

# Non Equilibrium Dissociation of HF in Electrical Discharges: The Role of Vibrational Excitation\*

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Dissociation rates of HF in electrical discharges have been calculated by solving a system of vibrational master equations, including e-V (electron-vibration), V-V (vibration-vibration) and V-T (vibration-translation) energy exchanges. The results show that large dissociation rates can be obtained by this mechanism only when the e-V pumping rates overcome the V-T deactivating rates. This occurs for electron number densities larger than  $10^{13} \text{ cm}^{-3}$ .

Finally the close connection of the present results with the corresponding ones obtained by using as vibrational excitation source an IR powerfull laser is shown and discussed.

## 1. Introduction

We have recently proposed a vibrational model for explaining the dissociation rates of homonuclear diatomic species in electrical discharges [1]. According to this model the electrons of the discharge populate the first vibrational levels of the ground electronic state of the molecule, thus introducing a vibrational disequilibrium with respect to the gas temperature.

The vibrational quanta are then transported up to the dissociation limit by means of V-V (vibration-vibration) energy exchanges. The V-T (vibration-translation) processes on the contrary tend to destroy this mechanism, by trying to restore a Boltzmann vibrational population at the gas temperature ( $T_g$ ).

This mechanism can be very effective for those molecules which possess large e-V (electron-vibration) rates combined with small V-T deactivating ones.

In this paper we extend this model to the HF molecule and the results will be compared with the values recently obtained by Kompa et al. [2], who studied the HF dissociation induced by IR pulsed laser.

## 2. Method of Calculation

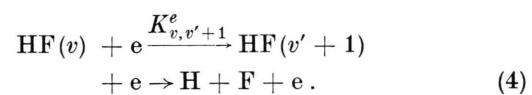
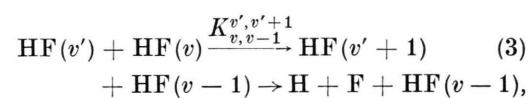
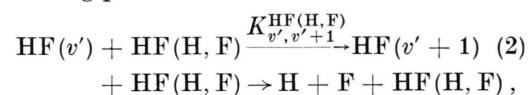
According to the vibrational mechanism outlined in Refs. [1, 2], the dissociation rate ( $\text{cm}^{-3} \text{ s}^{-1}$ ) of

the HF in electrical discharges can be written as

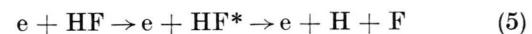
$$v_D = \frac{\partial N_{v'+1}}{\partial t} = \sum_{i=1}^3 N_i N_{v'} K_{v', v'+1}^i + N_{v'} \sum_{v=1}^{v'} N_v K_{v, v-1}^{v', v'+1} + n_e \sum_{v=1}^{v'} N_v K_{v, v'+1}^e \quad (1)$$

where  $N_v$  is the population density of  $v$ th level ( $v'=19$  is the last bound vibrational level of the ground electronic state of HF and  $v'+1$  is the dissociation level [1, 2]) and  $i=1, 2, 3$  corresponds respectively to HF, H, F.

The rate coefficients appearing in Eq. (1) refer to the following processes



It should be noted that we are considering only the dissociation rate of the pure vibrational mechanism, i.e. contributions coming from the direct electronic mechanism



and from the dissociative attachment



are not considered in the present paper.

Equation (1) is then coupled to a system of  $v'$  vibrational master equations [1], which describe

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the temporal evolution of the vibrational levels under the action of e-V, V-V and V-T energy exchanges.

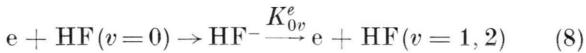
A typical equation of this system [1, 2] is written as

$$\begin{aligned} \frac{\partial N_v}{\partial t} = & \sum_{i=1}^3 N_i [N_{v-1} K_{v-1,v}^i + N_{v+1} K_{v+1,v}^i \\ & - N_v (K_{v,v-1}^i + K_{v,v+1}^i)] \\ & + \sum_{w=0}^{v'} N_w [N_{v-1} K_{w,w-1}^{v-1,v} + N_{v+1} K_{v+1,v}^{w,w+1} \\ & - N_v (K_{v,v-1}^{w,w+1} + K_{w,w-1}^{v,v+1})] \quad (7) \\ & + \sum_{w=0}^{v'} n_e [N_w K_{w,v}^e - N_v K_{v,w}^e] \\ & + N_{v+1} A_{v+1,v} - N_v A_{v,v-1} \end{aligned}$$

( $A_{v,v-1}$  is the spontaneous emission coefficient).

It should be noted that Eqs. (1), (7) disregard the recombination process, taking into account the deactivation of vibrational energy by the atoms (H, F). As for the rate coefficients appearing in Eqs. (1), (7), they have been calculated as follows.

1) The e-V rates



have been obtained by numerical integration of the experimental cross section of Rohr and Linder [3] over a Maxwell electron distribution function. This last hypothesis does not affect too much the e-V rates, because the thresholds of these processes overlap with the bulk of electron distribution function, which in turn is not affected by inelastic processes [4].

The missing e-V rates have been simply obtained by imposing  $K_{01}^e = K_{1,2}^e = K_{2,3}^e$  and so on ( $K_{0v}^e = 0$ ,  $v > 2$ ), while the detailed balance has been used for the e-V reverse rates.

2) V-T and V-V rates have been taken from the work of Kompa et al. [2], even though other rates have appeared in the literature since this work [5]. However their incorporation in our work is not done for a consistent comparison of dissociation rates induced by electrons and by IR laser.

The system of  $v'+1$  differential equations has been numerically integrated with the following initial condition

$$\begin{aligned} N_v(t=0) &= 0 \quad \text{for } v \neq 0, \\ N_v(t=0) &= N_{HF}^0, \quad v = 0, \\ N_H &= N_F = 0 \end{aligned} \quad (9)$$

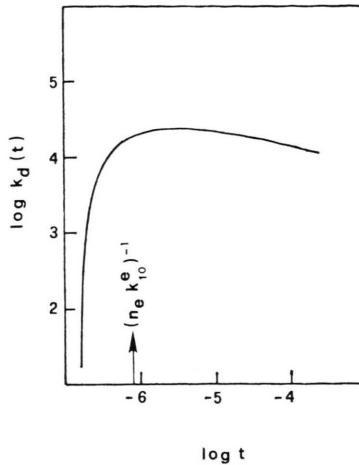


Fig. 1. Dissociation constant ( $s^{-1}$ ) as a function of time ( $n_e = 10^{14} \text{ cm}^{-3}$ ,  $T_g = 300 \text{ K}$ ,  $p = 3 \text{ torr}$ ,  $T_e = 10000 \text{ K}$ ).

at different gas temperatures ( $300 \text{ K} \leq T_g \leq 1000 \text{ K}$ ), pressures ( $3 \leq p \leq 60 \text{ torr}$ ), electron densities ( $10^{11} \leq n_e \leq 10^{14} \text{ cm}^{-3}$ ). In all calculations the electron temperature has been considered equal to  $T_e = 10000 \text{ K}$ , which gives very high e-V rates minimizing the dissociation processes coming through other channels.

After a transient period, which is approximately given by  $(n_e K_{01}^e)^{-1}$ , the pseudofirst order constant  $k_d(t) = v_D / \sum_0^{v'} N_v$  settles to a quasistationary value  $k_d^s$  [1], as can be appreciated in Figure 1. This value can be taken as an indication of the effectiveness of the vibrational mechanism in dissociating HF.

### 3. Results

HF is an interesting system from the point of view of the vibrational kinetics, presenting in fact large e-V rates ( $K_{01}^e \sim 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  at  $T_e = 10000 \text{ K}$ ) combined, unfortunately, with high deactivation rates of the process



In our previous works [1] (see also Ref. [6]) we have shown that the efficiency of the vibrational mechanism in dissociating diatomic species is strictly related to the possibility of creating a large "vibrational" temperature  $\Theta_1 = E_{10} / \ln(N_0 / N_1)$  ( $E_{10}$  is the energy of the transition  $0 \rightarrow 1$  and  $N_0$ ,  $N_1$  denote in this order the population densities of the

ground and of the first vibrational level. Large  $\Theta_1$  values can be obtained when the pumping rate ( $n_e K_{01}^e$ ) overcomes the most important V-T deactivation process (in this case  $N_{HF} K_{1,0}^{HF}$ ). To obtain large  $\Theta_1$  values, therefore, one must consider HF electrical discharges with electron densities  $n_e$  ( $\text{cm}^{-3}$ ) obeying the inequality

$$n_e > \frac{K_{10}^{HF}}{K_{01}^e} N_{HF}. \quad (11)$$

Values of  $(K_{10}^{HF}/K_{01}^e) N_{HF}$  can be calculated at different  $T_g$  and pressures. One can note that appreciable "vibrational temperatures" can be only obtained at high  $n_e$ .

As an example, at  $T_g = 300 \text{ K}$ ,  $p = 3 \text{ torr}$  one must have at least  $n_e = 2.4 \cdot 10^{13} \text{ cm}^{-3}$  to hope for the vibrational kinetics, while at the same gas temperature and pressure = 60 torr, we must exceed  $n_e = 4.7 \cdot 10^{14} \text{ cm}^{-3}$ . The numerical results confirm these considerations.

Figure 2, in fact, shows the behaviour of  $k_d^s$  as a function of pressure ( $n_e = 10^{14} \text{ cm}^{-3}$ ,  $T_e = 10000 \text{ K}$ ,  $T_g = 300 \text{ K}$ ). One can note that the quasistationary  $k_d^s$  values decrease from approximately  $10^4 \text{ s}^{-1}$  to  $10^3 \text{ s}^{-1}$  by increasing the pressure from  $p = 3$  to

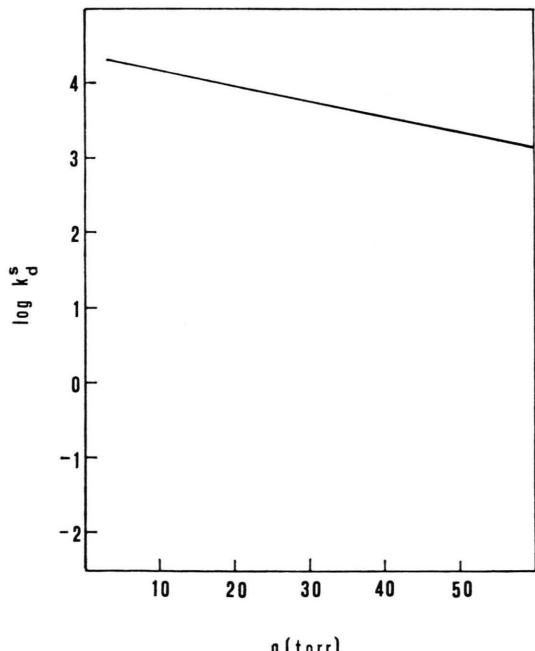


Fig. 2. Values of  $k_d^s$  ( $\text{s}^{-1}$ ) as a function of pressure (same conditions of Fig. 1).

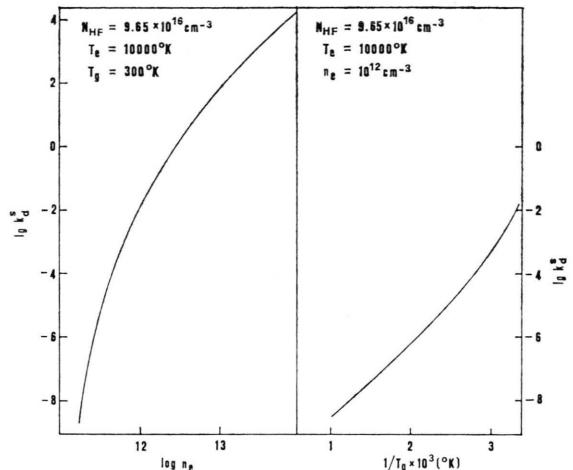


Fig. 3. a) Values of  $k_d^s$  as a function of  $n_e$  ( $\text{cm}^{-3}$ ) ( $p = 3$  torr,  $T_g = 300 \text{ K}$ );  
b) Values of  $k_d^s$  as a function of  $1/T_g$  ( $N_{HF}^0 \cong 10^{17} \text{ cm}^{-3}$ ,  $n_e = 10^{12} \text{ cm}^{-3}$ ).

60 torr, while the vibrational temperatures decrease from 4200 K to 2500 K.

Figure 3a shows the behaviour of  $k_d^s$  as a function of  $n_e$ , while Fig. 3b reports  $k_d^s$  values as a function of  $1/T_g$ .

The trend of  $k_d^s$  versus  $n_e$  can be understood on the qualitative considerations previously reported.

As for the dramatic decrease of  $k_d^s$  with increasing  $T_g$ , this is in line with our previous work [1]. It can be understood by recalling that the increase of  $T_g$  increases the reverse V-V processes, thereby destroying the V-V up mechanism discussed in References [1-2]. Figure 4 shows typical  $N_v$  distributions at different times for the conditions which, in the present work, yielded the largest  $k_d^s$  values. In the same figure we have also reported the atom concentration ( $\text{cm}^{-3}$ ) as a function of time. It should be noted that the  $N_v$  distribution does not present a Boltzmann tail for the conditions of Figure 4. This means that the V-V processes dominate the V-T ones, due to the large vibrational temperature obtained at  $n_e = 10^{14} \text{ cm}^{-3}$ ,  $T_g = 300 \text{ K}$  and  $p = 3 \text{ torr}$ . As for the atom production, we can see (Fig. 4) that our mechanism without recombination is able to dissociate all HF molecules in a time of the order of  $10^{-4} \text{ s}$ . It is worth noting that the atom concentration reaches a value of  $2.10^{15} \text{ cm}^{-3}$  at  $t = 10^{-6} \text{ s}$ , which is the characteristic time for pulsed discharges with  $n_e = 10^{14} \text{ cm}^{-3}$  (see for example Ref. [7]).

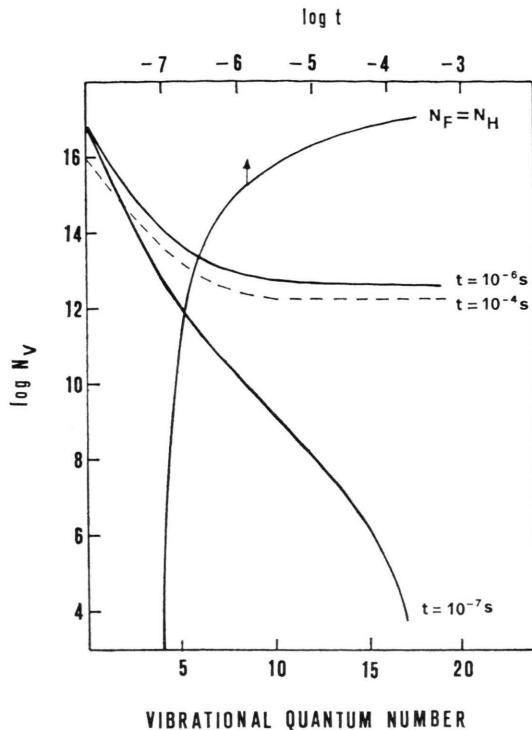


Fig. 4. Vibrational distribution  $N_v$  ( $\text{cm}^{-3}$ ) as a function of the vibrational quantum number at different times and atom concentration ( $\text{cm}^{-3}$ ) as a function of time (s) (same conditions of Figure 1).

A balance between the vibrational quanta introduced by e-V energy exchanges and the corresponding quanta lost by decay channels can be approximately written as follows [6]

$$n_e N_{v=0} K_{01}^e \cong n_e N_1 K_{10}^e + \sum_{i=\text{HF, H, F}} N_i \sum_{v=1}^{v'} N_v K_{v,v-1}^i + N_{\text{HF}} k_d^s D/E_{10}, \quad (12)$$

where the three terms at the right of Eq. (12) represent in that order the vibrational quanta lost by superelastic collisions (the reverse of process (8)), V-T deactivation and dissociation.

This last term destroys  $D/E_{10}$  quanta ( $D$  is the dissociation energy) for any reactive collision [6]. It should be noted that V-V terms do not appear in Eq. (12), since V-V collisions conserve vibrational quanta. Equation (12) applied to the  $N_v$  distribution of Fig. 4 shows that all three decay channels of Eq. (12) are important in destroying vibrational quanta.

#### 4. Comparison with the IR Laser Induced Process

The results reported in the present paper are very similar to those discussed by Kompa et al. [2], who studied the same mechanism induced by IR laser. These authors considered also the rotational structure of the first vibrational levels ( $v \leq 4$ ) of HF due to the coupling of these levels with the laser input.

To a first approximation we neglect the rotational structure and we consider the pumping rate  $0 - 1$  induced by the IR pulsed HF laser (duration 400 ns) used in Reference [2].

At the laser power  $W = 27 \cdot 10^6 \text{ W/cm}^2$ , we obtain a pumping rate

$$P_{01} \sim \sigma_{01} W_{01}/E_{10} \sim 3 \cdot 10^9 \text{ s}^{-1} \quad (13)$$

$(\sigma_{01} \sim 10^{-16} \text{ cm}^2, W_{01} \sim 10\% \text{ W}, E_{10} = 7.86 \cdot 10^{-20} \text{ joules}).$

This large pumping rate is able to overcome the vibrational deexcitation of process (10), thereby introducing vibrational quanta in the HF system. V-V processes will transport these quanta up to the dissociation limit.

The vibrational distributions obtained in Ref. [2] are very similar to those reported in the present work, while the dissociation constant calculated by Kompa et al. ( $p_{\text{HF}} = 60 \text{ torr}, W = 27 \cdot 10^6 \text{ W/cm}^2$ ) is several orders of magnitude larger than our  $k_d^s$  value obtained at the same pressure with  $n_e = 10^{14} \text{ cm}^{-3}$  ( $T_g = 300 \text{ K}$ ). This is due to the fact that the IR pumping rates used in Ref. [2] strongly exceed our e-V rates ( $n_e K_{01}^e \sim 10^6 \text{ s}^{-1}$  at  $n_e = 10^{14} \text{ cm}^{-3}, T_e = 10000 \text{ K}$ ).

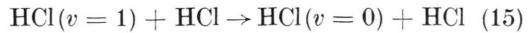
#### Conclusions

It should be interesting as a conclusion to predict how the present results can be extended to other similar systems.

Let us consider an HCl electrical discharge. In this case the e-V pumping rate of the process



has the same order of magnitude as the process (8), while the deactivation rate of the process



is several orders of magnitude smaller than process (10).

Apparently, therefore, one should expect that the production of H, Cl atoms by the pure vibrational mechanism could occur at electron number densities lower than those necessary for HF [8].

However, small quantities of H and Cl atoms strongly deactivate the vibrational content of HCl through the process [9]



selflimiting the atom production by the pure vibrational mechanism.

On the other hand, if the atoms come through other channels (direct electronic mechanism, dissociative attachment) the vibrational content of

HCl will be completely destroyed by process (16) which has a very large deactivation rate.

This means that, once again, the dissociation of HCl through a vibrational mechanism will occur only at very high electron densities, similar to those discussed for HF.

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