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

\[
\frac{\partial N_v}{\partial t} = \sum_{i=1}^{3} \left[ N_i \left( N_{v-1} K_{i,v-1,v}^{i} + N_{v+1} K_{i,v+1,v}^{i} - N_v (K_{i,v-1}^{i} + K_{i,v+1}^{i}) \right) \right]
\]

\[
+ \sum_{w=0}^{v'} n_e \left[ N_w K_{v,v}^{w,v} - N_v K_{v,v}^{w,v} \right]
\]

\[
+ N_{v+1} A_{v+1,v} - N_v A_{v,v-1}
\]

(\(A_{v,v-1}\) 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

\[
e + \text{HF}(v=0) \rightarrow \text{HF}^+ \rightarrow e + \text{HF}(v=1, 2)
\]  

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 \((K_{v=0}^{e} = 0, v \geq 2)\), 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

\[
N_v(t = 0) = 0 \quad \text{for} \quad v = 0,
\]

\[
N_v(t = 0) = N^0_{v,\text{HF}}, \quad v = 0,
\]

\[
N_H = N_F = 0
\]
ground and of the first vibrational level. Large \( \Theta_1 \) values can be obtained when the pumping rate \((n_eK_{e0})\) overcomes the most important V-T deactivation process (in this case \( N_{HF}K_{10}^{HF} \)). To obtain large \( \Theta_1 \) values, therefore, one must consider HF electrical discharges with electron densities \( n_e \) (cm\(^{-3}\)) obeying the inequality

\[
n_e > \frac{K_{10}^{HF}}{K_{e0}} N_{HF}\tag{11}
\]

Values of \((K_{10}^{HF}/K_{e0})N_{HF}\) 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 \( T_g = 300 \) K, \( p = 3 \) torr one must have at least \( n_e = 2.4 \cdot 10^{13} \) cm\(^{-3}\) to hope for the vibrational kinetics, while at the same gas temperature and pressure = 60 torr, we must exceed \( n_e = 4.7 \cdot 10^{14} \) cm\(^{-3}\). The numerical results confirm these considerations.

Figure 2, in fact, shows the behaviour of \( k_d^s \) as a function of pressure \((n_e = 10^{14} \) cm\(^{-3}\), \( T_e = 10000 \) K, \( T_g = 300 \) K). One can note that the quasistationary \( k_d^s \) values decrease from approximately \( 10^4 \) s\(^{-1}\) to \( 10^3 \) s\(^{-1}\) by increasing the pressure from \( p = 3 \) to 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 \( 1/T_g \) \((N_{HF} \approx 10^{17} \) cm\(^{-3}\), \( n_e = 10^{12} \) cm\(^{-3}\)).

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 (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 \( n_e = 10^{14} \) cm\(^{-3}\), \( T_g = 300 \) K and \( p = 3 \) 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 \( 10^{-4} \) s. It is worth noting that the atom concentration reaches a value of \( 2 \cdot 10^{15} \) cm\(^{-3}\) at \( t = 10^{-6} \) s, which is the characteristic time for pulsed discharges with \( n_e = 10^{14} \) cm\(^{-3}\) (see for example Ref. [7]).
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 ($\nu \leq 4$) 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 $0 \rightarrow 1$ induced by the IR pulsed HF laser (duration 400 ns) used in Reference [2].

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

$$P_{01} \sim \sigma_{01} \frac{W_{01}}{E_{10}} \sim 3 \times 10^9 \text{ s}^{-1}$$

($\sigma_{01} \sim 10^{-16}$ cm$^2$, $W_{01} \sim 10^6$ W, $E_{10} = 7.86 \times 10^{-20}$ joules).

This large pumping rate is able to overcome the vibrational deactivation 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. ($p_{HF} = 60$ torr, $W = 27 \times 10^6$ W/cm$^2$) is several orders of magnitude larger than our $k_{d}^a$ value obtained at the same pressure with $n_e = 10^{14}$ cm$^{-3}$ ($T_g = 300$ K). This is due to the fact that the IR pumping rates used in Ref. [2] strongly exceed our e-V rates ($n_e K_{01}^e \sim 10^6$ s$^{-1}$ at $n_e = 10^{14}$ cm$^{-3}$, $T_e = 10000$ 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

$$e + \text{HCl}(v = 0) \rightarrow e + \text{HCl}(v = 1)$$

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

$$\text{HCl}(v = 1) + \text{HCl} \rightarrow \text{HCl}(v = 0) + \text{HCl}$$

(15) 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]
\[ \text{HCl}(v = 1) + \text{H(Cl)} \rightarrow \text{HCl}(v = 0) + \text{H(Cl)}, \]  
(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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