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Non-Equilibrium Vibrational, Attachment and Dissociation Kinetics of HCl in XeCl Selfsustained Laser Discharges

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Abstract. The vibrational kinetics of HCl in a Ne-buffered XeCl selfsustained laser discharge is self-consistently calculated by coupling the vibrational master equation with the chemical one, the Boltzmann equation for electron transport and the circuit equations. The results show the limits of the classical simplified schemes of HCl vibrational kinetics used in the literature. Problems connected with the neglection of HCl depletion instabilities in the calculations are discussed using a parallel resistor network model.

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When realizing a numerical model of XeCl selfsustained discharge laser [1, 2], the nonequilibrium vibrational kinetics of HCl has a paramount importance. Vibrationally excited HCl molecules, infact, are supposed to enhance dissociative attachment leading to Cl^- ions and thus to excimer molecules through Cl^- recombination with Xe^+ or Xe-containing positive molecular ions.

At the same time, dissociative attachment to vibrationally excited HCl molecules is supposed to be the main channel for electron destruction, and therefore the most important mechanism leading to both global stability and local instability of the laser discharge.

Very simplified descriptions of HCl vibrational kinetics have been used in the numerous models of XeCl laser available in the literature due to problems of computational time: usually no more than three vibrational levels are taken into account. Some models using four vibrational levels of HCl have been occasionally discussed [3, 4]. Also, vibrational quanta quenching and transfer, as well as direct dissociation of HCl by electron impact, has been usually disregarded. A remarkable exception is the model of an *e*-beam pumped XeCl laser of Kannari et al. [5] which, however, refers to a different pumping scheme.

Far more wide vibrational kinetics have been used, as a rule, in papers devoted to HCl laser modeling, see for example [6].

Due to the explosion of literature about XeCl selfsustained discharge laser modeling and the general agreement on using a quite restricted vibrational manifold, more detailed calculations appear necessary to test the consistence of these simplified approaches to HCl vibrational kinetics and their domain of applicability.

Previous calculations of Gorse et al. [7] have shown the importance of highly excited levels in a preliminar model of HCl kinetics in Ne/Xe/HCl discharges. The model was based on a HCl chemical kinetics coupled with a Boltzmann equation taking into account also elastic and inelastic collisions of electrons with Ne and Xe, at fixed values of electric field and electron concentration.

In this paper the vibrational kinetics of HCl is calculated in the framework of a self-consistent model of the 10 liters XeCl selfsustained discharge laser developed at ENEA laboratories, Italy (see [8]) in the case of a Ne-buffered mixture.

1 Method of Calculation

The model used for these calculations is fundamentally the one used by Gorse [9] but taking into account in more detail the HCl vibrational kinetics. In particular:

a) 7 vibrational levels (including the ground level) are inserted,

b) direct dissociation by electron impact of HCl molecules in both ground and excited vibrational levels

$$e + \mathrm{HCl}(0, \ldots, 6) \rightarrow e + \mathrm{H} + \mathrm{Cl}$$

is taken into account,

c) the following vibrational quanta quenching (or VT, which stands for vibration-translation) processes:

$$\mathrm{HCl}(v) + \mathrm{H} \rightarrow \mathrm{HCl}(v-q) + \mathrm{H}$$

$$\mathrm{HCl}(v) + \mathrm{Cl} \rightarrow \mathrm{HCl}(v-q) + \mathrm{Cl} \qquad q = 1, \ldots, v$$

$$\mathrm{HCl}(v) + \mathrm{HCl}(0) \rightarrow \mathrm{HCl}(v-1) + \mathrm{HCl}(0)$$

and the following vibrational quanta transfer (or VV, which stands for vibration–vibration) processes:

$$\mathrm{HCl}(v) + \mathrm{HCl}(w) \rightarrow \mathrm{HCl}(v-1) + \mathrm{HCl}(w+1)$$

are taken into account using the rate coefficients reported by Capitelli et al. [6].

The master equation for the vibrational manifold is a part of the most general one for the chemical kinetics of all the relevant species (Ne, Xe, H, Cl atoms, HCl molecules, excited atoms and molecules, atomic and molecular ions, XeCl molecules, photons); this last has been coupled to the two-term Boltzmann equation for calculating the electron energy distribution function (eedf), from which the rate coefficients for some reactions involving electrons are determined.

The Boltzmann equation is solved in a time-dependent way taking into acount superelastic collisions of electrons with excited species (electronic and vibrational) and electron–electron collisions.

The cross sections used for electron collisions with Ne and Xe are the same as used in [10].

Concerning vibrational excitation cross sections, we have used for any one-quantum and two-quanta transitions the cross sections for HCl(0) excitation to HCl(1) and HCl(2) of Davies [11] respectively, and the corresponding ones for vibrational superelastic collisions have been calculated using detailed balance.

For the dissociative attachment, the cross sections calculated by Teillet-Billy and Gauyacq [12] have been used up to $v = 2$, and the cross section for attachment to HCl(2) has been used for $3 \leq v \leq 6$.

Two different assumptions about the cross sections for direct dissociation by electron impact of HCl molecules in the ground and excited vibrational levels have been used: according to the first one, the dissociation cross sections calculated by Cacciatore and Capitelli [13] have been used. The other possibility is to use as dissociation cross section of HCl(0) the cross section for electronic excitation of HCl(0) to $\mathrm{HCl}^*(A)$ derived by Davies [11] and translate this one to lower energy by steps equal to the vibrational excitation threshold (0.35 eV) to obtain the corresponding cross sections for HCl(v).

The discharge kinetics is coupled to the equations for the pumping circuit, whose imputs are the electron concentration and mobility (calculated from the eedf) and whose output is the instantaneous value of the electric field, which is needed to solve the Boltzmann equation.

The assumed scheme for the electrical pumping circuit is shown in Fig. 1. The values of the electrical quantities are: $C_1 = 640\,\mathrm{nF}$, $C_2 = 2.4\,\mathrm{nF}$, $R_\mathrm{p} = 38\,\mathrm{m\Omega}$, $L_\mathrm{p} = 63\,\mathrm{nH}$, $L_\mathrm{L} = 10\,\mathrm{nH}$. The electrodes are plane, rectangular, with dimensions 100 cm × 10 cm, the distance between them is 10 cm.

2 HCl Kinetics: Results and Discussion

In the initial conditions, the only species present are neon, xenon, HCl(0), electrons and Xe^+ ions: the xenon partial pressure is 10 Torr, the HCl(0) partial pressure is variable, the initial electrons and Xe^+ ions concentration (due to preionization) is $10^{10}\,\mathrm{cm}^{-3}$; the neon partial pressure is adjusted to obtain a total pressure of 3 atm.

A first calculation has been performed using cross sections from [13] for direct dissociation of HCl, at a partial pressure of HCl of 1.5 Torr and with an initial voltage on the main capacitor bank of 55 kV.

In Fig. 2 the populations of vibrational levels of HCl as a function of time are plotted as solid lines: as can be seen, after the vibrational manifold has relaxed to the quasi-stationary condition, all the considered levels are significantly populated, the population of $(v+1)^{\mathrm{th}}$ level being approximately one-third of that of the v^{th} one. In the same figure the populations calculated neglecting VV and VT processes are plotted as broken lines: as can be seen, the latter processes influence sensibly the vibrational kinetics of HCl. In particular, VT processes involving H atoms depopulate the excited vibrational levels of HCl as the concentration of H atoms rises: this phenomenon is not observed in the kinetics neglecting VT processes even at the end of the voltage plateau (at approximately 800 ns, in our model) because the vibrational excitation

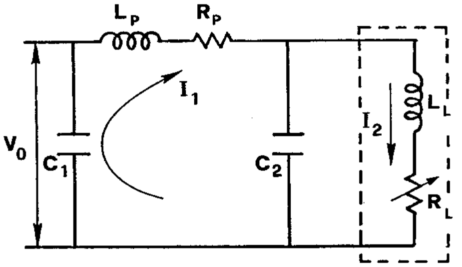

Fig. 1. Scheme of the electrical pumping circuit used in the calculations. V_0 is the initial voltage on the main capacitor bank

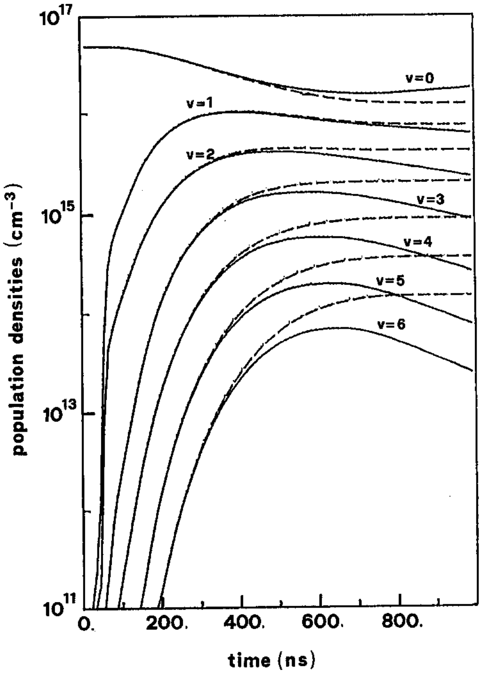

Fig. 2. Populations, in cm^{-3}, of the vibrational levels of HCl calculated for $p\mathrm{HCl} = 1.5\,\mathrm{Torr}$, $V_0 = 55\,\mathrm{kV}$, using Cacciatore and Capitelli cross sections for direct dissociation of HCl, including (full lines) and disregarding (dashed lines) VV and VT processes in the kinetics

and deexcitation rates of HCl depend only slightly upon the value of the electric field. Due to this evidence of the importance of VV and VT processes, we will be taking them into account in the following, if not otherwise specified.

In Fig. 3a and b the contributions of different vibrational levels to the rate coefficient for dissociative attachment and direct dissociation of HCl by electron impact are shown: the n^{th} curve from below refers to the sum of contributions from the ground level to the n^{th} one, therefore, the uppermost curve refers to the total rate.

It should be observed from Fig. 3a that at least five levels of HCl are necessary to correctly describe the attachment dynamics of the vibrational manifold. Also, observation of the results in Fig. 3b makes clear that all the levels of the considered manifold contribute significantly to the total rate coefficient for direct dissociation. This is due to the strong increase of the calculated cross section as a function of vibrational quantum number.

By comparison of the uppermost curves in Fig. 3a and b it can be observed that the total rate coefficient for direct dissociation of HCl is much lower than the attachment one in this condition.

However, it is not obvious that this conclusion will be still valid when considering the cross section for $HCl^*(A)$ electronic excitation of Davies as a dissociation cross section, as explained above. To test the effect of changing the cross section for direct dissociation of HCl by electron impact another calculation has been performed in the same conditions, but using the other set of cross sections.

In Fig. 4a and b the contribution to the rate coefficients for dissociative attachment and total dissociation calculated with this assumption are plotted: it can be seen that the total dissociation rate is no more negligible with respect to the total attachment one.

Calculations have also been performed for different HCl partial pressures, to see the effect of variations of composition of the laser mixture.

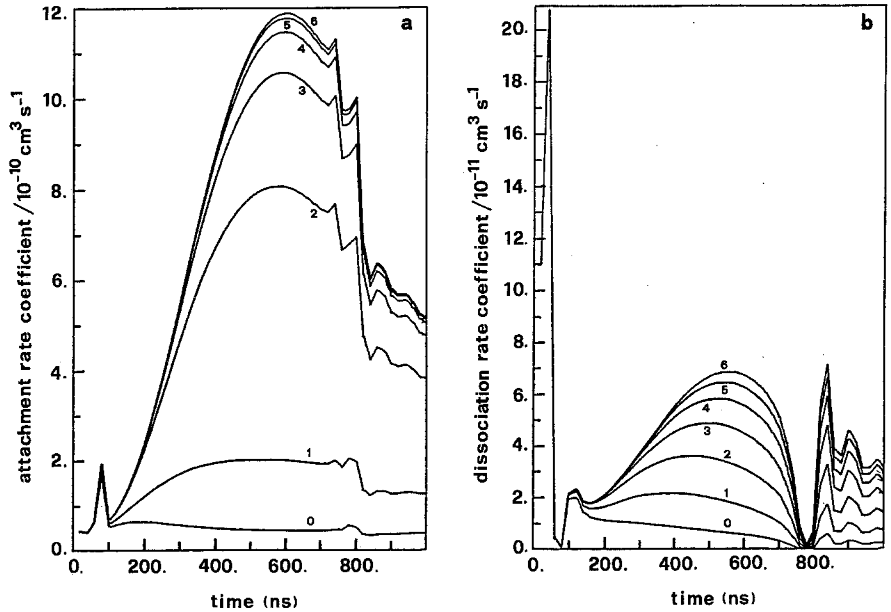

Fig. 3. **a** Contributions of vibrational levels of HCl to the rate coefficient for dissociative attachment, calculated with the same conditions as in Fig. 2 (the various curves refer to the sum of the different contributions up to the relevant v^{th} level). **b** Contributions of vibrational levels of HCl to the rate coefficient for direct dissociation, calculated with the same conditions as **a**

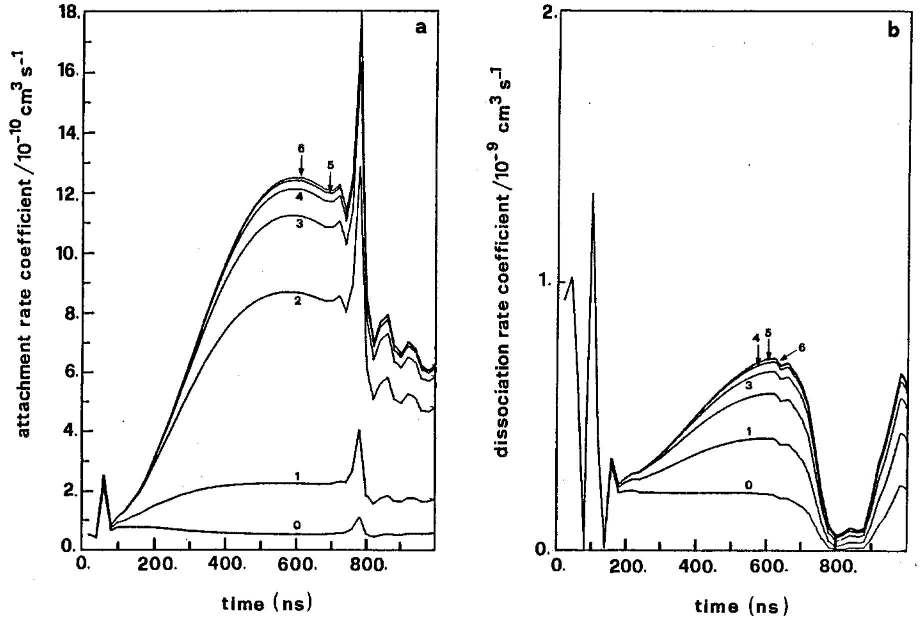

Fig. 4. **a** Contributions of vibrational levels of HCl to the rate coefficient for dissociative calculated for pHCl = 1.5 Torr, V_0 = 55 kV, using Davies $HCl^*(A)$ excitation cross section for direct dissociation of HCl (see text). **b** Contributions of vibrational levels of HCl to the rate coefficient for direct dissociation, calculated with the same conditions as **a**

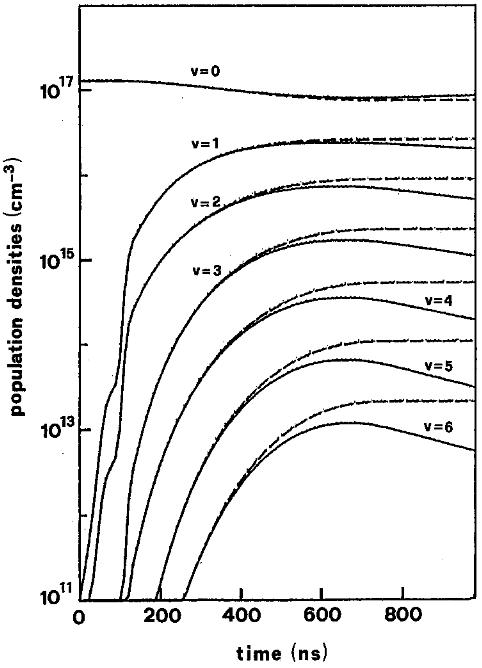

Fig. 5. Same of Fig. 2, but pHCl = 4 Torr

In particular, we have performed a calculation for pHCl = 4 Torr, using the first set of cross sections for direct dissociation of HCl.

The calculated evolution of populations of vibrational levels in this condition is shown in Fig. 5, while in Fig. 6a and b the contributions of different vibrational levels to dissociative attachment and direct dissociation are shown. In Fig. 5 the populations calculated neglecting VV and VT processes are also reported to show also the importance of these processes in this condition.

It can be seen that the importance of direct dissociation increases when increasing the HCl partial pressure. This behaviour seems to be due to a much lower vibrational excitation needed to stabilize the discharge as seen by the circuit (global stability), because of the greater quantity of HCl present.

Using this self-consistent approach it is possible to validate a posteriori a crucial assumption made in [7], where some of the present results were anticipated using a pure HCl chemical kinetics and therefore neglecting the channels of destruction of HCl due to the Ne/Xe kinetics, that is the harpooning

$$\mathrm{Xe}^* + \mathrm{HCl}(v) \rightarrow \mathrm{XeCl}^* + \mathrm{H}$$

and the direct dissociation

$$\mathrm{Xe}^* + \mathrm{HCl}(0, v) \rightarrow \mathrm{H} + \mathrm{Cl} + \mathrm{Xe}.$$

To do this, new calculations have been performed at pHCl = 1.5 Torr and using Cacciatore and Capitelli cross sections, but neglecting harpooning and direct dissociation of HCl by Xe* impact. The results for the contributions of vibrational levels to the dissociative attachment and direct dissociation by electron impact are reported in Fig. 7a and b, respectively.

By comparing Fig. 7a, b and Fig. 3a, b it can be noticed that neglection of these processes has no relevant effect on the results of the calculations: some difference could be noticed only in the system of peaks around t = 800 ns, which will be discussed in the next section.

3 Effect of Halogen Depletion Instability

The peaks in the curves in Fig. 2a, b at about t = 800 ns and other similar features in the following figures are the result of a secondary breakdown due in turn to an excessive electron destruction by dissociative attachment at the end of the first half-wave of the discharge voltage. This breakdown is not observed in the actual discharge [8], probably because the latter undergoes an halogen depletion instability triggered by preionization disuniformities.

We have observed this secondary breakdown to disappear, acording to experimental results, when performing one-dimensional calculations with a simplified parallel resistor network model similar to that used by Kushner

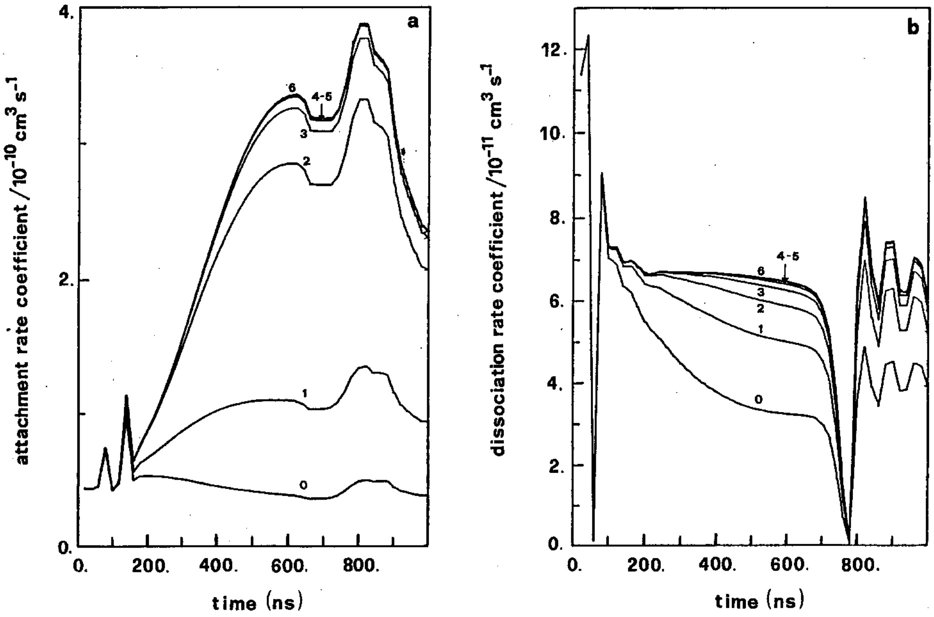

Fig. 6. Same of Fig. 3, but pHCl = 4 Torr

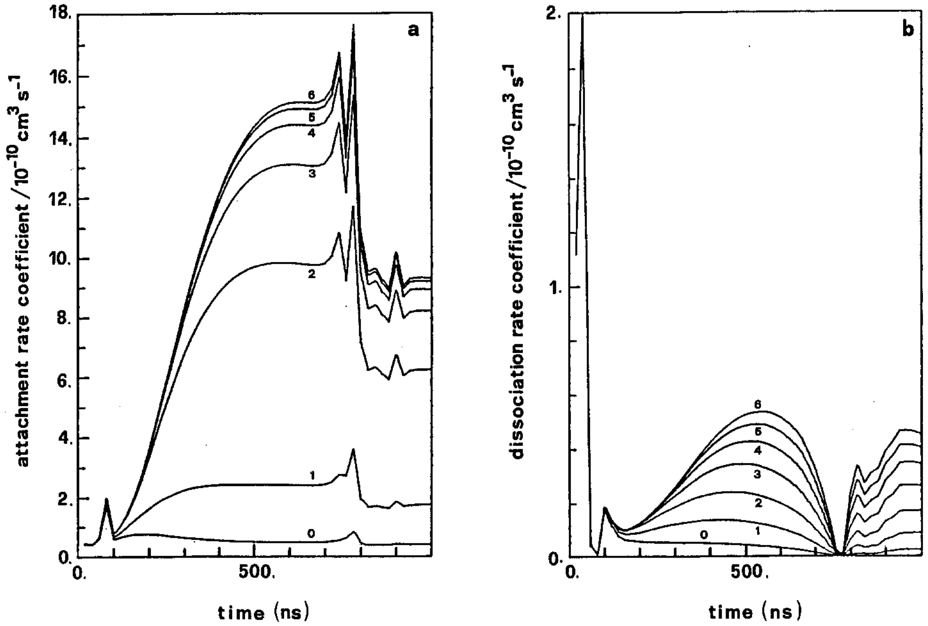

Fig. 7. Same of Fig. 3, but neglecting any $Xe^* + HCl$ process

[14] and Belasri et al. [15] using the same circuit of Fig. 1 and allowing for the experimental preionization shape [16].

The model is based on a parallel network of resistors with independent chemical kinetics: the resistance of each one is calculated from the local electron concentration and the total resistance is used in the circuit equation, giving in turn the value of the electric field. This last value is common to all the resistors, since the electrodes are plane and border effects are assumed to be negligible.

The 1D model we have used takes into account the following simplified scheme for chemical reactions:

1′ $Xe + e \leftrightarrow Xe^* + e$
rate: Boltzmann equation

2′ $Xe + e \rightarrow Xe^+ + 2e$
rate: Boltzmann equation

3′ $Xe^* + e \rightarrow Xe^+ + 2e$
rate: Boltzmann equation

4′ $HCl + e \leftrightarrow HCl(1) + e$
rate: Boltzmann equation

5′ $HCl(1) + e \rightarrow H + Cl^-$
rate $= 1.2 \times 10^{-9}\,cm^3\,s^{-1}$

6′ $Xe^* + HCl(0,1) \rightarrow Xe + H + Cl$
rate $= 5.6 \times 10^{-10}\,cm^3\,s^{-1}$

7′ $HCl(0,1) + e \rightarrow H + Cl + e$
rate $= 0.6 \times 10^{-9}\,cm^3\,s^{-1}$

8′ $Xe^+ + Cl^- \rightarrow XeCl^*$
rate: Flannery equation

The rate coefficients for the processes 1′–4′ have been previously calculated as a function of the electric field by finding a stationary solution for the Boltzmann equation using the same cross sections of the 0D model and the cold gas approximation. The rate coefficients of 5′ and 7′ match the typical values of the total rates calculated with the whole kinetics taking into account 7 levels and they are reported in [7]. The other rates are from [9]. $XeCl^*$ is supposed to decay in $Xe + Cl$ by spontaneous and stimulated emission with negligible effects on the circuit behaviour. The voltage and current behaviours calculated assuming uniform preionization and allowing for the experimental one using 20 equivalent parallel resistors are reported in Fig. 8a and b, respectively. The reported voltage includes the inductive contribution due to L_L.

It can be observed how the negative voltage peak of Fig. 8a is replaced by a smooth oscillating trend. Furthermore, in Fig. 8b further halfwaves of current are observed which are strongly damped in the 0D result.

These different behaviours are due to a different concentration of HCl molecules in the volume actually involved in the discharge in the two cases: in the uniform discharge the remaining quantity of HCl in vibrational excited states causes an almost full destruction of the electrons as soon as the voltage drops and the $Xe \rightarrow Xe^* \rightarrow Xe^+$ channel slows down. On the contrary, the contracted discharge contains only a negligible quantity of HCl molecules due the action of attachment and dissociation by the more and more concentrated electrons during the development of the instability.

The 1D curves agree better than the 0D ones with the experimental curves reported in the same figures expecially for the long-time behaviour, which the 0D theory completely fails to predict.

The disagreement of both models with the experimental results concerning the first voltage peak are due to the limited bandwidth of the measuring apparatus, which can be effectively taken into account by modeling the measuring apparatus as a part of the circuit as shown in [17]; the difference in the values of the plateau voltage are probably due to the simplifications used in the kinetics (for example, this simplified scheme neglects the effect of the Xe^* ionization process on the eedf).

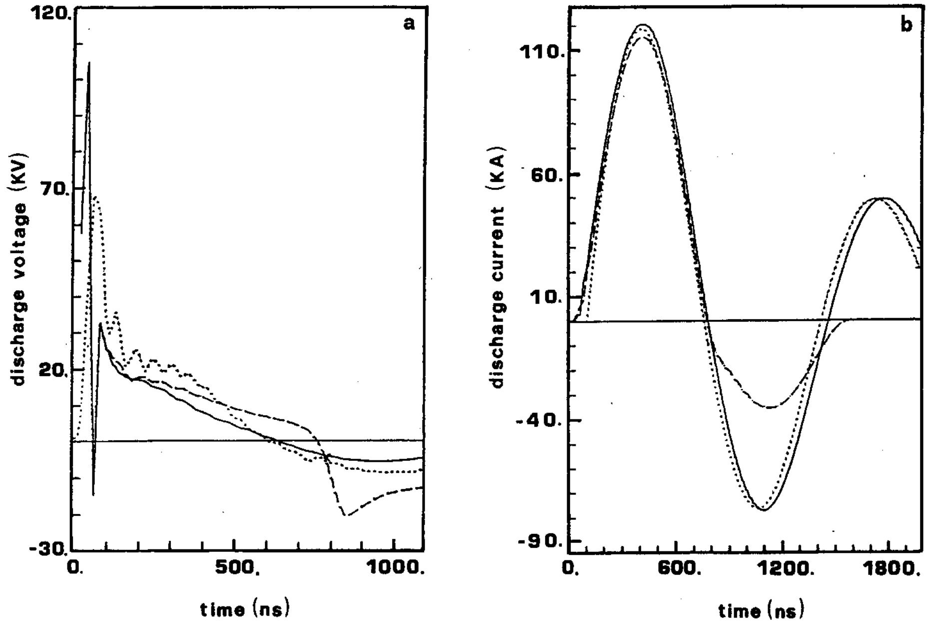

Fig. 8a, b. Discharge voltage (**a**) and current (**b**) calculated with a parallel resistor network model taking into account preionization disuniformities (full line) and neglecting them (broken line). Dotted line: experimental behaviour [8]

The most important point, however, is that the theoretical secondary breakdown appears to be due only to the neglection of preionization disuniformities triggering an halogen depletion instability. Owing to the strong differences between the two behaviours, we believe that this point will remain unchanged when performing a more detailed dimensional modeling of this discharge.

This result confort us in considering our 0D calculations with detailed kinetics as quite accurate for an idealized Frascati device with perfectly uniform preionization and probably for any device not so strongly affected by discharge instabilities (for example lasers of smaller active volume).

4 Conclusions

The most important result of this calculation is the importance of the dissociation and electronic excitation processes: the dissociation process becomes more and more relevant with increasing HCl partial pressure even if the one of the two sets of cross sections discussed here which gives the smaller effect is used.

Also, it should be observed that to take into account the total effect of dissociation it is sometimes necessary to follow a number of vibrational levels of HCl.

Furthermore, vibrational populations of highly excited levels calculated neglecting VV and VT processes are quite different from those obtained including these processes.

From this first result it should be concluded that a simplified approach to HCl vibrational kinetics neglecting direct VV, VT processes and direct dissociation and including only 3 or 4 vibrational levels cannot be used in any condition and in any case it can be used only as a first approximation. In particular it appears to be quite rough at high HCl partial pressure, where *high* depends on the electrical circuit used, and therefore could be lower than the usual operating one for some of the devices modeled in the literature.

The results about the process associated with Davies' $HCl^*(A)$ excitation cross section show that if this cross section is assumed as a dissociation one, then the dissociation of HCl by electron impact is no longer negligible even at low HCl partial pressure, and has to be included in the chemical kinetics.

In any case, due to very high calculated frequency of the process $e + HCl \rightarrow e + HCl^*(A)$, the subsequent chemical kinetics should be taken into account in the modeling.

This results show the relevance and need for further investigation of the behaviour of the HCl vibrational manifold in XeCl laser operation. In particular further researches should be performed to understand if our present knowledge of HCl vibrational kinetics suffices to calculate in a reliable manner the effect of an halogen depletion instability not only on the circuit behaviour, but also on the laser pulse.

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