ELECTRONIC DISSOCIATION AND IONIZATION CROSS-SECTIONS OF DIATOMIC MOLECULES IN DIFFERENT VIBRATIONAL LEVELS

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ABSTRACT

Dossociation and ionization cross sections of diatomic species (H_2, O_2, HCl) in different vibrational levels have been calculated with the classical Gryzinski's approximation. A satisfactory agreement has been found between the present results and those obtained by other authors with quantum mechanical methods.

1. INTRODUCTION

The study of dissociation and ionization of diatomic species in electrical discharges require the knowledge of cross sections of the type

$$e + A_2(v) \rightarrow e + A_2^* \rightarrow e + 2A \qquad (a)$$

$$e + A_2(v) \rightarrow e + A_2^+ + e \qquad (b)$$

where $A_2(v)$ represents a molecule in the vth vibrational level of the ground electronic state and A_2^* is a corresponding excited electronic state. In general cross sections for processes (a) and (b) are known only for v=o, so that one must estimate the cross sections involving vibrationally excited molecules ($v \neq o$). This problem can be in principle solved by using complicated quantum mechanical methods, which often give unsatisfactory results despite the large computing times. On the other hand one can use classical and semiclassical methods, which in many cases give as good results as the quantum mechanical methods, by strongly reducing, however, the computing times.
In this note we want just to apply the classical Gryzinski's approximation for calculating the cross sections of processes (a) and (b) [1].

2. METHOD OF CALCULATION AND RESULTS

The formulation of the dissociation cross sections is slightly different according to A_2^* represents i) a completely repulsive state ii) a completely bound state which dissociates after the interaction iii) a bound state with minimum shifted with respect to the ground state, so that the in-

teraction occurs on the repulsive part of the potential.
The following examples will be discussed for the three cases
i)

$$e + H_2(X'\Sigma_g, v) \rightarrow e + H_2(b^3\Sigma_U) \quad (c)$$

$$e + HCl\ (X'\Sigma, v) \rightarrow e + HCl\ (A'\Pi) \quad (d)$$

ii)

$$e + H_2(X'\Sigma_g, v) \rightarrow e + H_2(e^3\Sigma_u^+,\ a^3\Sigma_g^+,\ c^3\Pi_u) \quad (e)$$

iii)

$$e + O_2(^3\Sigma_g^-, v) \rightarrow e + O_2(A^3\Sigma_u^+) \quad \text{Herzberg Continuum}$$

$$e + O_2(^3\Sigma_g^-, v) \rightarrow e + O_2(B^3\Sigma_u^-) \quad \text{Schumann Continuum}$$

The dissociation cross section for point i) and iii) can be written as |2|

$$\sigma_D(E_2) = \int_{U_o}^{E_2} \frac{d\sigma_D}{dU_v}\, dU \quad (1)$$

$$\frac{d\sigma_D}{dU_v} = q_{c,v}\ \{Q_g(E_2,E_1,U_v) - Q_g(E_2,E_1,E_1)\} \quad (2)$$

where E_2 and E_1 are in the order the energies of the incident and of the bound electron and U_v is the energy in the continuum.
A_g in the Gryzinski's cross section which assumes different forms for optically allowed and forbidden transitions |2|, q_{cv} is the Franck-Condon density defined as

$$q_{cv} = \left| \int_o^\infty \Psi_v(A_2)\ \Psi_c(A_2^*)\ dR_i \right|^2 \quad (3)$$

A very simple formula for q_{cv} is obtained by considering the wave functions of the continuum states ($\Psi_c(A_2^*)$) as a δ function. In this case eq.3 reduces to

$$q_{cv} = \left(\frac{dV}{dR}\right)^{-1}_{R=R_c} \quad (\Psi_v(R_c))^2 \quad (4)$$

which requires the kowledge of the vibrational wave functions of the electronic ground state ($\Psi_v(R_c)$) at the relevant turning points R_c and the gradient of the repulsive potential at R_c.
The cross sections of point ii) as well as the ionization cross sections can be directly calculated by using the Franck-Condon factors (bound-bound transition) in combination with the Gryzinski's approximation |2|. The potential energy curves for the bound states have been fitted by means of Morse potential, while the exponential repulsive potential has been used for the repulsive stetes. The vibrational wave functions necessary for the calculation of the Franck-Condon density and Franck-Condon factors have been calculated as in ref. |3|.
The most serious incertitudes in the calculation of Gryzinski cross sections lies in the choice of n+l state which can be excited during the excitation of the nth state and in the choice of the number of effective electron N_e. A discussion of these points can be found in ref. |2|.

Figures 1-4 show some of the calculated cross sections for different vibrational levels as a function of electron energy. One can note that in all cases the threshold of the process decreases by increasing the vibratioanl quantum number v, the reverse being true for the maximum value of the cross section. The only exception is represented by the oxygen transitions, which present maxima decreasing with increasing v. This behaviour can be ascribed to the fact that the oxygen transitions belong to point ii) i.e. the excited state is a bound state with maximum shifted with respect to the ground state. Figure 5 reports a comparison of the present results with the quantum mechanical close coupling calculations of Chung and Lin |4| for the triplet states of hydrogen. The agreement can be considered satisfactory specially for the repulsive state $b\ ^3\Sigma_u^+$. A similar agreement has been found by comparing the present results of Herzberg and Schumann transition with other experimental and theoretical v=o cross sections |5|.
Fig. 6 reports the H_2 ionization cross sections for different vibrational levels for energies near the threshold of the process. A comparison of the v=o cross section with the experimental results of |6| shows a good agreement, the differences not exceeding a factor of 2.

3. CONCLUSIONS

In the previous paper we have presented a very simple way of calculating electronic cross sections for dissociation and ionization cross sections involving vibrationally excited levels. The satisfactoty agreement found between the present results and those of other authors indicate that the Gryzinski's formulation can be confidently used to provide input data for the vibrational kinetics |7|. It should be noted that in general the cross sections are averaged in the rates by means of the electron energy distribution function and that errors in this cross sections do not propagate to the same extent in the rates |8|. Moreover, since in many cases, one knows the v=o cross section, the Gryzinski formulation can be used as scaling law.

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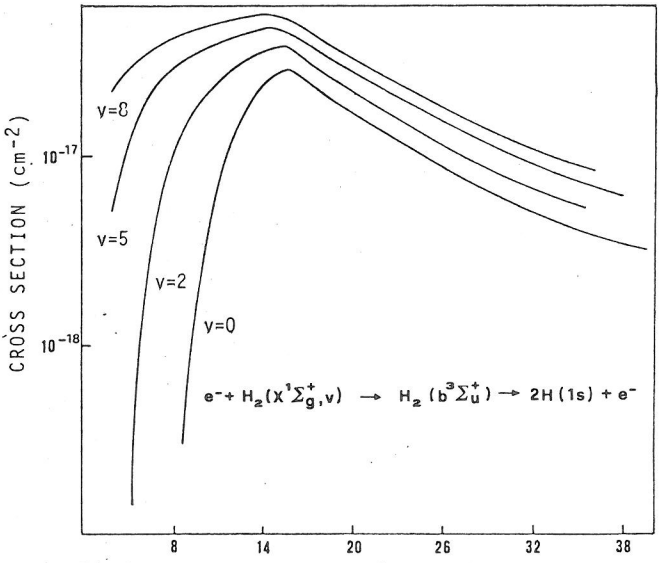
CROSS SECTION (cm^{-2})
10^{-17}
10^{-18}
v=8
v=5
v=2
v=0
$e^- + H_2(X^1\Sigma_g^+, v) \rightarrow H_2(b^3\Sigma_u^+) \rightarrow 2H(1s) + e^-$
8
14
20
26
32
38
ELECTRON ENERGY (eV)

Fig.1

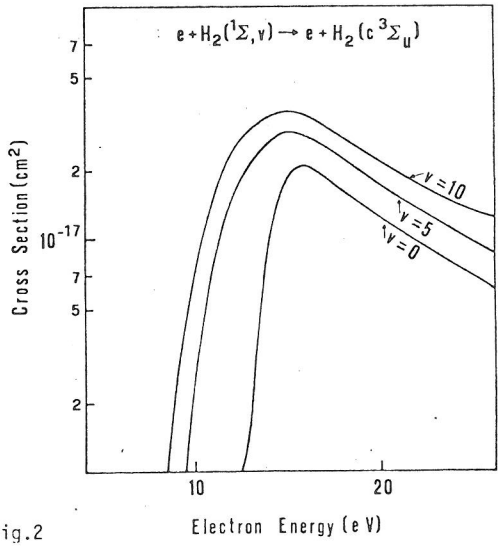
$e + H_2(^1\Sigma, v) \rightarrow e + H_2(c\,^3\Sigma_u)$
Cross Section (cm^2)
7
5
2
10^{-17}
7
5
2
v=10
v=5
v=0
10
20
Electron Energy (eV)

Fig.2

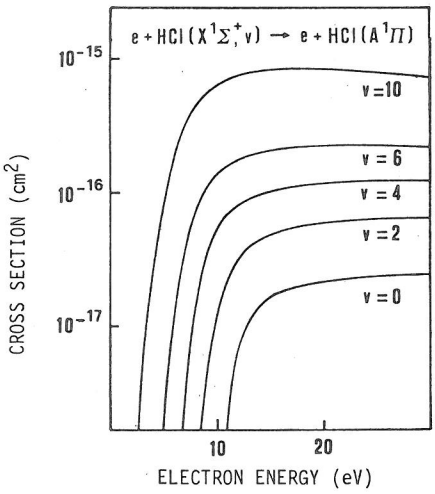
e + HCl(X¹Σ⁺,v) → e + HCl(A¹Π)
10⁻¹⁵
10⁻¹⁶
10⁻¹⁷
v=10
v = 6
v = 4
v = 2
v = 0
CROSS SECTION (cm²)
10
20
ELECTRON ENERGY (eV)

FIG. 3

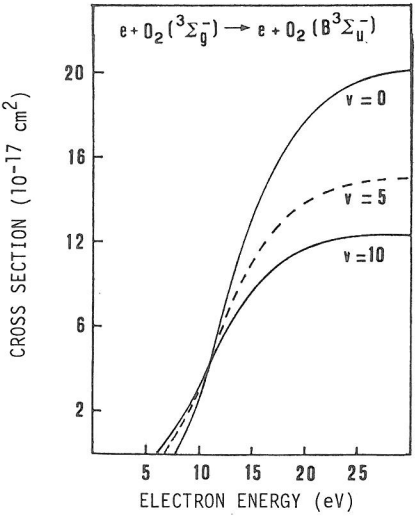
e + O₂(³Σg⁻) → e + O₂(B³Σu⁻)
20
16
12
6
2
v = 0
v = 5
v =10
CROSS SECTION (10⁻¹⁷ cm²)
5
10
15
20
25
ELECTRON ENERGY (eV)

FIG. 4

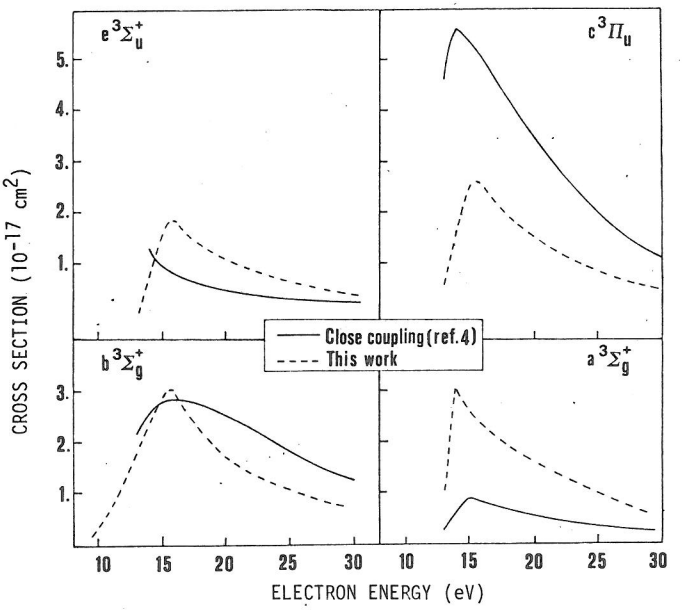
$e\,^3\Sigma_u^+$
$c\,^3\Pi_u$
$b\,^3\Sigma_g^+$
$a\,^3\Sigma_g^+$
Close coupling (ref.4)
This work
CROSS SECTION (10^{-17} cm^2)
ELECTRON ENERGY (eV)

FIG.5

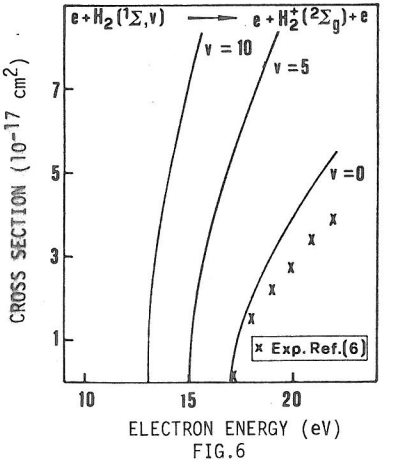
$e + H_2(^1\Sigma, v) \longrightarrow e + H_2^+(^2\Sigma_g) + e$
v = 10
v = 5
v = 0
x Exp. Ref.(6)
CROSS SECTION (10^{-17} cm^2)
ELECTRON ENERGY (eV)

FIG.6