PROGRESS IN THE KINETICS OF CHEMICAL REACTIONS IN NON-EQUILIBRIUM PLASMAS

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Abstract - The dissociation kinetics of diatomic species in non-equilibrium
plasmas is presented and discussed on the basis of three mechanisms: 1) the
direct electron impact mechanism (DEM); 2) the pure vibrational mechanism
(PVM); the joint vibroelectronic mechanism (JVE).
Calculated dissociation rates from PVM are in satisfactory agreement with
the experimental ones in N_2, while in CO the agreement with the experimen-
tal results is better achieved by the JVE rates.
The coupling between JVE and Boltzmann equation for the electron energy di-
stribution function is then discussed for H_2 and O_2. DEM plays an important
role in dissociating these molecule at high E/N, by determining in the pre-
sence of recombination process   a new dissociation mechanism, called a
recombination assisted dissociation process.
Finally the effect of vibrational non-equilibrium in the synthesis of NO
and on the dissociation of polyatomic molecules is discussed.

INTRODUCTION

Chemical reactions carried out under non-equilibrium plasmas are generally thought as occur-
ring through the action of the electrons, which either pump vibrational energy in the ground
electronic state of the molecules or promote electronic transitions to dissociative states of
the molecules. In general the first point has been overlooked by many authors although under
laboratory plasmas the energy input mainly occurs through the vibrational degree of freedom.
This point can be understood from fig. 1, which reports the fractional power input for N_2 and
CO as a function of E/N (E, electric field; N, total number density) obtained from calculated
electron energy distribution functions (Ref. 1). One can note that the power input goes essen-
tially through the vibrational excitation of the ground state, at least up to a given E/N va-
lue. This energy, under favorable conditions which will be discussed in the next pages, can
be utilized in chemical reactions.
In general, the input of vibrational energy generates vibrational temperatures of the ground
state higher than the translational temperature, thereby creating non-equilibrium conditions
(Refs. 2,3). Figure 2 shows such a situation for H_2 and D_2, while similar results can be found
for N_2 (Ref. 3)
The importance of the vibrational non-equilibrium conditions on chemical reactions has been
reported by different authors (Refs. 4,5), who pointed out the impossibility of explaining
chemical reactions (in particular dissociation) by means of a simple direct electronic impact
mechanism. Figure 3 reports such conclusions for N_2 (Ref. 4). The dashed line of this figure,
which represents the dissociation constant from a pure electronic mechanism, can not explain
the experimental data. Similar conclusions can be found for H_2 (Ref. 5).
As a result of all these considerations, many authors have developed theoretical models in
order to explain the importance of vibrational non-equilibrium on plasmachemistry reactions
(Refs. 6,8). The aim of this paper is to review these attempts, emphasizing the connections
between theory and experimental results.

THEORETICAL MODELS

Three models have been essentially developed in these last years to explain the dissociation
of diatomic molecules in electrical discharges:
1) the direct electron impact mechanism (DEM);
2) the pure vibrational mechanism (PVM);
3) the joint vibroelectronic mechanism (JVE).
According to DEM, the electrons of the discharge promote electronic transitions to dissocia-
tive states of diatomic molecules

$$e + A_2(v=o) \rightarrow e + A_2^* \rightarrow e + 2A \qquad (1)$$

with a first order dissociation constant defined as

$$n_e k_d^e(v=o) = n_e \int_o^\infty q_d(u) f_e(u) v(u) du \qquad (2)$$

where $q_d(u)$ is the dissociation cross section of process (1), $f_e(u)$ is the electron energy distribution function, $v(u)$ is the electron velocity and n_e is the electron density. To simplify the problem, many authors assumed a Maxwellian distribution function for $f_e(u)$ and considered the dissociation process as occurring only from the ground vibrational level of the diatomic molecule $(A_2(v=o))$.
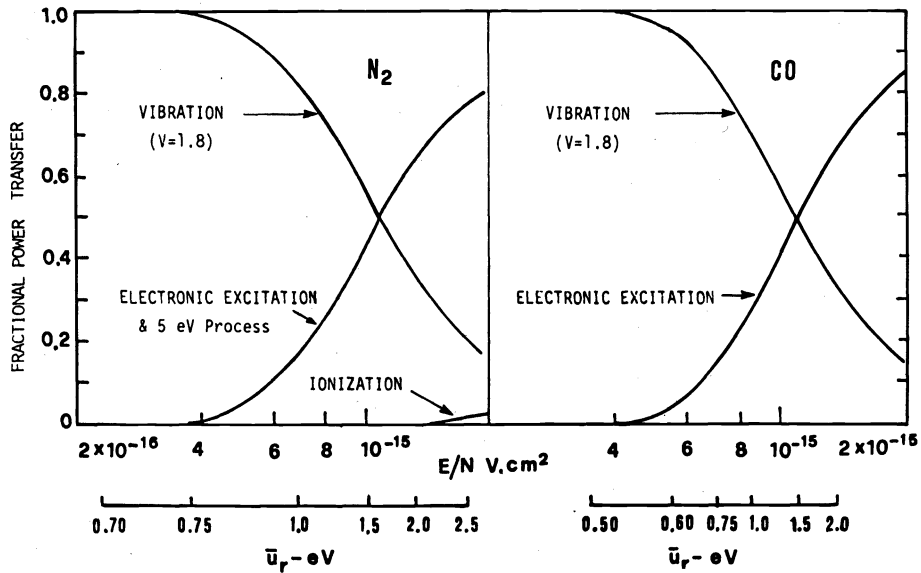

Fig. 1 Fractional power transfer as a function of E/N (and of the reduced energy $\bar{u}_r$) in N_2 and CO (From Ref. 1).
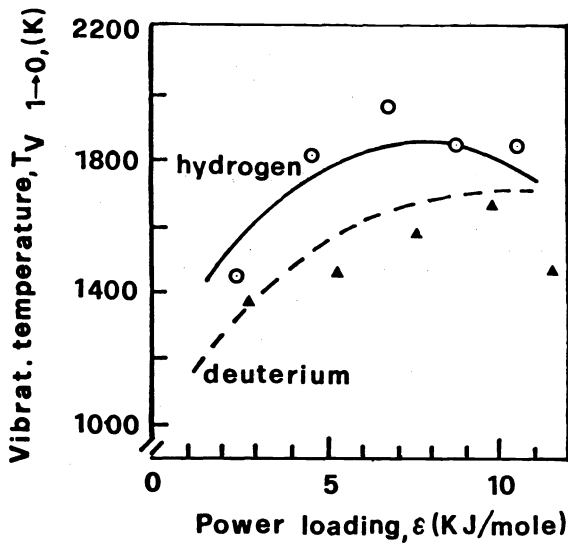

Fig. 2 Experimental vibrational temperature as a function of power loading in H_2 and D_2 plasmas (————— calculations for H_2; — — — — — calculations for D_2) (From Ref. 2).

The pure vibrational mechanism (PVM), on the contrary, considers the dissociation mechanism as a result of   three steps (see ref. 6):
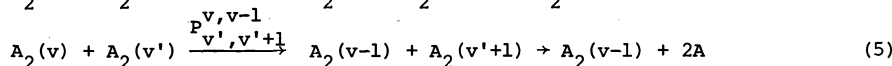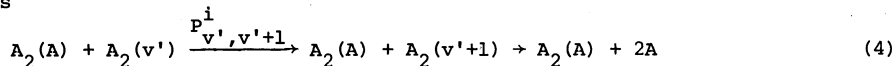i) the electrons introduce vibrational quanta in the diatomic molecule by means of e-V (electron-vibration) energy exchanges

$$e + A_2(v) \xrightarrow{k^e_{v,w}} e + A_2(w) \qquad (3)$$

ii) vibration-vibration (V-V) energy exchanges redistribute the introduced quanta on the whole vibrational manifold;
iii) vibration-translation (V-T) energy exchanges tend to relax the vibrational quanta over the first vibrational levels of the molecule.
As a result of various energy exchange process the vibrational quanta can reach the last vibrational level (v') of the diatomic molecule and then dissociate according to the following processes

$$A_2(A) + A_2(v') \xrightarrow{p^i_{v',v'+1}} A_2(A) + A_2(v'+1) \to A_2(A) + 2A \qquad (4)$$

$$A_2(v) + A_2(v') \xrightarrow{p^{v,v-1}_{v',v'+1}} A_2(v-1) + A_2(v'+1) \to A_2(v-1) + 2A \qquad (5)$$

The dissociation rate v_d can be written as

$$v_d = dN_{v'+1}/dt = N_{v'} \Sigma \ N_i p^i_{v',v'+1} + N_{v'} \Sigma N_v p^{v,v-1}_{v',v'+1} = k_d(t) \Sigma N_v \qquad (6)$$

where $N_{v'}$ represents the number density of level v' and N_i is the number density of species i (molecules and parent atoms). To calculate v_d one needs the vibrational distribution N_v, which in turn can be obtained by coupling eq.(6) with a system of v' vibrational master equations of the type

$$dN_v/dt = (dN_v/dt)_{e-V} + (dN_v/dt)_{V-V} + (dN_v/dt)_{V-T} + (dN_v/dt)_{se} + (dN_v/dt)_{rec} \qquad (7)$$

The different terms of eq.(7) represent in the order the vibrational relaxation rate due to electron-vibration (e-V), vibration-vibration (V-V), vibration-translation (V-T), spontaneous emission (se) and recombination (rec) process. Explicit expressions can be found elsewhere (ref.6). The possibility of a successful action of PVM in dissociating diatomic species in electrical discharges is linked to a 'crossing' of favorable conditions such as 1) large e-V rates 2) large V-V rates 3) small V-T rates. Points 1,2), in fact, determine a large pumping of vibrational quanta in the molecule and a successive redistribution of the introduced quanta on the vibrational ladder, while point 3) determines the conservation of the introduced quanta.
Table 1 shows the relevant rates for different systems. One notices that N_2 and CO represent the most promising molecules from the point of view of PVM. A problem arises at the onset of dissociation process, since the produced atoms are in general very effective in removing vibrational energy through V-T energy exchanges.

TABLE 1. V-V, V-T and e-V "effective" rates ($cm^3 s^{-1}$) in N_2, CO and O_2 systems (T_g = 500 °k, $\bar{u}_r$ ~ 1 e-V)

System	$p^{0,1}_{1,0}$	$p^{A2}_{1,0}$	$p^A_{1,0}$	$k^e_{o,v}$
N_2	$2.5 \ 10^{-13}$	$1.7 \ 10^{-21}$		~$1.5 \ 10^{-8}$
CO	$2.1 \ 10^{-12}$	$9.2 \ 10^{-19}$	$1.9 \ 10^{-13}$	~$1.5 \ 10^{-8}$
O_2	$6.3 \ 10^{-13}$	3.10^{-17}	$5.9 \ 10^{-17}$	~$1.2 \ 10^{-10}$

Finally in the joint vibroelectronic mechanism (JVE), the dissociation process occurs both through process (1) from all vibrational levels

$$e + A_2(v) \xrightarrow{k^e_d(v)} e + A^*_2 \to e + 2A \qquad (8)$$

and through the processes (4,5).
The dissociation rate can be now   written as

$$v_d = v_d(PVM) + n_e \sum_{v=o}^{v'} N_v k^e_d(v) = k_{dj}(t) \ N_v \qquad (9)$$

where $v_d(PVM)$ represents eq. (6)
Equation (9) is coupled with a system of vibrational master equations (see eq.(7)) which add a relaxation term due to the electron dissociation process

$$(dN_v/dt)_{e-D} = n_e N_v k^e_d(v) \qquad (10)$$

To obtain accurate values of dissociation rates in all mechanisms one must carefully know the electron energy distribution function (edf) which determine the electron rate coefficients (e-V and e-D rates). This point will be analyzed in the next pages.
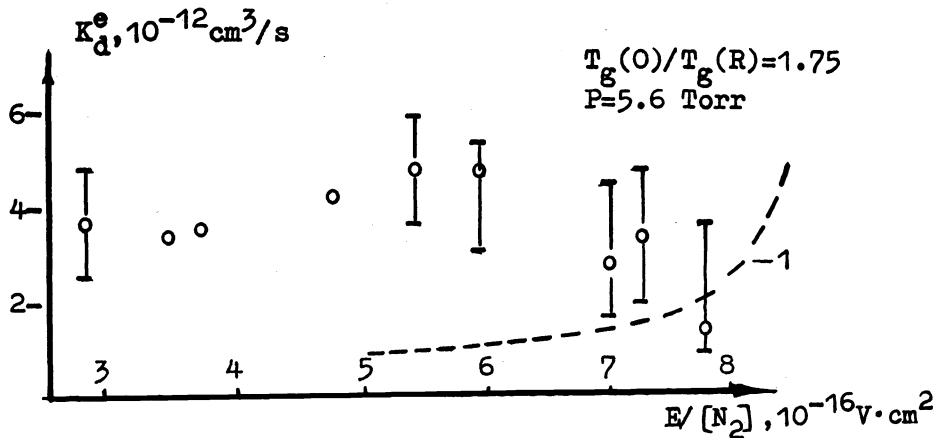
Fig. 3 Experimental dissociation constant as a function of E/N (---------
         calculations from DEM) (From Ref. 4).

RESULTS

Nitrogen
The nitrogen system presents the favorable conditions (large e-V and V-V and small V-T rates)
discussed in the previous pages. As a consequance PVM should be effective in dissociating N_2.
An attempt to model PVM for N_2 (ref. 9) gave the results reported in fig. 4. One can appre-
ciate that large dissociation rates are obtained in the gas temperature range $500 \leq T_g \leq 2000$ °K.
The non-equilibrium character of PVM can also be appreciated by comparing the quasistationary
k_d^s values with the corresponding ones obtained under thermal conditions ($n_e = 0$). In this last
case, in fact, k_d^s follows an Arrhenius type law with an activation energy approximately given
by the dissociation energy, while under the electrical conditions ($n_e \neq 0$) the activation
energy is approximately equal to zero. Figure 5 shows the corresponding N_v distributions ta-
ken from Ref. 9. One can appreciate the lack of the Boltzmann tails at T_g over the vibratio-
nal levels near to the continuum, thereby indicating that N_2 is a system in which V-T deacti-
vation can be neglected as compared with V-V pumping up. It should be however pointed out
that the results reported in Figs. 4,5 disregard the presence of nitrogen atoms, which can be
effective in removing vibrational energy. At the moment, however, vibrational relaxation ra-
tes of the process $N_2(v)-N$ are practically unknown.
Concerning the role of DEM in dissociating N_2, Fig. 4 shows that this mechanism yields disso-
ciation rates one order of magnitude smaller than the corresponding ones in PVM. Moreover it
can be shown that at lower electron energies DEM practically disappears.
A comparison between experimental results (Fig. 3 from Ref. 4) and theoretical values (Ref.9)
can be done by scaling the thoretical results by using the following equation

$$n_e \sum_v k_{0,v}^e v \quad = \quad k_d^s D/E_{1,0} \tag{11}$$

where D and $E_{1,0}$ is the dissociation energy and the energy of the first vibrational level re-
specitively. Equation (11) has been obtained under the hypothesis that the input of vibratio-
nal quanta by means of e-V energy exchanges is balanced by the corresponding loss through the
dissociation process. Equation (11) express a linear dependence of k_d^s on n_e and on the effec-
tive vibrational rate coefficients. By using this scaling law, one obtains that the theoreti-
cal values (Ref. 9) are one order of magnitude larger than the experimental values (Ref. 4).
This discrepancy however may be eliminated by improving the V-V rates used in Ref. 9. Recent
calculations performed by Billing (Ref. 10) have shown that the V-V rates of Ref. 9 are one
order of magnitude larger than the corresponding rates obtained by using semiclassical me-
thods. The use of the new set of V-V rates should bring an excellent agreement between theory
and experiments. It has been, in fact, shown (Ref.9) that decreasing by a factor 10 the V-V
rates one obtains approximately the same decrease in the dissociation constant.
An other possibility of explaining the discrepancy between theoretical values and experimen-
tal ones lies in the neglect of two quantum V-V transitions (Ref. 9). Their inclusion seem to
decrease by one order of magnitude the dissociation rate of N_2, as shown recently by Oraeskii
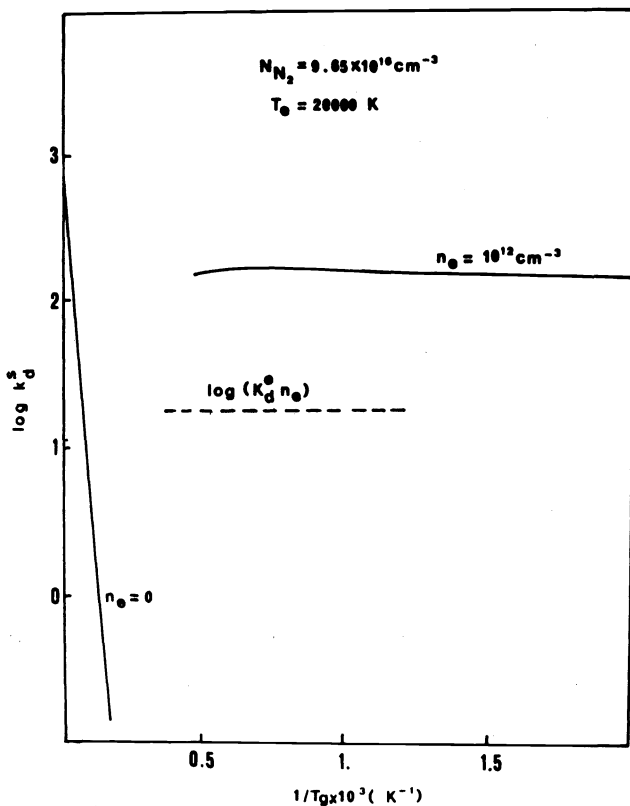et al (see Fig. 6 taken from Ref. 11).

Fig. 4 Quasistationary dissociation constant in N_2 as a function of $1/T_g$
(———— calculated values from PVM; —————— calculated values from
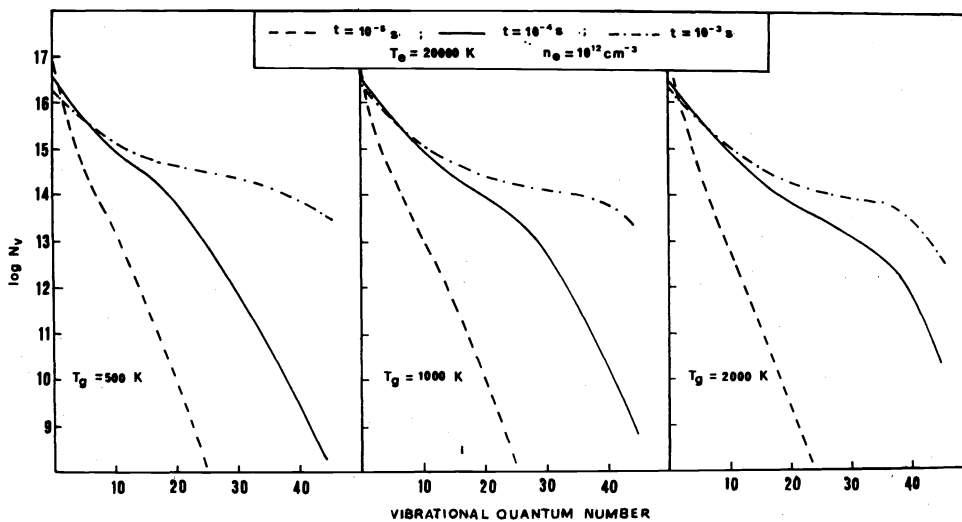DEM) (From Ref. 9).

Fig. 5 Vibrational N_v distributions as a function of vibrational number at
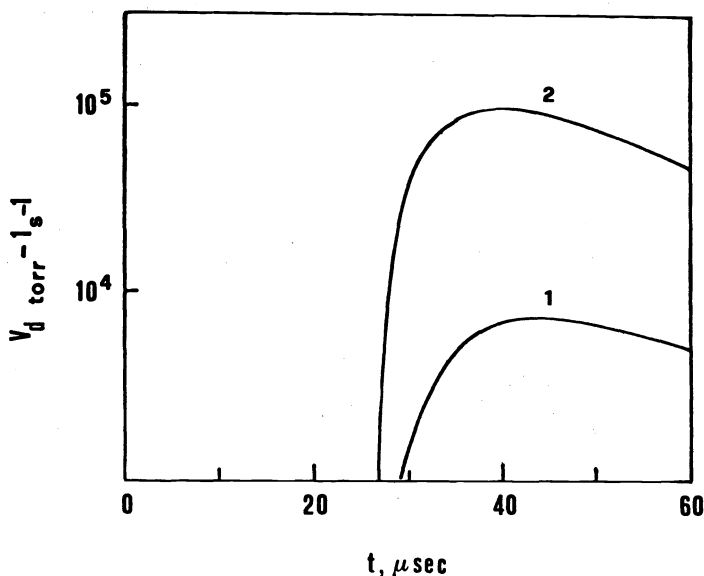different times calculated in PVM (From Ref. 9).

Fig. 6 Dissociation rate as a function of time in N_2 (curve 1: calcula-
tions taking into account two quantum V–V energy exchanges; cur-
ve 2: without two quantum V–V energy exchanges) (pump pulse ener-
gy 0.8 J/cm^3; T_g = 100 °K) (From Ref. 11).

Carbon Monoxide

Carbon monoxide will be illustrated as the second example which presents the 'crossing' of fa-
vorable conditions for dissociating according to PVM. This molecule in fact presents large
e–V and V–V and small V–T rates. On the contrary the CO(v)–O V–T rates are large, thereby in-
dicating a strong destruction of vibrational quanta at the onset of the dissociation process.
Figure 7 reports the dissociation constant and the degree of dissociation of CO calculated
according to PVM (Ref. 12) as a function of time, while Fig. 8 reports the N_v distributions
at different times. The method of calculation (Ref. 12) differs from that utilized for N_2
(Ref. 9), since in the CO case the influence of oxygen atoms on the N_v distributions and on
the dissociation constant has been taken into account. Moreover the gas temperature in the CO
case was allowed to change during the temporal evolution of N_v distributions. The results of
Figs. 7–8 are very similar to those presented for nitrogen. The dissociation constant evolves
toward a quasistationary value and then falls off to small values for the occurrence of oxy-
gen atoms and to the increase of gas temperature. The dissociation degree reaches a value of
0.1% under the conditions of Fig. 7. The N_v distributions present the usual form, being made
by three portions i) the Treanor's distribution ii) the plateau iii) the Boltzmann tail at T_g.
The results reported in Figs. 7–8 shows the possibility of PVM in dissociating CO in electri-
cal discharges. The experimental support for these calculations can be found on the dissocia-
tion rate measured by D'Amico and Smith (Ref. 13). These authors, in fact, found a characte-
ristic dissociation time of 30 s at a reduced energy of 0.5 eV and n_e = 10^{10} cm^{-3}. Dissocia-
tion by DEM in these conditions yields an approximate value of 10^4 s. An appropriate scaling
of the theoretical values reported in Fig. 7 to the experimental conditions, based on the
considerations reported for nitrogen, yields a characteristic time in good agreement with the
experimental one. This agreement does however appear optimistic, in view of 3% dissociation
under the experimental conditions (Ref. 13). The presence of oxygen atoms will deplete the
tails of N_v distributions, thereby the dissociation constant obtained in PVM will result lo-
wered. A more realistic model should make use of the joint vibroelectronic mechanism previou-
sly discussed. An approximate calculation based on a judicious estimate of $k_d^e(v)$ rates
yields a dissociation rate of JVE two orders of magnitude larger than $k_d^e(v=o)$, i.e. a charac-
teristic dissociation time of 100 s, to be compared with the experimental value of 30 s.
It should be furthermore pointed out that chemical dissociation channels such as

$$CO(v) + CO(v) \rightarrow C+O+CO(v') \qquad (12a)$$
$$CO(v) + CO(v) \rightarrow CO^*+CO(v') \qquad (12b)$$
$$CO^* + CO(v) \rightarrow CO_2+C \qquad (12c)$$
$$CO(v) + CO(v) \rightarrow CO_2+C \qquad (12d)$$

can be activated by the presence of vibrationally excited molecules (Refs. 12,14).
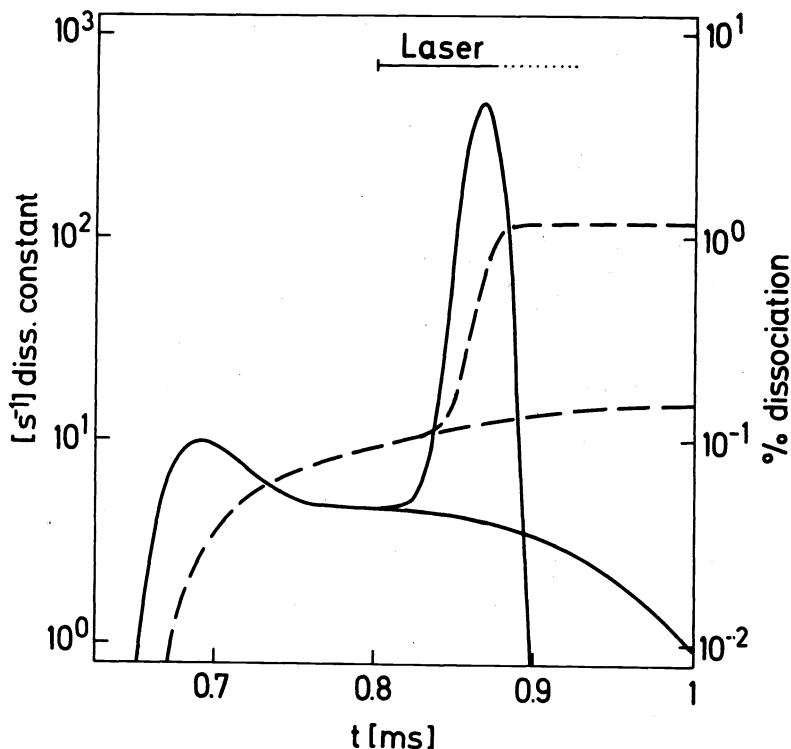
Fig. 7   Dissociation constant (full lines) and dissociation degree (dashed
         lines) as a function of time in CO electrical discharge with (up-
         per curves) and without (lower curves) the superposition of an IR
         pulsed CO laser ($n_e = 10^{12}$ cm^{-3}, E/N = $8 \cdot 10^{-16}$ V cm^2, $N_{CO} =$
         $= 10^{17}$ cm^{-3}) (From Ref. 12).

This last point is indirectly confirmed by the experiments of Rich and coworkers (Ref. 15)
who found dissociation of CO induced by an IR CO laser operating on several v → (v-1) transi-
tions. In this case the IR laser pumps vibrational quanta on the first vibrational levels of
CO and the V-V pumping up mechanism redistribute the vibrational quanta over the higher vibra-
tional levels. Figure 9, which reports the experimental N_v distributions measured by Rich and
coworkers, shows that only levels up to v=40 can be pumped by PVM and that the N_v distribu-
tions present Boltzmann tails at T_g. This means that under the experimental conditions (Ref.
15) a pure vibrational mechanism can not dissociate the CO molecule. The dissociation process,
monitored by the C_2 emission bands, may be explained by chemical reactions, activated by PVM
(see Refs. 12,14). The experimental N_v distributions reported in Fig. 9 are indeed very impor-
tant, showing the possibility for a diatomic molecule to reach very high vibrational levels.
An attempt to obtain the rate coefficient of reaction (12 d) was performed by Legasov et al.
(Ref. 16) under the following assumptions i) the cross sections for process (12 d) were cal-
culated within the framework of the bimolecular reaction statistical theory ii) a Treanor's
distribution was assumed to hold for the vibrational distribution. Under these assumptions,
Legasov et al. found the following equation for k_r:

$$k_r = k_o(T_g) \, (T_v/E_a)^2 \, (\omega_{CO}/\omega_{CO_2})^2 \exp(-h\omega_{CO}T_g/4x_e T_v^2) \qquad (13)$$

where $k_o(T_g)$ represents the elastic scattering rate constant which depends on the translatio-
nal temperature T_g, E=6eV is the reaction activation treshold, T_v is the vibrational tempera-
ture, x_e is the anharmonicity of CO and ω is the main frequency of vibration. Calculations of
k_r by means eq. (13) shows that the k_r values are larger than the corresponding thermal values
by several orders of magnitude.
Finally Figs. 7-8 also show the influence of a pulsed CO laser on the dissociation rate and
on the N_v distributions of CO prepared by an electrical discharge (Ref. 12). One can see that
the dissociation constant is increased by two orders of magnitude and the degree of dissocia-
tion by a factor 6 as compared with the corresponding values obtained without laser pulse.
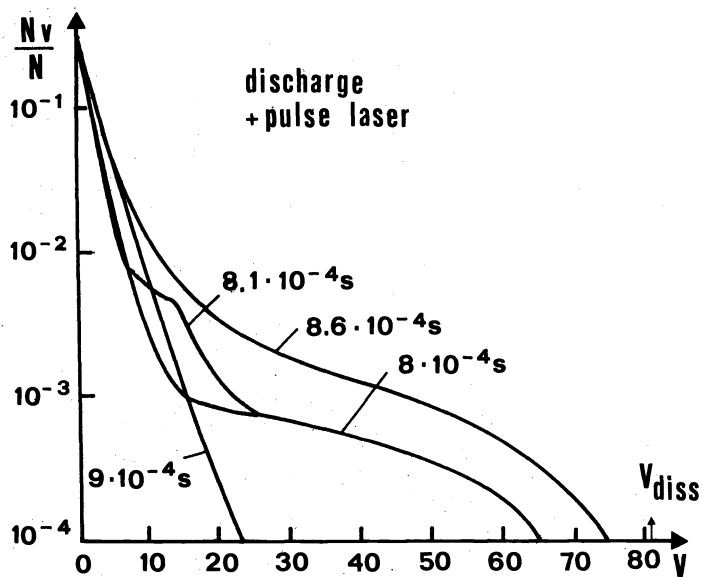
Fig. 8   Vibrational distribution as a function of vibrational quantum
         number at different times before, during and after the laser
         pulse in CO electrical discarges (same conditions of Fig. 7).
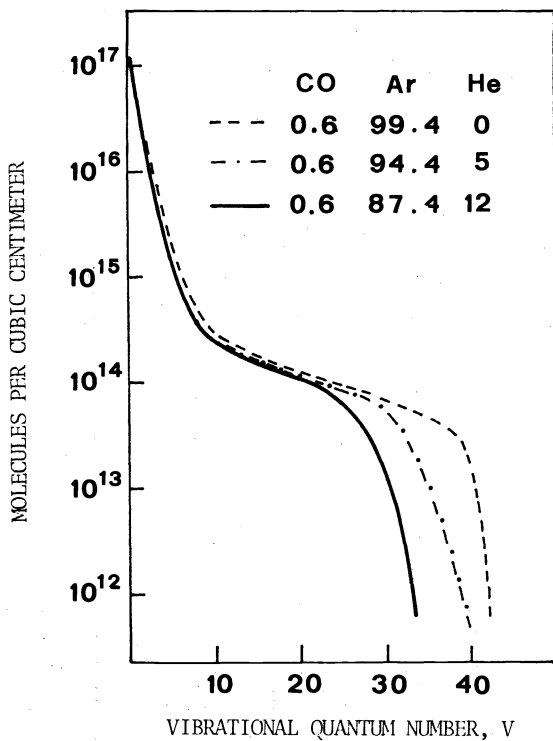
Fig. 9   Vibrational distribution N_V as a function of vibrational quantum
         number in cold CO induced by a cw CO laser in different mixtures.
         (From Ref. 15).

ELECTRON ENERGY DISTRIBUTION FUNCTIONS AND VIBRATIONAL KINETICS

In this section we want to present some examples showing the importance of coupling the vibrational kinetics (including the dissociation process) and the electron energy distribution function (edf). The electron energy distribution function, in fact, drastically changes in going from a cold molecular gas to a vibrationally excited molecular gas and finally to a gas essentially formed by parent atoms. This point can be appreciated in Fig. 10, where edf's for $H_2(v=o)$, $H_2(v)$ and $H_2(v=o)/H$ mixtures have been reported as a function of energy at different E/N values (Ref. 17). It can be shown that the electron energy distribution functions are completely different in the three cases. In particular the presence of vibrationally excited molecules and of parent atoms strongly increases the tail of edf as compared with the cold gas approximation.

In general one must expect a temporal evolution of edf during the temporal evolution of N_v and of the parent atoms. Three characteristic times need to be examined:

1) at t=o all molecules are in the ground vibrational level of the diatomic molecule. In this case the e-V and e-D rates must be calculated from edf in the cold gas approximation (Ref.17);

2) at times of the order of the electron vibration relaxation time $\tau_{e-V} = (n_e k^e_{1,0})^{-1}$ the molecular gas contains vibrationally excited molecules. The electron energy distribution functions must include the effect of superelastic vibrational collisions (Ref. 17);

3) at times of the order of the dissociation relaxation time $\tau_D = k_d^{-1}$ a fraction of molecules is dissociated in parent atoms. Edf now must include the presence of atoms and molecules.

Steps 1-3 can not in general be separated, so that one must solve the Boltzmann equation for edf coupled to the system of vibrational master equations (Ref. 18). The main aspects of this coupling will be illustrated for O_2 and H_2 in the next pages.
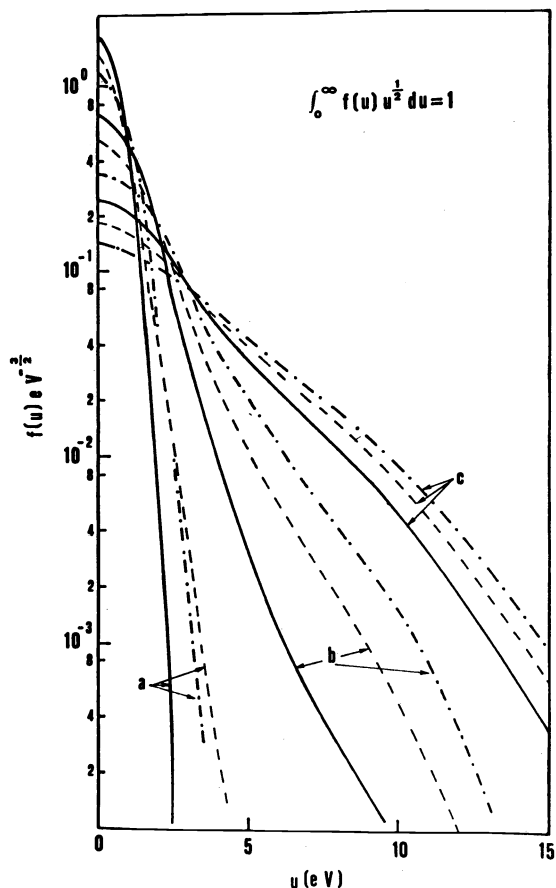

$$\int_0^\infty f(u) u^{\frac{1}{2}} du = 1$$

Fig. 10   Electron energy distribution functions as a function of energy at
          different E/N values in H_2 (———: cold molecular gas; - - -: vi-
          brationally excited molecular gas with T_v = 3500 °K; —·—·—: H_2/H
          1/1 mixtures) (a: E/N = 10^{-16} Vcm^2. B: E/N = $3 \cdot 10^{-16}$ Vcm^2; c: E/N=
          = $6 \cdot 10^{-16}$ Vcm^2) (From Ref. 17).

Oxygen

The characteristic features to be considered for the oxygen system are the following:

1) e-V pumping rates are small;
2) V-V rates overcome V-T ones in the molecular system;
3) Process $O_2(v)-O$ is very effective in removing vibrational energy by V-T transfer;
4) Dissociation via direct electron impact to both the A Σ_u^+ and the $B^3\Sigma_u^-$ excited electronic states is very effective.

In order to obtain a large contribution of vibrational levels to the dissociation rate one must choose electrical conditions which maximize e-V rates with respect to e-D ones (Refs. 19 20). These conditions occur at very small E/N values (E/N$\leqslant 10^{-16}$Vcm^2), as can be appreciated by looking at the fractional power transferred in the different degrees of freedom (Ref. 21). Figure 11 reports electron energy distribution functions selfconsistent with the N_v distributions of Fig. 11b (E/N = $0.8 \cdot 10^{-16}$ V cm^2). One can note that at times of the order of the electron vibration relaxation time the selfconsistent electron energy distribution functions, which include the effect of superelastic vibrational collisions, present tails one order of magnitude more populated than the corresponding ones at t = 0. This situation propagates particularly in the electron dissociation coefficients, as can be appreciated in Fig. 11c. $k_d^e(v=o)n_e$, which is the sum of the Herzberg and Schumann transitions, increases by a factor 2 by passing from t = o to t = τ_{e-v}. In this situation the other vibrational levels contribute to k_{dj}, which is two times larger than $k_d^e(v=o)n_e$. The strong decrease of both k_{dj} and $k_d^e(v=o)n_e$ for t>τ_{e-v} is due to the deactivating action of oxygen atoms, which tend to destrcy the vibrational energy content of the molecules. It should be noted that for E/N<$0.8 \cdot 10^{-16}$ Vcm^2 the differences between k_{dj} and $k_d^e(v=o)n_e$ tend to increase as a consequence of the smaller production of oxygen atoms (Ref. 18). Figure 12 reports such a case for E/N = $0.4 \cdot 10^{-16}$ Vcm^2. It is worth noting that for this condition, k_{dj} overcomes $k_d^e(v=o)n_e$ by a factor 5 and that the contribution of PVM is of the same order of magnitude as $k_d^e(v=o)n_e$.
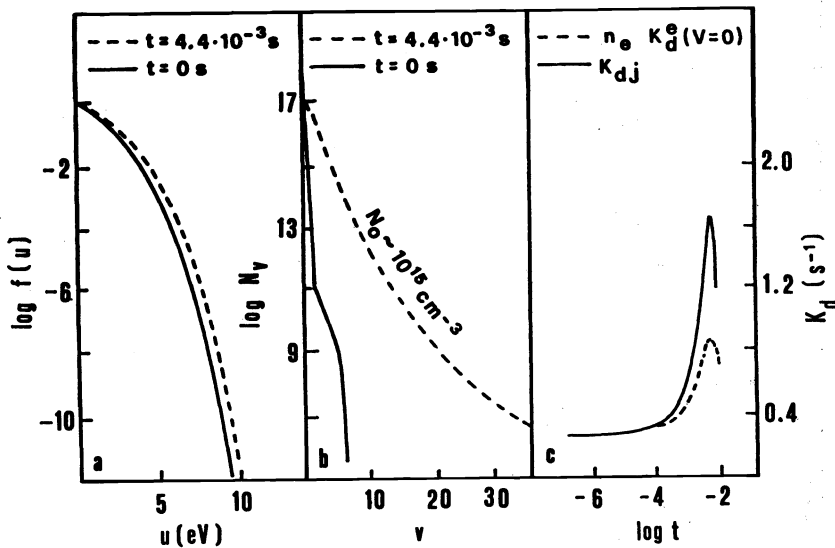

Fig. 11   a) Electron energy distribution function selfconsistent with the
          vibrational kinetics in O_2; b) vibrational distributions N_v as a
          function of vibrational quantum number at different times; c)dis-
          sociation constants as a function of time (E/N = $8 \cdot 10^{-17}$ Vcm^2,
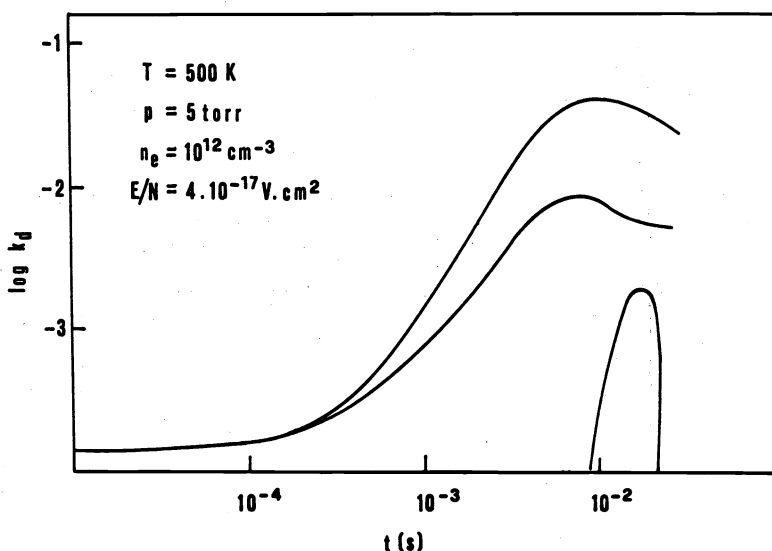 $n_e = 10^{12}$ cm^{-3}, $N_O = 10^{17}$, T_g = 500 °K).

Fig. 12   Dissociation constants (s^{-1}) as a function of time in O_2 (upper
curve: k_{di}; middle curve: $k_d^e(v=o)n_e$; lower curve: contribution
from PVM).

Let us now consider an E/N value greater than 10^{-16} Vcm^2, at which one should expect that the
production of oxygen atoms will be sufficient to completely deactivate the vibrational con-
tent of the molecules. Figure 12 gives the N_v distributions for E/N = $3 \cdot 10^{-16}$ Vcm^2. Apparen-
tly the N_v distributions look very similar to those reported for the other system. A most ac-
curate inspection, however, shows that the levels near to the ground vibrational level are
several orders of magnitude underpopulated as compared with the corresponding values of
Figs. 5,8,9,11. This means that the plateau present in Fig. 12 of vibrational levels exten-
ding from the continuum to the low lying vibrational levels has a nature completely dif-
ferent from those previously reported for CO, N_2 and O_2 at low E/N. In all these cases, in
fact, the plateau of vibrational levels is due to the prevailance of near resonant V-V energy
transfers (Ref. 6). The plateau of Fig. 12 is generated by the recombination process (Ref.
20), which feeds vibrational energy on the last vibrational level v' of O_2. This energy is
then redistributed on all other levels by the following cascade:

$$O + O + O_2(O) \rightarrow O_2(v') + O_2(O) \tag{14a}$$

$$O_2(v') + O_2(O) \rightarrow O_2(v'-1) + O_2(O) \tag{14b}$$

and so on. It can be shown (Ref. 20) that the population density of vibrational levels belon-
ging to the plateau changes in time as

$$N_v = (P^i_{v'+1,v'}/P^i_{v,v-1})N_O^2 \tag{15}$$

where N_O is the oxygen atom number density.
This plateau can redissociate leading to a recombination assisted dissociation process,
which increases the total dissociation rate. This last point can be appreciated in Fig. 14,
where the different contributions to the dissociation rate have been reported as a function
of time. One notices that the contribution of the recombination assisted dissociation pro-
cess (i.e. the reverse of process 14a) is approximately 20% of DEM from v=o, while the con-
tribution coming from DEM involving vibrationally excited levels is indeed very small.
The recombination assisted dissociation process can help to understand the O_2 dissociation
mechanism. Cramarossa et al. (Ref. 22) very recently performed an experimental determination
of the dissociation degree of O_2, under essentially the same electrical conditions reported
in Figs. 13,14. The experimental dissociation degree (Ref. 22) was reproduced by a first or-
der kinetc law, without considering the recombination process. Cramarossa et al. concluded
their analysis with the suggestion that the suppression of the recombination process could
be due to the recombination assisted dissociation process operating not only on the ground
electronic state but also on the metastable states near to the dissociation limit of O_2
Finally we want to point out that very recently Lawton and Phelps (Ref. 22) proposed to con-
sider the Schumann's transition (i.e. the state $B^3\Sigma_u^-$) as the only dissociation state of O_2.
This point does not change the qualitative conclusions reported in the present work. However
since in our calculations for E/N<10^{-16} Vcm^2 DEM for O_2 occurs mainly through the Herzberg
transition (i.e. the state $A^3\Sigma_u^+$), the conclusions of Lawton and Phelps should give more im-
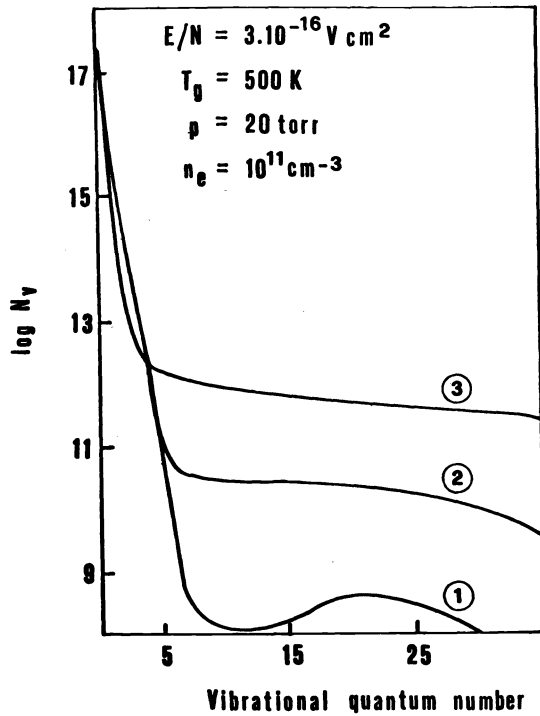portance to PVM for E/N<10^{-16} Vcm^2.

Fig. 13   Vibrational populations N_v as a function of vibrational quantum
number in O_2 (curve 1: t= $2 \cdot 10^{-4}$s, $N_O=2.5 \cdot 10^{15}$cm^{-3}; curve 2: t=
= $2.3 \cdot 10^{-3}$s, $N_O=3.3 \cdot 10^{16}$ cm^{-3}; t=$8.7 \cdot 10^{-3}$s, $N_O=2.7 \cdot 10^{17}$ cm^{-3}).
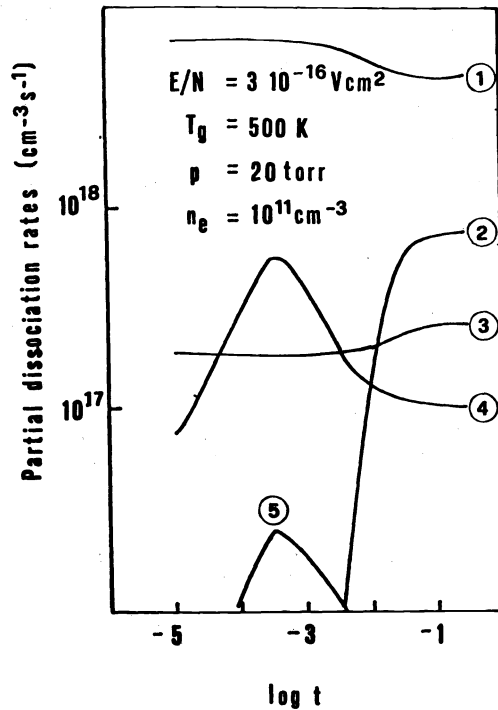

Fig. 14   Partial dissociation rates in O_2 as a function of time (curve 1:
$n_e N_{v=o} k_d^e(v=o)^H$; curve 2: $N_{v'} N_O P_{v'}^O,_{v'+1} + N_{v'} N_{O_2} P_{v',v'+1}^{O_2}$; curve 3:
$n_e N_{v=o} k_d^e(v=o)^S$; curve 4: $n_e N_{v=1} k_d^e(v=1)^H$; curve 5 : $n_e N_{v=1} k_d^e(v=1)^S$.
H = Herzberg transition; S = Schumann transition).

This point should confirm the validity of our previous work on PVM (Refs. 19,20). On the other hand, for $10^{-16}<E/N<10^{-15}$ Vcm^2 the presence of vibrationally excited molecules should affect JVE at least for short times (before the appearance of oxygen atoms). This last point can be understood in Fig. 15 where the partial dissociation rates for the same conditions of Fig. 14 have been reported as a function of time under the assumption that only the Schumann's transition is effective in dissociating oxygen. One notices that the results of Fig. 15 follow qualitatively those of Fig. 14, the only exception being represented by the increased importance of $v\neq o$ vibrational levels in affecting the dissociation rate.
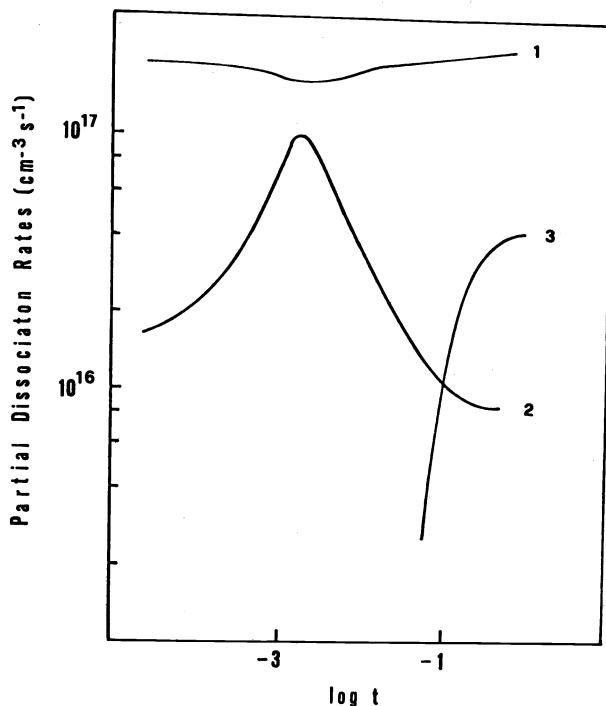

Fig. 15 Partial dissociation rates in O_2 as a function of time calculated by taking into account only the Schumann transition as electronic dissociation channel (curve 1: $n_e N_{v=o} k_d^e(v=o)^S$; curve 2: $n_e \sum_{v\neq o} N_v k_d^e(v)^S$; curve 3: $N_v, N_O P_{v',v'+1}^O + N_v, N_{O_2} P_{v',v'+1}^{O_2}$).

Hydrogen
The following points must be taken into account to understand the behaviour of this molecule:
1) e-V rates are between those of O_2 and N_2;
2) V-V rates overcome V-T ones in the molecular system at low gas temperature;
3) Process $H_2(v)$-H is very effective in removing vibrational energy by V-T energy transfer particularly at high temperature (Refs. 24,25);
4) Dissociation by DEM occurs at $E/N>2\cdot10^{-16}$ Vcm^2.
The effect of vibrational excitation on the dissociation rate may be therefore important at low T_g and E/N (Ref. 26). This point is shown   in Fig. 16, where the dissociation constant k_{dj} calculated in JVE has been compared with the corresponding $k_d^e(v=o)n_e$ value. One notices that at E/N = $3\cdot10^{-16}$ Vcm^2 k_{dj} is larger than $k_d^e(v=o)n_e$ by a factor 5, the differencesdo not exceed a factor 2 at E/N = $5\cdot10^{-16}$ Vcm^2. The values reported in Fig. 16 have been obtained by coupling edf and system of vibrational master equations including the processes of dissociation and recombination. The superelastic vibrational collisions affect the tails of edf thereby increasing the e-D rates, as can be appreciated in Fig. 16 by looking at the temporal evolution of $k_d^e(v=o)n_e$. The results reported in Fig. 16 show that vibrational excitation in H_2 can be achieved only for times shorter than the dissociation relaxation time.
In several cases, however, the residence time under laboratory plasmas is longer than τ_d. Moreover the gas temperature is greater than 300 $^\circ$K. As a consequence one should expect a strong influence of H-atoms on the vibrational content of H_2 molecules. These points can be seen in Fig. 17 a-c, where edf, vibrational populations and degree of dissociation have been reported as a function of electron energy, vibrational quantum number and time respectively. It is worth noting that edf progressively changes from the cold gas approximation to a mixture essentially made by hydrogen atoms. The N_v distributions are now populated by the recombination process as in O_2 at $E/N>10^{-16}$ Vcm^2.
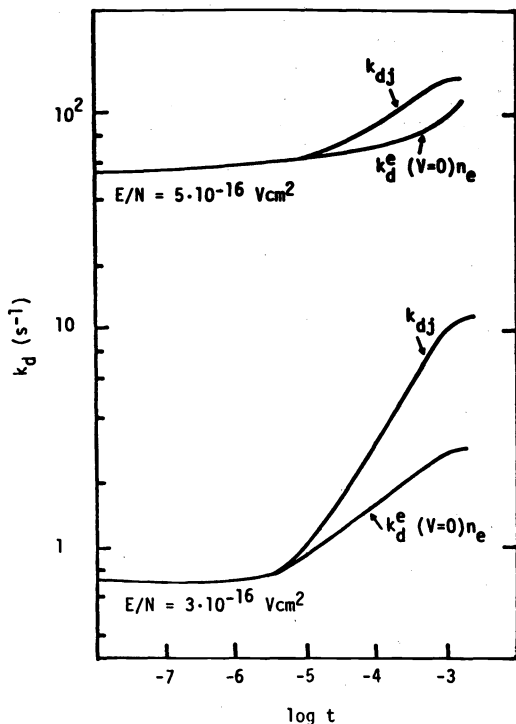
Fig. 16 Dissociation constants as a function of time for H_2 at two different E/N values (T_g = 300 °K, N_{H_2} = 10^{17} cm^{-3}, n_e = 10^{12} cm^{-3}).
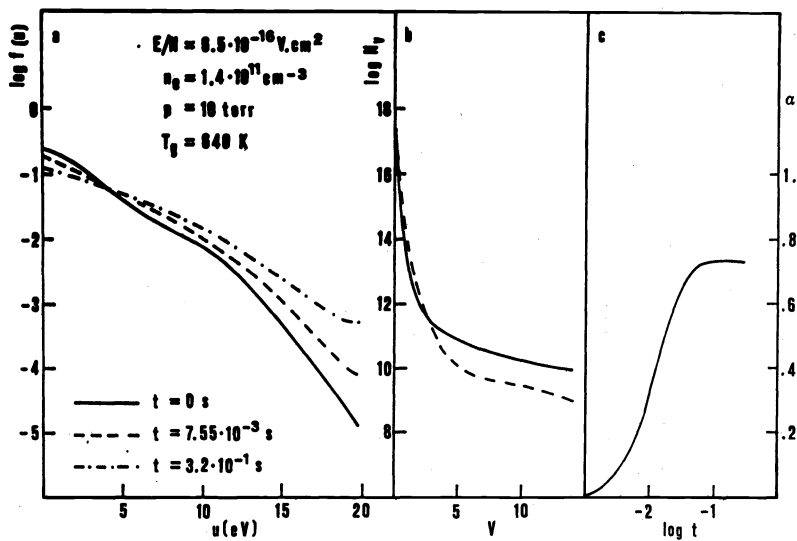

Fig. 17 a) Electron energy distribution functions selfconsistent with the vibrational distributions in H_2; b) vibrational distributions as a function of vibrational quantum number at different times (——— t=7.55·10^{-3}s; ----- t=3.2·10^{-1}s) dissociation degree of H_2 as a function of time.

Figure 18 reports the partial dissociation rates for the conditions of Fig. 16. One notices that $k_d^e(v=o)n_eN_{v=0}$ is the largest contribution to the total dissociation rate, the contribution coming from the excited vibrational levels being negligible. The recombination assisted dissociation process contributes up to 25%. It should be also noted that the dissociation constant $k_d^e(v=o)n_e$ increases by approximately a factor 4, passing from t=o to t=0.1s, following the temporal evolution of edf (see Fig. 19). This last point may be very important in explain; the experimental dissociation rates (Ref.5) (see also Ref. 17).
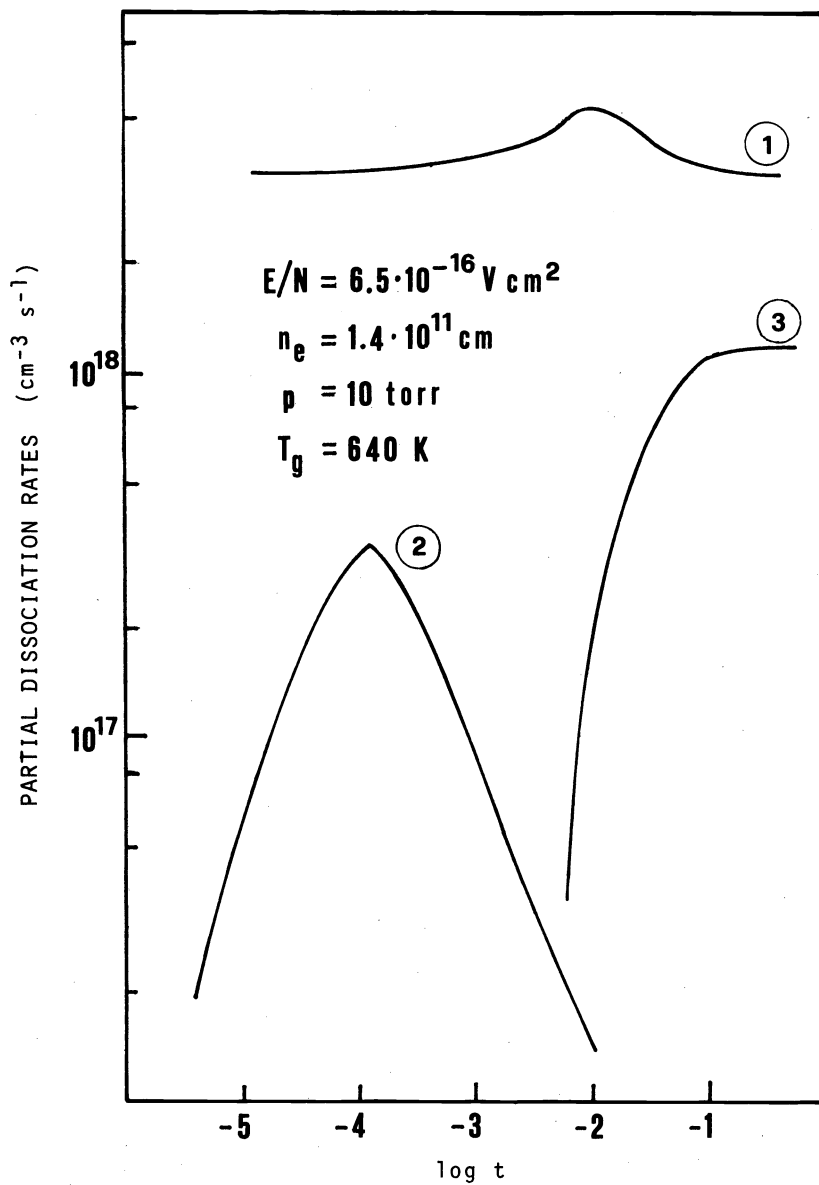

Fig. 18   Partial dissociation rates as a function of time in H_2 (curve 1:
$n_eN_{v=o}k_d^e(v=o)$; curve 2: $n_e\sum_{v\neq o}N_vk_d^e(v)$; curve 3: $N_{v'}N_HPH_{v',v'+1}^+$
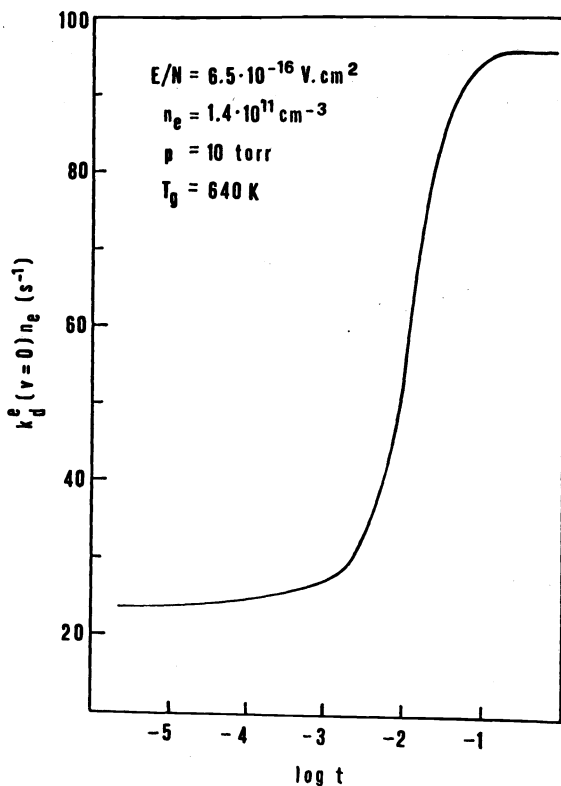$+N_{v'}N_{H_2}P_{v',v'+1}^{H_2}$

Fig. 19   Dissociation constant $k_d^e(v=o)$ as a function of time.

VIBRATIONAL EXCITATION AND CHEMICAL REACTIONS

The synthesis of NO

The role of vibrational excitation on the synthesis of NO from vibrationally excited N_2 and oxygen atoms

$$N_2(v) + O \rightarrow NO + N \qquad (16)$$

has been reported by Legasov et al. (Ref. 16). These authors, by making the same assumptions discussed for CO(v)-CO(v) chemical reactions, obtained the following rate coefficient for reaction (16)

$$k_r(T_v) = k_o(T_g) \rho (v=E_a/h\omega) (T_v/E_a) (1+T_g/T_v)^3 \exp(-E_a/T_v) \qquad (17)$$

where $\rho(v=E_a/h\omega)$ is the increase of the geometry cross section calculated at $v=E/h\omega$, E_a being the activation energy of process (16). Inspection of Eq. (17) shows that k_r at the vibrational temperature T_v is much larger than the corresponding value at T_g.

An other very simple expression for the rate coefficient of process (16) was found by Legasov et al. under the hypothesis that the loss of vibrational quanta by V-T energy exchanges can be neglected as compared with the corresponding loss by chemical reactions. In this case the reaction rate of process (16) can be written as

$$v_r = n_e N_{N_2} k_{o,v}^e h\omega/E_a \qquad (18)$$

where $k_{o,v}^e$ is an effective electron vibration rate coefficient.

It should be, however, noted that the neglect of V-T losses in the $N_2(v)$-O system is a poor approximation, since this process presents large deactivation rates (Ref. 27).

The best way of modelling the $N_2(v)$+O process is therefore to follow a master equation approach with the addition to eq. (7) of a relaxation term due to reaction (16). The V-T relaxation term should also include the $N_2(v)$-O term. The rate coefficients of process (16), calculated by Polak (Ref. 7), have been reported in Fig. 20 as a function of $1/T_g$. One notices the strong increase of the rate coefficient with increasing the vibrational quantum number. This means that, if a consistent population of vibrational levels can be achieved in an electrical discharge, the contribution of vibrationally excited molecules to process (16) can exceed the corresponding contribution from v=o. An experimental evidence of non-equilibrium

effects on the NO synthesis has been reported by Legasov et al. The close analogy between the process initiated by electrical discharges and the corresponding one induced by laser excitation can be found by looking at the experimental results quoted by Basov et al.(Ref.28).These authors in fact, excited directly the first vibrational level of N_2 by combinational Raman scattering from a Ruby laser. V-V pumping up then transported the vibrational quanta to vibrational levels able to react with cold O_2
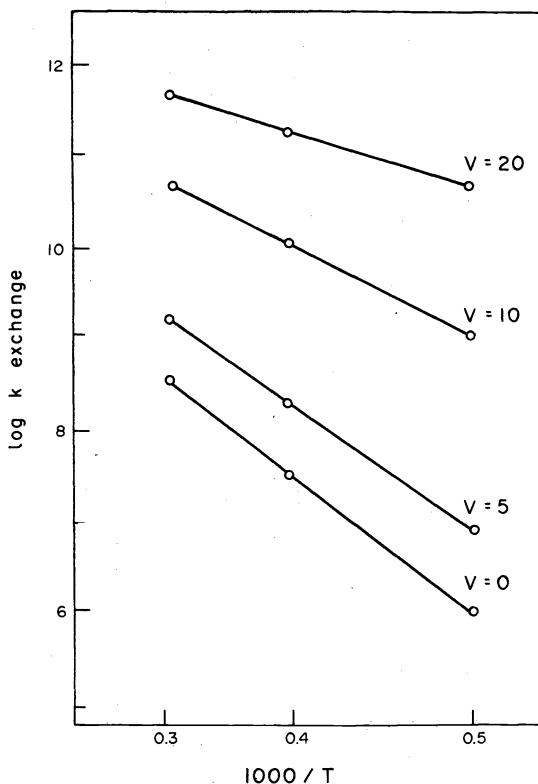

Fig. 20 Dissociation rates for the exchange reaction $N_2(v)+O \rightarrow NO+N$ as a function of 1/T for different vibrational levels (From Ref. 7).

Polyatomic molecules

The role of vibrational excitation in affecting chemical reactions involving polyatomic molecules is at the first stage of understanding. An experimental evidence of these effects has been reported by Capezzuto et al.(Ref.29) for the dissociation of CO_2 in electrical discharges. Figure 21 reports the ratio between calculated $k_d^e(v=o)n_e$ for DEM and the corresponding experimental value k_{exp}. One notices that a pure electronic mechanism can not represent the unique mechanism of dissociation. The contribution of DEM to the observed rates decreases with decreasing the reduced energy $\bar{u}_r$, becoming negligible at $\bar{u}_r=0.8eV$. In these conditions one can see that the fractional power input goes essentially in the vibrational degree of freedom (Ref. 1). Similar results have been reported by the same authors (Ref.30) in the cracking of hydrocarbons.

An attempt to model chemical reactions involving polyatomic molecules is under study in our laboratory. The model used is similar to that adopted by Lyman (Ref.31) for explaining the dissociation rate of polyatomic molecules induced by IR laser interaction in the collision regime. In our case the electrons have the same effect of IR laser in introducing vibrational quanta, which then can be used for the chemical reaction.

CONCLUDING REMARKS

The results reported in the previous pages have shown the importance of vibrational non-equilibrium conditions in affecting chemical reactions in electrical discharges.Many problems have been, however, overlooked in this review. Among them we mention the role of rotational non-equilibrium and the presence of metastable states in affecting chemical reactions.All these problems, which have been separately discussed by different authors, must be now inserted in a master equation formalism including vibrational non-equilibrium, rotational non-equilibrium, presence of atoms and of metastable species. The overal problem represents a formidable kinetic problem to be solved in the next years.
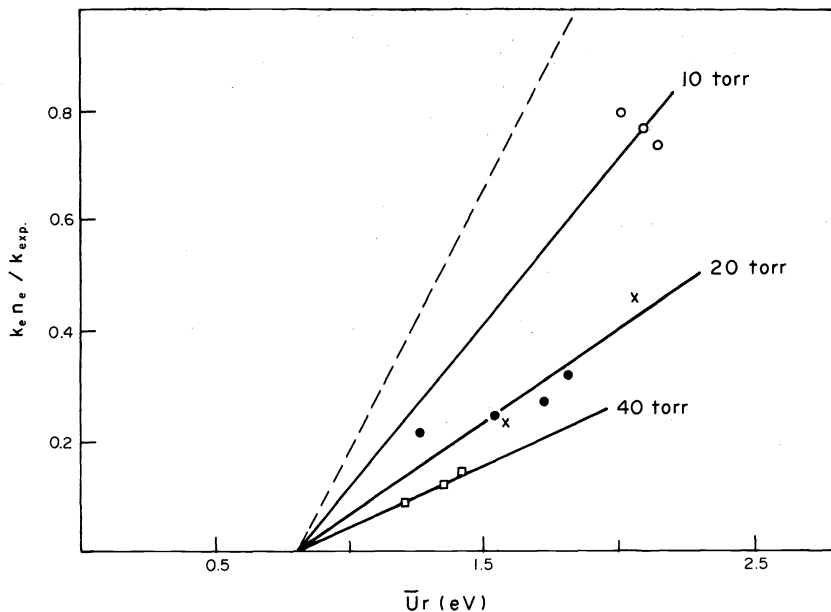
Fig. 21 Values of $k_e n_e/k_{exp}$ as a function of reduced energy at different
pressures in CO_2 (for the dashed line see Ref.29; $k_e n_e = k_d^e(v=o)n_e$).

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