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Self-consistent relaxation of the electron energy distribution function in excited H_2 postdischarges

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A collisional radiative model for both H and H_2 species coupled with a time-dependent Boltzmann equation is used to show structures in the electron energy distribution function in the post discharge regime. These structures are due to collisions of the second kind between cold electrons and vibrationally and electronically excited H* and H_2* species. [S1063-651X(99)09203-X]

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The relaxation of the electron energy distribution function (EEDF) in cold and vibrationally excited H_2 has been the subject of many papers devoted to investigations of the different elementary processes affecting the whole relaxation dynamics [1,2]. However, EEDF relaxation in electronically hot H_2/H mixtures has never been investigated. Very recently Capitelli *et al.* [3] showed that small concentrations of electronically excited states (molar fraction $<10^{-7}$) were able to create structures in the EEDF of H_2 plasmas at low reduced electric fields E/N as a result of collisions of the second kind. Extrapolation of these results to post-discharge conditions (i.e., $E/N=0$) should amplify this kind of structure, the magnitude of which strongly depend on the concentration of vibrationally and electronically excited states created in the discharge before the turn off of the electrical field. This means that only self-consistent kinetic models, including detailed kinetics of vibrationally and electronically excited states, can give a realistic description of the EEDF relaxation in post discharges. To this end, we apply a self-consistent kinetic model, recently developed by Hassouni, Gicquel, and Capitelli [4] to follow the coupled relaxation of the EEDF and excited state distributions in a post discharge regime ($E/N=0$).

The model includes (1) a Boltzmann equation for determining the EEDF; (2) a nonequilibrium vibrational kinetics for describing the vibrational distribution function (vdf) of H_2; (3) two collisional-radiative (cr) models describing the population of H_2 and H electronically excited states; (4) a chemistry model involving H_2, H, H^+, $H_2{}^+$, $H_3{}^+$, H^- and e^-; (5) a quasihomogenous plasma transport model for the estimation of species losses at the plasma reactor wall; and (6) a total energy balance equation for estimating the gas temperature (T_g).

The details of the model and the associated cross section and rate coefficient data may be found in Ref. [4]. In this paper we present just the main peculiarities of the model. The Boltzmann equation for the EEDF is written in the form

$$dn(\varepsilon,t)/dt=dJ_f/de+dJ_e/de-I_n-S_{\mathrm{up}}, \tag{1}$$

where $n(\varepsilon,t)$ is the density of electrons at a time t with energy in the range $[\varepsilon-d\varepsilon/2,\ \varepsilon+d\varepsilon/2]$. J_f and J_e denote the electron fluxes in energy space due to the electric field and to electron-heavy species elastic collisions. I_n and S_{up} are the source terms due to inelastic and superelastic collisions respectively (see Ref. [2] for explicit terms).

The inelastic source term includes numerous electron energy losses due to the collisions of electrons with both atomic and molecular species. The superelastic source term contains all the reverse processes which return energy to electrons. In particular we consider the following superelastic vibrational and electronic collisions:

$$e+H_2(v)\Rightarrow e+H_2(w),\quad v>w \tag{2}$$

$$e+H_2{}^*\Rightarrow e+H_2, \tag{3}$$

$$e+H^*\Rightarrow e+H. \tag{4}$$

Note that we are solving a time-dependent Boltzmann equation for the EEDF, since the time to reach quasistationary distributions is longer than the lifetime of some electronically excited states. In Ref. [2] it is in fact shown that the EEDF in the post discharge regime of vibrationally excited H_2 reaches quasistationary values in time of the order of $10^{-9}-10^{-7}$ s, which is comparable with the lifetimes of many H_2*/H* excited states.

A complete vibrational kinetics is solved for the vdf including e-V and E-V processes as well as V-V and V-T energy exchange processes. The latter includes also the deactivation of vibrationally excited molecules by atomic hydrogen. The pumping of vibrational energy proceeds by the resonant e-V and indirect E-V processes, i.e.,

$$e+H_2(v)\Rightarrow H_2{}^-\Rightarrow e+H_2(w), \tag{5}$$

$$e+H_2(v)\Rightarrow e+H_2(B\,{}^1\Sigma_u^+,C^1\Pi_u)\Rightarrow e+H_2(w)+h\nu, \tag{6}$$

The E-V rates have been modulated by the factor $\nu_r/(\nu_r+\nu_q)$ (ν_r is the radiative decay frequency, and ν_q is the quenching frequency) to take into account the loss of singlet states by quenching. The cr model for electronically excited atomic hydrogen considers excited states up to the principal quantum number $n=20$. These states are linked by electron and atom collision processes as well as by radiative transitions. Note that the plasma investigated in this work are optically thin except for the Lymann α radiation.

The cr model for H_2* considers the singlet and triplet states reported in Table 1 of Ref. [4]. These states are connected by electron collisions and radiative processes dis-

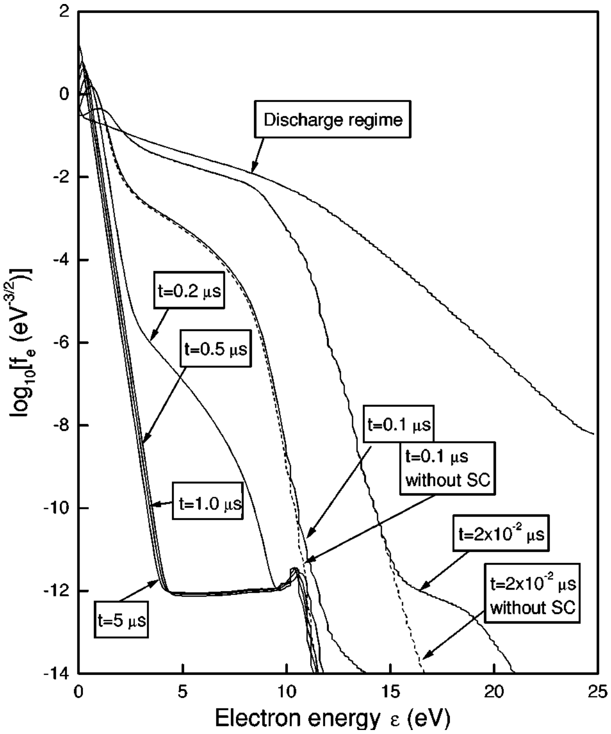

FIG. 1. Time relaxation of the electron energy distribution function (f_e). The dashed curves for $t=2\times10^{-2}$ and 10^{-1} μs and labeled ''without SC'' have been calculated without taking into account the superelastic collisions from H_2^* and H^*.

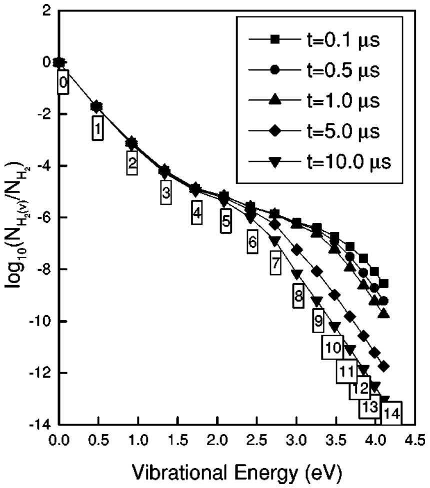

FIG. 2. Time relaxation of the vibrational distribution function. The numbers in the boxes denote the vibrational quantum numbers.

cussed in Refs. [4,5]. One of the major process which govern H_2^* populations is the collisional quenching which leads to the formation of H atoms. Very large quenching cross sections (around 100 A^2) have been reported for $n=2$ states and some of the $n=3$ states [6]. The same cross section value has been assumed for $n>2$ H_2 excited states. The resulting quenching rate, around $10^{-8}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$, is responsible for the small concentrations of H_2^* in moderate pressure plasmas.

The chemistry model contains the most important dissociation, ionization and ion conversion processes. In particular, a crucial role is played by the reaction

$$H(2s)+H_2 \Rightarrow H_3^+ + e, \tag{7}$$

which shows a cross section for thermal energies of about 50 A^2 [6].

Since the predominant positive ion is H_3^+, which is stable up to 1 μs with a mole fraction around 10^{-6}, the reverse process of (7) is also important in post discharge regimes. It results in a relatively high H ($n=2$) concentration, which sustains the EEDF during a large period of relaxation. For a given discharge conditions (E/N and pressure), the coupled set of species, electron Boltzmann and total energy equations were solved to yield the stationary plasma composition, vdf, EEDF, and T_g in the discharge regime. These stationary values were used as initial conditions in a time-dependent code, which solves the same set of equations, for investigating the plasma relaxation after the electric field switch off.

We present results corresponding to an initial discharge condition characterized by a power of 50 W and a pressure of 5 mbar. Figures 1–4, respectively, show the time relaxation of the EEDF, vdf, and H_2, and H electronically excited state distributions.

Let us first examine the relaxation of the EEDF. The first distribution reported in Fig. 1 represents the one obtained in the discharge regime. We can see that the corresponding high value of the reduced electrical field in the microwave discharge is such to spread the electrons uniformly along the energy axis and to hide the effect of all superelastic collisions.

After the electric field switches off, the EEDF relaxation results in a strong decrease of low (0–4 eV) and high (>12 eV) energy electrons ending for $t>0.5\,\mu$s in the formation of a long quasistationary plateau in the energy range 4–12 eV. For $t>0.5\,\mu$s we observe a strong decrease of the EEDF in the energy range 12–15 eV and a repetition of the plateau from approximately 15 eV on. The magnitude of this second plateau is so small ($\approx 10^{-22}\,\mathrm{eV}^{-3/2}$), so that we decided not to report it in the figure.

The low energy part of the EEDF reaches, at $t>0.5\,\mu$s, a quasistationary Maxwellian distribution which is strongly coupled to the low energy part of vdf reported in Fig. 2. We

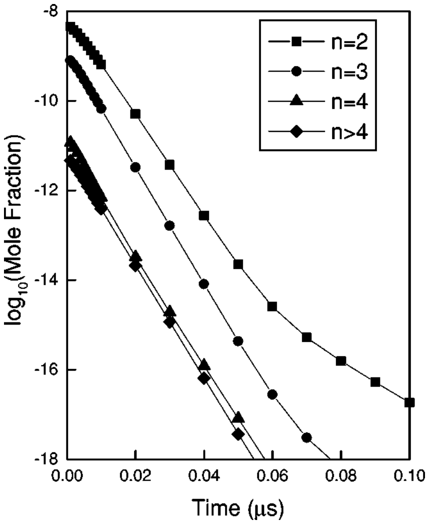

FIG. 3. Time relaxation of the electronically molecular excited state distribution.

see in fact that the first part of the vdf is roughly stable in the time interval taken into consideration. For $t > 0.5\,\mathrm{ms}$, the slope of the vdf for the first vibrational levels ($v = 0-4$) is approximately equal to that of the EEDF in the low energy range ($\varepsilon = 0-4\,\mathrm{eV}$), thus implying that the vibrational temperature based on the $v = 0-4$ levels is approximately equal to the electron temperature obtained by the slope of the EEDF in the energy range 0–4 eV. The long plateau in the vdf, generated by e-V and E-V processes, does not significantly affect the relaxation of the EEDF.

The long quasistationary plateau present in the EEDF for $t > 0.5\,\mu\mathrm{s}$ is mainly due to superelastic electronic collisions from H ($n = 2$). The main effect of the remaining H* and H_2* excited species on electron kinetics consists of slowing down the decay of the high energy part ($\varepsilon > 12\,\mathrm{eV}$) of the EEDF during the early relaxation. As a matter of the fact, inspection of Figs. 3 and 4 shows that, except in the case of H ($n = 2$), the concentration of H_2* and H* species strongly decreases with time. In particular, H_2* species show very small concentrations, and may be considered as nonexistent for $t > 0.1\,\mu\mathrm{s}$. Conversely, during the early relaxation (times in the range $10^{-2}-10^{-1}\,\mu\mathrm{s}$) the molar fractions of H_2*, especially the $n = 2$ and 3 states, keep relatively important values which generate structures in the EEDF and slow down its relaxation especially for high energy electrons ($\varepsilon > 12\,\mathrm{eV}$). This effect may be seen in Fig. 1, which shows that, for $t = 2 \times 10^{-2}$ and $10^{-1}\,\mu\mathrm{s}$, EEDF's calculated with and without taking into account the superelastic collisions may differ by several order of magnitude for $\varepsilon > 12\,\mathrm{eV}$.

This difference is due in particular to these states with energy level ε_1, in the range 11.8–12.2 eV for $n = 2$ and 13.4–14 eV for $n = 3$. Collisions of the second kind with these states transport the electrons from the low energy part of the EEDF to the plateau through the processes

$$e(\varepsilon \approx 0) + H_2^*(\varepsilon_1) \Rightarrow e(\varepsilon \approx \varepsilon_1) + H_2. \tag{8}$$

These sources of hot electrons are superimposed on similar processes involving superelastic collisions from atomic excited states with energy $13.6(1 - 1/n^2)$.

For $t > 0.2\,\mu\mathrm{s}$, the only excited state present in the post discharge is the H ($n = 2$) state which pumps electrons at 10.2 eV. Again elastic collisions transport electrons from this energy up to approximately 4 eV, which leads to the formation of the plateau in the range $\varepsilon = 4-10\,\mathrm{eV}$. Note that due to the small mass of H_2/H species, elastic collisions are very effective (see also Ref. [7]). For ε in the range 0–4 eV, electrons lose and gain energy through inelastic and superelastic vibrational collisions. The interplay of these processes, as well as elastic collisions, is such to determine the behavior of the EEDF in the energy range 0–4 eV.

It is worth noting that the form of the low energy Maxwell distribution plus the plateau reflect themselves in the high energy part of the EEDF. In any case, the concentration of this part of the EEDF is so small as to not allow any possibility of detection.

We would like to point out that the whole kinetic problem has been also solved using a quasistationary assumption for the EEDF [i.e., $dn(\varepsilon,t)/dt = 0$]. A comparison of these results with those reported in Figs. 1–4 shows in general a good agreement for long time values ($t > 0.5\,\mu\mathrm{s}$), while strong deviations in the EEDF are observed in its early relaxation.

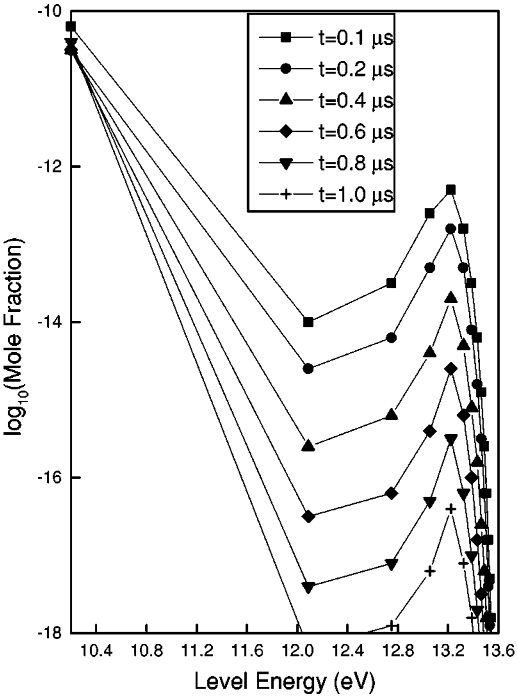

FIG. 4. Time relaxation of the electronically atomic excited state distribution.

These results show the strong coupling between the simultaneous relaxation of the EEDF and the distributions of vibrationally and electronically excited states. In particular, the first part of the EEDF (0–4 eV) relaxes in the presence of a stable vdf, while the structures present in the bulk and in the tail of the EEDF come from the interplay of second kind and elastic collisions. The quasistationary plateau present for $t > 0.5\,\mu\mathrm{s}$ is governed by the relaxation of H($2s$) produced through the recombination of H_3^+.

As a conclusion we want to spend few words about the possibility of experimental determination of our numerical results. The first part of the EEDF up to 8 eV contains fraction of electrons which may hopefully be experimentally determined for $t < 0.5\,\mu\mathrm{s}$. Keeping in mind that the electron and H_3^+ concentrations are equal, we can say that dedicated Langmuir probe measurements (see, for example, Ref. [8]) could be probably successful in determining the structures in the EEDF, especially for the early part of the evolution ($t < 0.5\,\mu\mathrm{s}$). This experiment is prohibitive at longer times ($t > 0.5\,\mu\mathrm{s}$) since the plateau contains for the reported conditions approximately 1 electron/cm^3, which can be hardly detected even with a repetitive experiment. Other plasma conditions should be studied to increase the density of electronically excited states, and therefore the plateau of the electron energy distribution function. Comparison between calculated and experimental EEDF's could help to set up a database for electron impact collisions involving excited molecular and atomic species, as well as to determine values of quenching rates of excited states.

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