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NON-EQUILIBRIUM DISSOCIATION OF NITROGEN

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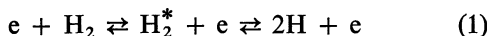
Résumé. — Les vitesses de dissociation de l'azote moléculaire ont été calculées en résolvant un système de *master* équations comprenant les transferts d'énergie V-V (vibration-vibration), V-T (vibration-translation) et e-V (électron-vibration).

Les résultats montrent que les vitesses de dissociation augmentent légèrement lorsque la température du gaz décroît dans l'intervalle de température 1 000-2 000 K pour une température des électrons $T_e = 20\,000$ K et pour une densité des électrons $n_e = 10^{12}$ cm $^{-3}$. Dans ce calcul nous avons montré que les vitesses de dissociation sont de deux ordres de grandeur plus élevées que celles obtenues par impact direct d'électrons.

Abstract. — Dissociation rates of molecular nitrogen in electrical discharges have been calculated by solving a system of master equations, including V-V (vibration-vibration), V-T (vibration-translation) and e-V (electron-vibration) energy transfers.

The results show that the dissociation rates slightly increase with decreasing gas temperature in the temperature range 1 000-2 000 K at the electron temperature $T_e = 20\,000$ K and electron density $n_e = 10^{12}$ cm $^{-3}$. In these calculations, dissociation rates are two orders of magnitude greater than the corresponding rates obtained by direct electron impact.

1. Introduction. — We have recently proposed a theoretical model to explain the high dissociation rates of molecular hydrogen in electrical discharges [1]. The model is based on a solution of the master equation for the populations of the vibrational states of the ground electronic state. Processes considered include vibration-vibration (V-V), vibration-translation (V-T) and electron-vibration (e-V) ⁽¹⁾ energy exchanges. In the case of molecular hydrogen, at low electron temperature ($kT_e \simeq$ leV), this model predicts dissociation rates greater than those obtained by direct electronic impact :



while at higher electron temperatures the two models predict dissociation rates of the same order of magnitude.

These rates were explained on the basis of an *anharmonic pumping* of higher vibrational levels by V-V and e-V energy transfers. The V-T processes, on the contrary, tend to depopulate the higher vibrational levels, thereby reducing the dissociation rates. The disso-

ciation rates were found to increase with decreasing gas temperature and pressure, due to the fact that both these parameters tend to increase the V-T energy exchanges. In this work we extend these calculations to pure nitrogen discharges. The choice of N₂ was motivated by the fact that the V-T rates of N₂-N₂ collisions are several orders of magnitude lower than

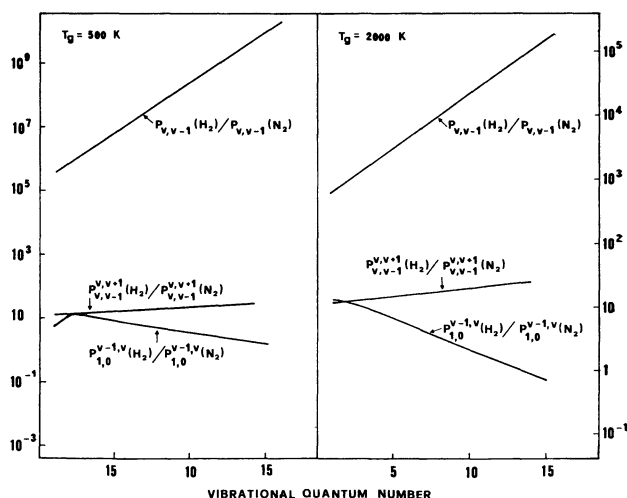


FIG. 1. — A comparison of V-V and V-T rate coefficients (non-dimensional) for H₂ and N₂ systems.

(1) The notation (e-V) should not be confused with the corresponding one indicating the transfer of electronic and vibrational energies.

The modified SSH theory [3, 4] has been used for calculating the V-T and V-V rate coefficients (cm^3/s), which appear in the form

$$P_{v,v-1} = Z_{11} P_{11} T_g [v/(1 - \delta v)] F(x_{v,v-1}) \quad (5a)$$

$$P_{v,v-1}^{w-1,w} = Z_{11} Q_{11} T_g [v/(1 - \delta v)] [w/(1 - \delta w)] F(y_{v,v-1}^{w-1,w}) \quad \text{for } w \leq v \quad (5b)$$

$$P_{v,v-1}^{w-1,w} = Z_{11} Q_{11} T_g [v/(1 - \delta v)] [w/(1 - \delta w)] F(y_{v,v-1}^{w-1,w}) \exp[(E_v + E_{w-1} - E_{v-1} - E_w)/kT_g] \quad \text{for } w > v \quad (5c)$$

$$x_{v,v-1} = (\frac{1}{2})^{3/2} (\theta'_{11}/T_g)^{1/2} (1 - 2\delta v)$$

$$y_{v,v-1}^{w-1,w} = 2\delta (\frac{1}{2})^{3/2} (\theta'_{11}/T_g)^{1/2} |v - w|$$

$$\theta'_{11} = 5.39 \times 10^6 \text{ K}$$

where Z_{11} is the $\text{N}_2\text{-N}_2$ collision frequency calculated on the basis of a collision diameter $\sigma = 3.75 \text{ \AA}$ (see ref. [2]).

The P_{11} values have been obtained by matching the equations to the experimental correlation data [5].

$$(p\tau)_{v-T} (\text{N}_2 - \text{N}_2) = 5.7 \times 10^{-12} \exp(234.9 T_g^{-1/3}) \text{ atm.s} \quad (6)$$

while the Q_{11} ones have been obtained by calculating $P_{0,1}^{1,0}$ by means of equation (22) of reference [6].

Figure 2 reports some of the calculated V-T and V-V rate coefficients.

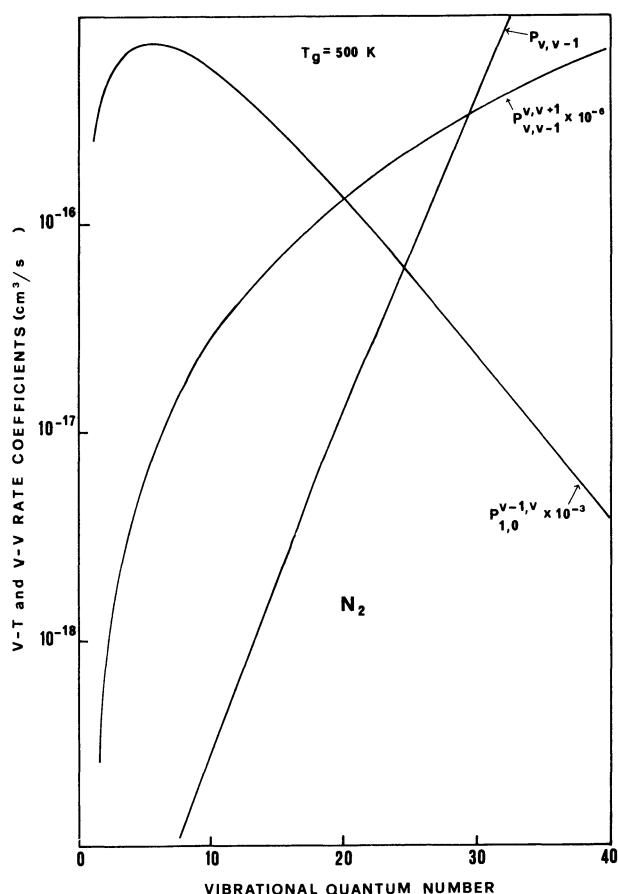


FIG. 2. — Rate coefficients for V-T and V-V processes (cm^3/s) as a function of vibrational quantum number for N_2 .

The e-V rate coefficients have been obtained by numerical integration of the experimental O-v ($v \leq 8$) cross sections [7] over a Maxwellian distribution function for the electrons, while those for h-v transitions ($h > 0$) have been assumed equal to the corresponding O-v transitions (i.e. $K_{0,1}^e = K_{1,2}^e = K_{2,3}^e$ and so on). Values of $K_{0,1}^e$ and of

$$\left(\sum_{i=1}^8 K_{0,i}^e \right)$$

have been reported in table I. The system of differential equations (2-3) written in vector form as

$$\delta \mathbf{n} / \delta t = \mathbf{f}(\mathbf{n}) \quad (7a)$$

has been integrated with the following numerical algorithm [8]

$$\mathbf{n}(t+h) = \mathbf{n}(t) + \left(\mathbf{I} - \frac{1}{2} h \mathbf{J} + \frac{1}{12} h^2 \mathbf{J}^2 \right)^{-1} h \mathbf{f}(\mathbf{n}(t)) \quad (7b)$$

where \mathbf{I} is the identity matrix, \mathbf{J} is the jacobian of the system calculated at time t and h is the step size.

TABLE I

Rate coefficients (cm^3/s) for e-V processes

T_e (K)	$K_{0,1}^e$	$\sum_{i=1}^8 K_{0,i}^e$	K_{eff}^e (a)	K_{eff}^e (b)
10 000	1.7 (—9) *	6.1 (—9)	1.3 (—8)	1.1 (—8)
20 000	2.4 (—9)	8.8 (—9)	2.6 (—8)	2.2 (—8)

* $1.7(-9) = 1.7 \times 10^{-9}$.

(a) Present results.

(b) Reference [16].

Most of the results have been obtained by imposing at $t = 0$ the following initial condition :

$$\begin{aligned} N_v(t=0) &= 0 \quad \text{for } v > 0 \\ N_0(t=0) &= N_{\text{N}_2} \end{aligned} \quad (8)$$

3. **Results.** — After a transient period, which is approximately given by $(n_e K_{0,1}^s)^{-1}$, $k_d(t)$ settles to a constant value k_d^s , the so called steady state dissociation constant (see Fig. 3). A true steady state disso-

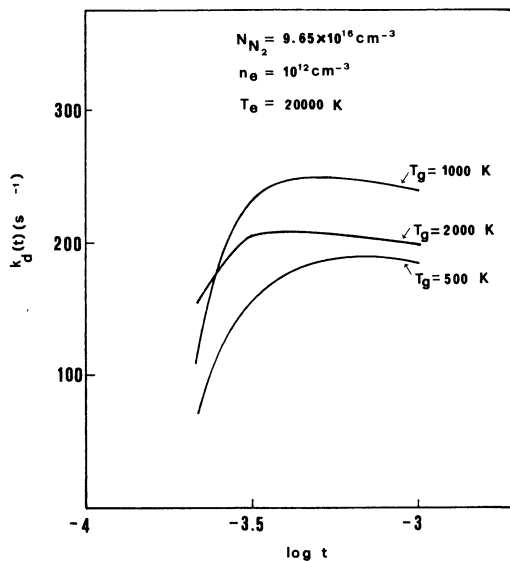


FIG. 3. — Temporal evolution of $k_d(t)$.

ciation constant cannot be achieved in our model because one neglects the recombination process and this yields $k_d(t = \infty) = 0$. The k_d^s values reported in the present work are therefore those corresponding to plateaus or maxima of $k_d(t)$ plots⁽³⁾.

Values of $\log k_d^s$ have been reported in figure 4 as a function of $1/T_g$ for $n_e = 10^{12} \text{ cm}^{-3}$ and $T_e = 20\,000 \text{ K}$. In the same figure we have also reported the values for $n_e = 0$.

It should be noted that the behaviour of k_d^s in the thermal conditions ($n_e = 0$) is completely different from that occurring in the discharges ($n_e \neq 0$).

For thermal conditions the dissociation constant strongly decreases with decreasing gas temperature. An activation energy of 250 kcal/mole is obtained in this case, which is 10 % higher than the nitrogen dissociation energy. A satisfactory agreement is found between theoretical and experimental k_d^s values [9, 10], as can be appreciated from table II. It should be noted that our results are always lower than the experimental ones. An increase of the theoretical dissociation rate is however expected when one considers the rotational and electronic degrees of freedom of diatomic molecule. This inclusion, for example, enhances the theoretical dissociation constant of oxygen in thermal conditions by a factor 9 at $T_g = 4\,500 \text{ K}$ [11].

(3) The k_d^s values reported in this work correspond to a pseudo-first order kinetic equation (see Eq. (2)), even though, due to the prevalence of V-V processes, a second order coefficient would be more revealing. We prefer, however, to keep the definition of equation 2 by analogy with the H_2 system of ref. [1].

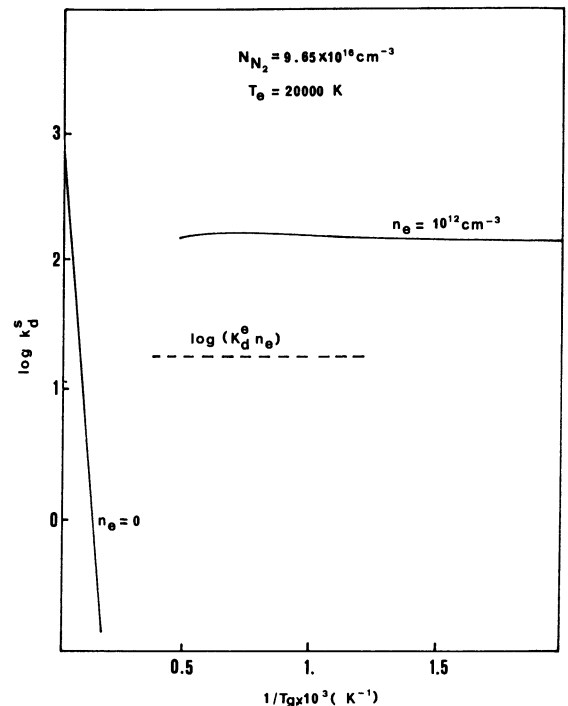


FIG. 4. — Values of $\log k_d^s$ and of $\log(k_d^s n_e)$ as a function of $1/T_g$.

TABLE II

A comparison between theoretical and experimental values of k_d^s (cc/mole.s) for thermal conditions ($n_e = 0$)

T_g (K)	k_d^s (a)	k_d^s (b)	k_d^s (c)
6 000	1.0 (+ 6) *	8.8 (+ 7)	3.5 (+ 6)
10 000	4.5 (+ 9)	2.8 (+ 10)	1.8 (+ 10)

* 1.0(+ 6) = 1.0×10^6 .

(a) Present results.

(b) Reference [9].

(c) Reference [10].

In the electrical conditions ($n_e = 10^{12} \text{ cm}^{-3}$) the dissociation constant slightly increases with decreasing gas temperature, yielding an apparent negative activation energy ($1\,000 \leq T_g \leq 2\,000 \text{ K}$).

To understand these results, we have reported in figure 5 the N_v distributions at different gas temperatures. It should be noted that these distributions are very similar, even though the population densities of higher vibrational levels ($v > 30$), which are responsible of the dissociation rate, decrease with increasing gas temperature. This is due : i) to the fact that the V-T processes, which tend to depopulate the higher vibrational levels, increase their importance with increasing gas temperature ; ii) the forward V-V processes, at low gas temperature, present rate coefficients much larger than the reverse ones, due to the fact that the Boltzmann factor which relates for-

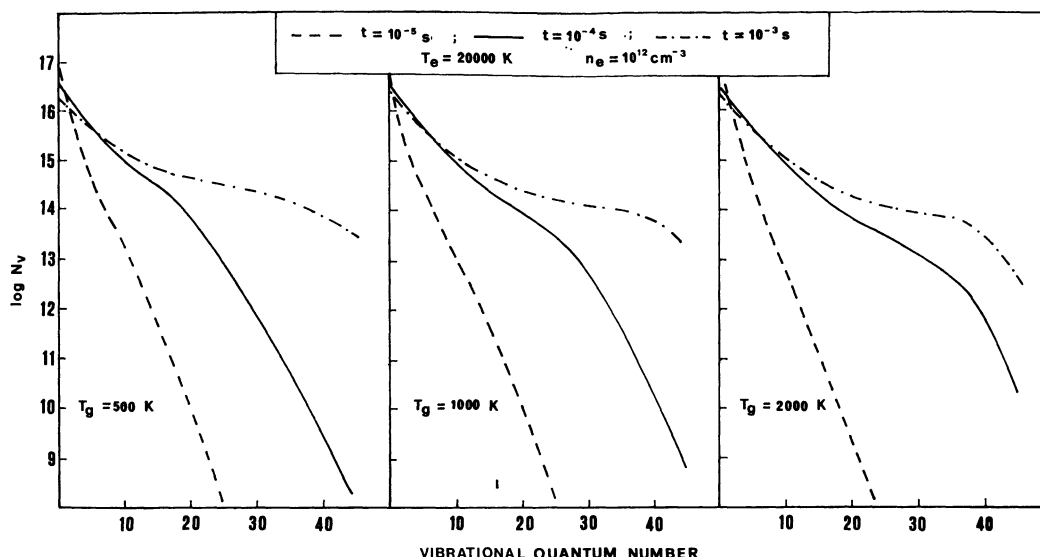


FIG. 5. — Population densities ($\log N_v$) as a function of vibrational quantum number at different times.

ward and reverse rate coefficients is small at low gas temperature. This last point is made clear by writing the ratio between forward and backward rate coefficients for the near resonant V-V processes :

$$P_{v,v-1}^{v,v+1}/P_{v-1,v}^{v+1,v} = \exp(2 E_{10} \delta/kT_g).$$

Point i) can be understood by looking at table III, where the V-T and V-V contributions to v_d have been reported at different T_g . One can note that the V-T

TABLE III

Values of the terms $N_{N_2} N_v P_{v',v'+1}$ ($\text{cm}^{-3} \text{s}^{-1}$)
(a) and

$$\sum_{v=1}^{v'} N_v P_{v,v-1}^{v',v'+1} N_{v'} \quad (\text{cm}^{-3} \text{s}^{-1}) \quad (b)$$

of equation (2) at different gas temperatures
($N_{N_2} = 9.65 \times 10^{16} \text{ cm}^{-3}$)

T_g (K)	a	b
500	1.8 (16)	1.6 (19)
1 000	6.1 (17)	1.8 (19)
2 000	6.0 (18)	1.3 (19)

$$1.8(16) = 1.8 \times 10^{16}.$$

processes are not important at $T_g = 500$ K, while their importance strongly increases at 2 000 K. It should be noted that at $T_g = 500$ K the dissociation constant is slightly less than the corresponding values at $T_g = 1 000, 2 000$ K, since the low temperature increase of N_v populations of higher vibrational levels is compensated by the corresponding increase of the rate coefficients appearing in equation (2).

Figure 6 shows the influence of pressure on k_d^s at $n_e = 10^{12} \text{ cm}^{-3}$. The behaviour of k_d^s with pressure as given in figure 6 is completely different from that

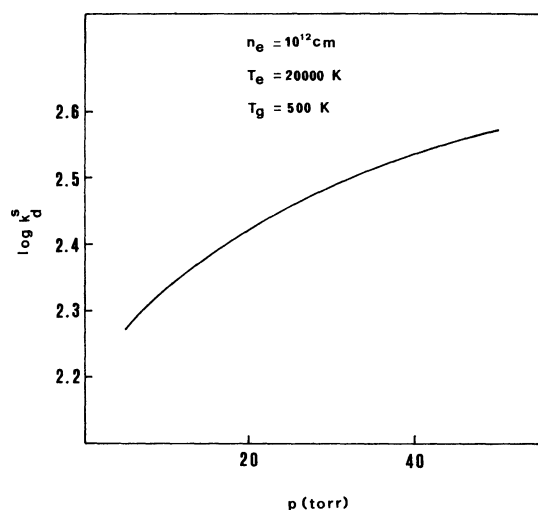


FIG. 6. — Values of $\log k_d^s$ as a function of pressure (torr).

found for H_2 , where k_d^s strongly decreased with increasing pressure. The present results can be attributed to the small importance of V-T exchanges in affecting the N_v distribution at $T_g = 500$ K. It should be pointed out that at 50 torr and $T_g = 500$ K the term $N_{N_2} N_v P_{v',v'+1}$ is small as compared to

$$\sum_{v=1}^{v'} P_{v,v-1}^{v',v'+1} N_v N_{v'}.$$

This last term increases with pressure, leading to an increase in the dissociation rate. The small increase of k_d^s with pressure (Fig. 6) is due to the fact that at n_e constant the pumping rate for molecule at 5 torr

is smaller than the corresponding one at 50 torr. A linear increase of k_d^s with pressure is then expected at $p/n_e = \text{constant}$. This is confirmed in table IVa where k_d^s is reported as a function of n_e at $p = 50$ torr. It should be noted that k_d^s (50 torr, $n_e = 10^{13} \text{ cm}^{-3}$) is about 10 times greater than the corresponding value at 5 torr and $n_e = 10^{12} \text{ cm}^{-3}$. Table IVb reports k_d^s values as a function of temperature. The increase of k_d^s with T_e ($T_e < 20\,000 \text{ K}$) is due to the increase of e-V rate coefficients with T_e (see table I).

TABLE IVa

Values of k_d^s (s^{-1}) as a function of electron density n_e (cm^{-3}) ($T_e = 20\,000$, $T_g = 500 \text{ K}$)

p (torr)	n_e	k_d^s
50	10^{12}	370.0
50	10^{13}	1 830.0
5	10^{12}	186.0

TABLE IVb

Values of k_d^s (s^{-1}) as a function of electron temperature (K) ($n_e = 10^{12} \text{ cm}^{-3}$, $T_g = 500 \text{ K}$, $p = 5$ torr)

T_e	k_d^s
10 000	46.0
20 000	186.0

The present results can be compared with similar models proposed in the literature by Caledonia and Center [12] and by Gordiets *et al.* [13]. According to the first authors, the non-equilibrium vibrational population of diatomic species is made up of three ranges: 1) the first controlled by a Treanor distribution [14] at a given vibrational temperature

$$\theta_1 = E_{10}/k \ln(N_0/N_1);$$

2) a plateau region in which the V-V near resonance processes dominate the distribution;

3) a deactivation region in which the N_v distribution follows a Boltzmann law at the gas temperature.

The onset of this deactivation region occurs at a vibrational quantum number v^* given by [12]

$$\frac{P_{v^*,v^*-1}}{P_{1,2}^{1,0} v^*} \simeq \frac{v_1 N_{v_1}}{N_{M_2}} \exp(-2 E_{10} \delta/kT_g) \quad (9)$$

where N_1 is the population density corresponding to the minimum of the Treanor distribution

$$v_1 = T_g/(2 \delta \theta_1) + 0.5. \quad (10)$$

Values of v^* and v_1 , calculated by means of equations (9) and (10) with the aid of θ_1 and N_{v_1} values taken from the numerical calculation at the maxima of k_d^s , have been reported in table V at different T_g .

TABLE V

Values of the vibrational quantum numbers v_1 (see Eq. (10)) v^* (see Eq. (9)) and v^{**} (see Eq. (11e)) at different T_g ($n_e = 10^{12} \text{ cm}^{-3}$, $N_{N_2} = 9.65 \times 10^{16} \text{ cm}^{-3}$, $T_e = 20\,000 \text{ K}$)

T_g (K)	θ_1 (K)	v_1	v^*	v^{**}	$\delta_{VT}^{(a)}$	$\delta_{VV}^{(a)}$
500	$\sim 7\,630$	~ 6	> 45	~ 69	0.311	0.296
2 000	$\sim 8\,200$	~ 20	> 45	~ 57	0.159	0.144

^(a) See text.

One can note that v^* is always greater than the last bound level of nitrogen molecule ($v' = 45$). As a consequence the Caledonia and Center criterion should not predict Boltzmann tails in the nitrogen system under the conditions studied in the present work, in agreement with our calculations.

The small tails ($v > 40$) present in our calculations do not follow a Boltzmann law at T_g and are probably due to the dissociation reaction which is not considered in the Caledonia and Center model.

The Gordiets *et al.* approach gives the following formulas for calculating the normalized population density of vibrational levels under non-equilibrium conditions.

$$f(v) = f(0) \exp \{ -v | E_1/\theta_1 - (v-1) \Delta E/T_g | \} \quad v < v_1 \quad (11a)$$

$$f(v) = \frac{C}{v+1} - \frac{P_{1,0} \exp(\delta_{VT} v)}{P_{1,0}^{0,1} \times \delta_{VT}(v+1)} \quad v_1 \leq v \leq v^{**} \quad (11b)$$

where E_1 and ΔE are our E_{10} and δ values expressed in K, δ_{VT} and δ_{VV} which enters in x are parameters appearing in the V-T and V-V rate constants, while C and x can be calculated from the equations reported in [13]. Values of δ_{VT} and δ_{VV} , which have been reported for some cases in table V, have been obtained by

matching our formulas (Eqs. (5)) with the corresponding ones used by Gordiets *et al.* (see Eqs. (2-3) of ref. [13]). Values of v^{**} (see [13]) for $T_g = 500 \text{ K}$ and $2\,000 \text{ K}$ have been reported in table V. Once again one can note that these values are greater than the last bound level of the nitrogen molecule, in agree-

ment with the Caledonia and Center criterion and with our calculations. A good agreement (see table VI) is observed up to vibrational levels far from dissociation ($v \leq 30$), while differences up to a factor of 100 can be noted above this level. It should be noted that Gordiets formulas for $k_d(\theta_1)$ cannot be used in the present calculations, because of $v^{**} > v'$.

TABLE VI

A comparison of the normalized population densities calculated by the Gordiets et al. method (see Eqs. (11a-b)) and the corresponding values calculated in the present work ($N_{N_2} = 9.65 \times 10^{16} \text{ cm}^{-3}$, $T_e = 20\,000 \text{ K}$, $n_e = 10^{12} \text{ cm}^{-3}$)

v	$f(v)$ ^(a)	$f(v)$ ^(b)
0	0.276	0.339
5	0.043	0.053
10	1.0 (– 2)	1.4 (– 2)
20	2.0 (– 3)	3.0 (– 3)
35	7.1 (– 4)	1.7 (– 3)
45	4.8 (– 5)	1.2 (– 3)

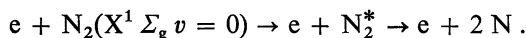
^(a) Present work.

^(b) Equations (11a-b).

1.0(– 2) = 1.0×10^{-2} .

It is interesting to compare the present k_d^s values with the corresponding values for the direct electronic mechanism from the ground vibrational level

$$(k_d^e(v=0) = k_d^e)$$



The k_d^e values, obtained by numerical integration of the experimental cross sections of Winters [15] over a Maxwellian distribution function for the electrons, are presented in figure 4. One can note that the present k_d^s values are always greater than the corresponding $k_d^e n_e$ (s^{-1}) values. It should be pointed out that the use of a Maxwellian distribution function for calculating k_d^e is a poor approximation, because the values of the actual distribution function strongly deviate from the Maxwellian in the energy range important for the calculation of k_d^e (i.e. $u > 10 \text{ eV}$, see Fig. 4 of Ref. [16]).

These deviations should increase k_d^s , since the Maxwellian assumption underestimates the tail of the distribution function (see Ref. [16]). Another factor which should increase k_d^s is the insertion of the higher vibrational levels in the direct electronic mechanism. Due to the lack of informations on the relevant cross sections, the following scaling law has been used to test the sensitivity of k_d^e on the higher vibrational levels

$$k_d^s(v) = k_d^s(v=0) (v+1). \quad (12)$$

The corresponding $\overline{k_d^e}$ values have been obtained by averaging the different contributions with the known vibrational distribution according to

$$\overline{k_d^e} = \sum_{v=0}^{v'} N_v k_d^e(v) / N_{N_2}. \quad (13)$$

With this assumption $\overline{k_d^e}$ has been found to be 6 times greater than the corresponding $k_d^e(v=0)$ value ($n_e = 10^{12} \text{ cm}^{-3}$, $T_e = 20\,000 \text{ K}$, $T_g = 500 \text{ K}$, $p = 5 \text{ torr}$).

4. Accuracy of the results. — The accuracy of the present results will be discussed in connection with the different assumptions made in the calculation.

In particular :

1) The use of SSH theory for calculating V-T and V-V rate coefficients, which, despite its wide use, is known to be a poor approximation (see for ex. [17]).

2) The extension of these cross sections, as well as those of e-V processes, to the continuum.

3) The use of a Maxwellian distribution function for calculating the rate coefficients of electron vibrational processes.

4) The neglect of the recombination process as well as the influence of atoms on the dissociation constant.

5) The number of vibrational levels considered in the present study.

The computer program has been successfully tested by comparing our results with the corresponding ones found by Polak [18].

To investigate the sensitivity of the present values to the V-T and V-V rate coefficients, we have varied some of the calculations ($T_e = 20\,000 \text{ K}$, $T_g = 500 \text{ K}$, $n_e = 10^{12} \text{ cm}^{-3}$, $p = 5 \text{ torr}$) i) by increasing by a factor 10 all V-T cross sections ; ii) by decreasing by the same factor all V-V cross sections. The response of N_v and k_d^s to this change can be appreciated from figure 7 and table VII. It should be noted that the results are completely insensitive to the variation in the V-T cross sections, while the corresponding V-V change affects proportionally the results.

This behaviour can be explained by the fact that the N_2 system, as already pointed out, practically does not present tails in the N_v distribution, due to the small importance of V-T cross sections. A factor 10 of change in these cross sections does not modify the situation, while a similar change in the V-V cross sections directly affects $P_{v,v-1}^{v',v'+1}$ appearing in equation (2) without appreciably altering the N_v distribution (see Fig. 7). It is evident, however, that at $T_g = 2\,000 \text{ K}$ the V-T cross sections are important in affecting the N_v distribution. The use of SSH cross sections for calculating the rate coefficients connecting bound states and the continuum (point 2), which is usually done in this kind of calculations, can be

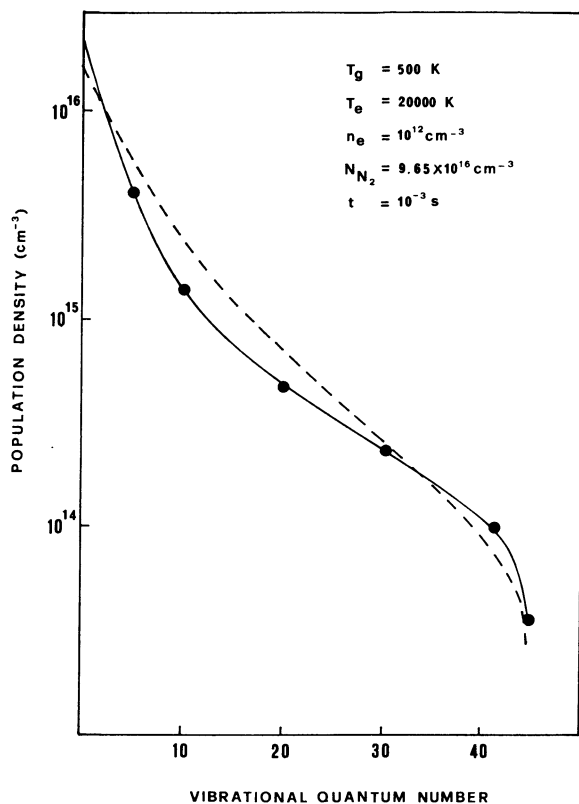


FIG. 7. — N_v distributions calculated with different assumptions (— normal V-T and V-V rate coefficients; --- V-V/10; ● V-T $\times 10$).

TABLE VII

Values of k_d^s (s^{-1}) obtained under different assumptions on V-V and V-T cross sections ($T_g = 500 \text{ K}$, $T_e = 20\,000 \text{ K}$, $N_{N_2} = 9.65 \times 10^{16} \text{ cm}^{-3}$, $n_e = 10^{12} \text{ cm}^{-3}$)

(a)	(b)	(c)
186.0	180.0	15.0

(a) Present results.

(b) V-T rate coefficients increased by a factor 10.

(c) V-V rate coefficients decreased by a factor 10.

only justified by the lack of information on these cross sections (especially for V-V transitions).

As for point 3, one can say that in the actual discharge conditions the electron distribution function in N_2 strongly deviates from a Maxwellian one especially for energies greater than 4 eV (see Fig. 4 of ref. [16]). At the lower energies which are important in the calculation of e-V rate coefficients, the ratio between the actual distribution function and the Maxwellian one presents an oscillatory behaviour. As a consequence one should expect a compensation in the e-V rate coefficients calculated by using Maxwell and non-Maxwell distribution functions due to the integrated nature of these coefficients.

This can be indirectly appreciated by comparing the *effective* electron vibrational excitation rates calculated by Nighan and the corresponding quantities calculated assuming a Maxwellian distribution function (see table I). It should be noted however that the superelastic collisions can alter the electron distribution function especially at high vibrational temperatures (see Fig. 5 of [16]). An estimation of the relevant energy decay channels (V-T deactivation, superelastic collisions, dissociation) based on equations (12), (22) of ref. [13] shows that the superelastic collisions and the dissociation reaction are the most important energy loss mechanisms for the conditions studied in the present work. This means that a portion of the pumping energy is returned to the electrons *via* superelastic collisions, thereby indicating that a self consistent computation of dissociation rates can be achieved only by coupling the Boltzmann equation for the electron distribution function to the system of vibrational master equations. This coupling is outside the scope of the present work and we will not pursue it any longer in the present paper.

As for the neglect of the recombination process (point 4) in our master equation, this can be justified by the fact that $k_d(t)$ achieves its stationary value when the concentration of dissociated molecules does not exceed 10%. It should be pointed out, however, that for times greater than 10^{-3} s the recombination process strongly affects both the dissociation constant of nitrogen and the $k_d(t)$ values.

The number of vibrational levels considered in the present work should not affect the dissociation constant k_d^s especially in the electrical conditions ($n_e \neq 0$). In these conditions in fact the lack of a true Boltzmann tail ensures small variations in the population densities of last vibrational levels. The addition of some levels, therefore, does not appreciably modify k_d^s .

5. Conclusions. — The results reported show that high dissociation rates can be predicted on the basis of a ladder climbing model of the vibrational levels of ground electronic state of diatomic species.

The accuracy of the present results depends on the set of V-T, V-V and e-V cross sections as well as on the different hypothesis made in the calculation (see points 1-5 of section 4). Moreover the inclusion of rotational processes as well as the multiple quantum transfers in heavy particles collisions should improve the present model.

The fact that the V-T deactivation in the nitrogen system can be neglected means that the dissociation is approximately balanced by the net pumping rate from electrons. From this it follows that our calculated rates can be only as accurate as the pumping rates utilized. These last quantities, however, depend on the superelastic collisions which alter the electron distribution function (and the pumping rates) as already pointed out in section 5.

As for the comparison between the present mechanism and the direct one, we can say that the present results indicate our $k_d^s > k_d^e n_e$, even though some assumptions (Maxwellian distribution function, neglect of the direct dissociation mechanism from the higher vibrational levels) could underestimate $k_d^e n_e$, while some cross sections (i.e. the V-V ones) could overestimate our k_d^s values.

Despite these uncertainties, however, we believe that the present mechanism must be taken into account in the dissociation of nitrogen either for its own importance as discussed in the previous pages, or for preparing the higher vibrational levels of the ground

electronic state to jump to dissociative electronic states. The present results, therefore, must be considered as a first step toward the understanding of the nitrogen dissociation in electrical discharges.

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