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On the Reactions of N2 with O

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Unimolecular decomposition of N_2O, quenching of $O(^1D)$ by N_2, and vibrational relaxation of N_2 in the presence of $O(^3P)$ are all believed to occur by the same curve crossing mechanism. This mechanism is examined making use of a complete theory of curve crossings that we have developed earlier. Good agreement with experiment is found for the unimolecular decomposition rate. The simple curve crossing mechanism does not explain the observed $O(^1D)$ quenching rate; this rate must be due to complex formation and/or additional crossings. At high temperatures, the calculated vibrational relaxation time is in good agreement with experiment, but at low temperatures there is a serious, unexplained discrepancy.

I. INTRODUCTION

Recently Fisher and Bauer[1] have presented a theoretical analysis of three reactions involving O and N_2: the unimolecular decomposition of N_2O, the quenching of $O(^1D)$ in collisions with N_2, and the vibrational relaxation of N_2 in the presence of $O(^3P)$. These reactions take place by a crossing of the ^1D and ^3P curves, which are coupled by spin–orbit terms in the Hamiltonian. Fisher and Bauer arrived at plausible results for the cross sections, but only by making some implausible assumptions. First, they treated the curve crossings by Landau–Zener theory, which can be shown to be inapplicable to this situation. Second, in order to arrive at results that are in agreement with experiment, they were obliged to assume a spin–orbit matrix element between $2\frac{1}{2}$ and 6 times as large as the spin–orbit coupling in isolated O; this is implausibly large.[2] Finally, they treated the vibrational relaxation of N_2 and the unimolecular decomposition of N_2O by somewhat different approximations. In fact, the two reactions are very similar, and should be treated the same way.

The purpose of these remarks is twofold. First, we wish to give a pedagogical application of the rigorous curve crossing theory that we have presented in a previous paper.[3] Second, we wish to display clearly the present level of understanding (or misunderstanding) of these N_2–O reactions.

II. UNIMOLECULAR DECOMPOSITION OF N_2O

The N_2O molecule is known to be most stable in the linear N–N–O configuration, and following Ref. 1, we adopt the working hypothesis that the decomposition also occurs mainly in the linear configuration. The potential curves have been obtained by the Augen method,[4] and are shown in Fig. 1. The adiabatic curves, obtained by diagonalizing the spin–orbit coupling, are shown as dotted lines; their splitting has been greatly exaggerated for clarity. To allow direct comparison with Ref. 1, we have used the same potentials, but we have assumed a spin–orbit coupling of 80 cm⁻¹, in contrast with the implausibly large 200–500 cm⁻¹. Since transitions from the bound ^1D state to the antibound ^3P state are likely only near the crossing, it follows that the molecule cannot dissociate unless its energy is above the energy of the crossing, about 2.6 eV above the ground state.

Before taking up the correct formulation of this problem, let us first dispense with the conventional wisdom regarding such processes. One of the fundamental tenets of reactive collision theory is the adiabatic theorem, which asserts that at sufficiently low velocities, the system will remain with certainty on the lowest adiabatic surface. This theorem is regularly invoked in studies of collision dynamics to justify the neglect of excited electronic states. If this theorem were applied to the present situation, it would lead us to a serious misconception: If the energy is barely above the crossing energy so that the O atom traverses the crossing region very slowly, it will remain with certainty on the lower adiabatic curve, thus with certainty making a transition from the ^1D to the ^3P state.[5] But the adiabatic theorem does not apply to curve crossings; if the coupling between the states is small, then the probability of remaining on the adiabatic curve goes to zero as $(V_{12})^2$, even in the limit of zero velocity. We shall display this quantitatively below.

A complete and exact quantum description of collisions involving curve crossings is provided by the "close coupling" method, in which one numerically solves a pair of coupled Schrödinger equations,

$$[-(\hbar^2/2M)(d^2/dR^2) + V_{11}(R) - E]$$
$$\times u_1(R) + V_{12}(R)u_2(R) = 0 , \quad (1)$$

and a corresponding equation for u_2. Such calculations are, however, very lengthy and tedious
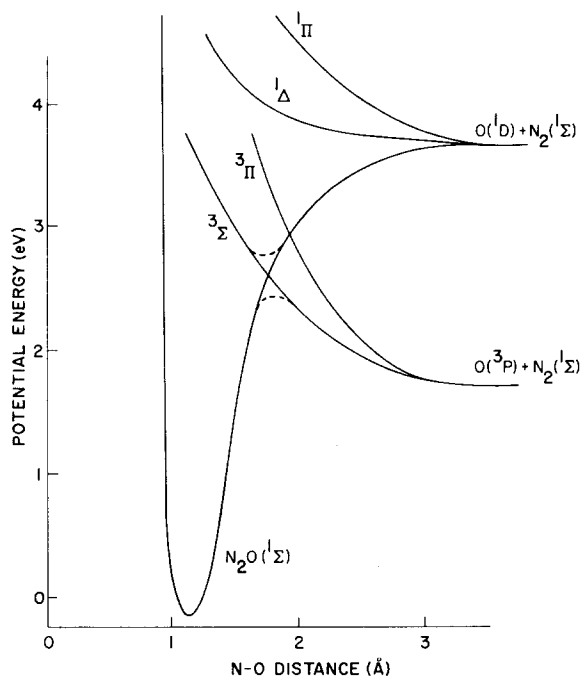
FIG. 1. Schematic potential curves for collinear NNO. The dashed lines are the adiabatic curves, including diagonalization of the spin—orbit coupling. The splitting between them has been greatly exaggerated for clarity.

because of the short de Broglie wavelength. Therefore almost all studies of phenomena associated with curve crossings have used some form of the classical trajectory formulation, in which the nuclei are assumed to move along a classical path $R(\tau)$ and the electrons obey a time-dependent Schrödinger equation.

$$i\hbar(d/d\tau)C_1 = V_{12}\exp\left[i/\hbar \int (V_{11}-V_{22})d\tau'\right]C_2, \quad (2a)$$

$$i\hbar(d/d\tau)C_2 = V_{21}\exp\left[i/\hbar \int (V_{22}-V_{11})d\tau'\right]C_1. \quad (2b)$$

This formulation has proved its usefulness for a wide variety of collision processes, and Tully and Preston have been successfully applying it to reactions involving surface crossings. In previous papers,[6] we have shown how the close coupled equations (1) reduce by a series of approximations to the classical trajectory equations (2). The formalism presented there clearly shows when the classical formulation is applicable and when it is not applicable. It is not applicable here. The classical approach fails if there are forces of opposite sign and the crossing point is close to a turning point.[6]

Nikitin[7] has shown that the close coupled equations can then be reduced to the time-dependent form (2) but only provided that a minus sign is added to Eq. (2b):

$$-i\hbar(dC_2/d\tau) = V_{12}\exp\left[i/\hbar \int (V_{22}-V_{11})d\tau\right]C_1. \quad (2b')$$

This minus sign adds considerable theoretical interest: The effective Hamiltonian is now anti-Hermitian, and the evolution operator is now antiunitary, so there is an anticonservation of probability,

$$|C_1|^2 - |C_2|^2 = 1.$$

The resulting equations may accordingly be called the "anticlassical trajectory equations." The unusual features of these equations reflect the nonclassical nature of the motion near the crossing point: The O atom may become trapped in the upper adiabatic well, or it may have to tunnel through the lower adiabatic barrier; obviously such processes cannot be described classically. Clearly, this change of sign must also affect the calculated transition probability; however, if the coupling is very weak, as in the present case, Eqs. (2b) and (2b') lead to the same result in first order.

In Ref. 1, the N_2O reactions were analyzed with the use of the Landau–Zener (LZ) formula. The derivation of this formula is based upon a special case of the time-dependent formulation and if the whole formulation fails, the formula cannot be expected to be correct. In addition, the LZ formula, like the adiabatic theorem, predicts that the transition probability (^1D to ^3P) goes to unity as the velocity goes to zero; however, the correct value is about 0.06, so the LZ formula is seriously in error.

The correct treatment of the unimolecular decomposition,[7] based upon the use of (2a) and (2b'), and taking the first-order ("distorted wave") approximation,

$$C_2 \simeq (-i\hbar)^{-1} \int_{-\infty}^{\infty} V_{12}\exp\left[i/\hbar \int (V_{22}-V_{11})d\tau'\right]d\tau$$

leads to the result for the transition probability,[3]

$$P = \pi^2 \beta^{4/3} Ai^2(-\epsilon\beta^{2/3}), \quad (3)$$

where

$$\beta = (4V_{12}/\hbar)\left[MV_{12}/F(F_1-F_2)\right]^{1/2},$$

$$E = (E-E_x)\left[(F_1-F_2)/2V_{12}F\right],$$

with M as the reduced mass of O, $E-E_x$ is the energy of O relative to crossing energy, E_x, V_{12} is the coupling at the crossing, assumed 80 cm^{-1}. $F = |F_1F_2|^{1/2}$ is the average force at the crossing, $F_i = -dV_{ii}/dR$ are the forces at the crossing. In Fig. 2 is shown the transition probability as a function of energy relative to the crossing using the Landau–Zener approximation and the (correct) first-order approximation. Even putting aside the fact that the LZ theory does not apply, it is not completely clear how one should use it even for comparison. If one assumes that transitions leading to decomposition can take place only on a single passage outward through the crossing region, then the appropriate formula is
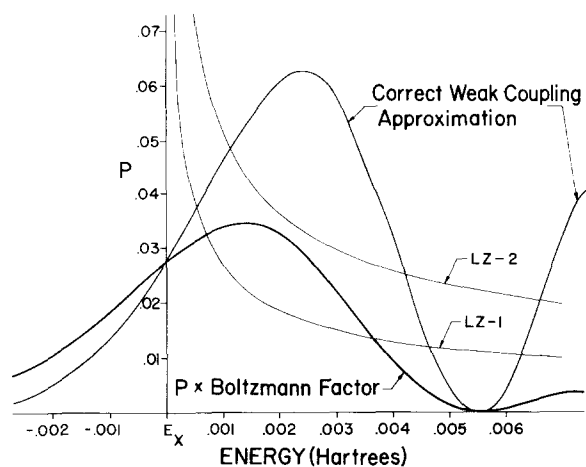
FIG. 2. Transition probability vs energy relative to crossing energy. Single crossing Landau–Zener (LZ-1) and double crossing Landau–Zener (LZ-2) are compared with the correct weak coupling approximation. The Boltzmann factor ($T = 888\,^\circ$K) heavily weights the region where LZ is worst.

$$P = P_1 = 1 - e^{-\pi T_0}, \quad T_0 = \beta/4\sqrt{\epsilon} \; . \tag{4a}$$

On the other hand, if one assumes that transitions can also take place during the subsequent passage inward (Fig. 1) then one is led to the result

$$P = P_1 + (1 - P_1)P_1(1 - P_1)$$
$$\simeq 2P_1 \quad (\text{if } P_1 \ll 1). \tag{4b}$$

Returning to Fig. 2, we see the following features.

(1) The LZ formula fails to account for transitions that occur below the crossing energy by tunneling through the barrier.

(2) At the crossing energy both LZ formulas have the wrong behavior; they agree with the incorrect prediction of the adiabatic theorem.

(3) Above the crossing energy, the actual transition probability oscillates above and below the LZ predictions; these oscillations result from interference between the two possible paths. The first peak is substantially higher than either LZ prediction.

(4) At large $E - E_x$ the double passage formula (4b) is better than the single passage one (4a).

On the whole, the LZ predictions are almost tolerable except in a narrow region close to the crossing energy. However, this region is weighted most heavily by the Boltzmann factor, so the LZ formula gets successively worse as the temperature decreases. In Fig. 2 is also shown the transition probability times the Boltzmann factor, for a temperature of 888 °K. This factor increases the relative importance of energies below and near the crossing energy, so that the energies for which the LZ formula is valid contribute negligibly to the reaction rate.

The rate constant for unimolecular decomposition is $k = P\bar{\nu}e^{-E^*/kT}$, where $\bar{\nu}$ is a certain average of the vibrational frequencies, E^* is the activation energy, and P is the probability of decomposing in a single vibration. Using $\bar{\nu} = 4.5 \times 10^{13}$ sec⁻¹, and $P = 0.055$ from averaging Fig. 2 and including the normalization constant, we obtain the pre-exponential factor 2.4×10^{12}, as compared to the experimental value[8] of 0.81×10^{12}. In view of the uncertainty about the detailed shapes of the potential curves, the anharmonicity of the ground state curve, the unknown coupling (assumed to be 80 cm⁻¹), and the uncertainty as to whether the reaction is collinear, this agreement is excellent.

III. QUENCHING OF O(^1D) by N₂

To give a theoretical prediction of the cross section for

$$O(^1D) + N_2 \rightarrow O(^3P) + N_2,$$
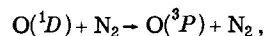
let us adopt the working hypothesis that the average transition probability in the quenching reaction is comparable to the average transition probability in the unimolecular decomposition. Then by using a "grey sphere" model, the total quenching cross section can be estimated as $\sigma \simeq g\bar{P}\pi R_x^2$, where g is a statistical factor[1] equal to $\frac{1}{5}$. The theoretical result is $\sigma \simeq 0.1$ Å² as contrasted with the experimental result[9] of $\sigma \simeq 2$–10 Å². Although our initial hypothesis is rather dubious, we know that it is *not* in error by a factor of 20. We conclude that the proposed mechanism does not account for the observed cross section for O(^1D) quenching.

There are two factors that may account for this discrepancy. The first is the possibility of complex formation due to collisions at small impact parameters. If a thermal energy O(^1D) atom approaches the N₂ end on, the very strong attractive forces cause them to slam together with more than 3 eV of relative kinetic energy. This must cause vibrational excitation of the N₂, and once this occurs, the O atom cannot escape. The complex can decompose into O(^1D) only if the N₂ gives up all its vibrational energy; however, it can decompose to O(^3P) any time the O atom passes through the crossing. If the lifetime with respect to ^1D decomposition is as much as 20 vibrational times, then it is virtually certain that the complex will decompose to the ^3P state. The cross section for ^1D quenching by complex formation may be written as

$$\sigma = g(\pi R_0^2)sP',$$

where g is again the statistical factor, R_0 is the

maximum impact parameter leading to complex formation (probably about 1 Å, the hard core radius of N_2), s is a steric factor (noncollinear collisions may be less likely to form complexes), and P' is the probability that the complex will decay into the ^3P state. Taking the maximum possible values, $s = 1$ and $P' = 1$, we obtain $\sigma \lesssim 0.6$ Å^2. We conclude that while complex formation almost certainly occurs and while it greatly enhances the quenching cross section, it does not by itself account for the observed quenching rate.

A second factor that may enhance the quenching cross section is the possibility of additional curve crossings. Chutjian and Segal[10] have calculated potential curves by the semiempirical INDO method, and their results suggest that the $^1\Delta$ state is only weakly repulsive in the collinear configuration and that one of its components may be attractive in the bent configuration. This state may then be strongly coupled to the $^1\Sigma^-$ state, which would allow complex formation and eventual decay to $O(^3P)$ by a variety of pathways. Taking into account the statistical factor ($\frac{1}{5}$), and assuming the $^1\Delta$ and $^1\Sigma^-$ cross at about 1.1 Å, the quenching cross section by this pathway could not exceed 1 Å^2. This is in fair agreement with the experimental result, and no better estimates can be made without much more detailed knowledge of the potential curves.

IV. VIBRATIONAL RELAXATION OF N_2

For the reaction

$$N_2(v=1) + O(^3P) \rightarrow N_2(v=0) + O(^3P),$$
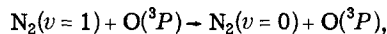
we follow Ref. 1 in assuming that a chemical mechanism associated with the curve crossing dominates the rate at high temperatures. The probability of a simultaneous vibrational and electronic transition at the curve crossing is equal to a Franck–Condon factor times the electronic probability calculated previously for N_2O decomposition. Because of the uncertainty in the magnitude of this Franck–Condon factor and the possibility of complex formation, it is not really possible to make a good estimate of the vibrational relaxation cross section. We made an honest estimate based on reasonable assumptions about the magnitude of these effects, and calculated the relaxation time,

$$P\tau = k_B T / k (1 + e^{-\epsilon/k_B T}),$$

with $k = \sigma \bar{v}\, e^{-E_a/k_B T}$ the reaction rate, k_B the Boltzmann constant, E_a the activation energy, ϵ the vibrational spacing of N_2, and $\bar{v}$ the average relative velocity. The result at $T = 3000$ °K, was $P\tau = 1.3$ μsec · atm, in excellent agreement with the experimental result.[11] This agreement is completely fortuitous; the uncertainty in the experimental result is about a factor of 2, and the un-

certainty in the theoretical result is much larger. Nevertheless, we can conclude that the proposed mechanism is compatible with the high-temperature experiments.

However, the theory predicts that the chemical mechanism must disappear at low temperatures because of the very large activation energy (almost 1 eV) required to reach the crossing. The experimental result[12] indicates that the chemical mechanism persists at low temperatures. If this result is correct, it presents a fundamental puzzle, because there is no chemical mechanism known for this system that does not have a large activation energy. Furthermore, it seems that any such mechanism should also affect the unimolecular decomposition rate.

We do not have a plausible explanation for this discrepancy. A possible explanation may be that vibrational changes are occurring mainly from very high vibrational states ($v = 5$ or 6) associated with the ^3P curves directly into the ground vibrational states associated with the ^1D curves. Such transitions would have much lower activation energy, of order 0.1–0.2 eV (see Ref. 1, Fig. 3). However, one would expect that tiny Franck–Condon factors would eliminate this possibility. This could be tested by measuring the relaxation rate as a function of N_2 vibrational temperature.

V. CONCLUSIONS

The results are summarized in Table I. For unimolecular decomposition, theory and experiment are in very good agreement. For $O(^1D)$ quenching, the simple curve crossing mechanism is not compatible with the experimental results, but

TABLE I. Comparison of theory and experiment.

Unimolecular decomposition rate (pre-exponential factor)	
Theoretical	2.4×10^{12} sec^{-1}
Experimental	0.81×10^{12} sec^{-1}
$O(^1D)$ Quenching cross section	
Theoretical	
simple curve crossing	0.1 Å^2
complex formation	< 0.6 Å^2
additional crossings	≤ 1.0 Å^2
total	<1.7 Å^2
Experimental	2–10 Å^2
N_2 Vibrational relaxation time ($P\tau$)	
$T = 3000$ °K	
Theoretical	1.3 μsec · atm
Experimental	1.3 μsec · atm
$T = 300$ °K	
Theoretical	no chemical mechanism
Experimental	10 μsec · atm

the possibility of complex formation and additional crossings enhances the cross section, and greatly improves the agreement. For vibrational relaxation of N_2, at high temperatures, the agreement with experiment is fortuitously excellent, but at low temperatures there is a serious discrepancy.

From a theoretical point of view, two steps are needed to increase our understanding. The first is an accurate and reliable calculation of the potential curves. Such a calculation is currently being performed.[13] When it is done, the second step is a classical trajectory analysis of the reaction dynamics, taking into account the electronic transitions. The present calculation of electronic transition probabilities should be quite accurate, but there are uncertainties about the dynamics, especially regarding the expected complex formation. Trajectory calculations will confirm or negate the estimates we have used in this paper. From the experimental point of view, another measurement of the low-temperature vibrational relaxation time would be most helpful.[14]

ACKNOWLEDGMENTS

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[14]*Note added in proof:* Such a measurement has recently been performed by G. A. Black and his collaborators and it confirms the result of McNeal *et al.*[12] [J. Chem. Phys. (to be published)].