THE THEORY OF VIBRATIONAL ENERGY TRANSFER BETWEEN SIMPLE MOLECULES IN NONREACTIVE COLLISIONS

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I. Introduction

In writing a review of vibrational energy transfer in gases, one must first cite the reviews of Takayanagi,[1,2] Herzfeld,[3,4] and Cottrell and McCoubrey.[5] To avoid excessive duplication of these earlier reviews, we have not exhaustively covered the history of the subject or assigned credits for the earliest contributions to a particular idea. Indeed, much of the groundwork in vibrational energy transfer was laid in the early 1930's. However, a number of important papers have been published on this subject in the last 5 years, and new insight can now be obtained on the meaning of the various procedures that can be used to calculate theoretically the energy transfer in collisions. In some ways, the relationships among various approximate methods are so basic and so important that they may be more significant than the actual results for vibrational energy transfer. No existing calculation is based on a collision model that is sufficiently realistic so that accurate results can be expected. However, these calculations, based on a crude collision model, lead to conclusions regarding which approximate methods can be employed in the future to solve the complicated equations resulting from a more rigorous collision model.

In this review, the plan is to concentrate on those papers that are most significant for exploring the validity of various approaches for the calculation of energy transfer in molecular collisions. The relationships among quantum, semiclassical, and classical procedures, when applied to energy transfer, are at least as interesting as the energy transfer itself. These will be explored in detail.

It is inevitable, in a review of this sort, that some papers that deserve to be mentioned will be left out or only briefly considered. We apologize in advance for any articles that are

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(1) K. Takayanagi, *Progr. Theor. Phys. Suppl.* (Kyoto), **25**, 1 (1963).

(2) K. Takayanagi, *Advan. At. Mol. Phys.*, **1**, 149 (1965).

(3) K. Herzfeld and T. A. Litovitz, "Absorption and Dispersion of Ultrasonic Waves," Academic Press, New York, N. Y., 1959.

(4) K. F. Herzfeld in "Thermodynamics and Physics of Matter," Princeton University Press, Princeton, N. J., 1965, Section H.

(5) T. L. Cottrell and J. C. McCoubrey, "Molecular Energy Transfer in Gases," Butterworth & Co., Ltd., London, 1961.

inadvertently neglected. This is not an exhaustive review with one sentence reserved for each and every paper in the literature, but rather an attempt to concentrate on those aspects that have the greatest general bearing on determining how future, more accurate calculations should be performed.

In this article, we shall be concerned with the calculation of vibrational–translational energy transfer for nonreactive collisions, in which energy exchange takes place between the lower vibrational levels. Consideration of very highly vibrationally excited molecules is specifically excluded. The physical applications of our restricted range of interest include rapid changes in gas temperatures in gas flows, ultrasonics, and chemical or laser production of non-Boltzmann distributions of vibrational energy levels. However, the vibrational energy exchange that occurs in collisions of highly excited molecules capable of unimolecular decomposition are not considered in detail in this article.

Vibrational–translational energy transfer may be depicted by the equation

$$A(v_i) + BC(n_i) \longrightarrow A(v_j) + BC(n_j)$$

In this process, a diatomic molecule BC in vibrational state n_i collides with a molecule or atom A, the relative collision velocity being v_i. After collision, BC is in vibrational state n_j, and the relative velocity of separation is v_j. If rotational transitions are neglected, the vibrational energy of BC is exchanged for relative translational energy of A and BC. We shall also be interested in "resonant" vibrational–vibrational energy transfer

$$AB(n_1) + AB(n_2) \longrightarrow AB(n_1') + AB(n_2')$$

In this process, no energy is exchanged between vibrational and translational modes and $n_1 + n_2 = n_1' + n_2'$. Strictly speaking, there is a small vibrational–translational energy exchange if the molecular vibrations are not perfectly harmonic, but this is usually very minor. In nonresonant energy transfer, $n_1 + n_2 \neq n_1' + n_2'$. To calculate cross sections or collision numbers rigorously for these energy exchange processes, the complete potential energy surface for all possible configurations should be determined, and the complete Schroedinger equation for the system would be solved subject to the appropriate boundary conditions. Such a calculation would be extremely complicated and laborious, and there is little likelihood that it will be carried out for any process in the next decade. Therefore, a simplified approximate collision model must be set up in order to carry through a calculation to completion. It is to be hoped that such an approximate calculation, although necessarily oversimplified, will nevertheless retain much of the essence of the real problem. Hence, the model would correctly predict the trends and general magnitudes of probabilities for vibrational energy exchange processes, although it may not be easy to determine whether this is so in any given case.

Certain approximations have often been made in order to obtain analytical solutions of the general equations. Since 1963, several approximations have been shown to be poor on the basis of comparison with more exact results obtained by computer solution of the collision equations. In some calculations, crude, but *a priori* assumptions are made for the collision model, and the results are compared with experiment. We believe that such calculations are more valuable than those containing adjustable parameters that are fitted to experiment, because the latter tend to explain everything and predict nothing.

II. Basic Theory of Vibrational–Transitional Energy Transfer for a Collinear Collision of a Particle A with a Harmonic Oscillator BC

A. SIMPLEST COLLISION MODEL

In this section, a simple collision model will be described that has been frequently used. Although it is rather crude, the model serves a useful purpose because it contains some elements of the real collision interaction, and because a number of different calculations may be carried out and compared on the basis of this model.

Consider a linear head-on collision of a mass point A with a diatomic molecule BC, as shown in Figure 1. The center of mass of BC is denoted as G, and the center of mass of the three particles is denoted as R. The positions of G and R are measured from a fixed origin denoted as O. The Cartesian coordinates of particles A, B, and C are denoted as $\tilde{x}_A$, $\tilde{x}_B$, and $\tilde{x}_C$, respectively. The positions of G and R are

$$\tilde{x}_G = (m_B\tilde{x}_B + m_C\tilde{x}_C)/(m_B + m_C) \tag{1}$$

$$\tilde{x}_R = (m_A\tilde{x}_A + m_B\tilde{x}_B + m_C\tilde{x}_C)/M \tag{2}$$

where $M = m_A + m_B + m_C$. The three coordinates $\tilde{x}_A$, $\tilde{x}_B$, and $\tilde{x}_C$ can be used to describe the positions of the particles, but it is more convenient to use $\tilde{x}_R$ as one of the coordinates, because the potential energy must be independent of $\tilde{x}_R$. A useful alternate set of coordinates is $\tilde{x}$, $\tilde{y}$, and $\tilde{x}_R$, where

$$\tilde{x} = \tilde{x}_A - \tilde{x}_G \tag{3}$$

$$\tilde{y} = \tilde{x}_B - \tilde{x}_C \tag{4}$$

In this coordinate system, $\tilde{x}_R$ specifies the position of the center of mass of all three particles, $\tilde{x}$ is the position of A relative to the center of mass of BC, and $\tilde{y}$ is the oscillator separation.

In general, the potential energy cannot depend on the coordinate $\tilde{x}_R$ so that the motion in $\tilde{x}_R$ is free. When $\tilde{x}$ is extremely large, the intermolecular potential simply reduces to the potential energy for an isolated diatomic molecule BC, denoted as $V_0(\tilde{y})$. For noninfinite $\tilde{x}$, the interaction between A and BC depends on both coordinates $\tilde{x}$ and $\tilde{y}$. The total potential may be written in the form

$$V(\tilde{x},\tilde{y}) = V_0(\tilde{y}) + V'(\tilde{x},\tilde{y}) \tag{5}$$

without loss of generality. The interaction term $V'(\tilde{x},\tilde{y}) \rightarrow 0$ as $\tilde{x} \rightarrow \infty$. Equation 5 is exact. In the simple approximate collision model, it is assumed that $V'(\tilde{x},\tilde{y})$ is an interaction between atoms A and *B*, so that $V'(\tilde{x},\tilde{y})$ depends only on the distance between mass points A and B. This distance is $\tilde{x} - \gamma\tilde{y}$, where $\gamma = m_C/(m_B + m_C)$. Thus

$$V(\tilde{x},\tilde{y}) \cong V_0(\tilde{y}) + V'(\tilde{x} - \gamma\tilde{y}) \tag{6}$$

It is usually assumed that $V'(\tilde{x} - \gamma\tilde{y})$ has the form of a typical intermolecular potential between saturated molecules, such as a Lennard-Jones, Morse, or Buckingham potential. In many calculations, the attractive part of the interaction potential is either neglected or treated crudely. The repulsive part of $V'(\tilde{x} - \gamma\tilde{y})$ is assumed to have exponential form

$$V'(\tilde{x} - \gamma\tilde{y}) = A\exp[-(\tilde{x} - \gamma\tilde{y})/L] \tag{7}$$

where A and L are constants. The parameter L is obtained by fitting this function to the best available intermolecular potential determined from experimental data on transport properties. Unfortunately, this procedure involves a number of crude assumptions. The intermolecular potentials are sensitive to weak glancing collisions and are not strongly dependent on the steepness of the inner repulsive potential. Vibrational energy transfer is extremely sensitive to the slope of the repulsive potential, which is not very well known. Potentials based on transport properties[6] are, in general, steep. Herzfeld[4] found that an equating of the exponential potential to the repulsive part of the Lennard-Jones transport property potential is obtained for $L \cong r_0/17.5$, where r_0 is the Lennard-Jones potential parameter. This result depends on the energy chosen for equating the two potentials.

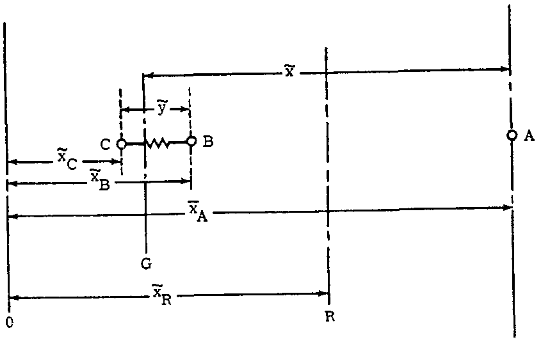

Figure 1. Collision coordinates. An origin fixed in space is at O, the center of mass of B and C is at G, and the center of mass of A + B + C is at R.

In some calculations, it is assumed that the amplitude of vibration of BC throughout the collision is small compared to L. By defining $\tilde{y}_0$ as the equilibrium value of $\tilde{y}$, we obtain

$$V' = (Ae^{\gamma\tilde{y}_0/L})e^{-\tilde{x}/L}\exp[\gamma(\tilde{y} - \tilde{y}_0)/L] \tag{8}$$

If $|\tilde{y} - \tilde{y}_0| \ll L$, the exponential may be expanded in $(\tilde{y} - \tilde{y}_0)$, and the *linearized* potential is

$$V' = A'e^{-\tilde{x}/L}[1 + \gamma(\tilde{y} - \tilde{y}_0)/L + \ldots] \tag{9}$$

where $A' = Ae^{\gamma\tilde{y}_0/L}$.

B. CLASSICAL DYNAMICAL CALCULATION OF ENERGY TRANSFER

1. General Equations

In the classical calculation, the atom A is initially at a large distance from the free oscillator BC. The beginning of the collision is the initial time $t = t_0$. Then the initial conditions are

$$\tilde{x}(t_0) = \tilde{x}_0 \tag{10}$$

$$\tilde{y}(t_0) - \tilde{y}_0 = B_i \sin(\omega t_0 + \delta_i) \tag{11}$$

where $\tilde{x}_0$ is a large positive number, $\tilde{y}_0$ is the equilibrium value of $\tilde{y}$, and B_i and γ_i are constants that determine the amplitude and phase, respectively, of the initial harmonic motion of BC. The equations of motion for the three-particle system A + BC can be shown to be

$$M\ddot{\tilde{x}}_R = 0$$

$$\tilde{m}\ddot{\tilde{x}} = -\frac{\partial V}{\partial \tilde{x}}(\tilde{x},\tilde{y}) = -\frac{\partial V'}{\partial \tilde{x}}(\tilde{x},\tilde{y}) \tag{12}$$

$$\mu\ddot{\tilde{y}} = -\frac{\partial V}{\partial \tilde{y}}(\tilde{x},\tilde{y}) = -f(\tilde{y} - \tilde{y}_0) - \frac{\partial V'}{\partial \tilde{y}}(\tilde{x},\tilde{y})$$

where f is the force constant for BC, $V_0(\tilde{y})$ is assumed to be $^1/_2f(\tilde{y} - \tilde{y}_0)^2$, and the mass terms are defined by

$$\tilde{m} = m_A(m_B + m_C)/(m_A + m_B + m_C) \tag{13}$$

$$\mu = m_Bm_C/(m_B + m_C) \tag{14}$$

Equations 12 must be solved subject to the initial conditions, eq 10 and 11. The equation for $\tilde{x}_R$ is trivial and need not be considered further. The center of mass of A + BC merely moves with uniform motion and does not affect the vibrational energy transfer. If eq 7 is used for V', the result is

$$\begin{aligned} \tilde{m}\ddot{\tilde{x}} &= (A/L)\exp[-(\tilde{x} - \gamma\tilde{y})/L] \\ \mu\ddot{\tilde{y}} &= -f(\tilde{y} - \tilde{y}_0) - (A\gamma/L)\exp[-(\tilde{x} - \gamma\tilde{y})L] \end{aligned} \tag{15}$$

We repeat for emphasis that f is the force constant of the oscillator. These equations can be solved on a computer by starting with the initial conditions, eq 10 and 11, and an arbitrary choice of t_0, $\tilde{x}_0$, B_i, and δ_i. It can easily be shown that the choice of t_0 has no bearing on the calculation, provided the integration is carried out to times that are sufficiently large compared to t_0. The choice of $\tilde{x}_0$ is also of no consequence, provided that $\tilde{x}_0$ is large enough that $\exp[-\tilde{x}_0/L] \ll 1$, except insofar as the choice of $\tilde{x}_0$ affects the initial phase.

Upon integration of eq 15, it will be found that as t increases, $\tilde{x}$ will at first decrease to a minimum, and then increase again. Eventually $\tilde{x}$ will return to $\tilde{x}_0$, and at this point the collision may be assumed to be ended. Near the end of the collision ($t \gg t_0$), the interaction energy is zero, and it will be found that $\tilde{y}$ varies with t according to some relation

$$\tilde{y} - \tilde{y}_0 = B_f \sin(\omega t + \delta_f) \tag{16}$$

The energy transferred to the oscillator in the collision is

$$\Delta E = \tfrac{1}{2}f[B_f^2 - B_i^2] \tag{17}$$

In general, ΔE will depend on both B_i and δ_i for arbitrary t_0 and $\tilde{x}_0$.

In any experiment, the energy transferred to an oscillator with a particular initial amount of excitation (*i.e.*, a fixed value of B_i) is measured. In order to compare with experiment, the values of ΔE calculated for fixed B_i but various δ_i should be phase averaged. Thus

$$\langle\Delta E(B_i)\rangle = (2\pi)^{-1}\int_0^{2\pi}\Delta E(B_i,\delta_i)\,d\delta_i \tag{18}$$

is the quantity that should be compared with an experimental ΔE for fixed B_i.

It can be shown that $\Delta E(B_i,\delta_i)$ does not depend on the choice of A, but is very sensitive to the value of L. To show this, A may be written in the form $e^{a/L}$, where a is a constant. If this is substituted for A in eq 15, it will be found that the form of eq 15 remains unchanged, but $\tilde{x}$ is replaced by $\tilde{x}' = \tilde{x} - a$. The solution of eq 15 does not depend on the initial position $\tilde{x}_0$, and hence it cannot depend on the initial value of $\tilde{x}'$. Since the constants A and a do not appear explicitly in the equations, it follows from eq 15 that the energy

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(6) J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, and E. L. Spotz in ref 4, Section D.

transfer must be independent of these constants. The results of numerical calculations on a large number of systems under various conditions are given by Kelley and Wolfsberg.[7]

2. *Approximate Solution*

Before discussing the exact numerical calculations, it is useful to first present an approximate solution derived by Landau and Teller,[8] Rapp,[9] Parker,[10] and Takayanagi.[1] This procedure involves the basic assumption that the vibrational amplitude of the oscillator is not driven to large values during the collision, so that

$$|\tilde{y} - \tilde{y}_0| \ll L \tag{19}$$

throughout the collision. Prior to the work of Wolfsberg and Kelley,[7] it had been thought that this condition is automatically satisfied for all low-velocity collisions. Actually, this is not the case, and the above authors have shown that condition 19 holds only for certain mass combinations of A, B, and C. This will be discussed in greater detail later.

If it is assumed that eq 19 is valid, then eq 9 may be used for the potential. Furthermore, since $\tilde{y}$ never deviates substantially from $\tilde{y}_0$, one can perform an approximate integration of eq 15 by setting $\tilde{y}(t)$ equal to $\tilde{y}_0$ in the exponential functions. Equations 15 then take the approximate form

$$\begin{aligned} \tilde{m}\ddot{\tilde{x}} &\cong (A'/L)e^{-\tilde{x}/L} \\ \mu\ddot{\tilde{y}} + f(\tilde{y} - \tilde{y}_0) &= -(\gamma A'/L)e^{-\tilde{x}/L} \end{aligned} \tag{20}$$

It is convenient to define $\tilde{x}_t$ as $\tilde{x}$ at the classical turning point, and $\tilde{X} = \tilde{x} - x_t$. Then eq 20 become

$$\begin{aligned} \tilde{m}\ddot{\tilde{X}} &= (A''/L)e^{-\tilde{X}/L} \\ \mu\tilde{y} + f(\tilde{y} - \tilde{y}_0) &= (\gamma A''/L)e^{-\tilde{X}/L} \end{aligned} \tag{21}$$

where $A'' = A'e^{-\tilde{x}_t/L}$. The first of eq 20 may now be integrated directly, if $t = 0$ is defined as the point where $\tilde{X} = 0$. The result is

$$e^{-\tilde{X}(t)/L} = \operatorname{sech}^2[(A''/2\tilde{m})^{1/2}t/L] \tag{22}$$

The beginning of the collision corresponds to $X = \infty$ and $t = -\infty$, and the end to $X = \infty$ and $t = +\infty$. If the initial relative velocity is v_0, then all the initial kinetic energy $(\tilde{m}v_0{}^2/2)$ is converted to potential energy at $t = 0$. Therefore, $A'' = \tilde{m}v_0{}^2/2$, and eq 22 may be written

$$e^{-\tilde{X}/L} = \operatorname{sech}^2(v_0t/2L) \tag{23}$$

This equation is based on the assumption that variations in $\tilde{y}(t)$ during the collision are small compared to L. It also implies that the energy transferred to the oscillator is small compared to the incident energy since the latter quantity is assumed independent of the excitation in the oscillator. If this equation is substituted into the second of eq 21, the result is

$$\mu\ddot{\tilde{y}} + f(\tilde{y} - \tilde{y}_0) = -(\gamma A''/L)\operatorname{sech}^2(v_0t/2L) \tag{24}$$

Equation 24 may be solved subject to the initial condition

$$\lim_{t\to-\infty}[\tilde{y}(t) - \tilde{y}_0] = B_i \sin(\omega t + \delta_i) \tag{25}$$

According to Slater and Frank,[11] the solution of eq 24, subject to eq 25, is

$$\lim_{t\to+\infty}[\tilde{y}(t) - \tilde{y}_0] = B_i\sin(\omega t + \delta_i) + (\mu\omega)^{-1}\int_{-\infty}^{t}(\gamma A''/L)\operatorname{sech}^2(v_0s/2L)\sin[\omega(t - s)]\,\mathrm{d}s \tag{26}$$

where the first term is the initial oscillation, and the second term is the change due to the transient force. Since $\operatorname{sech}^2(v_0s/2L)$ is an even function, it can be shown that

$$\lim_{t\to+\infty}[\tilde{y}(t) - \tilde{y}_0] = \left[B_i\cos\delta_i + (\mu\omega)^{-1}\int_{-\infty}^{\infty}(\gamma A''/L)\operatorname{sech}^2(v_0s/2L)\cos(\omega s)\,\mathrm{d}s\right]\sin(\omega t) + B_i\sin\delta_i\cos(\omega t) \tag{27}$$

It then follows that the approximate energy transfer to the oscillator is

$$\Delta E_{\mathrm{ap}} = (f/2)\left\{(2B_i/\mu\omega)\cos\delta_i\int_{-\infty}^{\infty}(\gamma A''/L) \times \operatorname{sech}^2(v_0s/2L)\cos(\omega s)\,\mathrm{d}s + (\mu\omega)^{-2}\left[\int_{-\infty}^{\infty}(\gamma A''/L)\operatorname{sech}^2(v_0s/2L)\cos(\omega s)\,\mathrm{d}s\right]^2\right\} \tag{28}$$

The phase-averaged approximate energy transfer does not contain the first term, since the average value of $\cos\delta_i$ is zero. Thus, the phase-averaged energy transfer $\langle\Delta E_{\mathrm{ap}}\rangle$ is

$$\langle\Delta E_{\mathrm{ap}}\rangle = (2\mu)^{-1}\left[\int_{-\infty}^{\infty}(\gamma A''/L) \times \operatorname{sech}^2(v_0s/2L)\cos(\omega s)\,\mathrm{d}s\right]^2 \tag{29}$$

Since this equation does not contain B_i, the phase-averaged value $\langle\Delta E_{\mathrm{ap}}\rangle$ is independent of the initial excitation in the oscillator. The result of integration is

$$\langle\Delta E_{\mathrm{ap}}\rangle = (2\pi^2\omega^2L^2\tilde{m}^2\gamma^2/\mu)\operatorname{csch}^2(\pi\omega L/v_0) \tag{30}$$

For calculational purposes, it is convenient to define the dimensionless quantities

$$m = \tilde{m}\gamma^2/\mu \tag{31}$$

$$\alpha = (\gamma^2\hbar/\mu\omega)^{1/2}L^{-1} \tag{32}$$

Then, eq 30 becomes

$$\langle\Delta E_{\mathrm{ap}}\rangle = (2\pi^2m^2/\alpha^2)(h\nu)\operatorname{csch}^2\left[\frac{\pi}{\alpha}\left(\frac{m}{2E_0/h\nu}\right)^{1/2}\right] \tag{33}$$

where $E_0 = A'' = \tilde{m}v_0{}^2/2$.

Except at very high velocities, $\pi\omega L$ is usually large compared to v_0. Therefore, under most conditions it is sufficiently accurate to expand $\operatorname{csch}^2(\pi\omega L/v_0)$, so that

$$\langle\Delta E_{\mathrm{ap}}\rangle \cong (8\pi^2\omega^2L^2\tilde{m}^2\gamma^2/\mu)e^{-2\pi\omega L/v_0} \tag{34}$$

The ratio of transferred to incident energy is

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[7] J. D. Kelley and M. Wolfsberg, *J. Chem. Phys.*, **44**, 324 (1966).

[8] L. Landau and E. Teller, *Physik. Z. Sowjetunion*, **10**, 34 (1936).

[9] D. Rapp, *J. Chem. Phys.*, 32, 735 (1960).

[10] J. G. Parker, *Phys. Fluids*, 2, 449 (1959).

[11] J. G. Slater and N. H. Frank, "Mechanics," McGraw-Hill Book Co., Inc., New York, N. Y., 1947.

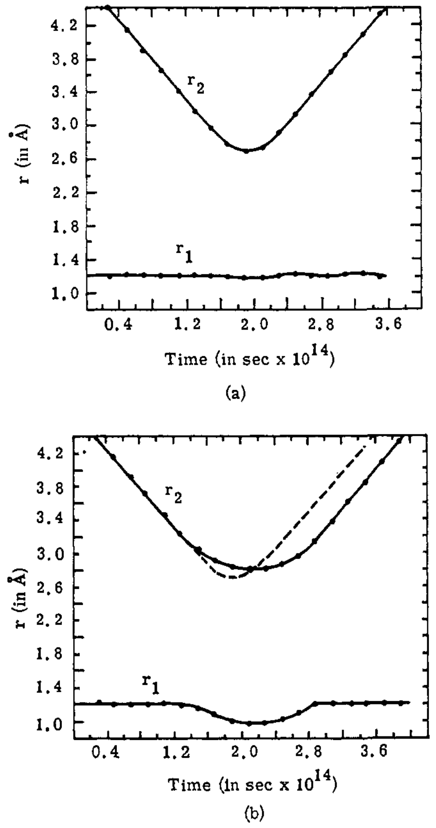

Figure 2. Variation of r_1 and r_2 (the BC and AB distances, respectively) with time during a collision. Case a corresponds to m = 0.0416, while case b corresponds to m = 6.0. In case a, $r_1(t)$ never deviates substantially from the equilibrium configuration of BC, and $r_2(t)$ is essentially identical with what one would calculate from the approximate method. In case b, $r_1(t)$ is heavily compressed during the middle of the collision, and the approximate treatment yields the dotted line for $r_2(t)$, whereas the exact treatment leads to the solid line for $r_2(t)$. Note that although $r_1(t)$ is heavily compressed during the middle of the collision, the final energy transfer to BC after the collision is over is small.

$$\langle \Delta E_{\mathrm{ap}} \rangle / E_0 = (16\pi^2\omega^2L^2\tilde{m}\gamma^2/\mu v_0^2)e^{-2\pi\omega L/v_0} \qquad (35)$$

Equations 34 and 35 can be given a simple interpretation. The quantity L/v_0 is a measure of the duration of the collision τ_c, and $2\pi/\omega = \tau_v$ is the vibrational period. Therefore, the exponential factor in eq 35 can be written as $\exp[-4\pi^2\tau_c/\tau_v]$. At low velocities, where $\tau_c \gg \tau_v$, the energy transfer is small because the oscillator can readjust adiabatically to the perturbation caused by the incident particle. At high velocities, $\tau_c \ll \tau_v$, and, when the oscillator is struck by the incident particle, large vibrational excitation is produced.

3. Exact Solution

In the limit of very high velocities, as $(v_0/\omega L) \rightarrow \infty$, the hyperbolic function in eq 30 may be expanded, and the hard sphere limit is

$$\lim_{v_0 \rightarrow \infty} \langle \Delta E_{\mathrm{ap}} \rangle = 4mE_0 \qquad (36)$$

Thus, the calculated approximate energy transfer will exceed the incident energy at high collision velocities if $m > 0.25$. Since this is not physically possible, it might be expected that even at low velocities the approximate calculation will be accurate only for $m \ll 0.25$, and not for $m > 0.25$. Wolfsberg and Kelley[7] have found this to be the case. For a number of selected examples, Kelley and Wolfsberg calculated $\langle \Delta E \rangle$, the exact energy transfer, and $\langle \Delta E_{\mathrm{ap}} \rangle$ at several collision velocities. Since $\langle \Delta E \rangle$ depends on the initial excitation of the oscillator ($\langle \Delta E_{\mathrm{ap}} \rangle$ does not), the calculation of ΔE was made for zero initial excitation. It was found that at low velocities ΔE is proportional, but not equal, to $\langle \Delta E_{\mathrm{ap}} \rangle$, and the ratio $\mathcal{R} = \langle \Delta E_{\mathrm{ap}} \rangle / \Delta E$ depends only on m. An approximate empirical relation that correlates this ratio at low collision velocities is

$$\mathcal{R} = e^{1.685m} \qquad (37)$$

For example, in a collision where m_A, m_B, and m_C are 13, 1, and 12, respectively, m = 6 and $\mathcal{R} > 100$. However, if m_A, m_B, and m_C are 2, 24, and 24, then m = 0.04, and the ratio is 1.06. Therefore, the approximate method should be limited to collisons between a light particle and a heavy oscillator, where m is small. The ratio $\mathcal{R}$ stays constant over a very broad range of velocities if $m \lesssim 0.5$. For example, in the collision[7] where m_A, m_B, and m_C are 2, 12, and 12, respectively (m = 0.0769), $\mathcal{R}$ is essentially constant over the entire range of incident energy from 0.3 to 20.3 eV. The value of $\mathcal{R}$ at low velocities appears to be independent of the force constant of the oscillator. Kelley and Wolfsberg show that calculations based on the approximate separation of $\bar{x}$ and $\bar{y}$ motion will be in error in proportion to the magnitude of the mass parameter m. For mass factors m less than about $^1/_2$, the approximate formula, eq 30, may be used, with eq 37 as a correction factor. For larger values of m, a complete computer solution is advisable.

A few calculations of the exact $\langle \Delta E \rangle$ were made for cases where the oscillator was initially vibrating. It was found that the energy transferred to the oscillator decreases when the initial excitation is increased.

The failure of the approximate method for large values of m is illustrated in Figures 2a and 2b, where r_1 is the $\overline{\mathrm{BC}}$ distance and r_2 is the $\overline{\mathrm{AB}}$ distance. Both figures depict exact computer solutions of eq 15 by plotting r_1 and r_2 simultaneously as functions of time. Case a corresponds to m = 0.0416, and case b corresponds to m = 6.0. In both examples, the oscillator is initially unexcited, the incident energy E_0 is 5.078 eV, and the energy transferred to the oscillator is less than $^1/_{1000}$ of E_0. In case a, where m is small, the distance $\overline{\mathrm{BC}}$ is a weak oscillatory function of time during the collision. The vibrational amplitude never exceeds 0.02 Å, and since $L \cong$ 0.2 Å the conditions for applicability of the approximate method are fairly well satisfied (note: $\mathcal{R}$ = 1.07 for case a).

In case b, by contrast, oscillator $\overline{\mathrm{BC}}$ is strongly compressed during the collision, despite the fact that the energy transfer is small after the collision. The compression of $\overline{\mathrm{BC}}$ at the heart of the collision is about equal to L. The time dependence of the $\overline{\mathrm{AB}}$ distance is the same in case a, whether calculated by the approximate or exact methods, but for case b the time dependence is greatly in error when calculated by the approximate method.

In summary, the completely classical calculation of energy transfer to an oscillator may be determined exactly by computer solution of eq 15. The energy transfer, which depends sensitively on L, increases with increasing collision velocity and decreases with increasing initial excitation of the oscillator. An approximate procedure, leading to a simple closed form expression for the energy transfer, can be used for small values of the mass parameter m. A correction factor that relates ΔE_{ap} to ΔE is found to be $e^{-1.685m}$ for $m \lesssim {}^1/_2$.

The failure of the approximate procedure is severe for large m, even when the energy transfer in the collision is quite small.

C. SEMICLASSICAL CALCULATION

1. General Equations

It should be emphasized that the classical calculation is based upon the treatment of the energy levels of the oscillator as a continuum. As such, there is no reference to vibrational quantum states, and only the total energy transfer to the oscillator can be calculated. In the semiclassical calculation, the molecule BC is treated as a quantum mechanical system with discrete energy levels. The motion of the incident particle is treated classically. The perturbation $V'(\tilde{x},\tilde{y})$ of the oscillator due to the incident particle can be converted to $V'(t,\tilde{y})$ by determining the classical motion $\tilde{x}(t)$ of the incident particle. This time-dependent perturbation is then inserted in the time-dependent Schroedinger equation, the solution of which gives the final state of the oscillator after the collision. In conventional applications of this procedure, the external motion in coordinate $\tilde{x}$ is determined by making the approximation $\tilde{y} \cong \tilde{y}_0$. The results obtained should therefore be analogous to the "approximate" and not the exact classical calculations. Because the energy in cooordinate $\tilde{x}$ is assumed to be large compared to the energy transferred, the time dependence of $\tilde{x}$ can be evaluated from eq 23, which is the solution of the first equation of (21).

The Schroedinger equation for an isolated diatomic molecule BC is written as

$$\mathcal{H}_0 H_n(\tilde{Y}) = \xi_n H_n(\tilde{Y}) \tag{38}$$

where H_n is the nth normalized harmonic oscillator wave function, $\xi_n = (n + {}^1/_2)\hbar\omega$, $\omega^2 = f/\mu$, $\tilde{Y} = \tilde{y} - \tilde{y}_0$, and $\mathcal{H}_0$ is the Hamiltonian operator for an isolated harmonic oscillator; *i.e.*

$$\mathcal{H}_0 = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial \tilde{Y}^2} + \frac{1}{2}f\tilde{Y}^2 \tag{39}$$

In the problem under consideration, the time-dependent perturbation potential is

$$V'(t,\tilde{Y}) = E_0 \operatorname{sech}^2(v_0 t/2L)\exp[\gamma\tilde{Y}/L] \tag{40}$$

which is obtained from eq 8 and 23. Therefore, the time-dependent Schroedinger equation for the perturbed oscillator is

$$\{\mathcal{H}_0 + V'(t,\tilde{Y})\}\Psi = \hbar i\frac{\partial\Psi}{\partial t} \tag{41}$$

The solution of this equation may be expanded in terms of the stationary-state wave functions $H_n(\tilde{Y})e^{-i\omega_n t}$

$$\Psi(t,\tilde{Y}) = \sum_n a_n(t)H_n(\tilde{Y})e^{-i\omega_n t} \tag{42}$$

where $\omega_n = \xi_n/\hbar$. When eq 42 is substituted into eq 41, and eq 38 is used to simplify, the result is a differential equation in terms of the expansion coefficients $a_n(t)$. If the result is multiplied by some arbitrary oscillator function $H_j(\tilde{Y})$, and integrated over $\mathrm{d}\tilde{Y}$, the result is

$$\mathrm{d}a_j/\mathrm{d}t = (\hbar i)^{-1}\sum_n a_n(t)V_{jn}'(t)e^{i\omega_{jn}t} \tag{43}$$

where $\omega_{jn} = \omega_j - \omega_n$, and

$$V_{jn}'(t) = \int_{-\infty}^{\infty} V'(t,\tilde{Y})H_j(\tilde{Y})H_n(\tilde{Y})\,\mathrm{d}\tilde{Y} \tag{44}$$

Equations 43 (for various j) constitute a set of coupled differential equations in the coefficients $a_n(t)$, with one equation for each term in the expansion eq 42. In principle, the complete set of functions should be used in eq 42, thereby leading to an infinite set of eq 43. In actual practice, a finite set of functions is used, and a heuristic procedure is adopted whereby the calculation is repeated by adding states until the calculated results do not change. It is then presumed that the transition probabilities are exact in the sense that they do not differ substantially from what would be obtained from a calculation that uses an infinite set of states.

Equations 43 are equivalent to the time-dependent Schroedinger equation, except that the time dependence of $\Psi(\tilde{Y},t)$ is given in terms of the time dependence of the expansion coefficients. The probability of finding the oscillator in state n at time t is $|a_n(t)|^2$. At $t = -\infty$, the oscillator is presumed to be in some definite initial state I, represented by the conditions

$$\begin{aligned} a_I(-\infty) &= 1 \\ a_n(-\infty) &= 0 \qquad n \neq I \end{aligned} \tag{45}$$

After the collision, the probability of finding the oscillator in any state j is $|a_j(\infty)|^2$ and the probability of the transition $I \rightarrow j$ is

$$P_{I\rightarrow j} = |a_j(\infty)|^2 \tag{46}$$

2. The First-Order Perturbation Approximation[9,12]

The solution of eq 43 must be accomplished on a digital computer unless additional assumptions are made. One approximate approach that is sometimes used is the first-order perturbation approximation (FOPA), by which it is assumed that the total transition probability out of the initial state is small. In this case, $a_I(t) \cong 1$, $a_n(t) \ll a_I(t)$ for all t, and eq 43 simplifies to

$$\mathrm{d}a_j/\mathrm{d}t \cong (\hbar i)^{-1}V_{jI}'(t)e^{i\omega_{jI}t} \tag{47}$$

so that

$$P_{I\rightarrow j} = |a_j(\infty)|^2 \cong \left|\hbar^{-1}\int_{-\infty}^{\infty} V_{jI}'(t)e^{i\omega_{jI}t}\,\mathrm{d}t\right|^2 \tag{48}$$

If it is assumed as before that $|\tilde{Y}| \ll L$, eq 40 may be expanded to give

$$V'(t,\tilde{Y}) \cong E_0 \operatorname{sech}^2(v_0 t/2L)[1 + \gamma\tilde{Y}/L + \ldots] \tag{49}$$

Then it follows that

$$V_{jI}'(t) = E_0(\gamma/L)\tilde{Y}_{jI}\operatorname{sech}^2(v_0 t/2L) \tag{50}$$

where

$$\tilde{Y}_{jI} = \int_{-\infty}^{\infty} H_j(\tilde{Y})\tilde{Y}H_I(\tilde{Y})\,\mathrm{d}\tilde{Y} \tag{51}$$

It can be shown[4] that $\tilde{Y}_{jI} = 0$, unless $|j - I| = 1$. For $|j - I| = 1$

$$\tilde{Y}_{I\pm1,I} = [(I + \tfrac{1}{2} \pm \tfrac{1}{2})/2\beta]^{1/2} \tag{52}$$

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(12) D. Rapp and T. E. Sharp, *J. Chem. Phys.*, 38, 2641 (1963).

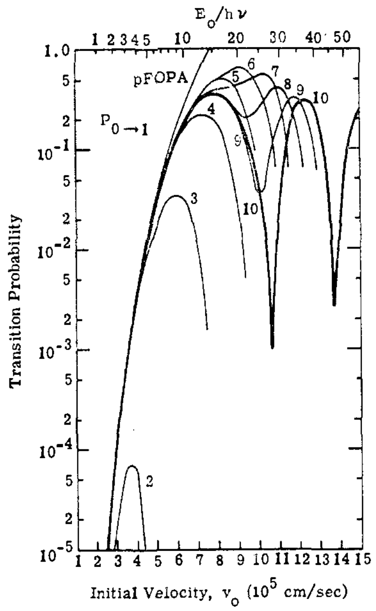

Figure 3. Probability for the 0 → 1 transition for $m = 0.5$ and $\alpha = 0.108$ *vs.* initial collision velocity according to computer solution of the semiclassical equations, using an eigenfunction expansion truncated at 2, 3, 4, . . . , 10 states.

where $\beta = (\mu f)^{1/2}/\hbar$. The net result upon substituting eq 50 and 52 into eq 48 is

$$P_{I\rightarrow I\pm 1} = (2\pi^2\omega\gamma^2\tilde{m}^2L^2/\hbar\mu) \times \operatorname{csch}^2(\pi\omega L/v_0)(I + \tfrac{1}{2} \pm \tfrac{1}{2}) \quad (53)$$

The approximate classical and semiclassical procedures may now be compared. According to the semiclassical result, the energy transferred to the oscillator is

$$\Delta E_{sc} = [P_{I\rightarrow I+1} - P_{I\rightarrow I-1}]\hbar\omega \quad (54)$$

therefore

$$\Delta E_{sc} = (2\pi^2\omega^2\gamma^2\tilde{m}^2L^2/\mu)\operatorname{csch}^2(\pi\omega L/v_0) \quad (55)$$

This is identical with eq 30 obtained from the approximate classical expression. The difference in interpretation[9] is as follows. In the classical description, the energy ΔE_{ap} (from eq 28) is transferred in every single collision with initial phase δ_i, and the phase-averaged energy transfer is $\langle\Delta E_{ap}\rangle$. In the semiclassical description, either an entire quantum is transferred or nothing is transferred in any single collision. The probability per collision is given in eq 53. When averaged over a large number of collisions, the average energy transfer per collision is identical with that calculated classically.

3. Multistate Computer Solutions[13]

Computer solutions of eq 43 were carried out by Rapp and Sharp[13] using various truncated wave-function expansions. The effect of including 2, 3, 4, . . . , and up to 10 states in the eigenfunction expansion was tested, and the results were compared with FOPA calculations.

For the 0 → 1 transition, the variation $P_{0\rightarrow 1}$ *vs.* collision velocity is shown in Figure 3 for various truncations of the eigenfunction expansion. Each succeeding $(N + 1)$-state calculation agrees with the N-state calculations over a range of collision velocities. The most accurate calculation is the 10-state calculation, and this can only be trusted over the range of velocities (*i.e.*, $E_0/h\nu < 20$) for which the 10-state and 9-state results are in agreement. The sharp resonances in $P_{0\rightarrow 1}$ at higher collision energies are mathematical artifacts due to the truncation of the eigenfunction expansion. It is found that the FOPA and exact calculations of $P_{0\rightarrow 1}$ agree for probabilities less than about 0.04. At high energies, values of $P_{0\rightarrow 1}$ obtained from the FOPA method actually exceed unity. It is noteworthy that the exact 2-state result for $P_{0\rightarrow 1}$ is a less accurate calculation than the FOPA procedure.

For nonadjacent transitions, the FOPA method becomes invalid. Despite the fact that $\tilde{Y}_{ij}$ is zero unless $|i - j| = 1$, multiple transitions can occur *via* a series of one-quantum transitions during a single collision. Thus, in the low-velocity regime, the 0 → 3 transition occurs primarily by the mechanism 0 → 1 → 2 → 3. A procedure, analogous to the FOPA, has been developed, in which processes of the general type $I \rightarrow I \pm 1 \rightarrow I \pm 2 \rightarrow \ldots \rightarrow j$ are treated as a series of one-quantum jumps during a collision. The result, based on the assumption that $a_I = 1$ and $a_{I+n} \ll a_I$, is called the Nth order perturbation approximation (NOPA). The probability for the transition $I \rightarrow j$ takes the form

$$P_{I\rightarrow j}{}^{(\mathrm{NOPA})} = (j!/\{I![(j - I)!]^2\})(P_{0\rightarrow 1})^{j-I} \quad (55a)$$

which reduces to

$$P_{0\rightarrow j}{}^{(\mathrm{NOPA})} = (P_{0\rightarrow 1})^j/j! \quad (55b)$$

for $I = 0$. At low velocities, these relations yield results that are good approximations to the exact calculated probabilities. The FOPA results for nonadjacent transitions are many orders of magnitude too small because they take into account only direct transitions from the initial to the final state. To obtain exact probabilities for transitions to nonadjacent levels, the initial, final, and all intermediate states must be included.

4. Exact Solution for a Potential Linear in $\tilde{Y}$

Equations 43 can be solved analytically without the use of the FOPA or other approximations, if eq 9 is used for the potential. The method, originated by Kerner[14] and Treanor,[15] produces a closed-form solution to the time-dependent Schroedinger equation; *i.e.*

$$\left[-(\hbar^2/2\mu)\frac{\partial^2}{\partial\tilde{Y}^2} + \frac{1}{2}f\tilde{Y}^2 - \tilde{Y}F(t)\right]\Psi(\tilde{Y},t) = \hbar i\frac{\partial\Psi}{\partial t}(\tilde{Y},t) \quad (56$$

where, according to eq 49, the classical force acting on the oscillator is

$$F(t) = E_0\operatorname{sech}^2(v_0t/2L) \quad (57)$$

The factor 1 in the term $(1 + \gamma\tilde{Y}/L)$ of eq 49 can be neglected because a perturbation that depends on t but not on $\tilde{Y}$ cannot produce vibrational transitions in an oscillator. A perturbation $F(t)$ merely produces a phase change in $\Psi(\tilde{Y},t)$, and therefore can be neglected. Kerner[14] and Treanor[15] wrote

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(13) T. E. Sharp and D. Rapp, *J. Chem. Phys.*, **43**, 1233 (1965).

(14) E. Kerner, *Can. J. Phys.*, **36**, 371 (1958).

(15) C. E. Treanor, *J. Chem. Phys.*, **43**, 532 (1965).

$$\Psi(\tilde{Y},t) = \varphi(\tilde{Y},t)\exp[\tilde{Y}g(t)] \tag{58}$$

where φ and g are general unspecified functions. This involves no loss of generality. The expression is substituted into eq 56, and the resulting equation contains partial derivatives with respect to the independent variables $\tilde{Y}$ and t.

A new set of independent variables is chosen as ξ and t, where

$$\xi(\tilde{Y},t) = \tilde{Y} - \mu(t) \tag{59}$$

and $\mu(t)$ is to be specified later. After converting partials with respect to $\tilde{Y}$ to partials with respect to ξ, the Schroedinger equation takes a form involving partial derivatives with respect to ξ and t. Since the mathematics was arranged with $g(t)$ and $\mu(t)$ being completely arbitrary, these functions are chosen so as to cancel certain terms in the resulting Schroedinger equation, thereby simplifying the calculation. The functions $u(t)$ and $g(t)$ are chosen so that

$$g(t) = i\mu\ddot{u}/\hbar \tag{60}$$

$$\mu\ddot{u} + fu = F(t) \tag{61}$$

Note that $g(t)$ is pure imaginary. Therefore, the exponential term in eq 58 has the form $e^{i\theta}$ and is merely a time-dependent phase factor attached to the wave function. It has no bearing on the transition probabilities and need not be considered further. Hence, $|\Psi(Y,t)|^2 = |\varphi(Y,t)|^2$. It is worth emphasizing that while the oscillator is treated by a strictly quantum mechanical procedure, the equation for the function $u(t)$ happens to be the classical equation of motion for an oscillator subjected to the transient force $F(t)$. Thus, the function $u(t)$ is the position (measured from equilibrium) that the oscillator would have if it were classical. Actually, $u(t)$ is not fully defined by eq 61 because two boundary conditions must be given to particularize the solution of a second-order differential equation. This shall be done later.

With eq 60 and 61 so chosen, the Schroedinger equation in terms of ξ and t takes the form

$$-(\hbar^2/2\mu)\left(\frac{\partial^2\varphi}{\partial\xi^2}\right)_t + [f\xi^2/2 + \delta(t)]\varphi = \hbar i\left(\frac{\partial\varphi}{\partial t}\right)_\xi \tag{62}$$

where $\delta(t) = -(fu^2/2) + (\mu\dot{u}^2/2)$. Except for the presence of the term $\delta(t)$, eq 62 is the same as the time-dependent Schroedinger equation for a free oscillator in terms of coordinates ξ and t. The term $\delta(t)$ can be removed mathematically by writing

$$\varphi(\xi,t) = \eta(\xi,t)\exp\left[-(i/\hbar)\int_{-\infty}^{t}\delta(t')\,\mathrm{d}t'\right] \tag{63}$$

The exponential term in this equation is a simple phase factor whose absolute square is unity; therefore, this term cannot affect the energy transfer. Substitution of eq 63 into eq 62 results in

$$-(\hbar^2/2\mu)(\partial^2\eta/\partial\xi^2)_t + (f\xi^2/2)\eta = \hbar i(\partial\eta/\partial t)_\xi \tag{64}$$

which is the Schroedinger equation for a free oscillator in coordinates ξ and t. Therefore, $\eta(\xi,t)$ can be any of the harmonic oscillator wave functions

$$\eta_n(\xi,y) = H_n(\xi)\exp\left[-i\int_{-\infty}^{t}(n + \tfrac{1}{2})\omega\,\mathrm{d}t'\right] \tag{65}$$

in which it is assumed that the (arbitrary) phase is such that $\eta_n \rightarrow H_n(\xi)$ as $t \rightarrow -\infty$. Inspection of eq 61 shows that, since $\xi = \tilde{Y} - u(t)$, these functions are centered on the position of a classical forced oscillator.

If eq 58, 60, 63, and 65 are combined, it is found that the nth exact solution of eq 56 is

$$\psi_n(\xi,t) = e^{i\mu\ddot{u}\tilde{Y}/\hbar}H_n(\xi) \times \exp\left[-(i/\hbar)\int_{-\infty}^{t}\{(n + \tfrac{1}{2})\hbar\omega + \delta(t')\}\,\mathrm{d}t'\right] \tag{66}$$

The general solution of eq 56 must be a linear combination of these functions, and since each is an exact solution, the expansion coefficients are time independent

$$\Psi = \sum_{n=0}^{\infty} c_n\psi_n(\xi,t) \tag{67}$$

To determine the expansion coefficients c_n, the initial condition

$$\lim_{t\rightarrow-\infty}\Psi = H_I(\tilde{Y}) \tag{68}$$

must be used. A comparison of eq 66, 67, and 68 shows that the coefficients c_n can be evaluated explicitly only if we choose a particular form for $u(t)$, which has so far been defined merely as a solution of eq 61. However, eq 61 is a second-order differential equation and requires two initial conditions to particularize any solution. It is simplest to choose the conditions $u(t) = \dot{u}(t) = 0$ at $t = -\infty$. With this definition, eq 66 reduces to $\psi_n(\xi,t) \rightarrow H_n(\tilde{Y})$ as $t \rightarrow -\infty$. Then, a comparison of eq 67 and 68 shows that at $t = -\infty$, $c_I = 1$, and all other coefficients are zero. Since this is true at $t = -\infty$, it must hold true for all subsequent times, and the general solution of eq 56, subject to the initial condition, is $\Psi = \psi_I(\xi,t)$.

The general solution is expressed in (ξ,t) space. In order to evaluate the transition probabilities, it is required that the wave function be expanded in terms of the usual harmonic oscillator wave functions in $(\tilde{Y},t)$ space. Thus, the function $\psi_I(\xi,t)$ is expanded in terms of the functions

$$\psi_n^0(\tilde{Y},t) = H_n(\tilde{Y})\exp\left[-i(n + \tfrac{1}{2})\omega\int_{-\infty}^{t}\mathrm{d}t'\right] \tag{69}$$

in the following way.

$$\Psi = \psi_I(\xi,t) = \sum_{n=0}^{\infty} b_{In}(t)\psi_n^0(\tilde{Y},t) \tag{70}$$

Because the functions $\psi_n^0(\tilde{Y},t)$ are not exact solutions of eq 56, the coefficients in this expansion are time dependent; therefore

$$b_{In}(t) = \int_{-\infty}^{\infty}\psi_n^{0*}(\tilde{Y},t)\psi_I(\xi,t)\,\mathrm{d}\tilde{Y} \tag{71}$$

The transition probability from state I to state n may be interpreted as

$$P_{I\rightarrow n} = |b_{In}(\infty)|^2 \tag{72}$$

Treanor[15] was able to integrate eq 71 and obtained the result

$$P_{I\rightarrow n} = I!n!e^{-\eta_0}\eta_0^{I+n}|E_{In}|^2 \tag{73}$$

in which

$$\eta_0 = [(fu^2/2) + (\mu\dot{u}^2/2)]/h\nu \tag{74}$$

In this equation, η_0 is the energy (measured in units of $h\nu$) that would be stored at $t = \infty$ in a classical oscillator initially at rest and subjected to the force $F(t)$. The term E_{In} is the sum

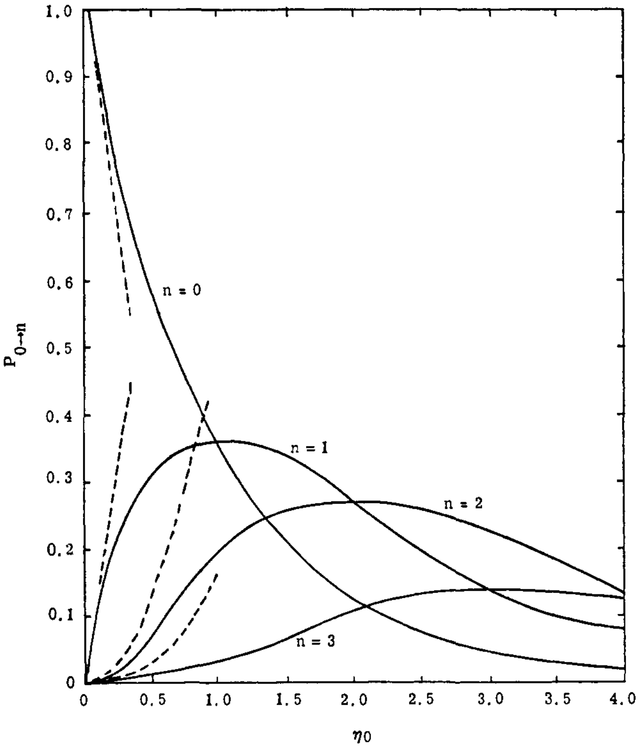

Figure 4. Exact semiclassical transition probabilities *vs.* η_0 according to the method of Kerner and Treanor. The solid lines are the exact probabilities (eq 76) and the dashed lines are approximations of eq 39. Note that the exact $P_{0\to n}$ reaches a maximum at $\eta_0 = n$.

$$E_{In} = \sum_{l=0}^{P} \frac{(-1)^l \eta_0^{-l}}{(I-l)!(n-l)!l!} \tag{75}$$

where p is the lesser of I or n.

For the special case of an oscillator that is initially in the ground quantum state, $I = 0$ and $E_{0n} = (n!)^{-1}$. Thus[15]

$$P_{0\to n} = \eta_0^{\,n} e^{-\eta_0}/n! \tag{76}$$

At low collision velocities, where the transition probabilities are small, the energy stored in a classical oscillator is a small fraction of a quantum. Therefore, $\eta_0 \ll 1$, and eq 73 simplifies to

$$P_{I\to n} \cong \frac{I!n!\eta_0^{(I+n-2p)}}{[(I-p)!(n-p)!p!]^2} \tag{77}$$

If the oscillator is initially in the state $I = 0$, eq 77 reduces to

$$P_{0\to n} \cong \eta_0!/n! \tag{78}$$

The quantity η_0 has already been implicitly calculated in the section on the classical calculation of vibrational energy transfer. Since η_0 is $\Delta E_{\mathrm{ap}}/h\nu$ for the case of zero initial excitation of the oscillator ($B_i = 0$), all one need do is divide eq 30 by $h\nu$ to obtain η_0. When transition probabilities to adjacent states are small, eq 77 can be used to obtain $P_{I\to I\pm1}$, and the results agree exactly with those of eq 53 for the usual FOPA time-dependent perturbation procedure.

The functional dependence of η_0 on collision velocity v_0 is monotonic in the sense that η_0 increases as v_0 increases. A plot of transition probability *vs.* η_0 is qualitatively equivalent to a plot of P *vs.* v_0. Consider eq 76 for the case of an initially unexcited oscillator. Each probability $P_{0\to n}$ rises to a maximum at $\eta_0 = n$, and then decreases at higher values of η_0. The probability of excitation to state n reaches a maximum at a collision velocity that would classically produce a vibrational excitation of $nh\nu$. A plot of eq 76 and 77 is shown in Figure 4. Each probability $P_{0\to n}$ is seen to rise to a maximum at a velocity such that $\eta_0 = n$. At low collision velocities, the 0 → 1 transition is dominant, and the Kerner–Treanor method leads to an exact semiclassical solution if the interaction potential is of the form $-\tilde{Y}F(t)$. This interaction potential follows from the assumption that $|\tilde{Y}| \ll L$, so that motion in $\tilde{x}$ may be calculated on the basis $\tilde{y} \cong \tilde{y}_0$, and the potential in $\tilde{Y}$ may be expanded to a linear term. To obtain an exact solution for which the first, but not the second, assumption is made, a digital computer solution as outlined in section II.C.3 is required. The computer solution can be obtained for an interaction of the general form $V(\tilde{Y})F(t)$. Recently, Treanor[16] showed that the exact computer solution compared well with the Kerner–Treanor solution for a potential linearized in $\tilde{Y}$.

5. A Possible Revised Semiclassical Calculation That Conserves Energy

The semiclassical calculations that have been discussed all correspond to the "approximate" classical method, because the trajectory $\tilde{x}(t)$ is determined with $\tilde{y}$ set equal to $\tilde{y}_0$. As a result, these calculations do not include the conservation of energy, and E_0 is assumed to remain as the energy in coordinate $\tilde{x}$, regardless of how much excitation occurs in the oscillator. To our knowledge, no one has performed a semiclassical calculation that is analogous to the classical "exact" calculation in which energy is conserved. To perform such a calculation, instead of using eq 15 as the coupled equations for solution on a computer, the equations

$$\tilde{m}\ddot{\tilde{X}} = (A'''/L)e^{-\tilde{X}/L}e^{\gamma\tilde{Y}/L} \tag{79}$$

$$\mathrm{d}a_j/\mathrm{d}t = (\hbar i)^{-1} \sum_n a_n(t) V_{jn}'(t) e^{i\omega_{jn}t} \tag{80}$$

are used. The coordinate $\tilde{X}$ is treated classically and $\tilde{Y}$ is treated quantum mechanically. To conserve energy, A''' must be interpreted as the instantaneous amount of energy in coordinate $\tilde{X}$; *i.e.*

$$A''' = E_0 - \sum_n |a_n(t)|^2 \xi_n \tag{81}$$

Similarly, $V_{jn}'(t)$ must be calculated from the interaction

$$V'(\tilde{X},\tilde{Y}) = A''' e^{-\tilde{X}/L} e^{\gamma\tilde{Y}/L} \tag{82}$$

with $X(t)$ chosen as the solution of eq 79 in which $\tilde{Y}$ is replaced by $\langle\tilde{Y}\rangle$, the expectation value of $\tilde{Y}$ for the oscillator at time t. Thus eq 79 and 80 become

$$\tilde{m}\ddot{\tilde{X}} = [A(t)/L]e^{-\tilde{X}/L} \exp[(\gamma/L) \sum_k \sum_l c_k^* c_l e^{i\omega_{kl}t} \tilde{Y}_{kl}] \tag{83}$$

$$\mathrm{d}a_j/\mathrm{d}t = (\hbar i)^{-1} \sum_n a_n(t) A(t) e^{-\tilde{X}/L} [\exp(\gamma Y/L)]_{jn} e^{i\omega_{jn}t} \tag{84}$$

These equations form a set of coupled differential equations in which coordinate $\tilde{X}$ obeys a classical equation of motion containing $\langle\tilde{Y}\rangle$, and coordinate $\tilde{Y}$ obeys the time-dependent Schroedinger equation. According to eq 81, energy is conserved. A computer solution of eq 83 and 84 should lead to the semiclassical analog of the "exact" classical calculation.

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(16) C. E. Treanor, *J. Chem. Phys.*, **44**, 2220 (1966).

D. THE PURELY QUANTUM CALCULATION

1. General Equations

In this section, we shall describe a purely quantum mechanical calculation of the energy transfer to an oscillator. The time-independent Schroedinger equation for the three-particle system, shown in Figure 1, is

$$-\frac{\hbar^2}{2}\left[\frac{1}{m_A}\frac{\partial^2}{\partial \tilde{x}_A{}^2}+\frac{1}{m_B}\frac{\partial^2}{\partial \tilde{x}_B{}^2}+\frac{1}{m_C}\frac{\partial^2}{\partial \tilde{x}_C{}^2}\right]\Psi + V\Psi = E_T\Psi \tag{85}$$

where Ψ is the total wave function, V is given in eq 6, and E_T is the total energy of the three particles. It is convenient to transform to the coordinates $\tilde{x}$, $\tilde{y}$, and $\tilde{x}_R$, as given in eq 2, 3, and 4. The Schroedinger equation becomes[17]

$$-\frac{\hbar^2}{2}\left[\frac{1}{M}\frac{\partial^2}{\partial x_R{}^2}+\frac{1}{\tilde{m}}\frac{\partial^2}{\partial \tilde{x}^2}+\frac{1}{\mu}\frac{\partial^2}{\partial \tilde{y}^2}\right]\Psi + V(\tilde{x},\tilde{y})\Psi = E_T\Psi \tag{86}$$

Since V does not depend on $\tilde{x}_R$ (the position of the center of mass), the variables may be separated: $\Psi(\tilde{x},\tilde{y},\tilde{x}_R) = \Psi(\tilde{x},\tilde{y})\cdot\xi(\tilde{x}_R)$, and $E_T = E + E_{CM}$, where $\psi(\tilde{x},\tilde{y})$ is the wave function in terms of the relative coordinates for a fixed center of mass, $\xi(\tilde{x}_R)$ is the wave function for the center of mass, E is the energy of relative motion, and E_{CM} is the energy of the center of mass of the three particles. It may be shown that $\xi(\tilde{x}_R)$ is simply a free particle wave function, which corresponds to the free motion of the center of mass with energy E_{CM}. This does not affect the energy transfer and need not be considered further.

When the expressions for Ψ and E_T are put into eq 86, the result is

$$-\frac{\hbar^2}{2}\left[\frac{1}{\mu}\frac{\partial^2}{\partial \tilde{y}^2}+\frac{1}{\tilde{m}}\frac{\partial^2}{\partial \tilde{x}^2}\right]\psi(\tilde{x},\tilde{y}) + V(\tilde{x},\tilde{y})\psi(\tilde{x},\tilde{y}) = E\psi(\tilde{x},\tilde{y}) \tag{87}$$

Equation 87 must be solved subject to the boundary conditions that an incident flux of particles A approaches BC from the right with relative velocity $v_I = \hbar k_I/\tilde{m}$, and the oscillator is in state $H_I(\tilde{y})$, while reflected fluxes move out to the right with relative velocity $v_n = \hbar k_n/\tilde{m}$, leaving the oscillator in state $H_n(\tilde{y})$. This may be seen by considering eq 87 for $\tilde{x} \cong \infty$, where $V(\tilde{x},\tilde{y}) \rightarrow V_0(\tilde{y})$.

Any function of the form $H_n(\tilde{y})\exp[\pm ik_n x]$ is a mathematical solution of eq 87 for large positive $\tilde{x}$, where

$$E = (n + \tfrac{1}{2})h\nu + \hbar^2 k_n{}^2/2\tilde{m} \tag{88}$$

Since the incident flux is monoenergetic, n must be equal to I for the minus sign to hold in the $\tilde{x}$ wave function, and the boundary condition at $\tilde{x} = +\infty$ can be written

$$\lim_{\tilde{x}\rightarrow\infty} \psi(\tilde{x},\tilde{y}) = H_I(\tilde{y})e^{-ik_I\tilde{x}} + \sum_{n=0}^{\infty} a_n H_n(\tilde{y})e^{ik_n\tilde{x}} \tag{89}$$

The constants a_n must be determined by solving eq 87. The boundary condition at $\tilde{x} = -\infty$ is

$$\lim_{\tilde{x}\rightarrow-\infty} \psi(\tilde{x},\tilde{y}) = 0 \tag{90}$$

since $V(\tilde{x},\tilde{y}) \rightarrow \infty$ at $\tilde{x} = -\infty$. The probability of a transition from state I to state n is the ratio of the reflected flux corresponding to state n to the incident flux; *i.e.*

$$P_{I\rightarrow n} = (k_n/k_I)\left|a_n\right|^2 \tag{91}$$

In order to solve eq 87, $V(\tilde{x},\tilde{y})$ is written in the form of eq 6, and the equation is multiplied by $(\mu/\hbar^2 f)^{1/2}$. By defining[18] new dimensionless coordinates x and y as

$$y = (f\mu/\hbar^2)^{1/4}(\tilde{y} - \tilde{y}_0) \tag{92}$$

$$x = (f\mu/\hbar^2)^{1/4}(\gamma^{-1}\tilde{x} - \tilde{y}_0) \tag{93}$$

it is found[18] that the Schroedinger equation takes the simple form

$$\left\{-\frac{1}{2m}\frac{\partial^2}{\partial x^2} - \frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}y^2 + U'(K[x - y])\right\}\psi(x,y) = \epsilon\psi(x,y) \tag{94}$$

where

$$\begin{aligned} m &= \tilde{m}\gamma^2/\mu \\ \epsilon &= E/h\nu \\ U' &= V'/h\nu \\ K &= (\hbar^2/f\mu)^{1/4}\gamma \\ K(x - y) &= \tilde{x} - \gamma\tilde{y} \end{aligned} \tag{95}$$

Thus, energy is measured in units of $h\nu$, and the A + BC problem reduces to a two-particle problem as in Figure 5 with an effective mass m for the incident particle. Note that Secrest and Johnson[18] measure energy in units of $h\nu/2$, not $h\nu$. The asymptotic conditions in terms of dimensionless variables are

$$\lim_{x\rightarrow-\infty} \psi(x,y) = 0$$

$$\lim_{x\rightarrow+\infty} \psi(x,y) = H_I(y)e^{-i\kappa_I x} + \sum_{n=0}^{\infty} a_n H_n(y)e^{i\kappa_n x} \tag{96}$$

where κ_n is defined as $\kappa_n = k_n(\hbar^2/f\mu)^{1/4}\gamma$, so that

$$\kappa_n{}^2/2m + (n + \tfrac{1}{2}) = \epsilon \tag{97}$$

2. Exact Solution Using Green's Function in Plane Waves

The solution of eq 94 is accomplished by a Green's function procedure. Secrest and Johnson[16] write (without loss of generality)

$$\Psi(x,y) = H_I(y)e^{-i\kappa_I x} + \psi_{scat} \tag{98}$$

where $\psi_{scat}(x,y)$ is completely general and represents the scattered waves. When this expression is substituted into eq 94, the result is

$$\left[-\frac{1}{2m}\frac{\partial^2}{\partial x^2} - \frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}y^2 - \epsilon\right]\psi_{scat} = -U'\Psi \tag{99}$$

where the equation

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}y^2\right]H_n(y) = \left(n + \frac{1}{2}\right)H_n(y) \tag{100}$$

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[17] D. Rapp, *J. Chem. Phys.*, **40**, 2813 (1964).

[18] D. Secrest and B. R. Johnson, *ibid.*, **45**, 4556 (1966).

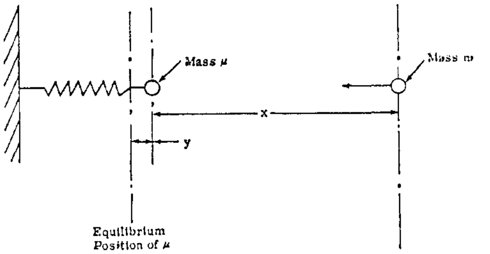

Figure 5. Equivalent two particle problem for A + BC collisions.

has been used for simplification. Equation 99 may be considered in operator form

$$\Omega(x,y)\psi_{\mathrm{scat}}(x,y) = -U'(x,y)\Psi(x,y) \qquad (101)$$

where $\Omega(x,y)$ is the operator in the square brackets of eq 99.

The Green's function for operator Ω can be found by standard techniques[19] to be

$$G(x,y;x',y') = mi\sum_{n=0}^{\infty} \kappa_n^{-1}H_n(y)H_n(y') \exp[i\kappa_n|x - x'|] \qquad (102)$$

From this it follows that[19]

$$\psi_{\mathrm{scat}}(x,y) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} G(x,y;x',y')[-U'(x',y')\,\Psi(x',y')]\,\mathrm{d}x'\mathrm{d}y' \qquad (103)$$

and

$$\psi(x,y) = H_I(y)e^{-i\kappa_I x} - mi\sum_{n=0}^{\infty} \kappa_n^{-1}H_n(y) \times \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} H_n(y') \exp(i\kappa_n|x - x'|)U'(x',y')\Psi(x',y')\,\mathrm{d}x'\mathrm{d}y' \qquad (104)$$

In the limit as $x \rightarrow +\infty$, $|x - x'|$ may be replaced by $(x - x')$ for all x'. Thus

$$\lim_{x\rightarrow\infty}\Psi(x,y) = H_I(y)e^{-i\kappa_I x} - mi\sum_{n=0}^{\infty} \kappa_n^{-1}H_n(y)e^{i\kappa_n x} \times \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} H_n(y')e^{-i\kappa_n x'}U'(x',y')\Psi(x',y')\,\mathrm{d}x'\mathrm{d}y' \qquad (105)$$

This is of the same form as eq 96, and a_n may therefore be identified as

$$a_n = -im\kappa_n^{-1}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} H_n(y')e^{-i\kappa_n x'}U'(x',y') \times \Psi(x',y')\,\mathrm{d}x'\mathrm{d}y' \qquad (106)$$

The wave function at $x = -\infty$ may be evaluated by taking $|x - x'|$ to be $(x' - x)$ for all x'. Then one finds

$$\lim_{x\rightarrow-\infty}\Psi(x,y) = H_I(y)e^{-i\kappa_I x} - mi\sum_{n=0}^{\infty}\kappa_n^{-1}H_n(y)e^{-i\kappa_n x} \times \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} H_n(y')e^{i\kappa_n x'}U'(x',y')\Psi(x',y')\,\mathrm{d}x'\mathrm{d}y' \qquad (107)$$

According to eq 96, this must be equal to zero. Therefore, it is required that

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} H_n(y')e^{i\kappa_n x'}U(x',y')\Psi(x'y')\,\mathrm{d}x'\mathrm{d}y' = -\delta_{nI} \qquad (108)$$

In general, one must solve eq 104 subject to the conditions of eq 108. This is not simple because eq 104 contains the unknown Ψ under the integral sign on the right side, and an iterative procedure is required. Secrest and Johnson[18] present a method for doing this, but, unfortunately, the method is not at all intelligible to us. We shall merely state that solutions for a_n in a number of examples were obtained and will be discussed in the next section.

Recently, a new paper[19a] has been written which, according to the authors, leads to results in essential agreement with those of Secrest and Johnson, but with much less calculational effort.

3. *Exact Solution with Green's Function in Distorted Waves*[20]

An alternate, but equivalent, method for calculating the quanf tum mechanical transition probabilities involves the use o- "distorted waves" rather than plane waves. Distorted waves are defined as solutions of the elastic scattering problem of A hitting BC, with BC kept in its equilibrium position. Thus, the distorted waves are defined as solutions of the equation

$$(2m)^{-1}(\mathrm{d}^2\varphi_n/\mathrm{d}x^2) + U'(x)\varphi_n = (\kappa_n^2/2m)\varphi_n \qquad (109)$$

where $U'(x)$ is $U'(x,y)$ at $y = 0$. In the limit as $x \rightarrow \infty$, $U'(x) \rightarrow 0$, and the distorted waves become plane waves. Two different solutions of eq 109 are defined[20] in terms of different asymptotic forms. The distorted wave of the first kind, $\varphi_{n1}(x)$, is the solution that goes to $(2\pi)^{-1/2} \exp(i\kappa_n x)$ as $x \rightarrow +\infty$. It should be noted that this solution diverges as $x \rightarrow -\infty$. The distorted wave of the second kind, $\varphi_{n2}(x)$, is defined as the solution of eq 109 that goes to zero as $x \rightarrow -\infty$. It can be shown that the asymptotic form, as $x \rightarrow +\infty$, may be taken as $(2/\pi)^{1/2} \cos(\kappa_n x + \eta_n)$, where η_n is a phase factor.

The equation to be solved is still eq 94, and the appropriate boundary conditions are, as before, given in eq 96. However, in the distorted wave procedure, eq 98 is replaced by the expression

$$\Psi = H_I(y)\varphi_{I2}(x) + \psi_{\mathrm{scat}} \qquad (110)$$

where the incident wave term is replaced by a distorted wave of the second kind containing incident and reflected waves corresponding to state I. The procedure is now analogous to that used for plane waves. Equation 110 is substituted into eq 94, and the result is

$$\{-(2m)^{-1}(\partial^2/\partial x^2) + U'(x) - \tfrac{1}{2}(\partial^2/\partial y^2) + \tfrac{1}{2}y^2 - \epsilon\}\psi_{\mathrm{scat}} = \Delta U'(x,y)\Psi(x,y) \qquad (111)$$

where $\Delta U'(x,y) = U'(x) - U'(x,y) = U'(x,0) - U'(x,y)$. The Green's function for the operator in braces in eq 111 can be shown[19] to be

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19) P. M. Morse and H. Feshbach, "Methods of Theoretical Physics," McGraw-Hill Book Co., Inc., New York, N. Y., 1953, pp 803–834.

(19a) S.-K. Chan, J. C. Light, and J. L. Lin, *J. Chem. Phys.*, 49, 86 (1968).

(20) D. Rapp and T. Kassal, *ibid.*, 48, 5287 (1968).

$$G(x,y;\,x',y') = (2\pi mi) \sum_{n=0}^{\infty} \kappa_n^{-1} e^{i\eta_n} H_n(y) \times H_n(y')\varphi_{n1}(x_>)\varphi_{n2}(x_<) \qquad (112)$$

in which $x_>$ and $x_<$ denote the greater and lesser of x and x', respectively. It can then be shown by standard procedures[19] that $\psi_{scat} = \psi_{s1} + \psi_{s2}$, where

$$\psi_{s1}(x,y) = (2\pi mi) \sum_{n=0}^{\infty} \kappa_n^{-1} e^{i\eta_n} H_n(y) \Big\{ \varphi_{n1}(x) \times \int_{-\infty}^{\infty}\int_{-\infty}^{x} \varphi_{n2}(x')H_n(y')\Delta U'(x',y')\varphi_{I2}(x')H_I(y')\,\mathrm{d}x'\mathrm{d}y' + \varphi_{n2}(x) \int_{-\infty}^{\infty}\int_{x}^{\infty} \varphi_{n1}(x')H_n(y')\Delta U'(x',y')\varphi_{I2}(x') \times H_I(y')\,\mathrm{d}x'\mathrm{d}y' \Big\} \qquad (113)$$

and

$$\psi_{s2}(x,y) = (2\pi mi) \sum_{n=0}^{\infty} \kappa_n^{-1} e^{i\eta_n} H_n(y) \Big\{ \varphi_{n1}(x) \times \int_{-\infty}^{\infty}\int_{-\infty}^{x} \varphi_{n2}(x')H_n(y')\Delta U'(x',y')\psi_{scat}(x',y')\,\mathrm{d}x'\mathrm{d}y' + \varphi_{n2}(x) \int_{-\infty}^{\infty}\int_{x}^{\infty} \varphi_{n1}(x')H_n(y')\Delta U'(x',y')\psi_{scat}(x',y')\,\mathrm{d}x'\mathrm{d}y' \Big\} \qquad (114)$$

In the limit as $x \to \infty$, the integrals from x to ∞ vanish. Similarly, the integrals from $-\infty$ to x vanish in the limit as $x \to -\infty$. Thus

$$\lim_{x\to\infty} \psi_{s1}(x,y) = (2\pi mi) \sum_{n=0}^{\infty} \kappa_n^{-1} e^{i\eta_n} H_n(y)\varphi_{n1}(x) \times \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \varphi_{n2}(x')H_n(y')\Delta U'(x',y')\varphi_{I2}(x')H_I(y')\,\mathrm{d}x'\mathrm{d}y' \qquad (115)$$

$$\lim_{x\to\infty} \psi_{s2}(x,y) = (2\pi mi) \sum_{n=0}^{\infty} \kappa_n^{-1} e^{i\eta_n} \varphi_{n1}(x) \times \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \varphi_{n2}(x')H_n(y')\Delta U'(x',y')\psi_{scat}(x',y')\,\mathrm{d}x'\mathrm{d}y' \qquad (116)$$

$$\lim_{x\to-\infty} \psi_{s1}(x,y) = \lim_{x\to-\infty} \psi_{s2}(x,y) = 0 \qquad (117)$$

Equation 117 follows from the asymptotic form of $\varphi_{n2}(x)$ as $x \to -\infty$.

If eq 115 and 116 are used to evaluate Ψ from eq 110 as $x \to +\infty$, a comparison with eq 96 leads to the coefficients a_n.

$$a_n = (2\pi mi)\kappa_n^{-1}(2\pi)^{-1/2} e^{i\eta_n} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \varphi_{n2}(x')H_n(y') \times \Delta U'(x',y')\{\varphi_{I2}(x')H_I(y') + \psi_{scat}(x',y')\}\,\mathrm{d}x'\mathrm{d}y' + (2/\pi)^{1/2}\delta_{In} \qquad (118)$$

The integral expression for a_n, eq 118, may be split into two parts, corresponding to the two terms in braces. The integral involving the first term may be evaluated without iteration. The calculation of the integral involving ψ_{scat} requires an iterative procedure because the equation for ψ_{s2} also contains ψ_{s2} under the integral sign on the right side of the equation. The iteration could begin by using ψ_{s1} as a first approximation to ψ_{scat} under the integral sign. The advantages of this method over the plane wave procedure are that ψ_{scat} automatically goes to zero as $x \to -\infty$, and a natural first choice for an iterative solution is suggested. Recently, Thiele[21] has carried out the distorted wave iteration procedure but it is not clear from his work whether the method converges properly.

As in the semiclassical multistate expansion procedure, the wave function is not actually summed over all states of the oscillator in numerical calculations. Instead, a heuristic procedure is adopted in which a truncated expansion involving N states is used. The calculation is then repeated with $N + 1$ states included in the expansion. If no significant change results in the calculated transition probability, it is assumed to be exact. If changes do occur, more terms must be added until the result does not change with further addition to the expansion. It is also implied that for an $I \to n$ transition the least number of terms required are all the inclusive states from I to n. When further terms are added, they should be adjacent to this set.

4. *The First-Order Distorted Wave Approximation (FODWA)*

The procedures outlined in the previous two sections are for the exact quantum mechanical calculation of vibrational transition probabilities. At low collision velocities, where the total transition probability out of the initial state is small, an approximate solution may be sought by using the "first-order distorted wave approximation" (FODWA). After deriving the general form of the FODWA by two methods, the specific evaluation of the appropriate integrals will be made for simple interaction potentials discussed in previous paragraphs.

The basis of the FODWA is that for purposes of calculating the inelastically scattered wave, the total wave function can be approximated by a function corresponding to elastic scattering by the potential. In eq 110, the first term, $H_I(y)\varphi_{I2}(x)$, corresponds to elastic scattering of particle A by BC, with BC in the initial state I. The second term, ψ_{scat}, contains all reference to states other than I. For small transition probabilities, the FODWA is made by assuming $|\psi_{scat}|$ is small compared to $|H_I(y)\varphi_{I2}(x)|$ for all x. The FODWA should become asymptotically correct at low velocities only if $m \ll 1$. If m is not small, $|\psi_{scat}|$ will not be negligible compared to $|H_I(y)\varphi_{I2}(x)|$ for all regions of x, even though the transition probabilities are small. The FODWA will then fail because of the invalidity of the basic assumption.

The effect of neglecting ψ_{scat} in eq 110 may be easily determined by examining eq 113–118. If follows that ψ_{s1} is not changed, but ψ_{s2} becomes equal to zero. Then a_n is given by[20]

$$a_n = (2\pi mi)\kappa_n^{-1} e^{i\eta_n} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \varphi_{n2}(x')H_n(y')\Delta U'(x',y') \times \varphi_{I2}(x')H_I(y')\,\mathrm{d}x'\mathrm{d}y' + (2/\pi)^{1/2}\delta_{In} \qquad (119)$$

The transition probability, according to the FODWA, is given by[20]

$$P_{I\to n} = (\kappa_n/\kappa_I)\,|a_n|^2 = (2\pi m^2/\kappa_I\kappa_n) \left| \int_{-\infty}^{\infty} \varphi_{n2}(x')\Delta U'_{nI}(x')\varphi_{I2}(x')\,\mathrm{d}x' \right|^2 \qquad (120)$$

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(21) E. Thiele and J. Weare, *J. Chem. Phys.*, 48, 2324 (1968).

where

$$\Delta U'_{nI}(x') = \int_{-\infty}^{\infty} H_n(y')\Delta U'(x',y')H_I(y')\,\mathrm{d}y' \qquad (121)$$

Equation 120 is the general expression for the FODWA.

An alternate procedure for deriving the FODWA, without the use of Green's functions, was given originally by Jackson and Mott.[22] In this procedure, the total wave function is written as in eq 110, which is substituted into eq 94, and eq 111 is obtained. The scattered wave is expanded in terms of the harmonic oscillator wave functions as

$$\psi_{\mathrm{scat}}(x,y) = \sum_{l=0}^{\infty} H_l(y)u_l(x) \qquad (122)$$

where the $u_l(x)$'s are general undefined functions of x. After substitution of eq 122 into eq 111 and utilizing eq 100, the result is

$$\sum_{l=0}^{\infty} \{-(2m)^{-1}(\partial^2/\partial x^2) + U'(x) - \kappa_l{}^2/2m\}H_l(y)u_l(x) = \Delta U'(x,y)\Psi(x,y) \qquad (123)$$

This equation is exact. The FODWA is made, as before, by assuming that $|\psi_{\mathrm{scat}}|$ is negligible compared to $|H_I(y)\varphi_{I2}(x)|$, so that $\Psi(x,y)$ may be approximated by $H_I(y)\varphi_{I2}(x)$ on the right side of eq 123. In order to solve the resulting equation, it must be multiplied by some arbitrary $H_n(y)$ and integrated over dy. The result is

$$\{-(2m)^{-1}(\partial^2/\partial x^2) + U_{nn}'(x) - \kappa_{s,}{}^2/2m\}u_n(x) = \Delta U_{nI}'(x)\varphi_{I2}(x) \qquad (124)$$

If the potential in y is linearized as in eq 9, then

$$U_{nn}'(x) = \int H_n(y)U'(x)[1 + \gamma\tilde{Y}/L]H_n(y)\,\mathrm{d}y = U'(x) \qquad (125)$$

because $\tilde{Y}_{nn} = 0$. Thus the FODWA is performed here only for a linearized potential in $\tilde{Y}$. The terms $U_{nn}'(x)$ in eq 124 may be replaced by $U'(x)$. Now, $u_n(x)$ is written in the form[22]

$$u_n(x) = g(x)\varphi_{n2}(x) \qquad (126)$$

which involves no loss of generality because $g(x)$ is a general unrestricted function. After multiplying through by $\varphi_{n2}(x)$, the result is

$$-(2m)^{-1}(\mathrm{d}/\mathrm{d}x)[\varphi_{n2}{}^2(x)(\mathrm{d}g/\mathrm{d}x)] - \Delta U_{nI}'(x)\varphi_{I2}(x)\varphi_{n2}(x) = 0 \qquad (127)$$

and eq 109 has been used for simplification. Equation 127 is integrated from $-\infty$ to x, by using the fact that $\varphi_{n2}(-\infty) = 0$, and one obtains

$$[\varphi_{n2}(x)]^2(\mathrm{d}g/\mathrm{d}x) = -2m\int_{-\infty}^{x} \varphi_{n2}(x')\Delta U_{nI}'(x')\varphi_{I2}(x')\,\mathrm{d}x' \qquad (128)$$

For large x, the integral on the right side of eq 128 is a constant, namely

$$\int_{-\infty}^{\infty} \varphi_{n2}(x)\Delta U_{nI}'(x)\varphi_{I2}(x)\,\mathrm{d}x = \text{“}Q\text{”} \qquad (129)$$

At any arbitrary large value of x, the asymptotic form of $\varphi_{n2}(x)$ may be used in the left side of eq 128, and the upper limit of the integral may be replaced by ∞. Thus, for large x

$$\mathrm{d}g/\mathrm{d}x = -2mQ(\pi/2)\sec^2(\kappa_n x + \delta_n) \qquad (130)$$

which can be integrated directly, with the result

$$\lim_{x\to\infty} g(x) = -\pi mQ\{\kappa_n{}^{-1}\tan(\kappa_n x + \delta_n) + C\} \qquad (131)$$

where C is a constant of integration. This constant must be chosen so that $u_l(x)$ contains only outgoing waves at $x = \infty$. It can be shown that $u_l(x) = g(x)\varphi_{l2}(x)$ contains only outgoing waves for large x if $C = -i\kappa_n{}^{-1}$. It is found that

$$\lim_{x\to\infty} u_n(x) = (2\pi)^{1/2}i\kappa_n{}^{-1}mQ\exp[i(\kappa_n x + \delta_n)] \qquad (132)$$

Upon comparison with eq 96, it follows that[22]

$$P_{I\to n} = (\kappa_n/\kappa_I)|a_n|^2 = 2\pi m^2Q^2/\kappa_I\kappa_n \qquad (133)$$

which is in agreement with eq 120.

To carry out the evaluation of the FODWA in detail for an exponential potential,[22] one must elucidate the distorted waves φ_{n2}, and then evaluate Q. The potential is written in the form

$$U'(x) = V'(x)/\hbar\omega = A'e^{-\tilde{x}_{tn}/L}e^{-\tilde{X}_n/L} \qquad (134)$$

where $\tilde{x}_{tn}$ is the classical turning point for incident energy $(\kappa_n{}^2/2m)\hbar\omega$, and $\tilde{X}_n = \tilde{x} - \tilde{x}_{tn}$. Because $\tilde{X}_n = 0$ at the classical turning point

$$A'e^{-\tilde{X}_{tn}/L} = \kappa_n{}^2/2m \qquad (135)$$

Therefore, eq 109 may be rewritten as[22]

$$(\mathrm{d}^2\varphi_{n2}/\mathrm{d}x^2) + \kappa_n{}^2[e^{-\tilde{X}_n/L} - 1]\varphi_{n2} = 0 \qquad (136)$$

But $\mathrm{d}x = (\mu\omega/\hbar\gamma^2)^{1/2}\,\mathrm{d}\tilde{X}_n$ and $\kappa_n = k_n(\hbar\gamma^2/\mu\omega)^{1/2}$; therefore

$$\mathrm{d}^2\varphi_{n2}/\mathrm{d}\tilde{X}_n{}^2 + k_n{}^2[e^{-\tilde{X}_n/L} - 1]\varphi_{n2} = 0 \qquad (137)$$

A new variable, ξ, is defined such that[22]

$$\xi = 2k_nLe^{-\tilde{X}_n/2L} = 2L(2\mu\omega m/\hbar\gamma^2A')e^{-\tilde{x}/2L} \qquad (138)$$

Note that ξ is the same for all n. In terms of the variable ξ, eq 137 takes the form of Bessel's equation of order $iq_n = i(2k_nL)$; *i.e.*

$$\xi^2(\mathrm{d}^2\varphi_{n2}/\mathrm{d}\xi^2) + \xi(\mathrm{d}\varphi_{n2}/\mathrm{d}\xi) + (\xi^2 - q_n{}^2)\varphi_{n2} = 0 \qquad (139)$$

The solution of this equation is the modified Bessel function

$$\varphi_{n2}(x) = (\text{constant})K_{iq_n}(\xi) \qquad (140)$$

The constant in this equation must be chosen for proper normalization of the wave function as $\tilde{X} \to \infty$. Since[22]

$$K_{iq_n}(\xi) \longrightarrow \left(\frac{\pi}{q_n\sinh(\pi q_n)}\right)^{1/2}\cos(k_n\tilde{x} + \delta_n) \qquad (141)$$

it can be seen that the constant in eq 141 must be chosen as

$$(\text{constant}) = [2q_n\sinh(\pi q_n)]^{1/2}/\pi \qquad (142)$$

To evaluate Q, $\Delta V_{nI}'(\tilde{x})$ must first be evaluated from eq 121. Using eq 9 for $V'(\tilde{x},\tilde{y})$

$$\Delta V_{nI}'(\tilde{x}) = A'e^{-\tilde{x}/L}(\gamma/L)\tilde{Y}_{nI} \qquad (143)$$

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(22) J. D. Jackson and N. F. Mott, *Proc. Roy. Soc.*, **A137**, 703 (1932).

Then

$$Q = (2/\pi^2)[q_n q_I \sinh(\pi q_n) \sinh(\pi q_I)]^{1/2}(\gamma/L)\tilde{Y}_{nI}A' \times \int_{-\infty}^{\infty} e^{-\bar{x}/L} K_{iq_n}(\xi) K_{iq_I}(\xi)\, \mathrm{d}x \tag{144}$$

The integral in eq 144 may be written

$$\frac{1}{A'}\left(\frac{\hbar^2}{4mL}\right)\left(\frac{\omega\gamma^2}{\mu\hbar}\right)^{1/2} \int_0^{\infty} K_{iq_n}(\xi) K_{iq_I}(\xi)\xi\, \mathrm{d}\xi \tag{145}$$

which is evaluated[22] by using the representation of the Bessel function

$$K_{iq_n}(\xi) = \int_0^{\infty} e^{-\xi \cosh(u)} \cos q_n u\, \mathrm{d}u \tag{146}$$

The integral in eq 145 is equal to

$$\frac{(\pi^2/4)(q_n^2 - q_I^2)}{[\cosh(\pi q_n) - \cosh(\pi q_I)]} \tag{147}$$

The final result for the FODWA is[22]

$$P_{I\to I\pm 1} = (8\pi^2\omega\gamma^2\tilde{m}^2L^2/\hbar\mu)\left(I + \frac{1}{2} \pm \frac{1}{2}\right) \times \frac{\sinh(\pi q_I)\sinh(\pi q_{I\pm 1})}{[\cosh(\pi q_I) - \cosh(\pi q_{I\pm 1})]^2} \tag{148}$$

The quantity πq_I is proportional to the ratio of the range of intermolecular forces (L) to the deBroglie wavelength for the incident particle, $\lambda_I = (2\pi/k_I)$. Thus

$$\pi q_I = 2\pi k_I L = 4\pi^2 L/\lambda_I \tag{149}$$

When this quantity is large, the x motion should be essentially classical, and the semiclassical approximation should be accurate. But if $\pi q_I \gg 1$, the hyperbolic functions may be approximately replaced by exponentials (*i.e.*, $\cosh(\pi q) \cong e^{\pi q}/2$). Thus, eq 148 reduces to

$$P_{I\to I\pm 1} = (2\pi^2\omega m\tilde{m}L^2/\hbar)\left(I + \frac{1}{2} \pm \frac{1}{2}\right) \times \operatorname{csch}^2\left[\frac{\pi}{2}(q_I - q_{I\pm 1})\right] \tag{150}$$

This is very similar to eq 53 in the semiclassical calculation. To draw the analogy further, one may write $\pi(q_I - q_{I\pm 1})$ as follows.

$$\frac{\pi}{2}(q_I - q_{I\pm 1}) = \pi L[k_I - k_{I\pm 1}] = \frac{\pi(k_I^2 - k_{I\pm 1}^2)L}{(k_I + k_{I\pm 1})} \tag{151}$$

But since $(\hbar^2/2\tilde{m})(k_I^2 - k_{I\pm 1}^2) = \mp\hbar\omega$

$$\pi(q_I - q_{I\pm 1}) = \mp\frac{\pi\omega L}{[(v_I + v_{I\pm 1})/2]} \tag{152}$$

where $v_n = \hbar k_n/\tilde{m}$. Thus, the argument of the csch² function in eq 150 is the same as that of eq 53, except that the single velocity v_0 of the semiclassical calculation is replaced by the arithmetic mean of velocities, before and after transition, in the quantum mechanical calculation. At high collision velocities, $v_I \cong v_{I\pm 1}$, since $\tilde{m}v_I^2/2$ will be large compared to $\hbar\omega$. Therefore, eq 150 goes to eq 53 at high velocities. Equation 150 may be written in the alternate form

$$P_{I\to I\pm 1} = (2\pi^2\omega\gamma^2\tilde{m}^2L^2/\hbar\mu)\left(I + \frac{1}{2} \pm \frac{1}{2}\right)\operatorname{csch}^2[\pi\omega L/\bar{v}] \tag{153}$$

where $\bar{v} = (v_I + v_{I\pm 1})/2$. It should be emphasized that the derivation of eq 153 from eq 148 is based on purely mathematical assumption, namely, that πq_I and $\pi q_{I\pm 1}$ are each large compared to unity. One then neglects $e^{-\pi q_I}$ compared to $e^{\pi q_I}$. In almost any case of physical interest, πq_I may vary from about 10 to 50, so the approximation is a good one.

In a very recent paper, Weare and Thiele[22a] studied purely quantum mechanical energy transfer from the scattering matrix viewpoint. In the usual calculations of energy transfer, a first-order calculation gives a good estimate of the order of magnitude of the transition probability to an adjacent state, if the probability is small. However, first-order calculations (both FOPA and FODWA) fail badly for nonadjacent transitions, even when the probabilities are small. This is due to the fact that stepwise transitions $I \to I + 1 \to I + 2 \ldots \to j$ during a single collision dominate over direct transitions $I \to j$. A usual FOPA or FODWA calculation will underestimate $P_{0\to 2}$ by many orders of magnitude, although it gives the correct order of magnitude for $P_{0\to 1}$. For an n-quantum jump, the minimum calculation required for the correct order of magnitude of the transition probability is a nth order perturbation approximation. The interesting thing about the calculation of Weare and Thiele[22a] is that, when the quantum mechanical equations are rewritten in scattering matrix form (instead of eq 123), the first-order solution appears to be equivalent to an nth order perturbation approximation for a final state, n quanta removed from the initial state. In other words, the first-order reaction matrix approximation (FORMA) appears to be equivalent to an nth order distorted wave approximation. If this is true, successive iterations of the equations in reaction matrix form may converge much faster than the usual equations. The nature of the reaction matrix is such that all paths from the initial to the final state are included, even when the solution is taken to first order. Weare and Thiele[22a] give the equation

$$P_{I\to I+m} = 4^{1-m} \prod_{l=0}^{m-1} P_{I+l\to I+l+1} \tag{154}$$

from this procedure for small $P_{I\to I+m}$, in terms of the small stepwise probabilities $P_{I\to I+1}$, $P_{I+1\to I+2}$, $\ldots$, $P_{I+m-1\to I+m}$. Equation 154 is very closely related to eq 55a which can be transformed to

$$P_{I\to I+m} = (m!)^{-2} \prod_{l=0}^{m-1} P_{I+l\to I+l+1} \tag{155}$$

E. COMPARISON OF CLASSICAL, SEMICLASSICAL, AND QUANTUM METHODS

1. Relation between Classical Energy Transfer and Quantum Transition Probabilities

In the purely classical methods, only the total energy transferred to the oscillator is calculated. There is no conceptual place for transition probabilities in such a deterministic calculation. Except for variations due to the phase of the initial motion of the oscillator, the classical ΔE is transferred to the oscillator in every single collision with initial velocity v_0. If the oscillator is initially vibrating, ΔE depends

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[22a] J. H. Weare and E. Thiele, *J. Chem. Phys.*, 48, 513 (1968).

on the phase, and $\langle \Delta E \rangle$ is the phase-averaged energy transfer per collision. If the oscillator is not originally excited, then ΔE is transferred in every collision.

In contrast to this description, the semiclassical and quantum treatments lead to transition probabilities from some initial state I to all final states n. It is impossible to specify the final quantum state of the oscillator for any particular collision. All that can be said is that in some large number, N_C, of collisions, $N_C P_{I \rightarrow n}$ will result in some arbitrary final state n. For a large number of collisions the total energy transferred to all the oscillators is

$$(\Delta E)_{\text{tot}} = \sum_{n=0}^{\infty} N_C[(n - I)h\nu]P_{I \rightarrow n} \tag{156}$$

Thus, the average energy transferred to an oscillator *per collision* is

$$\Delta \epsilon = \Delta E/h\nu = (\Delta E)_{\text{tot}}/N_C = \sum_{n=0}^{\infty} (n - I)P_{I \rightarrow n} \tag{157}$$

If $I = 0$, eq 157 reduces to

$$\Delta \epsilon = \sum_{n=0}^{\infty} nP_{0 \rightarrow n} \tag{158}$$

To compare quantum and classical calculations, $\Delta\epsilon$ should be compared for both procedures.

2. *Comparison of Exact and "Approximate" Classical Procedures*[7,9]

When an exact classical calculation is performed, the energy transferred is denoted ΔE. If the approximation is made that the $\bar{x}$ and $\bar{y}$ motions may be treated independently, the approximate result ΔE_{ap} is calculated. Wolfsberg and Kelley[7] have found that the ratio $\Delta E_{\text{ap}}/\Delta E = \mathcal{R}$ depends principally on the mass parameter m. For fixed values of the collision parameters m, ω, and L, and an initially unexcited oscillator, the ratio $\Delta E_{\text{ap}}/\Delta E$ is essentially independent of v_0 for $m \lesssim 0.5$. The value of $\mathcal{R}$ depends primarily on m, and is independent of large changes in L and ω.

An empirical correlation for $\mathcal{R}$, in terms of m, was given in eq 37. The approximate method has the advantage of yielding direct, closed-form expressions for the energy transfer, and treats the phase-averaged $\langle \Delta E_{\text{ap}} \rangle$ for an initially vibrating oscillator as equal to ΔE_{ap} for an initially unexcited oscillator. This is a good approximation for $m \ll 1$. Unless $m \ll 0.5$, the exact phase-averaged $\langle \Delta E \rangle$ for an initially excited oscillator may be considerably different from ΔE for an unexcited oscillator.

For calculational purposes, ΔE_{ap} may be put in the form

$$\Delta \epsilon_{\text{ap}} = (2\pi^2 m^2/\alpha^2)\,\text{csch}^2\left[\frac{\pi}{\alpha}\left(\frac{m}{2(\epsilon - \frac{1}{2})}\right)^{1/2}\right] \tag{159}$$

where $\Delta\epsilon_{\text{ap}}$ is measured in units of $h\nu$; ϵ is the *total* energy (units of $h\nu$) of oscillator + particle and is equal to $[{}^1/{}_2h\nu + (mv_0^2/2)]/h\nu$ if the oscillator is initially in the ground state; and

$$\alpha = (\gamma^2\hbar/\mu\omega L^2)^{1/2} \tag{160}$$

Values of $\Delta\epsilon$ must be obtained from an exact computer solution of the appropriate coupled equations. An example[7] of the relation between $\Delta\epsilon$ and $\Delta\epsilon_{\text{ap}}$ is given in Figure 6 for the special case $\alpha = 0.1287$, $m = {}^1/{}_{13}$, and zero initial excitation. In this case, $\mathcal{R} = \Delta\epsilon_{\text{ap}}/\Delta\epsilon \cong 1.13$ over the range of ϵ considered.

3. *Comparison of Classical "Approximate" and Semiclassical Calculations*

By using the semiclassical procedure, it can easily be shown that the energy transferred per collision, $\Delta\epsilon_{\text{sc}}$, to an oscillator in initial state ($I = 0$) is equal to the energy transferred according to the "approximate" classical procedure, $\Delta\epsilon_{\text{ap}}$. To do this, eq 76 for $P_{0 \rightarrow n}$ is used in eq 157. It is found that

$$\Delta\epsilon_{\text{sc}} = \sum_{n=0}^{\infty} nP_{0 \rightarrow n} = \eta_0 e^{-\eta_0} \sum_{n=1}^{\infty} \eta^{n-1}/(n - 1)! = \eta_0 \tag{161}$$

Since $\Delta\epsilon_{\text{ap}} = \eta_0$, it may be concluded that $\Delta\epsilon_{\text{ap}} = \Delta\epsilon_{\text{sc}}$. It can also be shown that, when $I \neq 0$, the FOPA transition probabilities satisfy the relation $\Delta\epsilon_{\text{ap}} = \Delta\epsilon_{\text{sc}}$ (*cf.* eq 54, 55, and 30).

In Figure 6, the exact semiclassical transition probabilities $P_{0 \rightarrow n}$ are presented along with $\Delta\epsilon_{\text{sc}} = \Delta\epsilon_{\text{ap}}$, and $\Delta\epsilon$ (exact classical calculation) for the case $m = {}^1/{}_{13}$, $\alpha = 0.1287$. At low collision energies, most transitions are 0 → 1, and $\Delta\epsilon_{\text{sc}} \cong P_{0 \rightarrow 1}$. The correspondence between the semiclassical and "approximate" classical energy transfer is due to the fact that both procedures involve solution for $\bar{x}(t)$ based on the assumption $\bar{y} \cong \bar{y}_0$. We have been unable to show $\Delta\epsilon_{\text{sc}} = \Delta\epsilon_{\text{ap}}$ for $I \neq 0$ unless the FOPA transition probabilities are used. It seems likely, however, that this relation would hold in general. To prove this, one would have to show (using eq 73)

$$\sum_{n=0}^{\infty} (n - I)I!n!e^{-\eta_0}\eta_0^{I+n}|E_{In}|^2 = \eta_0 \tag{162}$$

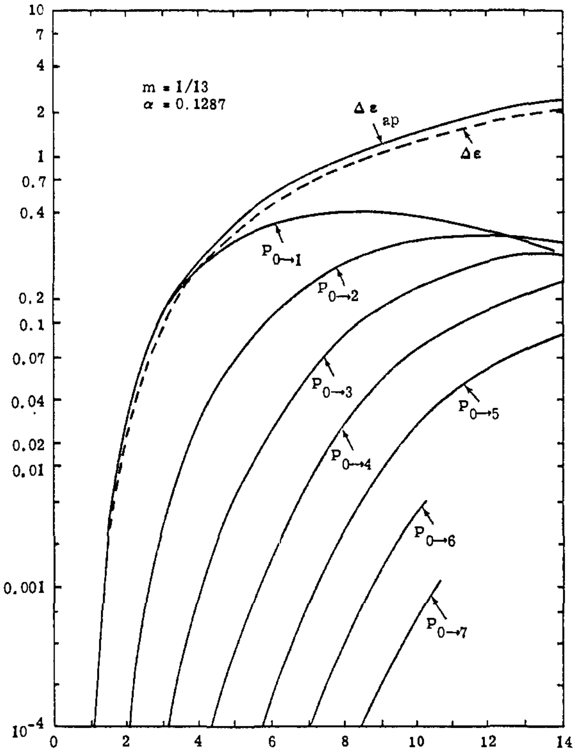

Figure 6. Transition probabilities *vs.* total energy of oscillator plus relative motion, according to the exact semiclassical procedure for $m = {}^1/{}_{13}$ and $\alpha = 0.1287$. The exact classical energy transfer $\Delta\epsilon$ is approximately 11.5% less than $\Delta\epsilon_{\text{ap}}$ over the range of incident velocity considered.

The semiclassical and classical methods yield a nonzero energy transfer below the initial energy threshold for excitation of one quantum. For the $0 \rightarrow 1$ transition, the total energy corresponding to threshold is $^3/_2$. Thus, $P_{0\rightarrow 1}$ should be zero at $\epsilon = {}^3/_2$. As may be seen from Figure 6, $P_{0\rightarrow 1}$ is calculated to be $\sim$0.0025 at this energy.

Since $\Delta\epsilon_{\text{ap}}$ is exactly the same as $P_{0\rightarrow 1}$ calculated from a FOPA semiclassical calculation (*i.e.*, eq 53), it can be seen that the FOPA and exact semiclassical results for $P_{0\rightarrow 1}$ begin to diverge when $P_{0\rightarrow 1}$ reaches about 0.05. This gives an indication of the range of validity of first-order approximations.

4. *Comparison of Exact Classical Energy Transfer with Exact Quantum Energy Transfer*

It would be most interesting to compare the $\Delta\epsilon$ calculated exactly by means of classical mechanics with the $\Delta\epsilon$ calculated exactly with quantum mechanics, for the same case. Unfortunately, the calculations of Wolfsberg and Kelley[7] are not sufficiently encompassing to enable such a comparison to be easily made. In Figure 7, for the case $m = {}^1/_{13}$ and $\alpha = 0.1287$, $\Delta\epsilon_{\text{ap}}$ and $\Delta\epsilon$ are plotted from the classical calculation, *based on no initial excitation of the oscillator.* On the same graph, $\Sigma nP_{0\rightarrow n}$ is plotted by using transition probabilities calculated quantum mechanically by Secrest and Johnson,[18] based on the initial energy of the oscillator chosen as $^1/_2h\nu$. The comparison is not really correct, because one should use a classical, phase-averaged, initial energy of $^1/_2h\nu$ in the oscillator Wolfsberg and Kelley[7] do not present enough results for this to be done. However, their general results do indicate that the energy transfer decreases as the initial excitation of the oscillator increases, the magnitude of the effect being qualitatively correct so that agreement will be shown to exist between exact classical and exact quantum energy transfer calculations.

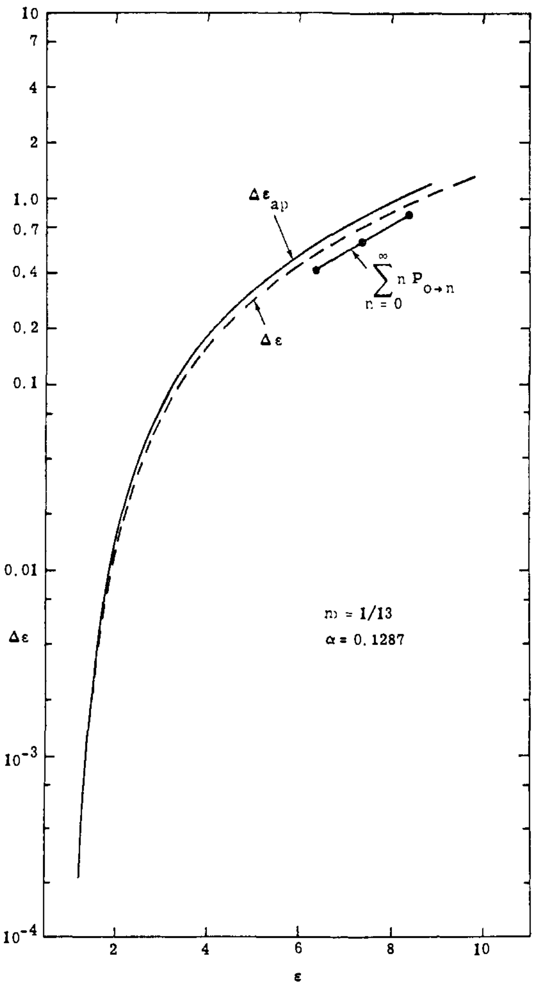

Figure 7. The energy transferred to an oscillator ($m = {}^1/_{13}$ and $\alpha = 0.1287$) as a function of total energy according to the approximate classical method ($\Delta\epsilon_{\text{ap}}$), the exact classical method for no initial excitation of the oscillator ($\Delta\epsilon$), and the exact quantum method for the oscillator initially in the ground quantum state $\langle \Sigma_{n=0}{}^{\infty} nP_{0\rightarrow n}\rangle$ (initial oscillator energy of $h\nu/2$).

Table I

Effect of Initial Excitation of Oscillator on the Phase-Averaged Classical $\langle\Delta\epsilon\rangle$

Initial collision energy[a]	*Initial oscillator energy*	$\langle\Delta\epsilon\rangle^a$	ϵ, *initial total energy*
17.1	0.902	5.18	18.0
17.1	0.353	5.58	17.45
17.1	0.171	5.68	17.27
17.1	0.000	5.81	17.1
17.1	0.500	5.46[b]	17.6
8.55	0.902	0.924	9.45
8.55	0.353	1.135	8.90
8.55	0.171	1.205	8.72
8.55	0.000	1.274	8.55
8.55	0.500	1.080[b]	9.05

[a] *hν* units. [b] By interpolation.

For the case $m = 0.5$ and $\alpha = 0.158$ (*i.e.*, $f = 5.312$ mdyn/Å and $L = 0.221$ Å), Wolfsberg and Kelley[7] have performed phase-averaged, energy-transfer calculations at two initial collision energies. They consider three possible initial amounts of excitation in the oscillator, none of which is $h\nu/2$. However, their results, which are presented in Table I, may be interpolated to yield a good estimate of the energy transfer for an initial oscillator energy of $h\nu/2$.

It may be concluded that the ratio of phase-averaged $\langle\Delta\epsilon\rangle$ to $\Delta\epsilon$ for zero initial oscillator energy is 0.940 at $\epsilon = 17.6$, and 0.848 at $\epsilon = 9.05$. Unfortunately, Secrest and Johnson[18] do calculations for $m = 0.5$ and $\alpha = 0.114$, but not for $\alpha = 0.158$. We shall assume that the ratio of $\langle\Delta\epsilon\rangle/\Delta\epsilon$ is independent of α and use their calculated transition probabilities. Thus, one may compare $\Delta\epsilon_{\text{ap}}$, $\Delta\epsilon$, $\langle\Delta\epsilon\rangle$, as well as the quantum mechanical energy transfer, for $m = 0.5$ and $\alpha = 0.114$. The results are given in Table II. Thus, the exact classical energy transfer, phase-averaged for an initial oscillator energy of $^1/_2h\nu$, agrees very well with the exact quantum mechanical energy transfer at $\epsilon = 9.05$.

5. *Comparison of FOPA (Semiclassical) and FODWA (Quantum) Methods*

The results of the first-order semiclassical and quantum methods will be compared in this section. The FOPA result is eq 53; the FODWA result is eq 148. However, the simpler

Table II

Comparison of $\Delta\epsilon_{ap}$, $\Delta\epsilon$, Based on No Initial Excitation of the Oscillator, and $\langle\Delta\epsilon\rangle$, Phase-Averaged for Initial Oscillator Energy $h\nu/2$

$\Delta\epsilon_{ap}$	$\Delta\epsilon$	$\langle\Delta\epsilon\rangle$	$\sum_{n=0}^{\infty} nP_{0\rightarrow n}$
0.122	0.051	0.044	0.044[a]

[a] The exact quantum energy transfer is $\sum_{n=0}^{\infty} nP_{0\rightarrow n}$.

expression, eq 153, is a very close mathematical approximation of eq 148, except at velocities near threshold. As an example, the transition probabilities according to eq 53, 148, and 153 are plotted in Figure 8 for the case $m = 0.2$ and $\alpha = 0.114$. It is found that there is no discernible difference between the expressions in eq 148 and 153 over the velocity range considered. Only in the very immediate vicinity of threshold do these expressions diverge. At threshold ($\epsilon = {}^3/_2$), eq 148 goes to zero, but eq 153 remains nonzero. There is a strong difference between eq 53 and 153, especially at the lower velocities. The use of the initial velocity in the FOPA, rather than the average velocity before and after transition (as required by the FODWA), leads to serious numerical errors.

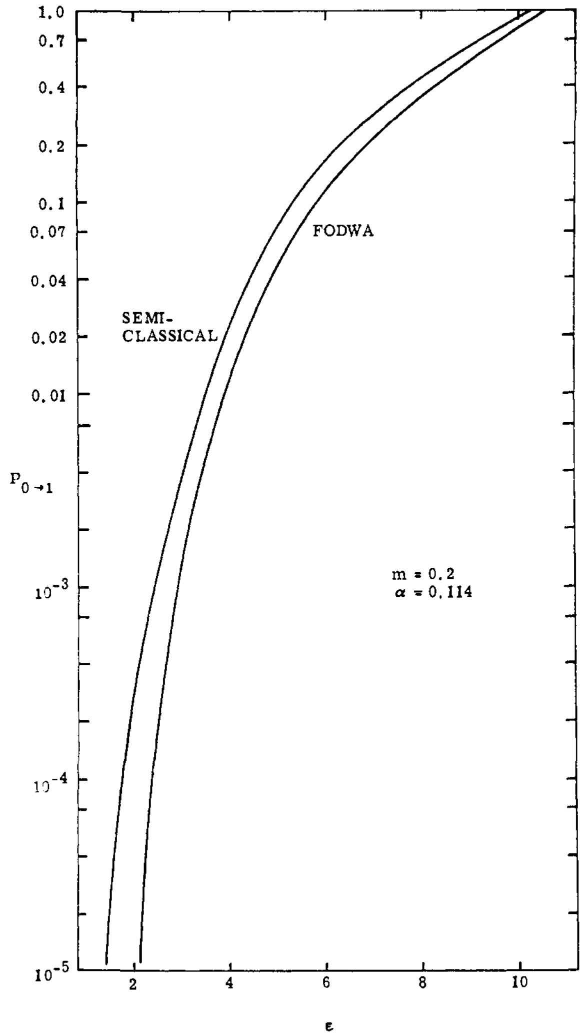

Figure 8. Comparison of the transition probability $P_{0\rightarrow 1}$ as a function of total energy for $m = 0.2$ and $\alpha = 0.114$ using the FODWA and FOPA procedures. The FOPA curve is calculated from eq 53. The FODWA result is eq 149. A close mathematical approximation to this expression is given in eq 151. The two expressions, eq 149 and 151, are in essentially complete agreement over the entire range of velocities considered.

It should be emphasized that the numerical errors are introduced into the semiclassical procedure by the assumption that the energy in coordinate x is independent of the excitation of the oscillator (*i.e.*, energy is not conserved). *The failure of the FOPA is not a failure of classical mechanics for coordinate x*, but the result of a model that does not conserve energy. If a semiclassical procedure were carried out in such a way as to conserve energy (*cf.* section II.E.5), the results would be very close to the quantum results. To show this, consider the quantity πq that occurs in eq 148 and 150. When $\pi q \gg 1$, the FODWA reduces to the semiclassical result, except that the initial velocity is replaced by the average velocity. It has been shown that $\pi q = 4\pi^2 L/\lambda$, and therefore that the condition $\pi q \gg 1$ is equivalent to the classical limit for coordinate x. A good measure of the degree to which coordinate x is nonclassical is the degree to which $e^{-\pi q}$ is not negligible compared to $e^{\pi q}$ in the hyperbolic functions in eq 148. Thus the error involved in assuming coordinate x is classical is roughly equal to $e^{-2\pi q}$. It can be shown that

$$2\pi q_n = (4\pi/\alpha)[2m(\epsilon - n - \tfrac{1}{2})]^{1/2} \qquad (163)$$

For most physical cases of interest, $\alpha \cong 0.1$ and $4\pi/\alpha \cong 120$. As long as $(\epsilon - n + {}^1/_2) \gtrsim 0.1$ the quantity $2\pi q_n$ will be very large, and coordinate x is essentially classical.

In summary, the main difference between the FOPA and the FODWA is that the FOPA is based on an expansion in states for which energy is not conserved, whereas the FODWA model involves an expansion in states with energy conservation. Each procedure leads to a different result for the transition probabilities. When the FODWA is taken to the classical limit for motion in x, it reduces to the same expression as one obtains from the FOPA, except that the average velocity appears where the initial velocity appeared in the FOPA. The numerical difference between these results is substantial and is due to the nonconservation of energy in the FOPA, and not a failure of the classical approximation.

6. *Comparison of Exact Quantum, Exact Semiclassical, FODWA, and FOPA Transition Probabilities*

There is only one truly rigorous procedure, namely an exact quantum method, such as was performed by Secrest and Johnson.[18] This may be used as a standard for comparison with various approximate procedures.

The FODWA is a first-order, quantum mechanical procedure that is based on two main assumptions. One is that the transition probabilities are small, and the other is that the wave function may be replaced by the incident and elastically scattered waves for purposes of calculation of the inelastic wave amplitudes. The first assumption leads to overestimates of the transition probabilities which are in excess of about 0.05. The second causes errors that are roughly velocity independent, and which depend mainly on the mass parameter m. Thus, at low velocities, where the transition probabilities are small, the exact quantum results do not reduce to the

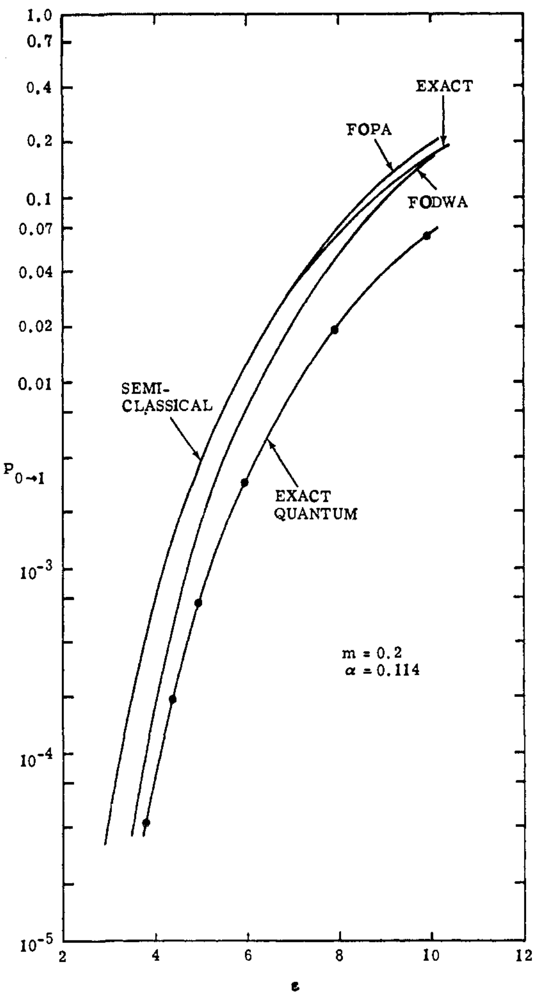

Figure 9. Comparison of quantum and semiclassical calculations of $P_{0\to 1}$ as a function of total energy, for $m = 0.2$ and $\alpha = 0.114$. The first-order semiclassical result agrees with the exact semiclassical result for transition probabilities less than about 0.04. The FODWA is never in agreement with the exact quantum probability, even for very small transition probabilities.

FODWA transition probabilities. It is found that the exact probabilities reduce to a factor $\mathcal{R}^{-1} = \exp(-1.685m)$ times the FODWA probabilities. This rather remarkable relationship to the exact and approximate classical calculations can be rationalized in terms of the basic assumption of the FODWA, that the elastically scattered wave with the initial velocity is used in lieu of the inelastically scattered wave to evaluate the inelastic scattering. At high velocities, the FODWA probabilities exceed unity and become meaningless. The behavior of the FODWA and the exact transition probabilities for the $0 \to 1$ transition are shown in Figures 9 and 10 for $m = 0.2$ and $m = 1.25$, respectively. The difference between the FODWA and exact probabilities is much greater for the larger value of m.

The lack of conservation of energy in the semiclassical procedure causes the probabilities to exceed the true quantum results for upward transitions, and to be less than the quantum probabilities for downward transitions. Results from the exact semiclassical calculation are plotted in Figures 9 and 10 for comparison with the exact quantum probabilities for the $0 \to 1$ transition with $m = 0.2$ and $m = 1.25$. It can be seen that the semiclassical probabilities are too large for this upward transition.

In contrast to the situation in the quantum calculation, where the exact quantum probabilities do not reduce to the FODWA results for small transition probabilities, the exact and FOPA semiclassical probabilities converge at low velocities. This is illustrated in Figures 9 and 10. As before, the FODWA tends toward the FOPA at high collision velocities.

Similar conclusions may be drawn for $0 \to n$ transitions. The difference between the semiclassical and quantum exact calculations becomes accentuated for transitions of more than 1 quantum. The results for the $0 \to 2$ transition, with $m = 0.2$, are illustrated in Figure 11. Although the semiclassical method gives the correct qualitative picture of the probabilities (as in Figure 6), it is quantitatively incorrect because the probabilities remain finite at energies that are below threshold. This is illustrated in Figure 12 for $m = {}^{1}/_{13}$ and $\alpha = 0.1287$. The exact semiclassical probabilities (solid lines) exceed the exact quantum probabilities (dotted lines) at all velocities.

In order to illustrate energy-transfer probabilities for an oscillator that is not necessarily in the ground state initially, Figures 13–15 have been prepared. The probabilities are from the exact quantum calculations of Secrest and Johnson.[18]

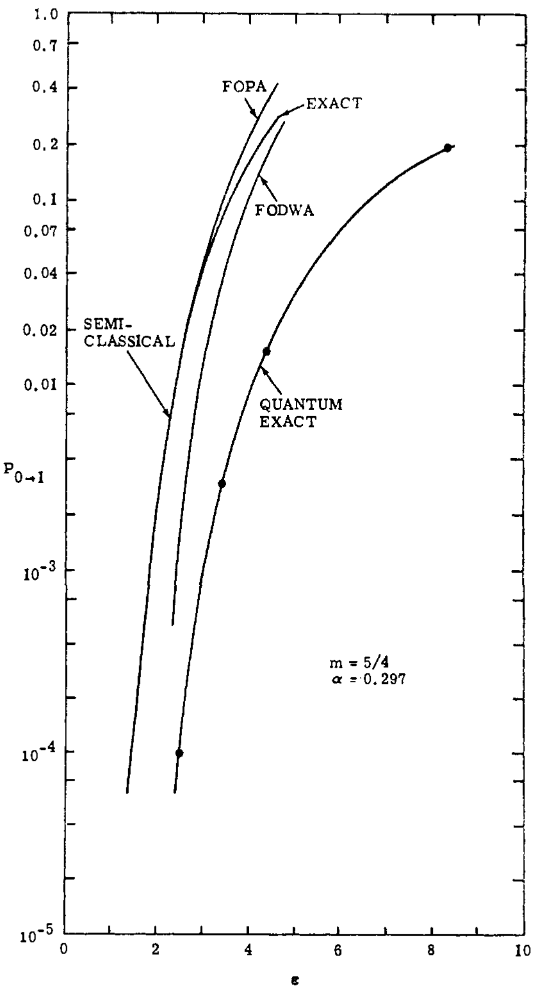

Figure 10. Comparison of quantum and semiclassical calculations of $P_{0\to 1}$ as a function of total energy, for $m = {}^{5}/_{4}$ and $\alpha = 0.297$.

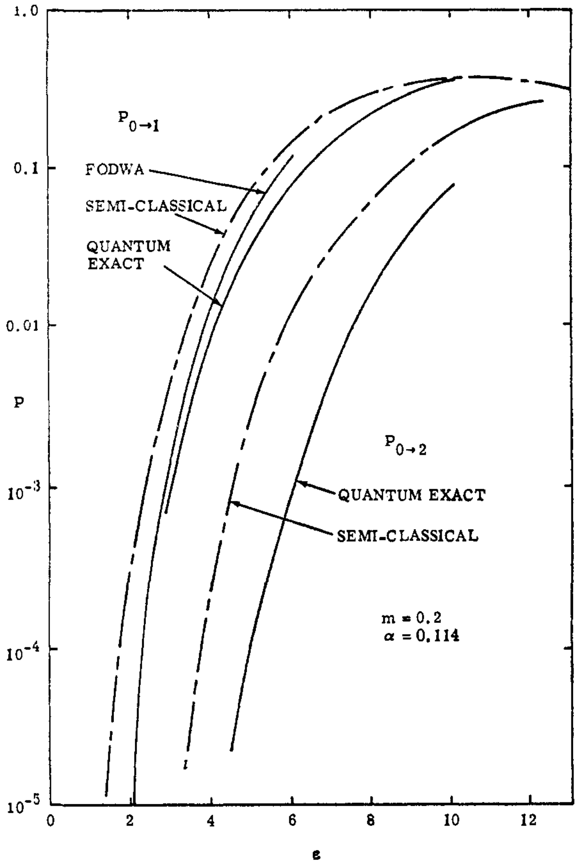

Figure 11. Comparison of quantum and semiclassical transition probabilities *vs.* ε for $m = 0.2$ and $\alpha = 0.114$. The exact semiclassical probabilities, shown by the intermittent lines, are shifted to the left of the exact quantum probabilities, shown by the solid lines. The shift to the left on the energy scale is more pronounced for upward transitions of several quanta.

7. *Comparison of Exact Quantum and FODWA Calculations. A Proposed Closed-Form Expression for $P_{0\to1}$*

In this section, an approximate semiempirical expression for $P_{0\to1}$ will be derived in a form that is useful for quick calculations. At low velocities (such that $P_{0\to1} \lesssim 0.05$), the exact quantum results for $P_{0\to1}$ are equal to $\exp(-1.685m)$ times the FODWA results. Since a closed-form expression for the FODWA exists, a semiempirical expression for the exact quantum probability is obtained by simply multiplying the FODWA expression by the correction factor $\exp(-1.685m)$. Thus, for $P_{0\to1} \lesssim 0.05$, the semiempirical expression

$$P_{0\to1} \cong p = e^{-1.685m}(2\pi^2 m^2/\alpha^2) \times \operatorname{csch}^2\left\{\frac{(\pi^2 m/2\alpha)^{1/2}}{\left(\epsilon-\frac{1}{2}\right)^{1/2}+\left(\epsilon-\frac{3}{2}\right)^{1/2}}\right\} \tag{164}$$

may be used. The quantity on the right side of the equation is defined as p, and $P_{0\to1}$ reduces to p for small transition probabilities.

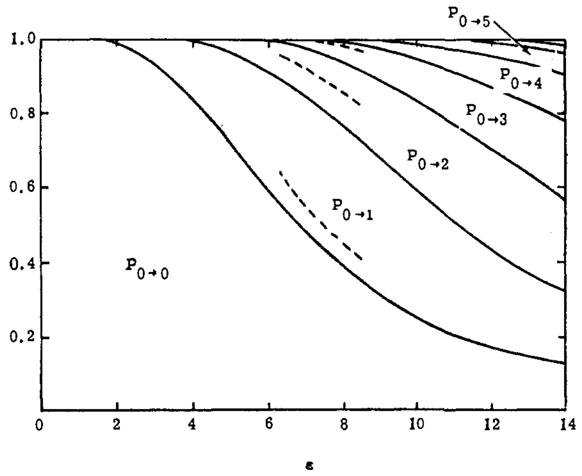

Figure 12. Transition probabilities *vs.* total energy out of the ground quantum state of an oscillator for $m = 1/_{18}$ and $\alpha = 0.1287$. The solid lines are the exact semiclassical results of Kerner and Treanor, and the dashed lines are the exact quantum results of Secrest and Johnson.

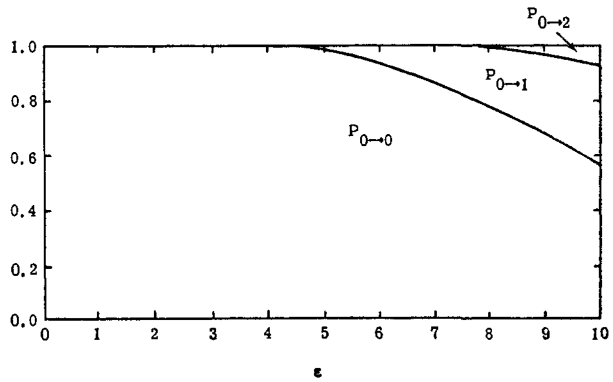

Figure 13. Exact quantum transition probabilities *vs.* total energy $P_{0\to n}$ for $m = 0.5$ and $\alpha = 0.114$.

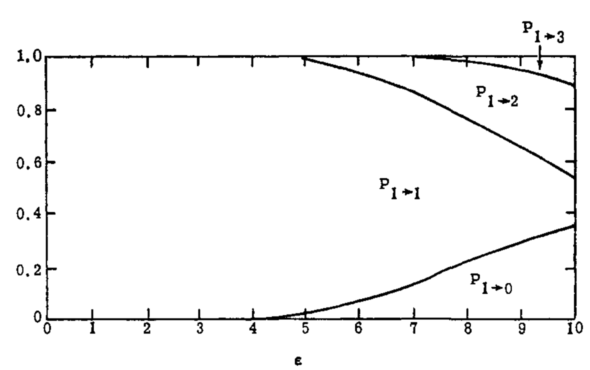

Figure 14. Exact quantum transition probabilities *vs.* total energy $P_{1\to n}$ for $m = 0.5$ and $\alpha = 0.114$.

In order to extend this procedure to large transition probabilities, it will be assumed that the known relationship between exact and first-order semiclassical probabilities can be used to relate the above semiempirical quantum first order and exact probabilities. According to the method of Kerner and Treanor, the semiclassical procedure leads to a first-order result for $P_{0\to1}$ equal to η_0, and an exact $P_{0\to1}$ equal to $\eta_0 e^{-\eta_0}$. By analogy, it is therefore assumed that the exact

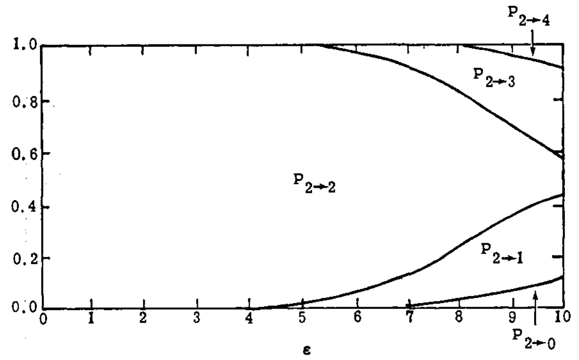

Figure 15. Exact quantum transition probabilities *vs.* total energy $P_{2\to n}$ for $m = 0.5$ and $\alpha = 0.114$.

quantum probability, even at high velocities, is approximately given by

$$P_{0\to 1} = pe^{-p} \qquad (165)$$

where p is defined in eq 164. For small values of p (low velocities), eq 165 reduces to eq 164. The approximate semiempirical expression in eq 165 is compared with the exact quantum results for $P_{0\to 1}$, for several values of m, in Figures 16a and 16b. The data points are the calculations of Secrest and Johnson,[18] and the lines are obtained from eq 165. The agreement is reasonably good.

III. More Sophisticated Collinear Collision Models

A. EFFECT OF ATTRACTIVE FORCES

1. Herzfeld's Procedure[4] of Fitting an Exponential Potential to a Lennard-Jones Potential

A crude procedure for determining the effect of a long-range attractive potential on the energy transfer was devised by Herzfeld.[4] In this method, it is assumed that the total potential between two molecules can be represented by a Lennard-Jones potential

$$V_1(r) = -4\varepsilon[(r_0/r)^6 - (r_0/r)^{12}] \qquad (166)$$

where ε and r_0 are constants determined by experiment, and r is the distance between centers of mass of the two molecules. Since the elementary models for energy transfer are based on an exponential potential, the exponential function

$$V_2(r) = Ae^{-r/L} - \varepsilon \qquad (167)$$

must be fitted to the Lennard-Jones potential. The constant $-\eta$ is introduced in eq 167 in order to make the slopes of the two potentials more compatible at small distances, which are most important for energy transfer. These two potentials are illustrated in Figure 17.

The minimum in $V_1(r)$ occurs at $r = 2^{1/6}r_0$, and the depth of the well is $-\varepsilon$. It is important that these two potentials coincide in the region of r that is of greatest importance in determining vibrational energy-transfer probabilities. At any arbitrary temperature, the range of collision velocities, important to vibrational energy transfer, will correspond to some minimum value of r, which will be called r_1, as shown in Figure 17. At $r = r_1$, the potentials and the slopes of the potentials are set equal. Thus, two equations are derived

$$A = \varepsilon e^{r_1/L}\{1 - 4\eta^6 + 4\eta^{12}\} \qquad (168)$$

$$-(A/L)e^{-r_1/L} = (24\varepsilon/r_1)(\eta^6 - 2\eta^{12}) \qquad (169)$$

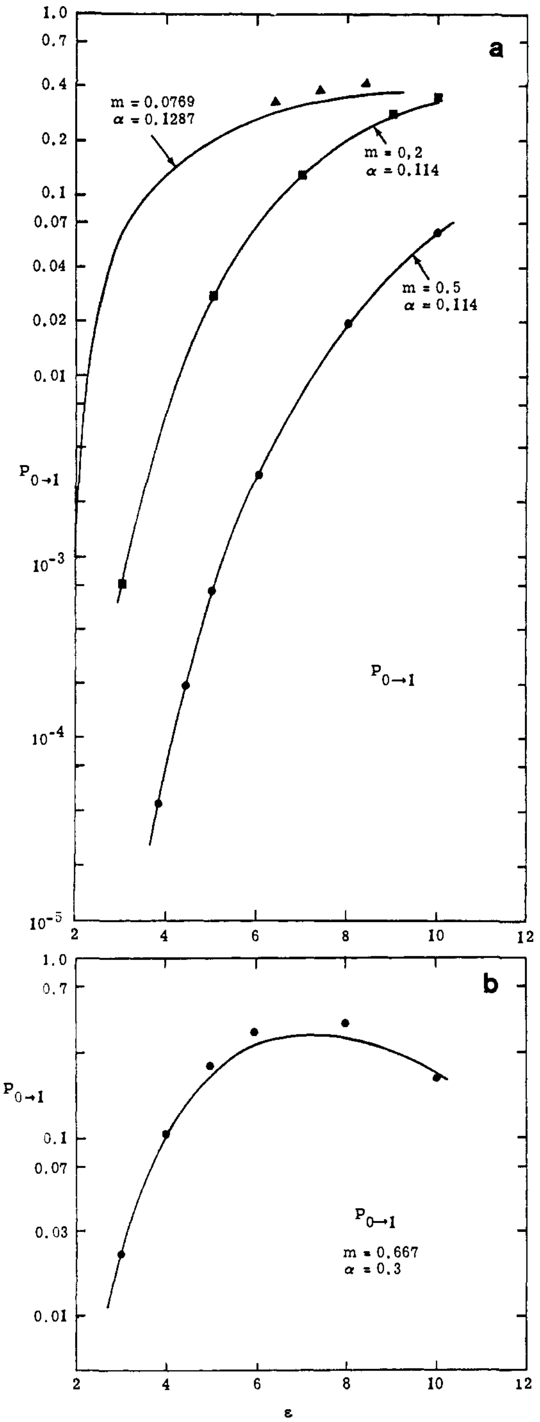

Figure 16. The semiempirical expression (eq 164 and 165) for $P_{0\to 1}$ tested against the exact calculations of Secrest and Johnson. The data points are the exact calculations and the lines are from eq 165.

where $\eta = r_0/r_1$ and is not to be confused with the symbol η used in the context of eq 74. If A is eliminated between these two equations an expression for L in terms of r_0 and r_1 is obtained.

$$r_0/L = 6\eta[1 - 2\eta^6][1 - \eta^6 - (4\eta^6)^{-1}]^{-1} \qquad (170)$$

A plot of this function is given in Figure 18. In many cases of physical interest, η lies in the range $1.2 \lesssim \eta \lesssim 1.3$ Therefore, the general approximate formula

$$L \cong r_0/17.5 \qquad (171)$$

may be deduced.

The potentials described in the previous paragraph refer to the over-all interaction between two molecules treated as point centers of force. The potential must also depend on the internal coordinate of one of the molecules for vibrational energy transfer to occur. If it is assumed that the $\tilde{Y}$ dependence of the interaction potential is exponential, and that it is unaffected by attractive forces in $\tilde{x}$, then r and $\tilde{x}$ may be equated. The potential in $\tilde{x}$ is multiplied by $\exp(\gamma\tilde{Y}/L)$ to obtain the complete interaction potential, including the dependence on the oscillator coordinate. Herzfeld's procedure[4] therefore amounts to the following. (1) Use eq 7 for the interaction potential in energy-transfer calculations, with L chosen as $r_0/17.5$. (2) For thermal averaging of transition probabilities, use a modified velocity distribution function such that all collisions are increased in energy by the amount ε. Since r_0 tends to be in the general range of magnitude ~3.5 Å for a number of molecules, $L \sim 0.2$ Å. The experiments generally used to determine r_0 and ε are most sensitive to the long-range attractive part of the potential and may lead to substantial errors in the extrapolation of the potential from r_0 to r_1.

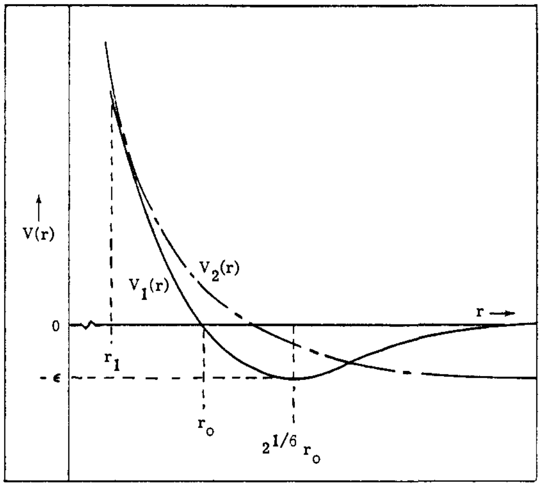

Figure 17. The exponential potential $V_2(r)$ fitted to the Lennard-Jones potential $V_1(r)$. The magnitudes and slopes of the potentials are set equal at $r = r_1$.

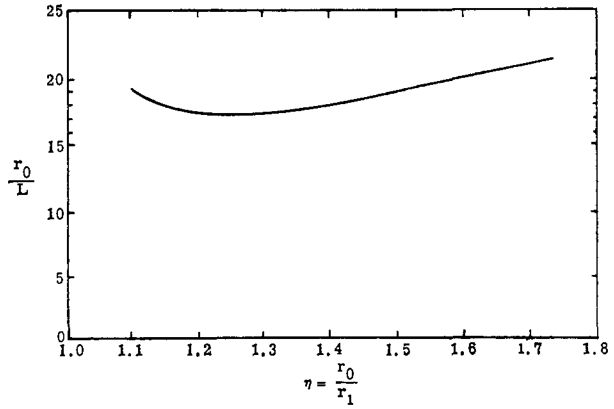

Figure 18. Dependence of r_0/L on the choice of r_1. A broad minimum with $r_0/L \cong 17.5$ is found for $\eta = r_0/r_1 \cong 1.3$.

2. The Morse Potential

A more rigorous procedure for taking attractive forces into account is to assume that the $\tilde{x}$ part of the intermolecular potential is a Morse potential instead of a simple exponential repulsion. The Morse potential contains both an exponential repulsive as well as a long-range exponential attractive term. The appropriate dynamic equations corresponding to the Morse potential should then be solved to determine the transition probabilities. This procedure has only been carried out to the first-order solution, with a potential linearized in $\tilde{Y}$. The assumed form of the potential is

$$V'(\tilde{x},\tilde{y}) = \varepsilon[e^{-\alpha(\tilde{x}-\tilde{x}_0)} - 2e^{-\alpha(\tilde{x}-\tilde{x}_0)/2}] \\ [1 + \gamma\tilde{Y}/L + \ldots] \qquad (172)$$

where ε is the well depth, and α is a constant related to L or r_0. A best fit of the x part of this potential to those in eq 166 and 167 can be made by methods given in section III.A.1. A rough approximation can be made to $V_2(r)$ in eq 167 by setting $\alpha = 1/L$ and $A = \varepsilon e^{\tilde{x}_0/L}$.

For the potential specified in eq 172, theoretical calculations of vibrational transition probabilities have been carried out by the FODWA and FOPA procedures. The FODWA result is[23]

$$P_{I\rightarrow I\pm1} = (8\pi^2L^2m^2\gamma^2\omega/\mu\hbar)\left(I + \frac{1}{2} \pm \frac{1}{2}\right)\left\{\frac{(Q_I + Q_{I\pm1})^2}{Q_IQ_{I\pm1}}\right\}\times \\ \left\{\frac{\sinh(2\pi q_I)\sinh(2\pi q_{I\pm1})}{[\cosh(2\pi q_I) - \cosh(2\pi q_{I\pm1})]^2}\right\} \qquad (173)$$

where

$$Q_I = \left|\Gamma\left[(-(2\tilde{m}\varepsilon)^{1/2}2L/\hbar) + 2ik_IL + \frac{1}{2}\right]\right|^2 \qquad (174)$$

and α is taken as $1/L$. This expression using the Morse potential is analogous to the FODWA expression for the transition probability of a simple exponential repulsive potential, eq 148. In the limit of a vanishing well depth in the Morse potential (*i.e.*, $\varepsilon \rightarrow 0$, and $x_0 \rightarrow \infty$ in such a way that $A = \varepsilon e^{\tilde{x}_0L}$ is constant), eq 172 reduces to eq 9. It is therefore not surprising that, in this same limit, eq 173 reduces identically to eq 148.

The FOPA semiclassical calculation has also been carried out for the Morse interaction potential. Cottrell and Ream[24] performed the calculation properly. Turner and Rapp[25] published a note purporting to correct an algebraic error in the work of Cottrell and Ream, but actually they were the ones who made the error, and their corrections should be disregarded. The result of Cottrell and Ream[24] can be put in the form

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(23) R. T. Allen and P. Feuer, *J. Chem. Phys.*, 40, 2810 (1964).
(24) T. L. Cottrell and N. Ream, *Trans. Faraday Soc.*, 51, 159 (1955).
(25) R. E. Turner and D. Rapp, *J. Chem. Phys.*, 35, 1076 (1961).

$$P_{I\rightarrow I\pm1} = (8\pi^2L^2\tilde{m}^2\gamma^2\omega/\mu\hbar)\,\text{csch}^2\,(2\pi\omega L/v_0) \times \cosh^2\left\{(\omega L/v_0)(2\varphi+\pi)\right\} \qquad (175)$$

where $\varphi = \arctan(2\varepsilon/\tilde{m}v_0^2)$. This expression is very similar to eq 53 obtained using the FOPA with an exponential repulsive potential. For collision energies that are high compared to the well depth, the effect of the attractive forces should vanish. This can be shown by allowing $2\varepsilon/\tilde{m}v_0^2$ to approach zero so that $\varphi \cong 0$. If $\pi\omega L/v_0 \ll 1$, as is necessary for the transition probabilities to be small, $\text{csch}^2(2\pi\omega L/v_0) \cong 4\exp(-4\pi\omega L/v_0)$, and $\cosh^2(\pi\omega L/v_0) \cong {}^1/_4 \exp(+2\pi\omega L/v_0)$. In this limit, eq 175 reduces to eq 53.

Allen and Feuer[23] have shown that the FODWA expression for the transition probability with a Morse potential can be put in a simplified form if it is assumed that q_I and $q_{I\pm1}$ are each $\gg 1$. The expression obtained is the same as eq 175, except that v_0 in the semiclassical calculation is replaced by $(v_I + v_{I\pm1})/2$ in the quantum FODWA calculation. Thus, just as in the case of an exponential repulsive potential, the FODWA for the Morse potential reduces to the FOPA for the Morse potential if the average velocity is used in the FOPA expression.

For purposes of calculation, eq 175 can be put into a more useful form (using $\bar{v}$ instead of v_0)

$$P_{I\rightarrow I\pm1} = (8\pi^2L^2\tilde{m}^2\omega/\hbar\mu)\,\text{csch}^2\,(2S) \times \left\{\cosh S \cosh T + \sinh S \sinh T\right\}^2 \qquad (176)$$

where $S = \pi\omega L/\bar{v}$ and $T = 2\varphi\omega L/\bar{v}$. For most cases of interest, $S \gg 1$, and $\cosh(S) \cong \sinh(S) \cong e^S/2$. In this case, eq 176 reduces to

$$P_{I\rightarrow I\pm1} = \left\{(8\pi^2L^2\tilde{m}^2\gamma^2\omega/\hbar\mu)e^{-2\pi\omega L/\bar{v}}\right\} \times \left\{\cosh T + \sinh T\right\}^2 \qquad (177)$$

The first term in the braces is the result one obtains for the exponential potential, and the second term in the braces may be regarded as a correction factor, $C(T)$, for attractive forces. This may also be put into dimensionless form

$$P_{0\rightarrow1} = (8\pi^2m^2/\alpha^2)\exp\left\{-(2\pi^2m/\alpha^2)^{1/2} \times \left[\left(\epsilon-\frac{1}{2}\right)^{1/2}+\left(\epsilon-\frac{3}{2}\right)^{1/2}\right]^{-1}\right\}C(T) \qquad (178)$$

$$T = (2m/\alpha^2)^{1/2}\left[\left(\epsilon-\frac{1}{2}\right)^{1/2}+\left(\epsilon-\frac{3}{2}\right)^{1/2}\right]^{-1} \times \arctan\left\{\frac{\eta/h\nu}{\left(\epsilon-\frac{1}{2}\right)}\right\} \qquad (179)$$

$$C(T) = (\cosh T + \sinh T)^2 \qquad (180)$$

where ϵ is again the total energy, and α is defined in eq 160. The effect of various well depths on transition probabilities will be illustrated for the special case $m = 0.2$ and $\alpha = 0.114$. In Table III, the correction factor $C(T)$ is shown for various total energies ϵ and various well depths ε.

The correction factor for attractive forces becomes appreciable only for large well depths and low collision energies. For many molecules, $\varepsilon/h\nu$ ranges from about 0.10 to 0.40, and the important range of ϵ is greater than 3. Thus, the correction due to attractive forces may be in the range 1.02 to about 1.5. Shin[26] has done similar calculations, using a Lennard-Jones 12–6 potential to include attractive forces, and a straight 12-repulsive potential. He obtains a ratio of calculated probabilities for inclusion of attractive forces and exclusion of attractive forces. He finds that the correction factor is about 10 for ϵ of the order of 1 to 2 and $\varepsilon/h\nu$ of the order of 0.05. This appears to be much larger than calculated herein. His procedure depends on a first-order distorted wave calculation in which only the exponent of the perturbation integral is evaluated (*cf.* section V.D). Since the preexponential factors for the 12 and 6–12 potentials may differ substantially, there is no reason to believe his calculation is correct. It is very possible that the preexponential factor for the 6–12 potential is lower than for the 12 potential. It is believed that Table III gives a better idea of the effect of attractive forces than Shin's results in his Table I.[26]

B. EFFECT OF ANHARMONICITY OF THE OSCILLATOR

1. *Effect of Anharmonicity on the General Quantum and Semiclassical Procedures of Section II*

In the exact quantum calculation of Secrest and Johnson,[18] and the equivalent calculation suggested by Rapp and Kassal,[20] there is no particular reason to limit the treatment to a harmonic oscillator. The entire calculation could be easily extended to the case of an anharmonic oscillator by simply replacing the harmonic BC wave functions, $H_n(y)$, by anharmonic wave functions. Only the perturbation integrals over dy would be different. No *exact* quantum mechanical calculations have been carried out for anharmonic oscillators.

Mies[27] has performed calculations to determine the effect of anharmonicity on first-order calculations. In general, his approach takes into account the case where the integrals $U_{nn}'(x)$ and $U_{II}'(x)$ are not necessarily equal (see eq 125 for the special case of a linearized potential). This can occur in two ways. If the potential given in eq 8 is used, and is *not* linearized as in eq 9, then

$$U_{nn}'(x) = U(x)\int H_n(\tilde{Y})e^{\gamma\tilde{Y}/L}H_n(\tilde{Y})\,\mathrm{d}\tilde{Y} \qquad (181)$$

instead of eq 125. With this potential, even the use of harmonic oscillator functions for $H_n(\tilde{Y})$ leads to $U_{nn}'(x) \neq U_{II}'(x)$ for $n \neq I$. Thus, in comparing the exact quantum calculations of Secrest and Johnson (who used eq 181) with the FODWA, the usual approximate procedure based upon the linearized potential as in eq 125 should not be used. Mies has given a revised FODWA, denoted here as RFODWA, which does not utilize the linearized potential in y, and should therefore be compared to the exact quantum results at low velocities.

Furthermore, Mies has shown that when anharmonic functions are used for $H_n(\tilde{Y})$ in eq 181, $U_{nn}'(x)$ and $U_{II}'(x)$ are substantially different for $n \neq I$, and the RFODWA differs from the usual FODWA. Finally, Mies has also shown[22] that use of the nonlinearized potential (so that $U_{nn}'(x) \neq$

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(26) H. K. Shin, *J. Chem. Phys.*, 41, 2864 (1964).

(27) F. H. Mies, *ibid.*, 40, 523 (1964).

$U_{II}'(x)$) in the FOPA semiclassical calculation leads to an analogous dissimilarity from the usual FOPA calculation.

2. *Effect of Nonequality of Diagonal Perturbation Matrix Elements on the FODWA. RFODWA*

Starting with eq 124, but using eq 181 instead of eq 125, Mies[27] carried through the RFODWA in a procedure analogous to that given by eq 126 through eq 133. For any transition $I \rightarrow n$, with total energy ϵ in units of $h\nu$, he found

$$[P_{I\rightarrow n}(\epsilon,\lambda)]_{\mathrm{RFODWA}} = [P_{I\rightarrow n}(\epsilon)]_{\mathrm{FODWA}}\mathfrak{F}(\epsilon,\lambda) \tag{182}$$

where $\lambda^2 = U_{nn}'(x)/U_{II}'(x)$, and $\mathfrak{F}$ is a correction factor that is less than unity.

For the special case $\lambda^2 = 1$, corresponding to harmonic oscillator functions and a linearized potential, $\mathfrak{F}(\epsilon,1) = 1$. For the general case, Mies[27] found

$$\mathfrak{F}(\epsilon,\lambda) = W_{nn}^{-2}\left|{}_2F_1[1 + (i/2)(q_I - q_n),\; 1 + (i/2)(q_I + q_n);2;1 - \lambda^{-2}]\right|^2 \tag{183}$$

where ${}_2F_1(a,b;c;Z)$ is the hypergeometric series, q_n is defined following eq 138, W_{nn} is defined as

$$W_{nn} = U_{nn}'(x)/U(x) \tag{184}$$

and eq 181 is used for $U_{nn}'(x)$. Since q_n may be regarded as $2\pi L/\lambda_n$, where λ_n is the deBroglie wavelength associated with collision velocity $v_n = \hbar k_n/\tilde{m}$, it can be seen that, when $2\pi L$ is large compared to λ_n and λ_I, $(q_I + q_n)$ will be $\gg 1$. In this limit, the motion in x is essentially classical, and $b \cong (i/2) \cdot (q_I + q_n)$ can be used in ${}_2F_1(a,b;c;Z)$ so that

$$ {}_2F_1(a,b;c;x/b) \xrightarrow[b\rightarrow\infty]{} {}_1F_1(a,c;x) \tag{185}$$

Thus, to this approximation, eq 183 reduces to

$$\mathfrak{F} \cong W_{nn}^{-2}\left|{}_1F_1(1 + i\rho,2;2i\Delta)\right|^2 \tag{186}$$

where

$$\rho = \tfrac{1}{2}(q_I - q_n) = L(k_I - k_n) = L(\Delta E)/\hbar\bar{v} \tag{187}$$

$$\Delta E = E_n^{(\mathrm{BC})} - E_I^{(\mathrm{BC})} \tag{188}$$

and

$$\Delta \cong (1 - \lambda^{-2})\,\tfrac{1}{4}(q_I + q_n) = (W_{nn} - W_{II})L\tilde{m}\bar{v}/\hbar W_{nn} \tag{189}$$

if $(q_I + q_n) \gg 1$.

3. *Effect of Nonequality of Diagonal Perturbation Matrix Elements on the FOPA. RFOPA*[28]

In the semiclassical FOPA calculation, the treatment resulting in eq 47 is not quite correct. One should actually write these equations as

$$\mathrm{d}a_I/\mathrm{d}t \cong (\hbar i)^{-1}a_I(t)V_{II}'(t) \tag{190}$$

$$\mathrm{d}a_n/\mathrm{d}t \cong (\hbar i)^{-1}\{a_I(t)V_{nI}'(t)e^{i\omega_{jI}t} + a_n(t)V_{nn}'(t)\} \tag{191}$$

Solution of eq 190 leads to

$$a_I(t) \cong \exp\left\{-(i/\hbar)\int_{-\infty}^{t} V_{II}'(t')\,\mathrm{d}t\right\} \tag{192}$$

Table III

Correction Factor $C(T)$ as a Function of ϵ for α = 0.114 and m = 0.2 and Various Well Depths η

$\frac{\eta}{h\nu}$ →	0.05	0.10	0.25	0.50
ϵ ↓				
2.5	1.12	1.26	1.77	3.24
3.5	1.06	1.12	1.34	1.85
6	1.02	1.04	1.12	1.25
10	1.01	1.02	1.05	1.10

If this is put into eq 191, the result is[28]

$$\mathrm{d}b_n/\mathrm{d}t \cong (\hbar i)^{-1}V_{nI}'(t)\exp\left\{i\left[\omega_{nI}t + \hbar^{-1}\int_{-\infty}^{t}\{V_{nn}'(t') - V_{II}'(t')\}\,\mathrm{d}t'\right]\right\} \tag{193}$$

where

$$b_n(t) = a_n(t)\exp\left\{-(i/\hbar)\int_{-\infty}^{t} V_{nn}'(t')\,\mathrm{d}t'\right\} \tag{194}$$

Since $|b_n(t)|^2 = |a_n(t)|^2$, and the initial condition is $a_I(-\infty) = 1$, it is found that

$$P_{I\rightarrow n} = |b_n(\infty)|^2 = \left|\hbar^{-1}\int_{-\infty}^{\infty} V_{nI}'(t)\exp\left\{i\left[\omega_{nI}{}^{t} + h^{-1}\int_{-\infty}^{t}\{V_{nn}'(t') - V_{II}'(t')\}\,\mathrm{d}t'\right]\right\}\mathrm{d}t\right|^2 \tag{195}$$

Each term $V_{nI}'(t)$, $V_{II}'(t)$, and $V_{nn}'(t)$ is written in the form

$$V_{nI}(t) = W_{nI}U'(t) \tag{196}$$

where the classical trajectory $x(t)$ is used to convert $U'(x)$ to $U'(t)$. The classical trajectory is different for each state of excitation of the oscillator. By relating to previously derived results (*cf.* eq 153), a trajectory is used with an average collision velocity $\bar{v} = (v_I + v_n)/2$. The average potential energy is $\overline{W}U(t)$, where $\overline{W} = (W_{nn} + W_{II})/2$. (Note that in the previous FOPA calculation (eq 48) it had been assumed that $W_{nn} \cong W_{II} \cong 1$.) Therefore, $U(t)$ must be taken as

$$U(t) = \overline{W}^{-1}\left(\frac{\tilde{m}\bar{v}^2}{2}\right)\mathrm{sech}^2(\bar{v}t/2L) \tag{197}$$

Equation 195 was integrated by Mies,[22] and we denote the result as the RFOPA (revised first-order perturbation approximation). His result may be put in the form

$$[P_{I\rightarrow n}(\epsilon,\lambda)]_{\mathrm{RFOPA}} = [P_{I\rightarrow n}(\epsilon)]_{\mathrm{FOPA}}\mathfrak{F}'(\epsilon,\lambda) \tag{198}$$

where $\mathfrak{F}'$, the correction factor, is

$$\mathfrak{F}' = \left|{}_1F_1(1 + i\rho,2;2i\Delta')\right|^2\overline{W}^{-2} \tag{199}$$

In this equation, ρ is as defined in eq 187, and Δ' is

$$\Delta' = (W_{nn} - W_{II})L\tilde{m}\bar{v}/\hbar\overline{W} \tag{200}$$

To the approximation that $\overline{W} \cong W_{nn}$, and $\Delta' = \Delta$, it follows that $\mathfrak{F}'$ is equal to $\mathfrak{F}$. This shows the over-all consistency of the classical limit of the RFODWA and the RFOPA.

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(28) F. H. Mies, *J. Chem. Phys.*, 41, 903 (1964).

4. The RFOPA for Harmonic BC, but Nonlinearized Potential in $\tilde{Y}$

The previous calculations may be applied to several examples. First, the effect of Mies' revised treatment will be derived for the case of a *harmonic* oscillator, with *nonlinearized* potential. In this case, W_{nn} is the matrix element of $\exp[\gamma\tilde{Y}/L]$ between two harmonic oscillator wave functions $H_n(\tilde{Y})$ over $\mathrm{d}\tilde{Y}$. It can be shown[18] that

$$W_{nm} = \{\exp[\gamma\tilde{Y}/L]\}_{nm} = e^{\alpha^2/4}(m!/n!)^{1/2}\mathfrak{L}_m{}^{n-m}(-\alpha^2/2) \quad (201)$$

where α is defined in eq 160 and $\mathfrak{L}$ is the LaGuerre polynomial. This leads to the result

$$W_{11} = e^{\alpha^2/4}(1 + \alpha^2/2) \text{ and } W_{00} = e^{\alpha^2/4} \quad (202)$$

so that

$$W_{11} - W_{00} = e^{2/4}(\alpha^2/2) \quad (203)$$

If $\alpha \ll 1$, as is usually the case, $W_{11} - W_{00} \cong \alpha^2/2$. Then, because Δ' is a small quantity, only the leading terms in the series expansion for ${}_1F_1$ need be taken. Thus, if it is assumed $W \cong 1$

$$\mathfrak{F}' = \left|1 + \frac{(1 + i\rho)(2i\Delta')}{2} + \frac{(1 + i\rho)(2 + i\rho)}{2\cdot 3\cdot 2!}(2i\Delta')^2 + \ldots\right|^2 \quad (204)$$

$$\mathfrak{F}' \cong 1 - 2\rho\Delta' + \left[(5\rho^2/16) - \frac{1}{3}\right](\Delta')^2 + \ldots$$

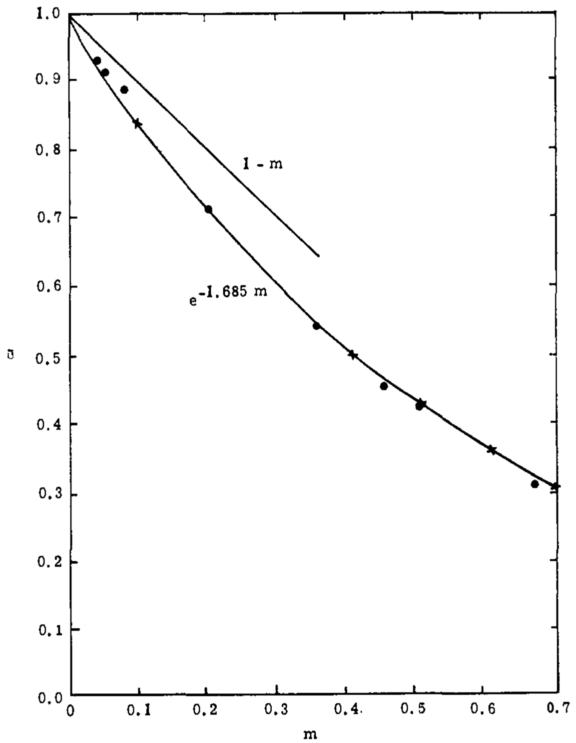

Figure 19. The ratio of energy transfer calculated exactly to the energy transfer calculated approximately (neglecting the change in velocity of A as BC becomes excited). The data dots are from the classical calculations of Kelley and Wolfsberg[7] and the data x's are from the quantum calculations of Secrest and Johnson.[18] The empirically fitted curve $e^{-1.685m}$ is drawn, along with the line $1 - m$ predicted by the RFOPA.

Table IV

Correction Factors due to Anharmonicity for the 0 → 1 Transition in Several Molecules as Calculated by Mies (Assuming L = 0.2 Å)

Diatomic molecule (BC)	*Incident molecule (A)*	*Total energy ε (units of hν)*	*Harmonic correction factor (1 − m)*	*Anharmonic correction factor* $\mathfrak{F}$
O_2	O_2	1.5	0.5	0.082
		5.5	0.5	0.071
		10.5	0.5	0.059
O_2	He	1.5	0.899	0.597
		5.5	0.899	0.585
		10.5	0.899	0.570
H_2	He	1.5	0.333	0.040
		5.5	0.333	0.014
		10.5	0.333	0.0015

For the case $n = 1$ and $I = 0$, it can be shown that if $\alpha \ll 1$ and $W = 1$, then $2\rho\Delta' = m$. Thus, eq 204 may be put in the form

$$\mathfrak{F}' \cong 1 - m + (\tfrac{5}{16})m^2 + \ldots \quad (205)$$

This is the correction factor predicted for the case of a harmonic oscillator with nonlinearized potential. For $m \ll 1$, the correction factor is approximately $\mathfrak{F}' \cong 1 - m$. In Figure 19 the calculated values of the correction factor from Secrest and Johnson,[18] and from Wolfsberg and Kelley,[7] and the line $(1 - m)$ are plotted. It can be seen that the procedure described in this section only partially corrects the FODWA toward the exact result.

5. The RFOPA for Anharmonic BC

By using Morse potential oscillator functions in eq 181, Mies was able to evaluate the matrix elements W_{01}, W_{00}, and W_{11}. The anharmonicities of typical molecules are sufficiently great that, when the spectroscopic Morse potential parameters are used, $W_{11} - W_{00}$ is substantially increased compared to the value calculated for the harmonic oscillator model. For example, in the relatively harmonic molecule N_2, $W_{11} - W_{00}$ is calculated to be 0.0261 for the Morse oscillator model, and 0.0065 for the harmonic oscillator. For the relatively anharmonic molecule H_2, $W_{11} - W_{00}$ is found to be 0.191 based on the Morse model and 0.0515 from the harmonic model. For the 0 → 1 transition in N_2, at $\bar{v} \cong 3 \times 10^5$ cm/sec, $\Delta' = 0.2$ based on the harmonic model, and $\Delta' \cong 0.5$ based on the Morse anharmonic model. Thus, the approximation of eq 204 breaks down badly for anharmonic oscillators because Δ' is not very small.

Mies has written a program to evaluate eq 183 and 199 for any special case. He finds the agreement between the two formulas to be very good. The correction factors $\mathfrak{F}(\epsilon)$ for various collision partners (*i.e.*, various values of λ) are given in some detail. A few of his results are summarized in Table IV. which indicates that the harmonic correction factor is never a good approximation, but fails worst for large values of m. For a light particle hitting a heavy molecule, the anharmonic correction factor is not far from unity. However, for anharmonic molecules and heavy incident molecules A, the anharmonic factors can be in the range 0.01–0.001. Thus, anharmonicity has a relatively large effect on the energy transfer in many cases of interest. The general effect is to reduce the energy transfer below that calculated from the harmonic model, the magnitude of the effect increasing sharply with the anharmonicity of BC and the mass of A relative to BC.

IV. Thermal Averaging of Transition Probabilities Using the Landau–Teller–Herzfeld Procedure

For a gas with translational energy in thermal equilibrium at temperature T, the average transition probability per collision is

$$\langle P_{I\rightarrow n}\rangle = \int_{v=0}^{\infty} P_{I\rightarrow n}(v)\,\mathrm{d}N(v) \tag{206}$$

where v is the initial relative velocity of collision, and $\mathrm{d}N(v)$ is the velocity distribution function normalized so that

$$\int_{v=0}^{v=\infty}\mathrm{d}N(v) = 1 \tag{207}$$

These integrations should be carried out vectorially over all coordinates for all orientations. However, $P_{I\rightarrow n}(v)$ is usually based on an approximate one-dimensional model, and $\mathrm{d}N(v)$ may also be considered in one dimension. When using a one-dimensional model, it is not immediately obvious which velocity distribution function is most appropriate. Herzfeld[4] has argued for use of either the distribution function characteristic of the component of relative velocity projected along the line of centers

$$\mathrm{d}N(v) = (\tilde{m}/kT)e^{-\tilde{m}v^2/2kT}v\,\mathrm{d}v \tag{208}$$

or the function characteristic of particles hitting an area of surface

$$\mathrm{d}N(v) = 2(\tilde{m}/2kT)^2v^3e^{-\tilde{m}v^2/2kT}\,\mathrm{d}v \tag{209}$$

The average probability is not very sensitive to the choice of the velocity distribution function.

Herzfeld[4,29] has presented an integration of eq 206 based on an approximate form of the FODWA for $P_{I\rightarrow n}(v)$. If it is assumed that $(2\pi\omega L/\bar{v}) \gg 1$, for small transition probabilities eq 153 reduces to the simple form (for the 1 → 0 transition)

$$P_{1\rightarrow 0} = (8\pi^2\omega\gamma^2\tilde{m}L^2/\hbar\mu)\exp(-2\pi\omega L/\bar{v}) \tag{210}$$

This expression may be further simplified[29] by assuming $(\tilde{m}\bar{v}^2/2) \gg h\nu$. The average velocity is written as $\bar{v} = (v_0 + v_1)/2$, and the initial velocity v_1 is simply called v. Then

$$\begin{aligned}\bar{v} = (v/2) + \tfrac{1}{2}(v^2 + 2h\nu/\tilde{m})^{1/2} ={}& \\ (v/2)\{1 + 2h\nu/\tilde{m}v^2)^{1/2}\} \cong{}& \\ v\{1 + h\nu/2\tilde{m}v^2 + \ldots\}&\end{aligned} \tag{211}$$

In many cases of physical interest, the conditions $2\pi\omega L/\bar{v} \gg 1$ and $\tilde{m}v^2/2 \gg h\nu$ are fairly well satisfied. The argument of the exponential function in eq 210 may then be written

$$-\frac{2\pi\omega L}{\bar{v}} \cong -\frac{2\pi\omega L}{v}\left\{1 - \frac{h\nu}{2\tilde{m}v^2} + \ldots\right\} \tag{212}$$

The integrand in eq 206 is a product of two terms with opposite dependence on v. The function $P_{1\rightarrow 0}(v)$ increases very rapidly as v is increased, while $\mathrm{d}N(v)$ possesses a maximum at a moderate value of v and decreases sharply as v increases in the range of physical interest. The integrand, therefore, possesses a sharper maximum than $\mathrm{d}N(v)$, and the maximum occurs at a higher value of v than for $\mathrm{d}N(v)$. This shows that the high-velocity "tail" of the velocity distribution is mainly responsible for the energy transfer. In order to locate the velocity v_m, at which the integrand is a maximum, an approximate procedure[8,29] is employed, which simply involves moving the factors that vary slowly with v out of the integral and treating them as constants evaluated at $v = v_m$. In terms of dimensionless variables, eq 210 and 212 yield

$$P_{1\rightarrow 0} \cong (8\pi^2m^2/\alpha^2)e^{h\omega^2L/2\tilde{m}v^3}e^{-2\pi\omega L/v} \tag{213}$$

If the terms v_m and $\exp(h\omega^2L/2\tilde{m}v_m^3)$ are treated as constants (using eq 208 for $\mathrm{d}N(v)$), the result is

$$\langle P_{1\rightarrow 0}\rangle \cong (8\pi^2m^2/\alpha^2)(\tilde{m}/kT)v_m\exp(h\omega^2L/2\tilde{m}v_m^3) \times \int_0^{\infty} e^{-\tilde{m}v^2/2kT}e^{-2\pi\omega L/v}\,\mathrm{d}v \tag{214}$$

The velocity v_m is determined by setting

$$\frac{\partial}{\partial v}[(\tilde{m}v^2/2kT) + (2\ \pi\omega L/v)] = 0 \tag{215}$$

Thus

$$v_m = (\pi\omega LkT/\tilde{m})^{1/3} \tag{216}$$

The integrand of eq 214 is now expanded in a power series about $v = v_m$. If the width of the peak in the integrand is not too large, only the first few terms of the series need be included. When this is done, it is found that

$$\begin{aligned}(\tilde{m}v^2/2kT) + (2\pi\omega L/v) ={}& [(\tilde{m}/2kT)v_m^2 + (2\pi\omega L/v_m)] + \\ & [(\tilde{m}v_m/kT) - (2\pi\omega L/v^2{}_m)](v - v_m) + \\ & \tfrac{1}{2}[(m/kT) + 4\pi\omega L/v_m^3](v - v_m)^2 + \ldots\end{aligned} \tag{217}$$

After substituting for v_m, it is found that

$$(mv^2/2kT) + 2\pi\omega L/v) = \frac{3}{2}\left(\frac{\tilde{m}}{kT}\right)v_m^2 + \frac{3}{2}\left(\frac{\tilde{m}}{kT}\right)(v - v_m)^2 + \ldots \tag{218}$$

and the coefficient of $(v - v_m)$ vanishes.

If eq 218 is substituted into eq 214, an integral is obtained that is easily evaluated, *viz.*

$$\langle P_{1\rightarrow 0}\rangle = (8\pi^2m^2/\alpha^2)(\tilde{m}/kT)(2\pi\omega LkT/\tilde{m})^{1/3}e^{\theta/2T} \times e^{3mv_m^2/2kT}\int_{-v_m}^{\infty}\exp\left[-\frac{3}{2}\left(\frac{\tilde{m}}{kT}\right) \times (v - v_m)^2\right]\mathrm{d}(v - v_m) \tag{219}$$

where $\theta = \hbar\omega/k$. To a high degree of approximation, the lower limit may be replaced by $-\infty$, and the integral is equal to $(2\pi kT/3\tilde{m})^{1/2}$. The final result is

$$\langle P_{1\rightarrow 0}\rangle = 2(2\pi/3)^{1/2}(\theta'/\theta)(\theta'/T)^{1/6}\exp\left[-\frac{3}{2}\left(\frac{\theta'}{kT}\right)^{1/3} + \frac{\theta}{2T}\right] \tag{220}$$

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(29) R. N. Schwartz, Z. I. Slawsky, and K. F. Herzfeld, *J. Chem. Phys.*, 20, 1591 (1952).

where

$$\theta' = 4\pi^2\tilde{m}L^2\omega^2/k \tag{221}$$

Herzfeld[4] added one more embellishment. Since the exponential intermolecular potential is asymptotic to $-\varepsilon$ at $x = \infty$ (*cf.* eq 167), the velocity distribution should be shifted to higher energies by the amount of energy ε. Thus, Herzfeld multiplied the velocity distribution function by $\exp(\varepsilon/kT)$. This factor carries all the way through to eq 220, and the final result, known as the "SSH theory," is

$$\langle P_{1\rightarrow0}\rangle = 2(2\pi/3)^{1/2}(\theta'/\theta)(\theta'/T)^{1/6} \times \exp\left[-\frac{3}{2}\left(\frac{\theta'}{T}\right)^{1/3} + \frac{\theta}{2T} + \frac{\varepsilon}{kT}\right] \tag{222}$$

It is based upon the usual assumptions of a harmonic oscillator, exponential repulsive potential, and one-dimensional collision model. It also involves use of the FODWA, and the assumptions $mv^2/2 \gg h\nu$ and $(2\pi\omega L/v) \gg 1$. Since the FODWA is a procedure based on small transition probabilities, one must be very careful that $P_{1\rightarrow0}(v_m)$ is small in applying eq 222. There are many physical cases of interest where $\langle P_{1\rightarrow0}\rangle$ is small because $dN(v_m)$ is small, and $P_{1\rightarrow0}(v_m)$ may be much too large to justify use of the FODWA. The fact that $\langle P_{1\rightarrow0}\rangle$ is $\gg$1 is no justification for use of eq 222. This is especially true when $\langle P_{1\rightarrow0}\rangle$ becomes as large as 10^{-3} to 10^{-2}. In some cases, these average probabilities correspond to $P_{1\rightarrow0}(v_m)$ that actually exceed unity.

Equation 222 is the basis of the often-used statement that $\log \langle P_{1\rightarrow0}\rangle$ is inversely proportional to $T^{1/3}$. This statement neglects the second two terms in the exponential that are inversely proportional to T. Although these terms are smaller than the first term, they are not negligible, and introduce substantial curvature into the plot of $\log \langle P_{1\rightarrow0}\rangle$ *vs.* $T^{-1/3}$. Temperature averaging of probabilities from more sophisticated calculations are probably best performed numerically. It is only because eq 222 is in very widespread use that its derivation has been given in detail.

V. Other Calculations

A. THOROUGH STUDY OF THE He + H$_2$ SYSTEM

1. The Energy Surface

A very significant contribution to the theory of vibrational energy transfer was made by Krauss and Mies[30,31] in two papers published in 1965. In the first,[30] a very detailed comprehensive study was made of the energy surface for potential interaction of He with H$_2$. In the second publicaton, Mies[31] utilized this essentially exact potential to evaluate the validity of approximate potentials commonly used in energy-transfer theory (as applied to He + H$_2$ collisions).

Before discussing the papers by Mies and Krauss, it is useful to make some general remarks about the over-all procedure used in energy-transfer calculations. When dealing with real molecular collisions between a particle A and a molecule BC, the calculated transition probabilities must somehow be averaged over all possible collision orientations. If the molecule BC is in thermal equilibrium translationally and rotationally (as is usually the case), the basic time periods involved in the collision are τ_c (the collision duration), τ_v (the vibrational period), and τ_R (the rotational period). Of course, τ_c cannot be precisely defined, but, in terms of some reasonable choice (range of time over which velocity increases from minimum to, say, 80% of value at infinite separation), it can be shown that τ_c and τ_v are comparable in many cases, whereas τ_R is at least 100 times larger than τ_c. Therefore, it is a very good approximation to treat the collision as if the orientation were constant.

It is useful to define the coordinate system shown in Figure 20, and assume that a particle enters along $\hat{x}$ with θ = constant and leaves along $\pi - \theta$ = constant. Because the innate probability of any angle θ occurring in the collision is proportional to $\sin\theta$ (consider a sphere of radius r drawn around BC; the area of an element corresponding to θ on the sphere is $2\pi r^2\,dr \sin\theta\, d\theta$), the average probability at any energy should be calculated as

$$\langle P(\epsilon)\rangle = \int_0^{\pi/2} P(\epsilon,\theta)\sin\theta\, d\theta \tag{223}$$

The probability $P(\epsilon,\theta)$ for a collision along the path of constant θ should be calculated from the general intermolecular interaction potential $V_T(\hat{x},\hat{y},\theta)$. This is defined as

$$V_T(\hat{x},\hat{y},\theta) = V_{BC}(\hat{y}) + V'(\hat{x},\hat{y},\theta)$$

where V_T is the total potential energy of the three-particle system ABC, and $V_{BC}(\hat{y})$ is the BC potential at $\hat{x} = \infty$. Except for the single paper by Krauss and Mies[30] for A = He and BC = H$_2$, there is relatively little knowledge of $V'(\hat{x},\hat{y},\theta)$ available for collisions, especially for relatively energetic collisions where $\hat{x}$ becomes small at the turning point.

The general assumption of the simple models used in most energy-transfer calculations is as follows. Since $V'(\hat{x},\hat{y},\theta)$ is essentially an unknown quantity, only the case $\theta = 0$ is considered, along with the assumption that the classical force on the oscillator at any angle θ is $\cos\theta$ times the force at $\theta = 0$. Since the energy transfer depends on the square of the force (*cf.* eq 29), it can be concluded that

$$\langle P(\epsilon)\rangle \cong P(\epsilon,0)\int_0^{\pi/2} \cos^2\theta \sin\theta\, d\theta = P(\epsilon,0)/3 \tag{224}$$

This must, of course, be considered a very crude argument. The factor of $^1/_3$ is considered to be a "steric factor."

It is common to take two approaches for approximating $V'(\hat{x},\hat{y},0)$. In one, the (spherically symmetric) potential between A and BC that was experimentally determined from transport property and virial coefficient data is fitted to an assumed form of the potential (see section III.A). Unfortunately, these properties are determined at low temperatures where they are most sensitive to the attractive part of the potential and are not very reliable for the inner repulsive part of the potential, which is the most important region for collisions involved in energy transfer. A procedure like that outlined in section III.A is used to extrapolate the known potential from large $\hat{x}$ (where the potential is known) to small $\hat{x}$. Since the calculated transition probabilities are very sensitive to the slope of the inner repulsive potential, this procedure can be very inaccurate. An alternate procedure used by some authors has been to give up hope of an *a priori* calculation of $V'(\hat{x},\hat{y},0)$ and merely assume a general form for this

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(30) M. Krauss and F. H. Mies, *J. Chem. Phys.*, 42, 2703 (1965).

(31) F. H. Mies, *ibid.*, 42, 2709 (1965).

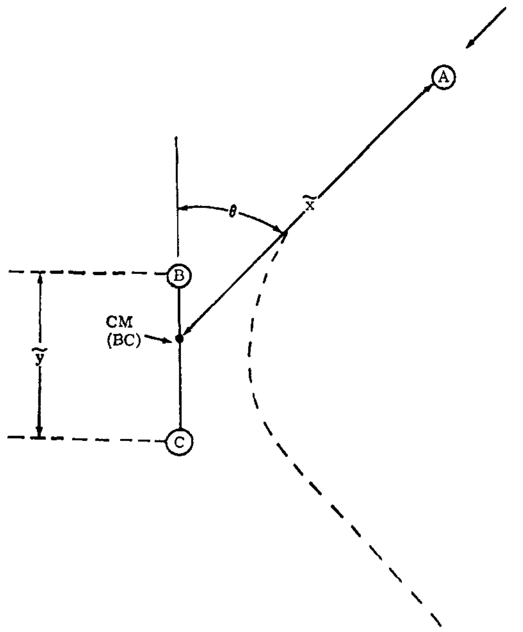

Figure 20. Collision coordinates for off-axis collisions. The distance between A and the center of mass of BC is $\tilde{x}$, the B–C distance is $\tilde{y}$, and θ is the angle between B–C and the initial direction of A.

potential in terms of parameters. The theory is fitted to available data and the parameters are chosen for the best fit. This procedure gives little indication as to the validity of the theory, since the effects of approximations are obscured by the choice of potential parameters. In each case, the assumed form of $V'(\tilde{x},\tilde{y},0)$ is an interaction that depends on the AB distance $\tilde{x} - \gamma\tilde{y}$.

Thus, the basic assumptions used in the theories are as follows.

1. Except for factors of the order of $^1/_3$, the average probability per collision is equal to $P(\epsilon,0)$.
2. The interacton $V'(\tilde{x},\tilde{y},0)$ depends only on the distance $\tilde{x} - \gamma\tilde{y}$.
3. In some calculations, $V'(\tilde{x},\tilde{y},0)$ is determined by fitting it to potentials measured in transport property and virial coefficient measurements, which are of dubious validity for small $\tilde{x}$.

2. Comparison with the "Dumbbell" Model

Mies and Krauss[30,31] have discussed the validity of the "dumbbell" model and have implied that the dumbbell model is automatically implied in the usual calculations on energy transfer. This is not the case. The dumbbell model uses the assumption that the potential

$$V'(\tilde{x},\tilde{y},0) = V_{AB}'(r_{AB}) + V_{AC}'(r_{AC}) \qquad (225)$$

is a sum of pairwise interactions between A and each of the atoms of BC. The model is a possible way of attempting to generalize a one-dimensional potential to off-axis collisions, but it leads to a θ dependence of $P(\epsilon,0)$ that is different from $\cos^2\theta$.

3. Effects on Energy-Transfer Calculations

Having made these preliminary observations, the calculations of Mies and Krauss[30] for He + H_2 will again be discussed. These authors performed a very elaborate quantum mechanical calculation of $V'(\tilde{x},\tilde{y},\theta)$ over the range $2.5a_0 \leq \tilde{x} \leq 3.9a_0$, $0 \leq \tilde{y} \leq 2a_0$, and for $\theta = 0$, $\pi/4$, and $\pi/2$.

The equilibrium value of $\tilde{y}$ is $1.4a_0$, and the range of vibrational amplitude of interest is perhaps $\pm 0.2a_0$. Thus the principal region of $\tilde{y}$ concerning vibrational energy transfer is $1.2a_0 \leq \tilde{y} \leq 1.6a_0$. The important region of $\tilde{x}$, corresponding to incident energies in the range 0.1–0.8 eV, is $2.9a_0 \leq \tilde{x} \leq 3.9a_0$. In this limited range of $\tilde{x}$ and $\tilde{y}$, a good approximation to the result of Krauss and Mies is

$$V'(\tilde{x},\tilde{y},\theta) = Ae^{-\tilde{x}/L}e^{\gamma\tilde{y}/L}e^{-K\tilde{y}\theta} \qquad (226)$$

where $A = 297$ eV, $L = 0.524a_0$, $\gamma = 0.403$, and $K = 0.109$.

This may now be compared to approximate procedures that are conventionally used in energy-transfer calculations. For the special case of head-on collisions (corresponding to $\theta = 0$), γ should be $m_C/(m_B + m_C) = {}^1/_2$ for H_2, according to the simple models. However, Krauss and Mies[30] find that $\gamma = 0.4$. Calculated transition probabilities are not very sensitive to the choice of γ, so this does not have an important numerical effect. They do, however, depend very strongly on the value of L. According to the simple model outlined in section III.A, a rough estimate of L is given by $L = r_0/17.5$. For H_2, r_0 is known to be $5.67a_0$, so one would calculate $L = 0.33a_0$ by this method. The approximate value of L is in poor agreement with the accurate value, $0.524a_0$, calculated by Krauss and Mies. According to Krauss and Mies, if a Buckingham (exp 6) potential is fitted to the low energy diffusion data, and this potential is extrapolated inward to smaller $\tilde{x}$, it is found that $L \cong 0.48a_0$, which is in much better agreement with the exact value. In the case of He + H_2, the procedure described in section III.A can lead to large errors in L, and very large errors in the calculated transition probabilities.

Mies finds the dumbbell model to be particularly bad for off-axis collisions near $\theta = \pi/2$. According to the dumbbell model, the force of A on BC for $\theta = \pi/2$ would be in the direction to spread the molecule and increase $\tilde{y}$. In the exact potential, the net force acting in a collision at $\theta = \pi/2$ is in a direction to compress BC, so the dumbbell model is not even qualitatively correct. However, this is not really relevant to the usual energy-transfer calculations.

Using the exact potential with the RFODWA, Mies calculated $P_{0\rightarrow 1}(\epsilon,0)$ *vs.* θ for $\epsilon = 6.5$. While the actual shape is not exactly the same, the net effect for $\langle P(\epsilon,\theta)\rangle$ is very similar to the result one would get by assuming $P(\epsilon,\theta) = P(\epsilon,0)\cos^2\theta$ (see Figure 7 of Mies' paper). Thus, it may be concluded (note that these conclusions are not exactly what Mies concludes) that: (1) the use of a one-dimensional model with a steric factor of $\sim{}^1/_3$ is a fair approximation for He + H_2 collisions; (2) the value $\gamma = m_C/(m_B + m_C)$ used in calculations is not correct in the case of He + H_2 (this does not have a serious numerical effect on calculated transition probabilities); (3) the value of L calculated by the procedure in section III.A is too small and leads to serious numerical errors for He + H_2 collisions; and (4) the correction for anharmonicity of BC should be included.

B. OTHER CLASSICAL CALCULATIONS

1. Benson and Coworkers

In a series of papers, Benson, Berend, and Wu have performed classical calculations of energy transfer for various collision models. In their first paper,[32] they assumed a hard-sphere interaction potential between particle A and atom B of molecule BC. They found on the basis of this model that if the oscillator is vibrating rapidly, and particle A approaches slowly, then a collision can only occur over a restricted range of phase angles near the maximum extension of the oscillator. At large extensions, the energy transfer is least efficient. They calculate the energy transfer as a function of phase at any incident velocity. For each incident velocity, only a partial range of oscillator phase is possible at collision (*i.e.*, φ cannot have all values between 0 and 2π). To calculate the average energy transferred per collision, one should average the energy transfer $\Delta E_{\text{vib}}(\varphi)$ over all accessible phases (*i.e.*, from C to D in Figure 6 of ref 32). However, Benson, Berend, and Wu used a different procedure, which seems reasonable at first glance, but is actually incorrect. They argued that if one is interested in the transition $1 \rightarrow 0$, then $P_{1\rightarrow 0}$ would be interpreted as the fraction of phases corresponding to $-2h\nu < \Delta E_{\text{vib}} < -h\nu$. This interpretation is fallacious. As was discussed in section II, one can only equate the total energy transferred quantally and classically. Therefore, the conclusions drawn in ref 32 regarding the dependence of transition probability on collision velocity are erroneous.

In the second paper,[33] a collinear collision of a particle with a diatomic molecule is solved exactly by using classical mechanics for two possible interaction potentials: one being harmonic with a finite cutoff, and the other a Morse potential. As in the case of their first paper,[32] the incorrect interpretation of the transition probability from the phase dependence of the classical energy transfer leads to an untenable sharp cutoff of the transition probability $P_{1\rightarrow 0}(v)$ at low velocities (see Figure 7 of ref 33). This incorrect interpretation leads to a velocity-averaged transition probability $\langle P_{1\rightarrow 0}\rangle$ that depends on T as $\exp[-c/T]$ instead of $\exp[-c'/T^{1/3}]$, as in the Herzfeld procedure (see section IV). The conclusions regarding the T dependence of $\langle P_{1\rightarrow 0}\rangle$ are not correct.

In the third paper,[34] Benson and Berend used the calculations of $\Delta E_{\text{vib}}(\varphi)$ from the second paper, but this time with the correct interpretation of $P_{0\rightarrow 1}$ as the phase-averaged ΔE_{vib} divided by $h\nu$. This eliminates the untenable sharp threshold in the dependence of $P_{0\rightarrow 1}$ on v predicted in the second paper and makes the results similar to those of Kelley and Wolfsberg.[7] Since the authors adjusted the potential parameters to fit the experimental data, it is impossible to compare the relative agreement of the two procedures with experiment.

In the fourth paper,[35] Benson and Berend considered the case of anharmonic oscillators, which are highly excited initially, and solved the classical equations of motion exactly for a Morse potential interaction with an incident particle. The use of classical mechanics for very high vibrational quantum numbers should be a good approximation. The calculations are probably of great significance in connection with the theory of unimolecular decomposition but do not really fall into the subject of the present review paper. However, we do wish to comment on one of the conclusions reached in the paper. We quote from the paper directly: "Figure 10 shows the values of $\Delta E_{\text{vib-de}}$ obtained for collisions of I_2 with Ar. . . . What is most striking is the relatively low values of $\Delta E_{\text{vib-de}}$($\sim$4 kcal) compared to the total vibrational energy in the system ($\sim$33 kcal). . . . These results provide justification for the assumption made by several authors that highly excited anharmonic oscillators will not lose large amounts of their energy in collisions. From detailed balancing we can also conclude that the inverse is true, namely, that the collisional population of the top most vibrational levels will come predominantly from the adjacent levels."

We believe that this statement might cause some misunderstanding. A vibrational deexcitation of 4 kcal in I_2 corresponds to a quantum jump at least ten vibrational levels. While it is true that a highly excited anharmonic oscillator will only lose about 10% of its vibrational energy per collision, this should be considered a *large* energy transfer. Excitation of upper levels of I_2 can come directly from states 10 or more levels below. The very sizable qualitative difference between energy transfer between the lower vibrational levels (say $0 \leq n \leq 4$) and energy transfer between levels near the dissociation limit should be stressed. In the former case, the transition probabilities are small, and, except at high temperature, transitions to adjacent levels are most important. In the latter case, the transition probabilities are much larger and direct transitions of many quanta are highly probable. It may be concluded that the average energy transferred per collision changes gradually from a small fraction of a quantum for low vibrational quantum numbers to many quanta for high vibrational quantum numbers of an anharmonic oscillator.

In the fifth paper, Benson and Berend[36] compare their results for $\langle P_{1\rightarrow 0}\rangle$ based on the method of their third paper[34] with data for a wide variety of diatomic molecules. They adjusted the repulsive potential in each case to obtain a best fit with experiment. It is unclear whether the potential parameters have been adjusted to compensate for approximations in the theory (such as neglect of anharmonicity and the one-dimensional collision model), or that the theory works satisfactorily. For some of the substances considered, at high temperatures, $\langle P_{1\rightarrow 0}\rangle$ is greater than 0.1. Since $\langle P_{1\rightarrow 0}\rangle$ is obtained from a velocity average of $P_{1\rightarrow 0}(v)$ (*cf.* section IV), the actual values of $P_{1\rightarrow 0}(v)$ involved in the collisions that contribute most to energy transfer are usually much greater than $\langle P_{1\rightarrow 0}\rangle$. This is due to the fact that $P_{1\rightarrow 0}(v)$ is a rapidly increasing function of v, while $dN(v)$ is a decreasing function of v. Thus, at high temperatures, multiple transitions probably dominate, and the method used to convert ΔE_{vib} to $P_{1\rightarrow 0}$ (*i.e.*, $P_{0\rightarrow 1} = \Delta E/h\nu$) breaks down badly. It may be concluded that all reported values of $\langle P_{1\rightarrow 0}\rangle$ greater than $\sim 10^{-3}$ are of dubious validity.

In their most recent (the sixth) paper,[37] Benson and Berend considered the effect of both rotation and vibration of BC in a collision with A, by using a two-dimensional model. They explored the effect of high initial rotational excitation of BC on vibrational transition probabilities. They used an exact, purely classical calculation with Morse potentials assumed between A and B, and between A and C. The cases considered had large amounts of initial rotational excitation of O_2 when hit by Ar. The initial rotational energies considered were 0.25, 1, and 2 eV, which correspond to 2500, 10,000, and

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(32) S. W. Benson, G. C. Berend, and J. C. Wu, *J. Chem. Phys.*, **38**, 25 (1963).

(33) S. W. Benson, G. C. Berend, and J. C. Wu, *ibid.*, **37**, 1386 (1962).

(34) S. W. Benson and G. C. Berend, *ibid.*, **39**, 2777 (1963).

(35) S. W. Benson and G. C. Berend, *ibid.*, **40**, 1289 (1964).

(36) S. W. Benson and G. C. Berend, *ibid.*, **44**, 470 (1966).

(37) S. W. Benson and G. C. Berend, *ibid*, **44**, 4247 (1966).

20,000°K, respectively. Later, it was claimed that the effect of rotation on their calculated curve of $\langle P_{1\rightarrow 0}\rangle$ *vs.* T (from ref 36) is to multiply $\langle P_{1\rightarrow 0}\rangle$ by a factor of $^1/_3$ and not change its shape. Since Benson and Berend apparently did not determine[37] the effect of initial rotational energy on $P_{1\rightarrow 0}(v)$, except for initial rotational energies large compared to those most probable at reasonable temperatures, it is difficult to understand how they obtained a thermal average. Their conclusion that one must multiply the previous calculated $\langle P_{1\rightarrow 0}\rangle$ (based on no initial rotational energy) by $^1/_3$ does not appear to follow from their calculations.

2. *Wilson and Coworkers*

A series of papers on the classical calculation of vibrational energy transfer have been published by Wilson and his coworkers.[38, 39] Although they are mainly concerned with energy transfer insofar as it is related to unimolecular decomposition, there is some overlap[39] with the subject matter of this review. Only a brief description of this work[39] will be given. A linear configuration for collisions of A upon BC was used with a Morse potential between B and C, and a 6–12 Lennard-Jones potential between A and B. Only Xe–Br_2 collisions were explicitly considered. The classical equations of motion, being good approximations for such heavy atoms, were solved exactly. In many ways, the calculations are analogous to those of Kelley and Wolfsberg[7] and Benson and Berend.[34] The energy transferred to an oscillator, initially at rest, is calculated for a wide range of relatively high initial velocities. The effect of initial excitation of the oscillator was also studied, and it was found that the energy transfer was substantially enhanced by increasing the initial excitation. A gradual change was observed from the case of an initially unexcited oscillator, where the energy transfer was small, to the case of a highly excited anharmonic oscillator, where a transfer of 10% of the dissociation energy in one collision was not unusual.

3. *Parker*

Parker[10] performed a classical calculation of the energy transfer between two diatomic molecules and demonstrated the equivalence of the approximate classical and FODWA quantum calculations at high collision velocities. This equivalence was used to justify his use of a classical procedure. The actual calculation involved a relatively elaborate model involving two diatomic molecules with arbitrary orientations for which classical equations of motion were derived based on an intermolecular potential consisting of the following terms.

Each diatomic molecule was assigned two symmetrically located centers of repulsion on the bond axis. The repulsion potential between two diatomic molecules was taken to be the sum of four terms, each of which is an exponential term $e^{-\alpha r}$, where r is the distance between a pair of repulsion centers on different molecules and α is a constant approximately equal to L^{-1} obtained from simpler potentials. An attractive potential was assigned to each pair of molecules and was taken to be $e^{-\alpha R/2}$, where R is the distance between centers of mass of the two molecules. Thus, Parker utilized a kind of generalized Morse potential. The total interaction potential was written as

$$V' = A[e^{-\alpha r_{ac}} + e^{-\alpha r_{ad}} + e^{-\alpha r_{bc}} + e^{-\alpha r_{bd}}] - Be^{-\alpha R/2} \quad (227)$$

where a and b are the repulsive centers on one molecule, c and d are the repulsive centers on the other molecule, and A and B are constants. The repulsive centers are assumed to be partway between the nuclei of the diatomic molecules. It is also assumed that R is large compared to the separation of repulsive centers d^*, and that the potential can be simplified by expansion of r_{ij} in d^*/R. The resulting classical dynamical equations were solved to the first order for the rotational energy transfer, by treating the molecules as nonvibrating. These results, while very interesting, fall outside the scope of this review.

Table V

The Interaction Constant α Determined by Fitting Parker's Theory to Experiment

Gas	r_0, Å	α, Å^{-1}
O_2	3.43	3.86
CO	3.59	4.02
F_2	3.65	4.06
N_2	3.68	4.07
Cl_2	4.12	3.52
Br_2	4.27	3.17
I_2	4.98	2.65

For purposes of calculating the vibrational energy transfer, Parker[10] determined the component of force exerted on center a relative to center b, along the bond axis $\overline{ab}$. He used this force to solve the classical equations of motion for the relative motion of an initially nonvibrating oscillator based on the assumption that the classical trajectory $R(t)$ is independent of the energy transfer. Thus, his calculation is analogous to the "approximate" classical procedure outlined in section II.B. After averaging over relative orientations, Parker used an expression for the energy transfer very similar to eq 33. This is not surprising since Parker's dynamical calculation of the energy transfer to the oscillator is essentially the same as that used in deriving eq 33. His main improvement is that he made the potential parameters orientation-dependent, and then averaged over-all orientations. It is to be expected that predictions based on Parker's procedure will be very close to those based on eq 33.

In the actual application to specific substances, there are two potential parameters in the theory, α and d^*. In his original paper, Parker selected values of these constants to obtain a best fit to experiment. The values of d^* ranged from $\sim ^1/_3$ to $\sim ^1/_2$ of the equilibrium bond distance of a molecule. The values of α tended to be somewhat less than L^{-1} predicted by the crude procedure of section III.A.

In a more recent paper, Parker[40] obtained a set of values of α and d^* for a number of molecules by again fitting his theory to experimental data. As before, he does not explicitly specify how he chooses the two parameters. However, it appears that the energy transfer is much more sensitive to α than to d^*. Therefore, the choice of α is of paramount importance. It was found that a best fit to experiment yielded the values of α listed in Table V. For convenience, the molecular diameters,

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(38) R. J. Harter, E. B. Alterman, and D. J. Wilson, *J. Chem. Phys.*, 40, 2137 (1964).

(39) E. B. Alterman and D. J. Wilson, *ibid.*, 42, 1957 (1965).

(40) J. G. Parker, *ibid.*, **41**, 1600 (1964).

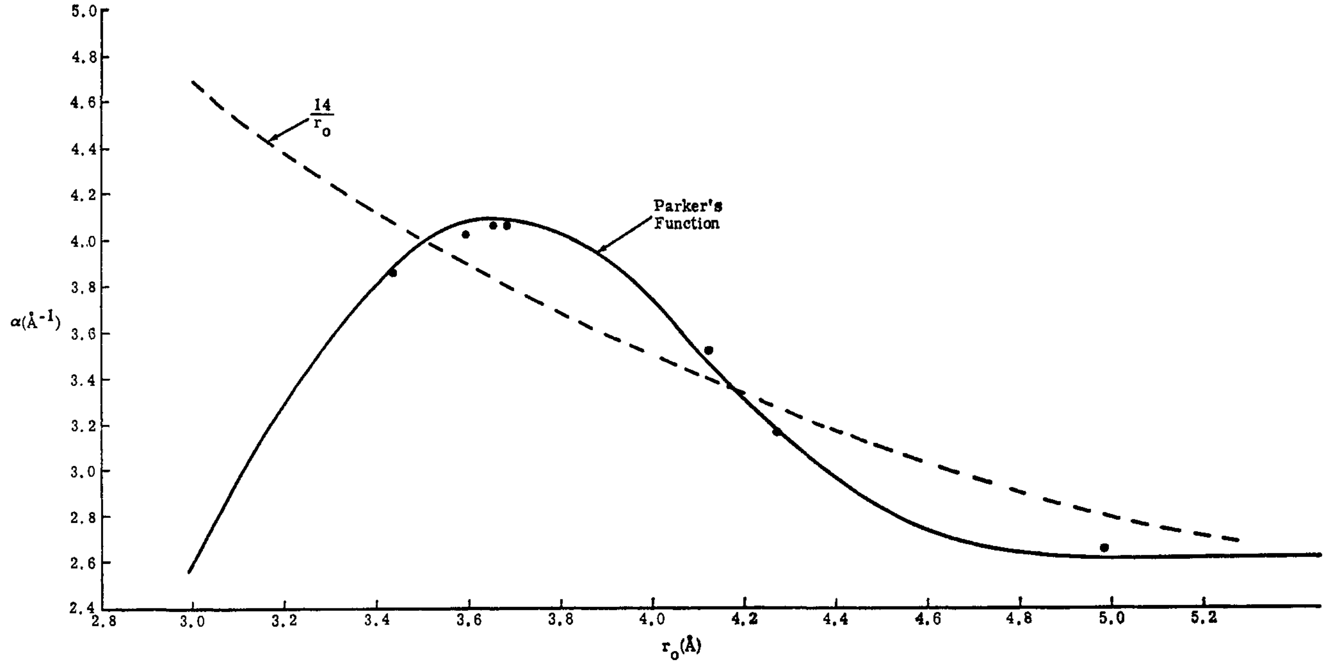

Figure 21. The values of α obtained by Parker[40] by fitting his approximate energy transfer theory to experimental data as a function o Lennard-Jones molecular diameter. Parker fitted an arbitrary function (eq 228) to his points. Another possible function is $\alpha = 14/r$ which has more theoretical basis. The two functions are widely divergent for small r_0.

r_0, determined from virial coefficients, and transport properties are also tabulated. According to the discussion of section III.A, there should be an inverse relationship between α and r_0.

In order to fit his theory to experiment, Parker attempted to draw an empirical relationship between the best value of α and the molecular diameter. He arbitrarily chose the dubious function

$$\alpha = 2.625\{1 - \exp[-(r_0/3.46)^6]\} + 6.117(r_0/3.46)^6 \exp[-(r_0/3.46)^6] \quad (228)$$

to correlate the results of Table V. This is one of an infinite number of arbitrary functions that correlate α with r_0 for the substances measured. It has no theoretical basis whatsoever and cannot be expected to lead to good values of α for r_0 outside the range measured. A plot of this function is presented in Figure 21, which shows that it goes to very small values of α for small r_0. According to section III.A, one might expect α to be inversely proportional to r_0 on theoretical grounds. A plot of the function $\alpha = 14/r_0$ is also given in Figure 21. If it is assumed that there is some scatter in the points, the fit is acceptable and leads to large values of α for small r_0.

The case of H_2 is a good example. Since $r_0 = 2.96$, Parker's equation leads to the value $\alpha = 2.5$ Å^{-1}, whereas the function $14/r_0$ is equal to 4.7 Å^{-1}. The calculation of Krauss and Mies for He + H_2 collisions (see section IV) leads to a value α = 3.6 Å^{-1}. This value is not really comparable because Parker's values of α are those necessary to fit a very approximate theory to experiment. Neglect of anharmonicity, for example, leads to very large errors that must be compensated by an adjusted value of α. It must be concluded that the sharp decrease in Parker's function $\alpha(r_0)$ for small r_0 is an artifact due to his use of a crude theory and his exact treatment of the lower four data points, the variation of which probably constitutes scatter. The agreement Parker finds between his theory and the experimental data for substances is due to his arbitrary choice of α. At the higher temperatures, when his calculated values of $\langle P \rangle$ approach 10^{-2}, the actual values of $P(v_m)$ (see section IV) are probably in excess of unity. For example, for O_2 at 10,000°K, Parker calculates $\langle P \rangle \cong 10^{-3}$. At this temperature, eq 216 leads to $v_m \cong 7 \times 10^5$ cm/sec. At this velocity, $P_{1\rightarrow 0}(v_m)$ is about 20 according to eq 153. Thus, the entire use of a first-order calculation is erroneous at these high temperatures.

C. EFFECTS OF ROTATION ON VIBRATIONAL ENERGY TRANSFER

This section deals only with a consideration of vibrational relaxation in a gas that is translationally and rotationally in thermal equilibrium. Since translational and rotational relaxation times are extremely short compared to vibrational relaxation times, this is the most usual case of physical interest. The effect of extremely high rotational quantum numbers on vibrational energy transfer[37] will not be discussed here.

For an equilibrium distribution of rotational states, the fraction of diatomic molecules in the Jth rotational state is given by

$$\frac{n_J}{N_{tot}} = \frac{(2J + 1)e^{-J(J+1)\theta_R/T}}{(T/\theta_R\sigma)} \quad (229)$$

where $\theta_R = \hbar^2/2Ik$, I is the moment of inertia, J is the rotational quantum number, and σ is the symmetry number. If this distribution is treated as a quasi-continuum, the most populated rotational quantum state is found to be

$$J_{max} \cong (T/2\theta_R)^{1/2} \quad (230)$$

This formula works best for $J_{\max} \gg 1$. It can also be shown[41] that the fraction of molecules with rotational quantum number in excess of some selected value, say J_0, is

$$z(J_0) \cong \exp[-J_0(J_0 + 1)\theta_{\mathrm{rot}}/T] \tag{231}$$

The rotational energy of the Jth state is $E_J = k\theta_R J(J + 1)$. If, for purposes of approximate analysis, a molecule in the Jth state is treated as a classical rotator, one would find the classical rotational period to be given by

$$\tau_{\mathrm{rot}} = 2\pi(I/2E_J)^{1/2} \tag{232}$$

The duration of a molecular collision cannot be precisely defined. However, for approximate purposes, the following crude definition may be used. For molecules that interact according to an exponential repulsive potential $Ae^{-\tilde{x}/L}$, the collision duration may be defined as $\tau_c = 2L/v$, where v is the initial relative collision velocity.

There are two calculations that are easily performed to illustrate the relative magnitudes of τ_c and τ_{rot}. One is to compare τ_c with $(\tau_{\mathrm{rot}})_M$ corresponding the most probable rotational state $J_{\max}$. The ratio is equal to

$$\frac{T_c}{(\tau_{\mathrm{rot}})_M} = (L/\pi v)(kT/I)^{1/2} \tag{233}$$

Typical values are $L \cong 2 \times 10^{-9}$ cm, $v = 2 \times 10^5$ cm/sec, $T = 700°$K, and $I = 2 \times 10^{-30}$ g cm^2. Thus, the general order of magnitude of $\tau_c/(\tau_{\mathrm{rot}})_M$ is ~ 0.01. Another indication is to calculate the fraction of molecules with rotational period less than the collision duration, that is, $z(J_0)$ where J_0 corresponds to $\tau_{\mathrm{rot}} = \tau_c$. When this is done, it is found that $z(J_0) \cong 10^{-80}$.

Therefore, it has been demonstrated that under most conditions of physical interest, the collision period is short compared to the rotational period of the most probable rotational state. The fraction of molecules with rotational periods that are short compared to the collision duration has been shown to be a very small number. Thus, the simple collisional models that utilize nonrotating coordinates with fixed orientation are demonstrated to be very good approximations.

D. THE LANDAU-WIDOM-SHIN PROCEDURE

In any calculation of transition probabilities for an inelastic collision process, one must always evaluate perturbation integrals of the form

$$Q = \int \Psi_{\mathrm{final}} V' \Psi_{\mathrm{initial}}\, \mathrm{d}\tau \tag{234}$$

In the classical limit, Ψ can be approximated by means of the WKB wave functions which diverge at the classical turning point. Therefore, the integrand in the perturbation integral goes to ∞ at the turning point, thereby preventing evaluation of the integral by usual techniques. In 1932, Landau[42] proposed an approximate method for evaluating the order of magnitude of such a perturbation integral with WKB wave functions. This is also briefly discussed in a quantum mechanics textbook.[43] Although Landau is undoubtedly correct, we cannot follow his arguments and do not understand his procedure. Landau's final result is that for a one-dimensional problem

$$Q \sim \int_{-\infty}^{\infty} \exp\left\{\frac{(2\tilde{m})^{1/2}}{\hbar}\left[\int_{\tilde{x}_{t_f}}^{\tilde{x}} [V'(\tilde{x}') - E_f]^{1/2}\,\mathrm{d}\tilde{x}' - \int_{\tilde{x}_{t_I}}^{\tilde{x}} [V'(\tilde{x}') - E_I]^{1/2}\,\mathrm{d}x'\right]\right\}\mathrm{d}\tilde{x} \tag{235}$$

where E_f and E_I are the energies in coordinate $\tilde{x}$ after and before transition, and $\tilde{x}_{t_f}$ and $\tilde{x}_{t_I}$ are the classical turning points corresponding to energies E_f and E_I.

The symbol $\sim$ between the left and right sides of eq 235 needs some explanation. The general magnitude of Q is determined by the right side of this equation; however, it is not an equal sign because other factors are involved. In a first-order calculation, the probability of a transition I → f is generally proportional to $|Q|^2$. Thus, the general statement of Landau's principle is that to first order, $P_{I \rightarrow f}$ is proportional to $|Q|^2$ as given in eq 235. The proportionality factor is not known.

Widom[44] applied the Landau principle to three potentials and obtained closed-form evaluations of Q for each case. He also averaged these expressions over an appropriate velocity distribution. Shin[26,45] proposed a mathematical technique for evaluating Q for almost any potential. His results agree with Widom's[41] for the cases considered. Shin's[45] final results for the velocity-averaged probabilities are

(1)
$$V'(\tilde{x}) = Ae^{-\tilde{x}/L} - \varepsilon \tag{236}$$

$$\langle P_{1\rightarrow 0}\rangle \sim \exp\left[-\frac{3}{2}\left(\frac{\theta'}{T}\right)^{1/3} + \frac{\theta}{2T} + \frac{\varepsilon}{kT}\right] \tag{237}$$

(2)
$$V'(\tilde{x}) = A/\tilde{x}^2 - \varepsilon \tag{238}$$

$$\langle P_{1\rightarrow 0}\rangle \sim \exp\left\{-\left[\frac{(2\tilde{m}A)^{1/2}\pi\omega}{k^2T^2}\right]^{1/3} + \frac{\theta}{2T} + \frac{\varepsilon}{kT}\right\} \tag{239}$$

(3)
$$V'(\tilde{x}) = D[e^{-\tilde{x}/L} - 2e^{-\tilde{x}/2L}] \tag{240}$$

$$\langle P_{1\rightarrow 0}\rangle \sim \exp\left\{-\frac{3}{2}\left(\frac{\theta'}{T}\right)^{1/3} + \frac{\theta}{2T} + \frac{16D}{3\pi^2kT} + \frac{4(\theta')^{1/6}D^{1/2}}{\pi T^{2/3}(2k)^{1/2}}\right\} \tag{241}$$

Shin also derived the appropriate expression for $\langle P_{1-0}\rangle$ corresponding to the Lennard-Jones potential

$$V'(\tilde{x}) = 4\varepsilon[(r_0/\tilde{x})^{12} - (r_0/\tilde{x})^6]$$

The meaning of the symbol $\sim$ in the Landau principle can be made more explicit by comparing eq 237 with eq 222. The only difference is the preexponential factor $2(2\pi/3)^{1/2}(\theta'/\theta)\cdot(\theta'/T)^{1/6}$. Since θ' tends to be about $\sim 3 \times 10^6$°K, and $\theta \cong 2000$°K, this factor generally is of magnitude 10^4–10^5. However, it is relatively insensitive to changes in temperature. One might guess, although there is certainly no proof, that for other potentials similar temperature-insensitive preexponential factors result.

The effect of the attractive part of the potential on calculated transition probabilities can be seen by comparison of eq 441 and 237. Equation 237 follows from use of a simple

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(41) B. Widom, Ph.D. Thesis, Cornell University, 1952.

(42) L. Landau, *Physik. Z. Sowjetunion*, 1, 81 (1932); 2, 26 (1932).

(43) L. Landau and E. M. Lifshitz, "Quantum Mechanics," Pergamon Press, Ltd., London, 1958, pp 178–183.

(44) B. Widom, *Discussions Faraday Soc.*, 33, 37 (1962).

(45) H. K. Shin, *J. Chem. Phys.*, 42, 59 (1965).

exponential repulsive potential that is asymptotic to $-\varepsilon$ at ∞, whereas eq 241 results from a potential that is the sum of an exponential repulsion plus a longer range exponential attractive potential. The difference between the extra terms in the exponentials illustrates the approximate nature of the term ε/kT in eq 237 as a correction for attractive forces.

Shin concludes[45] from this work that the calculated probabilities are strongly dependent on the assumed form of the interaction potential. He does not, however, attempt to evaluate the differences in calculated probabilities if the potentials are fitted to one another, for example, as in section III.A.

In more recent work, Shin[45a] has attempted to deal with off-axis collisions by using an angle-dependent potential and solving the problem at a fixed orientation. He uses a "dumbbell" model (*cf.* section V.A) in which the potential between A and B_2 is assumed to be a sum of potentials between A and each atom B of B_2, The collision is assumed to take place at a fixed orientation, as shown in Figure 20. With this model, Shin[45a] finds that the transition probability for any value of $P(\epsilon,\theta)$ is equal to $P(\epsilon,0)$ times a correction factor $f(\theta)$, which is independent of ϵ. He then uses eq 223 and finds that $\langle P(\epsilon,\theta)\rangle \cong 0.1P(\epsilon,0)$. The small value he obtains for the steric factor is due to his use of the dumbbell model. He finds that $P(\epsilon,\theta)$ falls off very rapidly as θ increases from 0. In typical cases, the transition probabilities at $\theta = \pi/4$ are about $^1/_{10}$ of those at $\theta = 0$. For He–H_2 collisions, where the angle-dependent potential is known fairly accurately,[30,31] the transition probability $P(\epsilon,\theta)$ does not fall off with θ as rapidly. At $\theta = \pi/4$, Mies[31] finds (see his Figure 7) that $P(\epsilon,\pi/4) = {}^1/_2P(\epsilon,0)$. Thus, the steric factor in this case should be much closer to $^1/_3$, as would be calculated from eq 224. It is highly doubtful that the dumbbell model is a good approximation in the cases considered by Shin,[45a] and the simple steric factor of $^1/_3$ in this case is preferred over the highly intricate calculated results of Shin.

E. THREE-DIMENSIONAL CALCULATIONS

1. The Breathing Sphere Model

Several authors[46–49] have utilized a "breathing sphere" model to extend the usual one-dimensional procedure to three dimensions. The oscillating molecule is treated as a spherical body that is capable of pulsations (changes in radius), while its spherical shape is rigidly maintained. The incident particle is represented by a point mass, and the intermolecular potential is assumed to be a function of the distance of the incident particle from the surface of the sphere. Standard methods for scattering by a spherically symmetric potential are then applied. The breathing sphere model is probably most appropriate for very rapidly rotating molecules because it approximates the average potential an incoming particle would encounter. However, it has already been demonstrated that for most cases of physical interest, the rotational periods are long compared to the collision durations. Therefore, the breathing sphere model is not expected to be a good description of three-dimensional effects in energy-transfer calculations.

Since the incident particle is treated as a point mass, it may be located by spherical polar coordinates r, θ, and φ, centered on an origin at the center of the breathing sphere whose radius is denoted as R. The Schroedinger equation for the total system of incident particle plus breathing sphere is analogous to eq 87. In terms of μ = the effective mass of the breathing sphere oscillator, $\tilde{m}$ = the reduced mass of incident particle and oscillator, and R_0 defined as the equilibrium value of R, it can be shown[48] that for a fixed center of mass of the entire system

$$\left[-\frac{\hbar^2}{2\mu}\nabla_R^2 - \frac{\hbar^2}{2\tilde{m}}\nabla_r^2 + \frac{1}{2}f(R - R_0)^2 + V'(R,r)\right]\Psi(R,r) = E\Psi(R,r) \qquad (242)$$

Since the interaction potential $V'(R,r)$ does not depend on θ or φ, a method of separation of variables can be employed to solve this equation. The first and third terms in eq 242 constitute the Hamiltonian for the isolated breathing sphere whose Schroedinger equation is

$$\left[-\frac{\hbar^2}{2}\nabla_R^2 + \frac{1}{2}f(R - R_0)^2\right]\varphi(R) = E_R\varphi(R) \qquad (243)$$

The solutions of eq 243 has the form

$$\varphi_n(R) = H_n(R)/R \qquad (244)$$

where $H_n(R)$ is a usual one-dimensional harmonic oscillator wave function. The energy of such a state is

$$E_{Rn} = \left(n + \frac{1}{2}\right)\hbar\omega \qquad (245)$$

and $\omega^2 = f/\mu$. A solution of eq 242 is therefore sought in the form

$$\Psi(R,r) = \sum_{n=0}^{\infty}\frac{H_n(R)}{R}\psi_n(r,\theta) \qquad (246)$$

Since the scattering potential is spherically symmetric, ψ_n cannot depend on the angle φ but can be expanded in terms of Legendre polynomials as[48]

$$\psi_n(r,\theta) = \sum_{l=0}^{\infty}[G_n{}^l(r)/r]\ P_l(\cos\ \theta) \qquad (247)$$

If eq 247 is substituted into eq 246, and the resultant expression for Ψ is substituted in eq 242, a set of radial equations[48] is obtained, *i.e.*

$$\left\{\frac{\partial^2}{\partial r^2} + \left[k_j{}^2 - \frac{l(l+1)}{r^2}\right]\right\}G_j{}^l(r) - \sum_{n=0}^{\infty}\langle j|V'(R,r)|n\rangle G_n{}^l(r) = 0 \qquad (248)$$

where

$$k_j{}^2 = (2\tilde{m}/\hbar^2)(E - E_{Rj} + E_{RI}) \qquad (249)$$

$$\langle j|V'(R,r)|n\rangle = \frac{2\tilde{m}}{\hbar^2}\int_0^{\infty}H_j(R)V'(R,r)H_n(R)\,\mathrm{d}R \qquad (250)$$

and I is the initial state. Equation 248 is essentially the same as the result obtained from a similar treatment of the collinear collision model (*cf.* eq 124) except for the centrifugal term $l(l+1)/r^2$.

(45a) H. K. Shin, *J. Chem Phys.*, 46, 3688 (1967); 47, 3302 (1967).
(46) R. N. Schwartz and K. F. Herzfeld, *ibid.*, 22, 767 (1954).
(47) K. Takayanagi, *Progr. Theor. Phys.* (Kyoto), 8, 497 (1952).
(48) F. H. Mies and K. Shuler, *J. Chem. Phys.*, 37, 177 (1962).
(49) H. K. Shin, *ibid.*, 46, 744 (1967).

In order to solve eq 248, the appropriate boundary conditions must be elucidated. As $r \rightarrow \infty$, it is necessary that $\psi_n(r,\theta)$ should take the form

$$e^{ik_I r \cos\theta} + \sum_{n=0}^{\infty} \sum_{l=0}^{\infty} g_n{}^l \frac{e^{ik_n r}}{r} P_l(\cos\theta) \qquad (251)$$

The first term is the incident wave, and the second term represents outgoing scattered waves, each with a wave number k_n, referring to the oscillator being left in state n. The l'th partial wave refers to the l'th quantized value of angular momentum for the incident particle. If eq 248 is examined for large values of r, the matrix element $\langle j| V'(R,r)|n\rangle$ and the centrifugal term $l(l + 1)/r^2$ both vanish. Therefore, in the limit $r \rightarrow \infty$, the solution of eq 248 takes the asymptotic form

$$G_j{}^l(r) \rightarrow a_j{}^l e^{-ik_j r} + b_j{}^l e^{+ik_j r} \qquad (252)$$

If this is substituted in eq 247, it can be seen that the constants $b_j{}^l$ may be identified with $g_j{}^l$. The constants $a_j{}^l$ must be chosen so that

$$\sum_{n=0}^{\infty} \sum_{l=0}^{\infty} a_n{}^l \frac{e^{-ik_n}}{r} P_l(\cos\theta) = e^{ik_I r \cos\theta} \qquad (253)$$

It can be shown that the $a_n{}^l$ must therefore be chosen so that

$$\begin{aligned} a_n{}^l &= 0 \qquad (n \neq I) \\ a_I{}^l &= (-1)^{l+1}(2l + 1)/2ik_I \end{aligned} \qquad (254)$$

That is, there can be no ingoing waves at $r = \infty$ corresponding to states of the oscillator other than the initial state. The coefficient $b_j{}^l$ of the outgoing wave $(e^{ik_j r}/r)P_l(\cos\theta)$ determines the contribution to the cross section for the transition $I \rightarrow j$ from the l'th partial wave. The total cross section for the transition $I \rightarrow j$ is a sum of contributions[48]

$$\sigma^l{}_{I\rightarrow j} = \pi(2l + 1)k_I{}^{-2}(k_j/k_I)|b_j{}^l/a_I{}^l + (-1)^l\delta_{Ij}|^2 \qquad (255)$$

rom the l'th partial wave; the total cross section is

$$Q_{I\rightarrow j} = \sum_{l=0}^{\infty} \sigma^l{}_{I\rightarrow j} \qquad (256)$$

In order to obtain the coefficients $b_j{}^l$, the set of coupled differential equations, eq 248, must be solved. For each value of l, a number of states must be included for the index n in $G_n{}^l(r)$. Trial and error are required to determine if enough states have been included. When a further increase does not lead to calculated changes in the cross section $\sigma^l{}_{I\rightarrow j}$, the cross section may be assumed to be exact. In cases of physical interest, somewhere between 10 and 20 values of n may be required[18] to calculate $\sigma^l{}_{I\rightarrow j}$, and then l must be summed from 0 to ∞. In practice, the latter summation is truncated when $\sigma^l{}_{I\rightarrow j}$ becomes small for large l. In typical cases of physical interest, several hundred values of l may have to be included and several hundred sets of perhaps 20 coupled differential equations must therefore be solved in order to calculate $Q_{I\rightarrow j}$ at one incident energy (*i.e.*, one value of k_I).

2. The "Modified Wave Number" Approximation (MWNA)

The MWNA was developed by Takayanagi[47] as an approximate method for solving the large number of equations involved in the breathing sphere model. A rigorous calculation requires an exact solution of eq 248 several hundred times, once for each significant value of l. At very large l, $\sigma^l{}_{I\rightarrow j}$ falls off rapidly with increasing l. In the MWNA it is assumed that the major contribution to the scattering is limited to a small region of r, over which $V'(r,R)$ varies rapidly with r, but $l(l + 1)/r^2$ is relatively constant. This is a reasonably good statement of the actual situation, as may be seen from section III.A, where it is shown that L (the range over which the potential varies) is roughly $^1/_{17.5}$ of the molecular diameter r_0. Therefore, for purposes of solving eq 248, the term $l(l + 1)/r^2$ may be replaced by the constant $l(l + 1)/r_*{}^2$, where r_* is the classical distance of closest approach. With this approximation, eq 248 takes the simpler form

$$\left[\frac{\partial^2}{\partial r^2} + \tilde{k}_j{}^2\right]G_j{}^l(r) - \sum_{n=0}^{\infty} \langle j| V'(R,r)|n\rangle G_n{}^l(r) = 0 \qquad (257)$$

and the modified wave number $\tilde{k}_j$ is defined by

$$\tilde{k}_j{}^2 = k_j{}^2 - l(l + 1)/r_*{}^2 \qquad (258)$$

Equation 257 is essentially identical with the equation one obtains for the wave function in a one-dimensional calculation, and the two solutions must be proportional. Let the equation for a one-dimensional treatment (*cf.* eq 123) be written as

$$\left[\frac{d^2}{dr^2} + k_j{}^2\right]F_j(r) - \sum_{n=0}^{\infty} \langle j| V'(R,r)|n\rangle F_n(r) = 0 \qquad (259)$$

which is solved subject to the asymptotic conditions as $r \rightarrow \infty$, such that

$$F_j(r) \sim e^{-ik_I r}\delta_{Ij} + B_j e^{ik_j r} \qquad (260)$$

This differs from eq 252 in that $a_I{}^l$, from eq 254, is not equal to unity. Therefore, it may be concluded that the proportionality factor relating $F_j(r)$ to $G_j{}^l(r)$ is simply $a_I{}^l$. Aside from this factor, the two functions are the same provided $\tilde{k}_j$ in eq 257 is equal to k_j in eq 259. This may be put in a different way if a dimensionless collision energy is defined as

$$\epsilon = \frac{(\hbar^2 k_I{}^2/2\tilde{m})}{h\nu} \qquad (261)$$

Then

$$G_j{}^l(\epsilon + \epsilon_*{}^l) = a_I{}^l F_j(\epsilon) \qquad (262)$$

where

$$\epsilon_*{}^l = \frac{\hbar^2 l(l + 1)}{2\tilde{m} r_*{}^2(h\nu)} \qquad (263)$$

In the one-dimensional treatment, a transition probability is calculated from the expression

$$P_{I\rightarrow j} = (k_j/k_I)|B_j|^2 \qquad (264)$$

Since $b_j{}^l$ [corresponding to total energy $(\epsilon - \epsilon_*{}^l)$] is equal to $a_I{}^l$ times B_j (corresponding to incident kinetic energy ϵ), it follows from eq 255 that for $j \neq I$

$$\sigma^l{}_{I\rightarrow j}(\epsilon + \epsilon_*{}^l) = \pi(2l + 1)k_I{}^{-2}P_{I\rightarrow j}(\epsilon) \qquad (265)$$

Thus $\sigma^l{}_{I\rightarrow j}$ for kinetic energy $\epsilon + \epsilon_*{}^l$ is proportional to $P_{I\rightarrow j}$ for energy ϵ. This may be written as

$$\sigma^l{}_{I\rightarrow j}(\epsilon) = \pi(2l + 1)k_I{}^{-2}P_{I\rightarrow j}(\epsilon - \epsilon_*{}^l) \qquad (266)$$

so that $\sigma^l{}_{I\rightarrow j}(\epsilon)$ is proportional to $P_{I\rightarrow j}(\epsilon - \epsilon_*{}^l)$. To evaluate the total cross section, eq 256 must be used. In view of the large number of angular momenta involved, the sum may be changed to an integral by multiplying each term in the sum by $\Delta l = 1$. The result is (for $I \neq j$)

$$Q_{I\to j}(\epsilon) = \int_0^{l_{\max}} \pi(2l + 1)k_I^{-2}P_{I\to j}(\epsilon - \epsilon_*^{\,l})\,\mathrm{d}l \quad (267)$$

The upper limit is $l_{\max}$, where $\epsilon_*^{\,l_{\max}} = \epsilon$.

Instead of regarding l as the independent variable, $(\epsilon - \epsilon_*^{\,l})$ = "ξ" may be regarded as the variable of integration. Using $\mathrm{d}\xi = -(\hbar^2/2\tilde{m})(r_*^{\,2}h\nu)^{-1}(2l + 1)\,\mathrm{d}l$, it follows that

$$Q_{I\to j}(\epsilon) = \frac{\pi r_*^{\,2}}{\epsilon}\int_0^{\epsilon} P_{I\to j}(\xi)\,\mathrm{d}\xi \quad (268)$$

If the average probability $\bar{P}_{I\to j}$ is defined as

$$\bar{P}_{I\to j}(\epsilon) = \frac{1}{\epsilon}\int_0^{\epsilon} P_{I\to 1}(\xi)\,\mathrm{d}\xi \quad (269)$$

eq 268 then takes the form (for $j \neq I$)

$$Q_{I\to j}(\epsilon) = \pi r_*^{\,2}\bar{P}_{I\to j}(\epsilon) \quad (270)$$

Thus, if the one-dimensional function $P_{I\to j}(\xi)$ is known, the three-dimensional breathing sphere cross section can be calculated from eq 270. Because eq 269 involves an integral of the one-dimensional probabilities over a wide range of energies, it is clear that any resonances or sharp variations of $P_{I\to j}(\xi)$ will be smoothed out in the calculation of $Q_{I\to j}(\epsilon)$. This was illustrated in the hard-sphere potential MWNA calculations of Mies and Shuler,[48] who used the one-dimensional probabilities of Zwanzig and Shuler.[50]

3. *Exact Solution*

An exact solution of the breathing sphere problem (eq 248) was performed numerically on a computer by Marriot[51] for a model representing CO–CO collisions. As pointed out previously, this procedure requires solving a set of coupled equations for each value of l at every collision energy. Usually, several hundred values of l contribute significantly to the total cross section. The general behavior of $\sigma^l_{I\to j}(\epsilon)$ *vs.* l is that $\sigma^l_{I\to j}$ rises from nearly zero at $l = 0$ to a maximum, and then falls off rapidly at high l to become negligible. At collision energies of roughly 2.5, 7.5, and 12.5 $h\nu$, the maxima in $\sigma^l_{0\to 1}$ are reached at $l \cong 40$, 60, and 80, respectively. The important range of $\sigma^l_{0\to 1}$ goes up to $l = 100$, 180, and 300, at these respective energies. The exact results are very similar to what one would predict from the MWNA. Examination of eq 266 shows that as l increases, $(2l + 1)$ increases and $P_{I\to j}(\epsilon - \epsilon_*^{\,l})$ decreases. A maximum in $\sigma^l_{I\to j}$ is reached at values of l in fairly good agreement with the exact results. The calculation of Marriot[51] serves as an interesting exact result for the breathing sphere model. However, it would have been much simpler to solve the problem for $l = 0$ and apply the MWNA; the results would have been almost as accurate.

4. *Application of the Landau–Widom–Shin Procedure to the Breathing Sphere Model*

Shin[49] applied the Landau–Widom–Shin procedure of section V.D to the breathing sphere model. First, Shin[49] modified the earlier Landau[43]–Widom[44]–Shin[45] procedure by performing an approximate evaluation of the perturbation integral, eq 234, including the preexponential factors. Shin did this by taking certain slowly varying functions out of the integral sign and evaluating them at the classical distance of closest approach. In certain ways, this is analogous to the MWNA approach. With this approximation, Shin[49] was able to solve eq 248 to the first-order distorted wave approximation, using the WKB wave functions to evaluate the perturbation integral. The functional form be obtained for $\sigma^l_{I\to j}(\epsilon)$ *vs.* l is very similar to that obtained by Marriot[51] at low collision energies. The total cross sections $Q_{I\to j}(\epsilon)$ are within a factor of 2 of those obtained using the MWNA with the one-dimensional probabilities calculated from Shin's procedure. This lends further support for the use of the MWNA in the breathing sphere calculations. It may be concluded that if the very approximate breathing sphere model is to be used at all, it may just as well be coupled with the MWNA to simplify the ensuing equations with minimal error. (Note: this is not exactly what Shin concludes. He apparently believes that factors of 2 are significant in this kind of calculation.)

VI. Comparison with Experiment

A. RELATION BETWEEN RELAXATION TIME AND TRANSITION PROBABILITIES[4]

In order to relate an experimental measurement to a theoretical transition probability, a kinetic analysis must be performed. Herzfeld[4] presents a clear exposition of this for several important special cases. In an experiment, a gas is rapidly disturbed causing a nonequilibrium distribution of vibrational states. The disturbance is terminated, and collisions bring about a spontaneous return (relaxation) to an equilibrium distribution. The translational and rotational degrees of freedom relax rapidly compared to vibrational excitation. Therefore, one may treat the vibrational relaxation as occurring in a gas that is in thermal equilibrium with respect to all other degrees of freedom.

At moderate temperatures, for most diatomic molecules, the equilibrium populations of excited states are small. For example, in O_2 at room temperature, about 99.9% of the molecules are in the ground vibrational state, 0.1% in the first excited state, 0.0001% in the second excited state, etc. Therefore, in studying vibrational relaxation of such a system, it is sufficient to use a two-state model. The instantaneous populations of states 0 and 1 are denoted n_0 and n_1, respectively, and the reactions considered are

$$n_0 + n_0 \underset{k_{10}}{\overset{k_{01}}{\rightleftarrows}} n_0 + n_1 \quad (271)$$

At equilibrium, the concentrations n_0^* and n_1^* are related by

$$\frac{n_1^*}{n_0^*} = e^{-(\epsilon_1 - \epsilon_0)/kT} = e^{-\theta_v/T} \quad (272)$$

By balancing the forward and backward rates of reaction at equilibrium, it is found that

$$\frac{k_{10}}{k_{01}} = \frac{n_0^*}{n_1^*} = e^{\theta_v/T} \quad (273)$$

In a nonequilibrium situation, where n_1 is made different from n_1^* by external perturbation, the rate of change of population of n_1 is given by

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(50) R. Zwanzig and K. Shuler, *J. Chem. Phys.*, **33**, 1778 (1960).

(51) R. Marriot, *Proc. Phys. Soc.*, **83**, 159 (1964).

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} = k_{01}n_0^2 - k_{10}n_1n_0 \tag{274}$$

If $n_0 \gg n_1$, n_0 can be considered as a constant, and the first-order rate constants may be defined by $k'_{01} = k_{01}n_0$ and $k'_{10} = k_{10}n_0$. Under these conditions eq 274 may be integrated, the final result being

$$(n_1(t) - n_1^*) = (n_1(0) - n_1^*)\exp\{-(k'_{01} + k'_{10})t\} \tag{275}$$

where $n_1(t)$ is the instantaneous value of n_1 at time t. Thus, the deviation from equilibrium of the population of the first excited state relaxes exponentially as

$$\Delta n_1(t) = \Delta n_1(0)e^{-t/\tau} \tag{276}$$

where $\Delta n_1 = n_1 - n_1^*$ and $\tau = (k'_{10} + k'_{10})^{-1}$. As $t \rightarrow \infty$, $\Delta n_1(t)$ approaches 0.

If the relaxation time τ is measured experimentally, the rate constant for deexcitation can be calculated from

$$k'_{10} = [\tau(1 + e^{-\theta_v/T})]^{-1} \tag{277}$$

The rate constant k_{10}' can be written as

$$k_{10}' = k_{10}n_0 = \langle P_{10}\rangle Cn_0 \tag{278}$$

where C is the rate constant for bimolecular collisions, and $\langle P_{10}\rangle$ is the average transition probability for $1 \rightarrow 0$ in a single collision. Therefore

$$\langle P_{10}\rangle = [Cn_0\tau(1 + e^{-\theta_v/T})]^{-1} \tag{279}$$

The reciprocal of the average transition probability per collision is the average number of collisions, Z_{10}, required for transfer of 1 quantum of energy. Thus

$$Z_{10} = \langle P_{10}\rangle^{-1} \tag{280}$$

This two-state model should only be applied for $n_0^* \gg n_1^*$, which implies that $\theta_v \gg T$. Therefore, the term $e^{-\theta_v/T}$ is very small.

At higher temperatures, where many vibrational states are substantially populated, a more general treatment is required. Landau and Teller[4,8] were able to show that if the first-order (FOPA or FODWA) transition probabilities are used

$$k_{j+1,j} = (j + 1)k_{10} \tag{281}$$

$$k_{j,j+1} = (j + 1)k_{01} = (j + 1)k_{10}e^{\theta_v/T} \tag{282}$$

and transitions to nonadjacent states do not occur. The equations giving the rates of change of the n_i are

$$\begin{aligned}
\partial n_0/\partial t &= -k'_{01}n_0 + k_{10}n_1 \\
\partial n_1/\partial t &= -k'_{12}n_1 - k'_{10}n_1 + k'_{21}n_2 + k'_{01}n_0 \\
&\ \ \vdots \\
\partial n_j/\partial t &= -k'_{j,j+1}n_j - k'_{j,j-1}n_j + k'_{j+1,j}n_{j+1} + k'_{j-1,j}n_{j-1}
\end{aligned} \tag{283}$$

and it is assumed that the total number of excited molecules is small compared to the number in the ground state so that n_0 may be considered as constant. The instantaneous amount of energy in all the excited states is

$$E = h\nu \sum_{j=1}^{\infty} jn_j \tag{284}$$

and this varies with time according to a relaxation equation

$$\frac{\partial E}{\partial t} = \frac{(E - E^*)}{\tau} \tag{285}$$

The value of E at thermal equilibrium is E^*, and

$$\tau = (k'_{10} - k'_{01})^{-1} \tag{286}$$

Thus

$$\langle P_{10}\rangle = [Cn_0\tau(1 - e^{-\theta_v/T})]^{-1} \tag{287}$$

for this model.

It should be noted that $\langle P_{10}\rangle$ is given by a function of τ which is different from that obtained using the two-state model. Thus, when several vibrational states are excited, the determination of transition probabilities from experimental relaxation times is not a trivial matter. For very high temperatures, where many excited states are substantially populated, careful attention must be paid to the physical significance of the measured relaxation time, and what approximations are used to calculate transition probabilities from the data.

B. CORRELATIONS OF EXPERIMENTAL DATA

It is not the intent of this article to critically review the experimental data on vibrational relaxation. It is hoped that this will be done in the near future by someone more competent in this area than the authors of this review. We shall merely be content to summarize some of the existing results.[36,40,52] There is a considerable amount of scatter in much of these data, and in some cases earlier results, obtained from gases that probably contained impurities, have been excluded. The results are given in Figure 22 where only an average of the scattered data obtained by discarding apparently dubious results and roughly drawing a curve through the remainder is presented. It is doubtful that the quality of the data justifies a more careful analysis. The dashed portions of the curves are felt to be much more uncertain than the solid lines. It will be noted that the magnitudes of the probabilities are in inverse order with the magnitudes of vibrational frequencies. The vibrational temperatures $\theta_v = h\nu/k$ are 3340, 3070, 2230, 310, 470, and 310°K, for N_2, CO, O_2, Cl_2, Br_2, and I_2, respectively.

C. COMPARISON OF THEORY AND EXPERIMENT

It is not a simple matter to compare theory with experiment because the important potential parameter L in the potential $e^{-z/L}$ is not very well known. Parker,[10,40] and Benson and Berend[36] adjusted this parameter to obtain a best fit of their theories to experiment for each substance. They were each able to obtain good fits of their respective theories to the data. The values of L obtained for each substance are summarized in Table VI.

It is impossible to determine whether the choice of the potential parameters is physically significant because all errors in the theory are compensated by the adjustable potential parameter. For example, neglect of anharmonicity leads to an error in $\langle P_{1\rightarrow 0}\rangle$ of from 10 to 100. Both Parker and Benson and Berend neglected this correction factor (*cf.* section III.B) and adjusted L to compensate for approximations in the theory. Thus, it is impossible to draw any conclusions as to the valid-

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(52) R. C. Millikan and D. R. White, *J. Chem. Phys.*, 39, 98 (1963).

ity of the theory from the work of these authors. Furthermore, at the higher temperatures, where $\langle P_{1\rightarrow 0}\rangle$ becomes as large as 0.01, first-order approximations cannot be justified at the most probable velocity for energy transfer. The assumption $\langle P_{1\rightarrow 0}\rangle = \Delta E/h\nu$ is not correct and must be replaced by eq 156.

In the "S-S-H" theory,[4,29] eq 222 is used, together with eq 171 for the potential parameters. This theory is *a priori* and can be tested by comparison with experiment. However, eq 222 should be multiplied by correction factors due to effects discovered since the original publication.[4,29] These include (a) correction for failure of the FODWA due to nonzero m, *i.e.*, $e^{-1.685m}$; (b) correction for anharmonicity of BC, $\mathfrak{F}$ from ref 27; (c) correction factor due to inadequacy of first-order approximation at high temperatures. (This may be approximately calculated from eq 165. If p is not too large, the effect is approximated by multiplying eq 222 by a factor e^{-p}, where p is calculated at v_m.) (d) It is assumed that the factor ε/kT in eq 222 adequately accounts for attractive forces. (e) A steric factor of ($^1/_3$) must be included (*cf.* section V.A). The results of a calculation are given in Table VII for $N_2 - N_2$ collisions, with θ = 3340°K, θ' = 5.60 × 10^6°K, and L = 0.221 Å. The correction for (c) was not made. The correction for (a) is simply 0.431, and the correction for (b) was estimated as roughly 0.07. Then the product of the three correction factors (a), (b), and (e) is simply ~0.01. Thus, eq 222 has simply been multiplied by 0.01. The values in Table VII lie about a factor of 10 lower than experiment which is all that can be expected from a crude calculation of this sort. This kind of theory correctly predicts that at any temperature, vibrational transition probabilities increase for the series N_2, CO, O_2, Cl_2, Br, I_2.

Table VI

Potential Parameter L (A°) in Vibrational Energy Transfer

Collision	*Parker*	*Benson and Berend*	*Eq 171*
N_2–N_2	0.25	0.27	0.21
CO–CO	0.25	0.25	0.21
O_2–O_2	0.26	0.26	0.20
Cl_2–Cl_2	0.28	0.30	0.23
Br_2–Br_2	0.32	0.32	0.24
I_2–I_2	0.38	0.37	0.29

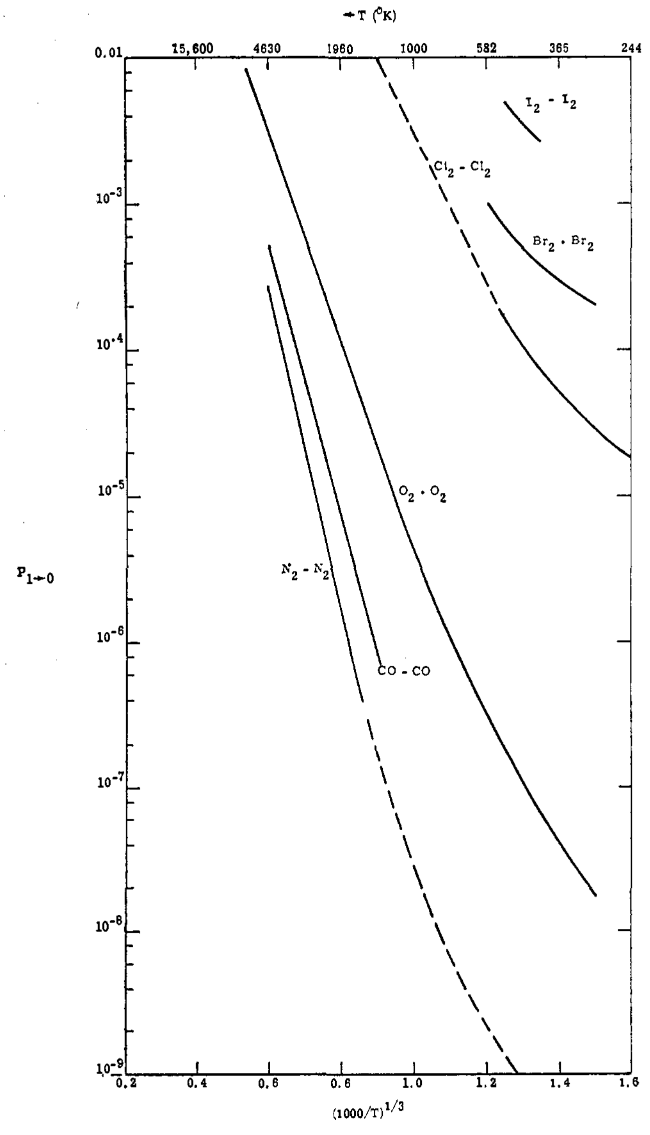

Figure 22. Summary of experimental data on vibrational relaxation.

VII. Vibrational–Vibrational Energy Transfer in Diatomic–Diatomic Collisions

A. SEMICLASSICAL FORMULATION OF THE PROBLEM

1. The Collision Model[29,53]

The calculations of vibrational–vibrational energy transfer between two diatomic molecules are based on the collinear collision model shown in Figure 23. The distance between centers of mass of AB and CD is $\mathfrak{x}$, and the internuclear distances are $\mathfrak{y}_1$ and $\mathfrak{y}_2$, respectively. The vibrational amplitudes measured from equilibrium are $\tilde{Y}_1$ and $\tilde{Y}_2$, which is analogous to the A + BC problem. The intermolecular potential is assumed to be a function of the distance between the center atoms of the molecules, $\mathfrak{x} - \gamma_1\mathfrak{y}_1 - \gamma_2\mathfrak{y}_2$, where $\gamma_1 = m_A/(m_A + m_B)$ and $\gamma_2 = m_D/(m_C + m_D)$. If the potential is assumed to be an exponential function of this distance, the potential may be written in the form

$$V'_1(\tilde{X},\tilde{Y}_1,\tilde{Y}_2) = A''e^{-\bar{X}/L}e^{\gamma_1\bar{Y}_1/L}e^{\gamma_2\bar{Y}_2/L} \qquad (288)$$

in analogy to eq 8 and 21, with $\tilde{X} = \mathfrak{x} - \mathfrak{x}_t$. In a semiclassical calculation for which energy is not conserved, A'' may be approximated by the incident energy E_0. Rapp and Sharp[12,53] also used another potential

$$V_2' = E_0 \operatorname{csch}^2 (k\tilde{X} + \xi)e^{\gamma_1\bar{Y}_1/L}e^{\gamma_2\tilde{Y}_2/L} \qquad (289)$$

for certain calculations. A best fit of eq 289 to 288 was obtained for $k = \pi/8L$ and $\operatorname{csch}^2 \xi = 1$. The two potentials are physically very similar.

In the semiclassical calculation, it is assumed that the vibrational amplitudes are small, and so the classical trajectory

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(53) D. Rapp and P. E. Golden, *J. Chem. Phys.*, 40, 573, 5123 (1964); D. Rapp, *ibid.*, 43, 316 (1965).

Table VII

Calculated $\langle P_{1\to 0}\rangle$ from a Modified "S–S–H" Calculation

Temp, °K	$\langle P_{1\to 0}\rangle_{\text{calcd}}$
4000	1.2×10^{-5}
2000	2.9×10^{-7}
1000	3.6×10^{-9}
500	2.0×10^{-11}
300	4.8×10^{-13}

$\tilde{X}(t)$ can be calculated from the classical equations of motion with $\tilde{Y}_1 \cong \tilde{Y}_2 \cong 0$. The result of this calculation for the potential V_1' is eq 13. For potential V_2', the result is[12]

$$\operatorname{csch}^2(k\tilde{X} + \xi) = \operatorname{sech}(2kv_0t) \tag{290}$$

For either potential, these results are used to convert $V'H(\tilde{X},\tilde{Y}_1,\tilde{Y}_2)$ to $V'(t,\tilde{Y}_1,\tilde{Y}_2)$, which in turn is used in a time-dependent quantum mechanical treatment of the oscillators. This potential may be written in the form

$$V'(t,\tilde{Y}_1,\tilde{Y}_2) = E_0A(t)B(\tilde{Y}_1,\tilde{Y}_2) \tag{291}$$

where $B(\tilde{Y}_1,\tilde{Y}_2) = e^{\gamma_1\tilde{Y}_1/L}e^{\gamma_2\tilde{Y}_2/L}$, and $A(t)$ is given by $\operatorname{sech}^2(v_0t/2L)$ for potential V_1' and $\operatorname{sech}(2kv_0t)$ for V_2'.

The Hamiltonian for the two oscillators, including the time-dependent coupling perturbation, may be written as

$$\mathcal{H} = \mathcal{H}^{(\mathrm{AB})}(\tilde{Y}_1) + \mathcal{H}^{(\mathrm{CD})}(\tilde{Y}_2) + V'(t,\tilde{Y}_1,\tilde{Y}_2) \tag{292}$$

where $\mathcal{H}^{(\mathrm{AB})}(\tilde{Y}_1)$ and $\mathcal{H}^{(\mathrm{CD})}(\tilde{Y}_2)$ are the Hamiltonians for the AB and CD molecules, respectively. The total wave function for the system of two oscillators is expanded in terms of the individual harmonic oscillator wave functions $H_j^{(\mathrm{AB})}(\tilde{Y}_1)$ and $H_n^{(\mathrm{CD})}(\tilde{Y}_2)$

$$\Psi = \sum_j\sum_n c_{jn}(t)H_j^{(\mathrm{AB})}(\tilde{Y}_1)H_n^{(\mathrm{CD})}(\tilde{Y}_2)e^{-i\omega_jt}e^{-i\Omega_nt} \tag{293}$$

where $\omega_j = (j + {}^1/_2)\omega^{(\mathrm{AB})}$ and $\Omega_n = (n + {}^1/_2)\omega^{(\mathrm{CD})}$.

When eq 293, 292, and 291 are substituted in the time-dependent Schroedinger equation

$$\mathcal{H}\Psi = \hbar i(\partial\Psi/\partial t) \tag{294}$$

and the result is multiplied by $H_r^{(\mathrm{AB})}(\tilde{Y}_1)H_s^{(\mathrm{CD})}(\tilde{Y}_2)$ and integrated over $\mathrm{d}\tilde{Y}_1\mathrm{d}\tilde{Y}_2$, the following equation is obtained

$$\mathrm{d}c_{rs}/\mathrm{d}t = (\hbar i)^{-1}E_0A(t)\sum_j\sum_n B_{rs,jn}e^{i\omega_{rj}t}e^{i\Omega_{sn}t}c_{jn}(t) \tag{295}$$

where $\omega_{rj} = \omega_r - \omega_j$, $\Omega_{sn} = \Omega_s - \Omega_n$, and

$$B_{rs,jn} = \iint H_r^{(\mathrm{AB})}(\tilde{Y}_1)H_s^{(\mathrm{CD})}(\tilde{Y}_2) \times B(\tilde{Y}_1,\tilde{Y}_2)H_j^{(\mathrm{AB})}(\tilde{Y}_1)H_n^{(\mathrm{CD})}(\tilde{Y}_2)\,\mathrm{d}\tilde{Y}_1\mathrm{d}\tilde{Y}_2 \tag{296}$$

If the oscillators AB and CD are initially in states I_1 and I_2' respectively, then the initial condition is

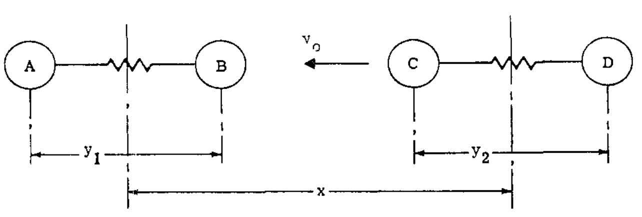

Figure 23. Collision model for AB + CD collisions. The distance between centers of mass is $\tilde{x}$ and the internuclear distances are $\tilde{y}_1$ and $\tilde{y}_2$.

$$c_{jn}(-\infty) = \delta_{jI_1}\delta_{nI_2} \tag{297}$$

The probability of the system ending up with AB in state r and CD in state s is

$$P_{I_1I_2\to rs} = |c_{rs}(\infty)|^2 \tag{298}$$

2. *Two-State Approximation at Exact Resonance*

Rapp and Golden[53] treated the resonant exchange process

$$\mathrm{AB(1) + AB(0) \longrightarrow AB(0) + AB(1)} \tag{299}$$

by assuming that only two terms in the expansion eq 293 need be considered, these corresponding to the initial and final states in eq 299. Thus, they set all coefficients in eq 293 equal to zero, except $c_{10}(t)$ and $c_{01}(t)$. In this case, eq 295 simplify to a set of only two coupled equations. If eq 289 is used for the interaction potential, a solution can be obtained in closed form, subject to the initial conditions $|c_{10}(-\infty)| = 1$, $c_{01}(-\infty) = 0$. The result is

$$|c_{10}(\infty)|^2 = \cos^2\left\{(E_0/\hbar)B_{01,10}\int_{-\infty}^{\infty}\operatorname{sech}(2kv_0t)\,\mathrm{d}t\right\}$$

$$|c_{01}(\infty)|^2 = \sin^2\left\{(E_0/\hbar)B_{01,10}\int_{-\infty}^{\infty}\operatorname{sech}(2kv_0t)\,\mathrm{d}t\right\} \tag{300}$$

$$P_{10\to 01} = |c_{01}(\infty)|^2 = \sin^2\{\pi\tilde{m}v_0B_{01,10}/4\hbar k\} \tag{301}$$

The matrix element $B_{01,10}$ is

$$B_{01,10} = \int_{-\infty}^{\infty} H_1(\tilde{Y}_1)e^{\gamma\bar{Y}_1/L}H_0(\tilde{Y}_1)\,\mathrm{d}\tilde{Y}_1 \times \int_{-\infty}^{\infty} H_0(\tilde{Y}_2)e^{\gamma\bar{Y}_2/L}H_1(\tilde{Y}_2)\,\mathrm{d}\tilde{Y}_2 \tag{302}$$

$$= \left\{\int H_1(\tilde{Y})e^{\gamma\tilde{Y}/L}H_0(\tilde{Y})\,\mathrm{d}\tilde{Y}\right\}^2 \tag{303}$$

$$\cong \hbar\gamma^2/2\omega\mu L^2 \tag{304}$$

where μ and f are the reduced mass and force constant of the oscillator, respectively.

According to eq 301, the probability of exchange of a quantum between two identical molecules varies sinusoidally with collision velocity. At low velocities, $P_{10\to 01}$ is small, and increases to unity with increasing velocity. When the velocity is increased further, the symmetrical nature of the interaction causes the probability to flow back to the initial oscillator. Thus, at high collision velocities, the quantum of vibrational energy tends to pass back and forth between the oscillators. If $L \cong 0.2$ Å and $\tilde{m} \cong 10$ amu

$$P_{10\to 01} \cong \sin^2[(5 \times 10^{-7})v_0] \tag{305}$$

with v_0 in cm/sec. If this is averaged over a normalized velocity distribution (*cf.* eq 208 and 206), the result is approximately

$$\langle P_{10\to 01}\rangle \cong 4 \times 10^{-6}T \tag{306}$$

provided that $5 \times 10^{-7}v_0 \ll 1$ over the range of significant velocities.

3. *Two-State Approximation for a Near-Resonance*

In the process

$$\mathrm{AB(1) + CD(0) \longrightarrow AB(0) + CD(1)} \tag{307}$$

there is a nonzero ΔE of interconversion of vibrational and translational energy. If the vibrational frequencies of AB and CD are not very different, the energy levels of the total system AB + CD will tend to be grouped together, with the lowest pair being states (1,0) and (0,1). The next higher group will be three states (2,0), (1,1), and (0,2), which, in the case of real molecules, are so far removed in energy that they will not be substantially populated, except at high collision velocities. Thus, the two-state approximation may be applied to this case as well as the case of exact resonance, and eq 295 again contain only two coefficients.

If eq 289 is used for the interaction potential, these equations can be solved in closed form,[53] and the result is

$$P_{10\rightarrow 01} = \sin^2\{\pi\tilde{m}v_0B_{01,10}/4\hbar k\}\ \mathrm{sech}^2\{\pi(\Delta E)/4\hbar kv_0\} \quad (308)$$

The argument of the sine function is the same as in eq 301 for the resonant case. Thus, the sech² function may be considered as a correction factor to the resonance expression when the frequencies of AB and CD are not identical. As $\Delta E \rightarrow 0$, the sech² function → 1, and, as ΔE increases, the sech² function becomes small. Thus, nonresonance tends to decrease the transition probability for exchange of vibrational energy. If the ΔE is expressed as a difference in wave numbers, $\Delta E = hc(\Delta\bar{\nu})$, where $\bar{\nu}$ is the vibrational frequency of a molecule measured in cm^{-1}, then eq 308 becomes

$$P_{10\rightarrow 01} \cong \sin^2(5\times 10^{-7}v_0)\ \mathrm{sech}^2\{740(\Delta\bar{\nu})/v_0\} \quad (309)$$

For a fixed value of $\Delta\bar{\nu}$, an increase in v_0 tends to make the sech² function → 1. Thus, for nonresonant process, the probability approaches a resonant probability at high velocities but becomes small at low velocities. If a velocity average of eq 309 is taken, the result is[53]

$$\langle P_{10\rightarrow 01}\rangle \cong 4\times 10^{-6}T\ \mathrm{sech}^2\{0.17(\Delta\nu)/T^{1/2}\} \quad (310)$$

A plot of this function for various values of $\Delta\bar{\nu}$ is given in Figure 24 along with some experimental values for vibrational–vibrational exchange for several processes.

4. Multistate Expansion Procedure[54]

Zelechow, Rapp, and Sharp[54] solved eq 295 without truncating the expansion, but with certain restrictive conditions. The restrictive conditions include: (1) that the interaction potential may be expanded in $\tilde{Y}$ with higher terms neglected, and (2) that the classical trajectory corresponding to the initial velocity may be used to convert the $\tilde{X}$-dependent part of the potential to a function of t. In effect, the problem becomes an extension of the Kerner–Treanor semiclassical method for the case of diatomic–diatomic collisions. In addition, only the symmetrical case of an AB–BA collision is considered.

The interaction potential is assumed to be of the form given by eq 288 and $\gamma_1 = \gamma_2 = \gamma$ since the collision is symmetrical. It is assumed that this may be approximated by the expansion

$$V'(\tilde{X},\tilde{Y}_1,\tilde{Y}_2) \cong A''e^{-\tilde{X}/L}[1 + \gamma(\tilde{Y}_1 + \tilde{Y}_2)/L + \gamma^2(\tilde{Y}_1 + \tilde{Y}_2)^2/2L^2 + \ldots] \quad (311)$$

Since the factor 1 in the brackets in eq 311 does not contain any oscillator coordinates, it does not contribute to vibrational transitions and may be neglected. The terms linear in $\tilde{Y}_1$ or $\tilde{Y}_2$ are responsible for vibrational transitions in one oscillator or the other, and the cross term $\tilde{Y}_1\tilde{Y}_2$ produces simultaneous transitions in both oscillators.

Equation 294 may be written in the specific form

$$\{-(\hbar^2/2\mu)[(\partial^2/\partial\tilde{Y}_1^2) + (\partial^2/\partial\tilde{Y}_2^2)] + {}^1/_2f(\tilde{Y}_1^2 + \tilde{Y}_2^2) + F(t)[\tilde{Y}_1 + \tilde{Y}_2 + (\gamma/2L)(\tilde{Y}_1 + \tilde{Y}_2)^2]\}\Psi = \hbar i(\partial\Psi/\partial t) \quad (312)$$

in which

$$F(t) = (\gamma A''/L)e^{-X(t)/L} = (\gamma A''/L)\,\mathrm{sech}^2(v_0t/2L) \quad (313)$$

Since the time-dependent coupling of the oscillators is symmetric, normal coordinates may be defined as

$$\begin{aligned}\tilde{Y}_S &= (\tilde{Y}_1 + \tilde{Y}_2)/\sqrt{2}\\ \tilde{Y}_A &= (\tilde{Y}_1 - \tilde{Y}_2)/\sqrt{2}\end{aligned} \quad (314)$$

With this transformation, the Schroedinger equation becomes

$$\{-(\hbar^2/2\mu)[(\partial^2/\partial Y_S^2) + (\partial^2/\partial\tilde{Y}_A^2)] + {}^1/_2[f + f'(t)]\tilde{Y}_S^2 + \tfrac{1}{2}f\tilde{Y}_A^2 + 2^{1/2}F(t)\tilde{Y}_S\}\Psi = \hbar i(\partial\Psi/\partial t) \quad (315)$$

in which $f'(t) = (2\gamma/L)F(t)$. This equation may be separated by writing $\Psi = \psi_s(\tilde{Y}_s)\psi_A(\tilde{Y}_A)$; the result is two differential equations, one for each normal mode.

$$\{-(\hbar^2/2\mu)(\partial^2/\partial\tilde{Y}_s^2) + {}^1/_2[f + f'(t)]\tilde{Y}_s^2 + \sqrt{2}F(t)\tilde{Y}_s\}\psi_s = \hbar i(\partial\psi_s/\partial t) \quad (316)$$

$$\{(-\hbar^2/2\mu)(\partial^2/\partial\tilde{Y}_A^2) + {}^1/_2f\tilde{Y}_A^2\}\psi_A = \hbar i(\partial\psi_A/\partial t) \quad (317)$$

Thus, $\psi_A(\tilde{Y}_A)$ is simply a wave function for a free unperturbed harmonic oscillator.

From eq 316 it can be seen that $\psi_s(\tilde{Y}_s)$ is the wave function of a harmonic oscillator with a time-dependent force constant $f_s(t) = f + f'(t)$ that is driven by a time-dependent force $2^{1/2}F(t)$. Under most cases of physical interest, $f \gg f'(t)$,

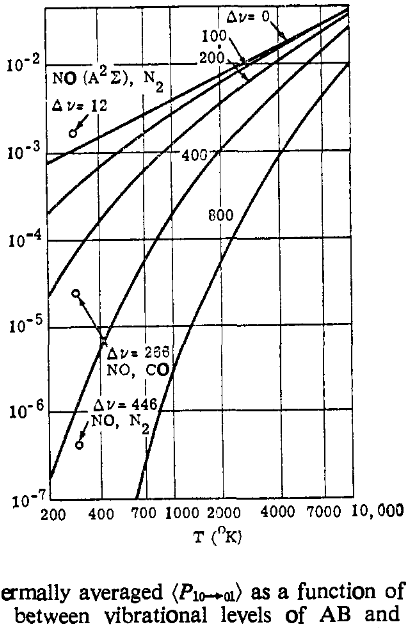

Figure 24. Thermally averaged $\langle P_{10\rightarrow 01}\rangle$ as a function of T with the nonresonance between vibrational levels of AB and CD as a parameter. The points are experimental data and the curves are predicted by eq 310.

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(54) A. Zelechow, D. Rapp, and T. E. Sharp, *J. Chem. Phys.*, 48, 286 (1968).

and the time-varying frequency $\omega_s(t) = (f_s(t)/\mu)^{1/2}$ is nearly constant, differing only slightly from $\omega_0 = (f/\mu)^{1/2}$. The general solution of eq 317 is a linear combination of harmonic oscillator wave functions.

If it can be assumed that $f \gg f'(t)$, eq 316 becomes essentially identical with eq 56. The general solution of this equation can therefore be put in the form of eq 66 and 67, a linear combination of the Kerner–Treanor functions. The general solution for Ψ is therefore a product of these two linear combinations of eigenfunctions, for the symmetric and antisymmetric normal modes. Whatever linear combinations correspond to the initial state ($t = -\infty$), they must persist after the collision is over at $t = +\infty$. In the limits as $t \rightarrow \pm\infty$, the perturbation $F(t) \rightarrow 0$, and the Kerner–Treanor functions become ordinary harmonic oscillator wave functions. Therefore the problem consists of three parts. First, one must transform the initial state from individual oscillator functions into terms of the normal mode wave functions. Secondly, the time-history of the normal mode wave functions from $t = -\infty$ to $t = +\infty$ is evaluated. Finally, the inverse transformation is performed to re-express the wave function at $t = +\infty$ in terms of the individual oscillator functions.

A function of the form $H_{n_1}(\tilde{Y}_1)H_{n_2}(\tilde{Y}_2)$ is written as (n_1,n_2), and a function $H_{n_s}(\tilde{Y}_s)H_{n_A}(\tilde{Y}_n)$ is written as $[n_s,n_A]$. At $t = -\infty$, the initial state is one particular function of the former type. It can be shown[54] that any function (n_1,n_2) can be expressed as a linear combintion of only those functions $[n_s,n_A]$ for which $n_s + n_A = n_1 + n_2 = n$. There are $n + 1$ such functions that would be degenerate in the absence of the perturbation. The functions (n_1,n_2) and $[n_s,n_A]$ may be ordered as

$$\begin{aligned} \varphi_j^{(n)} &= (n - j + 1,\ j - 1) \qquad n = n_1 + n_2 \\ \Phi_j^{(n)} &= [n - j + 1,\ j - 1] \qquad n = n_s + n_A \end{aligned} \tag{318}$$

Then the transformation between such functions with common values of n is written as

$$\Phi_k^{(n)} = \sum_{j=1}^{n+1} C_{kj}^{(n)} \varphi_j^{(n)} \tag{319}$$

A closed form expression for $C_{kj}^{(n)}$ is given in ref 54, where the inverse matrix $[C_{kj}^{(n)}]^{-1}$ is also evaluated. The initial wave function may be denoted $\varphi_I^{(n)}$. This is expressed as

$$\Psi(t = -\infty) = \varphi_I^{(n)} = \sum_{j=1}^{n+1} [C_{Ij}^{(n)}]^{-1}\Phi_j^{(n)} = \sum_{j=1}^{n+1} C_{jI}^{(n)}\Phi_j^{(n)} \tag{320}$$

The time dependence of the wave function may now be obtained in terms of the time dependence of the solutions of eq 316 and 317 for initial states $\Phi_1^{(n)}, \Phi_2^{(n)}, \ldots, \Phi_{n+1}^{(n)}$. The solution of eq 316 and 317 corresponding to the initial state $\Phi_g^{(n)}$ is[54]

$$\sum_{j=0}^{\infty} b_{n-g+1,j}(t)\Phi_g^{(j+g-1)} \times \exp\left\{-i\int_{-\infty}^{t} [\Omega_j(t') + \omega_{g-1}(t')]\,\mathrm{d}t'\right\} \tag{321}$$

where $\omega_g = (g + {}^1/_2)\omega_0$, $\Omega_j = (j + {}^1/_2)\Omega_s$, and $b_{gj}(t)$ is defined[15] in eq 71. Therefore, as $t \rightarrow +\infty$, the total wave function becomes

$$\Psi(t = \infty) = \sum_{g=1}^{n+1}\sum_{j=0}^{\infty} C_{g1}^{(n)} b_{n-g+1,j}(\infty)\Phi_g^{(j+g-1)} \times \exp\left\{-i\int_{-\infty}^{\infty} [\Omega_j(t) - \omega_{g-1}(t)]\,\mathrm{d}t\right\} \tag{322}$$

The functions $\Phi_g^{(j+g-1)}$ are now transformed back into φ functions, with $j + g - 1$ defined as "m." Thus

$$\Phi_g^{(m)} = \sum_{k=1}^{m+1} C_{gk}^{(m)} \varphi_k^{(m)} \tag{323}$$

and

$$\Psi(t = \infty) = \sum_{j=0}^{\infty}\sum_{k=1}^{m+1}\sum_{g=1}^{n+1} C_{gI}^{(n)} C_{gk}^{(m)} b_{n-g+1,j}(\infty)\varphi_k^{(m)} \times \exp\left\{-i\int_{-\infty}^{\infty} [\Omega_j(t) - \omega_{g-1}(t)]\,\mathrm{d}t\right\} \tag{324}$$

This has the general form

$$\Psi(t = \infty) = \sum_{m=0}^{\infty}\sum_{k=1}^{m+1} S_k^{(m)} \varphi_k^{(m)} \tag{325}$$

Thus, the probability of the transition $(n - I + 1, I - 1) \rightarrow (m - k + 1, k - 1)$ is

$$P_{(n-I+1,I-1)\rightarrow(m-k+1,k-1)} = |S_k^{(m)}|^2 \tag{326}$$

In the actual calculation,[54] it was assumed that $f \gg f'(t)$ in order to evaluate $\Omega_j(t)$. The final result is a general expression for the probability of a transition from state $(n - I + 1, I - 1)$ to state $(m - k + 1, k - 1)$. The expression is rather complicated[54] and will not be reproduced here. It represents the extension of the Kerner–Treanor procedure to diatomic–diatomic collisions subject to the assumption that $\gg f'(t)$. Under most conditions of physical interest, this is a good approximation. The general result is given in terms of two parameters $\bar{\eta}_0$ and ρ. The first parameter $\bar{\eta}_0$ is the energy that would be stored in a classical oscillator at $t = \infty$ if the oscillator were subjected to the force $-\sqrt{2}F(t)$ and was initially at rest with zero displacement. Since there is a factor of $\sqrt{2}$ here, $\bar{\eta}_0$ is simply twice η_0 (see eq 74). For the exponential potential

$$\bar{\eta}_0 = 2\eta_0 = [4\pi^2\omega_0^2L^2(m^2/\mu)\gamma^2/\hbar\omega_0]\,\mathrm{csch}^2(\pi\omega L/v_0) \tag{327}$$

The parameter ρ is given by

$$\rho = 2\tilde{m}v_0\gamma^2/L\omega_0\mu \tag{328}$$

It was found that the magnitude of $\bar{\eta}_0$ determines the magnitude of transitions with change of energy level ($m \neq n$), while ρ determines the distributions of magnitudes of transitions to the degenerate states of any energy level. For the special case of both oscillators initially unexcited, it is found that

$$P_{(0,0)\rightarrow(m-k+1,k-1)} = [\bar{\eta}_0 e^{-\bar{\eta}_0}/m!]\,|C_{1k}^{(m)}|^2 \tag{329}$$

A closed form expression for $C_{jk}^{(m)}$ is given in ref 54. The total probability of excitation to energy level m, including all $m + 1$ degenerate states, is

$$\sum_{k=1}^{m+1} P_{(0,0)\rightarrow(m-k+1,k-1)} = \bar{\eta}_0^{\,m} e^{-\bar{\eta}_0}/m! \tag{330}$$

which is of the same form as eq 76.

For a system initially in the state (1,0), the probabilities

Table VIII

Transition Probabilities $P(\varphi_1^{(1)} \rightarrow \varphi_k^{(m)})$ from the Initial State (1,0)

Final state $\varphi_k^{(m)}$	Final state $(m - k + 1,\ k - 1)$	*Exact probability*	*Approx probability for $\bar{\eta}_0 \ll 1$*
$\varphi_1^{(0)}$	(0,0)	$\bar{\eta}_0 e^{-\bar{\eta}_0/2}$	$\bar{\eta}_0/2$
$\varphi_1^{(1)}$	(1,0)	$\frac{e^{-\bar{\eta}_0}}{4}\{2 - 2\bar{\eta}_0 + \bar{\eta}_0^2 + 2(1 - \bar{\eta}_0)\cos\rho\}$	$(1 + \cos\rho)/2 = \cos^2\rho/2$
$\varphi_2^{(1)}$	(0,1)	$\frac{e^{-\bar{\eta}_0}}{4}\{2 - 2\bar{\eta}_0 + \bar{\eta}_0^2 - 2(1 - \bar{\eta}_0)\cos\rho\}$	$(1 - \sin\rho)/2 = \sin^2\rho/2$
$\varphi_1^{(2)}$	(2,0)	$\frac{e^{-\bar{\eta}_0}}{16}\{8\bar{\eta}_0 - 4\bar{\eta}_0^2 + \bar{\eta}_0^3 - 4\bar{\eta}_0(\bar{\eta}_0 - 2)\cos\rho\}$	$\bar{\eta}_0(1 + \cos\rho)/2$
$\varphi_2^{(2)}$	(1,1)	$\frac{e^{-\bar{\eta}_0}}{8}(4\bar{\epsilon}_0 - 4\bar{\eta}_0^2 + \bar{\eta}_0^3)$	$\bar{\eta}_0/2$
$\varphi_3^{(2)}$	(0,2)	$\frac{e^{-\bar{\eta}_0}}{16}\{8\bar{\eta}_0 - 4\bar{\eta}_0^2 + \bar{\eta}_0^3 + 4\bar{\eta}_0(\bar{\eta}_0 - 2)\cos\rho\}$	$\bar{\eta}_0(1 - \cos\rho)/2$
$\varphi_2^{(3)}$	(3,0)	$\frac{e^{-\bar{\eta}_0}}{96}\{18\bar{\eta}_0^2 - 6\bar{\eta}_0^3 + \bar{\eta}_0^4 - 6\bar{\eta}_0^2(\bar{\eta}_0 - 3)\cos\rho\}$	$\bar{\eta}_0^2(1 + \cos\rho)(3/16)$
$\varphi_3^{(3)}$	(2,1)	$\frac{e^{-\bar{\eta}^0}}{96}\{30\bar{\eta}_0^2 - 18\bar{\eta}_0^3 + 3\bar{\eta}_0^4 - 6\bar{\eta}_0^2(\bar{\eta}_0 - 3)\cos\rho\}$	$\frac{\bar{\eta}_0^2}{16}(5 + 3\cos\rho)$
$\varphi_4^{(3)}$	(1,2)	$\frac{e^{-\bar{\eta}_0}}{32}\{10\bar{\eta}_0^2 - 6\bar{\eta}_0^3 + \bar{\eta}_0^4 + 2\bar{\eta}_0^2(\bar{\eta}_0 - 3)\cos\rho\}$	$\frac{\bar{\eta}_0^2}{16}(5 - 3\cos\rho)$
$\varphi_4^{(3)}$	(0,3)	$\frac{e^{-\bar{\eta}_0}}{96}\{18\bar{\eta}_0^2 - 6\bar{\eta}_0^3 + \bar{\eta}_0^4 + 6\bar{\eta}_0^2(\bar{\eta}_0 - 3)\cos\rho\}$	$\frac{\bar{\eta}_0^2}{16}(3 - 3\cos\rho)$

for going to various final states are listed in Table VIII. It should be particularly noted that the probability of the transition (1,0) → (0,0) is very closely related to $P_{1\rightarrow 0}$ for a single oscillator in eq 76. If $\bar{\eta}_0 \ll 1$, the two results become identical since $\bar{\eta}_0/2 = \eta_0$. When $\bar{\eta}_0 \ll 1$, so that transitions to states with $m \neq n = 1$ have small probabilities, only the two final states (1,0) and (0,1) need be considered. These probabilities are (for $\bar{\eta}_0 \ll 1$)

$$\begin{aligned} P_{(1,0)\rightarrow(1,0)} &\cong \cos^2(\rho/2) \\ P_{(1,0)\rightarrow(0,1)} &\cong \sin^2(\rho/2) \end{aligned} \tag{331}$$

which is exactly the same as the two-state result, eq 300.

If the initial state is $(n,0)$ the probability of a transition to final state $(n - k + 1, k - 1)$ for $\bar{\eta}_0 \ll 1$ is given by

$$P_{[(n,0)\rightarrow(n-k+1,k-1)]} \cong \left\{\frac{n!}{(n - k + 1)!(k - 1)!}\right\} \times \cos^{2(n-k+1)}(\rho/2)\sin^{2(k-1)}(\rho/2) \tag{332}$$

This shows that for moderately low velocities, where ρ is small, the transition probabilities decrease as k increases.

For most molecules in the range of interesting velocities, ρ is of the order of 0.1–1.0 and varies slowly with v_0, whereas $\bar{\eta}_0$ may range from very small values to about unity and is sensitive to the value of v_0. For the initial state $(n - I + 1, I - 1) = \varphi_I^{(n)}$, the dependence of various transition probabilities on collision velocity will be as follows. At low velocities, $\bar{\eta}_0 \ll 1$, ρ may be of the order of $\sim$0.1, and only transitions to final states $\varphi_k^{(n)}$ with the same total energy are important. The dominant transitions will be to states $\varphi_{I\pm 1}^{(n)}$. As the collision velocity is increased to moderate values, transitions to final states $\varphi_k^{(n)}$ with $k \neq I \pm 1$ will become increasingly important as ρ increases. However, $\bar{\eta}_0$ will still be small, and transitions to states $\varphi_k^{(m)}$ with $m \neq n$ will be negligible. At high velocities, $\bar{\eta}_0$ will become sufficiently large so that transitions to states $\varphi_k^{(n\pm 1)}$ will become important. At very high velocities, transitions to all possible final states $\varphi_k^{(m)}$ will occur.

5. *Effect of the Long-Range Dipole Potential*

In resonant vibrational–vibrational energy transfer, the initial and final states have the same energy. Therefore, if the FOPA is applied, $\omega_{jI} + \Omega_{Ij}$ in eq 295 will be zero, and even a weak perturbation $B_{jI,Ij}$ acting for a sufficiently long time can lead to large transition probabilities. In the calculations described in sections VII.A.1–4, the strong repulsive potential at small distances has been chosen as the perturbation. This perturbation is proportional to the collision energy $E_0 = {}^1/_2\bar{m}v_0^2$. Because eq 295 requires an integration over $dt = d\bar{x}/v_0$, the result for $P_{Ij\rightarrow jI}$ will be proportional to E_0. Thus, as has been demonstrated in the previous subsection, the probability of resonant vibrational–vibrational energy exchange (due to a repulsive potential) is proportional to E_0 for small transition probabilities. On the other hand, if there is a long-range potential leading to a nonzero $B_{jI,Ij}$ that is independent of v_0, then eq 295 would lead to a $P_{Ij\rightarrow jI}$ that is inversely proportional to E_0. Since the perturbation is independent of E_0, the longer the perturbation acts, the greater is the transition probability.

Mahan[55] considered an approximate model for such a potential. When two diatomic molecules are separated by a large distance $\bar{x}$ compared to their bond distances $\bar{y}_1$ and $\bar{y}_2$, one term in the long-range attractive potential is due to the

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(55) B. H. Mahan, *J. Chem. Phys.*, 46, 98 (1967).

change in dipole moment with bond distance. For heteronuclear molecules, the potential has the form

$$V' = (\mathrm{d}D/\mathrm{d}\tilde{Y})^2(\tilde{Y}_1\tilde{Y}_2/\tilde{x}^3)[-2\cos\theta_1\cos\theta_2 + \sin\theta_1\sin\theta_2\cos(\varphi_2 - \varphi_1)] \quad (333)$$

where $\tilde{Y}_i = \tilde{y}_i - \tilde{y}_i^{(\mathrm{eq})}$, $(\mathrm{d}D/\mathrm{d}\tilde{Y})$ is the rate of change of dipole moment with bond distance (at the equilibrium separation), and θ_i, φ_i define the orientation of molecule i with respect to the line joining the centers of mass of the two molecules. This is a long-range potential which is independent of E_0, but dependent on the oscillator coordinates. Therefore, it can (in principle) lead to large transition probabilities for sufficiently slow collisions. This potential should only be used for $\tilde{x} \gg \tilde{y}$. For homonuclear molecules, $\mathrm{d}D/\mathrm{d}\tilde{Y} = 0$, and the potential term is negligible.

Mahan deals with the process

$$\mathrm{AB}(n_1,J_1,m_1) + \mathrm{AB}(n_2,J_2,m_2) \longrightarrow \mathrm{AB}(n_1',J_1',m_1') + \mathrm{AB}(n_2',J',m_2') \quad (334)$$

where n, J, and m are the vibrational, rotational, and magnetic quantum numbers, respectively. According to eq 296, one must evaluate the matrix element

$$B_{n_1'n_2',n_1n_2} = \langle (n_1',J_1',m_1')(n_2',J_2',m_2')|B| \times (n_1,J_1,m_1)(n_2,J_2,m_2)\rangle \quad (335)$$

and use the classical trajectory to convert $\tilde{x}$ to t. Each wave function (n, J, m) is a product of a vibrational wave function H_n times a rotational function $Y_J^m(\theta,\varphi)$. Integration over the vibrational coordinates leads to the result $(\mathrm{d}D/\mathrm{d}\tilde{Y})^2(\tilde{Y}_{n_1',n_1})(Y_{n_2',n_2})$, and the matrix elements vanish unless $n_1' - n_1 = \pm 1$ and $n_2' - n_2 = \pm 1$. Integration over the rotational coordinates leads to the selection rules $J_i' - J_i = \pm 1$; $m_i' - m_i = 0, \pm 1$; and i can be 1 or 2. It is also found that the matrix element is zero unless $|J_1 - J_2| = 1$, but there are no restrictions on $m_1 - m_2$. The final result for the matrix element depends on m_1 and m_2 in a complicated way. However, it can be shown that if J is the greater of J_1, J_2, then the root-mean-square value (averaged over all m_1, m_2) of the matrix element for large J and $|J_1 - J_2| = 1$ is

$$E_0A(t)B_{n_1'n_2',n_1n_2} = 6^{-1/2}(\mathrm{d}D/\mathrm{d}\tilde{Y})^2\tilde{Y}_{n_1',n_1}Y_{n_2',n_2}[\tilde{x}(t)]^{-3} \quad (336)$$

The expression for $\tilde{Y}_{n',n}$ is given in eq 52. For the case considered by Mahan,[55] $n_1 = 2$, $n_1' = 1$, $n_2 = 0$, $n_2' = 1$, and

$$E_0A(t)B_{n_1'n_2',n_1n_2} = (2\sqrt{3})^{-1}(\mathrm{d}D/\mathrm{d}\tilde{Y})^2(\hbar/\omega\mu)[\tilde{x}(t)]^{-3} \quad (337)$$

Since the intermolecular potential (eq 333) is a good approximation only for large $\tilde{x}$, an appropriate collision model is one in which the AB molecule moves with velocity v_0 past the other AB molecule along a straight line with impact parameter b. The distance along this path is vt, and the distance between molecules is $\tilde{x} = [(vt)^2 + b^2]$. If b is large compared to a bond distance, the model should be reasonable. If $\mathrm{d}t$ is replaced by $v_0^{-1}(\tilde{x}^2 - b^2)^{-1/2}2\tilde{x}\,\mathrm{d}\tilde{x}$, and eq 337 is written with $\mathrm{E}_0A(t)B_{n_1'n_2',n_1n_2} = C[\tilde{x}(t)]^{-3}$, then eq 295 takes the form

$$P_{[(2,0)\rightarrow(1,1)]} = \frac{4C^2}{\hbar^2v_0^2}\left|\int_b^\infty \frac{\mathrm{d}\tilde{x}}{\tilde{x}^2(\tilde{x}^2 - b^2)^{1/2}}\right|^2 = \frac{4C^2}{\hbar^2v_0^2b^4} \quad (338)$$

for those collisions with $|J_1 - J_2| = 1$, averaged over m_1 and m_2. The value of C is

$$C = (2\sqrt{3})^{-1}(\mathrm{d}D/\mathrm{d}\tilde{Y})^2(\hbar/\omega\mu) \quad (339)$$

Mahan[55] has shown that for a molecule such as CO, C is numerically equal to about 6×10^{-39} cgs unit. At a velocity $v_0 = 8 \times 10^4$ cm/sec, eq 338 becomes

$$P_{[(2,0)\rightarrow(1,1)]} \cong 2/b^4 \quad (340)$$

with b in Å units. For values of b in the range 6–10 Å, the probabilities are in the range 10^{-3}–10^{-4}. For smaller impact parameters, it is difficult to evaluate what happens. Mahan assumes that the average probability is about $^1/_3$ (since there are three final states: (2,0), (1,1), and (0,2)) for close encounters with small b. Thus, he assumes $P(b) = {}^1/_3$ for the range $b = 0$ to $b = b_0$, where b_0 is the impact parameter required to make eq 338 give a probability of $^1/_3$. He then uses eq 338 for all impact parameters greater than b_0, and obtains a cross section

$$\sigma = (4\pi/\sqrt{3})(C/\hbar v_0) \quad (341)$$

that is inversely proportional to v_0.

For CO–CO collisions, $\sigma \cong 4 \times 10^{-11}/v_0$ in cgs units. However, the value of b_0 at $v_0 = 8 \times 10^4$ cm/sec is about 1.5 Å. It is extremely doubtful that eq 333 is at all reasonable for b less than about 6 Å. It seems more likely that for small values of b, eq 333 can be used for the approach to collision, but, once the molecules get in close, the repulsive forces take over and eq 341 becomes dubious.

The calculations described here refer to collisions for which $|J_1 - J_2| = 1$. Thus, the probabilities and cross sections so calculated should be multiplied by the fraction of collisions for which this condition holds. For CO at room temperature, the fraction is about 0.06. After multiplying eq 341 by this factor, Mahan[55] concludes that the (2,0) → (1,1) transition is about ten times faster by this process than by repulsive forces. We cannot accept this conclusion and would propose an alternate procedure in which eq 338 was used for $\infty > b \gtrsim 6$ Å, and the value of P at $b \cong 6$ Å is used for all b less than $\sim$6 Å. If this were done, it would be found that for CO–CO collisions σ would be about a factor of 50 less than that predicted by eq 341. This would make the transition probability due to the dipole force comparable to that produced by the repulsive forces.

It should be particularly emphasized that the average probability per collision due to the dipole forces decreases as the temperature increases, whereas the probability due to repulsive forces increases with temperature.

B. QUANTUM MECHANICAL CALCULATION

A formulation of the FODWA calculation of vibrational–vibrational energy transfer was given by Schwartz, Slawsky, and Herzfeld.[29] The results are essentially the same as that obtained in section VII.A for the case of small transition probabilities in the two-state approximation. It should be particularly noted that for a process of the type (1,0) → (0,1), there is no change in external collision velocity, and the semiclassical FOPA becomes essentially the same as the FODWA. That is, the average velocity, before and after transition, is equal to the initial velocity.

Riley and Kuppermann[56] have set up the quantum mechanical equations corresponding to the same collision model as in section VII.A.1. The Schroedinger equation that is anal-

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(56) M. E. Riley and A. Kuppermann, *Chem. Phys. Letters*, **1**, 537 (1968).

ogous to eq 87, but that corresponds to *two* diatomic molecules, is

$$\left\{-\frac{\hbar^2}{2}\left[\frac{1}{\mu_1}\frac{\partial^2}{\partial \tilde{y}_1{}^2}+\frac{1}{\mu_2}\frac{\partial^2}{\partial \tilde{y}_2{}^2}+\frac{1}{\tilde{m}}\frac{\partial^2}{\partial \tilde{x}^2}\right]+ V(\tilde{x},\tilde{y}_1,\tilde{x}_2)\right\}\psi(\tilde{x},\tilde{y}_1,\tilde{y}_2) = E\psi(\tilde{x},\tilde{y}_1,\tilde{y}_2) \quad (342)$$

The total wave function may be expanded in terms of the eigenstates of the unperturbed system (neglecting the intermolecular interaction). Riley and Kuppermann[56] present a very brief description of their procedure for obtaining an exact solution of this problem. Their results are analogous to those of Secrest and Johnson[18] for atom–diatomic collisions. A number of calculations are presented for H_2–H_2 collisions with L chosen as 0.212 Å in the interaction potential eq 288. These results may be compared with the results of ref 54.

According to eq 331, at low collision velocities

$$P_{[(1,0)\rightarrow(0,1)]}, = \sin^2 \rho/2 \cong \rho^2/4 = (\tilde{m}v_0{}^2/2\hbar\omega)(2\tilde{m}\gamma^4\hbar/2L^2\omega\mu^2) \quad (343)$$

For H_2–H_2 collisions with $L \cong 0.2$ Å, the factor $(2\tilde{m}\gamma^4\hbar/2L^2\omega\mu^2) = 0.88$. Thus, one would predict that for low collision velocities the probability of the (1,0) → (0,1) transition would be 0.88ϵ, where $\epsilon = \tilde{m}v_0{}^2/2\hbar\omega$. Riley and Kuppermann[56] find the probability to be about 0.95ϵ. It is surprising that the agreement is not even better. When the initial state is (2,0), Riley and Kuppermann find that the (1,1) final state is greatly favored over the (0,2) final state. Their results are in good agreement with eq 332 from the semiclassical procedure.

In the case of V–V–T energy transfer, the results of Riley and Kuppermann[56] are expected to be much more accurate than those of Zelechow, Rapp, and Sharp[54] because the latter utilize the semiclassical procedure with the *initial* velocity. The relation between these results should be analogous to the relation between those of Secrest and Johnson[18] and Treanor.[15]

Riley and Kuppermann[56] point out that the FODWA works quite well for the (1,0) → (0,1) and (2,0) → (1,1) transitions. Each of these involves single quantum jumps for each oscillator. For the (2,0) → (0,2) process, however, the first-order calculation is too small by a factor of ~100. This is due simply to the fact that it occurs primarily by successive 1-quantum jumps in a single collision. Thus, (2,0) → (1,1) → 0,2) is the preferential route. Even for small transition probabilities, a second-order calculation is required for the correct order of magnitude.