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SOME ASPECTS OF ENERGY TRANSFER IN MOLECULAR AND ATOMIC COLLISIONS

George Elias Zahr
(Ph. D. thesis)

November 1976

Prepared for the U. S. Energy Research and Development Administration under Contract W-7405-ENG-48

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SOME ASPECTS OF ENERGY TRANSFER IN MOLECULAR
AND ATOMIC COLLISIONS

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DEDICATION

To the people who are struggling for freedom, justice, and peace. To the people of Palestine with deep respect and love.
ACKNOWLEDGMENTS

I wish to express my sincere gratitude for the encouragement and guidance of Prof. William H. Miller, under whose direction this work was made possible.

Special thanks are due to Dr. Richard K. Preston whose collaboration with the quenching of O(1D) problem is deeply appreciated.

Thanks are also to Prof. Henry F. Schaefer III for stimulating discussions and valuable suggestions on the potential energy surface calculations of the N$_2$-Na problem.

This work was supported in part by the U.S. Energy Research and Development Administration and National Science Foundation Grant GP-41509X.
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SOME ASPECTS OF ENERGY TRANSFER IN ATOMIC AND MOLECULAR COLLISIONS

By

George Elias Zahr

ABSTRACT

In part one it is maintained that quenching of $O(^1D)$ by collision with $N_2$ and the ionization of Na by collision with vibrationally excited $N_2$ proceed via the formation of a collision complex. Once the complex is formed, even a weak coupling between the two states involved, can induce a large transition probability because the crossing seam of the two potential energy surfaces is passed many times during the life of the complex. Qualitatively reasonable potential energy surfaces for $O(^1D) + N_2$ are constructed and classical trajectory calculations carried out to show that the cross section for complex formation is indeed appreciable; a statistical model is used to determine the quenching probability of the complex; results are in good agreement with experiment. Ab initio (SCF) potential energy surface calculations are carried out for $N_2$-Na, $N_2$-Na$^+$, and $N_2$-Na$^+$ systems; the points are fit to simple standard functions; a statistical model is developed for the ionization of Na by vibrationally excited $N_2$.

In part two the classical S-Matrix theory is applied to rotational excitation of CO by collision with He; the results are in qualitative agreement with quantum mechanical calculation.
POTENTIAL ENERGY SURFACE CROSSING PHENOMENA

I. INTRODUCTION

Any problem in theoretical chemistry can be solved exactly and completely if the Schrödinger equation for the system can be solved. However, at the present stage of mathematical advancement it is not possible to solve the Schrödinger equation for many systems, as a matter of fact the Schrödinger equation of very few simple systems has been solved exactly, and most of the work in the field deals with introducing approximate solutions that work in some cases and do not work in others. A very important approximation in Quantum Mechanics that made it possible to simplify Schrödinger equation to solve many problems is the Adiabatic Approximation. (1) This approximation is based on the simple fact that the masses of the nuclei are very large compared to the masses of the electrons, so they move much slower than the electrons. This makes it possible to separate the nuclear motion from the electronic motion on the basis that the energy associated with the nuclear motion is negligible compared to the energy associated with the electronic motion, and thus the electrons do not feel the nuclear motion.

The Hamiltonian for a system of nuclei and electrons (molecule) has the form

\[ H = \sum_N T_N + H_{el} \]  

(1.1)

where \( T_N \) is the Kinetic energy for nucleus \( N \) and \( H_{el} \) is the electronic
Hamiltonian which has the form

$$H_{el} = \sum_n T_n + V$$

(1.2)

where $T_n$ is the kinetic energy for electron $n$, and $V$ is the electrostatic potential among all the electrons and nuclei.

In the Zeroth order approximation assuming the nuclei are stationary, the problem reduces to solving the Schrödinger equation

$$H_{el} \Phi_i(r;R) = U_i(R) \Phi_i(r;R)$$

(1.3)

where $r$ is the electrons coordinates and $R$ is the nuclear coordinates. The wave function $\Phi_i(r;R)$ is parametrically dependent on $R$.

Now, it is possible to expand the wave function of the total Hamiltonian in the form

$$\psi(r,R) = \sum_i X_i(R) \Phi_i(r;R)$$

(1.4)

and solve the Schrödinger equation

$$H \psi(r,R) = E \psi(r,R)$$

(1.5)

substituting (1.1) and (1.4) in (1.5) one gets

$$\left( \sum N T_N + H_{el} \right) \sum_i X_i(R) \Phi_i(r;R) = E \sum_i X_i(R) \Phi_i(r;R)$$

using (1.3) and multiplying from the left by $\Phi_j^*(r;R)$ and integrating over $r$ the electrons coordinates

$$\sum_i \langle \Phi_i(r;R) | \sum N T_N X_i(R) \Phi_i(r;R) \rangle + U_j(R) X_j(R) = E X_j(R).$$

Let us assume that we only have two states

$$\sum_{i=1}^2 \langle \Phi_i(r;R) | \sum N T_N X_i(R) \Phi_i(r;R) \rangle + U_1(R) X_1(R) = E X_1(R)$$

(1.6-a)
\[ \sum_{i=1}^{2} \langle \phi_2 (r; R) | \sum_N T_N | X_i (r; R) \phi_1 (r; R) \rangle + U_2 (R) X_2 (R) = E X_2 (R) \] (1.6-b)

\[ T_N = \frac{1}{2 M_N} V_N^2 \] (4)

where \( M_N \) is the mass for nucleus \( N \)

\[ X_i = X_i (r; R), \quad \phi_i = \phi_i (r; R) \]

\[ T_N | X_i \phi_i \rangle = \frac{1}{2 M_N} V_N \left[ | \phi_1 \rangle V_N X_i + | \phi_1 \rangle V_N X_i + \right] \]

\[ = \frac{1}{2 M_N} \left[ V_N | \phi_1 \rangle V_N X_i + | \phi_1 \rangle V_N X_i + V_N^2 | \phi_1 \rangle X_i + \right] \]

\[ \left( T_N | X_1 \phi_1 \rangle \right) = \frac{1}{2 M_N} \left[ V_N | \phi_1 \rangle V_N X_1 + | \phi_1 \rangle V_N X_1 + V_N^2 | \phi_1 \rangle X_1 + \right] \]

with some mathematical manipulation we can show for a two state system (see Appendix A)

\[ \langle \phi_1 | V_N^2 | \phi_1 \rangle = - [\langle \phi_1 | V_N | \phi_2 \rangle]^2 \] (1.8-a)

\[ \langle \phi_2 | V_N^2 | \phi_2 \rangle = - [\langle \phi_2 | V_N | \phi_1 \rangle]^2 \] (1.8-b)

\[ \langle \phi_1 | V_N | \phi_1 \rangle = 0 \] (1.8-c)

\[ \langle \phi_1 | V_N^2 | \phi_2 \rangle = V_N \left[ \langle \phi_1 | V_N | \phi_2 \rangle \right] \] (1.8-d)

\[ \langle \phi_2 | V_N^2 | \phi_1 \rangle = V_N \left[ \langle \phi_2 | V_N | \phi_1 \rangle \right] \] (1.8-e)

substituting 1.8 and 1.7 into 1.6 and writing it in a matrix form

\[
\begin{bmatrix}
H_{11} - U_1 & H_{12} \\
H_{21} & H_{22} - U_2
\end{bmatrix}
\begin{bmatrix}
X_1 \\
X_1
\end{bmatrix}
= 0
\]
where

\[ H_{11} = \sum_N \frac{1}{M_N} \left[ \nabla_N^2 - \langle \phi_1 | \nabla_N | \phi_2 \rangle^2 \right] + E \]

\[ H_{12} = \sum_N \frac{1}{M_N} \left[ 2 \langle \phi_1 | \nabla_N | \phi_2 \rangle \nabla_N + \nabla_N - \phi_1 | \nabla_N | \phi_2 \rangle \right] \]

\[ H_{21} = \sum_N \frac{1}{M_N} \left[ 2 \langle \phi_2 | \nabla_N | \phi_1 \rangle \nabla_N + \nabla_N - \phi_2 | \nabla_N | \phi_1 \rangle \right] \]

\[ H_{22} = \sum_N \frac{1}{M_N} \left[ \nabla_N^2 - \langle \phi_2 | \nabla_N | \phi_1 \rangle^2 \right] + E \]

The adiabatic approximation is based on the assumption that \( \langle \phi_i | \nabla_N | \phi_j \rangle \) is negligible compared to other terms. The Schrödinger equation simplifies to the following form

\[ \left[ \sum_N \frac{1}{M_N} \nabla_N^2 + U_i \right] X_i = E X_i \]

Here the electronic eigenvalue is the potential energy that describes the nuclear motion. However the adiabatic approximation is valid only if \( U_1(R) \) and \( U_2(R) \) are not close to each other.\(^{5}\) When \( U_1(R) \) and \( U_2(R) \) are close to each other, terms of the form \( \langle \phi_i | \nabla_N | \phi_j \rangle \) are not negligible\(^{6}\) and we cannot anymore interpret \( U_i(R) \) as the potential energy that describes the nuclear motion. Such situations arise when the two potential energy surfaces (curves) cross each other or have an avoided crossing. In the area of the nuclear space around the crossing point the adiabatic approximation is not valid and we can't talk in terms of potential energy surfaces. The coupling between the two states that causes this effect is called the Nonadiabatic Coupling.
To overcome this problem of nonadiabatic coupling an approximate method had been developed in which the nonadiabatic coupling is confined to the crossing seam (point) and the adiabatic approximation is assumed to be valid everywhere else.

Molecular and atomic collision problems which involve more than one state are of the most important problems that include this type of potential energy surface crossing. Interest in solving these problems has risen very much in the past decade due to the advancements made in the field of molecular and atomic beam experiments which started providing very detailed data about molecular and atomic collisions.

An example is shown in Fig. 1; let us assume that the interaction between the two species A and B in the ground state is described by the potential energy curve 1, and that the interaction between them in the excited state is described by the potential curve 2. Let us also assume that the two curves cross each other at the point \( R = R_0 \); where \( R \) is the distance between A and B. This example represents a very common problem in chemical kinetics, and there are many questions about this problem that we have to find answers for: If A and B are in one of their two states described above before the collision, what is the probability of finding them in the other state after the collision?; what is the probability of forming an AB complex?; how long this complex lives?; or what is the effect of internal degrees of freedom in both A and B on the course of the collision?; and many
Figure 1. A model example of potential energy curve crossing; where curve 1 describes the excited state, curve 2 describes the ground state, and $R_0$ is the crossing point. (Internal degrees of freedom of A and B are not included in the Figure.)
Figure 1
other questions of this sort. To show how we deal with the above questions within the framework of the adiabatic approximation, let us try to answer the first one. Assume that A and B were in the excited state (state 2, Fig. 1) before the collision; what is the probability of finding them in the ground state (state 1) after the collision?

The motion of the two species as they approach each other \( R > R_0 \) is described by curve 2 until they get to the point \( R = R_0 \). At this point there is a nonadiabatic coupling between the two states and thus there is a specific probability \( (P_{12}) \) to continue on curve 1 and a probability of \( (1 - P_{12}) \) to continue on curve 2. The two species continue approaching each other until they get to the turning points on both curves. Again on the way back there is also the same probability of changing curves at \( R = R_0 \), assuming that the internal motion of both species A and B is frozen. With this simple analysis we see that the probability of being in the ground state after the collision is

\[
P_{1+2} = P_{12}(1 - P_{12}) + (1 - P_{12})P_{12}.
\]

The first term represents the probability of changing to curve 1 as A and B approach each other multiplied by the probability of staying on curve 1 as they depart. The second term represents the probability of staying on curve 2 as the two particles approach each other multiplied by the probability of changing to curve 1 as they depart.

It is clear in the above problem that the crossing point has been passed twice during the collision. However if the internal degrees of freedom of both A and B are included, the problem gets more
complicated and the crossing point will be a crossing line or may be even a crossing surface depending on the number of degrees of freedom involved. Also the number of times the crossing seam (point, line or surface) is passed during the collision depends on the nature of the two potential energy surfaces that describe the system. The transition probability is not the same either, its value depends on the nature of the potential energy surfaces at the specific point at which the passing of the crossing seam occurs, and it also depends on the amount of kinetic energy in the degrees of freedom involved in the passing of the crossing seam.

Two specific systems have been chosen to demonstrate the above complicated aspects of these types of problems. The first system is the quenching of oxygen (\(^1\text{D}\)) state atoms to oxygen (\(^3\text{P}\)) state by collision with nitrogen molecules. This system is discussed extensively in Chapter II. The second system is the penning ionization of Sodium by colliding with vibrationally excited \(\text{N}_2\). This system is discussed in Chapter III.

Footnotes and References

(1) This is also called Born-Oppenheimer Approximation; for more details see any standard quantum mechanics book e.g., L. Schiff, Quantum Mechanics, McGraw-Hill, New York, New York, 1955, pp. 289-290.
(2) Spin is excluded in this Hamiltonian.

(3) Where $X_i(R)$ a function that depends on nuclear coordinates $R$ only.

(4) $\hbar$ has been dropped on the assumption that atomic units are used where $\hbar = 1$.


II. QUENCHING OF O(1D) BY N₂

Reactions of electronically excited O(1D) has been the focus of many experimental studies, due to the importance of O(1D) in the chemistry of the atmosphere. This initiated many theoretical studies among which is the quenching of O(1D) by N₂. N₂ is considered to be the most important quencher of O(1D) in the upper atmosphere, thus making the study of this reaction an important one.

The quenching of O(1D) by N₂ has been a puzzle for theoreticians for some time, although the nature of the interaction that causes the transition is known to be the spin-orbit coupling between the two potential energy surfaces, the singlet "O(1D) and N₂" and the triplet "O(3P) and N₂". Attempts to explain this process without including the internal degrees of freedom of N₂ by using the simple atom-atom model had two major problems. First, since in this model the crossing point of the singlet and triplet curves is passed only twice - once as the particles approach each other and once as they depart - the spin-orbit coupling is too weak to explain the large transition probability for the process. Second, there is no way for the atom-atom model to explain the 2eV vibrational excitation of the N₂ product. To be able to explain these two experimental results of this reaction, internal degrees of freedom of N₂ have to be included.
Since the singlet potential energy surface is attractive, it is reasonable to assume that as the $^1D_0$ and $N_2$ collide, enough translational energy transfers to rotational and/or vibrational degrees of freedom of $N_2$ to trap the $^1D_0$ in an $N_2O$ complex. For example, at thermal energies this requires only a rotational excitation by six rotational levels ($\Delta j = 6$). It is clear now that if the trapping occurs the crossing point is passed much more than twice, and the small transition probability due to the weak spin-orbit coupling adds up as many times as the passing of the crossing point occurs to produce the known large transition probability for the process. Also due to the trapping enough energy from the $N_2$-O degree of freedom transfer to the N-N degree of freedom to produce the approximately 2eV vibrational excitation in the product $N_2$.

The approach in this chapter is very similar to that of Tully; however, the cross section for complex formation was not estimated from the potential as Tully did, but was evaluated from classical trajectories, and the statistical approximation used here is somewhat different from that of Tully.

The rest of this chapter formulates this problem and presents calculations that support this point of view presented above. Sections A, B, C, and D describe the model and present the theoretical formulation for the reaction, section E has the potentials used, section F has the results and section G concludes this chapter with some final remarks.
A. The Model

There are more than one singlet potential energy surface arises as $O(1D)$ and $N_2$ approach each other, however only one of these surfaces is attractive ($X^1E^+$) which is the one we are interested in. Also there are more than one triplet potential energy surface arise as the $O(3p)$ and $N_2$ approach each other, and these surfaces are close to each other which makes it possible to simplify the problem and deal with them as one surface (Fig. 2). So the process

$$O(1D) + N_2 \rightarrow O(3p) + N_2$$

is now described by two potential energy surfaces; one is an attractive singlet designated as $V_1$, and one is a repulsive triplet designated as $V_2$. These two surfaces cross each other and at the crossing seam the transition occurs.

The above process can be adequately described by the Tully-Preston "surface hopping" model; in this model the adiabatic approximation is assumed to be valid all over the space except at the avoided crossing seam; thus transition from one potential surface to another is only possible at the crossing seam; the transition probability is given by a Landau-Zener like formula. In Tully and Preston's original work on the $H^+ + H_2$ reaction they calculated classical trajectories on the "adiabatic" potential energy surfaces that have an avoided crossing; if a transition occurs from one surface to another they had to adjust the velocity, because there is a gap between the two adiabatic surfaces
Figure 2. Schematic drawing of the potential energy curves that describe the N₂O molecule in the N₂ - O degree of freedom.
Figure 2
at the avoided crossing seam; this gap is caused by the relatively large electrostatic coupling between the two states. The present problem is more straightforward because the spin orbit coupling between the two states is small; this makes it possible to run the classical trajectories on the "diabatic" potential energy surfaces that actually intersect; since transition occurs at the crossing seam where the two potential energy surfaces have the same value, there is no need to adjust the velocity when a transition occurs.

In accordance with this model trajectories are started on surface $V_1$ with the two species separated and then run until the two species are separated again; as the trajectory goes on it passes the crossing seam many times and transition probability accumulates. To pick the initial conditions for the trajectory a maximum impact parameter $b_{\text{max}}$ is found first; this $b_{\text{max}}$ is the maximum value of impact parameter at which passing of the crossing seam is possible and any larger value of impact parameter is not of interest in this problem; then the initial conditions are selected by the usual Monte Carlo sampling methods. The quenching cross section $\sigma_Q$ is given by

$$\sigma_Q = \pi b_{\text{max}}^2 N^{-1} \sum_{n=1}^{N} p_Q(p_1^{(n)}, q_1^{(n)})$$

(2.2)

where $N$ is the total number of trajectories; $q_1$ and $p_1$ are initial cartesian coordinates and momenta of the trajectory; $n$ denotes the specific set of initial conditions for the $n^{\text{th}}$ trajectory; $p_Q(p_1^{(n)}, q_1^{(n)})$ is the quenching probability for the $n^{\text{th}}$ trajectory that starts with the initial conditions $p_1$ and $q_1$. 
The next step is to evaluate \( P_q(p_1, q_1) \); the Landau-Zenar approximation for not changing surfaces (diabatic surfaces) at a given crossing encounter is

\[
P = \exp\left(-\frac{2\pi}{\hbar} \frac{V_{12}(q(t))^2}{|\frac{d}{dt} \Delta V(q(t))|}\right)
\]

where \( V_{12}(q(t)) \) is the spin orbit coupling between the two states; \( \Delta V(q(t)) = V_2(q(t)) - V_1(q(t)) \); and all the variables are evaluated at \( t = t_0 \), \( t_0 \) being the root of the equation \( \Delta V(q(t)) = 0 \) (i.e., the time when the trajectory is at the seam). The probability of changing potential energy surfaces is \( 1 - P \). Within this surface-hopping model the net quenching probability \( P_Q \) is a sequence of probability factors \( P \)'s and \( 1 - P \)'s; one factor for each time the trajectory passes the crossing seam. Since the spin-orbit coupling \( V_{12} \) is very small the transition probability \( P \) in equation 2.3 is almost one and the probability of changing surfaces \( 1 - P \) is much smaller than one; it is essentially no approximation in such circumstances to neglect recrossing. This in reality means that once the trajectory has crossed from the singlet surface to the triplet one it has no chance of coming back to the singlet surface again. (According to Fig. 3, if the trajectory crossed on the way out it has no chance of passing the crossing seam again anyway, and if it crossed on the way in it has only one chance of passing the crossing seam). On the basis of the above assumption the only way of not quenching is not to quench every time the crossing seam is passed; thus the probability of not quenching \( 1 - P_Q \) is the product of the probabilities of not quenching at every single time the crossing seam is passed.
Figure 3. A sketch of the lowest singlet, $V_1(r)$, and a typical triplet, $V_2(r)$, potential curves for the O-N$_2$ system. The arrow depicts a thermal energy collision of O($^1$D) and N$_2$ which results in sufficient rotational/vibrational excitation of N$_2$ (occurring predominantly at the inner classical turning point) to form a collision complex.
where $P_k$ is the probability of not quenching at the kth time of passing the crossing seam. Substituting Equation 2.3 in 2.4 the net probability of not quenching is given by

$$1 - P_Q = P_1 P_2 \cdots P_k \cdots$$

(2.4)

$$1 - P_Q = \exp \left[ - \sum_k \frac{2\pi}{h} V_{12}(q(t))^2 / \left| \frac{d}{dt} \Delta V(q(t)) \right|_{t=t_k} \right]$$

(2.5)

where $t_k$ is the time at which the kth passing of the crossing seam occurs.

Now within the above described model classical trajectories should be run on the singlet surface; the probability of not quenching should be evaluated at every single time the crossing seam is passed and then the net probability of not quenching is calculated.

However as mentioned in the introduction of this chapter there is a complex formation; i.e., as the two particles approach each other on the singlet surface a large portion of the trajectories get trapped in the well. It is extremely difficult numerically, if not impossible, to follow precisely the dynamics of these trapped trajectories; this is due to the accumulation of numerical error in such long-lived trajectories. To alleviate this problem a statistical approximation has been developed.
B. Statistical Approximation

\[ 1 - P_Q = \exp \left[ -\sum \frac{2\pi}{h} V_{12}(q(t))^2 \right] \frac{d}{dt} \Delta V(q(t)) \bigg|_{t=t_k} \]

\[ = \exp \left[ -\int_{-\infty}^{+\infty} dt \, V_{12}(q(t))^2 \delta(\Delta V(q(t))) \right]. \quad (2.6) \]

Equation 2.6 for the probability of not quenching or the survival probability has the form of an exponential decay

\[ 1 - P_Q = \exp \left[ -\int_{-\infty}^{+\infty} dt \, \Gamma(t) / h \right] \quad (2.7) \]

where \( \Gamma(t) \) has the golden rule like expression

\[ \Gamma(t) \equiv \Gamma(q(t)) = 2\pi V_{12}(q(t))^2 \delta(\Delta V(q(t))) \]. \quad (2.8) \]

The quenching probability to be used in Equation 2.2 is given now by

\[ P_Q = 1 - \exp \left[ -\int_{-\infty}^{+\infty} dt \, \frac{2\pi}{h} V_{12}(q(t))^2 \delta(\Delta V(q(t))) \right] \quad (2.9) \]

where \( q(t) \) in the exponent is the coordinates of the system that are described by the classical trajectories on the singlet surface. Since, as mentioned earlier, it is difficult to follow the dynamics of the trajectory precisely one invokes the ergotic hypothesis. This hypothesis assumes random distribution of energy in the different degrees of freedom,
thus making it possible to replace the time integral in Equation 2.9 by a phase space average; to demonstrate that, consider the quantity $A(p_1, q_1)$ the exponent in Equation 2.9.

$$A(p_1, q_1) = \int dt \Gamma(q(t, p_1, q_1)/\hbar$$

(2.10)

The trajectory $q(t, p_1, q_1)$ is determined by its initial conditions $p_1$ and $q_1$. If this trajectory forms a collision complex that lives long enough we can assume that the trajectory behaves ergodically, i.e., the energy distribution in the different degrees of freedom of the collision complex is random, thus any combination of coordinates and momenta that is permitted by the total energy and total angular momentum is equally probable. This means that the trajectory will be the same as any other trajectory that has the same total energy, the same total angular momentum and forms a long lived collision complex. The dependence of the quantity $A(p_1, q_1)$ on $p_1$ and $q_1$, the initial conditions of the trajectory, will be only through the constants of the motion, total energy $E$ and total angular momentum $J$; and the time average of $\Gamma(q(t, q_1, p_1))$ can be replaced by a phase space average. In mathematical formulation this means

$$A(p_1, q_1) = \tau \left[ \frac{1}{\tau} \int dt \Gamma(q(t, p_1, q_1))/\hbar \right]$$

(2.11-a)

$$\Rightarrow \tau < \Gamma/\hbar >_{E, J} = A(E, J)$$

(2.11-b)
where the phase space average \( \langle x \rangle_{E,J} \) for any function \( x(p,q) \) is defined by

\[
\langle x \rangle_{E,J} = \rho^{-1}(E,J) \int dp \int dq \ x(p,q) \delta(E-H(p,q)) \delta(J-J(p,q)) h(f(q))
\]

and

\[
\rho(E,J) = \int dp \int dq \ \delta(E-H(p,q)) \delta(J-J(p,q)) h(f(q))
\]

where \( \delta(\ ) \) is the usual delta function

\[
\delta(x) = \begin{cases} 
1 & \text{for } x = 0 \\
0 & \text{for } x \neq 0
\end{cases}
\]

\( h(\ ) \) is the step function

\[
h(x) = \begin{cases} 
1 & \text{for } x > 0 \\
0 & \text{for } x < 0
\end{cases}
\]

\( H(p,q) \) is the Hamiltonian, which is the value of total energy of the system at the phase space point \( (p,q) \). \( J(p,q) \) is the value of total angular momentum of the system at the phase space point \( (p,q) \) and \( f(q) \)\(^{(16)} \) is the function that defines the collision complex by the following way: the equation \( f(q) = 0 \) defines a closed surface in the phase space inside of which is the collision complex; \( f(q) > 0 \) being the inside of this "critical surface" and \( f(q) < 0 \) being the outside of it. The values of
total energy \( E \) and total angular momentum \( J \) are determined by the initial conditions

\[
E = H(p_1, q_1)
\]

\[
J = J(p_1, q_1)
\]

If we look now at the phase space average in Equation 2.12 we notice that the step function eliminates all phase space points outside the critical surface that defines the collision complex. This happens because the value of the step function is zero for all these points \((f(q)<0)\); also the two delta functions limit the integral to those points that correspond to total energy \( E \) and total angular momentum \( J \), i.e., they fulfill the following equations

\[
E = H(p, q) \quad (2.13-a)
\]

\[
J = J(p, q) \quad (2.13-b)
\]

Thus the phase space average in Eq. 2.12 is over all points that are accessible by the energy and momentum restrictions at which a collision complex is formed.
The average life time \( \tau = \tau(E,J) \) in Eq. 2.11) for the collision complex is given also by the statistical theory; it is the reciprocal of the average rate of flux out through the critical surface \( f(q) \).

\[
\tau(E,J)^{-1} \equiv \frac{d}{dt} h(f) h(-\frac{df}{dt}) >
\]  

(2.14)

where the first term evaluates the total flux across the surface \( f(q) = 0 \), and the second term keeps only the flux that is going out by having the value zero if \( \frac{df}{dt} > 0 \) and having the value one if \( \frac{df}{dt} < 0 \), i.e. if \( f(q) \) is decreasing (going from inside to out) the average is kept, otherwise it is put to zero.

Since

\[ h'(x) \equiv \delta(x), \]

\[
\tau(E,J)^{-1} = < S(f) \ f \ h(-\dot{f}) >, \quad (2.15)
\]

since the flux in and the flux out is equal, Eq. 2.15 can be simplified to

\[ \tau(E,J)^{-1} = < \frac{1}{2} \delta(f) \ |\dot{f}| > \quad (2.16) \]

where the absolute value added to \( \dot{f} \) make both flux in and flux out positive and then the average of half of that is taken to represent the flux out.
\[ f(q) = \frac{d}{dt} f(q) = \frac{3f(q)}{\partial q} \cdot \frac{p}{m} \]  

(2.17)

The quenching probability is now given by

\[ P_Q(p_1, q_1) = P_Q(E, J) \]  

(2.18)

where

\[ E = H(p_1, q_1) \]

\[ J = J(p_1, q_1) \]

and where

\[ P_Q(E, J) = 1 - \exp \left\{ -\tau(E, J) \frac{\Gamma}{\hbar} \delta(E, J) \right\} \]

(2.19-a)

\[ = 1 - \exp \left\{ -\frac{2\pi}{\hbar} \sqrt{\frac{2}{m}} \frac{\delta(\Delta V)}{\delta(\delta(p))} \frac{\delta(\delta(p))}{\delta(E, J)} \right\} \]

(2.19-b)

Due to mathematical complexity in the application of this theory for the specific problems we are dealing with here in this chapter and the one in the next chapter, an additional approximation is made; the conservation of angular momentum is not taken into account, i.e., the delta function involving the total angular momentum is dropped. (17)
As a result of that the average quenching probability is given only as a function of total energy and Equation 2.19 becomes

\[ P_Q(E) = 1 - \exp \left[ -\tau(E) \frac{\Gamma}{h} \right] \quad \text{(2.20-a)} \]

\[ = 1 - \exp \left[ -\frac{2\pi \sqrt{2}}{\hbar} \delta(\Delta V) \frac{\delta(f)}{\delta(f)} \frac{\delta(f)}{\delta(f)} \right] \quad \text{(2.20-b)} \]

where now the phase space average \( \langle x \rangle_E \) for any function \( x(p,q) \) is the microcanonical average, and in this specific case, over the region of the collision complex only.

\[ \langle x \rangle_E = \rho(E)^{-1} \int dp \int dq \, x(p,q) \delta(E-H(p,q)) \, h(f(q)) \quad \text{(2.21-a)} \]

\[ \rho(E) = \int dp \int dq \, \delta(E-H(p,q)) \, h(f(q)) \quad \text{(2.21-b)} \]

Appendix B gives details about the evaluation of the phase space integrals in Eq. 2.21.

With the above statistical approximation the model is simpler and especially with the quenching probability depends only on total energy; for the cross section for quenching, it gets much simpler and it can be separated into two terms.
\[ \sigma_Q(E) = \sigma_c(E) \cdot P_Q(E) \]  \hspace{1cm} (2.22)

where \( P_Q(E) \) is the quenching probability of the collision complex which can be evaluated by solving Equation 2.20, and \( \sigma_c(E) \) is the cross section for complex formation which can be evaluated from classical trajectories as follows:

\[ \sigma_c(E) = \pi b_{\text{max}}^2 \left( \frac{N_c}{N} \right) \]  \hspace{1cm} (2.23)

where \( b_{\text{max}} \) is the maximum impact parameter as described before in Section A, \( N_c \) is the number of trajectories that get trapped in the well and form a collision complex, and \( N \) is the total number of trajectories. It is important to say that initial conditions for these trajectories are chosen by the monte carlo method. \(^{(13)}\)

Now we have the quenching cross section as the cross section for complex formation multiplied by the average quenching probability for this complex.

C. Distribution of Product States

To obtain rigorously the product vibrational energy states distribution one has to go back to the above described Tully-Preston's "surface hopping model" and follow up the trajectories until they come back to the asymptotic region. As mentioned earlier, following up these
trajectories is extremely difficult due to the long-lived collision complex formation. Even if the trajectories are followed the accumulation of numerical errors is a problem that cannot be avoided. However the portion of energy that appears as a vibrational excitation of the product $N_2$ can be evaluated within the spirit of the above described statistical approximation.

Although the ergodicity assumption permits continuous energy transfer from one degree of freedom to another in the collision complex, one can safely assume that as the fragments of the complex depart there is no more exchange in energy between the newly becoming translational degree of freedom and the internal degrees of freedom of the fragments. In this specific case the assumption is that as the $N_2$ and $O$ depart there is no energy exchange between the relative translational energy and the vibrational energy of $N_2$. Since after the transition from the singlet to the triplet surface the fragments depart, then the amount of energy in the N-N degree of freedom of the collision complex at the point of transition is the same amount of energy that should appear as the product $N_2$ vibrational energy. The probability $P(E, \varepsilon)$ for a collision complex to quench and for the energy $\varepsilon$ to be the product $N_2$ vibrational energy is proportional to

$$P(E, \varepsilon) \sim \Gamma h \delta(\varepsilon - h_{\text{vib}}) \quad (2.24)$$

where $h_{\text{vib}}$ is the Hamiltonian for N-N vibration and the delta function
\[ \delta(\varepsilon - \hbar_{\text{vib}}) \] picks those points in the phase space where the amount of energy in the N-N vibration is equal to \( \varepsilon \).

Probability conservation says that

\[ P_Q(E) = \int d\varepsilon \, P_Q(E,\varepsilon) \quad (2.25) \]

and thus

\[ P_Q(E,\varepsilon) = P_Q(E) \frac{\Gamma/\hbar \cdot \delta(\varepsilon - \hbar_{\text{vib}})}{< \Gamma/\hbar >_E}. \quad (2.26) \]

The cross section for quenching with product N\(_2\) vibrational energy equal to \( \varepsilon \) is now given by

\[ \sigma_Q(E,\varepsilon) = \sigma_c(E) \, P_Q(E,\varepsilon). \quad (2.27) \]

As a result of probability conservation there is a cross section conservation and integrating \( \sigma_Q(E,\varepsilon) \) over all \( \varepsilon \) will give the total quenching cross section

\[ \sigma_Q(E) = \int d\varepsilon \, \sigma_Q(E,\varepsilon). \quad (2.28) \]
D. Additional Theoretical Comments

In the above described theoretical model there are two important outcomes that will not be used directly in this work, but it would be very useful to point out:

1. The model described by Equations 2.2 and 2.9 dealt with one potential energy surface crossing another; however it is easy to see that this model extends easily for the case where one potential energy surface crosses more than one other surface or a continuum of surfaces. This last case is one of importance because it describes penining ionization problems of the type

\[ A^* + BC \rightarrow A + BC^+ + e \]  \hspace{1cm} (2.29)

These problems are easier in some ways since the earlier assumption of neglecting recrossing is rigorously valid here; this is so because when the crossing occurs the electron leaves the scene of the reaction thus making the reaction irreversible. There is a modification that has to be made to make the model fit; the width function \( \Gamma(q) \) is no longer restricted to a single crossing seam and hence the delta function \( \delta(\Delta V) \) that picks the crossing seam has to be changed to a density of states \( \rho(q) \) since the final states are a continuum of states instead of a single state.
\[ \delta(\Delta V) \rightarrow \rho(q) \quad (2.30) \]

As a matter of fact the delta function itself describes the density of states in the quenching problem and it is a delta function only because the final state is discrete. The modification makes the model applicable to solve penning ionization problems like the one described in Equation 2.29.

2. Another outcome of this model is an expression for the rate of unimolecular decay for \( \text{N}_2\text{O} \). It can easily be seen that a vibrational excited state of the molecule acts very much like a collision complex, and the decomposition of an excited state of the molecule is very much like the framentation of a collision complex. The unimolecular theory gives the rate constants for unimolecular decay as

\[
K_{\text{uni}}(\omega) = Q_0(\beta)^{-1} \int dE \, \rho(E) \, e^{-\beta E} \frac{\omega k(E)}{\omega + k(E)}
\]

(2.31)

where \( \omega \) is the collision frequency with both molecules, and \( Q_0(\beta) \) is the partition function

\[
Q_0(\beta) = \int dE \, \rho(E) \, e^{-\beta E}
\]

(2.32)

where \( \beta = \frac{1}{kT} \), \( k \) is the boltzmann constant, \( T \) is the temperature, and \( \rho(E) \) is as defined in Eq. 2.21-b. The statistical model gives the microcanonical unimolecular decay rate as: the average rate of flux
out through a critical surface placed at the crossing seam multiplied by the probability of transition (quenching) to the triplet potential energy surface.

\[ k(E) = \tau(E)^{-1} P_Q(E) \]  

(2.33)

where \( \tau(E)^{-1} \) describes the flux as in Equation 2.16 and the critical surface \( f(q) \) is chosen such that \( f(q) = \Delta V(q) \); \( P_Q(E) \) is the same as described in Equation 2.19.

Now in the strong coupling limit \( (V_{12} \to \infty) \) the two adiabatic surfaces are largely separated and the transition probability \( P_Q(E) \to 1 \) (see Fig. 4) and the microcanonical unimolecular decay rate becomes the flux out through the critical surface,

\[ \lim_{V_{12} \to \infty} k(E) = \tau(E)^{-1} = \frac{1}{2} \delta(f) |f| > \]  

(2.34)

and that is the standard RRKM unimolecular decay rate for a single potential energy surface where the "rate determining step" is the rate of reaching the critical surface and crossing it. In the weak coupling limit \( (V_{12} \to 0) \)

\[ P_Q = 1 - \exp\left[ -\tau(E) < \Gamma / \hbar >_E \right] \]

since the coupling is small \( \Gamma / \hbar \) is very small and we can use the
Figure 4. A schematic drawing of two potential energy surfaces avoiding crossing; (a) shows the large coupling limit where the adiabatic surfaces have a large separation at the crossing point; (b) shows the small coupling limit where the adiabatic surfaces have a small separation at the crossing point.
Figure 4

Critical Surface
approximation

\[ p_Q = \tau(E) <\Gamma/h>_E \]  \hspace{1cm} (2.35)

and \( k(E) \) becomes

\[
\lim_{V_{12} \to 0} k(E) = \tau(E)^{-1} p_Q(E) = \tau(E)^{-1} \tau(E) <\Gamma/h>_E = <\Gamma/h>_E = \\
= <\frac{2\pi}{h} V_{12}^2 \delta(\Delta V)>_E \]  \hspace{1cm} (2.36)

where the "rate determining step" here is the transition from the singlet to the triplet surface.

E. Potential Energy Surfaces

To determine the cross section for complex formation it is necessary to know the singlet potential energy surface; by running classical trajectories on this surface all the information to evaluate \( \sigma_c \) in Eq. 2.23 can be obtained. For the quenching probability it is necessary to know both potential energy surfaces: the singlet and the triplet, and the coupling between them.

There is no exact form for these surfaces that is known at the present time, however there is enough spectroscopic and chemical data about \( N_2O, N_2, O^{(1)D}, \) and \( O^{(3)P} \) that we can use to build up a functional
Figure 5. A drawing of the N₂O molecule shows all the variables; r is the N-N distance, R is the distance between the oxygen atom and the center of mass of N₂, and γ is the angle between the two vectors r and R.
form for these two potential energy surfaces that will include their main features. \( V_1 \) the singlet surface is the one that there is more information about since it describes \( N_2O \) in its ground state. Two different model potentials for \( V_1 \) are used here. All parameters that appear in this section are in Table 1, and all variables are described by Fig. 5.

The first model potential surface \( V_1^I \) involves only translational-rotational coupling, and thus, in the trapping process that forms the collision complex only translational to rotational energy transfer can occur to cause the trapping. The function includes two terms: the first, describes the vibration of \( N_2 \) and uses only spectroscopic data about \( N_2 \); the second, describes the attractive potential between \( N_2 \) and \( O(1D) \), and includes the coupling between the rotational motion of \( N_2 \) and the translational motion. The coupling in this second term comes around due to the change in the depth of the well that the \( N_2 \) forms with \( O(1D) \) - as the system goes from the perpendicular case (\( \gamma=90^\circ \)) to the linear case (\( \gamma=0^\circ \) or \( 180^\circ \)). More specifically \( V_1^I \) has the form

\[
V_1^I(r,R,\gamma) = V_{N_2}^I(r) + V_{\text{int}}^I(r,R,\gamma)
\]  

(2.37)

where \( V_{N_2}^I \) is the morse potential for an isolated \( N_2 \) molecule

\[
V_{N_2}^I(r) = V_{N_2}(r) = D_1 \left[ e^{-2 \beta_{N_2} (r-r_{N_2})} - 2e^{-\beta_{N_2} (r-r_{N_2})} \right]
\]  

(2.38)
and \( V_{\text{int}}^{\text{I}}(r,R,\gamma) \) is an attractive Morse potential in which the well depth changes smoothly - from its value - for linear \( \text{N}_2\text{O} \) to its value for perpendicular \( \text{N}_2\text{O}^{(21)} \) - as \( \gamma \) changes from 0° or 180° to 90°.

\[
V_{\text{int}}^{\text{I}}(r,R,\gamma) = \left[ D_2 (1-\zeta(1-\cos^2 \gamma)) \right] \left[ e^{-2\alpha(R-R_e)} - 2e^{-\alpha(R-R_e)} \right]. \tag{2.39}
\]

The second model potential surface \( V_{\text{I}}^{\text{II}} \) includes translational-vibrational coupling in addition to the translational-rotational coupling. This is expected to change the cross section for complex formation; this change in the cross section will be a direct indication of the relative importance of the translational to vibrational energy transfer compared to the translational to rotational energy transfer in this mechanism. Translational-vibrational coupling was introduced by two adjustments added to \( V_{\text{I}}^{\text{I}}(r,R,\gamma) \): first, by allowing the Morse parameters in the first term to change their values as \( \text{O}^{(1D)} \) approaches \( \text{N}_2 \); when \( \text{N}_2 \) and \( \text{O}^{(1D)} \) are separated they have the values for an isolated \( \text{N}_2 \) molecule; as the \( \text{O}^{(1D)} \) gets close to \( \text{N}_2 \) they have values that give correct bonds force constants for \( \text{N}_2\text{O} \). Second, by replacing the distance \( R \) between \( \text{O}^{(1D)} \) and the center of mass of \( \text{N}_2 \) by the distance between \( \text{O}^{(1D)} \) and the closer \( \text{N} \) atom for the linear molecule. Thus the formula for the second model potential \( V_{\text{I}}^{\text{II}} \) is

\[
V_{\text{I}}^{\text{II}}(r,R,\gamma) = D_1 \left[ e^{-2\beta_1(r-r_1)} - 2e^{-\beta_1(r-r_1)} \right] + \left[ D_2 (1-\zeta(1-\cos^2 \gamma)) \right] \left[ e^{-2\alpha(R-r/2-r_0)} - 2e^{-\alpha(R-r/2-r_0)} \right]. \tag{2.40}
\]
where $\beta_1$ and $r_1$ depend on $R$ as follows:

$$\beta_1 \equiv \beta_1(R) = \beta_{N_2O} + (\beta_{N_2} - \beta_{N_2O}) S(R) \quad (2.41-a)$$

$$r_1 \equiv r_1(R) = r_{N_2O} + (r_{N_2} - r_{N_2O}) S(R) \quad (2.41-b)$$

and $S(R)$ is a "switching function"

$$S(R) = \frac{1}{2} + \frac{1}{2} \tanh(\lambda(R - R_0)) \quad (2.41-c)$$

where both $\lambda$ and $R_0$ are picked in such a way that

$$S(R) = \begin{cases} 1 & \text{large } R \\ 0 & \text{small } R. \end{cases}$$

So now for large $R$ where $N_2$ and $O(1^1D)$ are separated, $\beta_1$ and $r_1$ are equal to $\beta_{N_2}$ and $r_{N_2}$ respectively, and for small $R$ where $N_2O$ exists $\beta_1$ and $r_1$ are equal to $\beta_{N_2O}$ and $r_{N_2O}$ respectively; it is those later values of $\beta_1$ and $r_1$ that are the ones that give the right bond force constants for $N_2O$.

Constructing a model potential for the triplet surface is an easier job since we do not need a very detailed knowledge of this surface; the only place where this surface will be used is to evaluate the potential difference ($\Delta V$) that is used in computing the transition
probability. It is known that this surface is repulsive and it is assumed that as O(\(^3\)P) approaches \(N_2\), the \(N_2\) molecule does not get disturbed, i.e., its potential stays the same as isolated \(N_2\). So the potential surface we assume consists of two terms: the first one is a morse potential that describes isolated \(N_2\) molecules, and the second term is an exponential repulsion between O(\(^3\)P) and the center of mass of \(N_2\). There is a very minor dependence of repulsion energy in the second term on the angle \(\gamma\); it is reasonably assumed that there is less repulsion if O(\(^3\)P) approaches \(N_2\) on a path perpendicular to the \(N_2\) axis. The triplet model potential \((V_2)\) is now

\[
V_2(r,R,\gamma) = VN_2(r) + A(1 - \zeta'(1-\cos^2\gamma))e^{-\alpha'R}.
\] (2.42)

Since the quenching probability depends mainly on the number of times the crossing seam is passed, it is reasonable to assume that the changes in \(V_{12}(q)\) due to its position dependence can be neglected and \(V_{12}(q)\) can be assumed to be a constant

\[
V_{12}(r,R,\gamma) \equiv V_{12} = 80 \text{ cm}^{-1}.
\]

The value 80 cm\(^{-1}\) was chosen because it is the best known value for this coupling.\(^{(3),(4)}\)

Since the \(N_2\) molecule dissociation energy is more than 9.0 eV the only variable that limits the complex formation on the singlet
Table 1. Potential Parameters\textsuperscript{a}

\begin{align*}
D_1 &= 0.364 & \alpha &= 1.785 \\
D_2 &= 0.138 & \beta_{N_2} &= 1.423 \\
r_{N_2} &= 2.07 & \beta_{N_2O} &= 1.135 \\
r_{N_2O} &= 2.13 & \zeta &= 0.8285 \\
r_o &= 2.25 & \zeta' &= 0.01 \\
R_e &= r_o + \frac{1}{2} r_{N_2} &= 3.28 & A &= 0.75 \\
R_o &= 4.9 & a' &= 0.7 \\
R_c &= 8.0 & \lambda &= 1.7 \\
\end{align*}

\textsuperscript{a}All in atomic units. These numerical values refer to the potential functions described in Section E.
surface is the distance $R$ between the $O(1D)$ atom and the center of mass of the $N_2$ molecule. Thus the function that defines the region of the complex is a function of $R$ only. It can be taken to be

$$f(r,R,\gamma) = f(R) = R_c - R$$

(2.43)

such that $R_c$ is out on the singlet surface before the attractive part starts; this way it is assured that all complex formations will be in the region of positive $f(R)$, i.e., where $R < R_c$. Although it can't be claimed that the above potential energy surfaces are the exact ones or the most accurate ones possible, it can be claimed that they are qualitatively reasonable and have the main features of the system. The above surfaces should be able to answer very important questions about this system, such as, is there a complex formation? How important is it? What is the cross section for the complex formation?, and what is the relative importance of rotational and vibrational excitation in the complex formation?

F. Calculation and Results

The following quantities have to be calculated at each total energy: the cross section for complex formation $\sigma_c(E)$, the total quenching probability $P_Q(E)$, the probability of quenching with energy $\varepsilon$ as a product $N_2$ vibrational energy $P(E,\varepsilon)$. This later quantity $P(E,\varepsilon)$ has to be calculated for a set of values of vibrational energy $\varepsilon$ for each value of total energy $E$. 
1. **Cross Section for Complex Formation**

Classical trajectories on the singlet potential energy surface are calculated to compute $\sigma_c(E)$. Each trajectory is started with $N_2$ in the ground vibrational state ($v=0$) and the sixth rotational level ($j=6$); these conditions represent the most probable state of $N_2$ under thermal conditions; the initial translational energy is what is left of the total energy after internal energy (vibrational and rotational) of $N_2$ is deducted out. The rest of the initial conditions are chosen by the Monte Carlo method. (11) Although the trajectories are calculated on the singlet surface only, however every time the trajectory passes the crossing seam the transition probability is calculated; this way a very small number of trajectories will quench directly and a small cross section for direct quenching is calculated, (22) this cross section has to be added to the quenching cross section calculated from the complex formation to make the total quenching cross section. To verify the complex formation, trajectories are followed up to ten vibrations in the $N_2$-$O$ degree of freedom to make sure that they are trapped. The trajectory calculations were performed at three different collision energies 0.03, 0.6, and 1.2. Tables 2 and 3 show these results for surfaces $V_1^I$ and $V_1^{II}$ respectively.

As expected surface $V_1^{II}$ which includes vibrational coupling in addition to the rotational coupling gave larger complex formation cross sections than $V_1^I$ which had only the rotational coupling. At low collision energy (0.03 eV) the inclusion of vibrational
<table>
<thead>
<tr>
<th>E in eV</th>
<th>$b_{\text{max}}$ in a.u.</th>
<th>Total no. of trajec.</th>
<th>Product Distribution</th>
<th>Product</th>
<th>No. of trajec</th>
<th>Cross section Å$^2$</th>
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<td>0.03</td>
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<td>203</td>
<td></td>
<td>$\text{N}_2\text{O}$ (complex)</td>
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<td>$O(^1D)$</td>
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<td>$O(^3P)$</td>
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<td>0.28</td>
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<tr>
<td>0.6</td>
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Table 3. Trajectory Results for Potential Energy $V_1^{II}$

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<th>Product distribution</th>
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</tr>
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</tbody>
</table>
coupling increased the cross section only by approximately 25%. This indicates that the rotational excitation of $N_2$ at this energy can count for the majority of the collision complex formation. However at higher collision energy this is not true anymore and an increase of 100% and 500% in complex formation cross section occurs at collision energies of 0.6 eV and 1.2 eV respectively. At those higher energies the vibrational excitation of $N_2$ becomes more important than rotational excitation in the formation of the collision complex. This is very reasonable since at higher collision energies the amount of translational energy that has to be transferred to internal energy (rotational and vibrational) to cause the trapping of the trajectories becomes larger and vibrational excitations - since they are larger in energy than rotational excitation - become the important factor in the collision complex formation.

2. Total Quenching Probability $P_Q(E)$

This quantity is evaluated by solving Equation 2.19 numerically. Fig. 6 shows these results. At low collision energy the quenching probability is almost unity and the quenching cross section is the same as that for complex formation; at these energies the life time for the complex is very long and it can be said that approximately the complex stays there until it quenches. At low collision energies almost all the energy in the complex in excess of the ground state of $N_2O$ has to be in the $N_2--O$ vibrational degree of freedom so that the complex can die; while at higher energies a portion of this energy can be in other degrees of freedom and the complex still can die; and as
Figure 6. The quenching probability as a function of initial collision energy $E$, as defined by Eq. 2.20; the lower (upper) curve is the result of using singlet potential surface I (II). The insert shows the low energy region with an expanded energy scale.
the collision energy increases this portion of energy that can be in
other degrees of freedom increases, and thus the probability that the
collision complex dies at higher collision energies is higher and the life time for the complex is shorter.

3. Probability of Quenching with Product N₂ Vibrational Energy \( P_Q(E,\varepsilon) \)

Fig. 7 shows the vibrational energy distribution of N₂ where \( P_Q(E,\varepsilon)/P_Q(E) \) is plotted against \( \varepsilon \) for the three different collision energies 0.03, 0.6, and 1.2 eV, using potential energy surface \( V_{1}^{II} \). As the collision energy increases the distribution curve broadens and the average vibrational excitation energy \( \langle \varepsilon \rangle \) increases.

\[
\langle \varepsilon \rangle = \int \varepsilon \, d\varepsilon \frac{P_Q(E,\varepsilon)}{P_Q(E)} \cdot \varepsilon .
\] (2.44)

At room temperature \((E=0.03 \text{eV})\) the vibrational excitation energy is approximately 20\% of the exoergicity of the reaction which is in good qualitative agreement with the latest experimental results.\(^{(9)}\)

4. Quenching Cross Section \( \sigma_Q(E) \) and Quenching Rate Constant \( K_Q(T) \)

\( \sigma_Q(E) \) is calculated at the three energies 0.03, 0.6, and 1.2 eV from Equation 2.22 with simple addition of the direct quenching cross section. The thermally averaged quenching rate constant \( K_Q(T) \) is

\[
K_Q(T) = \frac{\int dE \, e^{-\beta E} K(E)}{\int dE \, e^{-\beta E}}
\] (2.45-a)
Figure 7. The distribution of vibrational energy $\varepsilon$ in the product $N_2$ molecule at three different initial collision energies $E$, as defined by Eq. 2.26; the quantity shown is also identical to the cross section ratio $\sigma_Q(\varepsilon,E)/\sigma_Q(E)$. Because the ratio of the probability distribution to the total quenching probability is plotted, the area under each curve is unity.
Figure 7

\[ P_Q(\epsilon, E)/P_Q(E) \]

- \( E = 0.03 \text{ eV} \)
- \( E = 0.6 \text{ eV} \)
- \( E = 1.2 \text{ eV} \)
and

\[ K(E) = \frac{1}{5} v(E) \sigma_Q(E) \]  \hspace{1cm} (2.45-b)

and

\[ K_Q(T) = \frac{1}{5} \frac{\int dE e^{-\beta E} v(E) \sigma_Q(E)}{\int dE e^{-\beta E}} \]  \hspace{1cm} (2.45-c)

\( \sigma_Q(E) \) is approximately constant in a small range of energy. In the denominator of Eq. 2.45-c the integral has value in a range of energy around \( E = kT \) and we can assume approximately that \( \sigma_Q(E) \) is a constant in that range. Thus

\[ K_Q(T) = \frac{1}{5} \frac{\int dE e^{-\beta E} v(E) \sigma_Q(E)}{\int dE e^{-\beta E}} \]  \hspace{1cm} (2.45-d)

\[ K_Q(T) = \frac{1}{5} \bar{v}(T) \sigma_Q(E) \]  \hspace{1cm} (2.46-a)

where

\[ E = kT \]  \hspace{1cm} (2.46-b)

and \( \bar{v}(T) \) is the thermally averaged velocity

\[ \bar{v}(T) = (8 kT/\pi r)^{1/2} \]  \hspace{1cm} (2.46-c)

and the 1/5 factor in Eq. 2.45-b accounts for the fact that out of the five potential energy surfaces that arise when \( N_2 \) and \( O(1D) \) approach each other only one of them is attractive; thus statistically
only 1/5 of the times that $N_2$ and $O^{(1)}D$ approach each other they get on the attractive singlet surface that causes the reaction to go. Table 4 shows the results for $c_Q(E)$ and $K_Q(T)$. At room temperature ($kT = 0.03$ eV) the rate constant of $3.9 \times 10^{-11}$ and $5.4 \times 10^{-11}$, using potential energy surfaces $V_1^I$ and $V_1^{II}$ respectively, is in excellent agreement with experimental value. (23) The values of the rate constant in Table 4 show that the rate constant is apparently not a sensitive function of temperature.

G. Concluding Remarks

The basic picture of the quenching mechanism - that as the reactants $O^{(1)}D$ and $N_2$ collide, enough translational energy goes into rotational and vibrational excitation of $N_2$ and a collision complex is formed; thus multiple passing of the crossing seam is permitted and probability is accumulated to explain the large quenching cross section - this picture is the same as that of Tully's. (5) However there are differences between this work and Tully's work that have to be pointed out.

Tully determines the cross section for the complex formation $\sigma_c(E)$ from a dispersion term, for the singlet state, of the form $C_6/R^6$; while in this work two potential energy surfaces $V_1^I$ and $V_1^{II}$ that include all degrees of freedom were used to represent that singlet state and neither of them includes a dispersion term; the cross section
Table 4. Results for Quenching of $^1D$ by $N_2$

<table>
<thead>
<tr>
<th>Surface I$^a$</th>
<th>Surface II$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E^b$</td>
<td>$\sigma_c^c$</td>
</tr>
<tr>
<td>0.03</td>
<td>26.2</td>
</tr>
<tr>
<td>0.6</td>
<td>1.6</td>
</tr>
<tr>
<td>1.2</td>
<td>0.4</td>
</tr>
</tbody>
</table>

$^a$The results using singlet potential surfaces $V_1^I$ or $V_1^{II}$, which are described in Section E.

$^b$The initial translational energy in eV.

$^c$The quenching cross section ($A^2$).

$^d$The rate constant ($cm^3$/mol. sec.) for quenching at a temperature $kT = E$, as defined by Eq. 2.46-a.

$^e$The average energy (eV) in vibrational excitation of product $N_2$, as defined by Eq. 2.44.
\(\sigma_c(E)\) was evaluated by running classical trajectories on these surfaces that are not exact and rather crude but they are qualitatively reasonable potential energy surfaces. The way in which the statistical approximation is used to determine the quenching probability is also somewhat different.

With the above differences taken into consideration, the qualitative agreement and even the semi-quantitative agreement, in the thermal rate constant and the amount of vibrational energy appearing in product \(N_2\), between this work and Tully's work is encouraging and reassuring. This is consistent with the thermal energy results from potentials \(V_1^I\) and \(V_1^{II}\) that demonstrate the very low sensitivity of these results to the details of the potential energy surface, and is also consistent with Tully's observation that his thermal energy results are rather insensitive to the \(C_6\) coefficient.

With all this similarity and agreement between this work and Tully's it is important to notice that the RRKM, like the nature of Tully's approach to calculate the cross section for complex formation \(\sigma_c(E)\), limits his approach to low collision energies, while the approach of classical trajectories that is used in this work remains valid at higher collision energies. The large difference between the results of potentials \(V_1^I\) and \(V_1^{II}\) at high energies demonstrate the need for more accurate potential energy surfaces to be able to obtain reliable results at high energies.
Recent experimental results of Lin and Shortridge\textsuperscript{(24)} on the quenching of \( \text{O}(^{1}\text{D}) \) by \( \text{CO} \) showed a reasonable amount of energy as a product \( \text{CO} \) vibrational energy; it has been found\textsuperscript{(25)} that this reaction also has a large thermal rate constant \((-7\times10^{-11} \text{ cm}^3/\text{molec. sec.})\) which makes it similar qualitatively to the \( \text{O}(^{1}\text{D}) \) and \( \text{N}_2 \) reaction; this is a reasonable expectation since both systems are isoelectronic and therefore their potential energy surfaces are similar. Because of this similarity our approach and our qualitative results for the \( \text{O}(^{1}\text{D}) \) and \( \text{N}_2 \) reaction apply equally well to the \( \text{O}(^{1}\text{D}) \) and \( \text{CO} \) reaction.

In conclusion this work demonstrates how the simple atom-atom picture can't always explain collisions that include more than the translational degree of freedom; it shows how important other degrees of freedom can be even in a simple atom-diatom problem, and how their participation in the dynamics can change the whole picture of the collision. This problem clearly shows that in a transition from one surface to another the knowledge of the mechanism is very important and how in this case because of the nature of the mechanism, the cross section for the reaction is practically independent of the magnitude of the coupling between the two states.
Footnotes and References


(2) J. C. Tully, J. Chem. Phys., 62, 1893 (1975), and references there.


(8) Fisher and Bauer had to assume an abnormally large value (300 cm\(^{-1}\)) for the spin orbit coupling in order to obtain a reasonable rate constant.

(10) The word "seam" is used here to mean either the crossing point, the crossing line, or the crossing surface depending on the number of degrees of freedom involved.


(15) This transformation used the fact:

\[ \int dx \, g(x) \, \delta(f(x)) = \int dx \, g(x) \, \frac{\delta(x-a)}{f'(x)} \]

where x=a is the solution for f(x) = 0.

(16) The function f(q) may include both coordinates and momenta as Tully did (Ref. 5),

\[ f(q,p) = 0 \]

and thus Eq. 2-17 has to be modified to include that.
(17) There are cases of "angular momentum-limited" reactions for which this approximation is poor; however the present reaction is not such a case.

(18) Notice that -

$$\int dx \, \delta(x) = 1$$

so

$$\int d\varepsilon \, P(Q(E, \varepsilon)) = \int d\varepsilon \, P(Q(E)) \, \frac{<\Gamma/h \cdot \delta(\varepsilon - \hbar_\text{vib})>}{<\Gamma/h>}$$

$$= P(Q(E))/<\Gamma/h> \cdot \int d\varepsilon <\Gamma/h \cdot \delta(\varepsilon - \hbar_\text{vib})>$$

$$= P(Q(E))/<\Gamma/h> \cdot <\Gamma/h> = P(Q(E)).$$

(19) Notice

$$\int d\varepsilon \, \sigma(Q(E, \varepsilon)) = \int d\varepsilon \, \sigma_c(E) \, P(Q(E, \varepsilon))$$

$$= \sigma_c(E) \int d\varepsilon \, P(Q(E, \varepsilon))$$

$$= \sigma_c(E) \, P(Q(E)) = \sigma(Q(E)).$$

(20) $1 - e^{-x} \approx x$ for small $x$.

(22) For more details of how this is done see R.K. Preston, Ph.D. Thesis, Yale Univ. (1972).


III. PENNING IONIZATION OF Na BY VIBRATIONALLY EXCITED N₂

The mechanism of collisioned ionization reactions of the form

\[ A^* + M + A + M^+ + e \]  

where \( A^* \) is an electronically excited species and \( M \) is an atom with ionization energy less than the excitation energy of \( A \), the mechanism of these reactions is relatively understood.\(^{(1)}\) For the reaction to occur the potential energy surface (curve) that describes the excited species \( A^* \) and the atom \( M \) is required to be higher in energy than the potential energy surface (curve) that describes the species \( A \) and the ionized atom \( M \) (see Fig. 8). In such a picture there is a continuum of potential curves that describe the ionic state and lie above curve II. All of these curves are parallel to curve II and are separated from it by an energy equal to the kinetic energy of the electron. The curve that describes the excited state crosses this continuum of curves, thus at each point on it there is a probability of transition to an ionic curve and releasing an electron with kinetic energy equal to the vertical distance between curves I and II at that point.

The ionization of sodium by collision with vibrationally excited nitrogen was studied by Schmidt and co-worker;\(^{(2)}\)

\[ \text{Na} + N_2 \overset{+}{\rightarrow} \text{Na}^+ + N_2 + e \]  

\((3.2)\)
Figure 8. A schematic drawing of three potential energy curves that describe the penning ionization problem in Eq. 3.1: curve I describes the excited state of A* and M, curve II describes A in the ground state and ionized M, and curve III describes both A and M in the ground state; the dashed area above curve II represents the continuum of ionic curves that describe A + M+ + e.
Figure 3

\[ E \]
\[ A^* + M \]
\[ A + M^+ + e (K.E. = 0) \]
\[ A + M \]

\[ R \rightarrow \]

XBL 7610 4675
They showed that if there is enough vibrational energy in the $N_2$ molecule to ionize the Na atom ($v \geq 21$), the reaction goes with a reasonably large cross section. This reaction is interesting, since the potential energy surface that describes the excited state ($N_2^+ + \text{Na}$) lies lower in energy than the potential energy surface that describes the ionic state ($N_2 + \text{Na}^+$). As a matter of fact, a search in space was conducted and the two surfaces were found to be almost parallel, with the surface ($V_1$) that describes the excited state 5.0 eV lower in energy than the surface $V_2$ that describes the ionic state (Fig. 9). Because of the inverted order of the above two surfaces it is not possible to explain this reaction within the framework of the generally accepted mechanism for collisional ionization that is described above. An abinitio SCF calculation was carried out to know more about these surfaces, and a third surface $V_3$ that describes $N_2^- + \text{Na}^+$ was also calculated, and was found to cross both of the previous surfaces as expected (Fig. 9). The presence of this third surface resolves the problem within the spirit of the mechanism of the quenching reaction (Eq. 2.1) that is described in the previous chapter and pertains the acceptable picture of collisional ionization described earlier; as the collision occurs a transition from surface $V_1$ to surface $V_3$ occurs and causes a complex formation; with internal energy transfer in the complex enough energy gets in the $N_2^-—\text{Na}^+$ degree of freedom to make it possible for the complex to reach that part of space where surface $V_3$ is higher in energy than surface $V_2$; when the complex reaches this part of space leakage from surface $V_3$ into the continuum of ionic surfaces above surface $V_2$ is possible and thus the reaction goes. Sections A, B,
Figure 9. A schematic representation of 3 potential energy surfaces that describe \( \text{N}_2 + \text{Na} \): \( V_1 \) describes \( \text{N}_2 + \text{Na} \) in the ground state, \( V_2 \) describes \( \text{N}_2 + \text{Na}^+ \), and \( V_3 \) describes \( \text{N}_2^- + \text{Na}^+ \); \( R \) is the distance between the sodium atom and the center of mass of the \( \text{N}_2 \) molecule.
Figure 9
and C describe the model and the theory in detail, Section D describes the potential energy surfaces and Section E gives the conclusion.

A. The Model

Although there are much more than three potential energy surfaces that are involved in this picture, namely all the surfaces that describe \( \text{N}_2 \) molecules and excited states of Na atom, using these three surfaces only will give the basic features of the mechanism; all those extra surfaces can be included in the picture if it turns out that they are important in the mechanism.

As the \( \text{N}_2 \) molecule and the Na atom approach each other on surface \( V_1 \) they get to the point where surfaces \( V_1 \) and \( V_3 \) cross, and at this point there is a high probability of transition to surface \( V_3 \); this high probability of transition is due to the low relative velocity at the crossing seam. As the two species continue approaching each other on surface \( V_3 \) it is assumed that enough energy from the highly vibrationally excited \( \text{N}_2 \) \( (v \geq 21) \) transfers to the translational degree of freedom \( (\text{N}_2---\text{Na}) \) and thus on the way back as the two species separate, the relative velocity as the system gets to the crossing seam is high enough to make the probability of recrossing back to surface \( V_1 \) very low. In subsequent vibrations in this \( \text{N}_2---\text{Na} \) degree of freedom more energy transfers to it from the highly excited N-N degree of freedom and thus reduces the probability of recrossing more and more in subsequent passes.
of the crossing seam. At this point a complex is formed,

$$N_2 + Na \rightarrow N_2^-Na^+$$  \hspace{1cm} (3.3-a)

Now this complex formed has one of two things to do, either to recross back to surface $V_1$ and come back to reactants or gain enough energy in the $N_2$-$Na$ degree of freedom from the N-N degree of freedom to be able to reach the region of space where surface $V_3$ is higher in energy than surface $V_2$ and leaks into the continuum of surfaces of $V_2$. In the region of space where surface $V_3$ is higher in energy than surface $V_2$ the $N_2^-$ and Na$^+$ are almost separated; $N_2^-$ is known to be very unstable and decomposes instantaneously to $N_2$ and an electron, thus it is reasonable to assume that if the complex gets to the region of space where surface $V_3$ is higher in energy than surface $V_2$ it leaks instantaneously to surface $V_2$ and decomposes to give $N_2 + Na^+ + e$,

$$N_2^-Na^+ \rightarrow N_2 + Na^+ + e.$$  \hspace{1cm} (3.3-b)

The ionization process in the above described model is a two step process: first the electron moves from the sodium atom to the nitrogen molecule to form the complex $N_2^-Na^+$ in the transition from surface $V_1$ to surface $V_3$; second the $N_2^-$ releases the electron and the complex decomposes in the transition from surface $V_3$ to surface $V_2$ (see Fig. 10). Since surface $V_2$ has a very shallow well, 0.5 eV, it is reasonable to expect a small percentage (~1%) of the final product not to have enough
Figure 10. These are the same potential energy curves as in Fig. 9.
The line with the arrows is a schematic representation of a reactive trajectory on these curves.
Figure 10
energy to separate any stay trapped in the well and form $N_2Na^+$ molecular ion that is detected experimentally as a product of this reaction.\(^{(2)}\)

B. Formulation

There are two quantities that have to be calculated to evaluate the cross section for this reaction, namely the cross section for complex formation and the probability for the separation of the ions and the release of the electron.

Probably the most direct way to calculate the cross section for a complex formation is to run classical trajectories on surface $V_1$ and then calculate transition probability when the crossing seam of surfaces $V_1$ and $V_3$ is reached and follow up the trajectory until the complex formation is assured. However recently Miller and co-workers\(^{(4)}\) have showed that transition state theory and classical trajectories give essentially the same results at energies few tenths of an eV above the barrier. In the present problem the crossing seam of surfaces $V_1$ and $V_3$ is very similar in nature to the barrier in a single potential surface reaction. For thermal energy collisions the relative velocity at the crossing seam of surfaces $V_1$ and $V_3$ is very low and thus if the same type of treatment as Miller's is used to calculate the cross section we will get essentially the same results of the classical trajectories with much less work,
where \( F(E) \) is the microcanonical average of reactive flux that forms the complex and \( F'_o(E) \) is the microcanonical average of incident flux per unit area (see Fig. 11).

The reactive flux is the flux across the crossing seam of surfaces \( V_1 \) and \( V_3 \) multiplied by the transition probability from surface \( V_1 \) to surface \( V_3 \),

\[
\sigma_c(E) = \frac{F(E)}{F'_o(E)} \tag{3.4}
\]

where \( F(E) \) is the microcanonical average of reactive flux that forms the complex and \( F'_o(E) \) is the microcanonical average of incident flux per unit area (see Fig. 11).

\[
F(E) = \int dq \int dp \delta(E-H)\delta(e_{vib}-h_{vib})\delta(e_{rot}-h_{rot})\cdot\frac{d(h(f_2(q)))}{dt} p(q,p) \tag{3.5}
\]

where \( q \) and \( p \) represent coordinates and momenta of the system respectively; \( \delta(\ ) \) and \( h(\ ) \) are the usual delta and step functions respectively; \( f_2(q) \) is a function such that \( f_2(q)=0 \) defines the crossing seam; \( E, e_{vib} \) and \( e_{rot} \) are the total energy of the system, the vibrational energy of the \( N_2 \) molecule and the rotational energy of the \( N_2 \) molecule respectively. \( H, h_{vib}, \) and \( h_{rot} \) are the total Hamiltonian, the vibrational Hamiltonian for \( N_2 \), and the rotational Hamiltonian for \( N_2 \) respectively; \( P(q,p) \) the transition probability from surface \( V_1 \) to surface \( V_3 \); the factor \( 1/2 \) was added to include flux in one direction only. In Equation 3.5 reactive flux is evaluated while the vibrational energy and the rotational energy of \( N_2 \) molecules is conserved thus eliminating any exchange of energy before the complex formation; this is a reasonable
Figure 11. These are the same potential energy curves as in Fig. 9:

\[ f_2(q) = 0 \] is a surface that is defined by the crossing seam of surfaces \( V_1 \) and \( V_3 \), 
\[ f_3(q) = 0 \] is a surface that is defined by the crossing seam of surfaces \( V_2 \) and \( V_3 \); 
\[ f_1(q) = 0 \] is a surface in the asymptotic region on surface \( V_1 \).
Figure 11
assumption because the crossing seam is reached while the distance between \( N_2 \) and \( Na \) is still large where chances for energy exchange are negligible.

\[
f_2(q) = \Delta V_{31} = V_3 - V_1 \tag{3.6}
\]

the Landau-Zener formula for transition probability is used and approximated as follows

\[
P(q_2, p_2) = \left[ 1 - \exp \left( -\frac{\frac{2\pi v_{13}^2}{h(\Delta V_{31})}}{d(\Delta V_{31})} \right) \right] = \frac{2\pi v_{13}^2}{h(\Delta V_{31})} \tag{3.7}
\]

where \( V_{13} \) is the coupling between surfaces \( V_1 \) and \( V_3 \); making use of the relation

\[
\frac{dh(f)}{dt} = \delta(f) \frac{df}{dt}
\]

and substituting 3.6 and 3.7 into 3.5,

\[
F(E) = \int dq \int dp \delta(E-H)\delta(e_{vib}\cdot h_{vib})\delta(e_{rot}\cdot h_{rot}) \cdot \frac{2\pi v_{13}^2}{h} \tag{3.8}
\]

The incident flux \( F_0(E) \) is the flux through a critical surface far out in the asymptotic region on surface \( V_1 \)

\[
F_0(E) = \int dq \int dp \delta(E-H)\delta(e_{vib}\cdot h_{vib})\delta(e_{rot}\cdot h_{rot}) \cdot \frac{d(h(f(q))))}{dt} \tag{3.9}
\]
all variables are the same as described before; \( f_1(q) \) is a function such that \( f_1(q) = 0 \) describes a critical surface in the asymptotic region; the simplest form for this function is

\[
f(q) = Z - Z_0
\]

where \( Z \) represents the \( Z \)-coordinate of the vector \( \vec{R} \) which describes the distance between \( Na \) and the center of mass of \( N_2 \); \( Z_0 \) is a large value such that \( Z = Z_0 \) is in the asymptotic region. Since \( F_0(E) \) is the incident flux per unit area,

\[
F_0(E) = \int dp \int d\vec{r} \int dZ \delta(E-H)\delta(\varepsilon_{\text{vib}} - \varepsilon_{\text{vib}})\delta(\varepsilon_{\text{rot}} - \varepsilon_{\text{rot}}) \cdot \frac{1}{2} \cdot \delta(Z-Z_0) \frac{dz}{dt} \tag{3.10}
\]

Appendix II shows the details of evaluating Equations 3.8 and 3.10.

It is important to notice here that the approximation for the transition probability in Equation 3.7 is a very crude approximation if the transition probability is large. However if that approximation is not used Equation 3.8 would be much more complicated.

As mentioned earlier there are only two things for the complex to do, either to cross to surface \( V_1 \) and thus reverse the first step or leak to surface \( V_2 \) and the reaction goes. This picture gives a problem similar to the one in the previous chapter where the critical surface that defines the complex is now at the crossing seam of surfaces \( V_2 \)
and \( V_3 \); whenever the system crosses this critical surface and gets outside the complex region the reaction goes and the electron flies away eliminating any possibility of reversing the reaction; meanwhile as the complex is still there, every time the crossing seam of surfaces \( V_1 \) and \( V_3 \) is passed there is a probability of reversing the first step and recrossing to surface \( V_1 \). The probability of leaking to surface \( V_2 \) or the probability of penning ionization

\[
P_{PI} = 1 - P_R \quad (3.11)
\]

where \( P_R \) is the probability of recrossing to surface \( V_1 \) or the probability of reversing the reaction.

The probability of reversing the reaction is exactly identical to the quenching probability in the previous chapter with only one difference, namely the position of the critical surface that encloses the complex in the previous chapter was out in the asymptotic region on the singlet surface, while here it is at the crossing seam of surfaces \( V_2 \) and \( V_3 \) (see Fig. 11). The same as \( P_Q \) in Equation (2.20-a)

\[
P_R = 1 - \exp \left[ -\tau(E)\langle \Gamma/h \rangle_E \right] \quad (3.12)
\]

where

\[
\Gamma/h = \frac{2\pi}{\hbar} V_{13}^2 \delta(\Delta V_{31})
\]
and \( \tau(E) \) is the reciprocal of the average rate of flux out through the critical surface \( f_3(q) \) (Fig. 11),

\[
\tau(E)^{-1} = <1/2 \cdot |\frac{d}{dt} h(f_3)| >_E = <1/2 \cdot \delta(f_3)| \frac{\dot{f}_3}{f_3} > \quad (3.13)
\]

where the microcanonical phase space average over the region of the collision complex for any function \( x(q) \)

\[
< x(q) > = \rho(E)^{-1} \int dq \int dp \ x(q) \ \delta(E-H) \ h(f_3(q)) \quad (3.14)
\]

and

\[
\rho(E) = \int dq \int dp \ \delta(E-H) h(f_3(q)) \quad (3.15)
\]

where all variables are as defined earlier in this chapter.

The cross section for the reaction \( \sigma(E) \) is now the cross section for complex formation \( \sigma_c(E) \) multiplied by the probability of Penning ionization

\[
\sigma(E) = \sigma_c(E) P_{PI} \quad . \quad (3.16)
\]

If other potential energy surfaces that describe \( N_2 \) and excited states of sodium are to be included, probability of passing to each of these surfaces has to be calculated the same way \( P_R \) is calculated and
the probability of penning ionization will be

$$P_{\text{PI}} = 1 - P_R \sum P_i$$  \hspace{1cm} (3.17)

where $P_i$ is the probability of leakage to the potential energy surface that describes $N_2$ molecules and excited states $i$ of the Na atom.

Depending on the magnitude of these probabilities ($P_i$), the lifetime of the complex may have to be adjusted to include the effect of the presence of these extra potential energy surfaces.

C. Additional Comments

The mechanism formulated in the previous two sections applies to a very wide set of reactions of alkali atoms and diatomic molecules like $N_2$ and CO that include a transition from one potential energy surface to another. Consider a model problem like the one in Fig. 12 where atom $A^*$ and molecule $BC$ collide to give atom $A$ and molecule $BC^+$,

$$A^* + BC \rightarrow A + BC^+.$$  \hspace{1cm} (3.18)

The mechanism for this reaction has to be through surface 3. The large cross section and the large product $BC^+$, vibrational energy of reactions of this sort\(^{(5),(6)}\) support a mechanism that includes a complex formation. Using the two step model developed earlier, it is easy to see that the
Figure 12. A schematic representation of a model problem where curve 1 represents the ground state, curve 2 represents the excited state, and curve 3 represents the ionic state; $f_1$ and $f_2$ are two critical surfaces that define the crossing seam of surfaces 1 and 3 and surfaces 2 and 3 respectively.
Figure 12
calculations of the cross section are the same as shown in Section B with the exception that surface 2 replaces surface $V_1$; also the coupling term in the transition probability and the position of the critical surface have to be changed to fit the new system.

The transition probability from surface 3 to surface 1 is the same as the quenching probability in the previous chapter except for the life time of the complex. The life time of the complex in this case is the reciprocal of the flux back to surface 2; this can be calculated easily by placing the critical surface that defines the complex at the crossing seam of surfaces 3 and 2 and multiplying the flux by the transition probability at this crossing seam.

$$\tau(E)^{-1} = \langle 1/2 \delta(f_2) | \hat{f}_2 | P_{32} \rangle$$  (3.19)

where now an approximation similar to the one presented in Equation 3.7 can be used and

$$\tau(E)^{-1} = \langle 1/2 \delta(f_2) \frac{2\pi V_{23}^2}{\hbar} \rangle$$  (3.20)

and

$$P_Q = 1 - \exp\left[-\frac{\tau(E)}{\langle \Gamma/\hbar \rangle_E}\right].$$  (3.21)
Another similar set of reactions are the quenching of vibrationally excited diatom by an alkali atom. Within the framework of the picture presented in this chapter these reactions have the opposite mechanism of this one; the cross section for complex formation can be calculated the same way as in Section B and the transition probability to surface 2 now is

\[ P = 1 - P_Q \]

where \( P_Q \) is the same as calculated earlier in this section.

D. Potential Energy Surfaces

A standard SCF program (Polyalom) was used to calculate the three potential energy surfaces involved in this system. Tables 5 and 6 show the double zeta basis used for both sodium and nitrogen respectively. With the simple picture of Penning Ionization in mind a wide range of space was investigated to find points in space where surface \( V_1 \) can be higher in energy than surface \( V_2 \). In that search both perpendicular and colinear arrangements were investigated; however as mentioned earlier both surfaces turned out to be almost parallel with surface \( V_1 \) approximately 5 eV lower in energy than surface \( V_2 \). The points evaluated were fit to simple standard functional forms for the potential energy; some of the known spectroscopic properties were also used in the fit. Fig. 13 shows the molecule and defines the coordinates used.
Table 5. Basis Set for Sodium Atom. The set is a \((^9S, ^5P)\) basis set contracted to \((^4S, ^2P)\) basis set

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Table 6. Basis Set for Nitrogen. The set is a \(^6S,^5P\) basis set contracted to \(^4S,^2P\) basis set.

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Figure 13. A schematic drawing of the arrangement of $N_2$ molecule and Na atom; $r$ is the N-N distance, $R$ is the distance between atom Na and the center of mass of $N_2$, and $\gamma$ is the angle between the vectors $\vec{r}$ and $\vec{R}$. 
Figure 13
This surface is known to be repulsive,\(^6\),\(^8\) and in both perpendicular and collinear arrangements it showed its repulsive character in the \(N_2\)-Na degree of freedom; there is hardly any effect on the nature of the potential of the \(N_2\) molecule due to the presence of the Na atom in the region investigated. Tables 7 and 8 have the points evaluated in both perpendicular and collinear configurations respectively. The best fit was to a function of the following form

\[ V_1 = V_{N_2} + D_1 \left( \frac{1}{R-R_{01}} \right)^{\alpha_1} \]  \hspace{1cm} (3.22)

where

\[ V_{N_2} = D_{N_2} \left[ 1 - e^{-\alpha_2 (r-r_{N_2})} \right]^2 \] \hspace{1cm} (3.23)

\(\alpha_1\) was fit to the points of the collinear case and imposed on the perpendicular one to make it easier for the calculations. The values of the potential energy parameters are in Table 9.

\[ N_2\text{Na}^+ \]

\(N_2\text{Na}^+\) molecular ion has been detected before,\(^2\),\(^9\) and a potential well is thus expected. The collinear arrangement showed a deeper well than the perpendicular one (collinear 0.49 eV and perpendicular 0.01 eV) which is similar to Staemmler's\(^{10}\) work on \(N_2\text{Li}^+\) where he also got a well in collinear arrangement (0.56 eV) that is
Table 7. Potential Energy Points for Perpendicular Configuration of $N_2Na$ ($\gamma = 90^\circ$). $r/2$ is half the distance between the N atoms, $R$ is the distance between the center of mass of $N_2$ and the Na atom. All units are in atomic units.

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Table 8. Potential Energy Points for Collinear N$_2$Na ($\gamma = 0^\circ$). a, b, and c are as shown here.

All Units are in Atomic Units.

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Table 9. Values of Parameters for the Potential Energy Functions in Section D; All Units are Atomic Units Unless Labeled Otherwise.

\[ D_{N_2}^a = 9.902 \text{ eV} \quad D_{3}^{a,b} = 8.25 \text{ eV} \]
\[ r_{N_2}^a = 2.06874 \text{ a.u.} \quad \alpha_{N_2}^b = 1.2823 \]
\[ \alpha_{N_2}^a = 1.423 \text{ a.u.}^{-1} \quad r_{N_2}^b = 2.2692 \]

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<th>Value for Perpendicular Conf.</th>
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a - units are eV

b - These are the values for a Moore potential of the form

\[ V_{N_2}^- = D_3 \left[ 1 - e^{-\alpha_{N_2}^a (r - r_{N_2}^-)} \right]^2 \]

that describes an isolated \( N_2^- \) molecular ion.
deeper than the perpendicular arrangement (0.20 eV). This can be explained on the basis that this bond is an ion-induced dipole bond. The presence of Na\(^+\) ion has negligible effect on the \(N_2\) molecule potential. Tables 10 and 11 have all the points evaluated in both perpendicular and collinear configurations respectively. The best fit was to a 6-12 Lennard-Jones potential in the \(N_2-\text{Na}^+\) degree of freedom

\[
V_2 = V_{N_2} + D_2 \left( \frac{\sigma}{R+R_{02}} \right)^{12} \left( \frac{1}{R+R_{02}} \right)^6
\]  

(3.24)

\(\sigma\) was fit to the collinear case and imposed on the perpendicular one. Table 9 shows all the parameters in Equation 3.24.

\[\text{Na}^+\text{N}_2^-\]

This potential energy surface has been proposed as the channel through which quenching of electronically excited Na by \(N_2\) occurs; however there is no reliable functional form for this potential. The calculation for this curve was more complicated than the two previous ones; due to symmetry problems, it was not possible to calculate the potential at large \(N_2^-\)–\(-\text{Na}^+\) distance; for distances larger than 5.4 a.u. the extra electron in \(N_2^-\) moves to the \(^3\text{P}\)-orbital in the Na during the energy minimization process, and the program calculates the potential energy for the \(N_2\) molecule and an excited Na atom. The potential energy curves for \(N_2^-\) and \(N_2\) were calculated to help in constructing the surface at large \(N_2^-\)–\(-\text{Na}^+\) distance. Tables 12 and 13 show all the calculated points for \(N_2^-\text{Na}^+\) for both perpendicular
Table 10. Potential energy points for perpendicular configuration of \( \text{N}_2\text{Na}^+ (\gamma = 90^\circ) \). \( r/2 \) is half the distance between the N atoms; 
R is the distance between the center of mass of \( \text{N}_2 \) and the Na atom. All units are in atomic units.

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Table 11. Potential energy points for collinear N$_2$Na$^+$ (γ=0°). a,b, and c are as shown here: N---N---Na. All units are in atomic units.

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Table 12. Potential energy points for perpendicular configuration of $\text{N}_2\text{Na}^+$ ($\gamma = 90^\circ$). $r/2$ is half the distance between the N atoms; $R$ is the distance between the center of mass of $\text{N}_2$ and the Na atom. All units are in atomic units.

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Table 13. Potential energy points for collinear $N_2^-Na^+$ ($\gamma = 0^\circ$). $a$, $b$, and $c$ are as shown here $N$--$b$--$N$--$Na$. All units are in atomic units.

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Table 14. Potential energy points for N\(_2^-\) and N\(_2^+\). \(r/2\) is half the distance between the two N atoms. All units are atomic units.

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<th>(E) for N(_2^-)</th>
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and collinear configurations respectively; Table 14 shows the points calculated for \( N_2^- \) and \( N_2 \). The best fit was to Moorse potentials in both the \( N_2^-\text{--Na} \) degree of freedom and the \( N-N \) degree of freedom,

\[
V_3 = D_3 \left[ 1 - \exp(-\alpha(r_3)) \right]^2 + D_4 \left[ 1 - \exp(-\beta(R_{e})) \right]^2 \tag{3.25}
\]

Table 9 has all the parameters in Equation 3.24.

E. Conclusion

In the calculation of these potentials the goal was to get a set of qualitative potentials that can be easily used in simple calculations; this was motivated by the results of the previous chapter where it was clear that having a qualitative set of potential energy surfaces can be very helpful in putting together a reasonable mechanism that can explain a lot of the details of the reaction. These potentials also set the basis for dealing with quenching of electronically excited sodium by \( N_2 \) where a process similar to the opposite of this one occurs. We feel that these quenching reactions go through a complex formation that causes the large vibrational excitation of \( N_2 \). \(^{(5)}\),\(^{(6)}\) Also reactions of quenching of vibrationally excited \( N_2 \) by alkali atoms \(^{(7)}\) go through the same type of mechanism of the present problem. Statements like "active \( N_2 \) is relaxed on sodium covered walls in nearly every collision"\(^{(7)}\) cannot be justified without a complex formation mechanism.
No calculations have been done until now on the present system, due to the inavailability of a reasonable value for the coupling between these different states and mainly between the ionic curve (Na\(^+\)N\(_2\)\(^-\)) and the neutral ground state one. We hope that in the near future these calculations will be possible.

Footnotes and References

(1) For a review of this type of reaction see E.E. Muschlitz, Jr., Advan. Chem. Phys. 10, 171 (1966); W.H. Miller, J. Chem. Phys. 52, 3563 (1970) and references there.


(3) See Section D of this chapter.


Appendix A. Coupling Terms for a Two State System

For two normalized states

$$\langle \phi_i | \phi_i \rangle = 1 \quad \text{(A-1)}$$

$$\langle \phi_i | \phi_j \rangle = 0 \quad \text{(A-2)}$$

The derivatives of both sides of Eq. A-1 with respect to $R$ gives

$$\nabla_R \langle \phi_i | \phi_i \rangle = \nabla_R \cdot 1$$

$$\langle \nabla_R \phi_i | \phi_i \rangle + \langle \phi_i | \nabla_R \phi_i \rangle = 0$$

$$\langle \nabla_R \phi_i | \phi_i \rangle = -\langle \phi_i | \nabla_R \phi_i \rangle \quad \text{(A-3)}$$

Since $\phi_i$'s are real

$$\langle \nabla_R \phi_i | \phi_i \rangle = \langle \phi_i | \nabla_R \phi_i \rangle \quad \text{(A-4)}$$

Equations A-3 and A-4 can be true only if

$$\langle \phi_i | \nabla_R \phi_i \rangle = 0 \quad \text{(A-5)}$$
Since we have only two states, when any operator operates on one of them the result can be expressed as a linear combination of both of them; thus

\[ \nabla_R \phi_i = \alpha_i(R) \phi_i + \alpha_j(R) \phi_j \]  \hspace{1cm} \text{(A-6)}

multiply by \( \phi_i \) from the left and integrate over \( r \)

\[ < \phi_i | \nabla_R | \phi_i > = \alpha_i(R) < \phi_i | \phi_i > + \alpha_j(R) < \phi_i | \phi_j > \]

\[ = \alpha_i(R) \]

using Eq. A-5

\[ \alpha_i(R) = 0 \]

so

\[ \nabla_R \phi_i = \alpha_j(R) \phi_j \]  \hspace{1cm} \text{(A-7)}

\[ \nabla_R^2 \phi_i = \nabla_R (\alpha_j(R) \phi_j) \]

\[ \nabla_R^2 \phi_i = \phi_j (\nabla_R \alpha_j(R)) + \alpha_j(R) (\nabla_R \phi_j) \]  \hspace{1cm} \text{(A-8)}

multiply by \( \phi_i \) from the left and integrate over \( r \)
\[
< \phi_i | \nabla_R^2 | \phi_i > = < \phi_i | \phi_j > \nabla_R \alpha_j (R) + \alpha_j (R) < \phi_i | \nabla_R | \phi_j >
\]

\[
< \phi_i | \nabla_R^2 | \phi_i > = \alpha_j (R) < \phi_i | \nabla_R | \phi_j >
\]  
(A-9)

multiply Eq. A-7 by \( \phi_j \) from the left and integrate over \( r \):

\[
< \phi_j | \nabla_R | \phi_i > = \alpha_j (R) < \phi_j | \phi_j >
\]

\[
< \phi_j | \nabla_R | \phi_i > = \alpha_j (R)
\]  
(A-10)

substituting Eq. A-10 in Eq. A-9

\[
< \phi_i | \nabla_R^2 | \phi_i > = < \phi_j | \nabla_R | \phi_i > < \phi_i | \nabla_R | \phi_j >
\]  
(A-11)

taking the derivatives of both sides of Eq. A-2 with respect to \( \sim \):

\[
< \nabla_R \phi_i | \phi_j > = 0
\]

\[
< \nabla_R \phi_i | \phi_j > + < \phi_i | \nabla_R | \phi_j > = 0
\]

\[
< \phi_j | \nabla_R | \phi_i > = - < \phi_i | \nabla_R | \phi_j >
\]  
(A-12)

substituting Eq. A-12 in Eq. A-11
multiplying Eq. A-8 by $\Phi_j$ from the left and integrating over $R$

$$<\phi_i|\nabla_R^2|\phi_i> = <\phi_i|\nabla_R|\phi_j>^2$$  \hspace{1cm} (A-13)

$$<\phi_j|\nabla_R^2|\phi_i> = <\phi_j|\phi_i> \nabla_R \alpha_j(R) + \alpha_j(R) <\phi_j|\nabla_R|\phi_j>$$  \hspace{1cm} (A-14)

substituting Eq. A-5 and Eq. A-10 in Eq. A-14

$$<\phi_j|\nabla_R^2|\phi_i> = \nabla_R <\phi_j|\nabla_R|\phi_i> .$$

**Appendix B. Phase Space Integrals**

The phase space integrals required in Chapter II Sections B, C, and D and in Chapter III Sections B and C are all of the form

$$<x>_E = \rho(E)^{-1}\int dp \int dq \ x(p,q) \delta(E-H(p,q))h(f(q))$$  \hspace{1cm} (B-1)

where

$$\rho(E) = \int dp \int dq \ \delta(E-H(p,q))h(f(q))$$  \hspace{1cm} (B-2)

(The normalization factor $\rho(E)$ is not required in order to compute $P_Q(E)$ and $P_Q(E,c)$ of Chapter II, Sections B and C, and $\sigma_c$ and $P_R$ of Chapter III, Section B, because they involve a ratio of phase space averages, but it would be required to determine the unimolecular rate
Choosing cartesian coordinates and momenta for the A + BC system

\[ q = \vec{r}, \vec{R} \]
\[ p = \vec{p}, \vec{P} \]

\((\vec{r}, \vec{p})\) being the cartesian variables for BC, and \((\vec{R}, \vec{P})\) the cartesian variables for A relative to BC, the Hamiltonian is

\[ H = \frac{\vec{p}^2}{2\mu} + \frac{\vec{P}^2}{2m} + V(r, R, \gamma) \quad \text{(B-3)} \]

where \(\mu\) and \(m\) are the appropriate reduced masses, \(\gamma\) the angle between \(\vec{r}\) and \(\vec{R}\), and \(V\) is the potential surface under consideration (e.g., in Chapter III it is the singlet potential surface).

If the function \(f\), which defines the collision complex as discussed, does not involve momenta—as we have assumed for the applications in this work—then it will depend only on the three coordinates \(r, R\), and \(\gamma\) which determine the size and shape of the A - B - C triangle.

The normalization factor \(\rho(E)\) is thus given by

\[ \rho(E) = \int d_3\vec{r} \int d_3\vec{R} \, h(f(r, R, \gamma)) \int d_3\vec{p} \int d_3\vec{P} \, \delta(E - V(r, R, \gamma) - \frac{p^2}{2\mu} - \frac{P^2}{2m}) \quad \text{(B-4)} \]
The momentum integrals can all be carried out, giving

\[ \rho(E) = 4\pi^3 (\mu m)^{3/2} \int d\tilde{r} \int d\tilde{R} \ h(f(r,R,\gamma))[E - V(r,R,\gamma)]^2 , \quad (B-5) \]

with the domain of integration restricted to the region for which

\[ E - V(r,R,\gamma) > 0 . \quad (B-6) \]

The integral over the three Euler angles which orient the A - B - C triangle can also be performed--i.e.,

\[ \int d\tilde{r} \int d\tilde{R} \ F(r,R,\gamma) = 8\pi^2 \int_0^\infty dr \int_0^\infty dR \int_{-1}^{+1} d(cos\gamma) F(r,R,\gamma) \quad (B-7) \]

for an arbitrary function F--so that \( \rho(E) \) is given finally by

\[ \rho(E) = 32\pi^5 (\mu m)^{3/2} \int dr \int dR \int d(cos\gamma) h[f(r,R,\gamma)] [E-V(r,R,\gamma)]^2 . \quad (B-8) \]

For the case

\[ X(p,q) = \Gamma(q)/\hbar = \frac{2\pi}{\hbar} V_{12}(r,R,\gamma)^2 \delta[\Delta V(r,R,\gamma)] \quad (B-9) \]

the momentum integrals and the integral over the three Euler angles can all be evaluated in the same manner as in the preceding paragraph, so that
Because of the delta function in the integrand of Eq. (B-10), one of the integrals can be evaluated directly, $\int dR$ say, and the remaining integrals over $r$ and $\cos \gamma$ carried out numerically.

In Chapter II, $\tau(E)^{-1}$, the reciprocal lifetime of the collision complex, corresponds to Eq. B-1 with

$$X(p,q) = \frac{1}{2} \delta(f(q)) \left| \frac{\partial f(q)}{\partial q} \right| \cdot \frac{p}{m},$$

and this involves the momenta in a way other than just in the Hamiltonian. The momentum integrations can still be carried out, however, giving

$$\tau(E)^{-1} \equiv \langle \frac{1}{2} \delta(f) | \vec{p} | \rangle_E$$

$$= \rho(E)^{-1} \frac{32\pi^2}{15} \mu m \int \frac{1}{2} \delta(f(q)) | \vec{p} |$$

$$\times \left[ [E-V(r,R,\gamma)]^{5/2} \left[ \frac{\partial f(q)}{\partial R} \right]^2 + \left[ \frac{\partial f(q)}{\partial r} \right]^2 \right]^{1/2} ,$$

where
Eq. B-6 also applies here, so that one obtains

\[
\tau(E)^{-1} = \rho(E)^{-1} \frac{256\pi^4}{15} (\mu m)^{3/2} \int dr \int dR R^2 \int d(cos\gamma) \delta[f(r, R, \gamma)] \\
\times [E - V(r, R, \gamma)]^{5/2} \left[ \frac{2}{\mu} \left| \frac{\partial f}{\partial R} \right|^2 + \frac{2}{\mu} \left| \frac{\partial f}{\partial \gamma} \right|^2 \right]^{1/2} . \quad (B-13)
\]

With \( f(r, R, \gamma) = R_C - R \) (Eq. 2.43) Eq. B-13 simplifies to

\[
\tau(E)^{-1} = \rho(E)^{-1} \frac{256\pi^4}{15} (\mu m)^{3/2} (2/\mu)^{1/2} R_C^2 \int dr \int d(cos\gamma) [E - V(r, R_C, \gamma)]^{5/2} \\
\quad (B-14)
\]

and the two remaining integrations were carried out numerically.

The vibrational energy distribution of \( N_2 \) in Chapter II corresponds to Eq. B-1 with

\[
X(p, q) = \delta(\epsilon - h_{\text{vib}}) \Gamma(q)/\hbar \\
= \frac{2\pi}{\hbar} V_{12}(q)^2 \delta[\Delta V(q)] \delta(\epsilon - h_{\text{vib}}) , \quad (B-15)
\]
where the vibrational Hamiltonian is

\[ h_{\text{vib}} = \frac{p_r^2}{2m} + v(r), \quad (B-16) \]

\[ p_r = \vec{p} \cdot \frac{\vec{r}}{r} \]

being the radial (i.e., vibrational) component of the B - C momentum and \( v(r) \) the \( \text{N}_2 \) vibrational potential. Thus

\[ < \delta (\varepsilon - h_{\text{vib}}) \Gamma / h >_E = \rho(\varepsilon)^{-1} \int d_3 \tilde{r} \int d_3 \tilde{\mathbf{R}} \ h[f(r, R, \gamma)] \frac{2\pi}{h} V_{12}(r, R, \gamma)^2 \]

\[ \times \delta(\Delta V(r, R, \gamma)) \int d_3 \tilde{p} \int d_3 \tilde{\mathbf{p}} \ \delta[E-V(r, R, \gamma) - p^2/2\mu - p^2/2m] \]

\[ \times \delta(\varepsilon - v(r) - (\tilde{p} \cdot \tilde{r})^2/2mr^2) \] . \quad (B-17)

Carrying our the momentum integrals and the integral over the three Euler angles in this case gives

\[ < \delta (\varepsilon - h_{\text{vib}}) \Gamma / h >_E = \rho(\varepsilon)^{-1} \frac{256\pi^4}{3} (\mu m)^{3/2} \int dr \int dR \int d(cos \gamma) \ h[f(r, R, \gamma)] \]

\[ \times \frac{2\pi}{h} V_{12}(r, R, \gamma)^2 \ \delta(\Delta V(r, R, \gamma)) \ [E-\varepsilon- \ V_{\text{int}}(r, R, \gamma)]^{3/2} \ [\varepsilon-v(r)]^{-1/2} \]

\[ \quad . \quad (B-18) \]

where

\[ V_{\text{int}}(r, R, \gamma) = V(r, R, \gamma) - v(r) \] .
The integral over R can be carried out by virtue of the delta function, and the remaining two integrals were evaluated numerically. [Note that since

\[ \int d\epsilon \left( E - \epsilon - V_{\text{int}} \right)^{3/2} \left( \epsilon - V(r) \right)^{1/2} = \frac{3\pi}{8} \left( E - V(r,R,\gamma) \right)^2, \]

the integral of Eq. B-18 over \( \epsilon \) gives, as it should, the result in Eq. B-10.]

In Chapter III the numerator \( F(E) \) in the cross section expression (Eq. 3.5) corresponds to Eq. B-1 with

\[
X(p,q) = \delta(\epsilon_{\text{vib}} - h_{\text{vib}}) \delta(\epsilon_{\text{rot}} - h_{\text{rot}}) \frac{1}{2} \delta(\Delta V_{31}) \frac{2\pi V_{13}^2}{h},
\]

\[ h_{\text{vib}} = \frac{p_r^2}{2m} + V(r) = \frac{p_r^2 \cos^2 \theta}{2m} + V(r), \]

\[ h_{\text{rot}} = \frac{p_r^2}{2m} \sin^2 \theta, \]

\[ F(E) = \frac{\pi V_{31}^2}{h^2} \int d_3 \mathbf{r} \int d_3 \mathbf{R} \delta(\Delta V_{31}) \int d_3 \mathbf{p} \delta(\epsilon_{\text{vib}} - v(r) - \frac{p_r^2}{2m} \cos^2 \theta) \times \]

\[ \delta(\epsilon_{\text{rot}} - \frac{p_r^2}{2m} \sin^2 \theta) \int d_3 \mathbf{p} \delta(E - H), \]

carrying out the momentum integrals.
the denominator \( F_0(E) \) corresponds to Eq. B-1 with

\[
X(p,q) = \delta(\epsilon_{\text{vib}} - h_{\text{vib}}) \delta(\epsilon_{\text{rot}} - h_{\text{rot}}) \frac{1}{2} \delta(Z - Z_0) \frac{dZ}{dt}
\]
carrying out the momentum integral and \( dZ \) integral

\[
F_0(E) = 2\sqrt{2} \pi^2 m^{3/2} \mu \int d3r \frac{E - \epsilon_{\text{vib}} - \epsilon_{\text{rot}}}{\sqrt{\epsilon_{\text{vib}} - V(r)}}
\]

In conclusion, it is interesting to consider a very primitive model which illustrates the qualitative nature of the vibrational energy distribution that is predicted by statistical theory. Suppose the total Hamiltonian \( H \) is the sum of that for two non-interacting systems 1 and 2,

\[
H = h_1 + h_2,
\]
and that \( h_1 \) and \( h_2 \) are a set of \( s_1 \) and \( s_2 \) oscillators, respectively. If \( P(\epsilon,E) \) is the probability that \( h_1 \) has an energy in the range \((\epsilon, \epsilon + d\epsilon)\), given that the total energy is \( E \), then one has

\[
P(\epsilon,E) = \int dp \int dq \delta(\epsilon - h_1) \delta(E - h_1 - h_2) / \int dp \int dq \delta(E - h_1 - h_2), \quad (B-19)
\]
and for a system of oscillators this is easily found to be

\[ P(E, E) = C \cdot \frac{E^{s_1-1} \cdot (E-E)^{s_2-1}}{E^{s_1+s_2-1}} \]  

(B-20)

where \( C \) is a numerical factor.

Often the distribution in \( E \) is observed experimentally to be linear on a semi-log plot for an appreciably range of \( E \). This implies that

\[ -\frac{d}{dE} \ln P(E, E) \neq \text{function of } E; \]  

(B-21)

from Equation B-20 one finds

\[ -\frac{d}{dE} \ln P(E, E) = \frac{s_2-1}{E-E} - \frac{s_1-1}{E} . \]

For \( s_1 = 1 \) and \( E \ll E \), this does not satisfy the condition in Eq. B-21, i.e., the \( E \)-distribution is Boltzmann, characterized by the temperature

\[ kT_E = E/(s_1 - 1) . \]

The fact that a sub-system of a much larger microcanonical system behaves canonically is, of course, a well-known phenomenon in statistical mechanics.
NUMERICAL APPLICATION OF THE CLASSICAL S-MATRIX THEORY TO THE EXCITATION OF CARBON MONOXIDE (CO) BY COLLISION WITH HELIUM (He)

The classical S-Matrix theory developed by W.H. Miller\textsuperscript{(1),(2)} for atom diatom systems shows how the classical limit of the time-independent quantum mechanical S-Matrix can be expressed in terms of quantities that can be obtained directly from the solution of the classical equations of motion; thus only processes that can be described by classical mechanics, i.e., classically allowed processes, are candidates to be described by this classical S-Matrix theory.

Rotational excitations in molecular collisions are in general classically allowed processes, i.e., there exists classical trajectories with initial conditions identical to the initial quantum state and final conditions that agree with the final quantum state; as a matter of fact, the classical cross section for rotational excitations usually rises from zero sharply as initial collision energy increases beyond its threshold value.\textsuperscript{(3)}

Rotational excitation of Carbon Monoxide (CO) by collision with Helium (He) was studied both quantum mechanically\textsuperscript{(4),(5)} and classically,\textsuperscript{(3)} and thus represents an excellent candidate to provide a new test for the applicability of the classical S-Matrix theory. It is important to test the ability of semiclassical mechanics (the classical S-Matrix theory)
to describe this system, since classical mechanics works relatively well\(^{(3)}\) for this system and gives results that agree qualitatively with quantum mechanical results. Since in the classical S-Matrix theory we have to find the specific trajectories that describe the transition between the two quantum states that we are concerned with, we have to go through a search process to find these trajectories; the number of initial variables for these trajectories is very essential, and if this number is more than one, the search gets very complicated and it sometimes becomes practically impossible to find all the trajectories that describe the transition. In this specific problem we implemented the helicity conserving approximation (\(J_z\) conserving) to limit the number of initial variables for the trajectories to one, namely the initial phase of the rotation. The potential energy surface used here is the same one formulated and used by Green and Thaddeus,\(^{(5)}\) which is based on the "electron gas model" calculations made by Gordon and Kim.\(^{(6)}\) The methodology is presented in Section I, calculations and results are in Section II, and Section III has the discussion and conclusions.

I. Methodology

The helicity representation for the classical Hamiltonian of an atom-diatom rigid rotor is\(^{(1)}\)

\[
H(P,j,M,R,q_j,q_M,J) = \frac{p^2}{Z\mu} + Bj^2 + V(R,\cos \gamma) + \\
+ \frac{1}{2\mu R^2} \left[ j^2 + j^2 - 2m^2 + 2(J^2 - M^2)^{1/2} (j^2 - M^2)^{1/2} \cos q_M \right] 
\]  

(1)
where

\[ \cos \gamma = \left(1 - \frac{M^2}{j^2}\right)^{1/2} \cos q_j, \]  \hspace{1cm} (2)

\( R \) is the distance between the atom (He) and the center of mass of the diatom rigid rotor (CO), and \( P \) is its conjugate momentum; \( j \) is the rotational angular momentum of the diatom (CO), it is the classical analogue of the rotational quantum number; \( q_j \) is the conjugate angle of the angular momentum \( j \), its value is between 0 and \( 2\pi \); \( M \) is the helicity, it is the projection of the diatom's rotational angular momentum \( j \) onto the relative velocity vector; \( q_M \) is the conjugate angle of the helicity \( M \), its value is between 0 and \( 2\pi \); \( J \) is the total angular momentum (rotational plus orbital), it is a fixed parameter in the Hamiltonian; \( \mu \) is the translational reduced mass

\[ \mu = m_{\text{He}} (m_C + m_O)/(m_{\text{He}} + m_C + m_O) \]

\( m \) is the internal reduced mass

\[ m = m_C \cdot m_O / (m_C + m_O) \]

and \( m_{\text{He}}, m_C, m_O \) are the masses of atoms Helium, Carbon, and Oxygen respectively; \( B \) is the diatom rotational constant

\[ B = \frac{1}{2mr^2} \]
and \( r \) is the distance between the C and O atoms; \( \gamma \) is the angle between \( \hat{R} \) and \( \hat{r} \); \( V(R,\cos \gamma) \) is the interaction potential between the atom (He) and the diatom rigid rotor (CO).

In the helicity conserving approximation or the "\( J_z \) - conserving approximation" the following replacement is made

\[
\left[ J^2 + j^2 - 2M^2 + 2(J^2 - M^2)^{1/2}(j^2 - M^2)^{1/2} \cos q_M \right] \rightarrow J^2
\]  

(3)

and the classical Hamiltonian becomes

\[
H(P,j,R,q_j;J,M) = \frac{P^2}{2\mu} + Bj^2 + \frac{J^2}{2\mu R^2} + V(R,\cos \gamma)
\]  

(4)

where \( q_M \) disappears from the Hamiltonian, and \( M \) becomes a constant of the motion and appears in the Hamiltonian only as a parameter.

The Hamiltonian in Eq. 4 has four variables, two of them (\( R \) and \( P \)) define the atom-diatom relative motion and the other two (\( j \) and \( q_j \)) define the diatom internal degrees of freedom. To apply the classical S-Matrix theory we have to find the classical trajectories that describe the specific transition we are interested in; the initial rotational quantum state of the diatom will define the initial value of \( j \); the total energy of the system and the initial value of \( j \) will define the initial value of \( P \); \( R \) has to be out in the asymptotic region where the interaction potential (\( V(R,\cos \gamma) \)) equals zero; now we are left with one initial
variable \((q_j)\) which we can change to make the final conditions of the trajectories fit the final quantum state desired (i.e., final rotational quantum number) and thus make the trajectories describe the specific transition under consideration. Now the application of classical \(S\)-Matrix theory should be easy since it requires only a one dimensional root search. The \(S\)-Matrix \((7)\) is

\[
S_{j_2,j_1}^{J,M} = \left( \frac{\partial j_2}{\partial q_{j_1}} \right)^{-1/2} e^{i\phi} \tag{5}
\]

where \(\phi\) is the classical action along the trajectory \((7)\)

\[
\phi = \int_{-\infty}^{+\infty} dt \left( \frac{dp}{dt} + q_j \frac{dj}{dt} \right) \tag{6}
\]

with \(q_{j_1}\) determined by

\[j_2(q_{j_1}) = \text{final rotational quantum number of the specific transition under consideration.}\]

If there are more than one trajectory that contributes to the transition

\[
S_{j_2,j_1}^{J,M} = \sum_{\text{all traj.}} \left[ 2\pi \left( \frac{\partial j_2}{\partial q_{j_1}} \right) \right]^{-1/2} e^{i\phi} \tag{7}
\]
the contribution of each J value to the cross section \( \sigma_{j_2^* j_1}^J \) and the total cross section \( \sigma_{j_2^* j_1} \) are

\[
\sigma_{j_2^* j_1}^J = \frac{\pi}{k_1^2 (2j_1 + 1)} \sum_{M} |S_{j_2^*, j_1}^J|^2 \\
\sigma_{j_2^* j_1} = \sum_{J=0}^{\infty} \sigma_{j_2^* j_1}^J
\]  

(8-a)

where \( k_1 \) is the initial momentum that is specified by the initial rotational state \( j \) and the total energy \( E \)

\[
k_1 = \left[ 2\mu (E - B j^2) - \frac{J^2}{R^2} \right]^{1/2}
\]

(9)

The Hamilton equations of motion for this system in the helicity representation with the helicity conserving approximation are:

\[
\frac{dR}{dt} = \frac{\partial H}{\partial P} = \frac{P}{\mu}
\]

(10-a)

\[
\frac{dP}{dt} = \frac{-\partial H}{\partial R} = \frac{J^2}{\mu R^3} - \frac{\partial V(R, \cos y)}{\partial R}
\]

(10-b)

\[
\frac{dq_j}{dt} = \frac{\partial H}{\partial q_j} = 2B j + \frac{M^2}{j^2(j^2 - M^2)^{1/2}} \cos q_j \frac{\partial V(R, \cos y)}{\partial (\cos y)}
\]

(10-c)

\[
\frac{dj}{dt} = \frac{\partial H}{\partial q_j} = \left( 1 - \frac{M^2}{j^2} \right)^{1/2} \sin q_j \frac{\partial V(R, \cos y)}{\partial (\cos y)}
\]

(10-d)
For the specific problem we are dealing with now, we will be looking at transitions from the initial state $j=0$. Since $M$ - the helicity - is the projection of the diatom's rotational angular momentum $j$ on the velocity vector, and since the initial value of $j$ is zero, then the initial value of $M$ is zero; if the helicity conserving approximation is applied, $M$ is a constant of the motion, and its value along the trajectory is its initial value; thus the value of $M$ is zero.

The Hamilton equations of motion (10) will be

\[
\begin{align*}
\frac{dR}{dt} &= \frac{P}{\mu} \quad (11-a) \\
\frac{dP}{dt} &= \frac{j^2}{\mu R^3} - \frac{3\partial V(R, \cos \gamma)}{\partial R} \quad (11-b) \\
\frac{dq_j}{dt} &= 2Bj \quad (11-c) \\
\frac{dj}{dt} &= \sin q_j \frac{3\partial V(R, \cos \gamma)}{\partial (\cos \gamma)} \quad (11-d)
\end{align*}
\]

The variable $q_j(t)$ does not take a constant value as $t_1 \to \infty$ (before the collision) or as $t_2 \to \infty$ (after the collision). This can easily be seen if Equation 11-c is integrated in the asymptotic region,

\[q_j = 2Bjt + \text{constant} \quad (12)\]

This time dependence of $q_j$ makes it inconvenient to specify its initial
value; to eliminate this problem we define a rotational angle \( \bar{q}_j \) by

\[
q_j = \bar{q}_j + 2BJ\frac{\mu R}{F}
\]

(13)

since

\[
R(t) = \frac{Pt}{\mu} + \text{constant}
\]

is the solution for \( R \) in the asymptotic region. It is clear now that \( \bar{q}_j(t) \) does take on a constant value as \( t \to \pm \infty \).

The rotation quantum number \( j_{QM} \) is defined by the usual semiclassical way,

\[
E_{rot} = B(j_{QM} + 1/2)^2.
\]

(14)

Thus the value of \( j \) in our calculations is,

\[
j = j_{QM} + 1/2
\]

(15)

and trajectories that describe transitions from \( j_{QM}=0 \) to \( j_{QM}=n \) should start with an initial angular momentum \( j = 0.5 \) and end with a final angular momentum \( j = n+0.5 \). However, the problem is not that simple and the function \( j^2_2(q^1_j) \) can have negative values; as a matter of fact, it we plot \( j^2_2 \) vs. \( \bar{q}_j^1 \), the point \( (j^2_2 = 0, \bar{q}_j^1 = n) \)
is approximately a center of symmetry in this function - this point will be a center of symmetry if \( j_1 \) was equal to zero; but since \( j_1 = 0.5 \), it is not exactly a center of symmetry - and there is approximately a negative value of \( j_2 \) for each positive one; this will be seen in the next section in Figures 1, 2, and 3. The question that arises is whether to include the trajectories that give a final \( j_2 = -(n + 0.5) \) as trajectories that contribute to the transition to \( j_{QM} = n \) (or \( j_2 = n + 0.5 \)); we argue that these trajectories should not be included since they correspond to a change in \( j \) equal to \( n + 1 \) and not \( n \) for a transition from \( j_{QM} = 0 \) to \( j_{QM} = n \). On the basis of this argument, we ignored all negative values of \( j_2 \); we also extend the argument to include even transitions for \( j_1 = 0 \) to \( j_2 = n \), even though in this case for \( j_2 = -n \) the change in angular momentum is only \( n \), but to be consistent with the previous argument we ignore negative values of \( j_2 \) for any transition we are looking into.

The initial conditions for the trajectories then, will be

\[
\begin{align*}
R_1 \text{ large} & \quad \text{(16-a)} \\
P_1 &= -\left[2\mu (E-Bj_1^2) - J^2/R^2 \right]^{1/2} \quad \text{(16-b)} \\
q_{j_1} &= \dot{q}_{j_1} + 2Bj_1 \frac{\mu R_1}{P_1} \quad \text{(16-c)} \\
j_1 &= j_{QM1} + 1/2 \quad \text{(16-d)}
\end{align*}
\]
II. Calculations and Results

The first step in the calculation was to find all the trajectories that contribute to each transition; although this is only a one dimensional root search, but it is not as simple as it sounds; the function $j_2(q_{j_1})$ is not a simple standard function, to calculate any point on this function a trajectory has to be calculated; the shape of this function can vary from one value of total angular momentum ($J$) to another, and to know what this function looks like, we had to calculate a set of trajectories for each value of $J$; as a matter of fact the way the roots of the function $j_2(q_{j_1})$ were found, was by making small increments in $q_{j_1}$ from 0 to $2\pi$ and looking for the roots along the path of the function. Figure 1 shows the function $j_2(q_{j_1})$ at $E=100 \text{ cm}^{-1}$, for a set of $J$ values 1, 5, 10, 15, and 20. Although these graphs look smooth, this is not true at all energies and all values of $J$; for small energies ($E < 40\text{ cm}^{-1}$) and small $J$ ($J < 10$) it is not possible to find all the roots of the function. There are so many roots that the results are not trusted at these values; Figure 2 is an example of the complicated structure of the function $j_2(q_{j_1})$; it is done at $E = 60\text{ cm}^{-1}$ and $J = 13.5$. From this graph we can see that this function is not a smooth function at all, and we may even doubt whether this much detailed evaluation of the function did bring out all the details of its structure. When the function was evaluated at $E = 60\text{ cm}^{-1}$ for $J = 12.5$ and $J = 14.5$, the function was much smoother; Figure 3 shows these results. The derivative $\frac{\partial j_2}{\partial q_{j_1}}$ which is equal to
Figure 1. This Figure is shown on the following five pages; it shows the function $j_2(\bar{q}_j)$ vs. $\bar{q}_j$ at $E = 100 \text{ cm}^{-1}$ for different values of J; a is for $J = 1$, b for $J = 5$, c for $J = 10$, d for $J = 15$, and e for $J = 20$. 
Figure 1-a

$E = 100 \text{ cm}^{-1}$

$J = 1$

$j_1 = 0.5$
Figure 1-b

\[ j_2(\bar{q}_{j_1}) \]

- \[ E = 100 \text{ cm}^{-1} \]
- \[ J = 5 \]
- \[ j_{1} = 0.5 \]
Figure 1-c

E = 100 cm$^{-1}$

$J = 10$

$j_\parallel = 0.5$
Figure 1-d

\[ j_2(\bar{q}_{ij_1}) \]

-2.0 \[ \rightarrow \]

0 \[ \rightarrow \]

2.0 \[ \rightarrow \]

4.0

\[ E = 100 \text{ cm}^{-1} \]
\[ J = 15 \]
\[ j_{i1} = 0.5 \]
Figure 1-e

$E = 100 \text{ cm}^{-1}$

$J = 20$

$j_{\parallel} = 0.5$
Figure 2. A plot of the function $j_2(\bar{q}_{j_1})$ vs. $\bar{q}_{j_1}$ at $E = 60 \text{ cm}^{-1}$ for $J = 13.5$. Notice the magnification of many regions on the graph and how some regions had to be magnified more than once. This is an example of the complexity of the function $j_2(\bar{q}_{j_1})$. 
Fig. 2
Figure 3. This Figure is shown on the following two pages; it shows the function $j_2(q_{j_{1}})$ vs. $q_{j_{1}}$ at $E = 60 \text{ cm}^{-1}$; a is for $J = 12.5$ and b is for $J = 14.5$; notice for both values of $J$ the function has a much smoother behavior than for $J = 13.5$ shown in Figure 2.
Fig. 3-a
Fig. 3-b
the derivative \( \frac{\partial j_2}{\partial q_{j_1}} \) that appears in Equation 5 was evaluated by running a second trajectory with \( q_{j_1} \) value equal to its root value plus a small increment; the derivative was found by difference.

The calculation was done for two sets of values of \( J \); the first set consisted of integer numbers from 1 and up, the second set consisted of half integer numbers from 1.5 and up; for the second set, the value of \( J \) used in Equation 8-a is the half integer number minus a half, which is similar to the usual semiclassical way of defining the rotational quantum number. Figure 4 shows a comparison of the contribution of each \( J \) value to the cross section \( \sigma_{j_2^*j_1}^J \) for the previous described two sets of values of \( J \) and quantum calculations done by Green and co-workers,\(^{(4),(5)}\) all the calculations in this Figure were done at \( E = 60 \) cm\(^{-1}\); the Figures are shown separate because the results will be too crowded on one graph. Figure 5 shows a comparison of the total cross section \( \sigma_{j_2^*j_1}^J \) for the two sets of values of \( J \) with classical\(^{(3)}\) and quantum mechanical results; all the calculations in this Figure were done at \( E = 100 \) cm\(^{-1}\).

Rasmussen and co-workers\(^{(8)}\) have applied this theory to nuclear spin; in their work they did not use the usual semiclassical way to define the spin quantum number but rather the classical way (i.e., their initial value of the spin was zero and not half and their final values were integer and not half integer). For the purpose of exploration and comparison we did calculation using the same kind of principle (i.e., \( E = B_{j_QM}^2, j_QM = j \)), where the initial rotational state was zero.
Figure 4. Comparison of $\sigma_{j_2+0}^J$ values at $E = 60 \text{ cm}^{-1}$ for different methods of calculation; the solid line that is shown in all graphs is the quantum calculation (close-coupling);(4) in addition to that, "a-1" and "a-2" show coupled state calculations(5) (points and dashed line), "b-1" and "b-2" show our calculations for the first set with integer values of J (points and dashed line), and "c-1" and "c-2" show our calculations for the second set with half integer values of J (points and dashed line).
Figure 4
Figure 5. Comparison of $\sigma_{j_2}^{+0}$ at $E = 100$ cm$^{-1}$; the solid line is the quantum calculations (close coupling);$^{(4)}$ in addition to that: "a" shows classical results$^{(3)}$ (points and dashed line), "b" shows our calculation for the first set of J with integer values, and "c" shows our calculation for the second set of J with half integer values (points and dashed line).
and the final rotational state was an integer; the total angular momentum J was given integer value the same as the first set in the previous calculations. Figure 6 shows a comparison of $\sigma_{j_2^*j_1}$ values from these results and from quantum results, all done at $E = 60 \text{ cm}^{-1}$; Figure 7 shows a comparison of $\sigma_{j_2^*j_1}$ values from these results and from quantum results, all done at $E = 100 \text{ cm}^{-1}$.

III. Discussion and Conclusion

These results are another test for the classical S-Matrix theory; Figures 4, 5, 6, and 7 show that this theory's results agree at least qualitatively with quantum results. It is very hard to judge whether any of the two sets of J used is better, and more tests are needed to know more about the differences between these two sets. However it is clear that in Fig. 4-c-1 the value of $\sigma_{j_2^*j_1}$ for $J = 13$ is out of trend in these results, and this may be due to the complicated structure of the function $j_2(q_{j_1})$ shown in Fig. 2; as a matter of fact, the calculation of Fig. 2 was done to try to understand the value 13 of $\sigma_{13}$ in Fig. 4.

The calculation done for $j_1 = 0$, $j_2 = n$ (n is an integer) and integer values of J shown in Figs. 6 and 7 is an interesting one, since it really shows better agreement with quantum calculations than calculation for $j_1 = 0.5$ and $j_2 = n + 0.5$ (n is an integer) for both sets of J; this is clearer if we compare Fig. 7 with Fig. 5-b and 5-c for calculations of the total cross section as a function of the final rotational state at $E = 100 \text{ cm}^{-1}$. 
Figure 6. Comparison of $\sigma_{J_2+0}^J$ values at $E = 60$ cm$^{-1}$; the solid line is quantum (close-coupling) results$^{(4)}$ and the dashed line and the points are our calculation with $j_1=0$, $j_2=n$ and $J$ is an integer.
Figure 7. Comparison of $\sigma_{j_2+0}$ values at $E = 100 \text{ cm}^{-1}$; the solid line is quantum (close-coupling) results$^{(4)}$ and the dashed line is our calculation with $j_1 = 0$, $j_2 = n$ and $J$ is an integer.
The complicated structure of the function $j_2(q_1)$ in this problem is a manifestation of the potential energy function used; thus this complicated structure does not necessarily exist for all systems; for a system with a less complicated structure of this function the whole calculation should be easier and more reliable.

Finally it has to be said that no final conclusion can be made without more calculations and more comparison for other values of energy for this system, and also applying the theory to other systems, where quantum results are available.

References and Footnotes


(4) S. Green, to be published.


These are similar to the S-Matrix and the action expressions in Ref. 2; the vibrational states in Ref. 2 are replaced by the rotational states here.

This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.