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Submitted to Journal of Chemical Physics

LBL-3192
Preprint c.1

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September, 1974

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

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THEORETICAL TREATMENT OF QUENCHING IN $O(^1D) + N_2$ COLLISIONS*

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ABSTRACT

It is maintained that quenching of $O(^1D)$ by collision with N_2 proceeds by formation of a collision complex on the lowest singlet potential surface. Once a collision complex is formed, even the weak spin-orbit interaction in O atom can induce quenching with essentially unit probability (at thermal energies) because the intersection of the singlet $[O(^1D) + N_2]$ and triplet $[O(^3P) + N_2]$ potential surfaces is crossed many times during the life of the complex. Rather crude, but qualitatively reasonable potential 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, $\sim 40\ \mathring{A}^2$ at thermal energy; a statistical model is used to determine the quenching probability of the collision complex. Values obtained for the magnitude of the thermal rate constant for quenching, and the fraction of the exoergicity which appears as vibrational excitation of N_2, are both in good agreement with experimental results.

I. INTRODUCTION

The quenching of $O(^1D)$ by N_2,

$$O(^1D) + N_2 \rightarrow O(^3P) + N_2 \quad , \tag{1.1}$$

has been somewhat of a puzzle for several years.[1,2] Although it is clear that the relevant interaction causing the transition is spin-orbit coupling (because of the spin change), an atom-atom curve crossing model--which treats N_2 as an atom--predicts much too small a rate constant; this is because in this model the crossing of the singlet and triplet potential curves is traversed only twice during the $O(^1D) + N_2$ collision--once as they approach and once as they separate--and the spin-orbit interaction is simply too weak to yield a large enough transition probability.[3] In addition, this atom-atom picture cannot explain the experimental observation[4] that a sizeable fraction of the approximately 2 eV exoergicity appears as vibrational excitation of the product N_2.

The picture which seems to explain both of these results--the relatively large rate of reaction (1.1) and the amount of vibrational excitation of product N_2--is to realize that N_2 is not an atom, that it has internal degrees of freedom, rotation and vibration. Since the singlet potential is strongly attractive, furthermore, it is reasonable to expect that the collision of $O(^1D) + N_2$ will excite sufficient rotation and/or vibration of N_2 to "trap" the oxygen atom, i.e., to form a collision complex; Figure 1 depicts this mechanism skematically. Considering rotational excitation

alone, for thermal energy collisions it requires only a $\Delta j = 6$ rotational excitation of N_2 from an initial rotational state $j = 6$ (the most probable one at 300° K) to result in trapping. If this complex formation does occur, then it is clear that even though the spin-orbit interaction is weak a sizeable quenching cross section can result--because the crossing point will be traversed many times--and that vibrational excitation of N_2 will be significant.

[Recent experiments by Lin and Shortridge[5] also show substantial vibrational excitation in the quenching of $O(^1D)$ by CO:

$$O(^1D) + CO \rightarrow O(^3P) + CO \quad . \tag{1.2}$$

This reaction has also been found[6] to have a large ($\sim 7 \times 10^{-11}$ cm^3/molec. sec.) thermal rate constant and is thus similar qualitatively to reaction (1.1); this is reasonable, of course, since O - CO and O - N_2 are isoelectronic and their potential energy surfaces therefore similar. Because of this similarity of potential surfaces, the qualitative results of our present work apply equally well to quenching of $O(^1D)$ by CO as by N_2.]

This paper presents calculations which support this point of view, i.e., which show that the cross section for complex formation on the ground state singlet potential surface is sizeable. We also show how a statistical treatment of the collision complex can be introduced to simplify the calculation of the quenching cross section and the distribution of product states. Of earlier theoretical treatments of this problem[1-2,7] our

approach is most akin to that of Tully;[7] the primary difference between the present work and Tully's is that we use classical trajectory calculations to determine the cross section for complex formation--rather than estimating it from a spherically symmetric C_6 coefficient--and the form of the statistical model that we develop is somewhat different from the one used by Tully.

Section II first discusses the formulation of the problem and develops the statistical approximation. Section III describes the potential surfaces used for the trajectory calculations, the results are presented in Section IV, and Section V concludes.

II. THEORY

A. Description of the Model.

Although more than one singlet potential surface arises when $O(^1D)$ and N_2 approach one another--and more than one triplet surface from $O(^3P)$ and N_2--we have considered a simplified model consisting of only one singlet and one triplet potential energy surface, designated V_1 and V_2, respectively. Section III describes the particular potential functions that we have used.

The process in Eq. (1.1) can be adequately described by a Tully-Preston "surface-hopping" model;[8] in this approach the nuclei move classically on potential energy surfaces, having the possibility of changing from one surface to another only when a trajectory crosses an intersection of the two potential surfaces; the probability of changing surfaces at an intersection is given by the Landau-Zener formula. The present application of this model is actually more straight forward than was Tully and Preston's[8] original work on the $H^+ + H_2$ reaction, for the spin-orbit interaction which couples the two electronic states is much weaker than the electrostatic coupling between the two states of the H_3^+ system. For the present application, therefore, the nuclei can be assumed to move on the "diabatic" potential surfaces which actually intersect, and there is no need for a velocity correction[8] to the trajectory when changing surfaces.

Within this model the quenching cross section, σ_Q, is given by

$$\sigma_Q = \pi b_{max}^2 N^{-1} \sum_{n=1}^{N} P_Q (\underset{\sim}{p}_1^{(n)}, \underset{\sim}{q}_1^{(n)}) \quad , \tag{2.1}$$

where $(\underset{\sim}{p}_1, \underset{\sim}{q}_1)$ denote the initial values for the cartesian coordinates and momenta of the A + BC collision system. These initial conditions are selected by Monte Carlo sampling methods in the usual way,[9] the index n denoting the specific set of initial conditions for the $n^{\underline{th}}$ trajectory; b_{max} is the maximum impact parameter that arises in the sampling of that variable (i.e., $b = b_{max}\sqrt{\xi}$, ξ a random number between 0 and 1). $P_Q\ (\underset{\sim}{p}_1, \underset{\sim}{q}_1)$ is the quenching probability for the trajectory that begins in the initial asymptotic region with initial conditions $(\underset{\sim}{p}_1, \underset{\sim}{q}_1)$.

The Landau-Zener approximation gives the probability of <u>not</u> changing surfaces at a given crossing encounter as

$$p = \exp\left[-\frac{2\pi}{\hbar}\ V_{12}\ (\underset{\sim}{q}(t))^2 / \left|\frac{d}{dt}\ \Delta V(\underset{\sim}{q}(t))\right|\right] \quad , \tag{2.2}$$

where

$$\Delta V(\underset{\sim}{q}) = V_2(\underset{\sim}{q}) - V_1(\underset{\sim}{q}) \quad ,$$

and evaluated at $t = t_o$, t_o being the root of the equation

$$\Delta V(\underset{\sim}{q}(t)) = 0 \quad , \tag{2.3}$$

i.e., the time when the trajectory is at the surface intersection; $V_{12}(\underset{\sim}{q})$ is the spin-orbit interaction which couples the two potential surfaces $V_1(\underset{\sim}{q})$ and $V_2(\underset{\sim}{q})$. The probability of changing potential surfaces is 1 - p. Within the surface-hopping model[8] the net probability of quenching, P_Q of Eq. (2.1), is in general the product of a sequence of probability factors, p's and (1-p)'s,

one factor for each crossing encounter. Because the spin-orbit interaction is so small, however, (1-p) is much smaller than unity and it is essentially no approximation in such circumstances to neglect recrossing, i.e., to assume that once the trajectory has crossed from the singlet to the triplet surface that it does not return to the singlet surface on any subsequent crossing encounters. (According to Figure 1 it would have at most only one chance to do so.) With this assumption the net probability of not quenching, $1 - P_Q$, is the product of the probabilities of not quenching at each individual crossing encounter; i.e., the only way of not quenching is not to quench every time the surface intersection is crossed:

$$1 - P_Q = p_1 p_2 p_3 \cdots \quad , \tag{2.4}$$

where the index k in $\{p_k\}$ refers to the different crossing encounters. The net probability of not quenching is thus given by

$$1 - P_Q = \exp\left[-\sum_k \frac{2\pi}{\hbar} V_{12}\,(\underset{\sim}{q}(t_k))^2 / \left|\frac{d}{dt}\Delta V(\underset{\sim}{q}(t))\right|_{t = t_k}\right], \tag{2.5}$$

where t_k is the time of the $k^{\underline{th}}$ crossing encounter; since

$$\sum_k V_{12}\,(\underset{\sim}{q}(t_k))^2 / \left|\frac{d}{dt}\,\Delta V\,(\underset{\sim}{q}(t))\right|_{t = t_k} \quad ,$$

$$= \int_{-\infty}^{\infty} dt\; V_{12}\,(\underset{\sim}{q}(t))^2\;\delta[\Delta V(\underset{\sim}{q}(t))] \quad , \tag{2.6}$$

Eq. (2.5) for the non-quenching or survival probability has the form of exponential decay:

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

where $\Gamma(t)$ is given by a "golden rule"-like expression:

$$\Gamma(t) \equiv \Gamma(\underset{\sim}{q}(t)),$$

$$\Gamma(\underset{\sim}{q}) = 2\pi\ V_{12}(\underset{\sim}{q})^2\ \ \delta[\Delta V(\underset{\sim}{q})] \quad . \tag{2.8}$$

The quenching probability in Eq. (2.1) is then finally given by

$$P_Q(\underset{\sim}{p}_1,\underset{\sim}{q}_1) = 1 - \exp\{- \int_{-\infty}^{\infty} dt\ \frac{2\pi}{\hbar}\ V_{12}\ (\underset{\sim}{q}(t))^2\ \delta[\Delta V(\underset{\sim}{q}(t))]\}, \tag{2.9}$$

where the trajectory $\underset{\sim}{q}(t)$ in the integrand of the exponent is the one which moves on the singlet potential surface with initial conditions $(\underset{\sim}{p}_1,\underset{\sim}{q}_1)$. As discussed in the Introduction, therefore, even though the quenching probability associated with a single crossing encounter is quite small, P_Q can be sizeable if many crossings occur; it is easy to see, in fact, that P_Q approaches unity in the limit of an infinite number of crossing encounters, i.e., a very long-lived collision complex.

As an aside, it is interesting to note that the above formula, Eqs. (2.1), (2.7)-(2.9), also pertain to the decay of an initial electronic state into a continuum of final electronic states, as is the case for describing Penning Ionization

$$A^* + BC \rightarrow A + BC^+ + e^- \quad . \tag{2.10}$$

Here, of course, the crossing is rigorously irreversable because the electron leaves the scene, whereas in the discrete-discrete process being considered above the irreversable nature of the transition arises because the probability associated with re-crossing is small. For the discrete-continuum process in Eq. (2.10) the width function $\Gamma(\underset{\sim}{q})$ is not restricted to a surface in coordinate space as in Eq. (2.8); the δ function factor is replaced by a density of states factor:

$$\delta[\Delta V(\underset{\sim}{q})] \rightarrow \rho(\underset{\sim}{q}) \quad . \tag{2.11}$$

(If the final state is discrete, then the "density of final states" should of course be a δ function.) With this modification, [Eq. (2.11)], therefore, the analysis developed in this section is directly applicable to collisional ionization problems such as Eq. (2.10).

B. Statistical Approximation.

With the above formulae one can proceed to carry out a Tully-Preston[8] surface-hopping calculation. This would be difficult for the present situation, for--as mentioned in the Introduction--many of the trajectories result in complex formation, and it is extremely difficult[10] numerically to follow such long-lived trajectories. Fortunately, however, the occurrence of complex formation allows one to invoke a statistical model to alleviate the need of following the dynamics precisely.

Specifically, one invokes the ergodic hypothesis to replace the time integrals in Eqs. (2.7) and (2.9) by phase space averages. Thus consider the quantity $A(\underset{\sim}{p}_1,\underset{\sim}{q}_1)$, the exponent in Eq. (2.9):

$$A(\underset{\sim}{p}_1,\underset{\sim}{q}_1) = \int dt\ \Gamma(\underset{\sim}{q}(t;\underset{\sim}{p}_1,\underset{\sim}{q}_1))/\hbar \quad , \tag{2.12}$$

where $\underset{\sim}{q}(t;\underset{\sim}{p}_1,\underset{\sim}{q}_1)$ is the particular classical trajectory that is determined by the initial condition $(\underset{\sim}{p}_1,\underset{\sim}{q}_1)$. If this trajectory forms a collision complex which lives sufficiently long to behave ergodically, then $A(\underset{\sim}{p}_1,\underset{\sim}{q}_1)$ will depend on $\underset{\sim}{p}_1$ and $\underset{\sim}{q}_1$ only through the constants of the motion--total energy E and total angular momentum J--and the time average of Γ can be replaced by an appropriate phase space average. More specifically, this means that

$$A(\underset{\sim}{p}_1,\underset{\sim}{q}_1) = \tau\left[\frac{1}{\tau}\int dt\ \ \Gamma(\underset{\sim}{q}(t;\underset{\sim}{p}_1,\underset{\sim}{q}_1))/\hbar\right] \tag{2.13a}$$

$$\simeq \tau < \Gamma/\hbar >_{E,J} \ \equiv\ A(E,J) \quad , \tag{2.13b}$$

where the phase space average implied by $<X>_{E,J}$ is defined for any function $X(\underset{\sim}{p},\underset{\sim}{q})$ by

$$<X>_{E,J} \equiv \rho(E,J)^{-1} \int d\underset{\sim}{p}\int d\underset{\sim}{q}\ X(\underset{\sim}{p},\underset{\sim}{q})\ \delta[E-H(\underset{\sim}{p},\underset{\sim}{q})]\ \delta[J-\mathcal{J}(\underset{\sim}{p},\underset{\sim}{q})]\ h[f(\underset{\sim}{q})] \tag{2.14a}$$

$$\rho(E,J) = \int d\underset{\sim}{p}\int d\underset{\sim}{q}\ \delta[E-H(\underset{\sim}{p},\underset{\sim}{q})]\ \delta[J-\mathcal{J}(\underset{\sim}{p},\underset{\sim}{q})]\ h[f(\underset{\sim}{q})] \quad , \tag{2.14b}$$

where $\delta(\ )$ is the usual delta function and $h(\ )$ the step function

$$h(x) = \begin{cases} 1, & x > 0 \\ 0, & x < 0 \end{cases} \quad .$$

$J(\underset{\sim}{p},\underset{\sim}{q})$ and $H(\underset{\sim}{p},\underset{\sim}{q})$ are the values of total angular momentum and total energy determined by the phase point $(\underset{\sim}{p},\underset{\sim}{q})$, and $f(\underset{\sim}{q})$ is the function which defines the collision complex, i.e., the collision complex is the inside of the closed surface in configuration space[11] defined by the equation

$$f(\underset{\sim}{q}) = 0 \quad , \tag{2.15}$$

$f(\underset{\sim}{q}) > 0$ (<0) being the inside (outside) of this "critical surface" defined by Eq. (2.15). The values E and J in Eqs. (2.13) and (2.14) are determined by the initial conditions $(\underset{\sim}{p}_1,\underset{\sim}{q}_1)$, i.e.,

$$E = H(\underset{\sim}{p}_1,\underset{\sim}{q}_1)$$

$$J = J(\underset{\sim}{p}_1,\underset{\sim}{q}_1) \quad .$$

The phase space average defined by Eq. (2.14) is thus over all phase space corresponding to total energy E and total angular momentum J and which is inside the critical surface that defines the collision complex.

The time $\tau \equiv \tau(E,J)$ in Eq. (2.13), the average lifetime of the collision complex for a given total energy and total angular momentum, is also given by statistical theory: It is the reciprocal of the average rate of flux out through the critical surface:

$$\tau(E,J)^{-1} \equiv \left\langle \frac{1}{2} \left| \frac{d}{dt} h\,(f) \right| \right\rangle_{E,J} \quad , \tag{2.16}$$

or (since $h'(x) \equiv \delta(x)$)

$$\tau(E,J)^{-1} = \langle \frac{1}{2}\, \delta(f)|\dot{f}|\rangle_{E,J} \quad , \tag{2.17}$$

where[11]

$$\dot{f}(\underset{\sim}{q}) \equiv \frac{d}{dt} f(\underset{\sim}{q}) = \frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{p}/m \quad ; \tag{2.18}$$

the factor $\frac{1}{2}$ appears in the definition of τ [Eq. (2.16)] because the absolute value of the flux across the critical surface has equal contributions from flux in and from flux out.

The statistical approximation for the quenching probability is thus given by

$$P_Q(\underset{\sim}{p}_1,\underset{\sim}{q}_1) = P_Q(E,J) \quad , \tag{2.19}$$

where

$$E = H(\underset{\sim}{p}_1,\underset{\sim}{q}_1) \tag{2.20a}$$

$$J = J(\underset{\sim}{p}_1,\underset{\sim}{q}_1) \quad , \tag{2.20b}$$

and where

$$P_Q(E,J) = 1 - \exp\left[- \tau(E,J)\, \langle\Gamma/\hbar\rangle_{E,J}\right] \tag{2.21a}$$

$$= 1 - \exp\left[- \langle\frac{2\pi}{\hbar} V_{12}{}^2\, \delta(\Delta V)\rangle_{E,J} \,/\, \langle\frac{1}{2}\, \delta(f)|\dot{f}|\rangle_{E,J}\right] \quad . \tag{2.21b}$$

For the applications made in this paper, however, an additional approximation was made, namely conservation of total angular momentum was not explicitly taken into account; i.e., the delta functions involving total angular momentum in the phase space average [Eq. (2.14)] were omitted. As a function only of total energy, therefore, the average quenching probability is given by

$$P_Q(E) = 1 - \exp\left[- \tau(E) \ \langle \Gamma/\hbar \rangle_E\right] \tag{2.22a}$$

$$= 1 - \exp\left[- \langle \frac{2\pi}{\hbar} \ V_{12}{}^2 \ \delta(\Delta V)\rangle_E \ / \ \langle \frac{1}{2} \ \delta(f) |\dot{f}| \rangle_E\right], \tag{2.22b}$$

where for any function $X(\underset{\sim}{p},\underset{\sim}{q})$ the average $\langle X \rangle_E$ is a microcanonical phase space average over the region of the collision complex:

$$\langle X \rangle_E \equiv \rho(E)^{-1} \int d\underset{\sim}{p} \int d\underset{\sim}{q} \ X(\underset{\sim}{p},\underset{\sim}{q}) \ \delta[E-H(\underset{\sim}{p},\underset{\sim}{q})] \ h[f(\underset{\sim}{q})] \tag{2.23a}$$

$$\rho(E) = \int d\underset{\sim}{p} \int d\underset{\sim}{q} \ \delta[E-H(\underset{\sim}{p},\underset{\sim}{q})] \ h[f(\underset{\sim}{q})] \quad . \tag{2.23b}$$

There are known examples of "angular momentum-limited" reactions for which this added approximation would be poor, but the present system should not be such a case. The Appendix gives more details of the evaluation of the phase space averages which appear in (2.22) and elsewhere in this section.

With this simplification, that the quenching probability depends only on the total energy, Eq. (2.1) for the quenching cross section takes an extremely simple form because the initial

conditions for the trajectories correspond to a fixed initial energy. The probability factor in Eq. (2.1) is thus the same for all trajectories which form complexes, so that Eq. (2.1) factors into two independent parts:

$$\sigma_Q(E) = \sigma_c(E)\, P_Q(E) \quad , \tag{2.24}$$

where $\sigma_c(E)$ is the cross section for complex formation,

$$\sigma_c(E) = \pi\, b_{max}^2\, (N_c/N) \quad , \tag{2.25}$$

N_c being the number of Monte Carlo-begun trajectories which form complexes, and with $P_Q(E)$ given by Eq. (2.22) above. (There are actually a small number of trajectories which quench without forming complexes, and the contribution from them should be added to the expression in Eq. (2.24). This cross section for "direct" quenching, however, was negligible in comparison of that from the complex mechanism for all cases studied.) The quenching cross section is thus the cross section for complex formation multiplied by the average probability that the collision complex quenches.

C. Distribution of Product States.

The fraction of the total energy which appears as vibrational excitation of product N_2 can only be obtained rigorously by following the complete trajectories through the long-lived collision complex to the final asymptotic region, i.e., by applying the surface-hopping model[8] *in toto*. As mentioned above, this would

be extremely difficult to do and is probably unwarranted. Within the spirit of the statistical approximation introduced above, however, one can obtain this quantity quite simply.

Consistent with the assumption of ergodicity of the collision complex, one may assume that all degrees of freedom of the collision complex are in microcanonical equilibrium. If one adds the additional assumption, common to statististical descriptions of final state distributions, that there is no energy transfer between translational and internal degrees of freedom as the fragments separate from the region of the transition, then the probability $P_Q(\varepsilon,E)$ that a collision complex with total energy E quenches and has an energy ε in vibrational excitation of N_2 is proportional to

$$P_Q(\varepsilon,E) \sim \langle(\Gamma/\hbar)\ \delta(\varepsilon-h_{vib})\rangle_E \quad , \tag{2.26}$$

where h_{vib} is the vibrational Hamiltonian for an isolated N_2 molecule (see the Appendix). Conservation of probability--

$$\int d\varepsilon \quad P_Q(\varepsilon,E) = P_Q(E) \tag{2.27}$$

--can then be used to determine $P_Q(\varepsilon,E)$ absolutely:

$$P_Q(\varepsilon,E) = P_Q(E)\ \langle(\Gamma/\hbar)\ \delta(\varepsilon-h_{vib})\rangle_E/\langle\Gamma/\hbar\rangle_E \quad , \tag{2.28}$$

with $P_Q(E)$ given above by Eq. (2.22). The cross section for quenching and having an internal energy ε is then given by

$$\sigma_Q(\varepsilon,E) = \sigma_c(E)\ P_Q(\varepsilon,E) \quad , \tag{2.29}$$

and one sees that the integral of this over all ε is the total quenching probability of Eq. (2.24):

$$\int d\varepsilon\ \sigma_Q(\varepsilon,E) = \sigma_Q(E) \quad . \tag{2.30}$$

D. Unimolecular Decomposition of N_2O.

For completeness we give the expressions for the rate of unimolecular decay of N_2O which result from the above model. If k(E) is the microcanonical unimolecular decay rate, then standard unimolecular theory[12] gives the effective (pressure dependent) unimolecular rate constant as

$$k_{uni}\ (\omega) = Q_o\ (\beta)^{-1} \int dE\ \rho(E)\ e^{-\beta E}\ \frac{\omega k(E)}{\omega + k(E)} \quad , \tag{2.31}$$

where ω is the collision frequency with bath molecules, and Q_o is the partition function for the complex:

$$Q_o\ (\beta) = \int dE\ \rho(E)\ e^{-\beta E}$$

where $\rho(E)$ is defined by Eq. (2.23b). The statistical model described in Section II B gives the microcanonical unimolecular decay rate as

$$k(E) = \tau(E)^{-1}\ P_Q(E) \quad , \tag{2.32}$$

where $\tau(E)^{-1}$ and $P_Q(E)$ are the same quantities as in Eq. (2.22); the function $f(\underset{\sim}{q})$ which defines the critical surface should in this case, however, be chosen as $f(\underset{\sim}{q}) = \Delta V(\underset{\sim}{q})$, i.e., the critical surface is the surface of intersection of the singlet and triplet. In the strong coupling limit, $V_{12} \to \infty$, $P_Q(E) \to 1$ so that

$$\lim_{V_{12}\to\infty} k(E) = \tau(E)^{-1} \equiv \left\langle \frac{1}{2}\,\delta(f)\,|\dot{f}|\right\rangle_E \quad , \tag{2.33}$$

the standard RRKM result for a single potential surface; i.e., in this limit the "rate determining step" is the rate of getting to the critical surface and crossing it, for once there the spin-orbit transition occurs instantaneously (since $V_{12} \to \infty$). In the weak coupling limit, $V_{12} \to 0$, one has

$$\begin{aligned} P_Q(E) &\equiv 1 - \exp\left[-\tau(E) \langle \Gamma/\hbar \rangle_E\right] \\ &\simeq \tau(E) \langle \Gamma/\hbar \rangle_E \quad , \end{aligned} \tag{2.34}$$

so that k(E) of Eq. (2.32) becomes simply a phase space version of Fermi's "golden rule":

$$\begin{aligned} \lim_{V_{12}\to 0} k(E) &= \tau(E)^{-1}\,\tau(E) \langle \Gamma/\hbar \rangle_E = \langle \Gamma/\hbar \rangle_E \\ &= \left\langle \frac{2\pi}{\hbar} V_{12}^{\,2}\,\delta(\Delta V)\right\rangle_E \quad ; \end{aligned} \tag{2.35}$$

here the "rate determining step" is the rate of singlet-triplet transitions induced by the spin-orbit interaction at the surface intersection.

III. POTENTIAL ENERGY SURFACES

Within the model described in the previous section it is necessary to determine the cross section for complex formation on the initial singlet potential surface and then an average quenching probability. The cross section for complex formation, which involves molecular dynamics only on the singlet potential energy surface, was determined by classical trajectory calculations with two different model potential surfaces (see below), and the quenching probability--which involves both the singlet and triplet potential surfaces--was obtained from Eq. (2.22). Numerical values of all potential parameters which appear in the expressions below are given in Table I.

The first potential surface, designated I, involves only translational-rotational coupling; vibration was uncoupled from these modes, so that loss of energy from translation can occur only via rotational excitation. Specifically, singlet potential surface I is

$$V_1^{I}(r,R,\gamma) = v_{N_2}(r) + V_{int}^{I}(r,R,\gamma) \quad , \tag{3.1}$$

where $v_{N_2}(r)$ is the vibrational potential of an isolated N_2 molecule (taken to be a Morse oscillator)

$$v_{N_2}(r) = D_1\left[e^{-2\beta_{N_2}(r-r_{N_2})} - 2\,e^{-\beta_{N_2}(r-r_{N_2})}\right] , \tag{3.2}$$

and the interaction term is a Morse function whose well depth is modulated by the angle γ between the diatom vector $\vec{r}$ and the center of mass translational coordinate vector $\vec{R}$:

$$V_{int}^{I}(r,R,\gamma) = D_2 \left[1 - \zeta(1-\cos^2\gamma)\right] \left[e^{-2\alpha(R-Re)} - 2\, e^{-\alpha(R-Re)}\right]. \quad (3.3)$$

The anisotropy parameter ζ was chosen to reproduce approximately the well depths of the collinear and perpendicular arrangements of N_2 and $O(^1D)$.[13]

Potential surface II for the singlet state included, in addition, vibrational coupling so that complex formation would occur <u>via</u> vibrational and rotational excitation. The same angular coupling as in surface I was retained, and the vibrational coupling was introduced by (1) allowing some of the Morse parameters of the N_2 vibrational potential to depend parametrically on the position of the O atom, and (2) having the distance in Eq. (3.3) refer, when $\gamma = 0$, to the N - O separation rather than to the distance between O and the center of mass of N_2. Thus potential surface II is

$$V_1^{II}(r,R,\gamma) = D_1 \left[e^{-2\beta_1(r-r_1)} - 2\, e^{-\beta_1(r-r_1)}\right]$$

$$+ D_2 \left[1 - \zeta\,(1-\cos^2\gamma)\right] \left[e^{-2\alpha(R - \frac{r}{2} - r_o)} - 2\, e^{-\alpha(R - \frac{r}{2} - r_o)}\right], \quad (3.4)$$

where β_1 and r_1 are functions of R:

$$\beta_1 \equiv \beta_1(R) = \beta_{N_2O} + (\beta_{N_2} - \beta_{N_2O})\, S(R) \tag{3.5a}$$

$$r_1 \equiv r_1(R) = r_{N_2O} + (r_{N_2} - r_{N_2O})\, S(R) \quad ; \tag{3.5b}$$

S(R) is the "switching function"

$$S(R) = \frac{1}{2} + \frac{1}{2}\tanh[\lambda(R-R_o)] \quad , \tag{3.6}$$

and is defined so that

$$S(R) = \begin{cases} 1, & R \gg R_o \\ 0, & R \ll R_o \end{cases} \quad .$$

For large R, therefore, $\beta_1(R)$ and $r_1(R)$ take on the values corresponding to the isolated N_2 molecule, and for small R their values were chosen so that potential II has the correct bond force constants for the N_2O molecule. Surface II degenerates into surface I with the replacements $\beta_1 \rightarrow \beta_{N_2}$, $r_1 \rightarrow r_{N_2}$, and $r \rightarrow r_{N_2}$ in the second term of Eq. (3.4) (i.e., $R_e \equiv r_o + \frac{1}{2} r_{N_2}$).

The triplet potential surface, which is needed only to construct the difference potential $\Delta V(\underset{\sim}{q})$ for use in computing the quenching probability from Eq. (2.22), was taken to have an exponential repulsion between $O(^3P)$ and the center of mass of N_2,

$$V_2(r,R,\gamma) = v_{N_2}(r) + A[1 - \zeta'(1-\cos^2\gamma)]\, e^{-\alpha' R} \quad , \tag{3.7}$$

and the spin-orbit interaction, $V_{1,2}(\underset{\sim}{q})$, was assumed to be independent of coordinates and have the value

$$V_{12}(r,R,\gamma) = V_{12} = 80 \text{ cm}^{-1} \quad . \tag{3.8}$$

The function $f(\underset{\sim}{q})$, which defines the region of the collision complex <u>via</u> Eq. (2.15), was taken as

$$f(r,R,\gamma) = R_c - R \quad . \tag{3.9}$$

Although none of these potential energy surfaces are expected to be a particularly accurate representation of the $O - N_2$ system, they are qualitatively reasonable in their gross features and should make it possible to answer the basic questions, namely, is there an appreciable cross section for $O(^1D) + N_2$ to form a collision complex. By comparing the results obtained from surfaces I and II it should also be possible to tell whether complex formation occurs primarily through rotational or vibrational excitation.

IV. RESULTS

Figure 2 shows the quenching probability, $P_Q(E)$ of Eq. (2.22), as a function of initial collision energy for potential surfaces I and II. (Since the initial state of N_2 is always taken as $v = 0$, $j = 6$, the total energy and the initial translation energy are related simply by an additive constant.) At thermal energies the quenching probability is close to unity, so that the cross section for quenching is essentially that for complex formation. At higher collision energies the probability falls because the lifetime of the complex is shorter and there is thus less chance of quenching.

Trajectory calculations to determine the cross section for complex formation on the singlet surface were carried out at collision energies 0.03, 0.6, and 1.2 eV for potential surfaces I and II. Table II gives the cross sections for complex formation which--multiplied by the appropriate quenching probability--give the cross sections for quenching, also listed in Table II.

The inclusion of vibrational coupling in surface II is seen to increase the cross section for complex formation, more so the higher the collision energy; thus σ_c is 25%, 100%, and 600% greater for surface II than for surface I at collision energies of 0.03, 0.06, and 1.2 eV, respectively. At thermal energy, therefore, rotational excitation accounts for $\frac{3}{4}$ of the complex formation, while at higher energies vibrational excitation is the dominant mechanism leading to complex formation.

An estimate of the thermally averaged rate constant can be obtained from the expression

$$k_Q(T) \simeq (\tfrac{1}{5})\ \bar{v}\ \sigma_Q(E) \quad , \tag{4.1}$$

for E = kT and where

$$\bar{v} = (8\ kT/\pi\mu)^{1/2} \quad ;$$

the factor $\frac{1}{5}$ in Eq. (4.1) is a statistical factor which accounts for the fact that only one of the five electronic states arising from $O(^1D) + N_2$ corresponds to the strongly attractive ground state. Eq. (4.1) gives a room temperature (i.e., kT = 0.03 eV) rate constant of 3.9×10^{-11} and 5.4×10^{-11} cm^3/mol. sec., respectively, for potential surfaces I and II, in excellent agreement with experimental values.[6] At kT = 0.6 eV the quenching rate has decreased only to 1.1×10^{-11} and 1.3×10^{-11} cm^3/mol. sec. for surfaces I and II, respectively, and thus appears not to be a sensitive function of temperature.

Figure 3 shows the vibrational energy distribution of product N_2, obtained using potential surface II, for the three different collision energies.

The average energy in vibrational excitation,

$$\bar{\varepsilon} = \int d\varepsilon\ \varepsilon\ P_Q(\varepsilon,E)/P_Q(E) \quad , \tag{4.2}$$

increases with increasing collision energy E, and the distribution broadens. At room temperature, E ≃ 0.03 eV, the average energy

in vibrational excitation of N_2 is approximately 20% of the exoergicity of reaction (1.1), also in good qualitative agreement with the latest experimental results.[4]

V. CONCLUDING REMARKS

Our basic picture of the quenching mechanism is the same as Tully's,[7] namely that $O(^1D) + N_2$ forms a collision complex on the singlet potential surface and thus passes through the intersection with the triplet state many times. The results presented in Section IV are also in qualitative, and even semiquantitative agreement with Tully's, specifically the magnitude of the thermal rate constant and the amount of energy which appears as vibrational excitation of product N_2.

The way in which complex formation is treated in the present work, however, and the nature of the potentials involved, are quite different from Tully's.[7] Tully uses only a dispersion term, $- C_6/R^6$, for the singlet potential in order to determine a cross section for complex formation, while our potential surfaces I and II do not even have such a dispersion term; the cross section for complex formation was determined in our case by actually computing classical trajectories for the assumed rather crude, but qualitatively reasonable potential surfaces. The way in which the statistical approximation is used to determine the average quenching probability of the collision complex is also somewhat different in the two approaches.

In view of these differences in approach between ours and Tully's,[7] it is reassuring that the results of the two treatments are in such good agreement. This is consistent with Tully's observation that his results at thermal energy are rather insensitive

to the C_6 coefficient he estimates and with the similarity of our thermal energy results for potential surfaces I and II. At higher collision energy Tully's model for determining the cross section for complex formation becomes invalid, while the classical trajectory approach is of course still applicable. Our results using potential surfaces I and II (cf. Table II) are quite different at these higher collision energies, however, indicating that a more accurate characterization of the potential surfaces is required to obtain reliable results at these energies.

In conclusion, this process is a dramatic demonstration of how different an atom-diatom collision can be from an atom-atom collision, and how radically the picture changes when additional degrees of freedom are available to participate in the collision dynamics. If this were an atom-atom collision system, the quenching cross section at thermal energy would be extremely small, proportional to the square of the spin-orbit coupling; for the present atom-diatom case the cross section is sizeable and essentially <u>independent</u> of the magnitude of spin-orbit coupling. It is interesting to contemplate what other surprises may lie in store as one learns more fully how to incorporate these additional degrees of freedom which are present in molecular systems.

Acknowledgment

The calculations reported in this paper were performed on a Datacraft 6024/4 minicomputer funded by NSF grant GP-39317.

Appendix: Phase Space Integrals

The phase space integrals required in Section II are all of the form

$$\langle X\rangle_E = \rho(E)^{-1} \int d\underset{\sim}{p} \int d\underset{\sim}{q}\; X(\underset{\sim}{p},\underset{\sim}{q})\; \delta[E-H(\underset{\sim}{p},\underset{\sim}{q})]\; h[f(\underset{\sim}{q})] \tag{A.1}$$

where

$$\rho(E) = \int d\underset{\sim}{p} \int d\underset{\sim}{q}\; \delta[E-H(\underset{\sim}{p},\underset{\sim}{q})]\; h[f(\underset{\sim}{q})] \quad . \tag{A.2}$$

(The normalization factor $\rho(E)$ is not required in order to compute $P_Q(E)$ and $P_Q(\varepsilon,E)$ of Sections IIB and IIC because they involve a ratio of phase space averages, but it would be required to determine the unimolecular rate constant of Section IID.) Choosing cartesian coordinates and momenta for the A + BC system

$$\underset{\sim}{q} \equiv \vec{r}, \vec{R}$$
$$\underset{\sim}{p} \equiv \vec{p}, \vec{P} \quad ,$$

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

$$H = \frac{P^2}{2\mu} + \frac{p^2}{2m} + V(r,R,\gamma) \quad , \tag{A.3}$$

where μ and m are the appropriate reduced masses, γ the angle between $\vec{r}$ and $\vec{R}$, and V is the singlet potential surface. If

the function f, which defines the collision complex as discussed regarding Eq. (2.15), does not involve momenta--as we have assumed[11] for the applications in this paper--then it will also depend only on the three coordinates r,R, and γ which determine the size and shape of the A - B - C triangle.

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

$$\rho(E) = \int d_3\vec{r}\int d_3\vec{R}\ h[f(r,R,\gamma)]\ \int d_3\vec{p}\int d_3\vec{P}\ \delta[E - V(r,R,\gamma) - P^2/2\mu - p^2/2m] \quad . \tag{A.4}$$

The momentum integrals can all be carried out, giving

$$\rho(E) = 4\pi^3\ (\mu m)^{3/2}\ \int d_3\vec{r}\int d_3\vec{R}\ h[f(r,R,\gamma)]\ [E - V(r,R,\gamma)]^2, \tag{A.5}$$

with the domain of integration restricted to the region for which

$$E - V(r,R,\gamma) \geq 0 \quad . \tag{A.6}$$

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

$$\int d_3\vec{r}\int d_3\vec{R}\ F(r,R,\gamma) = 8\pi^2 \int_0^\infty dr\ r^2 \int_0^\infty dR\ R^2 \int_{-1}^{1} d(\cos\gamma)\ F(r,R,\gamma); \tag{A.7}$$

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

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

For the case

$$X(\underset{\sim}{p},\underset{\sim}{q}) = \Gamma(\underset{\sim}{q})/\hbar = \frac{2\pi}{\hbar} V_{12}(r,R,\gamma)^2 \, \delta[\Delta V(r,R,\gamma)] \qquad (A.9)$$

the momentum integrals and the integral over the three Euler angles can all be evaluated in the same manner as in the preceeding paragraph, so that

$$\langle\Gamma/\hbar\rangle_E = \rho(E)^{-1} \, 32\pi^5 \, (\mu m)^{3/2} \int dr \, r^2 \int dR \, R^2 \int d(\cos\gamma) \, h[f(r,R,\gamma)]$$

$$\times \frac{2\pi}{\hbar} V_{12} \, (r,R,\gamma)^2 \, \delta[\Delta V(r,R,\gamma)] \quad [E - V(r,R,\gamma)]^2 . \qquad (A.10)$$

Because of the delta function in the integrand of Eq. (A.10), one of the integrals can be evaluated directly, $\int dR$ say, and the remaining integrals over r and cos γ carried out numerically.

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

$$X(\underset{\sim}{p},\underset{\sim}{q}) = \frac{1}{2} \, \delta[f(\underset{\sim}{q})] \, \left|\frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{p}/m\right| \quad , \qquad (A.11)$$

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

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

$$= \rho(E)^{-1} \frac{32\pi^2}{15} \, (\mu m)^{3/2} \int d_3\vec{r} \int d_3\vec{R} \quad \delta[f(r,R,\gamma)]$$

$$[E-V(r,R,\gamma)]^{5/2} \quad [\frac{2}{\mu} \left|\frac{\partial f}{\partial \vec{R}}\right|^2 + \frac{2}{m} \left|\frac{\partial f}{\partial \vec{r}}\right|^2]^{1/2} \quad , \qquad (A.12)$$

where

$$\left|\frac{\partial f}{\partial \vec{R}}\right|^2 = \frac{\partial f}{\partial \vec{R}} \cdot \frac{\partial f}{\partial \vec{R}}$$

$$\left|\frac{\partial f}{\partial \vec{r}}\right|^2 = \frac{\partial f}{\partial \vec{r}} \cdot \frac{\partial f}{\partial \vec{r}} \quad .$$

Eq. (A.6) also applies here, so that one obtains

$$\tau(E)^{-1} = \rho(E)^{-1} \frac{256\ \pi^4}{15} (\mu m)^{3/2} \int dr\ r^2 \int dR\ R^2 \int d(\cos\gamma)\ \delta[f(r,R,\gamma)]$$

$$[E - V(r,R,\gamma)]^{5/2} \left[\frac{2}{\mu} \left|\frac{\partial f}{\partial \vec{R}}\right|^2 + \frac{2}{m} \left|\frac{\partial f}{\partial \vec{r}}\right|^2 \right]^{1/2} . \qquad (A.13)$$

With $f(r,R,\gamma)$ given by Eq. (3.9) for the present applications, Eq. (A.13) simplifies to

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

and the two remaining integrations were carried out numerically.

Finally, the vibrational energy distribution of N_2 corresponds to Eq. (A.1) with

$$X(\underset{\sim}{p},\underset{\sim}{q}) = \delta(\varepsilon - h_{vib})\ \Gamma(\underset{\sim}{q})/\hbar$$

$$= \frac{2\pi}{\hbar} V_{12}(\underset{\sim}{q})^2\ \delta[\Delta V(\underset{\sim}{q})]\ \delta(\varepsilon - h_{vib}) \quad , \qquad (A.15)$$

where the vibrational Hamiltonian is

$$h_{vib} = p_r^{\ 2}/2m + v(r) \quad , \qquad (A.16)$$

$p_r = \vec{p} \cdot \vec{r}/r$ being the radial (i.e., vibrational) component of the B - C momentum and $v(r)$ the N_2 vibrational potential. Thus

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

$$X\ \delta[\Delta V(r,R,\gamma)]\ \int d_3\vec{p}\int d_3\vec{P}\ \ \delta[E-V(r,R,\gamma) - P^2/2\mu - p^2/2m]$$

$$X\ \delta[\varepsilon- v(r) - (\vec{p} \cdot \vec{r})^2/2mr^2] \quad . \qquad (A.17)$$

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

$$< \delta(\varepsilon-h_{vib})\ \Gamma/\hbar >_E = \rho(E)^{-1}\ \frac{256\ \pi^4}{3}\ \ (\mu m)^{3/2} \int dr\ r^2\int dR\ R^2\int d(\cos\gamma)$$

$$h[f(r,R,\gamma)]\ \frac{2\pi}{\hbar}\ V_{12}(r,R,\gamma)^2\ \delta[\Delta V(r,R,\gamma)]\ [E-\varepsilon-V_{int}(r,R,\gamma)]^{3/2}[\varepsilon-v(r)]^{-1/2}, \qquad (A.18)$$

where

$$V_{int}(r,R,\gamma) = V(r,R,\gamma) - v(r) \quad .$$

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

$$\int d\varepsilon\ [E-\varepsilon-V_{int}]^{3/2}\ [\varepsilon-v(r)]^{-1/2} = \frac{3\pi}{8}\ [E-V(r,R,\gamma)]^2 \quad ,$$

the integral of Eq. (A.18) over ε gives, as it should, the result in Eq. (A.10).]

In concluding, 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,

$$H = h_1 + h_2 \quad ,$$

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

$$P(\varepsilon,E) = \int d\underset{\sim}{p}\int d\underset{\sim}{q}\ \delta(\varepsilon-h_1)\ \delta(E-h_1-h_2)/\int d\underset{\sim}{p}\int d\underset{\sim}{q}\delta(E-h_1-h_2) \quad , \tag{A.19}$$

and for a system of oscillators this is easily found to be

$$P(\varepsilon,E) = C\ \varepsilon^{s_1-1}\ (E-\varepsilon)^{s_2-1}/E^{s_1+s_2-1} \quad , \tag{A.20}$$

where C is a numerical factor.

Often the distribution in ε is observed experimentally[5] to be linear on a semi-log plot for a an appreciable range of ε. This implies that

$$-\frac{d}{d\varepsilon}\ \ln P(\varepsilon,E) \neq \text{function of } \varepsilon \quad ; \tag{A.21}$$

from Eq. (A.20) one finds

$$-\frac{d}{d\varepsilon}\ \ln P(\varepsilon,E) = \frac{s_2-1}{E-\varepsilon} - \frac{s_1-1}{\varepsilon} \quad .$$

For $s_1 = 1$ and $\varepsilon \ll E$, this does satisfy the condition in Eq. (A.21), i.e., the <u>ε-distribution is Boltzmann</u>, characterized by the temperature

$$kT_\varepsilon = E/(s_2 - 1) \quad .$$

The fact that a sub-system of a much larger microcanonical system behaves canonically is, of course, a well-known phenomenon in statistical mechanics.

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* Supported in part by the U. S. Atomic Energy Commission, and by the National Science Foundation under grants GP-34199X and 41509X.

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11. It may sometimes be desirable to define the collision complex by a surface involving coordinate <u>and</u> momentum space, i.e., by an equation of the form

$$f(\underset{\sim}{p},\underset{\sim}{q}) = 0 \quad ;$$

this is actually the case for the orbiting model used by Tully (ref. 7). Eq. (2.18) would then be modified according to

$$\dot{f}(\underset{\sim}{p},\underset{\sim}{q}) \equiv \frac{d}{dt} f(\underset{\sim}{p},\underset{\sim}{q}) = \frac{\partial f}{\partial \underset{\sim}{q}} \cdot \dot{\underset{\sim}{q}} + \frac{\partial f}{\partial \underset{\sim}{p}} \cdot \dot{\underset{\sim}{p}}$$

$$= \frac{\partial f}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{p}/m - \frac{\partial f}{\partial \underset{\sim}{p}} \cdot \frac{\partial V}{\partial \underset{\sim}{q}} \quad .$$

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TABLE I. Potential Parameters[a]

D_1	=	0.364	α	=	1.785
D_2	=	0.138	β_{N_2}	=	1.423
r_{N_2}	=	2.07	β_{N_2O}	=	1.135
r_{N_2O}	=	2.13	ζ	=	0.8285
r_o	=	2.25	ζ'	=	0.01
R_e	=	$r_o + \frac{1}{2} r_{N_2} = 3.28$	A	=	0.75
R_o	=	4.9	α'	=	0.7
R_c	=	8.0	λ	=	1.7

[a]All in atomic units. These numerical values refer to the potential functions described in Section III.

TABLE II. Results for Quenching of $O(^1D)$ by N_2.

	Surface I[a]			Surface II[a]			
E^b	$\sigma_C{}^c$	$\sigma_Q{}^d$	$k_Q{}^e$	$\sigma_C{}^c$	$\sigma_Q{}^d$	$k_Q{}^e$	$\bar{\varepsilon}^f$
0.03	38	26	3.9×10^{-11}	48	36	5.4×10^{-11}	0.34
0.6	13	0.7	1.1×10^{-11}	26	2	1.3×10^{-11}	0.54
1.2	3	0.1	0.4×10^{-11}	19	1	0.7×10^{-11}	0.75

[a] The results using singlet potential surface I, or II, which are described in Section III.

[b] The initial translational energy in eV.

[c] The cross section ($\mathring{A}^2$) for complex formation, as defined by Eq. (2.25).

[d] The quenching cross section ($\mathring{A}^2$), as defined in Eq. (2.24).

[e] The rate constant (cm^3/mol. sec.) for quenching at a temperature kT = E, as defined by Eq. (4.1).

[f] The aveage energy (eV) in vibrational excitation of product N_2, as defined by Eq. (4.2).

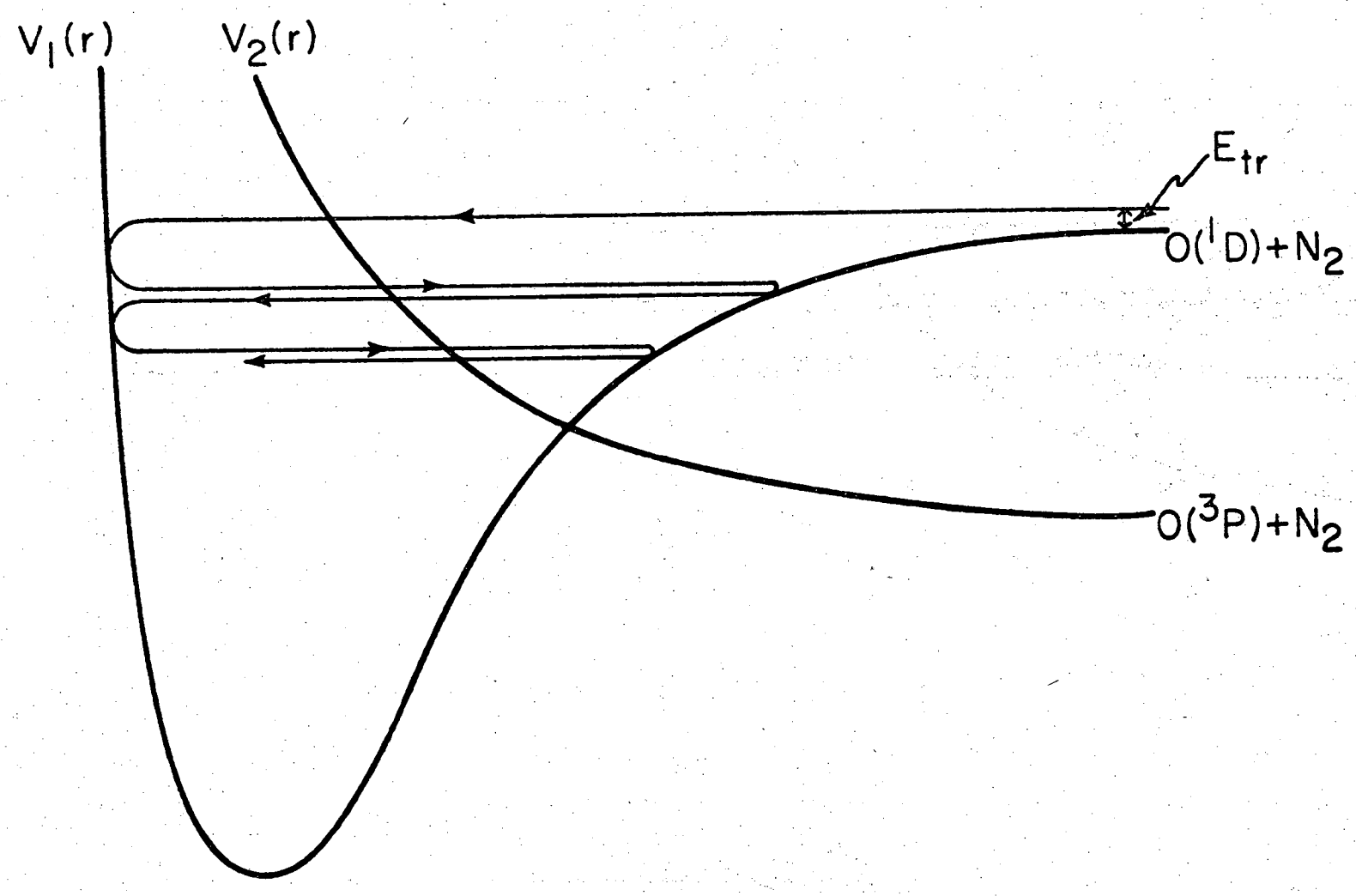
Figure Captions

Figure 1. A sketch of the lowest singlet, $V_1(r)$, and a typical triplet, $V_2(r)$, potential curve for the $O - N_2$ system. The arrow depicts a thermal energy collision of $O(^1D)$ and N_2 which results in sufficient rotational/vibrational excitation of N_2 (occuring predominantly at the inner classical turning point) to form a collision complex.

Figure 2. The quenching probability as a function of initial collision energy E, as defined by Eq. (2.22); 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.

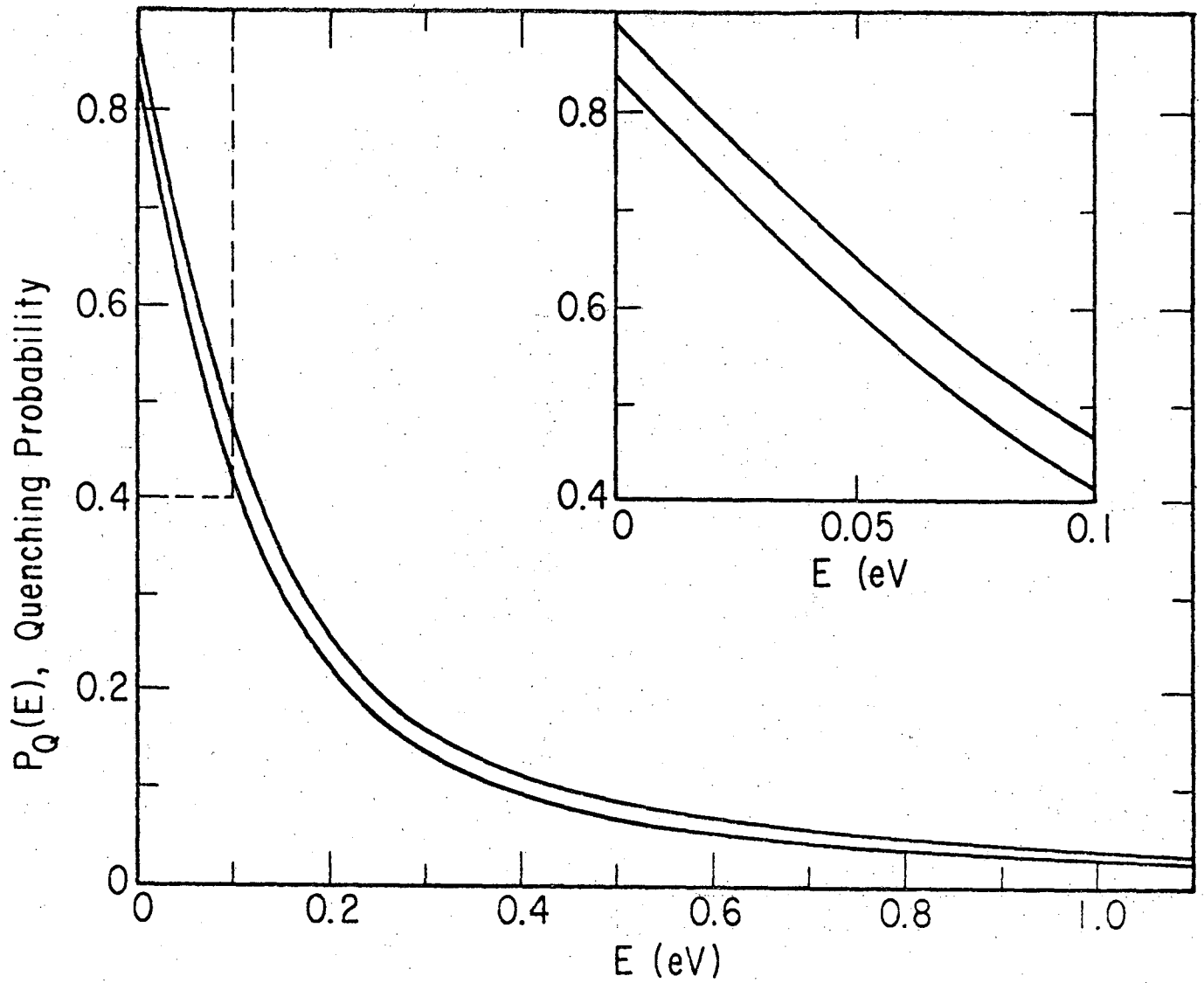
Figure 3. The distribution of vibrational energy ε in the product N_2 molecule at three different initial collision energies E, as defined by Eq. (2.28); the quantity shown is also identical to the cross section ratio $\sigma_Q(\varepsilon,E)/\sigma_Q(E)$. Because the ratio of the probability distribution to the total quenching probability is plotted, the area under each curve is unity.

0 0 0 0 4 2 0 1 9 9 9



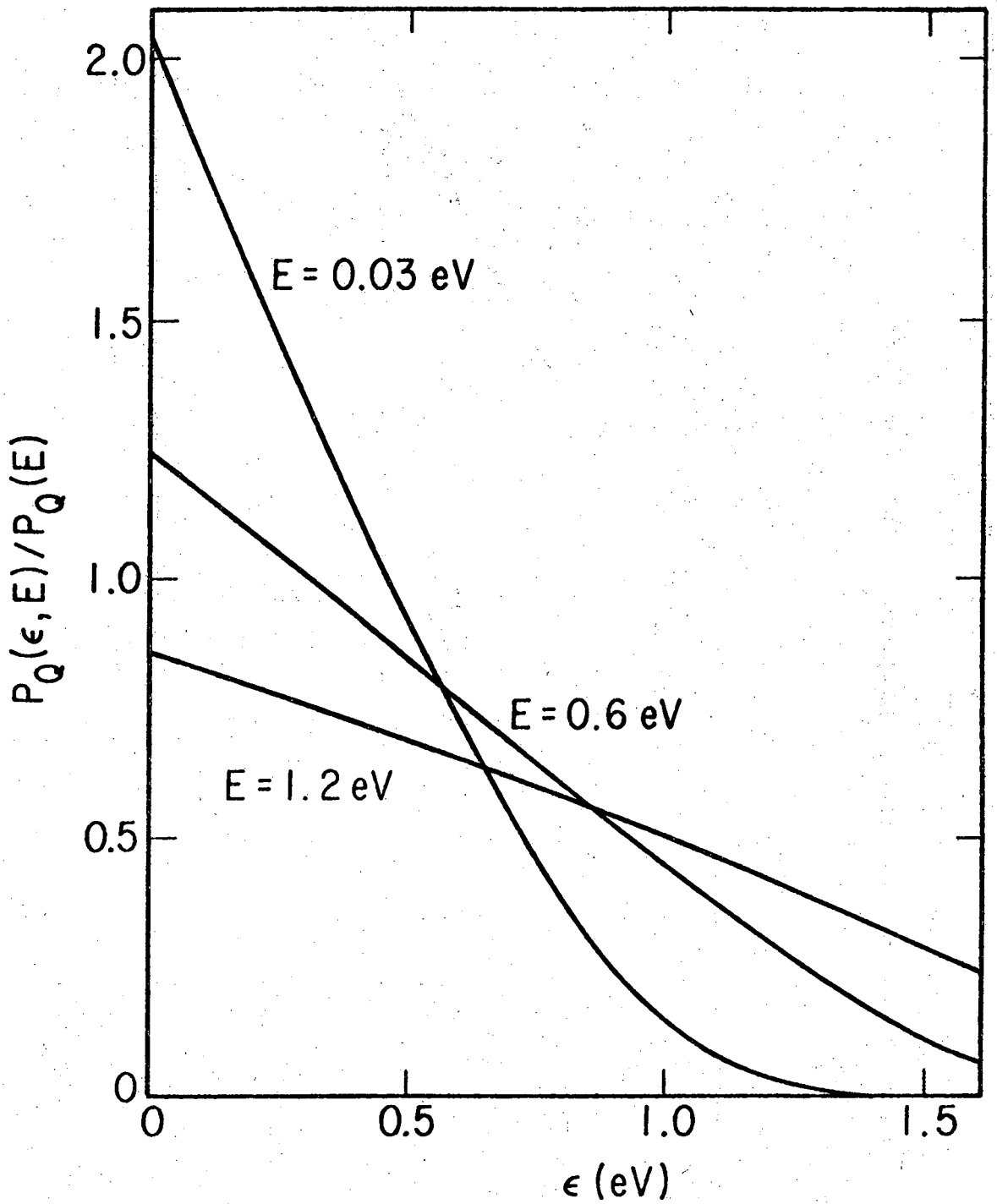
XBL 749-7224

Fig. 1



XBL 749-7225

Fig. 2



XBL 7410-7380

Fig. 3

0 0 0 0 4 2 0 2 0 0 1

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