2</sub>-N<sub>2</sub>) rate coefficients for the reverse reaction of (6)

$$Q_{v',v'-1}^{\mathrm{H}_2-\mathrm{N}_2} = \frac{[\mathrm{N}_2]}{[\mathrm{H}_2]} \sum_{v=1}^{45} \delta_{v-1} P_{v-1,v}^{v',v'-1}$$
(21)

and

$$Q_{v'-1,v'}^{H_2-N_2} = \frac{[N_2]}{[H_2]} \sum_{v=1}^{45} \delta_v P_{v,v-1}^{v'-1,v'}$$
(22)

calculated for L = 0.3 Å,  $T_g = 400$  K,  $[N_2]/N = 0.9$ ,  $[H_2]/N = 0.1$ , and for the vibrational temperature in N<sub>2</sub>,  $T_v(N_2) = 4000$  K. Equations (21) and (22) show that for v' < 9 the coefficients Q originate in H<sub>2</sub> the same kind of effect of an V-T exchange. Further, in present conditions, of a 90%N<sub>2</sub>-10%H<sub>2</sub> mixture, the depopulating effect of the V-V(H<sub>2</sub>-N<sub>2</sub>) exchanges are considerably larger than that due to the V-T(H<sub>2</sub>-H<sub>2</sub>) exchanges. The coefficients shown in figure 3 pass through a maximum at v' = 9, which corresponds to a nearly resonant V-V exchange with v = 0 in N<sub>2</sub>.

In what concerns the V-T rate coefficients of  $N_2$ -H<sub>2</sub> exchanges given by (7), we have used the data on the vibrational relaxation times deduced by White [25]

$$p\tau(\text{atm s}) = 2.42 \times 10^{-9} \exp(80.6T_g^{-1/3})$$
 (23)

which allows us to obtain for the  $\upsilon=1\to 0$  transition of  $N_2$  in the  $N_2\text{--}H_2$  system

$$P_{1,0}^{N_2-H_2}(\text{cm}^3\text{s}^{-1}) = 5.63 \times 10^{-14} T_g \exp(-80.6T_g^{-1/3}).$$
(24)



**Figure 3.** Composed coefficients for the V-V(H<sub>2</sub>-N<sub>2</sub>) exchanges given by formulae (21) and (22),  $Q_{v',v'-1}^{H_2-N_2}$  (full curve) and  $Q_{v'-1,v'}^{H_2-N_2}$  (broken curve), in a 90%N<sub>2</sub>-10%H<sub>2</sub> mixture, as a function of the v'th quantum number in H<sub>2</sub> and for L = 0.3 Å,  $T_v(N_2) = 4000$  K and  $T_g = 400$  K. For comparison the two chain curves represent the V-T(P\_{v',v'-1}, curve A) and V-V(P\_{v',v'-1}^{v',-1,v'}, curve B) rate coefficients in pure H<sub>2</sub> for  $T_g = 400$  K calculated in [10].

The rate coefficients for other V-T exchanges have been calculated from the SSH theory with L = 0.3 Å. Figure 4 shows that the V-T rate coefficients for N<sub>2</sub>-H<sub>2</sub> collisions are several orders of magnitude larger than those calculated for the N<sub>2</sub>-N<sub>2</sub> exchanges [13, 14]. Even in a 99%N<sub>2</sub>-1%H<sub>2</sub> mixture, where the former coefficients must be multiplied by 0.01/0.99 in equation (2), the effective V-T rates for N<sub>2</sub>-H<sub>2</sub> exchanges are still larger by more than one order of magnitude.

Finally, we have discarded the V-T( $H_2-N_2$ ) exchanges in depopulating  $H_2$  as the corresponding rate coefficients are negligibly small as compared to those for the V-T( $H_2-H_2$ ) exchanges due to the large differences between both molecular mass.

#### 4. Theoretical results

#### 4.1. Vibrational kinetics

As pointed out in section 2, the independent variables for this self-consistent problem as formulated here are: the ratio of the electric field to the total gas density E/N, the degree of ionization  $n_e/N$ , the gas temperature and of course the fractional composition of the mixture. For a set given of variables we have a unique solution composed by a EDF and the VDFs for N<sub>2</sub> and H<sub>2</sub>. Both VDFs are characterized by vibrational temperatures,  $T_v(N_2)$  and  $T_v(H_2)$ , and, in practice, it is useful to consider one of these temperatures as an independent parameter in place of  $n_e/N$ .



**Figure 4.** Rate coefficients for the V–T(N<sub>2</sub>–H<sub>2</sub>) exchanges for  $T_g = 400$  K and an intermolecular potential length L = 0.3 Å (curve A). Curve B shows the effective rates in a 99%N<sub>2</sub>–1%H<sub>2</sub> mixture, i.e. represents curve A ×(1/99). In this figure we also represent the V–T(N<sub>2</sub>–N<sub>2</sub>) rates. The various curves are as a function of the vth quantum number in N<sub>2</sub>.



**Figure 5.** Vibrational temperature  $T_v(H_2)$  as a function of the fractional concentration of  $H_2$  in a  $N_2$ - $H_2$  mixture, for  $E/N = 5 \times 10^{-16}$  V cm<sup>2</sup>,  $T_g = 400$  K and the following constant values of  $T_v(N_2)$  in K: curve A, 3500; B, 4000; C, 5000.

Figure 5 shows the vibrational temperature in H<sub>2</sub> as a function of the fractional concentration of this gas in the N<sub>2</sub>-H<sub>2</sub> mixture, for  $E/N = 5 \times 10^{-16}$  V cm<sup>2</sup>,  $T_g = 400$  K and for various constant values of  $T_v(N_2) =$ 3500, 4000 and 5000 K. The analysis of this figure allows us to conclude that the vibrational temperatures in H<sub>2</sub> are largely smaller than those in N<sub>2</sub> ( $T_v(H_2)$  is smaller by a factor of 1/3). As we will show in section 5 a ratio of this order between both temperatures is in satisfactory agreement with measurements using the CARS diagnostic. Moreover, we can note that the values of  $T_v(H_2)$  only slowly increase with the fractional concentration [H<sub>2</sub>]/N, except in the case of the highest values for  $T_v(N_2)$  where a relatively rapid increase in  $T_v(H_2)$  occurs for the lowest concentrations of H<sub>2</sub>.

The values of the degree of ionization necessary to produce the curves on figure 5 are not kept constant as long as  $[H_2]/N$  varies. Table 2 shows such values for the

**Table 2.** Values of the degree of ionization and of the vibrational temperature in H<sub>2</sub>, as a function of the fractional H<sub>2</sub> concentration, for  $E/N = 5 \times 10^{-18}$  V cm<sup>2</sup>,  $T_v(N_2) = 4000$  K,  $T_g = 400$  K.

[H <sub>2</sub> ]/N	<i>n</i> ₀/N (×10 <sup>−8</sup> )	n <sub>e</sub> /[H <sub>2</sub> ]	τ <sub>v</sub> (H <sub>2</sub> ) (K)
0	8.26		
0.01	7.69	7.69(×10 <sup>-6</sup> )	1293
0.02	7.66	3.83(×10 <sup>-6</sup> )	1299
0.05	7.50	1.50(×10 <sup>-6</sup> )	1316
0.10	7.10	7.10(×10 <sup>−7</sup> )	1335
0.20	6.40	3.20(×10 <sup>-7</sup> )	1365
0.35	5.30	1.51 (×10 <sup>−7</sup> )	1398
0.50	4.40	8.80(×10 <sup>-8</sup> )	1430

conditions of curve B (i.e. for  $T_{y}(N_2) = 4000$  K). This table indicates that for this constant value of  $T_{\rm v}(N_2)$ there is a reduction of about 50% in  $n_e/N$  as  $[H_2]/N$ increases from 0 (pure N<sub>2</sub>) up to 50%. On the other hand, if we look at the  $n_e/[H_2]$  values, there exists a strong decrease of these values as  $[H_2]/N$  increases as expected. At this point we note that the slow increase of  $T_{\rm v}({\rm H}_2)$  with  $[{\rm H}_2]/N$  is apparently in opposing sense to the rapid decrease of  $n_e/[H_2]$  as  $[H_2]/N$  increases. The vibrational temperatures  $T_{\rm v}({\rm H}_2)$  are determined by the e-V populating rates and these rates (in  $\text{cm}^3 \text{ s}^{-1}$ ) are dependent on  $n_e/[H_2]$ . Nevertheless, as  $[H_2]/N$ increases the effective rates of the  $V-V(H_2-N_2)$  processes given by the reverse reaction of (6), which are proportional to  $[N_2]/[H_2]$  (see equation (21)), decrease as well and these processes constitute a depopulating mechanism for H<sub>2</sub>. Thus, as  $[H_2]/N$  increases,  $T_v(H_2)$ is determined by the simultaneous effect of both decreasing functions  $n_e/[H_2]$  (populating) and  $[N_2]/[H_2]$ (depopulating).

It is interesting at this point to compare the predicted vibrational temperature  $T_v(H_2)$  in an N<sub>2</sub>-H<sub>2</sub> mixture to that obtained in pure H<sub>2</sub>. Thus, figure 6 shows values of  $T_v(H_2)$  against  $n_e/[H_2]$  for the same conditions as in table 2 as well as the vibrational temperature in pure H<sub>2</sub> calculated before [10].

Figure 7 shows the calculated vibrational temperature in N<sub>2</sub>,  $T_v(N_2)$ , as a function of the fractional concentration of H<sub>2</sub>, for  $E/N = 5 \times 10^{-16}$  V cm<sup>2</sup>,  $T_{\rm g} = 400$  K, and for  $n_{\rm g}/[N_2] = 4 \times 10^{-8}$  and  $6 \times 10^{-8}$ . For these two relatively low values of  $n_e/[N_2]$ ,  $T_v(N_2)$ presents a rapid increase in the region of the lowest concentrations of  $H_2([H_2]/N \leq 1\%)$  followed by a slow decrease for the highest concentrations. The explanation for such behaviour is as follows: (i) in the range going from pure  $N_2$  to approximately 1%  $H_2$ , the vibrational temperature in N2 increases due to the  $V-V(N_2-H_2)$  exchanges, which constitute a populating mechanism in N<sub>2</sub> (and therefore a depopulating one in H<sub>2</sub>) as a result of the different energy differences between two vibrational levels in both molecules; (ii) for  $H_2$  concentrations higher than ~ 1% the destruction of vibrational quanta by  $V-T(N_2-H_2)$  exchanges becomes predominant relatively to the former populating mechanism. We note that as will be discussed in section 5, this



**Figure 6.** Vibrational temperature  $T_v(H_2)$  as a function of the degree of ionization defined as  $n_e/[H_2]$ , for the case of a N<sub>2</sub>-H<sub>2</sub> mixture (curve A) and for pure H<sub>2</sub> (curve B). Both curves are for  $E/N = 5 \times 10^{-16}$  V cm<sup>2</sup> and  $T_g = 400$  K. Curve A is for  $T_v(N_2) = 4000$  K. The broken curve represents the corresponding values for  $[H_2]/N$  in N<sub>2</sub>-H<sub>2</sub>.



**Figure 7.** Vibrational temperature in N<sub>2</sub> as a function of the fractional concentration of H<sub>2</sub> in a N<sub>2</sub>-H<sub>2</sub> mixture, for  $E/N = 5 \times 10^{-16}$  V cm<sup>2</sup>,  $T_g = 400$  K and the following values of  $n_e/[N_2]$ : curve A,  $4 \times 10^{-8}$ ; B,  $6 \times 10^{-8}$ .

same behaviour for  $T_v(N_2)$  against  $[H_2]/N$  has been experimentally detected by emission spectroscopy using a rare gas actinometry technique.

The effects of  $V-T(N_2-H_2)$  exchanges are extremely important for the VDF in N<sub>2</sub>, causing a rapid fall-off at the highest vth levels and consequently a very sharp decrease in the rate of dissociation by the V-V and V-T processes given by equation (9), even for relative  $H_2$  concentrations as small as 0.5%. Figure 8 shows the VDFs in N<sub>2</sub> calculated for  $E/N = 5 \times 10^{-16}$  V cm<sup>2</sup>,  $T_{\rm v}({\rm N}_2) = 4000$  K and  $T_{\rm g} = 400$  K, for pure N<sub>2</sub> (curve A) and for various values of  $[H_2]/N$  ranging from 0.5% to 10%. In turn, figure 9 shows the VDFs in  $H_2$  calculated self-consistently with those in N<sub>2</sub> for H<sub>2</sub> concentrations of 1%, 10%, 50%. We note that the VDFs in H<sub>2</sub> are sharply decreasing due to their small vibrational temperatures ( $T_{\rm v}({\rm H}_2)$  ranging from 1293 to 1430 K; see table 2). It is worth noting at this point that this fact justifies our neglect of the V-T processes with H atoms referred to in section 2. As shown previously [10] for pure  $H_2$  the V-T exchanges with H atoms originate a strong decrease in the VDF of H<sub>2</sub> for  $v' \ge 3$ . However, in a N<sub>2</sub>-H<sub>2</sub> mixture and for the range of  $n_e/N$  values



**Figure 8.** Vibrational distribution functions in N<sub>2</sub> for  $E/N = 5 \times 10^{-16}$  V cm<sup>2</sup>,  $T_v(N_2) = 4000$  K,  $T_g = 400$  K and for the following values of H<sub>2</sub> concentration, [H<sub>2</sub>]/N: curve A, 0; B, 0.5%; C, 1%; D, 2%; E, 5%; F, 10%.

under consideration, the VDF of  $H_2$  presents such small values that the inclusion or the absence of processes with H atoms is irrelevant.

In figure 8 we have seen that as  $[H_2]/N$  increases the VDF in  $N_2$  is sharply depleted at high vth levels due to the V-T(N<sub>2</sub>-H<sub>2</sub>) processes and this fact promotes a strong decrease in the rate of dissociation of N<sub>2</sub> by the V-V and V-T processes given by equation (9). Figure 10 shows the rate of dissociation, per electron and at unit N<sub>2</sub> density, due to the V-V and V-T(N<sub>2</sub>-N<sub>2</sub>) processes, calculated in the conditions of figure 8 and as a function of the H<sub>2</sub> concentration. Figure 10 indicates that a fractional  $H_2$  concentration of about 0.5% is large enough to produce a decrease of two orders of magnitude in the rate of dissociation. We note that this behaviour is in accordance with observations in various experiments conducted either in a microwave (2.45 GHz) post-discharge for steel surface nitriding [26], where it has been observed that a sharp inhibition of the post-discharge afterglow results from N atom reassociation when a few per cent of H<sub>2</sub> is added to N<sub>2</sub>, or in a radiofrequency (27 MHz) discharge [27], in which it has been observed that the dissociation of N<sub>2</sub> mainly occurs by direct electron impact.

#### 4.2. Electron kinetics

Figure 11 shows the EDF in the N<sub>2</sub>-H<sub>2</sub> mixture calculated in the conditions of table 2 ( $E/N = 5 \times 10^{-16}$  V cm<sup>2</sup>,  $T_v(N_2) = 4000$  K,  $T_g = 400$  K) for pure N<sub>2</sub> (curve A) and for fractional H<sub>2</sub> concentrations of 50% (curve B) and 90% (curve C). The self-consistently calculated vibrational temperatures in H<sub>2</sub> are 1430 and 1472 K for curves B and C, respectively. For comparison we have also plotted the EDF in pure H<sub>2</sub> (curve D) for  $E/N = 5 \times 10^{-16}$  V cm<sup>2</sup>,  $T_g = 400$  K, and for the same vibrational temperature in H<sub>2</sub> as in curve C.

The EDF presents only small differences as long as  $[H_2]/N$  is smaller than 50%. For higher  $H_2$  concentrations, as the electron cross sections for vibrational



**Figure 9.** Vibrational distribution functions in H<sub>2</sub> for  $E/N = 5 \times 10^{-18}$  V cm<sup>2</sup>,  $T_v(N_2) = 4000$  K,  $T_g = 400$  K and for the following values of  $[H_2]/N$ : curve A, 1%; B, 10%; C, 50%. The corresponding vibrational temperatures in H<sub>2</sub> are respectively: 1293; 1335; 1430 K.



**Figure 10.** Rate of dissociation of N<sub>2</sub>, per electron and at unit N<sub>2</sub> density, by the V-V and V-T processes in a N<sub>2</sub>-H<sub>2</sub> mixture, as a function of [H<sub>2</sub>]/N and for  $E/N = 5 \times 10^{-16}$  V cm<sup>2</sup>,  $T_v(N_2) = 4000$  K and  $T_g = 400$  K.

excitation are considerably smaller in  $H_2$  than in  $N_2$ , an increase in  $[H_2]/N$  produces an enhancement of the high energy region of the EDF. We note that the increase of the tail of the EDF is a result of the difference in magnitude of the electron cross sections for vibrational excitation in both gases and not a consequence of the increase of the effects produced by the e-V superelastic collisions in  $H_2$ , as the vibrational temperature in  $H_2$  is always vanishingly small.

The effects of e-V superelastic collisions in both gases can be conveniently analysed in figure 12. In this figure we present the EDF in pure N<sub>2</sub> for  $T_v(N_2) = 4000$  K and  $T_v(N_2) = T_g = 400$  K, the EDF in pure H<sub>2</sub> for  $T_v(H_2) = 3000$  K and = 400 K, as well as the EDF in



**Figure 11.** Electron energy distribution functions in a N<sub>2</sub>-H<sub>2</sub> mixture for  $E/N = 5 \times 10^{-16}$  V cm<sup>2</sup>,  $T_v(N_2) = 4000$  K,  $T_g = 400$  K and the following fractional H<sub>2</sub> concentrations: curve A, 0 (i.e. pure N<sub>2</sub>); B, 0.5; C, 0.9. The corresponding vibrational temperatures in H<sub>2</sub> are: B, 1430; C, 1472 K. Curve D represents the EDF in pure H<sub>2</sub> for  $E/N = 5 \times 10^{-16}$  V cm<sup>2</sup>,  $T_g = 400$  K and  $T_v(H_2) = 1472$  K.

a mixture of  $50\%N_2-50\%H_2$  for  $T_v(N_2) = 4000$  K and  $T_{\rm v}({\rm H_2}) = 3000 {\rm K}$  (that is, under no self-consistent conditions) and for  $T_v(N_2) = T_v(H_2) = 400$  K. The value of E/N is kept constant and equal to  $5 \times 10^{-16}$  V cm<sup>2</sup>. Figure 12 shows that the effects of e-V superelastic collisions are extremely large in N2 and small in H2, even when we increase the vibrational temperature  $T_v(H_2)$ beyond its self-consistent limit. These results demonstrate that an increase in the H<sub>2</sub> concentration enhances the tail of the EDF and, therefore, produces an increase in the electron rate coefficients for excitation of upper electronic states. However, a reverse tendency must be expected for the case of low E/N and, simultaneously, high  $T_{\rm v}({\rm N}_2)$  values. Figure 13 shows the EDF calculated for  $E/N = 10^{-16}$  V cm<sup>2</sup> in pure N<sub>2</sub> ( $T_v = 400$  and 4000 K) and in pure H<sub>2</sub> ( $T_v = 400$  and 3000 K). For the highest  $T_{\rm v}({\rm N}_2)$  and  $T_{\rm v}({\rm H}_2)$  temperatures the effects of the e-V superelastic collisions in N2 are dominant in determining the EDF and, therefore, an increase in  $[H_2]/N$  produces a decrease in the high-energy tail of the EDF.

The changes in the EDFs caused by the increase of the fractional  $H_2$  concentration or by using of different vibrational temperatures affect the electron transport parameters and rate coefficients in the way illustrated in figures 14–16.

Figure 14 shows the electron kinetic temperature  $2/3\langle u \rangle$ , where  $\langle u \rangle$  denotes the mean electron energy as a function of  $[H_2]/N$  for  $E/N = 10^{-16}$ ,  $5 \times 10^{-16}$  and  $10^{-15}$  V cm<sup>2</sup>, for the cases:  $T_v(N_2) = 4000$  K and  $T_v(H_2) = 3000$  K;  $T_v(N_2) = 4000$  K and  $T_v(H_2) = 4000$  K;  $T_v(N_2) = T_v(H_2) = 4000$  K. This figure shows an increase of  $2/3\langle u \rangle$  with  $[H_2]/N$  for the higher values of



**Figure 12.** Electron energy distribution functions in a  $N_2-H_2$  mixture for  $E/N = 5 \times 10^{-16}$  V cm<sup>2</sup>,  $T_g = 400$  K and the following values of  $[H_2]/N$ : curve A, 0 (pure  $N_2$ ); B, 0.5; C, 1 (pure  $H_2$ ). The full curves are for  $T_V(N_2) = 4000$  K and  $T_V(H_2) = 3000$  K, while the broken ones are for  $T_V(N_2) = T_V(H_2) = T_g$ .



**Figure 13.** Electron energy distribution functions for  $E/N = 10^{-16}$  V cm<sup>2</sup> and  $T_g = 400$  K, in pure N<sub>2</sub> (curves A) and pure H<sub>2</sub> (curves B). The full curves are for  $T_v(N_2) = 4000$  K or  $T_v(H_2) = 3000$  K, while the broken ones are for  $T_v(N_2) = 400$  K or  $T_v(H_2) = 400$  K.

E/N and an inverse behaviour for the case of the lowest value  $10^{-16}$  V cm<sup>2</sup>, which is a consequence of the effect discussed in figure 13. This figure also demonstrates that the effects of e-V superelastic collisions in N<sub>2</sub> are by far more effective than in H<sub>2</sub>, although in figure 14 we have even chosen to plot a vibrational temperature in H<sub>2</sub> which is clearly larger than that obtained from self-consistent predictions.

Figure 15 shows the electron rate coefficients for excitation of both electronic triplet states in N<sub>2</sub>,  $A^3 \Sigma_u^+$  and  $B^3 \Pi_g$ , calculated as a function of  $[H_2]/N$ , for the same



**Figure 14.** Electron kinetic temperature  $2/3\langle u \rangle$  as a function of the fractional H<sub>2</sub> concentration for the following vibrational temperatures in K: curve A,  $T_v(N_2) = 4000$ ,  $T_v(H_2) = 3000$ ; B,  $T_v(N_2) = 4000$ ,  $T_v(H_2) = 400$ ; C,  $T_v(N_2) = T_v(H_2) = 400$ . The lower, intermediate and upper curves are for  $E/N = 10^{-16}$ ,  $5 \times 10^{-16}$  and  $10^{-15}$  V cm<sup>2</sup> respectively.

pairs of values for  $T_v(N_2)$  and  $T_v(H_2)$  as in figure 14, and for  $E/N = 5 \times 10^{-16}$  V cm<sup>2</sup>. The effects of the e-V superelastic collisions in H<sub>2</sub> are always small even when a value of  $T_v(H_2)$  as high as 3000 K is chosen. This is the reason why in figures 12–15 we have chosen to present various situations which clearly do not correspond to self-consistent conditions. Figures 12–15 demonstrate that the use of different values for  $T_v(H_2)$  provokes only minor modifications in the EDF and in the electron transport parameters and rate coefficients. On the contrary, the effects of e-V superelastic collisions in N<sub>2</sub> are extremely important for  $E/N = 5 \times 10^{-16}$  V cm<sup>2</sup> and become increasingly less important as E/N increases (see [8]).

Finally, figure 16 shows the rate of dissociation of N<sub>2</sub>, per electron and at unit N<sub>2</sub> density,  $v_{diss}/n_e[N_2]$ , by electron collisions and by the V-V and V-T processes. Both contributions have been calculated self-consistently from the present model for  $E/N = 5 \times 10^{-16}$  V cm<sup>2</sup>,  $T_v(N_2) = 4000$  K and  $T_g = 400$  K. Figure 16 shows that as the fractional H<sub>2</sub> concentration increases the rate of dissociation by electron collisions monotonically increases as well, but this enhancement only occurs for considerably higher concentrations of H<sub>2</sub> than those for which dissociation by the V-V and V-T processes is completely inhibited (a concentration [H<sub>2</sub>]/N ~ 0.8% is large enough to produce  $v_{diss}^u/n_e[N_2] < 10^{-14}$  cm<sup>3</sup> s<sup>-1</sup>, while  $v_{diss}^e/n_e[N_2]$  slowly increases from 3.6 × 10<sup>-14</sup> to 4.6 × 10<sup>-13</sup> cm<sup>3</sup> s<sup>-1</sup> as [H<sub>2</sub>]/N varies from 0 up to 50%).

#### 5. Experimental results for metal surface nitriding

In this section we will discuss experimental results obtained in two different reactors for metal surface nitriding. Although these results have not been obtained



Figure 15. (a) Electron rate coefficient for excitation of the N<sub>2</sub>( $A^3\Sigma_{u}^+$ ) state in a N<sub>2</sub>-H<sub>2</sub> mixture, as a function of [H<sub>2</sub>]/N, for  $E/N = 5 \times 10^{-16}$  V cm<sup>2</sup>,  $T_{g} = 400$  K and the following vibrational temperatures in K: curve A,  $T_v(N_2) = 4000$ ,  $T_v(H_2) = 3000$ ; B,  $T_v(N_2) = 4000$ ,  $T_v(H_2) = 400$ ; C,  $T_v(N_2) = T_v(H_2) = 400$ . (b) As in (a) but for excitation of the N<sub>2</sub>(B <sup>3</sup>Π<sub>g</sub>) state.

in the conditions of a classical positive column, that is in the conditions of a nearly homogeneous medium and relatively weak electric field, they corroborate in part our previous theoretical predictions of section 4 regarding the vibrational kinetics in a  $N_2$ -H<sub>2</sub> mixture.

Figure 17 shows a typical reactor for surface treatments such as metal nitriding. A discharge voltage is applied to a N<sub>2</sub>-H<sub>2</sub> gas mixture at low pressures (p = 1-5 Torr) introduced into a reactor to perform the plasma nitriding at a chosen cathode temperature ,  $(T_K = 840$  K for a steel surface). A glow discharge is performed between the metal surface to nitride which is the cathode K and the reactor walls (the anode) at ground potential. The glow discharge fulfils both functions of heating the metal surface by ion bombardment and to create the active species for metal nitriding. The best observed nitriding conditions for a steel cathode have been found for a total pressure of 2.5 Torr and



**Figure 16.** Rate of dissociation of N<sub>2</sub>, per electron and at unit N<sub>2</sub> density, by the V–V and V–T processes  $v_{diss}^{v}/n_{e}[N_{2}]$  (curve A) and by electron impact  $v_{diss}^{e}/n_{e}[N_{2}]$  (curve B), as a function of  $[H_{2}]/N$ , for  $E/N = 5 \times 10^{-16}$  V cm<sup>2</sup>,  $T_{v}(N_{2}) = 4000$  K and  $T_{g} = 400$  K.



Figure 17. Experimental set-up for steel surface nitriding: A, anode; K, steel cathode; O, hole and pin-holes in the reactor; L, optical lens; PM, photomultiplier; P, picoammeter; R, recorder. Gas flow  $1-5 \text{ I} \text{ h}^{-1} \text{ stp.}$ 

a current density of 1-5 mA cm<sup>-2</sup>. In these conditions an abnormal glow discharge is produced whose negative glow near the cathode is analysed by emission spectroscopy. The light emitted by the plasma has been collected through a hole of 1 cm diameter in the plasma reactor as shown in figure 17 and detected using a HRS Jobin-Yvon grating spectrometer in the visible range. The spectrometer resolution has been adjusted to 0.2 Å for rotational structure analysis. Various pin holes (diameter = 2 mm) are localized along the reactor wall allowing the analysis of the axial distribution of the negative glow.

The identified species are reported in table 3 with the corresponding optical transitions, characteristic spectral lines and excitation thresholds. The  $N_2^+$  first negative bands are the most intense spectral lines. In N<sub>2</sub>-H<sub>2</sub> mixtures these lines remain the most intense even for 90%H<sub>2</sub> in the mixture. From the N<sub>2</sub><sup>+</sup> (B<sup>2</sup>  $\Sigma_{\mu}^+$ , 0  $\rightarrow X^2 \Sigma_{g}^+$ , 0), 391.4 nm emission, the roTable 3. Most intense spectral lines observed in a  $N_2\text{-}H_2$  negative glow discharge for steel surface nitriding.

Species	Optical transition	Spectral line (nm)	Excitation threshold (eV)
N <sup>+</sup>	$B^2\Sigma^+_{\mu} \rightarrow X^2\Sigma^+_{\sigma}$	<b>391.4(0 → 0)</b>	18.7
N <sub>2</sub>	$C^3\Pi_u \to B^3\Pi_g$	$337.1(0 \rightarrow 0)$ $380.4(0 \rightarrow 2)$	11.1
N <sub>2</sub>	$B^3\Pi_g \rightarrow A^3\Sigma_u^+$	662.3(6 → 3)	7.4
NH	$A^3\Pi \rightarrow X^3\Sigma^{-1}$	$336.0(0 \rightarrow 0)$	3.7
Н	Balmer series	656.3(H <sub>α</sub> ) ΄ 486.1(H <sub>β</sub> )	12.1 12.7
N	$2p^23p \rightarrow 2p^23s$	746.8	12
N <sup>+</sup> F₀	2p3p → 2p3s	568.0 561.6	20.66 5.54

tational structure of the R branch has been recorded and the  $N_2^+$  rotational temperature,  $T_R(B^+)$ , has been calculated from the Boltzmann graph [2]. This rotational temperature has been found to be close to the cathode temperature  $T_K$  which has been measured with a thermocouple [2, 3].

This discharge has already been characterized in a previous publication [2] and the reader should refer to this paper for further details. Here, we are mainly concerned with a few aspects linked to the vibrational kinetics of  $N_2(X, v)$  and  $H_2(X, v')$ , such as the analysis of the dependence of the vibrational temperature  $T_v(N_2)$  on the fractional  $H_2$  concentration.

Although emission spectroscopy does not permit one to relate the detected excited states to the corresponding ground state, such a correspondence can be established by using an actinometry method. This makes use of a rare gas impurity allowing selection of the experimental conditions in which such connection is possible, that is the conditions where excitation occurs mainly by direct electron collisions. Thus, by using a 2% argon impurity in the N<sub>2</sub>-H<sub>2</sub> mixture the following relationship can be written for a direct electron excitation of the N<sub>2</sub>(C<sup>3</sup> $\Pi_u$ ) state

$$\frac{I_2}{I_1} \alpha \frac{[N_2]}{[Ar]} \frac{C_e^{N_2}}{C_e^{Ar}}$$
(25)

where  $I_1$  is the intensity of the Ar I 750.4 nm emission,  $I_2$  is the intensity of the nitrogen second positive 337.1 nm emission,  $C_e^{N_2} = \langle v \sigma_e^{N_2} \rangle$  is the electron rate coefficient ( $\sigma_e^{N_2}$  and v denote the electron cross section and the electron velocity, respectively) for excitation of the  $N_2(C,0)$  state with an excitation threshold of 11.1 eV, and  $C_e^{Ar}$  is the electron rate coefficient for excitation of the Ar(4p) state at 13.5 eV. Owing to the small difference between both thresholds and the similar shapes of the electron cross sections, the  $C_e^{N_2}/C_e^{Ar}$  ratio is approximately constant. If direct electron excitations are the main processes for Ar(4p) and  $N_2(C)$  states, the ratio  $I_2/I_1$  must be directly proportional to the N<sub>2</sub> concentration for a constant value of Ar concentration. This is really what is observed in figure 18 for a distance z = 1 cm above the cathode, i.e. in the beginning of the negative glow. We note that the quenching



**Figure 18.** Intensity ratio of N<sub>2</sub> (337.1 nm) and Ar I (750.4 nm) lines,  $I_{N_2}/I_{Ar}$ , against the  $[N_2]/[Ar]$  density ratio, in a 2%Ar impurity N<sub>2</sub>-H<sub>2</sub> plasma, at a distance z = 1 cm above the cathode of the reactor shown in figure 17.

of the metastable states of Ar impurity by the  $N_2$ -H<sub>2</sub> main gases is sufficiently strong that we do not have to consider excitation other than direct excitation.

Based on the same approach, but now using a 2% neon impurity in the N<sub>2</sub>-H<sub>2</sub> plasma, the N<sub>2</sub><sup>+</sup> (B<sup>2</sup>  $\Sigma_{u}^{+}$ , 0) state at 18.7 eV can be compared to the Ne(3p) state at 18.6 eV. From inspection of the ratio between the N<sub>2</sub><sup>+</sup> (391.4 nm) and Ne(585.2 nm) line intensities we can deduce the [N<sub>2</sub>]/[Ne] concentration ratio. Our results also show in this case that the N<sub>2</sub><sup>+</sup> (B) state is directly excited from the ground state for a relative H<sub>2</sub> concentration in the N<sub>2</sub>-H<sub>2</sub> mixture larger than 10% and for z = 1 cm. Thus, this method shows that at the beginning of the negative glow near the cathode fall, that is for  $z \leq 1$  cm, the N<sub>2</sub>(C) and N<sub>2</sub><sup>+</sup> (B) states are populated by electron collisions directly from the ground state.

Direct electron collisions for excitation of  $N_2(C)$ and  $N_2^+(B)$  states can be used to determine the vibrational temperature of  $N_2(X)$  ground state. By using the Franck–Condon factors connecting the  $N_2(C)$  and  $N_2^+(B)$  states to the  $N_2(X)$  ground state and supposing a  $N_2(X, v)$  vibrational distribution with a shape of a Gordiets-like [28] distribution, the vibrational temperature of  $N_2(X)$  can be deduced from those of  $N_2(C)$ and  $N_{2}^{+}(B)$  states. Figure 19 shows the vibrational temperatures  $T_v(C)$  and  $T_v(B^+)$ , as well as that of the electronic ground state  $T_v(X)$  and the cathode temperature  $T_{\rm K}$  as a function of H<sub>2</sub> concentration in the mixture for a total gas pressure p = 2.7 Torr and a discharge voltage of 500 V. It can be observed in figure 19 that  $T_{v}(C) > T_{v}(B^{+})$  and that the same  $T_{v}(X)$  values are approximately deduced using either  $T_v(C)$  or  $T_{\rm v}({\rm B}^+)$  temperatures. These results confirm that these excited states were effectively populated by direct electron collisions at  $z \leq 1$  cm. The  $T_v(X)$  temperature is about four times larger than the cathode temperature presenting both the same dependence on the  $H_2$ concentration. The  $T_v$  curve shows a flat maximum at 10% of H<sub>2</sub> which is in agreement with our theoretical predictions shown in figure 7, although in that case the maximum of  $T_v$  has been found at ~ 1% H<sub>2</sub>.

In figure 7 we have shown a small maximum in the



**Figure 19.** Characteristic vibrational temperatures, as a function of the fractional H<sub>2</sub> concentration and for a total gas pressure 2.7 Torr, corresponding to the following electronic states: o, N<sub>2</sub>(C<sup>3</sup>II<sub>u</sub>); ( $\Delta$ )N<sub>2</sub><sup>+</sup>(B<sup>2</sup>Σ<sub>u</sub><sup>+</sup>); •, N<sub>2</sub>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) deduced from N<sub>2</sub>(C<sup>3</sup>II<sub>u</sub>); ( $\Delta$ )N<sub>2</sub>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) deduced from N<sub>2</sub><sup>+</sup>(B<sup>2</sup>Σ<sub>u</sub><sup>+</sup>) (see text). *T*<sub>K</sub> denotes the cathode temperature.

**Table 4.** Discharge current, rotational temperature of the N<sub>2</sub><sup>+</sup> (B  $^{2}\Sigma_{u}^{+}$ ) state and a measure of the degree of ionization  $n_{e}/[N_{2}]$  (see text), as a function of the fractional H<sub>2</sub> concentration in a N<sub>2</sub>-H<sub>2</sub> mixture, for p = 2.6 Torr and V = 500 V in the reactor of figure 17.

[H <sub>2</sub> ]/N	/ (mA)	7 <sub>R</sub> (B <sup>+</sup> ) (K)	П <sub>R</sub> (B <sup>+</sup> )/(1 – [H <sub>2</sub> ]/N) (А К)
0	62	870	54
0.1	90	810	81
0.2	90	810	91
0.3	85	810	98
0.5	75	770	116
0.6	70	700	123
0.7	60	660	132
0.9	38	550	209

curve of  $T_v(N_2)$  against  $[H_2]/N$ , for a given constant value of  $n_e/[N_2]$ , at about 1% of H<sub>2</sub>, as a result of the V-V and V-T(N<sub>2</sub>-H<sub>2</sub>) energy exchanges. Although in figure 19 the values of  $n_e/[N_2]$  are not kept constant, this figure exhibits a quite similar behaviour which cannot be explained as a simple dependence of  $T_v(N_2)$  on  $n_e/[N_2]$ . Table 4 shows the discharge current I and the N<sub>2</sub><sup>+</sup> rotational temperature  $T_R(B^+)$  measured in the reactor of figure 17 for p = 2.6 Torr, an applied voltage of 500 V and for various values of the fractional H<sub>2</sub> concentration. If we suppose the degree of ionization  $n_e/[N_2]$  to be given by

$$\frac{n_{\rm e}}{[N_2]} = \frac{n_{\rm e}}{N(1 - [H_2]/N)} \alpha \frac{IT_{\rm R}({\rm B}^+)}{(1 - [H_2]/N)}$$
(26)

we readily observe in table 4 that this function is always increasing and, therefore, it cannot explain the observed feature in figure 19.

Figure 20 shows a second plasma reactor for steel surface nitriding which is formed by a discharge tube of



Figure 20. Plasma reactor for steel surface nitriding used in the experiments by CARS. K, steel surface cathode (diameter = 3 cm); A, anode.

diameter 2 cm connected to a vessel of diameter 15 cm. A glow discharge in flowing N<sub>2</sub> can be switched on between the anode (a side-armed cylindrical electrode in nickel, diameter = 0.8 cm) and the cathode, which is the steel sample to be nitrided. The glow discharge is made up of a positive column along the discharge tube and a negative glow and cathode fall at the end of the discharge tube in front of the cathode surface [4]. The vibrational populations of N<sub>2</sub>(X<sup>1</sup>\Sigma<sup>+</sup><sub>g</sub>, v) and H<sub>2</sub>(X<sup>1</sup>\Sigma<sup>+</sup><sub>g</sub>, v') have been measured by CARS (coherent anti-Stokes Raman scattering) [29] both in the negative glow and in the cathode fall. The steel cathode K in figure 20 can be translated along the discharge axis in order to change the distance between the laser beams and its surface.

In case of the N<sub>2</sub>(X<sup>1</sup> $\Sigma_{g}^{+}$ , v) distribution, our measurements have been performed up to v = 11 yielding a characteristic vibrational temperature  $T_v = \theta_1 = \Delta E_{1,0}/[K \ln(N_0/N_1)]$ , of about  $T_v \simeq 4000$  K in the negative glow and of  $T_v \simeq 2500$  K in the cathode fall as shown in figure 21. At this point it is worth noting that the values of  $T_v$  in the cathode fall are in reasonable agreement with those presented in figure 19, which have been measured at the start of the negative glow near the cathode fall of reactor shown in figure 17. Moreover, figure 21 indicates that the values of  $T_v$ in the cathode fall are significantly smaller than those in the other regions of the discharge.

By introducing small concentrations (1-5%) of H<sub>2</sub> in the flowing gas, the characteristic vibrational temperature for both N<sub>2</sub> and H<sub>2</sub> has been obtained by CARS. Table 5 shows the values of  $T_v(N_2)$  and  $T_v(H_2)$ , either in pure N<sub>2</sub> or in a 5%H<sub>2</sub>-95%N<sub>2</sub> mixture, for discharge currents I = 30 and 50 mA [5]. The relation between both temperatures is in satisfactory agreement with that previously predicted in this work using our theoretical model. It is worth remembering here that in figure 5 we have shown to exist the following correspondence between both vibrational temperatures: 3500 K in N<sub>2</sub>- ~ 1200 K in H<sub>2</sub>; 4000 K- ~ 1400 K; which agrees reasonably well with these measurements.



**Figure 21.** Characteristic vibrational temperature in N<sub>2</sub> measured by CARS as a function of the distance from the cathode K, for p = 2 Torr, I = 50 mA and a gas flow of 0.9 l min<sup>-1</sup> stp.

**Table 5.** Vibrational temperatures in N<sub>2</sub> and H<sub>2</sub> measured by cars diagnostic in the reactor shown in figure 20, for p = 2 Torr and a gas flow of 0.14 1 min<sup>-1</sup>.

[H₂]/N	/ (mA)	τ <sub>v</sub> (N <sub>2</sub> ) (K)	7v(H₂) (K)
0	30	2550	
0.05	30	3260	1630
0	50	3210	
0.05	50	3170	1640

#### 6. Conclusions

In this paper we have carried out a detailed analysis of the electron and the vibrational kinetics in a  $N_2$ -H<sub>2</sub> homogeneous glow discharge, at low pressures and moderate currents, from which we can point out the following main conclusions. (i) The vibrational temperature of molecules in the electronic ground state is smaller in  $H_2$  than in  $N_2$  by a factor of 1/3. (ii) The vibrational temperature in N<sub>2</sub> rapidly increases as we introduce small concentrations of H<sub>2</sub> and keep constant the degree of ionization  $n_e/[N_2]$ , but for concentrations of H<sub>2</sub> higher than ~ 1%,  $T_v(N_2)$  is a slowly decreasing function of  $[H_2]/N$  (at least for  $n_e/[N_2]$  values within the range for this parameter chosen in this paper). (iii) Very small concentrations of H<sub>2</sub> (~ 0.5%) are large enough to produce a strong deactivation at the highest vth levels of the vibrational distribution of  $N_2$  due to the V-T ( $N_2$ -H<sub>2</sub>) exchanges. (iv) It follows from (iii) that small concentrations of H<sub>2</sub> in a N<sub>2</sub>-H<sub>2</sub> discharge produce a complete inhibition of the dissociation mechanism in N<sub>2</sub> by the V-V and V-T energy transfer exchanges. (v) As the fractional concentration of  $H_2$  increases the tail of the EDF is significantly enhanced, which produces an increase of the electron transport parameters and rate coefficients for excitation and ionization, except for the case of low E/N and, simultaneously, high  $T_v(N_2)$  values where a decrease in the high-energy region of the EDF as  $[H_2]/N$  increases exists.

This paper also reports measurements by emission spectroscopy and by CARS in the negative glow of a  $N_2-H_2$  discharge for steel surface nitriding, which, even

though they were not performed in a positive column where the electric field remains constant, allow us to confirm most of our theoretical predictions linked to the vibrational kinetics of both gases in such a mixture.

With regard to the neglect of composed radicals in a  $N_2-H_2$  discharge, such as the NH species we note that, as observed in [27], the addition of a small concentration of  $H_2$  produces a rapid decrease of the NH (336.0 nm) emission line. This fact suggests that the formation of NH occurs through a mechanism involving vibrationally excited molecules  $N_2(X, v)$  at the highest v levels, which, as we have seen, are strongly destroyed even for concentrations of  $H_2$  as small as 0.5%.

Finally, we must also stress that one source of error could be linked to the collisional data for the V–V and V–T exchanges involving different collision partners,  $N_2$  and  $H_2$ . In the present paper we have calculated these coefficients using the SSH theory, but further work is needed in order to obtain more reliable V–V and V–T rates.

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#### References

- [1] Lebrun J P, Michel H and Gantois M 1972 Mem. Sci. Rev. Met. 69 727
- [2] Petitjean L and Ricard A 1984 J. Phys. D: Appl. Phys. 17 919-29
- [3] Ricard A 1985 Proc. 17th Int. Conf. on Phenomena in Ionized Gases (Budapest, 1985) ed J S Bakos and Zsuzsa Sörlei pp 320–32
- [4] Ricard A 1989 Revue Phys. Appl. 24 251-6

- [5] Lefebvre M and Péalat M 1987 Rapport ONERA 6/3644
   PY (Office National d' Etudes et de Recherches Aérospatiales, Châtillon, France)
- [6] Pitchford L C and and Phelps A V 1982 Phys. Rev. A 25 540-54
- [7] Frost L S and Phelps A V 1962 Phys. Rev. 127 1621-33
- [8] Loureiro J and Ferreira C M 1986 J. Phys. D: Appl. Phys. 19 17-35
- [9] Loureiro J and Ferreira C M 1989 J. Phys. D: Appl. Phys. 22 67-75
- [10] Loureiro J and Ferreira C M 1989 J. Phys. D: Appl. Phys. 22 1680–91
- [11] Cacciatore M, Capitelli M and Gorse C 1982 Chem. Phys. 66 141-51
- [12] Treanor C E, Rich J W and Rehm R G 1968 J. Chem. Phys. 48 1798–807
- [13] Billing G D and Fisher E R 1979 Chem. Phys. 43 395-401
- [14] Capitelli M, Gorse C and Billing G D 1980 Chem. Phys. 52 299–304
- [15] Loureiro J, Ferreira C M, Capitelli M, Gorse C and Cacciatore M 1990 J. Phys. D: Appl. Phys. 23 1371-83
- [16] Schwartz R N and Herzfeld K F 1954 J. Chem. Phys. 22 767-73
- [17] Schwartz R N, Slawsky Z I and Herzfeld K F 1952 J. Chem. Phys. 20 1591-9
- [18] Keck J and Carrier G 1975 J. Chem. Phys. 43 2284-98
- [19] Bray K N C 1968 J. Phys. B: At. Mol. Phys. 1 705-17
- [20] Rapp D 1960 J. Chem. Phys. 32 735-7; 1965 J. Chem. Phys. 43 316-17
- [21] Rapp D and Sharp T E 1963 J. Chem. Phys. 38 2641-8
- [22] Rapp D and Englander-Golden P 1964 J. Chem. Phys. 40 573-5; 3120-1
- [23] Kiefer J H 1972 J. Chem. Phys. 57 1938-56
- [24] Billing G D and Fisher E R 1976 Chem. Phys. 18 225-32
- [25] White D R 1967 J. Chem. Phys. 46 2016-17
- [26] Ricard A, Oseguera-Pena J E, Falk L, Michel H and Gantois M 1990 IEEE Trans. Plasma Sci. 18 940-4
- [27] de Benedictis S, Gicquel A and Cramarossa F 1987 Proc. 8th Int. Symp. on Plasma Chem. (Tokyo, 1987) ed K Akashi and A Kinbara pp 631-6
- [28] Gordiets B F, Mamedov Sh S and Shelepin L A 1975 Sov. Phys.-JETP 40 640-6
- [29] Massabieaux B, Gousset G, Lefebvre M and Péalat M 1987 J. Physique 48 1939–49