

ELECTRON DIATOMIC MOLECULE WEIGHTED TOTAL CROSS SECTION CALCULATION

I. PRINCIPLES FOR CALCULATION

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Received 17 July 1979

Revised 23 January 1980

We propose a method to calculate total cross sections in inelastic collisions between electrons and diatomic molecules for the excitation, ionization and dissociation processes. Calculations take into account the relative populations of the vibrational–rotational levels belonging to the initial configuration and the internuclear distance. Analytical expressions for elementary cross sections between real levels are those proposed by Drawin [1] and Gryzinski [2].

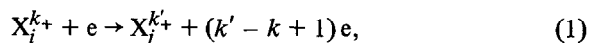
1. Introduction

We consider a target gas composed of diatomic molecules characterized by the same electronic energy term T_1 and by different vibrational and rotational quantum numbers v and J . A monokinetic electron beam interacts with this target. Our purpose is the calculation of a cross section which allows the determination of the number of molecules which after collision are in a different potential energy state. Two possibilities are considered in this paper:

i) The electron energy term after collision is $T_2 \neq T_1$ and the molecular potential energy corresponds to a stable molecular state. Such a collision process leads to an excitation or an ionization.

ii) Potential energy after collision corresponds to an unstable molecular state: collisions cause a molecule dissociation.

In an atomic gas for a collision process the following equation holds:



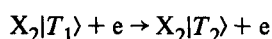
where i and j denote excited levels of an atom X in ionization stages k and k' . The cross section value σ depends only on the energy gap between the two considered levels and the kinetic energy ϵ of the incoming

electron; the shape of the curve $\sigma(\epsilon)$ is particularly dependent on the possibility of an optical transition between $X_j^{k'+}$ and X_i^{k+} . The reaction threshold of such a process is a well determined value and the reaction rate is easy to calculate if the electron energy distribution function is known. Experimental cross section values can be used for such a calculation.

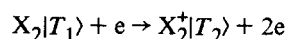
For a molecular gas, the situation is fundamentally similar to an atomic gas if transitions between molecular states $|T_1, v_1, J_1\rangle$ and $|T_2, v_2, J_2\rangle$ are considered.

The problem studied here is different. Our aim is to define a cross section which can be applied to a set of molecules with an electronic energy term T_1 and different vibrational and rotational energies $G(v)$ and $F(J)$, to compute the number of molecules which, after collision, have an electronic energy T_2 , whatever $G(v_2)$ and $F(J_2)$ be, provided that this potential energy situation corresponds to a stable molecular state if the excitation or ionization processes are considered, or to an unstable molecular state if dissociation is being studied.

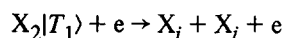
The three kinds of reactions considered in this paper can be written as follows:



(excitation with cross section $Q_{T_1}^{T_2}$),



(ionization with cross section $Q_{T_1}^{T_2^*}$),



(dissociation with cross section $Q_{T_1}^D$). (2)

For reactions such as (2) a fundamental difference appears with respect to the atomic case. In reactions (2) impact energies corresponding to the reaction threshold and cross section values for a given impact energy are functions of relative population number densities of the different vibrational and rotational levels belonging to the set of $|T_1\rangle$ levels. Consequently these values depend on the gas temperature Θ^* . Experimental cross section values for the processes in question can be found in the literature. These values are generally obtained by interaction between an electron beam and a target gas at room temperature ($\Theta = 300$ K). In such temperature conditions only a few rotational levels with $v = 0$ of molecules in their electronic ground state are appreciably populated. Experimentally measured reaction thresholds are thus very close to the asymptotic value $T_2 - T_1$. Consider now an ionized gas in which complete local thermodynamic equilibrium is approximately realized. Neutral particle temperature may reach several thousand kelvin. It is the situation encountered for example in a high current high pressure discharge. Excited levels with a vibrational quantum number greater than 0 may have a population number density of the same order of magnitude as that for the first vibrational level ($v = 0$). In such a situation, reactions (2) may be produced by electrons characterized by an energy smaller than $T_2 - T_1$. In other words, cross section values for such processes may be quite different from experimental values obtained for $\Theta = 300$ K. Consequently the experimental data are generally useless for computing reaction rates in hot molecular gases.

* It is to be noted that the population number densities of vibrational–rotational levels in an ionized gas depend on the gas and electron temperatures. This will be discussed in another paper.

2. Principles for calculations of the cross section

2.1. Model used for potential energy curves

For a diatomic molecule, the potential energy of a level belonging to an electronic state defined by an energy T_e^* and characterized by vibrational and rotational quantum numbers v and J depends on the inter-nuclear distance r . In our calculations, we use the Morse approximation and the potential energy is expressed by

$$U(r, J, v, T_e) = T_e + G(v) + (D_e - G(v)) \times [1 - \exp - \beta_e(r - r_e)]^2 + \frac{h}{8\pi c^2 \mu} \frac{J(J+1)}{r^2}. \quad (3)$$

The notations are those classically used in molecular spectroscopy (cf. Herzberg [3] or Rosen [4] for example).

In fig. 1, curves are drawn corresponding to variations of the potential energy of some rotational levels belonging to the first vibrational states of the nitrogen molecule in the electronic configuration $X^1\Sigma_g^+$.

Numerical values of the main parameters ω_e , $\omega_e x_e$, $\omega_e y_e$, α_e , D_e , etc. . . . are those given by Rosen [4].

The shape and evolution of the curves show that:

- i) For each value of the vibrational quantum number v , a limiting rotational quantum number value $J_L(v)$ exists such that $\partial U/\partial r < 0$ whatever r , if $J > J_L(v)$. For $J > J_L(v)$ the potential curve corresponds to a dissociated molecular state.
- ii) For each electronic state, a limiting vibrational quantum number $v_L(T_e)$ exists such that $\partial U/\partial r < 0$ whatever the r or J values, if $v > v_L(T_e)$.

In table I, $J_L(v)$ values are given for some electronic states of the N_2 molecule. To distinguish the $v_L(T_e)$ value we have made $J_L(v_L + 1) = 0$. It is to be noted that these limit values have to be used in the internal molecular partition function as a cut-off procedure on summations on v and $J(v)$ values (see appendix A).

* In several spectroscopic data tables an ambiguity between T_e and T_{00} exists. T_e is often given as being equal to 0 for the electronic ground state of the molecule. In fact for this level T_e has a negative value because the fundamental level is defined by $T_e + G(0) + F(0) = 0$. The small departure between T_e and T_{00} may induce noticeable errors in the internal molecular partition functions and in our method for computing cross section values.

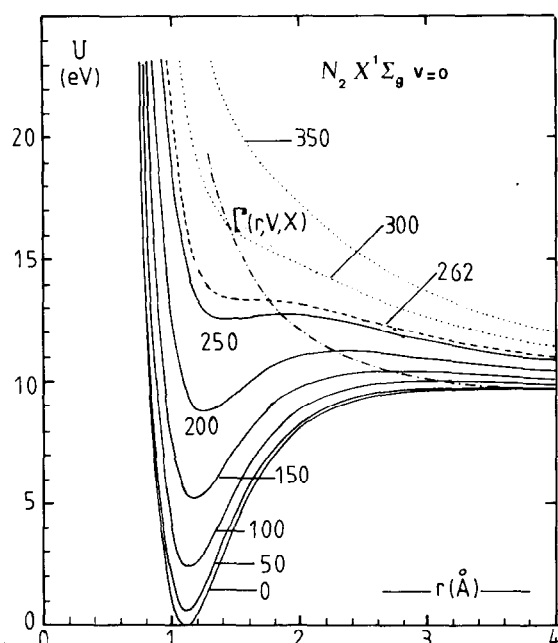


Fig. 1. Potential energy curves $U(r, J, v, T)$ versus internuclear distance for the electronic ground state level of the N_2 molecule, at $v = 0$, for different values of J from 0 to 350.

2.2. Stability area for an electronic state

The potential curve for a $|T, v, J\rangle$ level may be divided into three zones according to the internuclear distance value.

—The first one is obtained for the smallest values of r ($r < r_e$). In this interval, $\partial U/\partial r$ is negative and the potential is a strongly repulsive one.

—For r values greater than the equilibrium internuclear distance r_e , the potential becomes attractive ($\partial U/\partial r > 0$).

—Lastly, for the highest values of r , according to the J and v values, the sign of $\partial U/\partial r$ changes again; the potential is repulsive: the molecule tends towards dissociation. Similarly any $|T_e, v, J > J_L(v)\rangle$ or $|T_e, v > v_L(T_e), J\rangle$ level is an unstable one leading to dissociation because $\partial U/\partial r < 0$, whatever the r value is.

From the study of the potential energy curves corresponding to an electronic state defined by T_e , we can conclude that:

- $U(r, 0, 0, T_e)$ is a lower limit for all curves $U(r, J, v, T_e)$.
- $U(r, J_L(0), 0, T_e)$ is an upper limit for all curves

Table I

Rotational quantum number limit for different v values

v	$X^1\Sigma_g^+$	$A^3\Sigma_u^+$	$B^3\Pi_g$	$C^3\Pi_u$	$a^1\Pi_g$	v	$X^1\Sigma_g^+$	$A^3\Sigma_u^+$	$B^3\Pi_g$	$a^1\Pi_g$
0	262	188	204	113	228	26	166	48	92	134
1	258	184	200	104	224	27	162	0	85	130
2	255	180	196	93	220	28	159		79	127
3	251	175	192	80	216	29	155		73	124
4	247	171	187	58	213	30	151		64	120
5	243	167	183	0	209	31	147		48	116
6	239	163	179		205	32	144		0	112
7	236	158	175		201	33	140			108
8	232	154	171		198	34	136			105
9	228	150	167		194	35	132			101
10	224	146	163		190	36	128			97
11	221	142	159		187	37	123			93
12	217	137	155		183	38	119			88
13	213	133	150		180	39	115			82
14	210	128	146		176	40	111			78
15	206	124	142		173	41	106			73
16	202	120	138		169	42	101			67
17	199	115	134		165	43	94			59
18	195	110	129		162	44	89			44
19	191	104	125		159	45	84			4
20	188	100	121		155	46	77			0
21	184	94	116		151	47	66			
22	181	88	111		148	48	47			
23	177	80	107		145	49	0			
24	173	73	102		141	50	0			
25	169	65	97		138	51	0			

corresponding to stable molecular states i.e. showing a more or less deep potential well.

iii) For a given value of v , we can define a curve $\Gamma(r, v, T_e)$, the geometrical locus of points $r_0, U(r_0, J, v, T_e)$ such that $(\partial U/\partial r)_{r=r_0} = 0$, with $r \geq r_e$. Any point on the r, U plane, defined by $r_1, U(r_1, J, v, T_e) > \Gamma(r, v, T_e)$ is representative of an unstable molecular state because $\partial U/\partial r < 0$, whatever $r \geq r_1$. In fig. 1 the associated Γ -curve is also shown.

An analytical expression for Γ curves is not easy to determine. It is a function of $1/r$ such that $\lim_{r \rightarrow \infty} \Gamma(r, v, T_e) = D_e$, the asymptotic value for the dissociation energy of the T_e electronic state.

In our calculations and for r values such as $r_e \leq r \leq 4r_e$, a least squares method was used to represent the Γ curves by the development

$$\Gamma(r, v, T_e) = A + B/r + C/r^2. \quad (4)$$

In table II we give the values so obtained of the A, B, C parameters for several vibrational levels belonging to some electronic states of N_2 and N_2^+ .

A study of the $\Gamma(r, v, T_e)$ curves shows that $\Gamma(r, 0, T_e)$ is an upper limit for all curves $\Gamma(r, v, T_e)$.

Hence it can be concluded that representative points on the r, U plane of stable molecular states with an electronic energy term T_e are within an area limited by the three curves

$$U(r, 0, 0, T_e) \quad U(r, J_L(0), 0, T_e) \quad \text{and} \quad \Gamma(r, 0, T_e).$$

3. Application for inelastic collisions

We assume that in accordance with the Franck–Condon principle, the internuclear distance does not vary during an inelastic collision.

3.1. Collision-induced excitation or ionization

A collision transition between an initial level belonging to the set of states characterized by an electronic energy term T_1 and a final state characterized by an electronic energy term T_2 (which may be an electronic state of the molecular ion) leads to an excitation (or an ionization) if the representative point of the molecule after collision in the r, U plane is within the stability area of the electronic state T_2 .

When this point is within the stability areas of several electronic states, it is assumed that the electronic state produced by the collision is that for which the sum (vibrational energy + rotational energy) is smallest. This means that we assume that energy released by the incoming electron is preferentially transferred to the electronic cloud of the molecule. This hypothesis will be debatable for molecule–heavy particle collisions, which we are not considering.

The discussion is illustrated in fig. 2 where stability areas for $X^1\Sigma_g^+, A^3\Sigma_u^+, B^3\Pi_g$ electronic states of the N_2 molecule can be found from the three curves associated with each electronic state.

An initial state is defined by A . Several final states correspond to points a, b, c, d . If the representative point of the final state is

i) a : only a change in the rotational and (or) vibrational term occurs but the electronic state remains $X^1\Sigma_g^+$. These points are not considered in our calculations.

ii) b : excitation of a level belonging to $A^3\Sigma_u^+$ is produced. This point is situated in the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ state stability areas but it is the latter electronic state for which the sum (rotational + vibrational energy) is smallest.

iii) c : the molecular state obtained belongs to the set of $A^3\Sigma_u^+$ levels but its representative point is situated above $\Gamma(r, 0, A^3\Sigma_u^+)$ and corresponds to an unstable level. Such a reaction produces an indirect dissociation (see next subsection).

iv) d : excitation of a level belonging to the set of $B^3\Pi_g$ state is possible if this representative point does not belong to the stability area of another electronic state the electronic energy of which is more important (the $W^3\Delta_u$ state for example).

The broad hatched zone in fig. 2 corresponds to points compatible with an excitation of the $A^3\Sigma_u^+$ electronic state from the $X^1\Sigma_g^+$ levels. It is clear that for each internuclear distance value there exists an upper and a lower limit of the energy loss to which the incoming electron is subject.

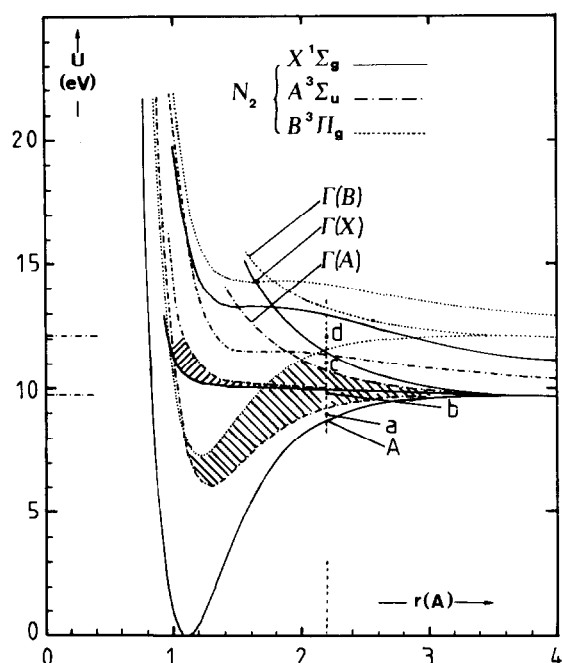
3.2. Collision-induced dissociation

Dissociation occurs if, from an initial state defined by a potential energy $U(r_1, J_1, v_1, T_1)$, we obtain, because of the energy loss of the incoming electron, a molecular state with potential energy U_2 such that

Table II

Parameters A , B and C for calculation of Γ -curves for some levels of N_2 and N_2^+

Level	v	A (eV)	B (eV \times cm)	C (eV \times cm ²)
$X^1\Sigma_g^+$	0	10.793	-1.15913×10^{-7}	2.86419×10^{-15}
	10	11.116	-1.14160×10^{-7}	2.32257×10^{-15}
	20	12.342	-1.58913×10^{-7}	2.43030×10^{-15}
	30	12.345	-1.55142×10^{-7}	1.94224×10^{-15}
$A^3\Sigma_u^+$	0	10.62682	-8.17476×10^{-8}	1.84784×10^{-15}
$B^3\Pi_g$	0	12.668117	-6.77368×10^{-8}	1.75428×10^{-15}
$N_2^+(X^2\Sigma_g^+)$	0	23.97618	-3.43277×10^{-8}	1.67553×10^{-15}

Fig. 2. Potential energy curves $U(r, 0, 0, T)$, $U(r, J_L(0), 0, T)$ and $\Gamma(r, 0, T)$ for some electronic states of N_2 molecules.

▨ area corresponding to the excitation of the $A^3\Sigma_u^+$ electronic state; ▩ area corresponding to the dissociation of the $X^1\Sigma_g^+$ electronic state.

$\partial U/\partial r < 0$, whatever $r \geq r_1$. As for the excitation or ionization processes, an upper and a lower limit for the electron energy loss exists for each r value.

Four situations can be encountered in a dissociation:

i) all molecule energy terms are modified:

$$U_2 = U(r_1, J > J_L(v_2), v_2, T_2);$$

ii) only the electronic energy term remains:

$$U_2 = U(r_1, J > J_L(v_2), v_2, T_1).$$

When only the rotational energy term is modified two cases must be distinguished:

$$\text{iii) } U_2 = U(r_1, J_2 > J_L(v_1), v_1, T_1);$$

$$\text{iv) } U_2 = U(r_1, J_2 < J_L(v_1), v_1, T_1),$$

but $\partial U/\partial r < 0$ whatever $r \geq r_1$.

The first situation need not be taken into account in the dissociation of the T_1 electronic state cross section calculation: it is in fact, a two-step dissociation. At first a level belonging to a set of T_2 levels is created. This level corresponds to an unstable situation and dissociation occurs according to the dissociation scheme of the T_2 electronic state. Taking into account such processes in the cross section calculation would mean that an N_2 molecule in its fundamental electronic state $X^1\Sigma_g^+$ would be able to be dissociated giving $N(^4S) + N(^2D)$ (products of dissociation of a molecule in the $B^3\Pi_g$ state).

If the indirect dissociation process does not contribute, it gives the upper limit of energy loss to which the incoming electron is subject.

Since $U(r_1, J_L(v_L(T_2)), v_L(T_2), T_2)$ corresponds to the minimum potential energy for unstable states with the electronic energy term T_2 , the maximum accept-

able energy loss for the incoming electron is

$$\Delta E_{\max} = U(r_1, J_L(v_L(T_2)), v_L(T_2), T_2) - U(r_1, J_1, v_1, T_1). \quad (5)$$

Using the same reasoning as before it will be shown that the minimum energy loss for an incoming electron to produce the dissociation of a molecule in a $|T_1, v_1, J_1\rangle$ state is

$$\Delta E_{\min} = U(r_1, J_L(v_L(T_1)), v_L(T_1), T_1) - U(r_1, J_1, v_1, T_1). \quad (6)$$

Firstly, consider an initial molecular state defined by $U(r_1, J_1, 0, T_1)$. To obtain the dissociation without any vibrational energy term modification, two situations are possible:

$$U_2 = U(r_1, J \geq J_L(0), 0, T_1),$$

or

$$U_2 = U(r_1, J \leq J_L(0), 0, T_1),$$

but $\partial U/\partial r < 0$ whatever $r \geq r_1$.

In the second situation, the representative point of the molecular state after collision in the r, U plane, is necessarily situated above the $\Gamma(r, 0, T_1)$ curve. The minimum energy loss is, according to the r value

$$\Delta E = \min \{U(r_1, J_L(0), 0, T_1); \Gamma(r_1, 0, T_1)\} - U(r_1, J_1, 0, T_1).$$

Consider now that dissociation can occur with a vibrational energy change. Since $\partial U(r, J_L(v), v, T)/\partial v < 0$ and $\partial \Gamma(r, v, T)/\partial v < 0$, we obtain, considering the set of vibration quantum numbers for the T_1 electronic state:

$$\Delta E = \min \{U(r_1, J_L(v_L(T_1)), v_L(T_1), T_1); \Gamma(r_1, v_L(T_1), T_1)\} - U(r_1, v_1, 0, T_1).$$

By generalizing the reasoning to any initial level with $U(r_1, J_1, v_1, T_1)$, relation (6) is obtained.

In fig. 2 the narrow hatched zone is the area corresponding to the (r, U) points obtained after collision between an electron and a N_2 molecule in its electronic ground state, leading to an effective dissociation.

4. Weighted total cross section calculation: weighted terms for levels of the initial electronic state

Total cross sections corresponding to a change in the electronic energy term or to a dissociation are obtained by a weighted summation of contributions from each $|T_1, v_1, J_1\rangle$ level. We define for each initial level and for a fixed value of the internuclear distance, an elementary cross section $q(r, J_1, v_1)$ which corresponds to the transition from this initial level to the set of levels of the final electronic state. So the weighted total cross section is defined by the expression:

$$Q_{T_1}^T(\epsilon) = \sum_{v_1=0}^{v_L(T_1)} P(v_1) \sum_{J_1=0}^{J_L(v)} P(J_1) \int_0^\infty P(r) q(r, J, v) dr. \quad (7)$$

$P(v_1)$ and $P(J_1)$ are probabilities corresponding to an initial state with v_1 and J_1 as quantum numbers for vibration and rotation. $P(r)$ is the probability of an internuclear distance value in the range $r, r + dr$. We assume that this probability can be treated within the approximation of the harmonic oscillator and that it depends only on the vibrational quantum number value. Thus $P(r)$ is written (see ref. 3, p. 113)

$$P(r) \equiv P_v(r) = \frac{1}{2^v v!} \sqrt{\frac{\alpha}{\pi}} \exp(-\alpha(r - r_e)^2) H_v^2(\chi), \quad (8)$$

with $\chi = \sqrt{\alpha}(r - r_e)$, $\alpha = 2\pi\sqrt{\mu k_0}/h$, $k_0 = 5.888 \times 10^{-2} \mu_A \omega_e^2$, H_v is the Hermitian polynomial of the v th degree.

In numerical computations, integration is replaced by a summation over an r range between 0.5 and 4 Å with a step of $dr = 0.01$ Å to obtain a good description of the $P_v(r)$ curves. For the highest gas temperature values considered in this work ($\Theta = 12000$ K), up to 20 vibrational quantum number values have to be

taken into account for the $N_2(X^1\Sigma_g^+)$ state. The curve $P_{20}(r)$ shows 21 maxima and 20 minima.

We assume that the target gas is in a situation where the hypothesis of Complete Thermal Equilibrium at the temperature Θ is fulfilled. In such conditions, probabilities $P(v)$ and $P(J)$ can be expressed from a "partial" internal partition function defined for each electronic state. This "partial" internal partition function is given by

$$Q_{\text{int}}^T(\Theta) = \sum_{v=0}^{v_L(T_1)} \exp -\frac{G(v)}{k\Theta} \left\{ \sum_{J=0}^{J_L(v)} (2J+1) \exp -\frac{F(J)}{k\Theta} \right\}. \quad (9)$$

If the vibrational energy $G(v)$ and the rotational energy $F(J)$ are expressed in cm^{-1} and Θ in kelvin, the Boltzmann constant k is 1.4392.

For a $|T_1, v_1, J_1\rangle$ level, the product $P(v_1)P(J_1)$ is then given by

$$P(v_1)P(J_1) = (2J_1 + 1) \times \exp(-(G(v_1) + F(J_1))/k\Theta)/Q_{\text{int}}^T(\Theta), \quad (10)$$

with

$$G(v_1) = (v_1 + 0.5)(\omega_e - (v_1 + 0.5) \times (\omega_e x_e - (v_1 + 0.5)\omega_e y_e)),$$

$$F(J_1) = J_1(J_1 + 1)(B_v - J_1(J_1 + 1)D_v).$$

The spectroscopic parameters $B_v, D_v, \omega_e, \omega_e x_e, \omega_e y_e$ have their classical meanings. The values used in the calculations are taken from the spectroscopic data table given by Rosen [4].

In order to reduce the time necessary to compute the cross sections, only v_1 and J_1 values such that

$$P(v_1)P(J_1) \geq 10^{-3}(P(v)P(J))_{\text{max}}$$

are taken into account. For a given gas temperature Θ , $(P(v)P(J))_{\text{max}}$ is the maximum value of $P(v)P(J)$. This value, for the $X^1\Sigma_g^+$ electronic state, is obtained for $v = 0$ and $8 \leq J \leq 52$ when Θ varies between 300 and 12000 K. Likewise, for each v_1 value, only r values such that $P_{v_1}(r) \geq 10^{-3}(P_{v_1}(r))_{\text{max}}$ are taken into account.

5. Models used for calculating the elementary cross section $g(r, J, v)$

5.1. Gryzinski's model [2]

Gryzinski's theoretical model gives a simple analytical expression for a cross section which corresponds to a minimum loss of kinetic energy $\Delta\epsilon$ of an incoming electron colliding with the optical electron of an atom or a molecule target. ϵ and E_1 being the kinetic energy of the incoming electron and binding energy of the optical electron of the target particle respectively, Gryzinski's cross section can be written [5]:

$$Q_G\{u, v\} = 4\pi a_0^2 \left(\frac{E_1^H}{\Delta\epsilon}\right)^2 \xi g(u, v) \quad (11a)$$

with

$$g(u, v) = \frac{1}{u} \left(1 - \frac{1}{u}\right)^{1+v/(v+1)} \left(\frac{u}{u+v}\right)^{3/2} \times \left\{1 + \frac{2v}{3} \left(1 - \frac{1}{2u}\right) \ln \left[e + \left(\frac{u-1}{v}\right)^{1/2}\right]\right\}, \quad (11b)$$

where u is the reduced kinetic energy of the incoming electron: $u = \epsilon/\Delta\epsilon$ and v the reduced binding energy of the optical electron: $v = E_1/\Delta\epsilon$; e is the natural logarithm base; ξ the number of equivalent electrons; E_1^H , the ionization potential of atomic hydrogen and πa_0^2 , the area of Bohr's first orbit ($8.8 \times 10^{-17} \text{ cm}^2$).

The use of Gryzinski's model for atomic gases is well known. To calculate the excitation cross section from the i th to the j th level, it is admitted that the cross section is the difference between cross sections for an energy loss of the electron greater or equal to $E_j - E_i$ and for an energy loss greater or equal to $E_{j+1} - E_i$, E_{j+1} being the potential energy of the $j+1$ th level that is to say:

$$Q_G^{i \rightarrow j} = Q_G\left\{\frac{E_1}{E_j - E_i}; \frac{\epsilon}{E_j - E_i}\right\} - Q_G\left\{\frac{E_1}{E_{j+1} - E_i}; \frac{\epsilon}{E_{j+1} - E_i}\right\}. \quad (12)$$

For an atomic gas, the optical electron binding energy is expressed in terms only of a Coulombian attachment and is given by $eV_i - E_i$. Thus in order to treat the ionization cross section ν is strictly equal to unity in eqs. (11a) and (11b).

For the electron-molecule collision processes, an analogy is made with the electron-atom collision. Consider an initial level belonging to the set of levels with an electronic energy term T_1 , and characterized by the four parameters r_1, J_1, v_1, T_1 . Calculate the contribution $q(r_1, J_1, v_1)$ of this level to the cross section of an inelastic process, for example the excitation from $|T_1\rangle$ levels to $|T_2\rangle$ levels. We then have:

$$q(r_1, J_1, v_1) = \sum_{v_2=0}^{\alpha(r_1)} \sum_{J_2=0}^{\beta(v_2, r_1)} q_{r_1, J_1, v_1, T_1}^{r_1, J_2, v_2, T_2}. \quad (13)$$

Limits α and β will be explained later. According to relation (12), we have:

$$q_{r_1, J_1, v_1, T_1}^{r_1, J_2, v_2, T_2} = Q \left\{ \frac{E_1}{\Delta\xi_{12}}; \frac{\epsilon}{\Delta\xi_{12}} \right\} - Q \left\{ \frac{E_1}{\Delta\xi_{13}}; \frac{\epsilon}{\Delta\xi_{13}} \right\}, \quad (14a)$$

with

$$\Delta\xi_{12} = U(r_1, J_2, v_2, T_2) - U(r_1, J_1, v_1, T_1),$$

$$\Delta\xi_{13} = U(r_1, J_2 + 1, v_2, T_2) - U(r_1, J_1, v_1, T_1). \quad (14b)$$

E_1 is the binding energy of the optical electron of the molecule in the $|T_1, v_1, J_1\rangle$ state. Its value will be discussed later.

The cross section for the excitation of level $|T_2, v_2, J_2 + 1\rangle$ is defined by:

$$q_{r_1, J_1, v_1, T_1}^{r_1, J_2+1, v_2, T_2} = Q \left\{ \frac{E_1}{\Delta\xi_{13}}; \frac{\epsilon}{\Delta\xi_{13}} \right\} - Q \left\{ \frac{E_1}{\Delta\xi_{14}}; \frac{\epsilon}{\Delta\xi_{14}} \right\}, \quad (15)$$

with

$$\Delta\xi_{14} = U(r_1, J_2 + 2, v_2, T_2) - U(r_1, J_1, v_1, T_1).$$

It is obvious that the set of transitions from the $|T_1, v_1, J_1\rangle$ level to levels with T_2 and v_2 corresponds to a cross section given by only one difference i.e.

$$q(r_1, J_1, v_1) = \sum_{v_2=0}^{\alpha(r_1)} Q \left\{ \frac{E_1}{\Delta\xi_{\min}}; \frac{\epsilon}{\Delta\xi_{\min}} \right\} - Q \left\{ \frac{E_1}{\Delta\xi_{\max}}; \frac{\epsilon}{\Delta\xi_{\max}} \right\}, \quad (16a)$$

with

$$\Delta\xi_{\min} = U(r_1, 0, v_2, T_2) - U(r_1, J_1, v_1, T_1),$$

$$\Delta\xi_{\max} = U(r_1, \beta, v_2, T_2) - U(r_1, J_1, v_1, T_1). \quad (16b)$$

Two situations can be distinguished for the $\Delta\xi_{\max}$ value, according to the impact energy of the incoming electron:

i) The kinetic energy of the incoming electron is high ($\epsilon \gg T_2 - T_1$). According to the internuclear distance value, the upper limit of potential energies of the $|T_2, v_2\rangle$ levels which can be excited is given either by the $U(r, 0, 0, T_3)$ curve, either the $\Gamma(r, v_2, T_2)$ curve. T_3 is the electronic energy term of the configuration which limits the $|T_1\rangle \rightarrow |T_2\rangle$ transitions. Consequently:

$$\Delta\xi_{\max} = \min \{ U(r_1, 0, 0, T_3); \Gamma(r_1, v_2, T_2) \} - U(r_1, J_1, v_1, T_1).$$

If $\Delta\xi_{\max}$ is determined from curve Γ , then $\beta(v_2, r_1)$ will be such that

$$\left(\frac{\partial U(r_1, \beta + 1, v_2, T_2)}{\partial r} \right)_{r=r_1} \leq 0.$$

In the other case, β will be defined by:

$$U(r_1, \beta, v_2, T_2) \leq U(r_1, 0, 0, T_3) \leq U(r_1, \beta + 1, v_2, T_2).$$

The limit α is calculated using the same reasoning. In particular, if for the r_1 value, $U(r_1, 0, 0, T_3)$

$> \Gamma(r_L, v_1(T_2), T_2)$ we have $\alpha = v_L(T_2)$. In the opposite case α is such that

$$U(r_1, \beta(\alpha), \alpha, T_2) \leq U(r_1, 0, 0, T_2)$$

$$\leq U(r_1, 0, \alpha + 1, T_2).$$

ii) The kinetic energy of the incoming electron is low. This situation is easier to treat because it is impossible to obtain the excitation of all the $|T_2\rangle$ levels. The α and β values are such that:

$$U(r_1, \beta(\alpha), \alpha, T_2) \approx \epsilon + U(r_1, J_1, v_1, T_1)$$

and $\epsilon/\Delta\xi_{\max}$ is close to 1. Equation (16a) can then be written

$$q(r_1, J_1, v_1) \approx \sum_{v_2=0}^{\alpha(r_1)} Q\left(\frac{E_1}{\Delta\xi_{\min}}; \frac{\epsilon}{\Delta\xi_{\min}}\right). \quad (17)$$

The use of Gryzinski's model, in particular for excitation cross section calculation, creates a problem because an ambiguity exists in the definition of the binding energy of the optical electrons of the molecules. This is an important question because the shape of the $g(u, v)$ curves as a function of u depends strongly on the v values [2].

It will be shown in the second part of this paper that a definition of binding energy based only on Coulombian interaction is inadequate. A better agreement with experimental cross section values will be obtained by assuming that the binding energy is expressed by

$$E_1' = U(r_1, J_L(v_L(T_2)), v_L(T_2), T_2)$$

$$- U(r_1, J_1, v_1, T_1),$$

instead of:

$$E_1 = U(r_1, 0, 0, T_1^+) - U(r_1, J_1, v_1, T_1),$$

which is the expression which corresponds to the definition used for atomic gases. In the latter E_1 expression, T_1^+ is the electronic energy term of the molecular ion in its electronic ground state.

With the new definition of the binding energy, it is clear that the v values ($v = E_1/\Delta\epsilon$) are smaller than the

"classical" ones ($v_{\text{class}} = E_1/\Delta\xi$) for the excitation processes and a little greater than unity for ionization; v_{class} is strictly equal to unity for such processes. The v value is unity for cross sections corresponding to dissociation.

5.2. Drawin's model

Various analytical expressions for the ionization and excitation cross sections have been given by Drawin [1]. They were successfully used for atomic gases. Different cases were considered:

i) If the optical transition between the j th level and the i th level is an electric dipole allowed one, the excitation cross section for the collisional transition $i \rightarrow j$ is given by:

$$q_{ij} = 4\pi a_0^2 \left(\frac{E_1^H}{E_j - E_i} \right)^2 \alpha_{ij} U_{ij}^{-1} (1 - U_{ij}^{-1}) f_{ij} \times \ln(1.25\beta_{ij} U_{ij}). \quad (18)$$

U_{ij} is a reduced incoming electron energy defined by $\epsilon/E_j - E_i$; E_1^H denotes the ionization potential of atomic hydrogen; f_{ij} is the absorption oscillator strength for the transition $i \rightarrow j$; β_{ij} is an adjustable constant of the order of unity.

ii) In the case where the optical transition $i \rightarrow j$ is forbidden, Drawin proposes several solutions:

—When no change in multiplicity occurs, the excitation cross section is given by the expression

$$q_{ij} = 4\pi a_0^2 \alpha_{ij} U_{ij}^{-1} (1 - U_{ij}^{-1}). \quad (19)$$

α_{ij} is an adjustable constant which may be theoretically calculated from quantum considerations.

—For forbidden transitions with a change in multiplicity, Drawin obtained a satisfactory agreement between experimental and theoretical cross section values using the following expressions:

$$q_{ij} = 4\pi a_0^2 \alpha_{ij} (U_{ij}^2 - 1)/U_{ij}^5 \quad \text{for singlet-triplet transitions,} \quad (20)$$

$$q_{ij} = 4\pi a_0^2 \alpha_{ij} U_{ij}^{-1} \quad \text{for triplet-singlet transitions.} \quad (21)$$

For ionization processes, Drawin used expression (18), putting $f_{ij} = 1$.

Application of these formulae to molecular gases is made using the same procedure as for Gryzinski's model. The contribution of an initial level $|T_1, v_1, J_1\rangle$ to the total cross section is obtained by means of a double summation on the v_2 and J_2 quantum number values of the final electronic configuration, i.e.:

$$q(r_1, J_1, v_1) = \sum_{v_2=0}^{\alpha(r_1)} \sum_{J_2=0}^{\beta(v_2, r_1)} q_D^{r_1, J_2, v_2, T_2, T_1} \quad (22)$$

q_D being, according to the process considered, one of the expressions (18) to (21). The α and β values have to be defined, as in the preceding case, for each internuclear distance value, taking into account the kinetic energy of the projectile electron.

6. Selection rules for the collisional transition between real levels

The elementary cross sections given by the expressions (13) or (22) are independent of any selection rule for collisional transitions between levels $|T_1, v_1, J_1\rangle$ and $|T_2, v_2, J_2\rangle$. As will be shown in the second part of this paper, giving the same weight to all transitions leads to cross section values which are very much greater than the experimental ones when Drawin's models are used. To obtain results which agree with the experimental data, the selection rules for collisional transitions between rotational levels established in Born's approximation by Gerjuoy and Stein [6] were introduced into the calculations.

These authors showed that collision cross sections for transitions between two levels with quantum numbers J_1 and J_2 are zero except if

$$J_1 = J_2 \pm 2. \quad (23)$$

Application of this selection rule reduces appreciably the number of summations on J_2 : for every $|T_1, v_1, J_1\rangle$ level, only two collision transitions have to be considered for each v_2 value.

7. Conclusion

Weighted total cross sections for the inelastic collision between electrons and diatomic molecules are

numerically obtained from the general expressions:

$$Q_{T_1}^{T_2}(\epsilon) = \sum_{v_1=0}^{v_L(T_1)} P(v_1) \sum_{J_1=0}^{J_L(v_1)} P(J_1) \int_0^\infty \left[P_{v_1}(r) \sum_{v_2=0}^{\alpha(r_1)} Q \left\{ \frac{E_1}{\Delta\xi_{\min}}, \frac{\epsilon}{\Delta\xi_{\min}} \right\} - Q \left\{ \frac{E_1}{\Delta\xi_{\max}}, \frac{\epsilon}{\Delta\xi_{\max}} \right\} \right] dr \quad (24)$$

when Gryzinski's formalism is used, and

$$Q_{T_1}^{T_2}(\epsilon) = \sum_{v_1=0}^{v_L(T_1)} P(v_1) \sum_{J_1=0}^{J_L(v_1)} P(J_1) \int_0^\infty \left[P_{v_1}(r) \sum_{v_2=0}^{\alpha(r_1)} \sum_{J_2=0}^{\beta(v_2, r)} \delta(J_1 - J_2 \pm 2) q_{v_1 J_1}^{v_2 J_2}(\epsilon) \right] dr, \quad (25)$$

$\delta(J_1 - J_2 \pm 2) \begin{cases} = 1 & \text{if } J_1 = J_2 \pm 2 \\ = 0 & \text{if } J_1 \neq J_2 \pm 2 \end{cases}$, if Drawin's models are used.

In both cases, the best choice for the elementary cross section is made by comparing calculated cross section values for a 300 K gas temperature with experimental data.

Appendix

For calculations of probabilities $P(v)P(J)$ used in cross sections determination we have to calculate for each electronic state T_e a partial partition function defined by:

$$Q_{\text{part}}^{T_e}(\Theta) = \sum_{v=0}^{v_L(T_e)} \exp - \frac{G(v)}{k\Theta} \left\{ \sum_{J=0}^{J_L(v)} (2J+1) \times \exp -F(J)/k\Theta \right\}.$$

From these values it is easy to determine the usual total partition function Q_{int} of N_2 and N_2^+ :

$$Q_{\text{int}}(\Theta) = \frac{1}{2} \left(\sum_{T_e} g_e \exp - T_e/k\Theta \right) Q_{\text{part}}^{T_e}(\Theta).$$

Table III
Internal partition functions for N_2 and N_2^+

T (K)	Q_{int} for N_2		Q_{int} for N_2^+	
	Ref. 7	Our work	Ref. 7	Our work
2000	430.5	433.0	925.8	926
3000	785.1	789.8	1754	1759.5
4000	1250	1258	2980	3004
5000	1828	1842	4723	4794.5
6000	2524	2545	7085	7250
7000	3339	3371	10140	10485
8000	4278	4329	13970	14600
9000	5351	5430	18610	19705
10000	6569	6698	24110	25910
11000	7950	8167	30520	33350
12000	9531	9890	37860	42130
13000	11340	11935	46180	52360
14000	13440	14370	55500	64130
15000	15870	17310	65850	77540

For the electronic state $^n\Sigma$ the electronic degeneracy is n ; for all other electronic states as $^n\Pi$, $^n\Delta$, $^n\phi$. . . the degeneracy is $2n$ due to Λ doubling. The factor $(1/2)$ is in connection with the homonuclearity of species considered here.

Calculations have been made taking into account 12 electronic states for N_2 and 5 for N_2^+ , spectroscopic parameters of which are taken from ref. 2. Contrary to work of Tarafdar [8] who limits the summations on J and v when $(T_e + G(v) + F(J))$ exceeds the dissociation energy asymptotic value D_e , in our calculation we take into account all (J, v) levels showing a potential well i.e. levels characterized by a positive derivative of the potential function when internuclear distance varies from 0 to theoretically infinite.

These so calculated partition functions can be compared with the values of Drellishak et al. [7]. For

lower temperatures, agreement is satisfying: our values differ by 1 or 2% from those of Drellishak. For higher temperatures, i.e. 8000 K and more, differences are more important (up to 15% for N_2^+ and 9% for N_2 at $\Theta = 15000$ K). In table III we compare Drellishak's values with our results.

These differences do not cause important deviations for the C.L.T.E. plasma composition but they have a stronger influence on calculated thermodynamic parameters as molar heat capacity, specific enthalpy etc. . . ., for which $dQ_{\text{int}}/d\Theta$ is needed.

Introduction of variations of ionization or dissociation energy versus Θ in plasma composition calculations according to the results presented in this paper may have a noticeable influence; such calculations will be presented in a separate paper.

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