

**ELECTRON TRANSFER COLLISIONS OF EXCITED
SODIUM ATOMS AND OXYGEN MOLECULES**

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ABSTRACT

The vibronic network model is here considered for excited sodium atoms and oxygen molecules collisions. Electronic to vibration transfer and reaction cross sections are computed with a single adjustable parameter : the ionic covalent matrix element. The comparison between the atom-molecule and the quasi-free electron models is presented.

I. INTRODUCTION

The electron transfer or harpoon mechanism is well known for the reaction of alkali atoms (1), chemiluminescence or chemi-ionization processes (2). When the alkali atoms are excited and collide with electron accepting molecules, the electronic to vibration energy transfer process (or quenching) competes with the reactive process, both go-

verned by the electron transfer which exhibits the following trend in the case of halogen molecules (3) : the electron transfer cross sections increase from ground states of the alkali atoms to the first resonant states due to the larger internuclear crossing distances between covalent and ionic states, then fall rapidly to zero for second resonant states and above.

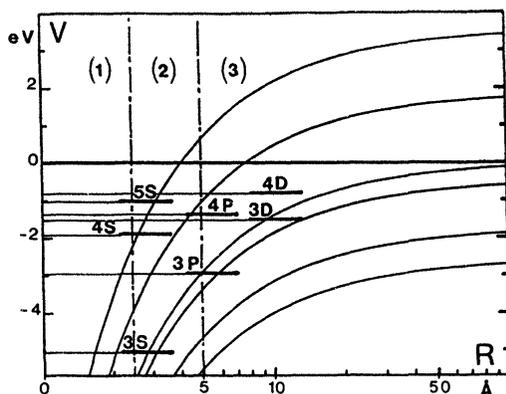


Figure 1 : Ionic-covalent curve crossings between excited states of sodium and molecules. Region (3) corresponds to negative molecular ions unperturbed by the presence of the Na^+ core. For $\text{Na} + \text{O}_2$, the ionic intermediate model is strictly valid for the 3P level and approximate for the 3S level.

The electron transfer process depends upon the overlap of the orbitals of the exchanged electron in the donor atom and the accepting molecule. If the donor atom is highly excited, its valence electron cloud has a lar-

ge size and the overlap with that of a strongly bound molecular negative ion will be rather poor. This is the case for halogens with electron affinities in between 1 and 3 eV. By contrast, molecules which possess very small vertical affinities and, thus, attach low energy electrons, will be of interest in collisions with excited atoms since the overlap will be more favorable due to the large spatial extension of the outer electron orbital of their negative ions.

Collisions of excited sodium atoms with oxygen molecules are here considered. The oxygen molecule has a rather small adiabatic electron affinity of .44 eV and a very small vertical affinity corresponding to molecular negative ions O_2^- loosely bound as compared to halogen negative ions. Experiments have been performed to measure the electronic to vibration energy transfer of the first resonant 3P state of sodium by oxygen molecules (4)(5) as well as reactive cross section of the 3P, 5S and 4D states (6).

A complete interpretation would require a calculation of the potential energy surfaces and their couplings, followed by trajectory computations on these surfaces. In the case of the reacting D state of sodium, for example, this would require dynamical studies over several tens of surfaces of different symmetries. The simpler approach of Bauer, Fischer and Gilmore (BFG) (7) was chosen. The validity of this model in the case of Na- O_2 collisions is examined in chapter II and the used atomic and molecular data are given. The results of this model are compared in chapter III to the experimental data of Barker (10) and

Hertel (4) for the quenching cross sections of the 3P state. The model is extended to the inter multiplet mixing cross sections and to the reactive cross sections in chapter IV. In this last case, a comparison is given between this multiple crossing model and the quasi-free electron model.

II. IONIC COVALENT CURVE CROSSING MODEL INCLUDING THE VIBRATIONAL DEGREE OF FREEDOM

A/ Principle

Two sets of states $|\phi_{c,v}\rangle$ and $|\phi_{i,v'}\rangle$ corresponding respectively to the covalent $\text{Na} + \text{O}_2(v)$ and ionic $\text{Na}^+ + \text{O}_2^-(v')$ systems, are considered. These sets are only coupled by potential coupling terms

$$(1) \quad \langle \phi_{i,v'} | H | \phi_{c,v} \rangle = H_{12}. \langle v | v' \rangle$$

At each curve crossing, a diabatic transition probability P_{12} is given by the Landau Zener expression

$$(2) \quad P_{12} = \exp \left[- 2 H_{12}^2 \langle v | v' \rangle / \hbar v_r \Delta S_{12} \right]$$

where v_r is the radial velocity at the crossing point and

$$(3) \quad \Delta S_{12} = \left| \frac{dV_i(R_c)}{dR} - \frac{dV_c(R)}{dR} \right|$$

The entrance channel is one of the covalent curve corresponding to an excited atom in one of the (n, l) state, with an approach angle θ in the molecular frame and an oxygen molecule in the $^3\Sigma_g^-$ and $v=0$ ground state. Due to the centrifugal barrier, the relative motion will be reversed at the turning point and the representating point will end up in one of the exit channels, generally an excited sodium atom in another (n', l') state with an oxygen molecule in one of the three electronic states

$^3\Sigma_g^-$, $^1\Delta_g$ and $^1\Sigma_g^+$. At thermal energies here considered, ion pair formation is energetically forbidden.

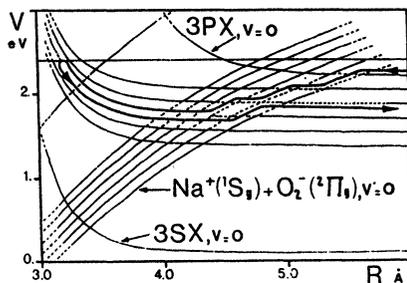


Figure 2a : In the vibronic network, motion of the Na-O_2 representing point for electronic to vibration transfer.

The representing point on the vibronic network may end up on an ionic curve after the first passage. The exit channel is then energetically forbidden and the representing point turns back towards another classical turning point. This is equivalent to a classical trajectory leading to complex formation (10).

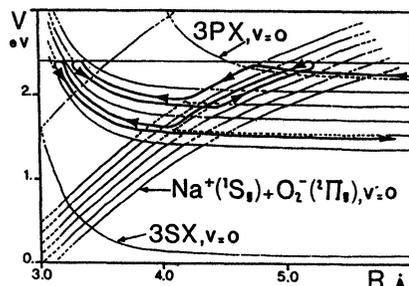


Figure 2b : Complex formation

The representing point may also appear on an ionic curve below the lowest ($3S, v=0$) covalent curve.

Reaction will then occur or not whether it is energetically allowed or not, and whether or not these initial dynamical conditions are favorable.

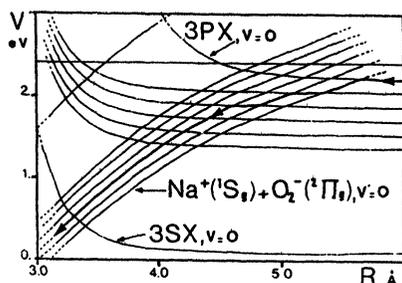


Figure 2c : Reaction

The validity of this many channel model of non adiabatic coupling has been examined by Child and Baer, and Klomp and Los. The BFG model does not allow for interferences between different paths in the vibronic network and requires a loss of memory of the vibrational phases between each crossing. For the excited sodium atom-oxygen molecule collisions at thermal energies here considered, the classical times between two electronic crossings are longer than $2 \cdot 10^{-14}$ s, vibrational period of O_2 , justifying the use of the BFG model.

For molecules such as N_2 or H_2 with negative electron affinities, the ionic intermediate model, corresponding to crossings bet-

ween ionic and covalent curves, has been compared to ab initio surface calculations. The internuclear crossing distances are of the order of magnitude of the atom and molecule sizes. The charge transfer between the excited atom and the molecule still exists, but the potential energy curves are very distorted as compared to the negative molecular ion curves.

On the contrary, for molecules with positive electron affinities, the crossings between ionic and covalent systems take place at large internuclear distances. From ab initio calculations on alkali-halogen systems, one can infer that the negative molecular ion curves are not perturbed by the presence of the Na^+ core at internuclear distances larger than 10 \AA . The ionic model is thus probably valid for sodium energy levels above the 3P state.

B/ Vibronic network

The covalent potential curves are approximated by Lennard Jones potential curves.

$$(4) \quad V_c(R) = -\frac{C_6}{R^6} + \frac{C_{12}}{R^{12}} - [IP(n, l) - EA(v, v')]]$$

where $IP(n, l)$ is the ionization potential of the considered excited state (n, l) of the sodium atom, $EA(v, v')$ the vertical affinity of oxygen between the v level of O_2 and v' level of O_2^- . The C_6 coefficients are given by

$$(5) \quad C_6 = 2\alpha_{\text{O}_2} n^{*2} \left[5n^{*2} + 1 - 3l(l+1) \right]$$

where the oxygen polarizability is equal to 1.59 \AA^3 and n^* is the effective quantum number of state (n, l) .

The C_{12} coefficients are given by

$$(6) \quad C_{12} = (.9 \pm .3) 10^{-16} (\rho_{Na^*} + \rho_{O_2}) \text{ erg}$$

where ρ_{Na^*} and ρ_{O_2} are the electronic radii of Na^* and O_2 .

The expression of the potential energy of the ionic system is given by

$$(7) \quad V_i(R) = -\frac{e^2}{4\pi\epsilon \cdot R} - \frac{\left(\alpha_{O_2^-} + \alpha_{Na^+} \right)}{4\pi\epsilon \cdot 2R^4}$$

where $\alpha_{O_2^-} = 2.64 \text{ \AA}^3$ and $\alpha_{Na^+} = .18 \text{ \AA}^3$

The Franck Condon factors $\langle v|v' \rangle$ between the $O_2 + e$ and the O_2^- systems are computed with O_2 and O_2^- potential curve Morse expressions. The autodetachment process of the O_2^- ion above $v' = 3$ is ignored since it corresponds to a time scale $10^{-10} - 10^{-12}$ s much longer than the mean collision time (10^{-13} s).

The only adjustable parameter which is used here is the ionic covalent coupling matrix element H_{12} . Following Smirnov, Olson and Los, this H_{12} matrix element can be written, in reduced form, as

$$(8) \quad H_{12}^* = A \cdot R_c^* \cdot \exp(-B \cdot R_c^*)$$

where

$$(9) \quad H_{12}^* = H_{12}(R_c) \left(IP(n, 1) - EA(v, v') \right)^{1/2}$$

$$(10) \quad R_c^* = R_c \left(2 \cdot IP(n, 1) \right)^{1/2}$$

The ionic-covalent crossing distance R_c is given by $V_i(R_c) = V_c(R)$.

From a simple LCAO calculation extending to highly excited states the method of Grice and Herschbach (9), we deduced the following numerical values of the A and B coefficients : A = 1.73, B = .7 corresponding to

the electron affinity of O_2 . Several values of B were tried in order to fit the available experimental data keeping the A coefficient constant.

Following Gislason (1), a simple estimate of the angular dependence of the ionic covalent coupling element upon the angle between the collision axis can be deduced from the respective symmetry properties of the covalent and ionic atom-molecule surfaces :

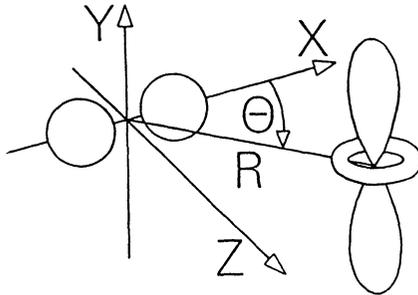


Figure 3 : Sodium-oxygen approach configuration

one combines the symmetry states of Na with those of O_2 in the three configurations corresponding to the three symmetry group $C_{\infty v}$, C_s and C_{2v} . When compared to the combined symmetries of Na and O_2 , two states are coupled or not whether they belong or not to the same irreducible representation. The H_{12} matrix elements are then approximated by

$$(11) \quad H_{12}(R, \theta) = H_{12}(R) F(\theta)$$

where $F(\theta)$ is a Legendre polynomial.

III. QUENCHING OF THE 3P STATE OF SODIUM BY OXYGEN MOLECULES.

The electronic to vibration energy transfer in collisions between the resonant 3P state of sodium by several molecules has been studied in beam experiments by Hertel (4) and Blais (5). By measuring the kinetic energy loss of the sodium atom after collision with a molecule, Hertel et al have determined the variation of the quenching cross section Q_q of the 3P state of Na as a function of the kinetic energy E_{cm} (in the center of mass frame) after collision. The experimental curve shown in figure (4) represents the energy dependance of the differential cross section $\left(\frac{dQ_q}{dE}\right) \cdot E_{cm}$.

The entrance channel $Na(3P) + O_2(^3\Sigma_g^-)$ corresponds to the three electronic states (with spin multiplicities 2 or 4) according to the three orbitals p_x , p_y , p_z of the sodium atom. Two cases are here considered in the molecular (and not the laboratory) frame : an equal mixture of the three p orbital of sodium or separately, the three p_x , p_y and p_z orbitals.

An alternative to the Landau Zener expression of the probability of the BFG model has been proposed by Barker, taking into account trajectories which are classically allowed on the lower adiabatic potential energy curves, but classically forbidden on the diabatic curves. The two expressions of the transition probabilities (BFG or Barker) have been tested and give very nearly the same results.

The best fit of the experimental data i. e. the total quenching cross section (10)

and the energy differential cross section (4) are displayed on figure 4.

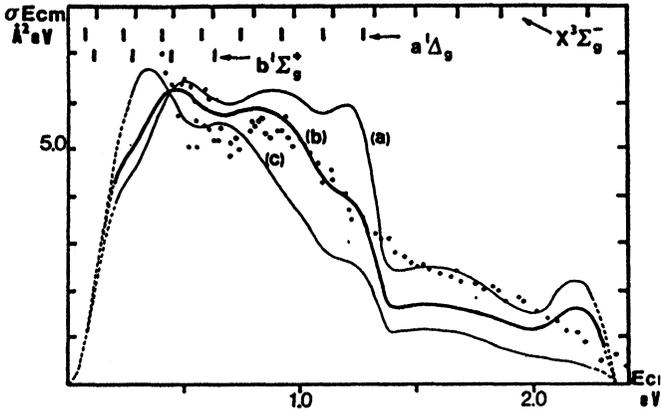
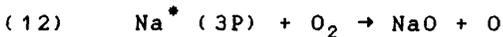


Figure 4 : Differential cross section for the quenching of the 3P state of sodium by oxygen molecules. Dots are experimental (reference 6). Curve (a) corresponds to the ionic-covalent H_{12} matrix element of Olson (ref 20), (b) to a B value of .8, (c) to a B value of .7.

The total quenching cross section does not appreciably vary for incident energies below .27 eV which corresponds to the energy threshold of the reaction



The influence of the values of the C_6 and C_{12} coefficients of the covalent potential (equations 5 and 6) has been tested by dividing these values by a factor of 2, leading to a 1% variation only of the total cross section.

In the vibronic network, the maximum number of 16 vibrational levels is necessary. If one reduces this number, for computation simplicity, to only 11 levels, the total cross

section does not appreciably diminish (41.4 \AA^2 instead of 42.3 \AA^2) but the bump of the experimental curve is not reproduced.

The internal reflexion which was first described in the BFG model, corresponds to exit channels on the ionic curves which are energetically forbidden and lead to several round trips as in complex formation. The behavior obtained in this work is similar to the results of Barker (10). Instead of considering an equal mixture of the orbitals of the Na atom, the cross sections have been calculated for the three entrance channels Na($3p_x$, $3p_y$, $3p_z$). The total cross-sections at relative energy of .15 eV are respectively 41.15, 43.1 and 43.8 \AA^2 . The energy transfer differential cross section depends strongly upon the prepared state.

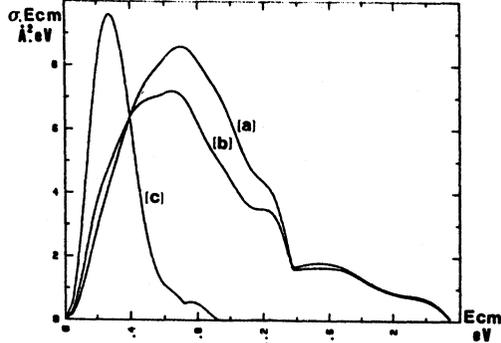


Figure 5 : Differential cross section for the Na $3p_x$ (a), $3p_z$ (b) and $3p_y$ (c) quenching by O_2 .

IV. INTERMULTIPLY MIXING AND REACTION.

The cross sections for collisional transfers from a given excited state of the

sodium atom towards the other excited levels, as well as the reaction cross section of these excited states with oxygen molecules have been calculated with the same preceding molecular parameters. For the reacting 4D state, it varies from 5 \AA^2 at .1 eV to 250 \AA^2 for .8 eV in good agreement with the experimental observations. The 4S state provides a cross section in between 2 and 20 \AA^2 in the same energy range. The main problem of this multiple crossing model is that the 5S and the 4D levels have reactive cross sections with the same order of magnitude, in contradiction with experiment. It is possible that for excited states, the exchanged electron behaves as if it were quasi-free. The selection rules for reaction become then those of creation of the O_2^- , the shape resonance is due to $l = 2$ (d wave) corresponding to a D state in the atomic symmetry group.

The multiple crossing model has been used with success by Gislason for the reaction of ground state alkali atoms with iodine. It is shown here that this model is able to predict the correct total cross section and reproduces the energy differential cross section for the quenching of a first resonant state by oxygen molecules. The intermultiplet quenching cross sections can be also predicted in the case of a large number of excited states involving more than hundred ionic and covalent potential energy curves without any approximation, but for rather highly excited states, this model must be used with caution when the symmetry of the reactants is taken into account.

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