# NON-EQUILIBRIUM DISSOCIATION OF DIATOMIC SPECIES OF LASER INTEREST: HCl

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## ABSTRACT

Dissociation rates of HCl in non-equilibrium plasmas have been calculated according to the pure vibrational mechanism and to the joint vibroelectronic mechanism. The results show the importance of vibrational non-equilibrium on the dissociation rate, even though the strong vibrational deactivation of the formed H, Cl atoms tend to destroy the vibrational content of the HCl molecules.

## 1. INTRODUCTION

We have recently studied the dissociation of homonuclear diatomic molecules under non-equilibrium conditions, emphasizing the importance of vibrational non-equilibrium on the dissociation rates (see for ex. ref. 1). In this work we extend these calculations to HCl, a molecule which could represent a possible candidate as infrared laser.

## 2. THE VIBRATIONAL KINETICS

### 2a. THE PURE VIBRATIONAL MECHANISM (PVM)

According to PVM the electrons of the discharge introduce vibrational energy by means of the electron-vibration (e-V) energy exchanges

$$e + HCl\ (v=0) \rightleftarrows e + HCl\ (v=1,2) \qquad a$$

vibration-vibration (V-V) energy exchanges distribute the introduced quanta over the whole vibrational manifold, while V-T (vibration-translation) energy exchanges tend to restore a Boltzmann distribution at the gas temperature. The dissociation occurs when the vibrational quanta reach the dissociation level (v'+1) located above the last bound level (v') of the molecule. The dissociation rate can be therefore expressed as [1]

$$r_d(\mathrm{PVM}) = \frac{\partial N_{v'+1}}{\partial t} = N_{v'} \sum_{i=\mathrm{HCl,H,Cl}} N_i \, P^{i}_{v',v'+1} + N_{v'} \sum_{v} N_v \, P^{v,v-1}_{v',v'+1} \quad (1)$$

where the rate coefficients appearing in eq. 1 correspond to V-T and V-V processes involving the last bound vibrational level of the molecule (see ref. 1).

Equation (1) is then coupled to a system of master equations which gives the temporal relaxation of the vth level in the presence of e-V, V-V, V-T and spontaneous emission processes. V-V and V-T rates involving HCl-HCl collisions have been taken from ref. 2, while the deactivation rates of vibrationally excited HCl molecules by H, Cl atoms have been derived from ref. 3. It should be noted that these last rates are very effective in removing vibrational energy from HCl. The e-V rates have been obtained by simultaneous solution of the Boltzmann equation for the electron energy distribution function (edf) with the system of vibrational master equations, the relevant e-V cross sections being taken from ref. 4.

A typical plot of the quasistationary dissociation constant ($k_d^s = r_d/N_{\mathrm{HCl}}$) as a function of $^1/T_g$ ($T_g$ is the gas temperature) is shown in fig. 1 for $E/N = 15 \cdot 10^{-16}$ V cm$^2$, $n_e = 10^{12}$ cm$^{-3}$ and $N_{\mathrm{HCl}} = 10^{17}$ cm$^{-3}$. The decrease of $k_d^s$ with increasing gas temperature is due to the increased importance of V-T relaxation accompanied by the decreased importance of V-V pumping up mechanism [1] The behaviour of $k_d^s$ in electrical discharges is completely different from the corresponding one occurring at $n_e = 0$ (thermal conditions) as can be appreciated in fig. 1.

## 2b. THE JOINT VIBROELECTRONIC MECHANISM (JVE)

According to JVE, the dissociation rate can be expressed as

$$r_d(\mathrm{JVE}) = \frac{\partial N_{v'+1}}{\partial t} = r_d(\mathrm{PVM}) + n_e \sum_{v} N_v \, k_d^e(v) \quad (2)$$

where $r_d$(PVM) is given by eq. (1) and $k_d^e(v)$ is the rate coefficient of the process

$$e + HCl(v) \rightleftarrows e + H + Cl \qquad b$$

Eq. (2) is then coupled to a system of vibrational master equations as in PVM with the addition of a relaxation term due to the dissociation process. Cross sections for process b have been calculated as outlined in ref. 1. The system of v'+1 differential equations has been coupled to the Boltzmann equation for edf. This last equation include processes b and the superelastic vibrational collisions (i.e. the reverse of process a), both depending on the vibrational population densities $N_v$. As a consequence the edf's change during the temporal evolution of $N_v$. In particular the tails of the electron energy distribution functions benefit for the presence of vibrationally excited molecules (see ref. 5). Values of the dissociation constant $k_{dj} = r_d(JVE)/N_{HCl}$ have been reported in fig. 2 as a function of time for different conditions and compared with the v=0 contribution $k_d^e(v=0)n_e$.

The temporal evolution of both $k_{dj}$ and $k_d^e(v=0)n_e$ follow the time evolutions of $N_v$ and edf. At t=0 $k_{dj}$ and $k_d^e(v=0)$ are coincident because of the initial condition $N_v = 0$ for $v \neq 0$. As the e-V processes populate the vibrational levels the contribution of $v \neq 0$ levels to the dissociation rate separates $k_{dj}$ from $k_d^e(v=0)n_e$. Both $k_{dj}$ and $k_d^e(v=0)n_e$ reache a maximum ($k_{dj}^m$) and then decrease due to the deactivating action of H, Cl atoms. Figures 3-4 report the maximum values of $k_{dj}(t)$ and $k_d^e(v=0)n_e$ as a function of pressure and gas temperature (fig. 3) and of reduced field E/N (fig. 4). It is worth noting that the differences in $k_{dj}$ and $k_d^e(v=0)n_e$ are emphasized at low $T_g$ and high $n_e$.

## 3. CONCLUDING REMARKS

The results presented in the present paper can be summarized as follows:

1) The dissociation of HCl in electrical discharges occurs through a joint vibroelectronic mechanism which is as more effective as smaller are the gas temperature and pressure and as greater is the

electron density

2) The contribution of the pure vibrational mechanism in dissociating HCl is indeed small, due to the fact that the electron dissociation mechanism is very effective in producing atoms which strongly deactivate the vibrational content of the molecule.
   This means that the results of fig. 1 must be considered as upper limits. PVM, on the other hand, can be important when the introduction of vibrational quanta is made by an IR laser of suitable frequency.
3) Electron energy distribution functions and related quantities must be calculated by the simultaneous solution of the Boltzmann equation with the system of vibrational master equations.

## 4. REFERENCES

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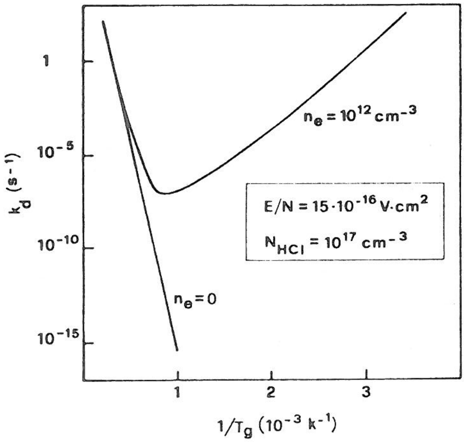

FIG. 1

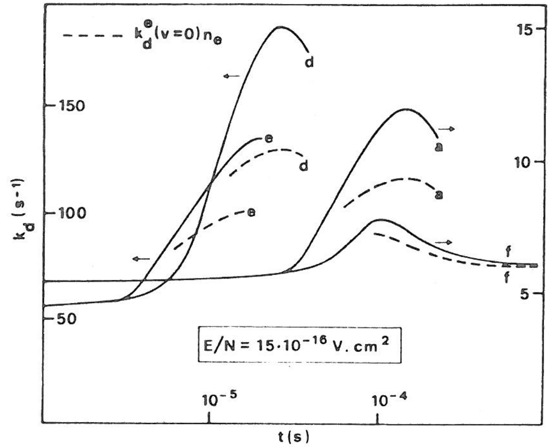

FIG. 2

a) $T_g = 300$, $P = 3$ torr, $n_e = 10^{11}$ cm⁻³
d) $T_g = 800$, $P = 8$ torr, $n_e = 10^{12}$ cm⁻³
e) $T_g = 300$, $P = 20$ torr, $n_e = 10^{12}$ cm⁻³
f) $T_g = 500$, $P = 20$ torr, $n_e = 10^{11}$ cm⁻³

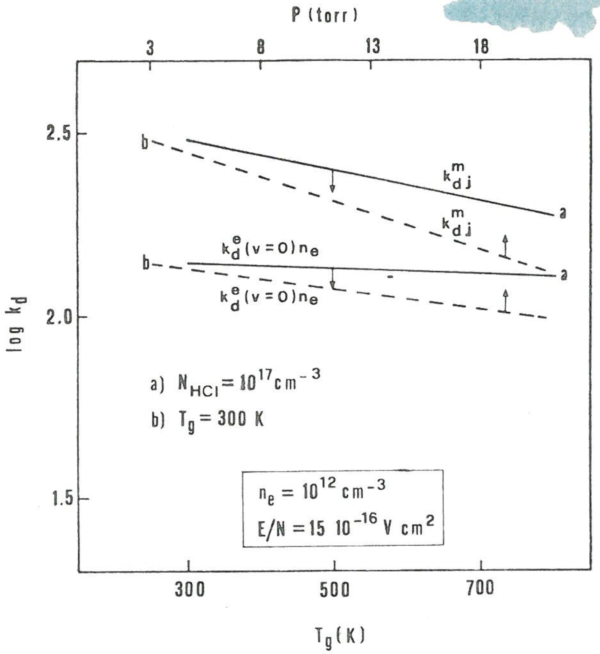
P (torr)
3
8
13
18
2.5
2.0
1.5
log $k_d$
b
a
$k^m_{dj}$
$k^m_{dj}$
$k^e_d(v=0)n_e$
$k^e_d(v=0)n_e$
a) $N_{HCl} = 10^{17} cm^{-3}$
b) $T_g = 300$ K
$n_e = 10^{12} cm^{-3}$
$E/N = 15\ 10^{-16}$ V $cm^2$
300
500
700
$T_g$(K)

FIG. 3

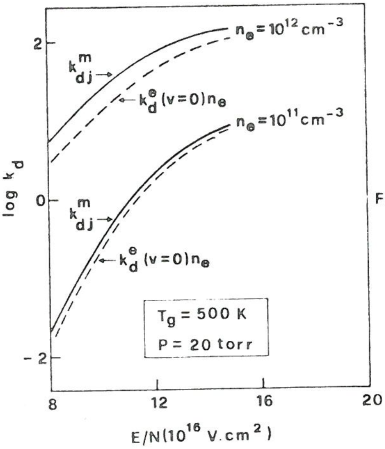
$n_e = 10^{12} cm^{-3}$
$n_e = 10^{11} cm^{-3}$
$k^m_{dj}$
$k^e_d(v=0)n_e$
$k^m_{dj}$
$k^e_d(v=0)n_e$
2
0
- 2
log $k_d$
$T_g$ = 500 K
P = 20 torr
8
12
16
20
$E/N(10^{16}$ V.$cm^2$)

FIG. 4