

## The Interchange of Translational and Vibrational Energy in an Asymmetric Molecular Potential Field

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They found that in this phase in both  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$  the depolarization ratios were essentially those of an ordered cubic crystal. The necessary condition that this be the case is that the symmetry axes of the cubic crystal remain intact or be only slightly perturbed. The model described is the only disordered structure in which this is the case. It is not the case, for example, in any model involving free rotation of the ammonium ions.

The infra-red spectra are also consistent with this model. It has been pointed out previously that the effect of coupling of neighboring ammonium ions is very small but that  $\nu_4$  is very sensitive to small displacements of the halide ions. The precise equilibrium position of each halide ion certainly depends on the orientation of the ammonium ions surrounding it. An example of such a displacement of the halide ions from their position in a cubic lattice is the  $D_{4h}$  structure of Phase III (see Fig. 1) whereas a configuration in which they are not displaced is the  $T_d$  structure of Phase III of  $\text{NH}_4\text{Cl}$ . In the disordered model the halide ions would be displaced by intermediate amounts and since the displacements vary statistically we might expect shifts in  $\nu_4$  varying from zero to a maximum value approximately equal to the splitting of  $\nu_4$  in Phase III of  $\text{NH}_4\text{Br}$  since this structure clearly gives a maximum halide displacement.

X-ray data might provide a further check on this model. If it is correct the halide ions are statistically distributed about their mean lattice positions in Phase II and some indications of disorder should be discernible. In any case, it is clear that the  $\lambda$ -point transition between Phase III and Phase II does not involve free rotation and it seems likely that it is a simple order-disorder transformation in the equilibrium orientations of the ammonium ions.

## The Interchange of Translational and Vibrational Energy in an Asymmetric Molecular Potential Field\*

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Reflection coefficients are calculated for a matter wave in a parabolic channel and in a square channel, each channel closed at one end by a vertical plane tilted slightly from the normal to the axis of the channel. The number of collisions necessary to dissipate one quantum of vibrational energy is given in terms of  $\lambda = \tan\theta$ , where  $\theta$  is the angular deviation of the plane end from the normal to the axis of the channel. Comparison with the data from measurements on sound dispersion shows good agreement for  $\text{N}_2\text{O}$  and  $\text{CO}_2$ . The temperature dependence of the average probability of transition per collision is compared with data for  $\text{Cl}_2$  and a mixture of  $\text{Cl}_2$  and  $\text{CO}$ .

### I. INTRODUCTION

THE probability of exciting internal energy states of a molecule in a collision is a quantity of importance in several physico-chemical phenomena. The Lindemann theory of unimolecular reactions supposes that activation occurs by this mechanism and the relative rates of activation and dissociation of the excited molecule determine the apparent pressure dependence of the reaction.

The dispersion of sound in gases likewise is governed by the rate of exchange of energy between translational and internal degrees of freedom of the molecule. Anything which prevents the internal degrees of freedom from taking up their equilibrium share of the heat of compression of the sound wave will diminish the effective

specific heat of the gas and increase the velocity of sound. As the frequency is increased, a point is reached where the time required to establish temperature equilibrium is of the same order as the period of the sound wave. An increase of sound velocity with frequency is then observed. From experimental data on dispersion, the number of collisions required to dissipate one quantum of vibrational energy can be calculated.

This problem of energy exchange between various degrees of freedom has been reviewed by Oldenburg and Frost.<sup>1</sup> The present discussion will be restricted to interchange between vibrational and translational energy. The simplest case is the collision of an atom with a diatomic molecule. This process can be represented classically by the motion of a mass-point on the appropriate energy surface in the configuration space of the triatomic complex. The surface upon which the complex moves during the collision is the same as that considered in the activated complex theory of chemical

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<sup>1</sup> O. Oldenburg and A. Frost, *Chem. Rev.* **20**, 99 (1937).

reaction rates. In the case of a simple collision, however, there is not enough energy for the complex to reach the activated state and we consider only a surface consisting of a channel with a closed end. The point-mass representing the complex is reflected by the surface and returns along the channel through which it came, but not necessarily in its initial vibrational state. Irregularities in the channel will cause a change in the components of momentum parallel and perpendicular to the path of least potential energy, which we shall call briefly the reaction path. This change in the momentum components of the point-mass represents a change in vibrational energy of the system. Inspection of the potential energy surfaces which have been calculated<sup>2</sup> shows that as the complex approaches the barrier, the surface rises and becomes assymmetric about the reaction path. This assymetry seems to bear the primary responsibility for the change in the vibrational energy of the system.

In quantum mechanics, the point-mass is replaced by a wave packet moving in the potential energy field represented by the surface. A steady stream of such packets is best treated by considering its Fourier plane-wave components in each vibrational state separately. The progressive wave is diffracted by irregularities in the potential energy (analogous to variations of the refractive index in the optical case) and is reflected and diffracted by the closed end of the channel. A particularly simple mathematical treatment is possible when the surface can be idealized to consist of two or more sections in each of which explicit solutions of the Schrödinger equation can be found. Boundary conditions and continuity conditions at the junctions of the several regions permit the solutions to be expanded in terms of eigenfunctions that represent plane waves incident and reflected in the incoming channel. The expansion coefficients give the relative transition probabilities for excitation to the higher vibrational states. This is similar to the "sudden" approximation in the quantum theory of the collisions of elementary particles.<sup>3</sup> A different approximation, based upon analytic continuation of the eigenfunctions, has been used by Hirschfelder and Wigner<sup>4</sup> for a continuous potential energy surface. Golden and Peiser<sup>5</sup> use still a different approach.

The energy surfaces shown in Figs. 1 and 2 represent collisions of hard spheres, one of which has a vibrational degree of freedom. They are of the same general type as that discussed qualitatively by Gershinowitz.<sup>6</sup> Zener<sup>7</sup> has used a more elaborate model. In a hard-sphere model, when the closing surface is normal to the channel axis, the Schrödinger equation separates into two equa-

tions for motion parallel and normal to the reaction path, respectively, and no vibrational transitions are induced by collision. Detailed reasons for this will be evident in the mathematical treatment that follows. The simplest modification that produces transitions is to incline the closed end slightly from the normal to the channel axis, as illustrated in Fig. 2. As atom *A* approaches diatomic molecule *BC* along the line of centers, the vibrations of *BC* become perturbed, being reduced in amplitude if no excitation occurs. This is effectively an anharmonicity introduced during the collision which induces an exchange of energy between translational and vibrational degrees of freedom. As might be expected, the reduced amplitude available favors transitions to higher energy levels in the case of a harmonic oscillator.

The parameter  $\lambda$ , the cotangent of the angle made by the closed end and the channel axis, measures the intensity of the interaction during the collision. If the angle is small, perturbation begins at large intermolecular distances. This model, however, allows no separate adjustment of both the anharmonicity and the duration of the perturbation. Thus a short range highly anharmonic interaction would have much the same representation as a long range, weakly anharmonic perturbation. Consequently, this model cannot be expected to give a quantitative account of the data, but may indicate important qualitative features of the interaction.

Both square and parabolic channels have been used

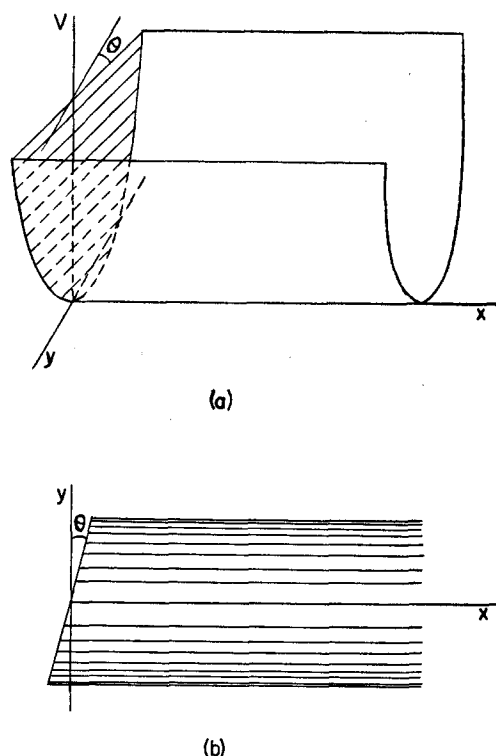


FIG. 1. The parabolic channel. (a)  $V(x)$  is infinite on the plane  $x = y \tan \theta$ , and is zero everywhere else. (b) Contour.

<sup>2</sup> Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), Chapter III.

<sup>3</sup> Cf. L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 207 ff.

<sup>4</sup> J. O. Hirschfelder and E. Wigner, *J. Chem. Phys.* **7**, 616 (1939).

<sup>5</sup> S. Golden and A. M. Peiser, *J. Chem. Phys.* **17**, 630 (1949).

<sup>6</sup> H. Gershinowitz, *J. Chem. Phys.* **5**, 54 (1937).

<sup>7</sup> C. Zener, *Phys. Rev.* **37**, 556 (1931).

to calculate reflection coefficients in detail. However, only the results from the parabolic channel will be used to interpret data.

## II. CALCULATION OF THE REFLECTION COEFFICIENTS

### The Parabolic Channel

The Schrödinger equation for the potential energy surface shown in Fig. 1 may be written

$$(-\hbar^2/2m)\nabla^2\psi + (k/2)y^2\psi = E\psi, \quad (1)$$

where  $\nabla^2$  is the two-dimensional Laplacian operator in rectangular coordinates. The solution to this equation is written in the form:

$$\psi_n = \sum_j [\exp(-ip_j x/\hbar)\delta_{nj} + R_{nj} \exp(ip_j x/\hbar)] H_j(\eta). \quad (2)$$

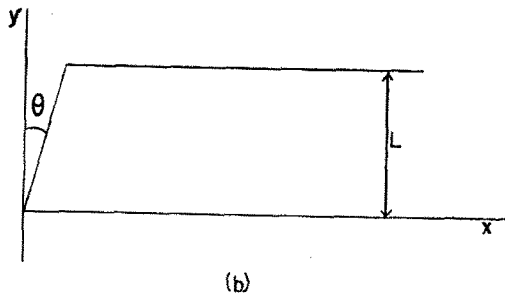
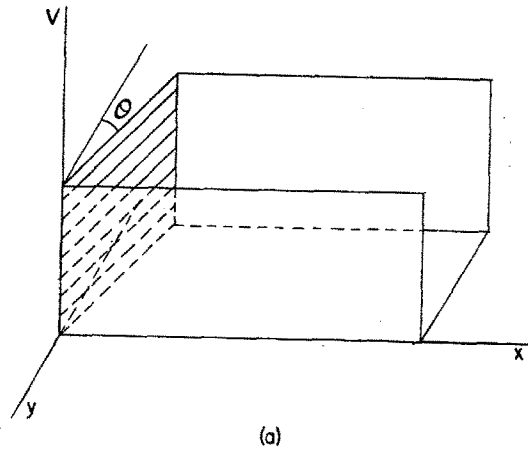


FIG. 2. The square channel. (a)  $V(x)$  is infinite on the plane  $x = y \tan \theta$ , and is zero everywhere else.  $V(y)$  is infinite on the planes  $y = 0$  and  $y = L$  and is zero in-between. (b) Contour.

This solution represents a system in the  $n$ th state incident upon the barrier with unit amplitude; the system is reflected from the barrier in various states,  $j$ , with the amplitudes  $R_{nj}$ . In this expression,  $H_j(\eta)$  is the normalized, weighted,  $j$ th Hermite polynomial;  $\beta = (mk/\hbar^2)^{1/2}$ ; and  $\eta = y\beta^{1/2}$ . The energy equation corresponding to this solution is

$$E/E_0 = r_j^2 + 2j + 1, \quad (3)$$

where  $E_0 = (\frac{1}{2})\hbar\nu_0$ ,  $p_j = r_j p$ , and  $p = (m\hbar\nu_0)^{1/2}$ .

The boundary condition requires that  $\psi_n = 0$ , when  $y = x/\tan\theta$ , that is, when  $\eta = \beta^{1/2}x/\tan\theta$ . Applying this condition and making the transformations:  $\lambda = \tan\theta$ ,  $\xi = \beta^{1/2}x/\lambda$ , Eq. (2) becomes

$$\sum_j [\exp(-ir_j\lambda\xi)\delta_{nj} + R_{nj} \exp(ir_j\lambda\xi)] H_j(\xi) = 0. \quad (4)$$

This equation must hold for all values of  $\xi$ .

The following expansions are then made:

$$\exp(-ir_j\lambda\xi) H_j(\xi) = \sum_k P_{jk} H_k(\xi) \quad (5)$$

$$\exp(ir_j\lambda\xi) H_j(\xi) = \sum_k Q_{jk} H_k(\xi), \quad (6)$$

where

$$P_{jk} = \int_{-\infty}^{\infty} \exp(-ir_j\lambda\xi) H_j(\xi) H_k(\xi) d\xi \quad (7)$$

$$Q_{jk} = P_{jk}^* = \int_{-\infty}^{\infty} \exp(ir_j\lambda\xi) H_j(\xi) H_k(\xi) d\xi. \quad (8)$$

Substitution of these expansions into Eq. (4) yields the result

$$\sum_j \sum_k [\delta_{nj} P_{jk} + R_{nj} Q_{jk}] H_k(\xi) = 0. \quad (9)$$

Setting the coefficient of each  $H_k(\xi)$  equal to zero, one obtains

$$P + RQ = 0, \quad (10)$$

where the equation has been written in matrix form. This equation immediately yields the formal solution:  $R = -PQ^{-1}$ . However, finding the inverse of  $Q$  is not a convenient method for evaluating the matrix elements of  $R$ .

The integrals  $P_{jk}$  and  $Q_{jk}$  can be evaluated explicitly; this is done in Appendix I. It is to be noted that  $P_{jk} = Q_{jk}^*$ , where the asterisk indicates the complex conjugate. The explicit form of  $Q_{jk}$  is

$$Q_{jk} = \left( \frac{j!k!}{2^{j+k}} \right)^{1/2} (ir_j\lambda)^{j+k} \times \exp[-(r_j\lambda/2)^2] \sum_{t=0}^{\infty} \frac{(-1)^t 2^t (r_j\lambda)^{-2t}}{t!(k-t)!(j-t)!}, \quad (11)$$

where the sum is from zero to the smaller of the values  $j$  or  $k$ .

Since there is no simple method of obtaining the inverse of a matrix such as  $Q$ , it will be convenient to use an alternate method to obtain approximate values of the  $R_{nj}$  when  $\lambda$  is small.

The exponential factor in the integrals  $P_{jk}$  and  $Q_{jk}$  is expanded before integrating and the resulting expression integrated term by term. This leads to an expansion of  $P$  and  $Q$  in powers of  $\lambda$  with matrix coefficients. The matrix  $R$  is also expanded in powers of

lambda with undetermined coefficients.

$$P = \sum_{n=0} P^{(n)} \lambda^n \quad (12a)$$

$$Q = \sum_{n=0} Q^{(n)} \lambda^n \quad (12b)$$

$$R = \sum_{n=0} R^{(n)} \lambda^n. \quad (12c)$$

Substituting these expansions in Eq. (10) yields:

$$\sum_n P^{(n)} \lambda^n + \sum_n \sum_s R^{(n)} Q^{(s)} \lambda^{n+s} = 0, \quad (13)$$

where

$$Q_{jk}^{(n)} = \frac{(ir_j)^n}{n!} \Phi_{jk}^{(n)}$$

$$P_{jk}^{(n)} = (-1)^n Q_{jk}^{(n)}$$

$$\Phi_{jk}^{(n)} = \int_{-\infty}^{\infty} \xi^n H_j(\xi) H_k(\xi) d\xi.$$

Again, Eq. (13) is an identity in lambda; consequently, the coefficient of each power of lambda must vanish. This gives the equation

$$P^{(n)} + \sum_s R^{(s)} Q^{(n-s)} = 0 \quad (14)$$

or the series of equations

$$\begin{aligned} P^{(0)} + R^{(0)} Q^{(0)} &= 0 \\ P^{(1)} + R^{(0)} Q^{(1)} + R^{(1)} Q^{(0)} &= 0 \\ P^{(2)} + R^{(0)} Q^{(2)} + R^{(1)} Q^{(1)} + R^{(2)} Q^{(0)} &= 0. \end{aligned} \quad (15)$$

Since  $P^{(0)} = Q^{(0)} = E$ , the unit matrix, we have immediately that  $R^{(0)} = -E$ . If this result is substituted in the second of Eqs. (15),  $R^{(1)}$  is determined.  $R^{(1)} = Q^{(1)} - P^{(1)}$ , or,  $R^{(1)} = 2Q^{(1)}$ . This procedure is repeated until the desired accuracy is obtained. Explicitly,

$$\begin{aligned} R_{jk}^{(0)} &= -\delta_{jk} \\ R_{jk}^{(1)} &= ir_j \sqrt{2} [j^{\frac{1}{2}} \delta_{j-1,k} + (j+1)^{\frac{1}{2}} \delta_{j+1,k}] \\ R_{jk}^{(2)} &= r_j \{ [j(j+1)^{\frac{1}{2}} r_{j-1} \delta_{j-2,k} \\ &\quad + [jr_{j-1} + (j+1)r_{j+1}] \delta_{jk} \\ &\quad + [(j+1)(j+2)^{\frac{1}{2}} r_{j+1} \delta_{j+2,k}] \}. \end{aligned} \quad (16)$$

These first three coefficients will be sufficient to give reflection coefficients correct to the power of  $\lambda^2$ .

The reflection coefficient is defined by the equation

$$\rho_{jk} = R_{jk} R_{jk}^* (r_k / r_j). \quad (17)$$

The value of  $\rho_{jk}$  is the probability that a system which strikes the barrier in the  $j$ th vibrational state will be reflected in the  $k$ th vibrational state. Conservation of matter as expressed by setting the probability current equal to zero—i.e.,

$$0 = \frac{\hbar}{2im} \left[ \psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right]$$

imposes the condition that  $\sum_k \rho_{jk} = 1$ .

Using the definition of the reflection coefficient, one obtains the expression

$$\rho_{jk} = \delta_{jk} + 2\lambda^2 r_k \{ jr_j \delta_{j-1,k} - [jr_{j-1} + (j+1)r_{j+1}] \delta_{jk} + (j+1)r_j \delta_{j+1,k} \}. \quad (18)$$

This form of  $\rho_{jk}$  can be shown to obey the summation condition. Also, it is readily shown that  $\rho_{jk} = \rho_{kj}$ .

Several remarks may be made concerning the reflection coefficient. It will be noted that there is a selection rule; the quantum number may change only by plus or minus one. Secondly, the diagonal terms de-

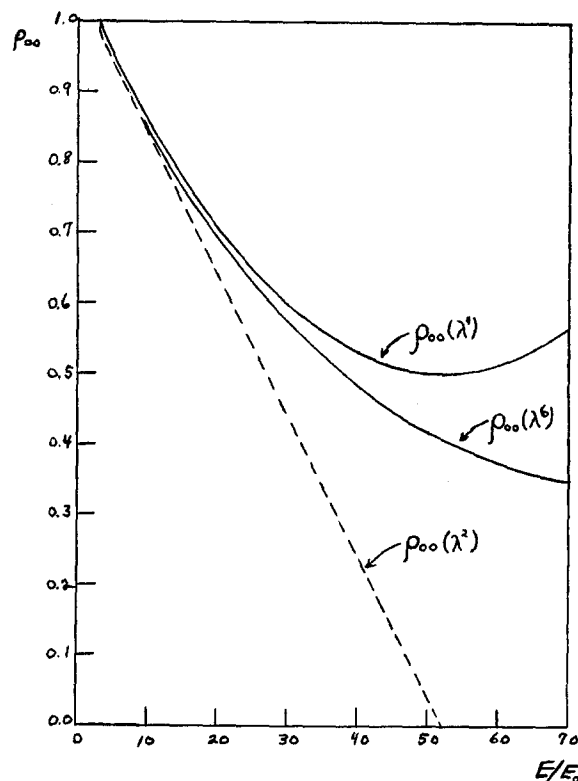


FIG. 3. Various approximations to  $\rho_{00}$ .

crease with increase in  $j$ , while the off-diagonal elements increase with increasing  $j$ . In other words, a system in a high vibrational state will have less chance of staying there than a system in a lower state. Furthermore, the off-diagonal elements are proportional to the product of the incident and reflected momenta; this indicates that the chance of a large change in the vibrational quantum number is small—a further confirmation of the selection rule. The ratio of the chance of jumping from  $j$  to  $j+1$ , to that for jumping from  $j$  to  $j-1$ , is  $(j+1)/j$ . This last result was obtained by Landau and Teller<sup>8</sup> by consideration of a perturbation energy which depends linearly on the coordinate of the vibration.

In Fig. 3 are plotted the curves for  $\rho_{00}$  corresponding to the first three approximations; that is, first including

<sup>8</sup> L. Landau and E. Teller as quoted by A. Eucken and H. Jaacke, *Zeits. f. physik. Chemie* **B30**, 96 (1935).

only the terms in  $\lambda^2$ , then adding the terms in  $\lambda^4$ , and finally adding the terms in  $\lambda^6$ . The various approximations diverge rapidly for large value of  $E/E_0$ , but lie closely together in the interesting range, 0–10 multiples of  $E/E_0$ . At very high energies, this approximation breaks down completely and another method must be employed. (See Appendix I.)

### The Square Channel

The solution of the Schrödinger equation in the square channel (Fig. 5) has the form

$$\psi_n = \sum_j [\delta_{nj} \exp(-ip_j x/\hbar) + R_{nj} \exp(ip_j x/\hbar)] \sin(\pi j y/L). \quad (19)$$

Again, the boundary condition requires that  $\psi_n = 0$  when  $y = x/\lambda$ , where, as before,  $\lambda = \tan\theta$ . Applying this condition and expanding in terms of  $\sin(k\pi x/L\lambda)$ , we are led again to the matrix equation (10), where now

$$P_{jk} = Q_{jk}^* = - \int_0^\pi \exp(-ir_j \lambda z) \sin jz \sin kz dz \quad (19)$$

and

$$z = \pi x/L\lambda; \quad E/E_0 = r_j^2 + j^2; \quad E_0 = \pi^2 \hbar^2/2mL^2$$

$$p_j = r_j \hbar; \quad p = \pi \hbar/L.$$

The reflection coefficient, expanded in powers of  $\lambda$ , is

$$\rho_{jk} = \left(1 - \frac{128\lambda^2}{\pi^2} j^2 r_j S_{jj}\right) \delta_{jk} + \frac{128\lambda^2 j^2 k^2 r_j r_k}{\pi^2 (j^2 - k^2)^4} [1 - (-1)^{j+k}] \Delta_{jk}, \quad (20)$$

where

$$S_{jj} = \sum_{m=0}^{\infty} m^2 r_m [1 - (-1)^{j+m}] \Delta_{jm} / (j^2 - m^2)^4 \quad (21)$$

and

$$\Delta_{jk} = 0 \quad \text{if } j = k; \quad \Delta_{jk} = 1 \quad \text{if } j \neq k.$$

This form for  $\rho_{jk}$  obeys the summation condition for  $j$  and  $k$ . The selection rule in this case allows only transitions between states of different symmetry. In addition, the resonance denominator effectively limits the transitions to those in which the quantum number changes by  $\pm 1$ . The general form for the reflection coefficient is much the same as for the parabolic case; however, the relative probability for an upward jump as compared to a downward jump does not have as simple a form as it did in the case of the parabolic channel. Figure 4 shows the variation of  $\rho_{jk}$  as a function of the energy ratio,  $E/E_0$ .

Because of the greater simplicity of the results and the more reasonable shape, only the results for the

parabolic channel will be used in discussing experimental data.

### III. THE AVERAGE PROBABILITY OF TRANSITION

The values of  $\rho_{jk}$  give the probability per collision for a system to leave the  $j$ th vibrational state and enter the  $k$ th vibrational state if the initial relative momentum is characterized by a given value of  $r_j$ . In order to calculate the average probability of transition per collision, the reflection coefficient must be multiplied by the number of collisions in the given velocity range and the resulting expression integrated over all possible values of the velocities.

The number of collisions between a molecule in state  $j$ , in the velocity range  $c_j, dc_j$ ; and all other molecules (of the first kind), in the velocity range  $c_1, dc_1$ , is given by the expression<sup>9</sup>

$$f_1 f_j g b d b d e d c_j d c_1, \quad (22)$$

where  $f_1$  is the distribution function for molecules of the first kind;  $f_j$  is the distribution function for molecules in the  $j$ th state;  $g$  is the relative velocity along the line of centers of the colliding molecules;  $b$  is an encounter variable which specifies the range of molecular interaction and which may depend upon  $g$ ;  $\epsilon_j$  is the

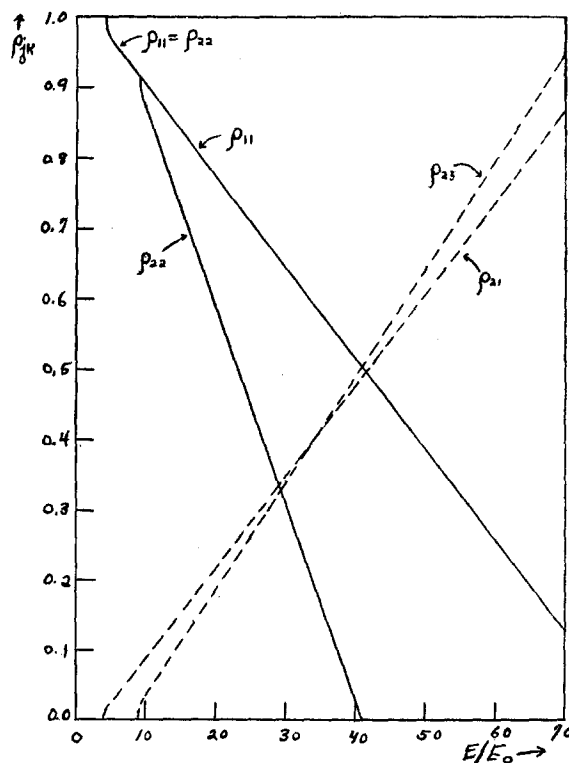


Fig. 4. Reflection coefficients as a function of the energy ratio (square channel).

<sup>9</sup> S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, London 1939), p. 61.

azimuth of the plane containing the orbit of the center of mass of the colliding system relative to a fixed plane of reference;  $\mathbf{c}_1$  and  $\mathbf{c}_j$  are the velocities of the two colliding molecules.

The total number of molecules per cubic centimeter going from state  $j$  to state  $k$  per second is:

$$\iiint \rho_{jk} f_1 f_j g b d b d \epsilon d \mathbf{c}_1 d \mathbf{c}_j. \quad (23)$$

The average probability per collision of leaving  $j$  and entering  $k$  is given by the expression:

$$\frac{\iiint \rho_{jk} f_1 f_j g b d b d \epsilon d \mathbf{c}_1 d \mathbf{c}_j}{\iiint f_1 f_j g b d b d \epsilon d \mathbf{c}_1 d \mathbf{c}_j}. \quad (24)$$

If the expression (24) is summed over all values of  $k$  except  $j$ , then the result is the average probability per collision of leaving state  $j$ . This quantity will be designated

$P_j$ .

$$P_j = \frac{\iiint (1 - \rho_{jj}) f_1 f_j g b d b d \epsilon d \mathbf{c}_1 d \mathbf{c}_j}{\iiint f_1 f_j g b d b d \epsilon d \mathbf{c}_1 d \mathbf{c}_j} \quad (25)$$

where the substitution  $\sum_{k \neq j} \rho_{jk} = 1 - \rho_{jj}$  has been made.

For the case of hard-sphere molecules,  $b$  does not depend upon  $g$ ; and, consequently, the integrations over  $b$  and  $\epsilon$  may be carried out immediately.† Since this integral occurs as a factor in both the numerator and the denominator, it cancels out and the equation becomes

$$P_j = \frac{\iint (1 - \rho_{jj}) f_1 f_j g d \mathbf{c}_1 d \mathbf{c}_j}{\iint f_1 f_j g d \mathbf{c}_1 d \mathbf{c}_j}. \quad (26)$$

The expressions for  $f_1$  and  $f_j$  are now substituted; since any numerical and normalizing factors will cancel out, only the factors involving  $c_1$  and  $c_j$  need be considered. The equation now becomes

$$P_j = \frac{\iint (1 - \rho_{jj}) \exp[-(m c_1^2 + m^* c_j^2)/2kT] g d \mathbf{c}_1 d \mathbf{c}_j}{\iint \exp[-(m c_1^2 + m^* c_j^2)/2kT] g d \mathbf{c}_1 d \mathbf{c}_j}, \quad (27)$$

where  $m$  is the mass of the impinging molecule, and  $m^*$  is the mass of the oscillator—i.e.,  $m^* = m_A + m_B$ , for a molecule  $A-B$ .

A change in variables is now effected;  $\mathbf{c}_1$  and  $\mathbf{c}_j$  are replaced by  $\mathbf{g}$  and  $\mathbf{G}$ , which are defined through the

relations

$$\begin{aligned} \mathbf{c}_1 &= \mathbf{G} - M_2 \mathbf{g} \\ \mathbf{c}_j &= \mathbf{G} + M_1 \mathbf{g} \\ g &= |\mathbf{g}|. \end{aligned}$$

Substitution into Eq. (27) yields

$$P_j = \frac{\iint (1 - \rho_{jj}) \exp[-m_0(G^2 + M_1 M_2 g^2)/2kT] g d \mathbf{g} d \mathbf{G}}{\iint \exp[-m_0(G^2 + M_1 M_2 g^2)/2kT] g d \mathbf{g} d \mathbf{G}} \quad (28)$$

where  $m_0 = m + m^*$ ,  $M_1 = m/(m + m^*)$ ,  $M_2 = m^*/(m + m^*)$ . Since  $\mathbf{g}$  is the relative velocity along the line of centers of the two colliding molecules, it is directly proportional to  $r_j$ , the velocity variable in the reflection coefficient. Since  $r_j$  and  $\mathbf{G}$  are independent, the latter variable may be integrated out in both the numerator and denominator. Furthermore, the orientation variables in the vector differential,  $d\mathbf{g}$ , can be integrated out; this leaves only the integration over the scalar

relative speed,  $g$ . Equation (28) reduces to

$$P_j = \frac{\int_0^\infty (1 - \rho_{jj}) \exp(-\mu g^2/2kT) g^3 dg}{\int_0^\infty \exp(-\mu g^2/2kT) g^3 dg}, \quad (29)$$

† For details of these integrations, see reference 9, p. 89 ff.

where  $\mu$  is the reduced mass of the colliding system— $\mu = mm^*/m_0$ .

The numerator and denominator are now transformed by substituting for  $g$  its equivalent in terms of  $r_j$ ;  $g = p_j/\mu$ , or  $g = r_j p/\mu$ . It is necessary to call attention

to the fact that in the expression for  $E$  [Eq. (3)], the mass,  $m$ , which occurred there is actually the reduced mass of the three-body system, and hence is equal to  $\mu$ .

The value of  $1 - \rho_{jj}$  is now substituted, with the result that

$$P_j = \frac{\int_0^\infty 2\lambda^2 r_j [j r_{j-1} + (j+1) r_{j+1}] r_j^3 \exp(-a r_j^2) dr_j}{\int_0^\infty r_j^3 \exp(-a r_j^2) dr_j} \quad (30)$$

where  $a = E_0/kT$ , ( $E_0 = \frac{1}{2} h\nu_0$ ).

Use is made of Eq. (3) to derive the formulas:

$$\begin{aligned} r_{j-1} &= (r_j^2 + 2)^{\frac{1}{2}} \\ r_{j+1} &= (r_j^2 - 2)^{\frac{1}{2}} \end{aligned}$$

Substituting these expressions in the numerator and integrating the denominator directly leads to the result

$$P_j = 4\lambda^2 a^2 \left[ j \int_0^\infty (r_j^2 + 2)^{\frac{1}{2}} r_j^4 \exp(-a r_j^2) dr_j + (j+1) \int_{\sqrt{2}}^\infty (r_j^2 - 2)^{\frac{1}{2}} r_j^4 \exp(-a r_j^2) dr_j \right] \quad (31)$$

Since the second term on the right-hand side of the equation does not contribute for values of  $r_j < \sqrt{2}$ , the lower limit of the integral must be taken as  $\sqrt{2}$ . The lower limit of the first integral is zero. The equation may be simplified further by changing the variable of integration to  $x = a r_j^2$  in the first integral, and to  $x = a(r_j^2 - 2)$  in the second integral. The expression for  $P_j$  now is

$$P_j = (2\lambda^2/a) [j J_1 + (j+1) \exp(-2a) J_2] \quad (32)$$

where

$$J_1(a) = \int_0^\infty [x(x+2a)]^{\frac{1}{2}} x^{\frac{3}{2}} \exp(-x) dx \quad (33)$$

$$J_2(a) = \int_0^\infty [x(x+2a)]^{\frac{1}{2}} (x+2a) \exp(-x) dx \quad (34)$$

These integrals will be approximated by the expressions

$$J_1(a) \approx 2(1+a)^{\frac{1}{2}} \quad (35)$$

$$J_2(a) \approx 2[(1+a)(1+2a+2a^2)]^{\frac{1}{2}} \quad (36)$$

The basis of this approximation is explained in Appendix II.

This gives the final form of  $P_j$ :

$$P_j = (4\lambda^2/a)(1+a)^{\frac{1}{2}} \times [j + (j+1) \exp(-2a)(1+2a+2a^2)^{\frac{1}{2}}] \quad (37)$$

Since  $P_j$  is the average probability of transition per collision,  $1/P_j$  is the average number of collisions which

the molecule undergoes before leaving the  $j$ th state. In Fig. 5,  $1/P_0$  is plotted against  $a = E_0/kT$ . The curve on the right is for a value of  $1/\lambda^2 = 692$ , while the curve on the left is for a value of  $1/\lambda^2 = 24,600$ . These values of  $1/\lambda^2$  have been obtained for helium and argon colliding with other molecules such as chlorine, nitrous oxide, and carbon dioxide from data on sound dispersion. Figure 5 illustrates the strong temperature dependence of the collision number as well as the striking difference between the efficiency of helium and argon in dissipating vibrational energy.

#### IV. DISCUSSION AND COMPARISON OF THE THEORY WITH EXPERIMENTAL DATA

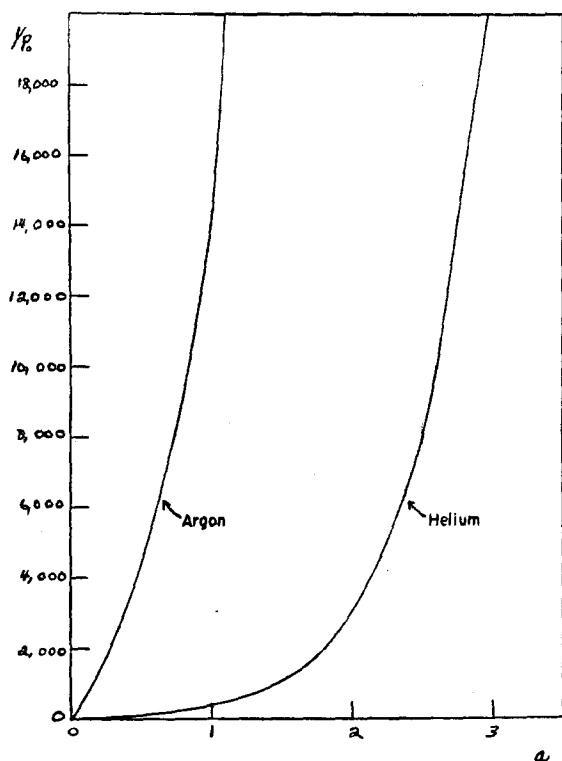
From their measurements of the dispersion of sound in gas mixtures, Eucken and Becker<sup>10</sup> calculated values for the number of collisions necessary to dissipate one quantum of vibrational energy. This collision number depends markedly on the partner in the collision. For example, chlorine at 18°C requires 900 collisions with an atom of helium in order to dissipate one quantum of vibrational energy, while, at the same temperature, 32,000 collisions with an argon atom are required.

One can interpret these collision numbers in terms of  $P_j$  [Eq. (37)], or, rather, in terms of  $1/P_0$ .  $P_0$  represents the average number of molecules leaving the zeroth level per collision. Since the average number leaving the zeroth level must be equal to the average number entering the zeroth level from the first level (cf. the selection rule in the reflection coefficient),  $P_0$  also represents the average number of quanta dissipated per collision; it is assumed that the number of molecules in higher levels is so small that contributions from this source may be neglected. Accordingly,  $1/P_0$  is the average number of collisions necessary to dissipate one quantum of vibrational energy.

In Table I, the parameter  $\lambda$  has been assumed to depend only upon the impinging molecule, i.e., the data for helium colliding with chlorine has been used to calculate a value of  $\lambda$ , which is then assumed to be characteristic of helium only. This value of  $\lambda$  is then used to calculate the number of collisions needed to

<sup>10</sup> A. Eucken and R. Becker, *Zeits. f. physik. Chemie* **B27**, 235 (1934). See also A. Eucken and E. Neumann, *Zeits. f. physik. Chemie* **B36**, 163 (1937).



FIG. 5. Variation of the collision number as a function of  $a$ .

dissipate one quantum when helium collides with carbon dioxide and nitrous oxide. The same procedure is repeated for argon-chlorine to calculate collision numbers for the systems argon-carbon dioxide, and argon-nitrous oxide.

In all three cases, helium has a much lower collision number. This has been explained heretofore by Eucken and Becker as being due to a deeper penetration of the structure of the oscillator by the small helium molecule. In terms of the above treatment the same explanation holds, of course. A larger value of  $\lambda$  in the case of helium as compared to argon simply means that the perturbation is larger in the case of helium. The calculated values in Table I are within the experimental error which is estimated to be between ten and thirty percent.

There is an obvious reason why the agreement should be better in the case of carbon dioxide than in the case of nitrous oxide. The vibration which is excited is the doubly degenerate bending vibration. Since carbon dioxide is symmetrical, the bending vibration is separable from the stretching vibrations—a fact which allows the use of the very simple surface which has been chosen (cf. Fig. 4). This energy surface pictures the collision as taking place between a helium molecule and a molecule of carbon dioxide, with the helium approaching the carbon dioxide molecule along a perpendicular bisector of the molecular axis; this configuration presumably represents an optimum condition for the excitation of the vibration.

### The Temperature Dependence of the Collision Number

Equation (37) also shows the temperature dependence of  $1/P_0$ . Unfortunately, experimental data are not available for systems involving rare gases; however, if it is assumed that in the collision of two molecules of chlorine, for example, that only one of them can be excited, then a comparison of theory and experiment can be made. The difficulty which presents itself is the choice of a value for the parameter  $\lambda$ . This choice can only be made by curve-fitting.

The curve-fitting has been done simply by averaging the values of  $\lambda$  calculated from experimental data at various temperatures. The average value of  $\lambda$  is used to draw the theoretical curve. For pure chlorine, the results are shown in Table II. The calculated values of  $P_0$  were obtained by using  $\lambda_{Av}^2 = 4.58 \times 10^{-5}$ . The results for chlorine colliding with carbon monoxide are given in Table III. Here  $\lambda_{Av}^2 = 6.31 \times 10^{-3}$ . These results are plotted in Figs. 6 and 7, respectively. All of the data are taken from Eucken and Becker.<sup>10</sup>

It is interesting to note that in the case of chlorine colliding with chlorine, the values of  $\lambda^2$  differ from the average value by an average of 14.7 percent; while in the case of chlorine and carbon monoxide,  $\lambda^2$  is more nearly constant, the values differing from the average value by an average of 6.4 percent. The theory seems to be better for the more reactive gas, although it might have been expected to be worse because of the use of a hard-sphere model.

It is difficult to associate the values of  $\lambda$  with features of known energy surfaces, chiefly because of the highly

TABLE I.

Oscillator	$\nu_0^a$	$T$	$a$	Helium $1/\lambda^2 = 692$			Argon $1/\lambda^2 = 24,600$		
				Obs. <sup>b</sup>	Calc.	Diff.	Obs. <sup>b</sup>	Calc.	Diff.
N <sub>2</sub> O	588.8 cm <sup>-1</sup>	291°K	1.44	1700 1400 <sup>c</sup>	1000	41% 23%	—	36,000	—
CO <sub>2</sub>	667.3 cm <sup>-1</sup>	291°K	1.64	1700	1500	12%	47,000	53,000	13%

<sup>a</sup> G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), pp. 274, 278.

<sup>b</sup> A. Eucken and R. Becker, see reference 10.

<sup>c</sup> A. Eucken and E. Neumann, see reference 10.

TABLE II. Chlorine-chlorine.

$T^\circ\text{K}$	$a$	$\lambda^2$	$P_0(\text{exp.})$	$P_0(\text{calc.})$
241	1.685	$3.92 \times 10^{-5}$	$1.66 \times 10^{-5}$	$1.94 \times 10^{-5}$
291	1.396	$3.90 \times 10^{-5}$	$2.94 \times 10^{-5}$	$3.45 \times 10^{-5}$
347	1.170	$4.65 \times 10^{-5}$	$5.55 \times 10^{-5}$	$5.47 \times 10^{-5}$
415	0.979	$5.86 \times 10^{-5}$	$10.5 \times 10^{-5}$	$8.21 \times 10^{-5}$

TABLE III. Chlorine-carbon monoxide.

$T^\circ\text{K}$	$a$	$\lambda^2$	$P_0(\text{exp.})$	$P_0(\text{calc.})$
241	1.685	$5.77 \times 10^{-3}$	$2.56 \times 10^{-3}$	$2.67 \times 10^{-3}$
291	1.396	$6.04 \times 10^{-3}$	$4.35 \times 10^{-3}$	$4.76 \times 10^{-3}$
347	1.170	$6.45 \times 10^{-3}$	$7.70 \times 10^{-3}$	$7.54 \times 10^{-3}$
415	0.979	$6.98 \times 10^{-3}$	$12.5 \times 10^{-3}$	$11.3 \times 10^{-3}$

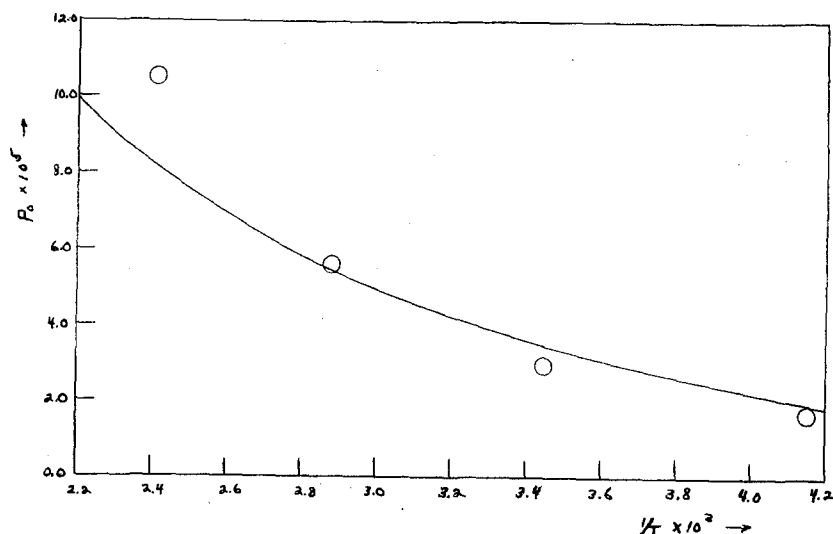


FIG. 6. Temperature variation of  $P_0$ . Chlorine-chlorine.

idealized nature of the model. As pointed out earlier, a weak interaction extending over a longer range than a strong interaction leads to the same value of  $\lambda$ . It is this circumstance, no doubt, which permits us to treat  $\lambda$  as a property of the rare gas, rather than of the colliding pair. The second virial coefficients of helium and argon show argon atoms to interact much more strongly than helium atoms, though at a somewhat greater distance. Our  $\lambda$  is much smaller for argon than for helium, suggesting that the penetration of the diatomic molecule is relatively more important for vibrational excitation than the strength of the van der Waals forces. However, we do not wish to push the quantitative significance of the model too far.

#### V. UNIMOLECULAR DECOMPOSITIONS

One can use the method of the preceding sections to derive explicit expressions for the various rate constants

which appear in the Lindemann mechanism for unimolecular decompositions. However, several difficulties arise in the application of these expressions to an actual chemical reaction. The value of  $\lambda$  is undetermined. Presumably, it can be determined by independent measurements on sound dispersion. However, one finds that for a unimolecular reaction to occur at a measurable rate at ordinary pressures, the values of  $\lambda$  which must be taken are several orders of magnitude larger than those which are found in sound dispersion. This result immediately breaks down the approximation which was used to derive values of the reflection coefficients.

Another difficulty presents itself if the results of the measurements of the inhibition of unimolecular reactions by foreign gases are considered. In the case of fluorine monoxide at 250°C it is found that argon is

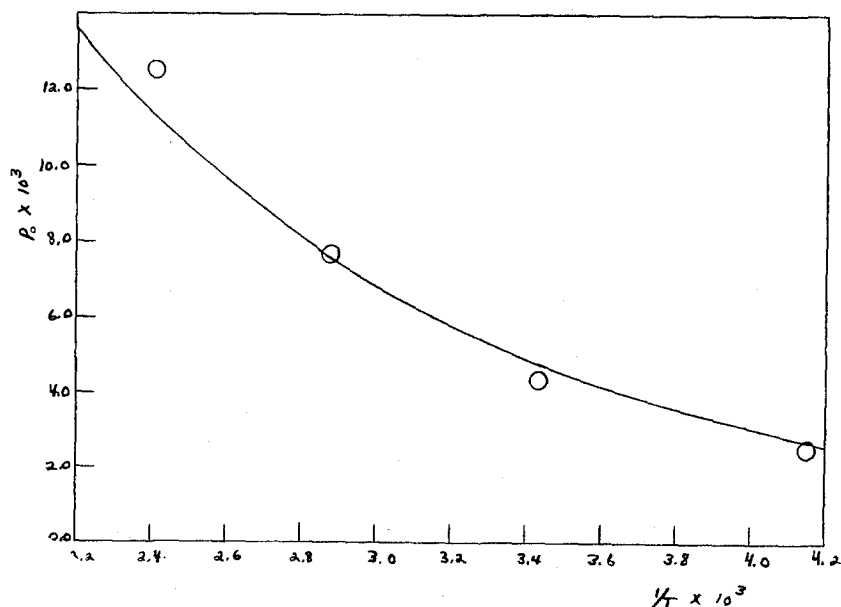


FIG. 7. Temperature variation of  $P_0$ . Chlorine-carbon monoxide.

twice as efficient as helium in producing excitation.<sup>11</sup> In the case of sound dispersion, the effect was in the opposite direction and helium was found to be 35 times as efficient as argon. In the case of nitrous oxide, helium is found experimentally to be three times as efficient as argon in chemical activation at least in this case the variation is in the same direction as for sound dispersion, although it differs by one order of magnitude. As Gershinowitz<sup>6</sup> has pointed out, there is no reason to expect that the collision efficiencies should be the same for sound dispersion as for activation. In sound dispersion the pertinent vibrational level is the first or, at most, the second, while in chemical activation the higher levels are involved. Furthermore, the individuality of the energy surface exerts a specific effect upon the collision process in activation; this is evidence by the change in the order of magnitude of the ratio of helium efficiency to that of argon in the case of nitrous oxide and the reversal in the case of fluorine monoxide.

It may thus be concluded that although the simple collision model considered here provides a fair representation of the collision process as it occurs in sound dispersion, it is much too idealized to represent the activation process in a chemical reaction. In addition, the process in sound dispersion is concerned mainly with the lowest vibration frequency in the molecule, while in the activation process the contributions of the other degrees of freedom to the activation of a particular bond may be considerable.

#### APPENDIX I

##### Evaluation of $P_{jk}$ and $Q_{jk}$

Integrals such as  $P_{jk}$  and  $Q_{jk}$  can be evaluated through the use of the generating function for the Hermite polynomials. If the integrals are stripped of normalizing coefficients and complicated notation, they can be written in the form

$$K_{jk} = \int_{-\infty}^{\infty} \exp(i2bx - x^2) H_j(x) H_k(x) dx, \quad (38)$$

where  $H_j(x)$  is the ordinary Hermite polynomial. The generating function for the Hermite polynomials is such that

$$\exp[x^2 - (z_1 - x)^2] = \sum_{n=0}^{\infty} H_n(x) z_1^n / n!. \quad (39)$$

If two equations such as (39) are multiplied together, the result multiplied on both sides by  $\exp(i2bx - x^2)$ , and the integral taken on both sides of the resulting equation, one obtains

$$\begin{aligned} \exp(-z_1^2 - z_2^2) \int_{-\infty}^{\infty} \exp[-x^2 + 2(z_1 + z_2 + ib)x] dx \\ = K_{n_s z_1^n z_2^s} / n! s!. \end{aligned} \quad (40)$$

<sup>11</sup> See, for example, reference 2, p. 291.

The variable of integration on the left-hand side of the equation is replaced by  $y = x - (z_1 + z_2 + ib)$ . This reduces the integral to a very simple form which integrates immediately to give

$$\begin{aligned} \exp(-b^2 + 2z_1 z_2 + i2bz_1 + i2bz_2) \\ = \sum_n \sum_s K_{n_s z_1^n z_2^s} / n! s!. \end{aligned} \quad (41)$$

The exponential factors on the left are now expanded in powers of  $z_1$  and  $z_2$ .

$$\exp(i2bz_1) = \sum_{p=0}^{\infty} (i2bz_1)^p / p!$$

$$\exp(i2bz_2) = \sum_{r=0}^{\infty} (i2bz_2)^r / r!$$

$$\exp(2z_1 z_2) = \sum_{t=0}^{\infty} (2z_1 z_2)^t / t!.$$

These expansions are substituted on the left for the exponentials with the result

$$\begin{aligned} (\pi)^{\frac{1}{2}} \exp(-b^2) \sum_p \sum_r \sum_t (i2b)^{p+r} 2^t z_1^{p+t} z_2^{r+t} / p! r! t! \\ = \sum_n \sum_s K_{n_s z_1^n z_2^s} / n! s!. \end{aligned} \quad (42)$$

Since Eq. (42) is an identity, the coefficients of  $z_1^k$  must be equal on both sides of the equation. On the right side this coefficient is

$$\sum_{s=0}^{\infty} K_{ks} z_2^s / k! s!.$$

On the left side, the sums are over all values of  $r$ , and over all values of  $p$  and  $t$  consistent with the relation:  $p+t=k$ . Thus,  $p$  is set equal to  $k-t$ , the sum over  $p$  disappears and the sum over  $t$  becomes a finite sum from 0 to  $k$ . Hence, setting the coefficients equal, one obtains the relation

$$\begin{aligned} (\pi)^{\frac{1}{2}} \exp(-b^2) \sum_{r=0}^{\infty} \sum_{t=0}^k (i2b)^{k-t+r} 2^t z_2^{t+r} / (k-t)! t! r! \\ = (1/k!) \sum_{s=0}^{\infty} K_{ks} z_2^s / s!. \end{aligned} \quad (43)$$

Applying the same argument to the coefficients of  $z_2^j$ , on the right side this coefficient is  $K_{kj} / k! j!$ ; while on the left, it is seen that for each value of  $t$ ,  $r = j - t$ . This leads to the equation

$$\begin{aligned} (\pi)^{\frac{1}{2}} \exp(-b^2) \\ \times \sum_{t=0}^k (i2b)^{j+k-2t} 2^t / (k-t)! (j-t)! t! = K_{kj} / k! j!. \end{aligned} \quad (44)$$

This yields immediately the value of the integral.

$$\begin{aligned} K_{kj} = (\pi)^{\frac{1}{2}} \exp(-b^2) (i2b)^{j+k} \\ \times \sum_{t=0}^k (-1)^t t! \binom{k}{t} \binom{j}{t} (\frac{1}{2} b^2)^t \end{aligned} \quad (45)$$

TABLE IV.

$J_1:$	$a$	Error	$J_2:$	$a$	Error
	0	0.0 percent	0	0.0 percent	
	$\frac{1}{2}$	+2.0	$\frac{1}{2}$	+2.2	
	1	+2.9	1	+3.8	
	2	+6.4	2	+6.6	
	$\infty$	+6.4	$\infty$	+12.8	

where  $\binom{k}{t}$  is the binomial coefficient. It can be shown that this formula for the integral satisfies the differential equation of the integral. The integral is symmetric in  $j$  and  $k$ , i.e.,  $K_{kj} = K_{jk}$ .

In order to obtain  $Q_{jk}$ , the substitutions:  $b = r_j \lambda / 2$ , and

$$H_j(x) \exp(-x^2/2) = [2^j j! (\pi)^{1/2}]^{1/2} H_j(x)$$

are made.

### The High Energy Region

For very high energies, the power series expansion of the matrices,  $P$  and  $Q$ , breaks down. To obtain an approximation in this region, Eq. (11) may be written

$$Q_{jk} = (2^{j+k} j! k!)^{-1/2} (ib_0)^{j+k} [1 - j(j+k)/\epsilon] \times [1 - 2kj/b_0^2] \exp(j\lambda^2/2) \quad (46)$$

where

$$r_j \lambda = b_0(1 - j/\epsilon); \quad b_0 = \lambda \epsilon^{1/2} \gg 1. \quad (47)$$

In the set, Eq. (9), since  $P = Q^*$ , all multiplicative factors independent of  $j$  cancel. Hence we may write

$$Q'_{jk} = F_j \cdot (1 - G_{jk}) = \sum_m F_{jm} (1 - G_{mk}) \delta_{jm} = (P'_{jk})^* \quad (48)$$

where

$$\left. \begin{aligned} F_{jm} &= (2^j j!)^{-1/2} (ib_0)^j \delta_{jm} \exp(j\lambda^2/2) \\ G_{mk} &= [\lambda^2 m(m+k) + 2km]/b_0^2 \end{aligned} \right\} \quad (49)$$

Thus

$$R = -PQ^{-1} = -P'(Q')^{-1} = -F^* F^{-1} = \|(-1)^{j+1} \delta_{jk}\|.$$

At very high energies, therefore, vibrations are not excited. Similar results are known for electronic excitation by electron impact.

## APPENDIX II

### Evaluation of the Integrals $J_1$ and $J_2$

The integral  $J_1$  is given by

$$J_1 = \int_0^\infty [x(x+2a)]^k \exp(-x) dx. \quad (50)$$

It is obvious that, since  $a$  is always positive,

$$\int_0^\infty x^2 \exp(-x) dx < J_1 < \int_0^\infty (x+2a)x \exp(-x) dx. \quad (51)$$

The following substitutions are made:

$$\begin{aligned} g(x) &= x \exp(-x) \\ f(x) &= x \\ h(x) &= (x+2a). \end{aligned}$$

The inequality now becomes

$$\int_0^\infty f g dx < \int_0^\infty (f h)^k g dx < \int_0^\infty h g dx. \quad (52)$$

Since the integrand in  $J_1$  is the geometric mean of the integrands at the two bounds of the interval,  $J_1$  has been approximated by taking the geometric mean of the two bounding integrals which are easily integrated. The same type of argument is used to evaluate  $J_2$ .

It will be noted that using this argument of the geometric mean is ambiguous in the case of  $J_2$ ; two different approximate formulas can be gotten. However, since the difference in the arithmetical values given by the two different approximations is less than 0.6 percent in the interesting range of values of  $a$ , the more convenient approximation given in Eq. (36) will be used.

Both integrals have been measured with a planimeter for values of  $a = \frac{1}{2}$ , 1, and 2. For  $a = 0$ , the approximation becomes exact in both cases. A comparison of the measured and calculated values of the integrals is given in Table IV.

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