Electron Energy Distribution Functions of Hydrogen: The Effect of Superelastic Vibrational Collisions and of the Dissociation Process *

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Electron energy distribution functions (EDF) of molecular H_2 have been calculated by numerically solving the Boltzmann equation including all the inelastic processes with the addition of superelastic vibrational collisions and of the hydrogen atoms coming from the dissociation process. The population densities of the vibrational levels have been obtained both by assuming a Boltzmann population at a vibrational temperature different from the translational one and by solving a system of vibrational master equations coupled to the Boltzmann equation.

The results, which have been compared with those corresponding to a vibrationally cold molecular gas, show that the inclusion of superelastic collisions and of the parent atoms affects the EDF tails without strongly modifying the EDF bulk. As a consequence the quantities affected by the EDF bulk, such as average and characteristic energies, drift velocity, 0—1 vibrational excitation rate are not too much affected by the inclusion of superelastic vibrational collisions and of parent atoms, while a strong influence is observed on the dissociation and ionization rate coefficients which depend on the EDF tail.

Calculated dissociation rates, obtained by EDF's which take into account both the presence of vibrationally excited molecules and hydrogen atoms, are in satisfactory agreement with experimental results.

1. Introduction

We have recently calculated the vibrational populations of different diatomic species in electrical discharges, with the aim of obtaining informations about a new dissociation mechanism operating under nonequilibrium conditions [1]. These calculations are based on the solution of a system of vibrational master equations, each of which describes the evolution of a given vibrational level under the action of e-V (electron-vibration), V-V (vibration-vibration) and V-T (vibration-translation) energy transfers. Similar problems are met in modelling gas laser discharges.

The starting point of these calculations lies in the e-V rates i.e. the rate coefficients of the processes

$$e + M_2 (v = 0) \rightarrow e + M_2 (v = k)$$

which were calculated in [1] by means of the Maxwell electron distribution function (MEDF).

Despite the fact that many non Maxwell EDF's are presently available [2—7], the problem of their incorporation in the vibrational kinetics can be open to question, since practically all calculated EDF's have been obtained by using i) a cold vibrational gas, ii) a completely molecular gas.

The importance of point i) in affecting EDF can be qualitatively understood by recalling that under many experimental discharge conditions the vibrational temperatures of diatomic species can reach high values ($1000 \leqq T_v \leqq 4000$ K) with respect to the translational temperature ($300 \leqq T_g \leqq 1000$ K). This means that a considerable number of molecules in the discharge are on vibrational levels different from the ground one. As a consequence a portion of the pumped energy is returned to the electrons via superelastic collisions (the reverse of process 1) thereby modifying EDF.

The presence of parent atoms (point ii)) on the other hand does modify EDF, due to the lack of rotational and vibrational losses in the atomic system and to the different cross sections for the other processes.

Both these problems (i.e. points i), ii)) will be examined in the present paper for H_2, the electron energy distribution functions of which have been calculated by different authors under the assumption of a cold vibrational gas [8—11] and for mixtures $H_2(v=0)/H$ [12].

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2. Method of Calculation

According to Ref. [13], the time evolution of the number density $n(u, t)\,\mathrm{d}u$ of electrons with energy between u and $u + \mathrm{d}u$ can be written as

$$\begin{aligned}\frac{\partial n}{\partial t} = &- \frac{\partial j_\mathrm{f}}{\partial t} - \frac{\partial j_\mathrm{el}}{\partial t} \\ &+ \sum_{s,j,j'} \Big\{ R_{s,j,j'}(u + u^*_{s,j,j'})\, n(u + u^*_{s,j,j'})\, N_j{}^s \\ &+ R'_{s,j,j'}(u - u^*_{s,j,j'})\, n(u - u^*_{s,j,j'})\, N^s_{j'} \\ &+ R^i_{s,j}(u + u^*_{s,i,j})\, n(u + u^*_{s,i,j})\, N_j{}^s \\ &+ \delta(u)\, N_j{}^s \int_{u_{s,i,j}}^{\infty} R^i_{s,j}(u)\, n(u)\, \mathrm{d}u \\ &- [R_{s,j,j'}(u)\, N_j{}^s + R'_{s,j,j'}(u)\, N^s_{j'} \\ &+ R^i_{s,j}(u)\, N_j{}^s]\, n(u) \Big\} . \end{aligned} \tag{1}$$

The first two terms on the rhs of Eq. (1) represent in the order of flux of electrons along the energy axis driven by the applied field E and by the elastic collisions. Explicit expressions for $\partial j_\mathrm{f}/\partial t$ and $\partial j_\mathrm{el}/\partial t$ can be found in Ref. [13]. The remaining terms represent the flux of electrons driven by inelastic and superelastic collisions.

$$R_{s,j,j'}(u) = \sigma_{s,j,j'}(u)\, v(u) \tag{2a}$$

is the rate at which electrons with velocity $v(u)$ excite species s to a vibrational or electronic state j' from the states, with energy loss $u^*_{s,j,j'}$ ($\sigma_{s,j,j'}$ is the appropriate cross section).

The term

$$R'_{s,j,j'} = \frac{u + u^*_{s,j,j'}}{u}\, \sigma_{s,j,j'}(u + u^*_{s,j,j'})\, v(u)$$

is the rate at which electrons deexcite species in a state j' to a lower state j, gaining the corresponding energy. $N_j{}^s$ and $N^s_{j'}$ are the population densities of states j and j' respectively. $R^i_{s,j}(u)$ is the ionization rate for species s in state j and the term under the integral sign represents the secondary electrons produced by ionization, the Dirac δ notation indicating that all these electrons are produced at zero energy.

Equation (1) is converted to a set of k-coupled ordinary differential equations by subdividing the electron energy axis into k cells of width Δ_u. (Typical values used in the present work are $\Delta_u = 0.2$ eV.)

At the stationary conditions, one obtains the number of electrons with energy in the k-th shell, n_k, which is related to the electron energy distribution f_k ($e\,V^{-3/2}$) by

$$f_k = n_k / (u_k{}^{1/2}\, u\, n_0)\,, \tag{3}$$

$$n_0 = \sum_k n_k\,. \tag{4}$$

The knowledge of n_k allows the calculation of important quantities such as average and characteristic energies, drift velocity, diffusion coefficient, rate coefficients and so on.

3. Results

Figure 1 shows some of the calculated EDF at different E/N values (E, electric field, N, total

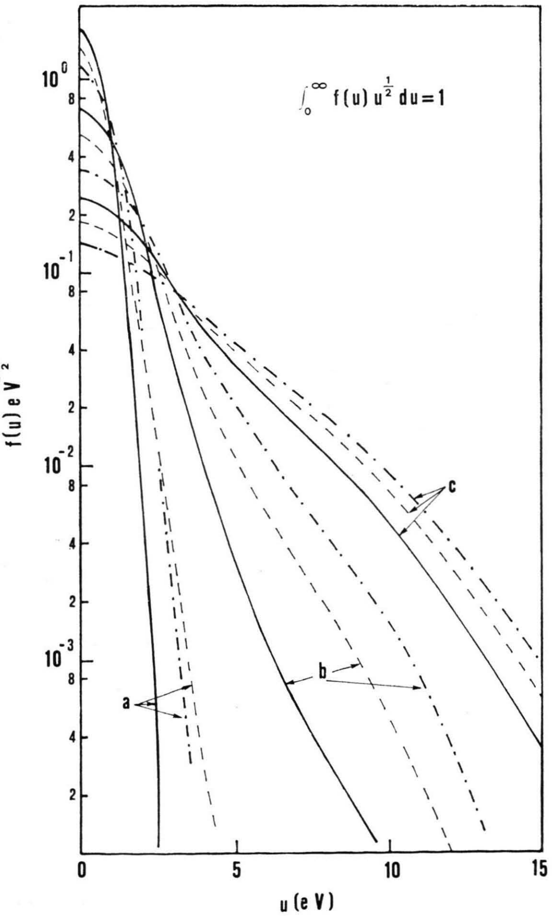

Fig. 1. Electron energy distribution functions $f(u)$ as a function of energy at different E/N values (—— (full lines): "cold" molecular gas; ---- (dashed lines): vibrationally excited molecular gas; -·-·- (dashed dot lines): H_2/H 1:1 mixture); (a: $E/N = 10^{-16}$ Vcm²; b: $E/N = 3.10^{-16}$ Vcm²; c: $E/N = 6.10^{-16}$ Vcm²).

number of particles) for the cases 1) vibrational cold gas, 2) vibrationally excited molecular gas, 3) mixture of $H_2(v=0)/H$ 1/1.

In 1) the following inelastic processes have been considered:

$$e + H_2(v=0) \rightarrow e + H_2(v=1,3)\,, \qquad a)$$

$$e + H_2(v=0) \rightarrow e + H_2^*\,, \qquad b)$$

$$e + H_2(v=0) \rightarrow e + 2\,H\,, \qquad c)$$

$$e + H_2(v=0) \rightarrow e + H_2{}^+ + e\,. \qquad d)$$

Cross sections for processes a)—d) have been taken from Refs. [14—15] and the momentum transfer cross sections from Ref. [16]. It should be noted that rotational excitation was disregarded in the present work. This point affects the calculations at $E/N < 10^{-16}$ V cm^2 as pointed out in [8].

In 2), besides processes a)—d) we have considered the superelastic vibrational collisions of levels (1)—(3) connected to the ground state $(v=0)$

$$e + H_2(v=1,3) \rightarrow e + H_2(v=0)\,. \qquad e)$$

The population densities of levels (1)—(3) have been obtained by means of a Boltzmann law at $T_v > T_g$ (in particular the results of Figs. 1—5 refer to $T_v = 3500$ K and $T_g = 300$ K).

In 3) we have solved the Boltzmann equation for a mixture of two species: $H_2(v=0)$ and H-atoms. Processes a)—d) have been considered for H_2 and

$$H(1\,s) + e \rightarrow H(2\,s, 2\,p) + e\,, \qquad f)$$

$$H(1\,s) + e \rightarrow H^+ + e + e \qquad g)$$

for hydrogen atoms.

Cross sections for processes f), g) have been taken from Refs. [17—19] and from Ref. [20] for momentum transfer.

It should be noted (Fig. 1) that the inclusion of superelastic collisions as well as of the parent atoms strongly affects the EDF tail, while the effect is less pronounced on the EDF bulk. As a consequence one

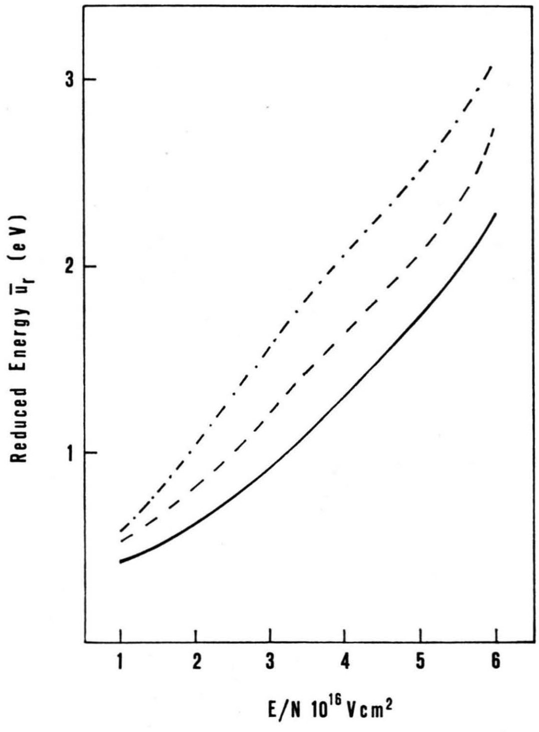

Fig. 2. Reduced averaged electron energies $\bar{u}_r$ as a function of E/N (——: "cold" molecular gas; – – –: vibrationally excited molecular gas; -·-·-: H_2/H 1:1 mixture).

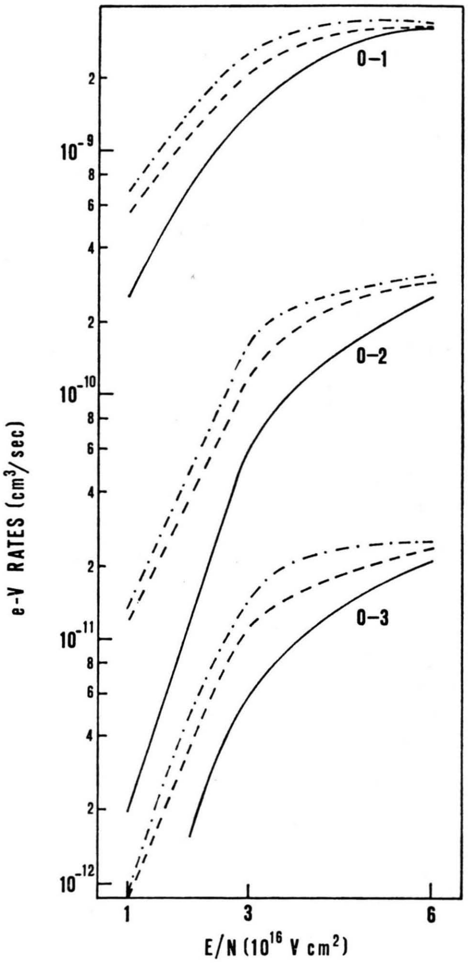

Fig. 3. e-V (electron-vibration) rates as a function of E/N (——: "cold" molecular gas; – – –: vibrationally excited molecular gas; -·-·-: H_2/H 1:1 mixture).

should expect that the quantities related to the EDF bulk such as average and characteristic energies and drift velocity will be slightly affected by the presence of superelastic collisions and of parent atoms. This is indeed the case as shown in Fig. 2 for the reduced average energy $\bar{u}_r = 2/3\ \bar{u}$.

As for the rate coefficients, the insertion of superelastic collisions and of the parent atoms will affect those rates, the thresholds of which overlap with the tail of EDF. As a result the 0—1 vibrational rate should not be affected by the presence of vibrationally excited molecules and parent atoms, while a larger influence is expected for the 0—2, 0—3 rate coefficients.

Figure 3 confirms these considerations. The maximum difference between the cold vibrational gas and the excited one is approximately a factor of 2 for the 0—1 transition, reaching a factor 10 for the 0—3 rate coefficient.

As for the rate coefficients depending on the tail of EDF, they are expected to strongly depend on the inclusion of superelastic collisions and of the parent atoms, as can be appreciated from Fig. 4 for the dissociation and ionization coefficients.

Finally Fig. 5 shows the fractional power losses in the three approximations.

The accuracy of the present results has been tested by comparing our EDF and related quantities with the corresponding ones of [8—11] for the cold gas and with those of Ref. [12] for the $H_2(v=0)/H$ mixture. A satisfactory agreement has been generally found.

Figure 6 shows a comparison of the present EDF in the cold gas approximation, obtained by using different dissociation cross sections. It should be

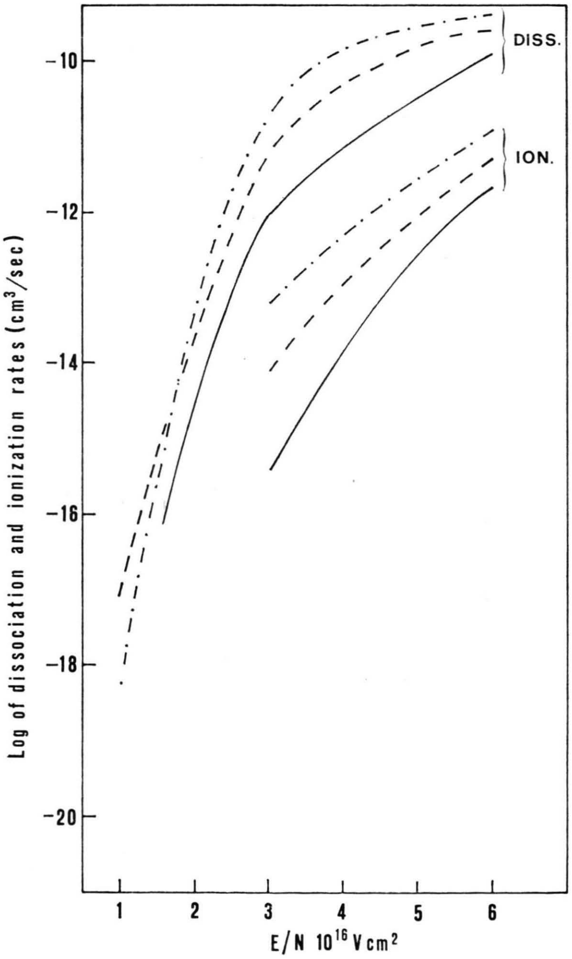

Fig. 4. Dissociation and ionization rates as a function of E/N (——: "cold" molecular gas; – – –: vibrationally excited molecular gas; -·-·-: H_2/H 1:1 mixture).

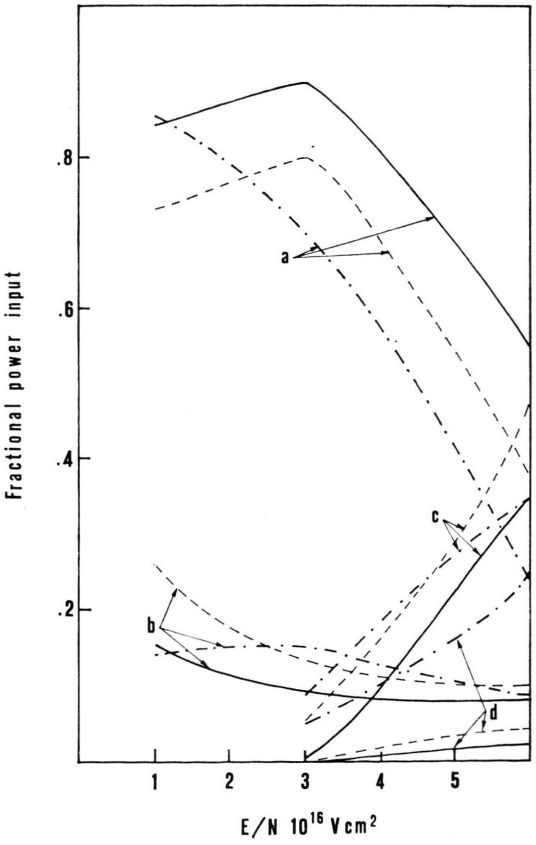

Fig. 5. Fractional energy power as a function of E/N (a: vibrational energy; b: elastic energy; c: dissociation energy; d: electronic excitation energy) (——: "cold" molecular gas; – – –: vibrationally excited molecular gas; -·-·-: H_2/H 1:1 mixture).

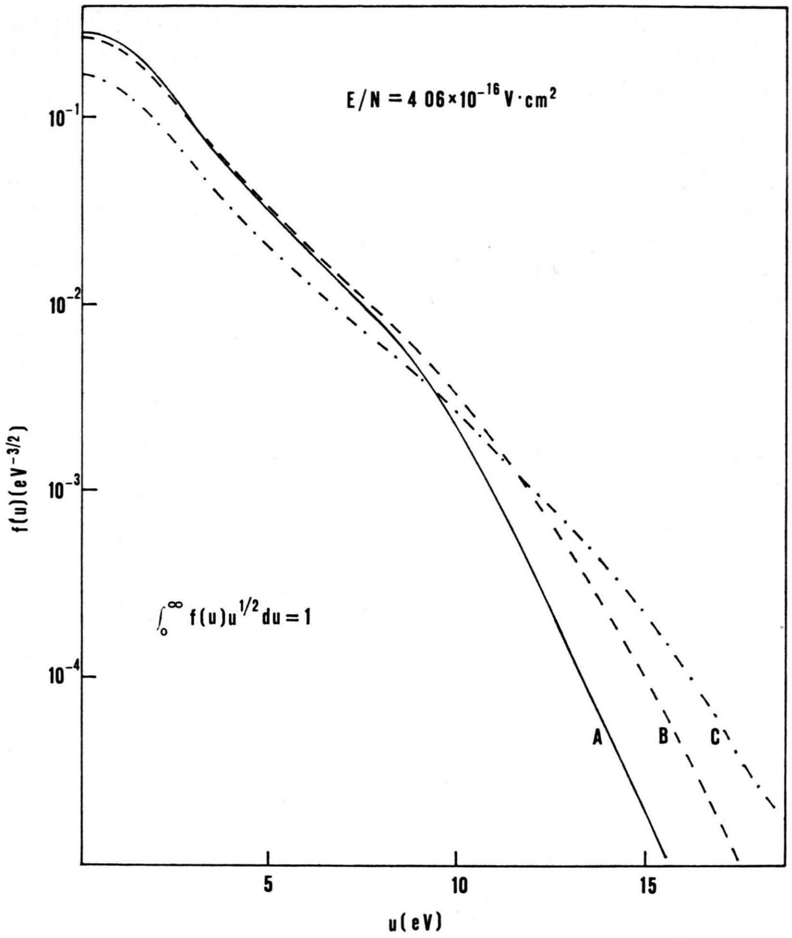

Fig. 6. Electron distribution energy functions obtained with different $v = 0$ dissociation cross sections (A: cross sections from Ref. [22]; B: cross sections from Ref. [8]; C: cross sections from Ref. [21]).

noted that the use of small cross sections as those of Ref. [21] tends to increase the number of electrons in the tail of EDF as compared with the use of the large cross sections of Refs. [8] and [22], which on the contrary tend to deplete the EDF tail. This of course generates a sort of compensation in the dissociation rate coefficients.

4. EDF and Dissociation Mechanisms

The results reported in the previous pages show the importance of superelastic vibrational collisions as well as of the parent atoms in affecting EDF. The results are in line with those reported by other authors for N_2 and CO.

It is interesting to estimate the possible effects of these results on the dissociation mechanisms discussed in our previous works [1]. Basically we have considered three different mechanisms: 1) the pure vibrational mechanism (PVM); 2) the direct electronic mechanism from the ground vibrational level (DEM); 3) the joint vibroelectronic mechanism (JVE).

According to PVM the electrons of the discharge introduce vibrational quanta by means of e-V processes. The introduced quanta reach the dissociation continuum by means of V-V energy transfers. As a consequence PVM depends only on the e-V rates (in particular on the 0—1 transition), which are not too much affected by the nonequilibrium state of the mixture (see Figure 3).

The other two mechanisms (DEM, JVE) depend on the electronic dissociative transitions from $v = 0$ as well as from excited vibrational levels

$$e + H_2(v) \xrightarrow{k_{d}^{e}(v)} e + 2\,H . \qquad h)$$

These rates are of course dependent on the inclusion of superelastic collisions and of the parent atoms as shown in Fig. 4 for $v = 0$, so that one should expect strong variations of DEM and JVE dissociation values on the calculated EDF. A selfconsistent calculation of EDF and of the system of vibrational master equations is therefore necessary to completely understand the dissociation mechanisms discussed in [1]. In particular one must consider both the coupling of EDF with the vibrational kinetics and with the presence of H-atoms coming from the dissociation process.

Figure 7a, b shows some of the calculated EDF which take into account the coupling of the Boltzmann equation with the system of vibrational master equations. The E/N, T_g, n_e, p values have been selected according to the experimental conditions of Ref. [23].

The different curves refer to the cold molecular gas (case 1), to the vibrationally excited gas (case 2) and to a mixture of vibrationally excited molecules and hydrogen atoms (case 3).

The vibrational populations N_v inserted in cases 2, 3 have been obtained by solving a system of $v' + 1$ vibrational master equations (v' is the number of vibrational levels in the molecule)

$$\mathrm{d}N_v/\mathrm{d}t = (\mathrm{d}N_v/\mathrm{d}t)_{\mathrm{e-V}} + (\mathrm{d}N_v/\mathrm{d}t)_{\mathrm{e-D}} + (\mathrm{d}N_v/\mathrm{d}t)_{\mathrm{V-V}} + (\mathrm{d}N_v/\mathrm{d}t)_{\mathrm{V-T}}, \quad (5\mathrm{a})$$

$$\begin{aligned} v_{\mathrm{D}} &= \mathrm{d}N_{v'+1}/\mathrm{d}t \\ &= n_{\mathrm{e}} \sum_v N_v \, k_d{}^e(v) + N_{\mathrm{H}_2} N_{v'} \, P_{v',v'+1} \quad (5\mathrm{b}) \\ &\quad + N_{v'} \sum_v N_v \, P_{v,v-1}^{v',v'+1} . \end{aligned}$$

The different terms of Eq. (5a) represent in implicit form the relaxation of the v-th level due to the electron vibration (e-V), electron-dissociation (e-D), vibration-vibration (V-V), vibration-translation (V-T) energy transfers (see Ref. [1] for the explicit form).

The rate coefficients appearing in Eq. (5b) refer to the following processes

$$\mathrm{H}_2 + \mathrm{H}_2(v') \xrightarrow{P_{v',v'+1}} \mathrm{H}_2 + \mathrm{H}_2(v'+1) \rightarrow \mathrm{H}_2 + 2\,\mathrm{H} \quad \mathrm{i)}$$

$$\mathrm{H}_2(v) + \mathrm{H}_2(v') \xrightarrow{P_{v,v-1}^{v',v'+1}} \mathrm{H}_2(v-1) + \mathrm{H}_2(v'+1) \rightarrow \mathrm{H}_2(v-1) + 2\,\mathrm{H} . \quad \mathrm{l)}$$

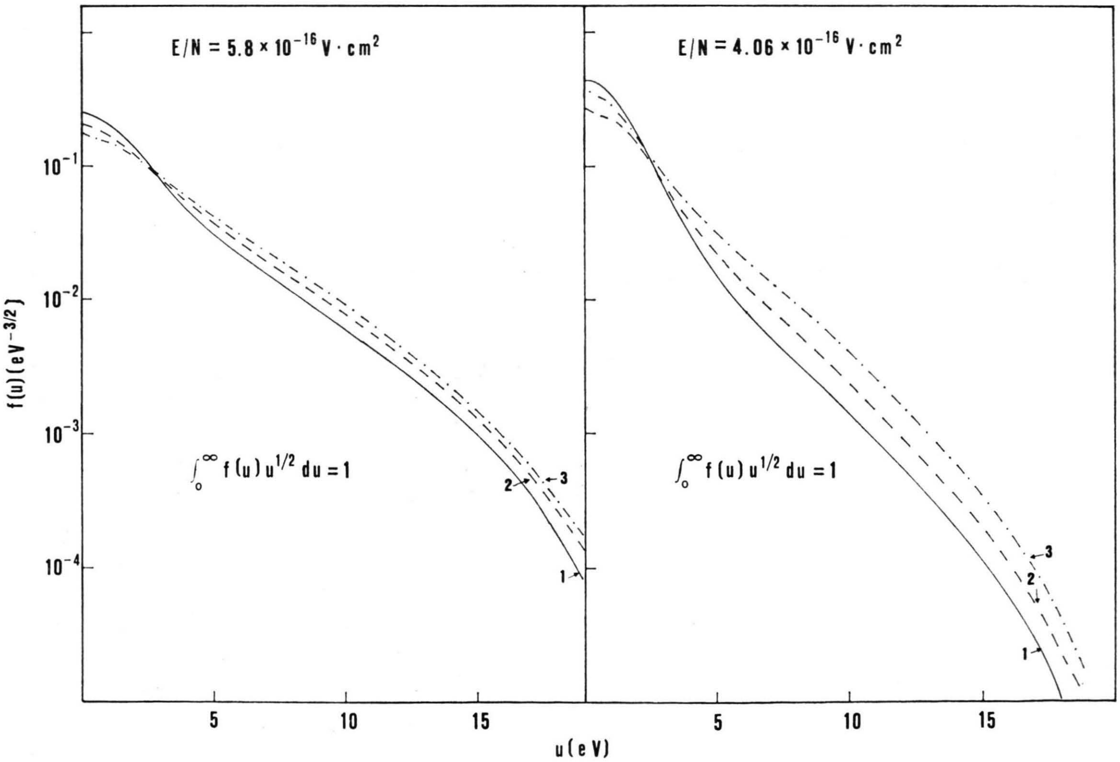

Fig. 7. Electron energy distribution functions for conditions typical of Ref. [23] (1: "cold" molecular gas; 2: vibrationally excited molecular gas; 3: mixture of vibrationally excited molecules and hydrogen atoms).

It should be noted that the electron energy distribution function determines the e-V and e-D rates.

The system of $v'+1$ differential equations is solved with the following initial condition

$$N_v(t=0)=0\,, \qquad v \neq 0\,, \tag{6a}$$

$$N_v(t=0)=N_{\mathrm{H}_2}\,, \quad v=0\,. \tag{6b}$$

At $t=0$, therefore, the e-V and e-D rates must be calculated with EDF of case 1. As the time evolves e-V, V-V and V-T energy exchanges populate the vibrational levels of the molecule, while the e-D processes become to dissociate H_2. EDF progressively changes from case 1) to cases 2), 3), with profound implications on the dissociation rates. A practical decoupling of the system of vibrational master equations from the Boltzmann equation can be obtained, by noting that the N_v populations strongly depend on the e-V, V-V and V-T rates, being practically independent of e-D ones. In turn the e-V rates are practically independent of the presence of vibrationally excited molecules and of parent atoms (see Figure 3). The practical self-consistency between EDF and system of master equations can be therefore reached a) by solving the Boltzmann equation for case 1 obtaining the e-V rates, b) by solving the system of vibrational master equations with the e-V rates of point a), obtaining the N_v populations, c) by solving the Boltzmann equation with N_v of point a), obtaining a new set of e-V and e-D rates, d) by repeating point b) with the rates of point c).

Curves 1, 2 of Fig. 7a, b correspond to points a) and c). Curve 3 on the contrary has been calculated by solving the Boltzmann equation with the N_v distribution of point d) and with a H-atoms concentration of 25%. This last value represents a good estimation of the H-atom concentration at the stationary conditions of [23].

Values of the dissociation constant $k_d^e(v=0)$ for the three cases above discussed have been reported in Table 1. One can note the strong increase of $k_d^e(v=0)$ from case 1 to case 3. Similar results have been obtained with the dissociation cross sections of [22].

As far the results have been obtained by neglecting the dissociation processes starting from vibrationally excited molecules, the contribution of which can be very important under given non-equilibrium conditions [21]. A complete set of e-D cross sections for the process

$$\mathrm{e} + \mathrm{H}_2(v) \rightarrow \mathrm{e} + \mathrm{H}_2(b\,{}^3\Sigma_\mathrm{u}) \rightarrow \mathrm{e} + 2\,\mathrm{H} \tag*{m)}$$

have been recently derived in [21]. By inserting these cross sections in cases 1—3 previously discussed we can generate both EDF and dissociation constants in DEM ($k_d^e(v=0)$) and JVE ($k_{dj}=v_d/N_{\mathrm{H}_2}$). The results which have been reported in Fig. 8 and Tables 1—2 are very similar to those obtained with the cross sections of [8].

Values of $k_d^e(v=0)\,n_\mathrm{e}(s^{-1})$ and $k_{dj}(s^{-1})$, calculated with the cross sections of [21] and with EDF which take into account both the presence of vibrationally excited molecules and parent atoms, have been reported in Table 2. One notices that $k_{dj}/k_d^e(v=0)\,n_\mathrm{e}$ is 1.19 and 1.14 at $E/N=4.1\cdot10^{-16}$ V cm^2 and $E/N=5.8\cdot10^{-16}$ V cm^2 respectively.

These ratios, which can be taken as an indication of the contribution of vibrationally excited molecules to the dissociation process in JVE, can be used to scale the $k_d^e(v=0)\,n_\mathrm{e}$ values obtained by using the $v=0$ dissociation cross sections of [8], [22].

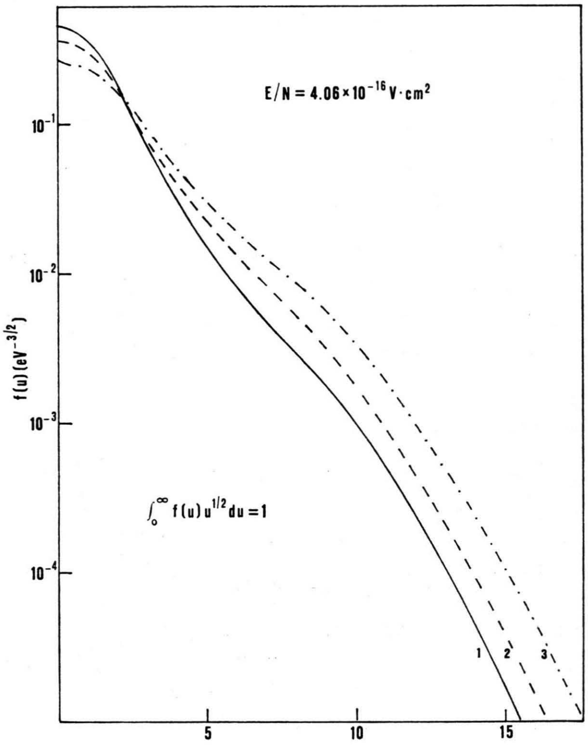

Fig. 8. Electron energy distribution functions for conditions typical of Ref. [23] obtained by using the cross sections of Ref. [21] (1: "cold" molecular gas; 2: vibrationally excited molecular gas; 3: mixture of vibrationally excited molecules and hydrogen atoms).

Table 1. Values of the dissociation constants ($cm^3\ s^{-1}$) calculated with different approximations on the electron energy distribution function.

E/N (V cm^2)	p (torr)	T_g (K)	n_e (cm^{-3})	k_d^e ($v = 0$)*	k_d^e ($v = 0$)**
5.8 (− 16)***	20	910	1.9 (11)	1.3 (− 10)	7.0 (− 11)[a]
				1.9 (− 10)	9.1 (− 11)[b]
				2.6 (− 10)	1.0 (− 10)[c]
4.1 (− 16)	20	700	3.1 (11)	1.8 (− 11)	1.2 (− 11)[a]
				3.6 (− 11)	2.1 (− 11)[b]
				7.5 (− 11)	3.6 (− 11)[c]

* Dissociation cross sections from [8].
** Dissociation cross sections from [21].
*** 5.8 (− 16) = 5.8×10^{-6}.
[a] EDF for a cold gas; [b] EDF for a vibrationally excited gas; [c] EDF for a vibrationally excited gas + 25% of hydrogen atoms.

Table 2. A comparison of the dissociation constants (s^{-1}) for DEM and JVE with the experimental values of [23].

E/N (V cm^2)	p (torr)	T_g (K)	n_e (cm^{-3})	k_d^e ($v = 0$) n_e	k_{dj}	k_{exp}
5.8 (− 16)**	20	910	1.9 (11)	19.2[a]	22.0[a]	149
				49.6[b]	56.8*	149
				65.5[c]	75.0*	149
4.1 (− 16)	20	700	3.1 (11)	11.3[a]	13.5[a]	114
				23.4[b]	27.9*	114
				30.8[c]	36.8*	114

In all cases the EDF have been calculated with the simultaneous presence of vibrationally excited molecules and hydrogen atoms (see text).
* Values obtained by scaling with the *a* values (see text).
** 5.8 (− 16) = 5.8×10^{-16}.
[a] Cross sections from Ref. [2]; [b] cross sections from Ref. [8]; [c] cross sections from Ref. [22].

In the same table we have also reported the experimental dissociation rates of [23]. The agreement between theory and experiments can be considered satisfactory.

5. Conclusions

The results reported in the previous pages show the importance of the non-equilibrium state of a reacting mixture in affecting the electron distribution function.

In particular the H_2 EDF calculated in the presence of vibrationally excited molecules and parent atoms present tails more populated than the corresponding "cold" EDF. The dissociation (and ionization) rates do benefit of this situation by attaining values higher than those obtained in the "cold" gas approximation. This point is particularly important for understanding chemical reactions under non-equilibrium conditions.

Some analogies with the results reported by other authors suggest a more general validity of the present results concerning the influence of vibrationally excited molecules on the electron energy distribution functions.

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