

THE PHYSICS OF FLUIDS

VOLUME 9, NUMBER 10

OCTOBER 1966

Transient Phenomena in Dissociative Reactions

CHARLES A. BRAU

Avco Everett Research Laboratory, Everett, Massachusetts

JAMES C. KECK

Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts

AND

GEORGE F. CARRIER

Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts

(Received 12 May 1966)

The "diffusion theory" of dissociation is used to analyze vibration-dissociation coupling in the early phases of dissociation behind a shock wave. It is shown that deviations from vibrational equilibrium introduce "incubation times" into the long-time behavior of macroscopic molecular observables, such as the number density. For example, if $Q(t)$ is some macroscopic observable whose value is Q_0 in vibrational equilibrium behind the shock wave with no dissociation, then at long times $Q(t) = Q_0 \exp[-(t - \tau_Q)/\tau_{Diss}]$, where τ_{Diss} is the dissociation time and τ_Q is the incubation time for the observable Q . The incubation times are experimentally observable quantities and may be positive or negative, depending on the observable, Q . Approximate methods are used to calculate incubation times according to a simplified Morse oscillator model. The results agree well with experimental measurements made by Wray in O_2 -argon mixtures. Incubation effects are found to increase rapidly in importance as the temperature increases, with $|\tau_Q/\tau_{Diss}| \gtrsim 10\%$ when $kT \gtrsim 15\%$ of the dissociation energy.

I. INTRODUCTION

BECAUSE the dissociation of diatomic molecules is strongly coupled with the vibrational relaxation of the molecules, one would expect to find transients in the dissociation reaction persisting for times of the order of the vibrational relaxation time. At sufficiently high temperatures for the vibrational relaxation time to be comparable to the dissociation time, one would expect transient effects to be quite noticeable. Such transients have been experimentally observed, and Wray¹ has measured an apparent "incubation time," or delay, in the dissociation of O_2 by argon behind shock waves.

Such an incubation time is predicted by the theories of Hammerling, Teare, and Kivel,² of Treanor and Marrone,³ and of Heims.⁴ However,

these theories are of a phenomenological nature, and do not properly treat the nonequilibrium behavior of the vibrational degrees of freedom. Therefore, in this paper the more elaborate theory "diffusion theory" of vibration-dissociation coupling⁵ is used to describe the transient effects in dissociation reactions behind shock waves.

II. GENERAL THEORY OF DISSOCIATION TRANSIENTS

For simplicity we consider the behavior of a species AB of diatomic molecules dispersed in an atmosphere of inert atoms, which we shall denote by X. Provided that the molecular concentration is sufficiently dilute compared with the concentration of inert atoms, the molecules will interact with the inert atoms and not with each other, nor with any atomic species A and B which may be formed. Moreover, the thermodynamic state of the inert atmosphere will not be appreciably affected by a

¹ K. L. Wray, *J. Chem. Phys.* **37**, 1254 (1962).

² P. Hammerling, J. D. Teare, and B. Kivel, *Phys. Fluids* **2**, 442 (1959).

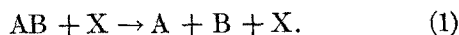
³ P. V. Marrone and C. E. Treanor, *Phys. Fluids* **6**, 1215 (1963).

⁴ S. P. Heims, *J. Chem. Phys.* **38**, 603 (1963).

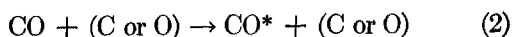
⁵ J. Keck and G. Carrier, *J. Chem. Phys.* **43**, 2284 (1965).

dilute concentration of molecules and will provide, in effect, a heat bath with which the molecules can interact.

In a shock-tube experiment to measure dissociation rates, the gas mixture is initially in thermal equilibrium at some temperature T_1 , near room temperature. Immediately behind a shock wave passing through the gas, the translational degrees of freedom of all species and the rotational degrees of freedom of the molecules will be in thermal equilibrium at the temperature T_2 , but the vibrational degrees of freedom of the molecules, which relax more slowly, will still be in their original state corresponding to the temperature T_1 . We shall be interested in describing the behavior of the vibrational degrees of freedom as they relax toward the temperature T_2 of the inert gas "heat bath," and the molecules begin to dissociate according to the reaction



We neglect the possible presence of electronically excited states of the atoms A, B, and X, and the molecules AB. Although no serious attempt has been made to experimentally determine the importance of excited atomic species, the equilibrium concentration of excited atomic species is generally small at the temperatures at which dissociation becomes important and dissociation rates have been measured. Electronically excited states of the molecules AB have been found to be important in the dissociation of CO by argon,⁶ but only at later times when the excited states of CO may be produced by reaction



of the CO with atomic C or O. We shall also neglect all chemical reactions except the dissociation reaction (1). For homonuclear molecules in an inert diluent this is usually the only important reaction, and for heteronuclear molecules other possible reactions can be minimized by further diluting the molecular species AB in the inert gas.

At temperatures sufficiently high for dissociation to take place, the spacing of the vibrational levels of the molecules is generally small compared with the vibrational energy of a typical molecule. The state of the vibrational degrees of freedom of the molecules may therefore be described by the classical distribution function $n(E, t)$, where $n(E, t)dE$ is interpreted as the number of molecules per unit volume whose vibrational energy lies in the range dE about E , at the time t . The total

number density of molecules, $N(t)$, and mean vibrational energy, $\bar{E}(t)$, are given by the formulas

$$N(t) = \int_0^D n(E, t) dE, \quad (3a)$$

$$N(t)\bar{E}(t) = \int_0^D n(E, t)E dE, \quad (3b)$$

where the dissociation energy D is the largest value which the vibrational energy may assume. Other macroscopic observables may be similarly calculated from appropriate moments of the distribution function. For example, if $\sigma(E)$ is the cross section for Shumann-Runge absorption of 1470-Å radiation by an oxygen molecule with the vibrational energy E , then the macroscopic absorption coefficient is given by the formula

$$N(t)\bar{\sigma}(t) = \int_0^D n(E, t)\sigma(E) dE. \quad (4)$$

When the vibrational degrees of freedom are in equilibrium at the temperature T , then the distribution function $n(E, t)$ will be of the form

$$n(E, t) = N(t)\Psi(E|T), \quad (5)$$

where $\Psi(E|T)$ is the normalized Boltzmann distribution,

$$\Psi(E|T) = g(E)Z^{-1}(T) \exp(-E/kT), \quad (6)$$

$g(E)$ is the density of vibrational states around the energy E , k is Boltzmann's constant, and $Z(T)$ is the partition function, defined by the expression

$$Z(T) = \int_0^D g(E) \exp(-E/kT) dE. \quad (7)$$

At equilibrium, the observables \bar{E} and $\bar{\sigma}$ have the values

$$\bar{E}_T = \int_0^D E \Psi(E|T) dE, \quad (8a)$$

$$\bar{\sigma}_T = \int_0^D \sigma(E)\Psi(E|T) dE. \quad (8b)$$

The equilibrium absorption coefficient $\bar{\sigma}_T$ has been measured, and is a well-known function of temperature.⁷

In the following discussion, it is convenient to make use of the "specific distribution function," $X(E, t)$, which is defined by the expression

$$X(E, t) = n(E, t)/\Psi(E|T_2). \quad (9)$$

Under the assumptions we have stated, and provided that molecules cannot make large vibrational transi-

⁶ A. R. Fairbairn, private communication.

⁷ M. Camac, J. Chem. Phys. 34, 448 (1961).

tions in collisions, the behavior of the distribution function $X(E, t)$ has been shown by Keck and Carrier⁵ and Brau⁸ to be described by a diffusion equation of the form

$$\Psi(E|T_2) \frac{\partial}{\partial t} X(E, t) = \frac{\partial}{\partial E} \left[\kappa(E) \Psi(E|T_2) \frac{\partial}{\partial E} X(E, t) \right]. \quad (10)$$

The "diffusion coefficient," $\kappa(E)$, will in general depend upon the number density and temperature of the background gas, as well as upon the vibrational energy E . Since there are no negative vibrational energy states, the point $E = 0$ acts as a reflecting barrier for the diffusion process. The appropriate boundary condition at this point is therefore

$$\lim_{E \rightarrow 0} \kappa(E) \frac{\partial}{\partial E} X(E, t) = 0. \quad (11)$$

When the molecules reach the uppermost states they may be dissociated by collisions with background atoms. If the atom concentration is sufficiently small that recombination may be neglected, the boundary condition at the dissociation limit is

$$\lim_{E \rightarrow D} \kappa(E) \frac{\partial}{\partial E} X(E, t) = -\alpha X(D, t), \quad (12)$$

where α is related to the rate of dissociation from the uppermost levels.

In studying the transient behavior of the distribution function $X(E, t)$, it is useful to consider the eigenvalues λ_n and eigenfunctions $\chi_n(E)$ of the associated eigenvalue equation

$$\frac{\partial}{\partial E} \left[\kappa(E) \Psi(E|T_2) \frac{\partial}{\partial E} \chi_n(E) \right] + \lambda_n \Psi(E|T_2) \chi_n(E) = 0, \quad (13)$$

with the boundary conditions (11) and (12). The eigenfunctions $\chi_n(E)$ are orthogonal to one another and may be normalized to unity, so that

$$\int_0^D \Psi(E|T_2) \chi_m(E) \chi_n(E) dE = \delta_{mn}, \quad (14)$$

where δ_{mn} is the Kronecker delta function.

If we expand the solution to the time dependent equation as an infinite sum of eigenfunctions of the form

$$X(E, t) = \sum_{n=0}^{\infty} A_n(t) \chi_n(E), \quad (15)$$

and use the properties (13) and (14), we find that

$$A_n = a_n \exp(-\lambda_n t), \quad (16)$$

where $a_n = A_n(0)$ is the n th expansion coefficient for the distribution function at the time $t = 0$. Immediately behind the shock wave the vibrational degrees of freedom are still in the equilibrium state which prevailed ahead of the shock, so the distribution function at time $t = 0$ is given by the expression

$$X(E, 0) = N(0) \Psi(E|T_1) / \Psi(E|T_2). \quad (17)$$

Therefore, the expansion coefficients a_n are given by the formula

$$a_n = N(0) \int_0^D \Psi(E|T_1) \chi_n(E) dE. \quad (18)$$

Collecting the results of Eqs. (16) and (18), we see that the distribution function for later times is described by the series

$$X(E, t) = \sum_{n=0}^{\infty} a_n \chi_n(E) \exp(-\lambda_n t), \quad (19)$$

while the macroscopic observables, N , \bar{E} , and $\bar{\sigma}$ are given by the series

$$N(t) = \sum_{n=0}^{\infty} a_n N_n \exp(-\lambda_n t), \quad (20a)$$

$$N(t) \bar{E}(t) = \sum_{n=0}^{\infty} a_n N_n \bar{E}_n \exp(-\lambda_n t), \quad (20b)$$

$$N(t) \bar{\sigma}(t) = \sum_{n=0}^{\infty} a_n N_n \bar{\sigma}_n \exp(-\lambda_n t), \quad (20c)$$

where

$$N_n = \int_0^D \Psi(E|T_2) \chi_n(E) dE, \quad (21a)$$

$$N_n \bar{E}_n = \int_0^D \Psi(E|T_2) \chi_n(E) E dE, \quad (21b)$$

$$N_n \bar{\sigma}_n = \int_0^D \Psi(E|T_2) \chi_n(E) \sigma(E) dE. \quad (21c)$$

From physical reasoning we see that all the eigenvalues λ_n must be positive, with λ_0 the smallest. Therefore, after a sufficiently long time the term corresponding to $n = 0$ will dominate the series (19) and (20), and we obtain the asymptotic results

$$X(E, t) / N(t) \rightarrow \chi_0(E), \quad (22a)$$

$$N(t) / N(0) \rightarrow (a_0 N_0 / N(0)) \exp(-\lambda_0 t), \quad (22b)$$

$$N(t) \bar{E}(t) / N(0) \bar{E}_{T_1} \rightarrow (a_0 N_0 \bar{E}_0 / N(0) \bar{E}_{T_1}) \exp(-\lambda_0 t), \quad (22c)$$

⁸ C. A. Brau, Ph.D. thesis, Harvard University (1965).

$$N(t)\bar{\sigma}(t)/N(0)\bar{\sigma}(t_2) \rightarrow (a_0 N_0 \bar{\sigma}_0 / N(0) \bar{\sigma}_{T_2}) \exp(-\lambda_0 t), \quad (22d)$$

as $t \rightarrow \infty$.

These equations have the following significance. From the first equation we see that after the initial transient the distribution function $X(E, t)$ assumes a "steady-state" (but nonequilibrium) shape which it keeps as long as recombination is not important. In general, λ_0/λ_1 is small compared with unity, being of the order of $\tau_{\text{vib}}/\tau_{\text{Diss}}$, where τ_{vib} is the vibrational relaxation time, and τ_{Diss} is the dissociation time. Therefore, the transients die out long before the lowest-order asymptotic terms shown in Eqs. (22), and the distribution function has the "steady-state" shape χ_0 through most of the dissociation process.

From Eq. (22b) we see that after the initial transient has subsided (and before recombination has become important), the molecules dissociate according to the law $dN/dt = -\lambda_0 N(t)$, so that the lowest eigenvalue λ_0 is related to the dissociation time by the formula

$$\tau_{\text{Diss}} = \lambda_0^{-1}. \quad (23)$$

From Eqs. (22c) and (22d) we see that after the initial transient, the vibrational energy, $N(t)\bar{E}(t)$, the absorption coefficient, $N(t)\bar{\sigma}(t)$, and all other moments of the distribution function also decay at the dissociation rate. This is due to the "steady-state" behavior of the shape of the distribution function. However, due to the coupling of the dissociation rate with the vibrational relaxation, the observable moments of the distribution function do not decay exponentially from the values they would have in vibrational equilibrium. Rather, if they are assumed to have this behavior they exhibit "incubation times," for, as we easily see, Eqs. (22) may be written in the form

$$N(t) \rightarrow N(0) \exp[-(t - \tau_N)/\tau_{\text{Diss}}], \quad (24a)$$

$$N(t)\bar{E}(t) \rightarrow N(0)\bar{E}_{T_2} \exp[-(t - \tau_E)/\tau_{\text{Diss}}], \quad (24b)$$

$$N(t)\bar{\sigma}(t) \rightarrow N(0)\bar{\sigma}_{T_2} \exp[-(t - \tau_I)/\tau_{\text{Diss}}], \quad (24c)$$

where the "incubation times," τ_N , τ_E , and τ_I , are given by the formulas

$$\tau_N/\tau_{\text{Diss}} = \ln [a_0 N_0 / N(0)], \quad (25a)$$

$$\tau_E/\tau_{\text{Diss}} = \ln [a_0 N_0 \bar{E}_0 / N(0) \bar{E}_{T_2}], \quad (25b)$$

$$\tau_I/\tau_{\text{Diss}} = \ln [a_0 N_0 \bar{\sigma}_0 / N(0) \bar{\sigma}_{T_2}]. \quad (25c)$$

These apparent "incubation times" arise from two effects. The first is the transient retardation of dis-

sociation during the period when the molecules are still in the lower vibrational levels, from which they are difficult to dissociate. This part of the incubation time is common to all observables, and is equal to $\ln [a_0 N_0 / N(0)]$. The second effect which contributes to the appearance of the incubation times in Eqs. (24) is the deviation of the "steady-state" distribution function from the equilibrium distribution, $X(E, t) = N(t)$. This effect is different for each moment of the distribution function, and gives rise to the terms $\ln (\bar{E}_0 / \bar{E}_{T_2})$, and $\ln (\bar{\sigma}_0 / \bar{\sigma}_{T_2})$ in the incubation times for the vibrational energy and absorption, respectively. It is interesting to note that the incubation-time formulas, Eqs. (25), depend only on moments of the lowest eigenfunction, $\chi_0(E)$, which (as we shall see) is the easiest eigenfunction to compute.

Certain simplifications are possible in the calculation of the moments $a_0/N(0)$ and $\bar{\sigma}_0/\bar{\sigma}_{T_2}$. The absorption cross section $\sigma(E)$ is not well known as a function of vibrational energy, but for radiation around 1470 Å it is known to be vanishingly small except for the first few energy levels.⁷ Since $\chi_0(E)$ is a slowly varying function near the origin, for $n = 0$ we may replace Eq. (21) with the approximate formula

$$N_n \bar{\sigma}_n \cong \chi_n(0) \int_0^D \Psi(E|T_2) \sigma(E) dE = \chi_n(0) \bar{\sigma}_{T_2}. \quad (26)$$

Similarly, the initial distribution, $X(E, 0) = N(0)\Psi(E|T_1)$, is vanishingly small except near $E = 0$. Therefore, for $n = 0$ we may replace Eq. (18) with the approximate formula

$$a_n \cong N(0)\chi_n(0) \int_0^D \Psi(E|T_1) dE = N(0)\chi_n(0). \quad (27)$$

Substituting these results into Eqs. (25) we obtain the formulas

$$\tau_N/\tau_{\text{Diss}} = \ln [N_0 \chi_0(0)], \quad (28a)$$

$$\tau_E/\tau_{\text{Diss}} = \ln [N_0 \bar{E}_0 \chi_0(0) / \bar{E}_{T_2}], \quad (28b)$$

$$\tau_I/\tau_{\text{Diss}} = 2 \ln \chi_0(0). \quad (28c)$$

III. EXACT ANALYSIS OF A SIMPLIFIED HARMONIC OSCILLATOR MODEL

The simplest molecular model, and the only one for which exact analytical solutions of the transient problem have been obtained, represents the molecule as a truncated harmonic oscillator and assumes that the diffusion coefficient, $\kappa(E)$, is independent of E . According to this model, the vibrational energy levels are uniformly spaced up to the dissocia-

tion energy, so that the equilibrium distribution function $\Psi(E|T)$ is given by the expression

$$\Psi(E|T) = \frac{\exp(-E/kT)}{kT[1 - \exp(-D/kT)]} \quad (29)$$

Actually the vibrational energy levels tend to crowd together near the dissociation limit, but we shall see that the use of Eq. (29) is not the major source of error. A more serious objection may be raised against the approximation of $\kappa(E)$ by a constant. However, the model gives qualitatively correct results, and permits the entire time history of $X(E, t)$ and the observables to be calculated. The results are interesting because they lead to some insight into the nature of the transients and the meaning of the incubation times. More realistic models are developed later.

It is convenient to use the dimensionless quantities

$$\begin{aligned} \epsilon &= E/kT_2, & \delta &= D/kT_2, \\ \beta &= \alpha kT_2/\kappa, & \Lambda_n &= k^2 T_2^2 \lambda_n/\kappa. \end{aligned} \quad (30)$$

In terms of these quantities, the eigenvalue equation has the form

$$\delta^2 \chi_n / \partial \epsilon^2 - \partial \chi_n / \partial \epsilon + \Lambda_n \chi_n = 0, \quad (31)$$

and the boundary conditions are expressed by the relations

$$\partial \chi_n / \partial \epsilon|_{\epsilon=0} = 0, \quad (32a)$$

$$\partial \chi_n / \partial \epsilon|_{\epsilon=\delta} + \beta \chi_n(\delta) = 0. \quad (32b)$$

The normalized solutions are conveniently written in the form

$$\chi_n(\epsilon) = C_n \exp\left(\frac{\epsilon}{2}\right) \sinh\left(\frac{\epsilon}{2} [1 - 4\Lambda_n]^{1/2} + \phi_n\right), \quad (33a)$$

$$\chi_n(\epsilon) = C_n \exp\left(\frac{\epsilon}{2}\right) \sin\left(\frac{\epsilon}{2} [4\Lambda_n - 1]^{1/2} + \phi_n\right), \quad n > 0. \quad (33b)$$

The eigenvalues are given by the formulas

$$\begin{aligned} \tanh\left(\frac{1}{2}\delta[1 - 4\Lambda_0]^{1/2}\right) &= [1 - 4\Lambda_0]^{1/2}/(1 + 2\Lambda_0/\beta), \end{aligned} \quad (34a)$$

$$\begin{aligned} \tan\left(\frac{1}{2}\delta[4\Lambda_n - 1]^{1/2}\right) &= [4\Lambda_n - 1]^{1/2}/(1 + 2\Lambda_n/\beta), \quad n > 0, \end{aligned} \quad (34b)$$

the phase angles are given by the formulas

$$\tanh \phi_0 + (1 - 4\Lambda_0)^{1/2} = 0, \quad (35a)$$

$$\tan \phi_n + (4\Lambda_n - 1)^{1/2} = 0, \quad n > 0, \quad (35b)$$

and the normalization constants are given by the formulas

$$C_0 = -2(1 - e^{-\delta})^{1/2} \left[\frac{1}{\Lambda_0} - \frac{1 + 2\beta}{\beta + \beta^2 + \Lambda_0} - 2\delta \right]^{-1/2}, \quad (36a)$$

$$C_n = 2(1 - e^{-\delta})^{1/2} \left[2\delta + \frac{1 + 2\beta}{\beta + \beta^2 + \Lambda_n} - \frac{1}{\Lambda_n} \right]^{-1/2}, \quad n > 0. \quad (36b)$$

The expansion coefficients and other moments of the eigenfunctions may be evaluated exactly from Eq. (33). The use of the approximate formula (26) in evaluating the coefficients $\bar{\sigma}_n$ introduces an unavoidable error into the calculations for large n . However, the higher eigenfunctions decay rapidly with time, and the final calculation will be in error only for very early times. The results are shown in Figs. 1(a) and 2(a) for the special case of $\delta \equiv D/kT_2 = 3.6$, $\beta \equiv \alpha kT_2/\kappa = 2.0$, and in Figs. 1(b) and 2(b) for the case of $\delta = 3.6$, $\beta = \infty$. The computations were made by truncating the series at twenty-five terms.

We see in Fig. 1 that the initial (nonequilibrium) Boltzmann distribution rapidly relaxes toward the "steady-state" distribution function, $\chi_0(E)$, in a time of the order of the dissociation incubation time. The lower levels ($E/D \lesssim 0.6$) are nearly in equilibrium ($\chi_0 \simeq 1$) in the steady state, but the upper levels are depleted by dissociation. Although the dissociation rate, $-dN/dt = \alpha\Psi(D|T_2)X(D, t)$, is proportional to the number of molecules near the dissociation limit, the process is controlled by the rate at which molecules can "diffuse" up the vibrational energy "ladder" due to the "concentration" gradient, dX/dE . In effect, the boundary

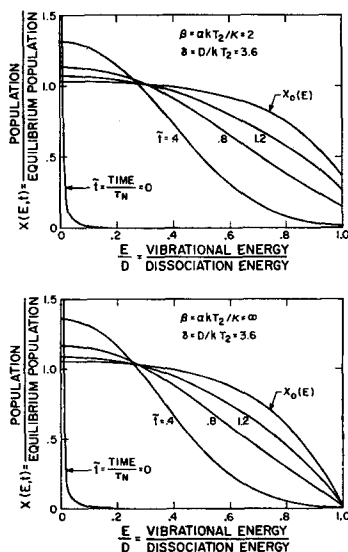


FIG. 1. Relaxation of vibrational distribution function to steady-state form during transient period.

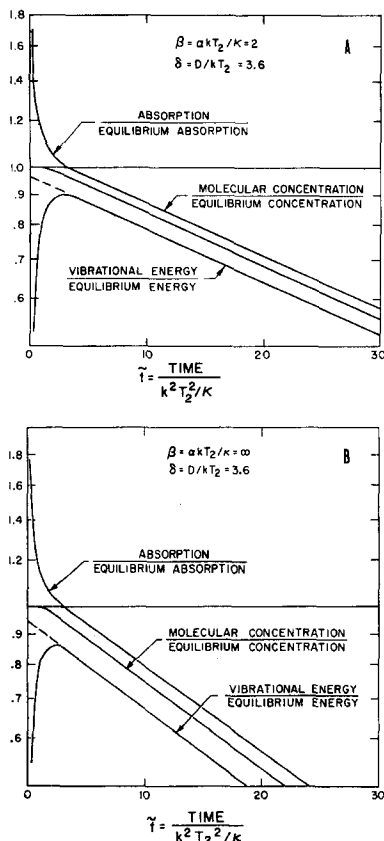


FIG. 2. Behavior of macroscopic observables during transient period.

condition makes $X(D, t)$ adjust itself so that the dissociation rate, $\alpha\Psi(D|T_2)X(D, t)$, is equal to the number of molecules diffusing up to the dissociation limit. As long as $\beta = \alpha k T_2 / \kappa$ is large enough to make $X(D, t)$ small, the gradients, and hence the diffusion process, will be relatively insensitive to the actual boundary condition. This explains the insensitivity of the results in Fig. 2 to the value of the parameter β .

In Fig. 2 we see that the initial dissociation rate, $-dN/dt$, is zero because the molecules are all in very low vibrational levels from which they cannot be dissociated. After a short "incubation time," which we call τ_N , the molecules reach the upper states and begin to dissociate. The Schumann-Runge absorption, which is caused by molecules in low vibrational levels, initially has a rather high value. This decreases rapidly at first, as the molecules move into higher vibrational levels, and slowly later on when the distribution function assumes its "steady-state" shape and decays at the dissociation rate. The absorption curve always remains above the number density curve because the upper levels are always depleted, making the lower levels excessively populated relative to the number of molecules present. This gives rise to a longer incubation

time for the absorption than for the number density, the difference in incubation times being of the order of the incubation times themselves. During the transient, the vibrational energy relaxes from an initially small value toward the equilibrium value corresponding to the temperature T_2 . However, removal of the most energetic molecules by dissociation keeps the vibrational energy below the equilibrium value so that the vibrational energy curve always remains below the number density curve. This gives rise to a *negative* contribution to the incubation time which is actually enough to make the apparent incubation time for the vibrational energy *negative*, as indicated by the dotted lines.

Although these results were calculated from a rather crude model, their qualitative features are shared by the more accurate model which will be discussed in the next sections.

IV. APPROXIMATE METHODS

To treat models which are more complicated than the simple model of Sec. III, it is necessary to resort to approximate methods. In this section we will develop a simple method of approximating the lowest eigenvalue and the lowest eigenfunction, from which we can calculate the dissociation rate and the incubation times.

We begin by converting the eigenvalue equation (13) and the boundary conditions (11) and (12) to an integral equation. Let the Green's function, $G(E|E')$, satisfy the inhomogeneous differential equation

$$\frac{\partial}{\partial E} \left[\kappa(E)\Psi(E|T_2) \frac{\partial}{\partial E} G(E|E') \right] + \delta(E - E') = 0 \quad (37)$$

and the boundary conditions (11) and (12). In Eq. (37), $\delta(x)$ is the Dirac delta function. If we multiply equation (37) through by $\chi_n(E) dE$ and integrate over the range $0 \leq E \leq D$, we obtain the expression

$$\int_0^D \chi_n(E) \frac{\partial}{\partial E} \left[\kappa(E)\Psi(E|T_2) \frac{\partial}{\partial E} G(E|E') \right] dE + \chi_n(E') = 0.$$

Integrating twice by parts and using Eq. (13) and the boundary conditions (11) and (12), we obtain the integral eigenvalue equation

$$\chi_n(E') = \lambda_n \int_0^D \Psi(E|T_2) G(E|E') \chi_n(E) dE, \quad (38)$$

which is equivalent to the original Sturm–Liouville system.

To find the Green’s function we observe that the solution of equation (37) for $E < E'$ which satisfies the boundary condition (11) is just a constant depending on E' . This is expressed by the relation

$$G(E|E') = g(E'), \quad E < E'.$$

However, Green’s functions possess the general property of symmetry, that is, $G(E|E') = G(E'|E)$. Thus, the solution for all E is expressed by the formula

$$G(E|E') = g(E_>), \tag{39}$$

where $E_>$ is the larger of the two quantities E and E' . To find the function $g(E)$, we integrate Eq. (37) from the point $E = E_1 < E'$, to the point $E = E_2 > E'$. Recalling that $\partial G(E|E')/\partial E = \partial g(E')/\partial E = 0$ for $E < E'$, we obtain the differential equation

$$dg(E)/dE = -1/\kappa(E)\Psi(E|T_2). \tag{40}$$

Integrating this equation from any point E to the point $E = D$, and using the boundary condition (12), we obtain the formula

$$g(E) = \frac{1}{\alpha\Psi(D|T_2)} + \int_E^D \frac{dE}{\kappa(E)\Psi(E|T_2)}, \tag{41}$$

which expresses the Green’s function as a definite integral.

To approximate the solution of the eigenvalue equation (38), we may substitute a trial function, $\chi^{(0)}(E)$, for the eigenfunction $\chi_n(E)$ in the integral. If we carry out the integral and call the result $\chi^{(1)}(E)$, we may repeat the process using $\chi^{(1)}(E)$ as the trial function. If we repeat the process n times, then for sufficiently large n , $\chi^{(n)}(E)$ will approximate the eigenfunction $\chi_0(E)$, corresponding to the lowest eigenvalue, λ_0 , to any desired degree of accuracy, in the sense of mean-square error.⁹ To show this, we adopt the shorthand notation

$$(f_1, f_2) \equiv \int_0^D \Psi(E|T_2)f_1(E)f_2(E) dE. \tag{42}$$

The eigenvalue equation (38) is then expressed by the formula

$$\chi_n = \lambda_n(G, \chi_n). \tag{43}$$

The n th approximation, $\chi^{(n)}(E)$, to the eigenfunction $\chi_0(E)$ (within a normalization constant) is

expressed by the formula

$$\chi^{(n)} = (G, \chi^{(n-1)}). \tag{44}$$

To assess the convergence of the method to $\chi_0(E)$, we expand the zeroth approximation, $\chi^{(0)}(E)$, in a series of eigenfunctions of the form

$$\chi^{(0)} = \sum_i b_i \chi_i. \tag{45}$$

If we iteratively improve the approximation n times by means of equation (44), we obtain the result

$$\chi^{(n)} = \sum_i \frac{b_i}{\lambda_i^n} \chi_i = \frac{b_0}{\lambda_0^n} \left[\chi_0 + 0 \left(\frac{b_1 \lambda_0^n}{b_0 \lambda_1^n} \right) \right]. \tag{46}$$

Since $0 < \lambda_0 < \lambda_1 < \dots$, the error may be made as small as desired.

We may obtain an excellent approximation, $\lambda^{(n)}$, to the lowest eigenvalue, λ_0 , by substituting the $(n - 1)$ th approximation to the eigenfunction, $\chi^{(n-1)}$, into the eigenvalue equation (43) and taking the inner product with $\chi^{(n)}$. Upon using Eq. (44), we obtain the formula

$$\lambda^{(n)} = (\chi^{(n)}, \chi^{(n-1)}) / (\chi^{(n)}, \chi^{(n)}). \tag{47}$$

To assess the accuracy of this formula, we use the expansion (46) of $\chi^{(n-1)}$ and $\chi^{(n)}$ and the orthogonality property $(\chi_m, \chi_n) = \delta_{mn}$ to obtain the result

$$\lambda^{(n)} = \frac{\sum_i b_i^2 \lambda_i^{1-2n}}{\sum_i b_i^2 \lambda_i^{-2n}} = \lambda_0 \left[1 + 0 \left(\frac{b_1^2 \lambda_0^{2n-1}}{b_0^2 \lambda_1^{2n-1}} \right) \right]. \tag{48}$$

For our purposes it will be sufficient to use one iteration with the trial function $\chi^{(0)}(E) \equiv 1$. This very simple trial function yields very good results because the true eigenfunction differs appreciably from unity only near the dissociation limit, and in this region the weighting function $\Psi(E|T_2)$ is small. We then obtain the simple formula

$$\begin{aligned} \chi_0(E') &= C\chi^{(1)}(E') \\ &= C \int_0^D \Psi(E|T_2)G(E|E') dE \end{aligned} \tag{49}$$

as our approximation to the lowest eigenfunction. The constant C is chosen so that $\chi_0(E)$ is normalized to unity, and is therefore given by the formula

$$C^{-2} = \int_0^D \Psi(E|T_2)\chi^{(1)}(E) dE. \tag{50}$$

Because $\chi^{(0)}(E) \equiv 1$, the number density moment $N^{(1)}$ is equivalent to the formula

$$N^{(1)} = C \int_0^D \Psi(E|T_2)\chi^{(1)}(E)\chi^{(0)}(E) dE,$$

⁹ F. B. Hildebrand, *Methods of Applied Mathematics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1952), pp. 442–443.

and the approximation (47) to the eigenvalue λ_0 reduces to the simple expression

$$\lambda_0 \cong \lambda^{(1)} = CN^{(1)}. \quad (51)$$

To estimate the accuracy of equations (49)–(51), we may use some results from the simple model discussed in Sec. III. By observing that the expansion coefficients b_n are given by the simple formula

$$b_n = (\chi^{(0)}, \chi_n) = (1, \chi_n) = N_n,$$

it may be shown that the lowest-order error term of the eigenfunction formula is of the order of

$$b_1\lambda_0/b_0\lambda_1 \cong 10^{-3}$$

while the lowest-order error term in the eigenvalue formula is of the order of

$$b_1^2\lambda_0/b_0^2\lambda_1 \cong 10^{-4}.$$

The errors in the incubation times are somewhat larger, but computations using the methods of this section have been carried out using the model of Sec. III, and the results never differ from the exact results by more than a few percent.

V. MORSE OSCILLATOR MODEL

Although the results of Sec. III are capable of providing a qualitatively correct description of the transient phenomena, they predict incubation times which are smaller than those observed for real molecules by about a factor of five. The difficulty lies in the molecular model used, that is, in the choice of the functions $\kappa(E)$ and $\Psi(E|T)$. In this section we shall use the approximate methods developed in Sec. IV to calculate incubation times for the more accurate Morse oscillator model.

The Morse potential function,

$$V(r) = D\{1 - \exp[-\beta(r - r_e)]\}^2, \quad (52)$$

in which r is the internuclear separation and D , β , and r_e are disposable parameters, has been found to represent the potential of diatomic molecules fairly well. In contrast with the truncated harmonic oscillator, the frequency of oscillation depends upon the energy, and the energy levels are not evenly spaced. Indeed, for a classical Morse oscillator the frequency ω is given by the formula

$$\omega = \omega_0(1 - E/D)^{1/2}. \quad (53)$$

The frequency of oscillation at the bottom of the well is given by the formula $\omega_0 = (2D\beta^2/\mu_{12})^{1/2}$, where μ_{12} is the reduced mass of the molecule. The energy transition rates of a classical Morse oscil-

lator have been investigated numerically by Keck⁵ and Woznick,¹⁰ who find that within their statistical errors the transition rate is given by the expression

$$\kappa(E)\Psi(E|T) \propto \frac{D^{\frac{1}{2}} - (D' - E)^{\frac{1}{2}}}{D^{\frac{1}{2}} + (D' - E)^{\frac{1}{2}}} \cdot \exp\left(-\frac{D' - E}{kT}\right) f_1(\omega\tau), \quad (54)$$

where E is the total (rotational plus vibrational) internal energy, D' is the maximum in the effective (true plus centrifugal) potential, and τ is the effective duration of a collision, given by the formula

$$\tau = \pi L(\mu_3/2kT)^{1/2}, \quad (55)$$

where μ_{13} is the reduced mass of the colliding particles, and L is the range of the interaction potential (assumed exponential) of the colliding particles. The adiabaticity factor, $f_1(\omega\tau)$, is closely approximated by the expression

$$f_1(x) \approx \left(\frac{4}{3}\right) \exp\left(-\frac{4}{3}x\right). \quad (56)$$

At high temperatures, where transient effects are important, the dissociation process tends to be limited by the rate at which molecules diffuse through the lower levels, rather than by what happens in the upper levels. If, therefore, we expand the expression (53), (54), and (56) about $E = 0$, keeping first-order terms, and neglect the effect on $\Psi(E|T)$ of level crowding near the dissociation limit, we obtain the simple expression

$$\kappa(E) = \kappa_0 E \exp(\mu E/kT), \quad (57)$$

where the adiabaticity coefficient μ is defined by the formula

$$\mu = 2\omega_0\tau/9\delta. \quad (58)$$

As before, δ is defined by the expression $\delta = D/kT_2$. If we define the "softness parameter" γ by the expression

$$\gamma = \left(\frac{1}{3}\pi\beta L\right)^2 \mu_3/\mu_{12}, \quad (59)$$

which depends only on the properties of the colliding molecules, the adiabaticity coefficient may be expressed by the formula

$$\mu = \frac{2}{9}(\gamma/\delta)^{1/2}. \quad (60)$$

Clearly γ (and μ) are larger for "softer" collisions. The model we have now obtained is equivalent to a truncated Landau-Teller harmonic oscillator model¹¹

¹⁰ B. Woznick, Avco Everett Research Laboratory Report 223 (1965).

¹¹ R. J. Rubin and K. E. Shuler, *J. Chem. Phys.* 25, 59 (1956).

except that the transition probabilities are augmented by an adiabaticity effect, $\exp(\mu E/kT)$, arising from the closer spacing of the upper levels.

The Green's function is obtained from Eq. (41). In terms of the dimensionless variables

$$\epsilon = E/kT_2, \quad \delta = D/kT_2, \quad (61a)$$

$$\beta = \alpha/\kappa_0, \quad \Lambda_n = kT_2\lambda_n/\kappa_0, \quad (61b)$$

$$G^* = (\kappa_0 G/kT_2)(1 - e^{-\delta})^{-1}, \quad (61c)$$

$$g^* = (\kappa_0 g/kT_2)(1 - e^{-\delta})^{-1},$$

the Green's function is given by the expression

$$G^*(\epsilon|\epsilon') = g^*(\epsilon_>) = \frac{e^\delta}{\beta} + \int_\epsilon^\delta \frac{e^{(1-\mu)x}}{x} dx \quad (62)$$

and the lowest eigenfunction is given by the expression

$$\chi_0(\epsilon) = C^* \left[\frac{e^\delta - 1}{\beta} + \int_\epsilon^\delta dx \frac{e^x - 1}{x} e^{-\mu x} \right]. \quad (63)$$

By expanding the exponential in a power series we find that

$$\chi_0(\epsilon) = C^* \{ (e^\delta - 1)\beta^{-1} + S([1 - \mu]\delta) - S(-\mu\delta) - S([1 - \mu]\epsilon) + S(-\mu\epsilon) \}, \quad (64)$$

where the function $S(x)$ is defined by the infinite series

$$S(x) = \sum_{m=0}^\infty \frac{x^m}{mm!}. \quad (65)$$

The coefficient C^* is found by integrating Eq. (50) by parts, using Eq. (63a) to evaluate $\chi'_0(\epsilon)$; the result is

$$\begin{aligned} \frac{1 - e^{-\delta}}{C^{*2}} &= \left[\frac{e^\delta - 1}{\beta} + S([1 - \mu]\delta) - S(-\mu\delta) \right]^2 \\ &- e^{-\delta} \left[\frac{e^\delta - 1}{\beta} \right]^2 \\ &- 2\beta^{-1}(e^\delta - 1)[S(-\mu\delta) - S(-[1 + \mu]\delta)] \\ &- 2P\left(\frac{-\mu}{1 - \mu} \mid (1 - \mu)\delta\right) \\ &+ 2P\left(\frac{-(1 + \mu)}{1 - \mu} \mid (1 - \mu)\delta\right) \\ &- 2P(1 \mid -\mu\delta) - 2P(1 + \mu^{-1} \mid -\mu\delta), \end{aligned} \quad (66)$$

where the function $P(a|x)$ is defined by the expression

$$P(a|x) = \sum_{n=1}^\infty \frac{a^n}{nn!} \int_0^x t^{n-1} e^t dt. \quad (67)$$

This function may be evaluated by expanding the exponential in the integrand, integrating and inverting the order of summation. However, a simpler expression may be obtained by integrating by parts N times to obtain the series

$$\begin{aligned} \int_0^x t^{n-1} e^t dt &= (-1)^n (n - 1)! e^x \sum_{m=n}^{n+N-1} \frac{(-x)^m}{m!} \\ &+ (-1)^n \frac{(n - 1)!}{(n + N - 1)!} \int_0^x dt e^t (-t)^{n+N-1}. \end{aligned}$$

The remainder term is smaller, in absolute value, than $(n - 1)! e^x x^{n+N}/(n + N)!$. Since this vanishes as $N \rightarrow \infty$, we may extend the sum to infinity. Substituting the result into Eq. (67), we obtain a double infinite series for $P(a|x)$. However by inverting the order of summation, we obtain the convenient formula

$$P(a|x) = e^x \sum_{n=1}^\infty \frac{(-x)^n}{n!} \sum_{m=1}^n \frac{(-a)^m}{m^2}. \quad (68)$$

The moments N_0 , $N_0 \bar{E}_0/\bar{E}_{T_2}$, and $N_0 \bar{\sigma}_0/\bar{\sigma}_{T_2}$ of the eigenfunction $\chi_0(E)$ are given by the formulas

$$\begin{aligned} N_0 &= C^* \left[\frac{\exp(\delta) - 1}{\beta} \right. \\ &\left. + \frac{S([1 - \mu]\delta) - 2S(-\mu\delta) + S(-[1 + \mu]\delta)}{1 - \exp(-\delta)} \right], \end{aligned} \quad (69a)$$

$$\begin{aligned} \frac{N_0 \bar{E}_0}{\bar{E}_{T_2}} &= C^* \left[\frac{\exp(\delta) - 1}{\beta} - \frac{1 - \exp(-\mu\delta)}{\mu [\exp(\delta) - \delta - 1]} \right. \\ &+ \frac{1 - \exp[-(1 + \mu)\delta]}{(1 + \mu) [\exp(\delta) - \delta - 1]} \\ &\left. + \frac{S([1 - \mu]\delta) - 2S(-\mu\delta) + S(-[1 + \mu]\delta)}{\exp(\delta) - \delta - 1} \right], \end{aligned} \quad (69b)$$

$$\begin{aligned} \frac{N_0 \bar{\sigma}_0}{\bar{\sigma}_{T_2}} &= \frac{a_0}{N(0)} \\ &= C^* \left[\frac{\exp(\delta) - 1}{\beta} + S([1 - \mu]\delta) - S(-\mu\delta) \right]. \end{aligned} \quad (69c)$$

In their numerical trajectory calculations, Woznick¹⁰ and Keck⁵ also find that within their statistical errors the net flux past the energy $E = D$ is related to the diffusion coefficient by the equation

$$\alpha\Psi(D|T_2) = 2\kappa(D)\Psi(D|T_2). \quad (70)$$

Using this formula with the diffusion coefficient of Eq. (57), we find that

$$\beta = 2\delta \exp(\mu\delta). \quad (71)$$

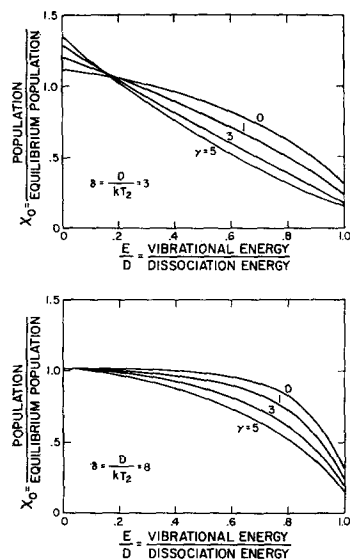


FIG. 3. Steady-state vibrational distribution functions according to the simplified Morse oscillator model.

The results are shown in Figs. 3, 4, and 5. Comparing Figs. 3(a) and 3(b), we observe that at higher temperatures (smaller δ 's) the nonequilibrium effects in the lower levels are more pronounced, and the "bottleneck" in the diffusion process is located further from the dissociation limit. Since the parameter γ reflects the "anharmonicity" of the molecular vibrations, ($\gamma = 0$ for a harmonic oscillator) we see that anharmonic behavior increases nonequilibrium effects at all vibrational energies, and moves the bottleneck into lower energy levels.

The incubation times τ_N , τ_E , and τ_I are plotted in Figs. 4 and 5. As was the case with the model discussed in Sec. III, the energy incubation time, τ_E , is negative, except at very high temperatures ($\delta \lesssim 2$). Comparing Figs. 4 and 5, we observe that the absorption incubation time, τ_I , is about twice the dissociation delay time, τ_N , for all values of γ and δ . That is, the apparent incubation time measured by Schumann-Runge absorption is due as much to the skewness of the "steady-state"

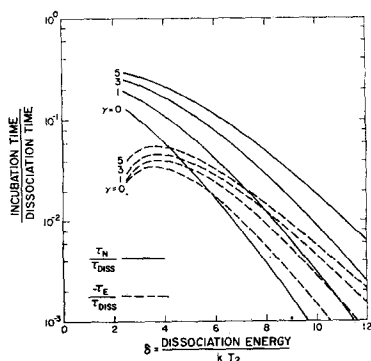


FIG. 4. Incubation time for the molecular number density and vibrational energy according to the simplified Morse oscillator model.

distribution function, $\chi_0(E)$, as to the actual delay in the onset of dissociation.

In Fig. 5 the calculated incubation times for Schumann-Runge absorption of 1470 Å radiation by oxygen are compared with some experimental data due to Wray.¹ Since the incubation times and dissociation times vary in the same way with pressure, the dimensionless ratio of the incubation time to the dissociation time should be independent of the pressure and of the mixture, so long as the concentration of molecules is small, and the data should all fall on a single curve. Unfortunately, there is a good deal of scatter in the data. Using reasonable values for the molecular constants,^{12,13} the appropriate value of the "softness parameter" for O_2 -Ar collisions is estimated to be $\gamma \simeq 2$. For this case the theory lies in the middle of the experiments at higher temperatures, but appears to fall below the experimental points at low temperatures. Although the "bottleneck" in the diffusion process controlling the dissociation rate moves toward the dissociation limit at low temperatures and we might expect the theory to be in error, it should

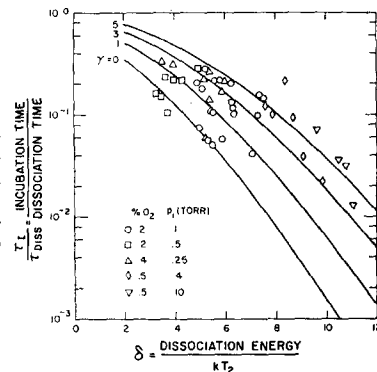


FIG. 5. Incubation times for the Schumann-Runge absorption coefficient according to the simplified Morse oscillator model, compared with experimental data due to Wray.⁹

be borne in mind that the data for $\delta \gtrsim 8$ are known to be less reliable than the other data.^{1,14} This is because at these temperatures the incubation time is very short compared with the dissociation time over which the experiment had to be carried out. As a result, the incubation times observed at these temperatures were smaller than the resolution times of the experiment, and in some cases appeared to be negative. The negative incubation times have not been plotted in Fig. 5. In view of this and the large scatter in all the data, it would be premature to confirm or reject the theory at this point.

¹² E. A. Mason and J. T. Vanderslice, *J. Chem. Phys.* **28**, 432 (1958).

¹³ K. F. Herzfeld and T. A. Litovitz, *Absorption and Dispersion of Ultrasonic Waves* (Academic Press Inc., New York, 1959), p. 324.

¹⁴ K. L. Wray, private communication.

VI. DISCUSSION

Due to the coupling of dissociation with vibrational relaxation, transients appear in the dissociation of diatomic molecules behind shock waves during the initial period of vibrational relaxation. During the transient period, the behavior of the macroscopic observables of the molecular species is generally rather complex. However, after the transient has passed, the overall effect of vibration-dissociation coupling is to introduce time shifts, or incubation times, into the exponential decay of the molecular observables as the molecules dissociate.

These incubation times may be calculated from the lowest eigenvalue and lowest eigenfunction of the coupled vibration-dissociation process, and arise from two effects. The first effect is due to an actual delay in the dissociation process due to the fact that the molecules start off in low vibrational levels, from which they are difficult to dissociate. This dissociation delay was predicted by several earlier theories,²⁻⁴ and is common to all molecular observables. The second effect giving rise to incubation times is the nonequilibrium shape of the vibrational distribution function during the "steady-state" phase of dissociation. The nonequilibrium shape is caused by the depletion of the upper levels by dissociation. The effect of this on the incubation time is different for each molecular observable, and can be more important than the delay of dissociation.

Approximate methods can be used to calculate the lowest eigenvalue and eigenfunction according to the "diffusion theory" of nonequilibrium dissociation. When a simplified Morse-oscillator molecular model is used, the results fall within the experimental scatter at high temperatures ($kT \gtrsim 10\%$ of the dissociation energy), where transient effects are most important.

However, the theory is still over-simplified, and

is subject to errors from two sources. The first is the approximations used to simplify the Morse oscillator model. These approximations could be avoided if one were willing to carry out some integrals on a computer, which is, in fact, not a very difficult task. A more serious source of error is the diffusion coefficient of Eq. (54), which was derived from a statistical analysis of classical trajectory calculations carried out on a computer. The formula was derived from collisions in which the molecule was within about $3kT$ of dissociating, although the dissociation energy was about $10kT$. Consequently, the validity of the formula for the low energy levels is subject to some doubt. Moreover, the formula takes only a crude account of rotations by using the total energy (vibrational plus rotational) as the coordinate, and describing diffusion as taking place with respect to the total energy D' necessary to dissociate a molecule with a given angular momentum. While this seems to work fairly well in the upper levels, and leads to fairly accurate predictions of dissociation rate constants,⁵ it still ignores the fact that the internal relaxation process is really a two-dimensional problem, with the vibrational energy as one coordinate and the rotational energy as the other. Since rotational transitions are often much faster than vibrational transitions, and do not depend on temperature in the same way, this could be a serious limitation, and further work should be done in this area.

ACKNOWLEDGMENTS

This work was supported jointly by Ballistic Systems Division Deputy for Ballistic Missile Reentry Systems, Air Force Systems Command, Norton Air Force Base, California, under Contract AF04(964)-690, and Advanced Research Projects Agency, monitored by the Army Missile Command, U. S. Army under Contract DA-01-021-AMC-12005(Z) (part of Project Defender).