Impulse approximation for three-dimensional inelastic atom—diatomic-molecule collisions

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The impulse approximation of Chew is applied to the calculation of the cross sections for rotational and vibrational excitation of diatomic molecules by collisions with an atom. The assumptions underlying the impulse approximation are discussed and found to be justified for these processes. A closure approximation is used to perform the sums over rotational quantum numbers in the expression for the vibrational-excitation cross section and the resulting expression depends on two factors; an oscillator form factor and the scattering amplitudes for atom-atom scattering. Vibrational-transition probabilities, evaluated for oxygen—carbon monoxide collisions assuming that the oscillator is harmonic and using a rough estimate for the typical atom-atom scattering amplitudes, are in qualitative agreement with experiment. Further refinements and extensions of the model are discussed.

I. INTRODUCTION

The study of vibrational and rotational energy transfer in gases has occupied chemists and physicists since the 1930's. The various approaches to the calculation of transition probabilities have been reviewed by a number of authors.[1-5] Recently, the impulse approximation of Chew[6] has been brought to bear on one-dimensional atom—diatomic-molecule collisions by Clinton, Cosgrove, and Henderson[7] and by Eckelt and Korsch.[8] In this paper we apply the impulse approximation to three-dimensional atom—diatomic-molecule collisions.

The assumptions underlying the impulse approximation are (1) the incident particle interacts with only one particle of the composite system at a time, (2) the amplitude of the incident wave falling upon constituents of the system is nearly the same as if that constituent were alone, and (3) binding forces between the constituents are negligible while the incident particle interacts strongly with the system.[9-11] Quantitative criteria for assumptions 1 and 2 have proven elusive[9-11]; assumption 1, however, seems justified when the range of the atom—diatomic-molecule interaction R is much less than the interatomic spacing of the diatomic molecule r_e,

$$R \ll r_e , \tag{1}$$

and assumption 2 will be satisfied when

$$\sigma \ll 4\pi r_e^2 (k r_e)^2 , \tag{2}$$

where σ is the cross section and k is the wave number of the incident atom.[9]

When the relative kinetic energy E_k is well above the rotational threshold, the atom—diatomic-molecule interaction is predominately a short-range interaction and Eq. (1) will be satisfied. For example,

Herzfeld has shown that an exponential repulsive potential of the form $e^{-r/L}$ with $L \approx r_c/17.5$ matches the Lennard-Jones 6-12 potential well for these energies where r_0 is the Lennard-Jones length parameter.[12] If we identify L with the range of the atom—diatomic-molecule interaction, Eq. (1) will be satisfied since r_0 and r_e are of the same order of magnitude.

The cross section is of the same order of magnitude as $4\pi r_e^2$, and Eq. (2) becomes

$$E_k /hc \gg (\mu_T /\mu_r) B_e > B_e$$

where $B_e = h/(8\pi^2 c \mu_r r_e^2)$ is the rotational term constant[13] and μ_T and μ_r are the reduced masses for vibrational motion and relative motion. Assumption 2 will also be satisfied when the kinetic energy is well above the rotational threshold.

Assumption 3 is valid when the duration of the collision τ_c is small compared to the period of oscillation of the bound system.[9] This is just the condition for the interaction to proceed so rapidly that the wave function cannot adjust itself adiabatically and implies that the transition probabilities will be appreciable.[14] Typical rotational and vibrational periods are 10^{-10} and 10^{-13} sec. If we let the collision duration be $\tau_c = L/V$ and $L \sim 10^{-9}$ cm, this assumption will be valid provided the relative velocity remains above 0.1 km/sec for vibrational excitation and 10 cm/sec for rotational excitation. All velocities of interest in molecular excitation are well above these limits except for the final relative velocities when the energy is just above a threshold.

We shall consider only vibrational excitation here so that assumptions 1 and 2 will be well satisfied and assumption 3 will be satisfied except near energy thresholds. The impulse approxima-

tion allows us to separate the vibrational part of the calculation from the scattering part. In Sec. II we derive the form that the impulse approximation takes for atom–diatomic-molecule scattering. The contribution of the molecular vibrations to the calculation is contained in a form factor that is discussed and calculated for a harmonic potential in Sec. III. In Sec. IV we discuss the scattering part of the calculation and present a sample calculation of the cross sections for the vibrational excitation of carbon monoxide by collision with atomic oxygen when both are in their electronic ground states. Since the ground state of atomic oxygen is a triplet state, the interaction will proceed along the potential curves for triplet CO_2 which are all repulsive.[15] We shall not consider possible contributions to this process from the crossing of the singlet and triplet CO_2 potential curves.[16]

Before proceeding, we should mention that the "sudden" approximation is also claimed to be valid when assumption 3 is justified.[17,18] In this approximation, the vibrational part of the calculation separates from the collision part, as in the impulse approximation, and the vibrational contribution to the interaction is contained in a form factor identical to ours. (In Treanor's one-dimensional theory as well, the same form factor appears.[19]) The essential differences between our approach and the sudden approximation are twofold. The first is that the scattering part is typically treated in a semiclassical manner in the sudden approximation, whereas our approach is in principle entirely quantum mechanical. In this paper we have used a rough estimate for the scattering amplitude, which is certainly no better than the semiclassical approach of the sudden approximation. We shall see, however, that our result does not depend strongly on this assumption, and an extension to a more realistic model is straightforward.

The other difference between these approximations is that the sudden approximation treats the scattering part of the interaction by letting the atom–diatomic-molecule potential be represented by a spherically averaged interaction and treating the residual interaction as a perturbation. In the impulse approximation, the atom–diatomic-molecule interaction is treated as the sum of two-body potentials between the incident atom and the constituents of the diatomic molecule and is handled exactly (subject to assumptions 1–3). It is this second difference that we feel makes the impulse approximation preferable to the sudden approximation.

Our results are summarized and discussed in Sec. V.

II. IMPULSE APPROXIMATION

We shall consider the scattering to be described by a Hamiltonian of the form

$$H = -\frac{\hbar^2}{2m_a}\nabla_a^2 - \frac{\hbar^2}{2m_b}\nabla_b^2 - \frac{\hbar^2}{2m_c}\nabla_c^2 + V_1(|\vec{r}_a - \vec{r}_c|)$$

$$+ V_2(|\vec{r}_a - \vec{r}_b|) + V_B(|\vec{r}_b - \vec{r}_c|) . \quad (3)$$

Although quantum-mechanical calculations of the potential for $H_2 + H$, $H_2 + H_2$, and $H_2 + He$ show that the interaction is not, in general, a sum of two-body potentials,[2] our knowledge of the true potential for heavier systems is so limited that this seems to be a reasonable choice for the present.

We may separate out the center-of-mass motion with the transformation to the center-of-mass system,

$$M\vec{R} = m_a\vec{r}_a + m_b\vec{r}_b + m_c\vec{r}_c , \quad (4)$$

$$\vec{r} = \vec{r}_a - (m_b\vec{r}_b + m_c\vec{r}_c)/(m_b + m_c) , \quad (5)$$

and

$$\vec{\tau} = \vec{r}_b - \vec{r}_c , \quad (6)$$

where $M = (m_a + m_b + m_c)$. The momenta conjugate to these coordinates are

$$\vec{K} = \vec{k}_a + \vec{k}_b + \vec{k}_c , \quad M\vec{k}_r = (m_b + m_c)\vec{k}_a - m_a(\vec{k}_b + \vec{k}_c),$$

$$(m_b + m_c)\vec{k}_\tau = m_c\vec{k}_b - m_b\vec{k}_c ,$$

and the Hamiltonian is

$$H(\vec{R}, \vec{r}, \vec{\tau}) = -\frac{\hbar^2}{2M}\nabla_R^2 + H_0(\vec{r}, \vec{\tau})$$

$$+ V_b(|\vec{r} + \beta_b\vec{\tau}|) + V_c(|\vec{r} + \beta_c\vec{\tau}|) , \quad (7)$$

where

$$H_0(\vec{r}, \vec{\tau}) = -\frac{\hbar^2}{2\mu_r}\nabla_r^2 - \frac{\hbar^2}{2\mu_\tau}\nabla_\tau^2 + V_B(|\vec{\tau}|) , \quad (8)$$

and where $\mu_r = m_a(m_b + m_c)/M$, $\mu_\tau = m_b m_c/(m_b + m_c)$, $\beta_b = -m_c/(m_b + m_c)$, and $\beta_c = m_b/(m_b + m_c)$.

The R dependence of Schrödinger's equation

$$H\Psi(\vec{R}, \vec{r}, \vec{\tau}) = E\Psi(\vec{R}, \vec{r}, \vec{\tau}) \quad (9)$$

may be factored

$$\Psi(\vec{R}, \vec{r}, \vec{\tau}) = e^{i\vec{K}\cdot\vec{R}}\psi(\vec{r}, \vec{\tau}) , \quad (10)$$

where $\psi(\vec{r}, \vec{\tau})$ is a solution of

$$[H_0(\vec{r}, \vec{\tau}) + V_b(|\vec{r} + \beta_b\vec{\tau}|) + V_c(|\vec{r} + \beta_c\vec{\tau}|)]\psi(\vec{r}, \vec{\tau})$$

$$= E'\psi(\vec{r}, \vec{\tau}) \quad (11)$$

and where

$$E' = E - \hbar^2 K^2/2M . \quad (12)$$

The solutions of Eq. (11) appropriate to the scattering of a plane wave in the z direction of atom a

by a bound state of molecule bc at rest with quantum numbers $n_0, l_0,$ and m_0 satisfy the integral equation[20,21]

$$\psi(\vec{r}, \vec{\tau}) = e^{i k_r z} \varphi_{n_0, l_0, m_0}(\vec{\tau}) + \sum_{n,l,m} \psi_{n,l,m}(\vec{r}, \vec{\tau}) ,$$

(13)

$$\psi_{n,l,m}(\vec{r}, \vec{\tau}) = -\frac{2\mu_r}{4\pi\hbar^2} \int d\vec{r}' \int d\vec{\tau}'$$

$$\times \varphi_{n,l,m}(\vec{\tau}) \frac{e^{i k_r' |\vec{r}' - \vec{r}|}}{|\vec{r}' - \vec{r}|} \varphi^*_{n,l,m}(\vec{\tau}')$$

$$\times [V_b(|\vec{r}' + \beta_b \vec{\tau}'|) + V_c(|\vec{r}' + \beta_c \vec{\tau}'|)] \psi(\vec{r}', \vec{\tau}') ,$$

(14)

where the functions $\varphi_{n,l,m}(\vec{\tau})$ are the solutions of the equation

$$\left(-\frac{\hbar^2}{2\mu_\tau} \nabla_\tau^2 + V_B(|\vec{\tau}|)\right) \varphi_{n,l,m}(\vec{\tau}) = \epsilon_{n,l} \varphi_{n,l,m}(\vec{\tau}) ,$$

(15)

$n, l,$ and m are the final quantum numbers of the bound states, and

$$k_r'^2 = 2\mu_r(E' - \epsilon_{n,l})/\hbar^2 .$$

(16)

The sum on $n, l,$ and m in Eq. (13) represents a sum over all discrete quantum numbers and an integral over all continuous quantum numbers.

We note that there is a contribution to the integral in Eq. (14) only from regions of $\vec{r}', \vec{\tau}'$ space where the potential is appreciable. When $|\vec{r}|$ is outside this domain, we have

$$\psi_{n,l,m}(\vec{r}, \vec{\tau}) \to \frac{e^{i k_r' r}}{r} \varphi_{n,l,m}(\vec{\tau}) f_{n,l,m}(\vec{k}_r', \vec{k}_r)$$

as $r \to \infty$

where

$$f_{n,l,m}(\vec{k}_r', \vec{k}_r) = -\frac{2\mu_r}{4\pi\hbar^2} \int d\vec{r}' \int d\vec{\tau}' e^{-i \vec{k}_r' \cdot \vec{r}'} \varphi^*_{n,l,m}(\vec{\tau}')$$

$$\times [V_b(|\vec{r}' + \beta_b \vec{\tau}'|) + V_c(|\vec{r}' + \beta_c \vec{\tau}'|)] \psi(\vec{r}', \vec{\tau}')$$

(17)

and where $\vec{k}_r'$ is a vector in the $\vec{r}$ direction with magnitude k_r'. The differential cross section for excitation of the level n, l, m is given by[20,21]

$$\sigma(\theta, \varphi) = (k_a^f/k_a) |f_{n,l,m}(\vec{k}_r', \vec{k}_r)|^2 ,$$

(18)

where $k_a^f = |\vec{k}_r' + m_a \vec{k}_a/M|$.

The expression for the scattering amplitude in Eq. (17) is exact, but can be calculated only if the true wave function $\psi(\vec{r}', \vec{\tau}')$ is known. In the Born approximation one assumes that the scattering is weak, and one lets $\psi(\vec{r}', \vec{\tau}') = e^{i k_r z'} \varphi_{n_0, l_0, m_0}(\vec{\tau}')$ in Eq. (17). This procedure will not work in the case considered here because of the strongly repulsive

nature of V_1 and V_2.

In the impulse approximation of Chew, the scattering amplitude is separated;

$$f_{IA}(\vec{k}_r', \vec{k}_r) = f_b(\vec{k}_r', \vec{k}_r) + f_c(\vec{k}_r', \vec{k}_r) ,$$

(19)

where

$$f_i(\vec{k}_r', \vec{k}_r) = -\frac{2\mu_r}{4\pi\hbar^2} \int d\vec{r}' \int d\vec{\tau}' e^{-i \vec{k}_r' \cdot \vec{\tau}'} \varphi^*_{n,l,m}(\vec{\tau}')$$

$$\times V_i(|\vec{r} + \beta_i \vec{\tau}|) \psi_i(r', \tau')$$

(20)

and the wave function $\psi_i(\vec{r}, \vec{\tau})$ is approximated by the exact expression for the scattering of atom a with momentum $\vec{k}_a$ by atom i with momentum $\vec{k}_i$ in the center-of-mass system, ignoring the presence of the other atom of the molecule except to average $\vec{k}_b$ and $\vec{k}_c$ over their momentum distribution in the initial state[6]; that is, for the case when the molecule is initially at rest,

$$\psi_c(\vec{r}_a, \vec{r}_b, \vec{r}_c) = (2\pi)^{-3/2} \int d\vec{k}_b \int d\vec{k}_c$$

$$\times e^{i(\vec{k}_b \cdot \vec{r}_b - \vec{k}_a \cdot \vec{R})} G_0(\vec{k}_b, \vec{k}_c) \Phi_{\vec{k}_a, \vec{k}_c}(\vec{r}_a, \vec{r}_c) ,$$

(21)

where

$$G_0(\vec{k}_b, \vec{k}_c) = (2\pi)^{-3} \int d\vec{r}_b \int d\vec{r}_c$$

$$\times e^{-i(\vec{k}_b \cdot \vec{r}_b + \vec{k}_c \cdot \vec{r}_c)} \varphi_{n_0, l_0, m_0}(\vec{r}_b - \vec{r}_c)$$

(22)

and where $\Phi_{\vec{k}_a, \vec{k}_c}(\vec{r}_a, \vec{r}_c)$ is the exact wave function for the scattering of atom a with momentum $\vec{k}_a$ by atom c with momentum $\vec{k}_c$. The factor $e^{-\vec{k}_a \cdot \vec{R}}$ in Eq. (21) removes the center-of-mass motion from the wave function. The expression for $G_0(\vec{k}_b, \vec{k}_c)$ may be simplified;

$$G_0(\vec{k}_b, \vec{k}_c) = \delta(\vec{k}_b + \vec{k}_c) g_0\left(\frac{m_c \vec{k}_b - m_b \vec{k}_c}{m_b + m_c}\right)$$

$$= \int d\vec{k}_\tau g_0(\vec{k}_\tau) \delta(\vec{k}_\tau - \vec{k}_b) \delta(\vec{k}_\tau + \vec{k}_c) ,$$

(23)

where

$$g_0(\vec{k}_\tau) = (2\pi)^{-3/2} \int d\vec{\tau} e^{-i \vec{k}_\tau \cdot \vec{\tau}} \varphi_{n_0, l_0, m_0}(\vec{\tau}) .$$

(24)

The expression for $\Phi_{\vec{k}_a, \vec{k}_c}(\vec{r}_a, \vec{r}_c)$ is also simplified in the a-c center-of-mass system

$$\vec{R}_{ac} = \frac{m_a}{m_a + m_c} \vec{r}_a + \frac{m_c}{m_a + m_c} \vec{r}_c$$

(25)

and

$$\vec{\rho} = \vec{r}_a - \vec{r}_c ,$$

(26)

with the conjugate momenta

$$\vec{k}_{ac} = \vec{k}_a + \vec{k}_c$$

(27)

and

$$(m_a + m_c)\vec{k}_\rho = m_c \vec{k}_a - m_a \vec{k}_c \;\; ; \tag{28}$$

$$\Phi_{\vec{k}_a, \vec{k}_c}(\vec{r}_a, \vec{r}_c) = e^{i\vec{k}_{ac} \cdot \vec{R}_{ac}} \chi_{\vec{k}_\rho}^{(c)}(\vec{\rho}) \; . \tag{29}$$

When Eqs. (23) and (29) are substituted into Eq. (21) we have

$$\psi_c(\vec{r}_a, \vec{r}_b, \vec{r}_c) = (2\pi)^{-3/2} \int d\vec{k}_\tau \, g_0(\vec{k}_\tau) \chi_{\vec{k}_\rho}^{(c)}(\vec{\rho}) \exp\{i[\vec{k}_\tau \cdot \vec{r}_b - \vec{k}_a \cdot \vec{R} + (\vec{k}_a - \vec{k}_\tau)\cdot(m_a \vec{r}_a + m_c \vec{r}_c)/(m_a + m_c)]\} \; , \tag{30}$$

where

$$\vec{k}_\rho = (m_c \vec{k}_a + m_a \vec{k}_\tau)/(m_a + m_c) \; . \tag{31}$$

We now may use the inverse of the transformation in Eqs. (4)–(6),

$$\vec{r}_a = \vec{R} + (m_b + m_c)\vec{r}/M \; ,$$

$$\vec{r}_b = \vec{R} - m_a \vec{r}/M + m_c \vec{\tau}/(m_b + m_c) \; ,$$

and

$$\vec{r}_c = \vec{R} - m_a \vec{r}/M - m_b \vec{\tau}/(m_b + m_c) \; ,$$

to express ψ_c in terms of $\vec{\rho}$ and $\vec{\tau}$;

$$\psi_c(\vec{r}, \vec{\tau}) = (2\pi)^{-3/2} \int d\vec{k}_\tau \, g_0(\vec{k}_\tau) \chi_{\vec{k}_\rho}^{(c)}(\vec{\rho})$$

$$\times \exp\{i (\vec{k}_\tau - m_b \vec{k}_a/M) \cdot [\vec{\tau} - m_a \vec{\rho}/(m_a + m_c)]\} \; , \tag{32}$$

since $\vec{r} = \vec{\rho} - m_b \vec{\tau}/(m_b + m_c)$. When $\vec{k}_b + \vec{k}_c = 0$, we have

$$\vec{k}_a = M\vec{k}_\tau/(m_b + m_c) \; , \tag{33}$$

and so the expression (20) for the partial scattering amplitude becomes

$$f_c(\vec{k}_r', \vec{k}_r) = -\frac{2\mu_r}{4\pi\hbar^2} (2\pi)^{-3/2} \int d\vec{k}_\tau \, g_0(\vec{k}_\tau) \int d\vec{\tau} \, \exp(i\vec{\tau} \cdot \{\vec{k}_\tau + [m_b/(m_b + m_c)]\vec{q}\}) \, \varphi_{n,l,m}^*(\vec{\tau})$$

$$\times \int d\vec{\rho} \, e^{-i\vec{\rho} \cdot (\vec{k}_\rho + \vec{q})} V_c(|\vec{\rho}|) \chi_{\vec{k}_\rho}^{(c)}(\vec{\rho}) \; , \tag{34}$$

where

$$\vec{q} \equiv \vec{k}_r' - \vec{k}_r \; . \tag{35}$$

Equation (34) and the similar expression for $f_b(\vec{k}_r', \vec{k}_r)$,

$$f_b(\vec{k}_r', \vec{k}_r) = -\frac{2\mu_r}{4\pi\hbar^2} (2\pi)^{-3/2} \int d\vec{k}_\tau \, g_0(\vec{k}_\tau) \int d\vec{\tau} \, \exp(i\vec{\tau} \cdot \{\vec{k}_\tau - [m_c/(m_b + m_c)]\vec{q}\}) \varphi_{n,l,m}^*(\vec{\tau})$$

$$\times \int d\vec{\rho}' \, e^{-i\vec{\rho}' \cdot (\vec{k}_\rho' + \vec{q})} V_b(|\vec{\rho}'|) \chi_{\vec{k}_\rho'}^{(b)}(\vec{\rho}) \; , \tag{36}$$

where

$$(m_a + m_b)\vec{k}_\rho' = m_b \vec{k}_a - m_a \vec{k}_\tau \; , \tag{37}$$

constitute the impulse approximation to the diatomic-molecule scattering amplitude.

All the quantities in Eqs. (34) and (36) may be calculated directly. Chew[6] has pointed out that since these equations (i) reduce to the Born approximation when $\chi_{\vec{k}_\rho}^{+}(\vec{\rho})$ is approximated by $e^{i\vec{k}_\rho \cdot \vec{\rho}}$ and (ii) give the exact expression for scattering when the binding potential $V_B(|\vec{\tau}|)$ is neglected, they may be viewed as an interpolation between these limits.

The function $g_0(\vec{k}_\tau)$ becomes vanishingly small for $\vec{k}_\tau > L^{-1}$, where L is the size of the target. Whenever $|\vec{k}_a| \gg m_a R^{-1}/m_c$ (and $k_a \gg m_a R^{-1}/m_b$), we may neglect the dependence of $\vec{k}_\rho$ (and $\vec{k}_\rho'$) upon $\vec{k}_\tau$ and factor Eqs. (34) and (36);

$$f_c(\vec{k}_r', \vec{k}_r) = (\mu_r/\mu_{ac}) \tilde{f}_c((\mu_{ac}/\mu_r)\vec{k}_r' + \vec{q}, (\mu_{ac}/\mu_r)\vec{k}_r)$$

$$\times \mathcal{F}_{n,l,m;n_0,l_0,m_0}(-m_b\vec{q}/(m_b + m_c)) \tag{38}$$

and

$$f_b(\vec{k}_r', \vec{k}_r) = (\mu_r/\mu_{ab}) \tilde{f}_b((\mu_{ab}/\mu_r)\vec{k}_r' + \vec{q}, (\mu_{ab}/\mu_r)\vec{k}_r)$$

$$\times \mathcal{F}_{n,l,m;n_0,l_0,m_0}(m_c\vec{q}/(m_b + m_c)) \; , \tag{39}$$

where we have introduced the reduced masses

$$\mu_{ac} \equiv m_a m_c/(m_a + m_c) \tag{40}$$

and

$$\mu_{ab} \equiv m_a m_b/(m_a + m_b) \; ,$$

the bound-state form factor

$$\mathfrak{F}_{n,l,m;n_0,l_0,m_0}(\vec{k}) \equiv \int d\tau \, e^{-i\vec{k}\cdot\vec{\tau}} \varphi^*_{n,l,m}(\vec{\tau})\varphi_{n_0,l_0,m_0}(\vec{\tau}) \, ,$$

$$(41)$$

and the free scattering amplitudes

$$\tilde{f}_i(\vec{k}_2, \vec{k}_1) \equiv -(2\mu_{ai}/4\pi\hbar^2) \int d\vec{\rho}\, e^{-i\vec{k}_2\cdot\vec{\rho}} V_i(\rho)\chi^{(i)}_{\vec{k}_i}(\rho)$$

$$(42)$$

III. BOUND-STATE FORM FACTOR

A number of interesting properties of the bound-state form factor follow immediately from its definition (41). Since the bound-state wave functions are orthonormal, we have

$$\mathfrak{F}_{n,l,m;n_0,l_0,m_0}(0) = \delta_{n,n_0}\delta_{l,l_0}\delta_{m,m_0} \, .$$

$$(43)$$

Also, since the bound-state wave functions are complete, we may identify $\mathfrak{F}_{n,l,m;n_0,l_0,m_0}(\vec{k})$ as the coefficient of $\varphi_{n,l,m}(\vec{\tau})$ in an expansion of $e^{-i\vec{k}\cdot\vec{\tau}}$ $\times \varphi_{n_0,l_0,m_0}(\vec{\tau})$;

$$e^{-i\vec{k}\cdot\vec{\tau}}\varphi_{n_0,l_0,m_0}(\vec{\tau}) = \sum_{n,l,m} \mathfrak{F}_{n,l,m;n_0,l_0,m_0}(\vec{k})\varphi_{n,l,m}(\vec{\tau}) \, ,$$

where the sum on n, l, and m represents a sum over all discrete quantum numbers and an integral over all continuous quantum numbers. If we multiply this by the similar expression for $e^{i\vec{k}\cdot\vec{\tau}}$ $\times \varphi^*_{n_1,l_1,m_1}(\vec{\tau})$ and integrate over $\vec{\tau}$, we have

$$\delta_{n_0,n_1}\delta_{l_0,l_1}\delta_{m_0,m_1}$$

$$= \sum_{n,l,m} \mathfrak{F}_{n,l,m;n_0,l_0,m_0}(\vec{k})\mathfrak{F}^*_{n,l,m;n_1,l_1,m_1}(\vec{k}) \quad (44)$$

and, in particular,

$$\sum_{n,l,m} |\mathfrak{F}_{n,l,m;n_0,l_0,m_0}(\kappa)|^2 = 1 \, .$$

$$(45)$$

Let us now approximate the binding potential with a harmonic-oscillator potential

$$V_B(|\vec{\tau}|) = \tfrac{1}{2}\mu_\tau\omega_0^2(\tau - \tau_e)^2 \, .$$

$$(46)$$

The solutions of Eq. (15) are of the form

$$\varphi_{n,l,m}(\vec{\tau}) = \tau^{-1}U_{nl}(\xi)Y_{lm}(\theta_\tau, \varphi_\tau) \, ,$$

$$(47)$$

where

$$\xi \equiv (\tau - \tau_e)/\sqrt{2}d \, ,$$

$$(48)$$

$$d \equiv (\hbar/2\omega_0\mu_\tau)^{1/2} \, ,$$

$$(49)$$

and

$$\xi_e \equiv \tau_e/\sqrt{2}d \, ,$$

$$(50)$$

and where $U_{nl}(\xi)$ satisfies the differential equation

$$\frac{\partial^2}{\partial\xi^2}U_{nl}(\xi) + \left(\frac{2\epsilon_{nl}}{\hbar\omega_0} - \frac{l(l+1)}{(\xi+\xi_e)^2} - \xi^2\right)U_{nl}(\xi) = 0 \quad (51)$$

for $-\xi_e < \xi < \infty$ with the boundary conditions

$$U_{nl}(-\xi_e) = 0$$

$$(52)$$

and

$$\lim_{\xi\to\infty} U_{nl}(\xi) = 0 \, .$$

$$(53)$$

The quantity $2\xi_e^2$ may be recognized as the ratio of the vibrational level spacing to the rotational constant and is large for most diatomic molecules [for CO, $\xi_e = (\omega_e/2B_e)^{1/2} = 23.7$].[13] We now make the approximation

$$-l(l+1)/(\xi+\xi_e)^2 \approx -l(l+1)/\xi_e^2$$

$$(54)$$

and let the boundary condition (52) become

$$\lim_{\xi\to-\infty} U_{nl}(\xi) = 0 \, .$$

$$(55)$$

The radial wave function $U_{nl}(\xi)$ is then given by

$$U_{nl}(\xi) = N_n H_n(\xi)e^{-(1/2)\xi^2} \, ,$$

$$(56)$$

where n is an integer,

$$2n + 1 = \frac{2\epsilon_{nl}}{\hbar\omega_0} - \frac{l(l+1)}{\xi_e^2} \, ,$$

$$(57)$$

$H_n(\xi)$ is a Hermite polynomial,[22] and the normalization constant N_n is given by

$$N_n = [\omega_0\mu_\tau/\hbar\pi2^{2n}(n!)^2]^{1/4} \, .$$

$$(58)$$

The approximations (54) and (55) are conventional in the treatment of diatomic-molecule spectra. Approximation (54) is equivalent to neglecting coupling between rotation and vibration. The solutions of

$$\frac{\partial^2}{\partial\xi^2}D_n(\sqrt{2}\xi) + (2n + 1 - \xi^2)D_n(\sqrt{2}\xi) = 0 \quad (59)$$

which are bounded as $\xi \to +\infty$ are all parabolic cylinder functions.[23] The approximation (55) restricts n to be zero or a positive integer, in which case $D_n(\sqrt{2}\xi)$ reduces to the product of an exponential and a Hermite polynomial as in Eq. (56). When the lower boundary condition is given by Eq. (52) and ξ_e is large, it can be shown that n must be slightly greater than an integer; however, the error in the energy eigenvalue associated with the approximation (55) is less than the error associated with the neglect of anharmonic terms in the potential.

When the bound wave functions are given by Eqs. (47) and (56), the form factor $\mathfrak{F}_{n,l,m;n_0,l_0,m_0}(\vec{k})$ is

$$\mathfrak{F}_{n,l,m;n_0,l_0,m_0}(\vec{k}) = \sum_{L,M} [4\pi(2l+1)(2l_0+1)(2L+1)]^{1/2} i^{-L}(-1)^m \begin{pmatrix} l & l_0 & L \\ -m & m_0 & M \end{pmatrix}\begin{pmatrix} l & l_0 & L \\ 0 & 0 & 0 \end{pmatrix} Y_{LM}^*(\theta_\kappa, \varphi_\kappa)$$

$$\times \int_{-\infty}^{\infty} d\xi\, H_n(\xi)H_{n_0}(\xi)e^{-\xi^2} N_n N_{n_0}\sqrt{2}\, dj_L(\sqrt{2}\,\kappa d(\xi+\xi_e)),\tag{60}$$

where we have expanded $e^{i\vec{k}\cdot\vec{r}}$ in spherical harmonics and made use of the properties of spherical harmonics and 3-j symbols [such as $\begin{pmatrix} l & l_0 & L \\ -m & m_0 & M \end{pmatrix}$].[24] In the expression for the inelastic cross section we require the square of the magnitude of the form factor to be averaged over the initial magnetic quantum numbers and summed over the final magnetic quantum numbers;

$$\frac{1}{(2l_0+1)}\sum_{m,m_0} |\mathfrak{F}_{n,l,m;n_0,l_0,m_0}(\vec{k})|^2$$

$$= \sum_L (2L+1)(2l+1)\begin{pmatrix} l & l_0 & L \\ 0 & 0 & 0 \end{pmatrix}^2 |(\pi 2^{n+n_0}n!n_0!)^{-1/2}$$

$$\times \int_{-\infty}^{\infty} d\xi\, H_n(\xi)H_{n_0}(\xi)e^{-\xi^2}j_L(\sqrt{2}\,\kappa d(\xi+\xi_e))|^2,\tag{61}$$

where we have again used angular momentum identities.

The expression in Eq. (61) is suitable for calculations of rotational- and vibrational-excitation cross sections. If we are interested only in the excitation of vibrational levels, we may sum this expression over the final orbital angular momentum l. An additional complication here is that ϵ_{nl}, and hence k'_r, $\tilde{f}_c(\vec{k}'_p,\vec{k}_p)$, and $\tilde{f}_b(\vec{k}'_p,\vec{k}'_p)$, all depend upon l. Fortunately, the dependence of ϵ_{nl} upon l is weak;

$$\epsilon_{nl} = (n+\tfrac{1}{2})\hbar\omega_0 + l(l+1)\hbar\omega_0/2\xi_e^2 \approx (n+\tfrac{1}{2})\hbar\omega_0\tag{62}$$

and may be neglected to a good approximation since the integral in Eq. (61) vanishes for large L. With the approximation (60), we may use the closure property of the 3-j symbols

$$\sum_l (2l+1)\begin{pmatrix} l & l_0 & L \\ 0 & 0 & 0 \end{pmatrix}^2 = 1$$

and the relation[24]

$$\frac{1}{2}\int_{-1}^{1} du\, e^{iu(z-y)} = \sum_L (2L+1)j_L(z)j_L(y),$$

to obtain

$$\frac{1}{(2l_0+1)}\sum_{l,m,m_0} |\mathfrak{F}_{n,l,m;n_0,l_0,m_0}(\vec{k})|^2 = (\pi 2^{n+n_0}n!n_0!)^{-1}\frac{1}{2}\int_{-1}^{1} du\, \left|\int_{-\infty}^{\infty} d\xi\, e^{i2^{1/2}\kappa du(\xi+\xi_e)}H_n(\xi)H_{n_0}(\xi)e^{-\xi^2}\right|^2.\tag{63}$$

The integral on ξ in Eq. (61) may be performed

$$\int_{-\infty}^{\infty} d\xi\, e^{i2^{1/2}\kappa du(\xi+\xi_e)}e^{-\xi^2}H_n(\xi)H_{n_0}(\xi) = e^{i2^{1/2}\kappa du\xi_e}e^{-\kappa^2 d^2 u^2/2}2^{(n_g+n_l)/2}\sqrt{\pi}\, n_l!(-i\kappa du)^{n_g-n_l}L_{n_l}^{(n_g-n_l)}(\kappa^2 d^2 u^2),$$

where n_l and n_g are the lesser and greater of n_0 and n and where $L_n^{(\alpha)}(x)$ is an associated Laguerre polynomial.[22] Equation (58) then becomes

$$\frac{1}{(2l_0+1)}\sum_{l,m,m_0} |\mathfrak{F}_{n,l,m;n_0,l_0,m_0}(\vec{k})|^2 = \frac{1}{2}\int_{-1}^{1} du\,(n_l!/n_g!)e^{-\kappa^2 d^2 u^2}(\kappa^2 d^2 u^2)^{n_g-n_l}[L_{n_l}^{(n_g-n_l)}(\kappa^2 d^2 u^2)]^2.\tag{64}$$

The interference term in the expression for the inelastic-scattering differential cross section may be reduced in a similar manner:

$$\frac{1}{(2l_0+1)}\sum_{l,m,m_0} \mathfrak{F}_{n,l,m;n_0,l_0,m_0}(-\beta_b\vec{q})\mathfrak{F}_{n,l,m;n_0,l_0,m_0}^*(-\beta_c\vec{q}) = \int_0^1 du\,\cos(\sqrt{2}\,\xi_e y)e^{-y^2(\beta_b^2+\beta_c^2)/2}(n_l!/n_g!)$$

$$\times(\beta_b\beta_c y^2)^{n_g-n_l}L_{n_l}^{(n_g-n_l)}(\beta_b^2 y^2)L_{n_l}^{(n_g-n_l)}(\beta_c^2 y^2) \approx 0,\tag{65}$$

where we have defined $y \equiv qud$ and noted that the integral will vanish because of the rapidly oscillating cosine term.

If the molecule is initially in the lowest vibrational state, the integral in Eq. (64) is

$$\frac{1}{(2l_0+1)}\sum_{l,m,m_0} |\mathcal{F}_{n,l,m:0,l_0,m_0}(\vec{k})|^2 = (n!\kappa d)^{-1}\int_0^{kd} dx\, e^{-x^2} x^{2n} \tag{66}$$

$$= \gamma(n+\tfrac{1}{2},\, \kappa^2 d^2)/(2n!\kappa d)\,, \tag{67}$$

where $\gamma(a,z)$ is the usual incomplete Γ function.[22] This expression is plotted in Fig. 1.

IV. CALCULATION OF THE INELASTIC-SCATTERING CROSS SECTION

The differential cross section for excitation of the nth vibrational level of a diatomic molecule initially unpolarized and in the lowest vibrational state is given by Eqs. (18), (19), (38), (39), (65), and (67);

$$\sigma_n(\theta,\varphi) = (k_a^f/k_a)[|(\mu_r/\mu_{ac})\tilde{f}_c((\mu_{ac}/\mu_r)\vec{k}_r + \vec{q},(\mu_{ac}/\mu_r)\vec{k}_r)|^2 \gamma(n+\tfrac{1}{2},\beta_c^2 q^2 d^2)/2n!qd|\beta_c|$$

$$+ |(\mu_r/\mu_{ab})\tilde{f}_b((\mu_{ab}/\mu_r)\vec{k}_r + \vec{q},(\mu_{ab}/\mu_r)\vec{k}_r)|^2 \gamma(n+\tfrac{1}{2},\beta_b^2 q^2 d^2)/2n!\,qd|\beta_b|]\,, \tag{68}$$

and does not depend on the initial angular momentum quantum number l_0 (or on the distribution of l_0 values). The initial momentum of atom a in the system in which the molecule bc is at rest is $\vec{k}_a$. The initial relative momentum $\vec{k}_r$ is given by

$$\vec{k}_r = (m_b + m_c)\vec{k}_a/M\,, \tag{69}$$

the final relative momentum satisfies

$$\hbar^2(k_r^2 - k_r'^2)/2\mu_r = \epsilon_{n,l} - \epsilon_{n_0,l_0} = n\hbar\omega_0\,, \tag{70}$$

and the final momentum of atom a in the bc rest system is

$$\vec{k}_a^f = \vec{k}_r' + m_a\vec{k}_r/(m_b+m_c)\,.$$

We shall neglect the recoil of the molecule bc here so the ratio k_a^f/k_a becomes

FIG. 1. Spherically averaged form factor for $0 \to n$ transitions $\gamma(n+\tfrac{1}{2}, \chi^2)/2n!\chi$. The parameter χ is the product of the oscillator length parameter d and the magnitude of the momentum transfer k.

$$k_a^f/k_a = k_r'/k_r\,. \tag{71}$$

In order to proceed further, we must calculate the free scattering amplitude $\tilde{f}_i(\vec{k}_2,\vec{k}_1)$ defined in Eq. (42). This is the Fourier transform of the product of the potential V_i and the true wave function for scattering of atom a by atom i when the initial relative momentum is $\vec{k}_1$. When $|\vec{k}_2|^2 = |\vec{k}_1|^2$, this is simply the scattering amplitude for elastic a-i scattering and may be determined from scattering experiments. Here, we require these scattering amplitudes for values of $|\vec{k}_2|^2$ not equal to $|\vec{k}_1|^2$ as well. These "off-the-energy-shell" T-matrix elements also appear in the integral equations of scattering theory[20] where they are related to the scattering wave function within the range of the potential.

Although the wave function $\chi^{(i)}_{\vec{k}_1}(\vec{\rho})$ and hence the free scattering amplitudes may be calculated exactly once the two-body potentials $V_i(\rho)$ are specified, we shall not make this calculation here but characterize the free amplitude by

$$|\tilde{f}_i(\vec{k}_2,\vec{k}_1)|^2 \approx |\hat{f}_i(\vec{k}_2,\vec{k}_1)|^2$$

$$\equiv (1 + k_1^2 r_i^2 e^{-|\vec{k}_2-\vec{k}_1|^2 r_i^2/4})\hat{\sigma}_i/8\pi\,. \tag{72}$$

This function is the sum of a constant term and a peak in the forward direction $(\vec{k}_2 = \vec{k}_1)$. The total elastic-scattering cross section in this approximation is

$$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta\, |\hat{f}_i(\vec{k}_2,\vec{k}_1)|^2_{k_2=k_1} = \hat{\sigma}_i(1 - \tfrac{1}{2}e^{-k_1^2 r_i^2}) \tag{73}$$

with the constant part of $|\hat{f}_i|^2$ contributing $\tfrac{1}{2}\hat{\sigma}_i$ and the forward peak contributing $\tfrac{1}{2}\hat{\sigma}_i(1 - e^{-k_1^2 r_i^2})$. The angular integration is facilitated by noting that

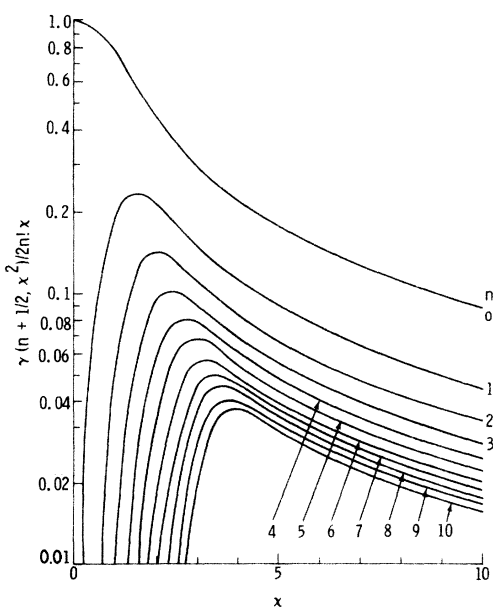$$q^2 \equiv |\vec{k}_2 - \vec{k}_1|^2 = k_1^2 + k_2^2 - 2k_1 k_2 \cos\theta$$

and hence

$$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta \, d\theta \, g(q^2) = 2\pi \int_{k_1-k_2}^{k_1+k_2} q \, dq \, g(q^2)/k_1 k_2 \; .$$

(74)

The approximation $\hat{f}_i$ is an attempt to characterize the scattering amplitude for a wide class of potentials for $k_i r_i \gg 1$, where r_i is the range of the potential $V_i(\rho)$. In the Born approximation, for example, $\hat{f}_i$ is given by

$$\tilde{f}_i(\vec{k}_1 + \vec{q}, \vec{k}_1)_{\text{Born}} = -(2\mu_{a_i}/\hbar^2)\int_0^{\infty} \rho^2 \, d\rho \, V_i(\rho) \sin q\rho/q\rho$$

(75)

and is clearly peaked about $q = 0$ with a width of the order of r_i^{-1}.

When $k_1 r_i$ is large, the exact amplitude for scattering by an infinitely repulsive sphere also exhibits a diffraction peak of width r_i [25] for values of $\vec{q}$ both on and off the energy shell and satisfies the relationship between the total elastic-scattering cross section σ_i and the forward-scattering amplitude

$$|\tilde{f}(\vec{k}_1, \vec{k}_1)|^2 = (1 + k_1^2 r_i^2)\sigma_i/8\pi \; .$$

The inelastic-scattering differential cross section Eq. (68) is the sum of two similar terms

$$\sigma_n(\theta, \varphi) = \sigma_n^{(b)}(\theta, \varphi) + \sigma_n^{(c)}(\theta, \varphi) \; ,$$

(76)

where

$$\sigma_n^{(i)}(\theta, \varphi) = \hat{\sigma}_i(k_r'/k_r)\gamma(n + \tfrac{1}{2}, \beta_i^2 \, q^2 d^2)$$

$$\times \frac{(\mu_r/\mu_{a_i})^2 + k_r^2 r_i^2 e^{-q^2 r_i^2/4}}{16\pi n! q d |\beta_i|}$$

(77)

and where we have used Eqs. (71) and (72). We may use Eq. (74) to integrate Eq. (77);

$$\sigma_n^{(i)} \equiv \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta \, d\theta \, \sigma_n^{(i)}(\theta, \varphi)$$

$$= \hat{\sigma}_i \int_{u_n^-}^{u_n^+} \chi \, d\chi \left(\frac{\gamma(n + \tfrac{1}{2}, \chi^2)}{2n! \, \chi}\right) \left[\left(\frac{\mu_r}{\mu_{a_i} u_0^+}\right)^2 + \eta_i e^{-\chi^2 \eta_i}\right]$$

for $(k_r d)^2 \geq n\mu_r/\mu_T$ (78a)

$= 0$ otherwise ,   (78b)

where

$$\eta_i \equiv (r_i/2\beta_i d)^2$$

(79)

and

$$u_n^{\pm} \equiv |\beta_i|(k_r \pm k_r')d$$

$$= |\beta_i|\{k_r d \pm [(k_r d)^2 - n\mu_r/\mu_T]^{1/2}\} \; .$$

(80)

Since the range of the potential r_i is of the same order of magnitude as the equilibrium oscillator spacing τ_e and $\xi_e^2 = \tau_e^2/2d^2$ is very large, η_i will be very large and will contribute to the integral (78a)

only for $\chi \ll 1$. We see from Fig. 1 that

$$\gamma(n + \tfrac{1}{2}, \chi^2)/2n! \chi \approx \delta_{n,0} \quad \text{for } \chi \ll 1 \; ,$$

hence the diffraction peak will contribute only when $n = 0$, and Eq. (78a) becomes

$$\sigma_n^{(i)} = \frac{1}{2} \hat{\sigma}_i \left[\delta_{n,0} + \frac{1}{n!}\left(\frac{\mu_r}{\mu_{a_i} u_0^+}\right)^2 [I_n(u_n^+) - I_n(u_n^-)]\right]$$

for $(k_r d)^2 \geq n\mu_r/\mu_T$,   (81)

where

$$I_n(u) = \int_0^u d\chi \, \gamma(n + \tfrac{1}{2}, \chi^2) = u\gamma(n + \tfrac{1}{2}, u^2) - \gamma(n + 1, u^2) \; .$$

(82)

The factor $(\mu_r/\mu_{a_i})^2$ in Eq. (81) arises from the attempt to relate f_i to the free particle scattering amplitudes $\tilde{f}_i$ in Eqs. (38) and (39) and always appears in the final expression for the cross section in the impulse approximation.[21] This factor does not appear multiplying the Kronecker δ because we have taken the height of the diffraction peak to be proportional to $(\mu_{a_i}/\mu_r)^2 k_r^2$.

Let us now consider the vibrational excitation of a stationary CO molecule by collision with a beam of oxygen atoms with velocity V_a. The ratio (μ_r/μ_{ai}) is given by

$$\mu_r/\mu_{ai} = (m_b + m_c)(m_a + m_i)/m_i(m_a + m_b + m_c) \; ,$$

(83)

hence $\mu_r/\mu_{c0} = \mu_r/\mu_T = 1.4849$, $\mu_r/\mu_{00} = 1.2727$, $|\beta_0| = 0.428\,57$, and $|\beta_c| = 0.571\,43$. Since $m_a V_a = \hbar k_a$, we have

$$(k_r d)^2 = \frac{\tfrac{1}{2} m_a V_a^2}{\hbar \omega_0}\left(\frac{(m_b + m_c)^2 m_a}{\mu_T M^2}\right) ,$$

(84)

where we have used Eqs. (33) and (49).

When we insert $\hbar\omega_0 = 0.268\,98$ eV [13] we find

$$k_r d = 1.8743 E_k^{1/2} = 0.539\,32 V_a ,$$

where $E_k = \tfrac{1}{2} m_0 V^2$ is the kinetic energy of the oxygen atom in electron volts and V_a is the velocity in km/sec. The only remaining quantities required to calculate the inelastic-scattering cross section are $\hat{\sigma}_0$ and $\hat{\sigma}_c$.

The transition probability per collision is

$$P_{0\to n} = (\sigma_n^{(0)} + \sigma_0^{(c)})/(\sigma_T^{(0)} + \sigma_T^{(c)}) ,$$

(85)

where

$$\sigma_T^{(i)} = \sum_n \sigma_n^{(i)}$$

(86)

is the contribution to the total cross section from a particular atom of the diatomic molecule. The transition probability will be between the limits $P_{0\to n}^{(0)}$ and $P_{0\to n}^{(c)}$ depending on the value of the ratio

TABLE I. Partial cross sections and excitation probabilities for oxygen-oxygen and oxygen-carbon collisions.

V (km/sec)	n [a]	OO $\sigma_n^{(0)}/\hat{\sigma}_0$	$P_{0\to n}^{(0)}$	OC $\sigma_n^{(c)}/\hat{\sigma}_c$	$P_{0\to n}^{(c)}$
1	0	1.282 226	1.000 000	1.537 623	1.000 000
	T	1.282 226		1.537 623	
2	0	1.211 575	1.000 000	1.389 568	1.000 000
	T	1.211 575		1.389 568	
3	0	1.123 927	0.937 138	1.235 458	0.903 083
	1	0.075 392	0.062 862	0.132 586	0.096 917
	T	1.199 319		1.368 044	
4	0	1.040 277	0.870 113	1.111 232	0.816 291
	1	0.125 045	0.104 591	0.180 834	0.132 837
	2	0.028 720	0.024 022	0.062 576	0.045 967
	3	0.001 523	0.001 274	0.006 677	0.004 905
	T	1.195 566		1.361 319	
5	0	0.969 512	0.811 919	1.017 983	0.749 746
	1	0.142 856	0.119 635	0.183 843	0.135 400
	2	0.058 368	0.048 880	0.094 415	0.069 537
	3	0.019 671	0.016 473	0.046 064	0.033 926
	4	0.003 693	0.003 093	0.015 466	0.011 391
	T	1.194 100		1.357 770	
6	0	0.912 272	0.764 504	0.947 774	0.698 691
	1	0.144 015	0.120 688	0.173 854	0.128 164
	2	0.074 241	0.062 215	0.102 318	0.075 428
	3	0.038 512	0.032 274	0.064 560	0.047 593
	4	0.017 362	0.014 550	0.039 382	0.029 032
	5	0.005 796	0.004 857	0.020 769	0.015 310
	6	0.001 067	0.000 894	0.007 452	0.005 494
	7	0.000 019	0.000 016	0.000 390	0.000 287
	T	1.193 286		1.356 498	
7	0	0.866 265	0.726 257	0.893 677	0.659 219
	1	0.138 525	0.116 137	0.161 165	0.118 883
	2	0.079 858	0.066 951	0.101 251	0.074 687
	3	0.049 565	0.041 554	0.070 216	0.051 795
	4	0.030 179	0.025 301	0.049 989	0.036 874
	5	0.016 838	0.014 117	0.035 101	0.025 893
	6	0.007 968	0.006 680	0.023 289	0.017 179
	7	0.002 871	0.002 407	0.013 603	0.010 034
	8	0.000 654	0.000 549	0.006 042	0.004 457
	9	0.000 057	0.000 048	0.001 328	0.000 980
	T	1.192 780		1.355 661	
8	0	0.828 941	0.695 161	0.850 944	0.628 021
	1	0.130 911	0.109 784	0.148 767	0.109 794
	2	0.080 286	0.067 329	0.097 081	0.071 648
	3	0.054 337	0.045 567	0.070 583	0.052 092
	4	0.037 679	0.031 598	0.053 546	0.039 518
	5	0.025 733	0.021 580	0.041 227	0.030 427
	6	0.016 708	0.014 012	0.031 633	0.023 346
	7	0.009 900	0.008 302	0.023 757	0.017 533
	8	0.005 083	0.004 262	0.017 037	0.012 574
	9	0.002 108	0.001 768	0.011 194	0.008 262
	10	0.000 636	0.000 534	0.006 240	0.004 605
	11	0.000 115	0.000 096	0.002 509	0.001 851
	12	0.000 007	0.000 006	0.000 444	0.000 327
	T	1.192 445		1.354 961	
9	0	0.798 241	0.669 545	0.816 429	0.602 762

TABLE I. *(Continued)*

V (km/sec)	n [a]	$\sigma_n^{(0)}/\hat{\sigma}_0$	$P_{0\to n}^{(0)}$	$\sigma_n^{(c)}/\hat{\sigma}_c$	$P_{0\to n}^{(c)}$
		OO		**OC**	
9	1	0.122 963	0.103 139	0.137 481	0.101 501
	2	0.078 383	0.065 746	0.091 967	0.067 898
	3	0.055 670	0.046 694	0.068 778	0.050 778
	4	0.041 180	0.034 540	0.053 983	0.039 855
	5	0.030 809	0.025 842	0.043 388	0.032 033
	6	0.022 853	0.019 169	0.035 237	0.026 015
	7	0.016 490	0.013 832	0.028 648	0.021 150
	8	0.011 322	0.009 496	0.023 117	0.017 067
	9	0.007 194	0.006 034	0.018 333	0.013 535
	10	0.004 085	0.003 427	0.014 093	0.010 405
	11	0.001 983	0.001 663	0.010 273	0.007 585
	12	0.000 775	0.000 650	0.006 839	0.005 049
	13	0.000 223	0.000 187	0.003 886	0.002 869
	14	0.000 041	0.000 034	0.001 653	0.001 220
	15	0.000 003	0.000 003	0.000 378	0.000 279
	T	1.192 215		1.354 481	
10	0	0.772 628	0.648 150	0.788 010	0.581 920
	1	0.115 357	0.096 772	0.127 446	0.094 115
	2	0.075 496	0.063 333	0.086 751	0.064 062
	3	0.055 271	0.046 366	0.066 102	0.048 814
	4	0.042 429	0.035 593	0.052 991	0.039 132
	5	0.033 285	0.027 922	0.043 655	0.032 238
	6	0.026 300	0.022 063	0.036 522	0.026 971
	7	0.020 704	0.017 368	0.030 804	0.022 748
	8	0.016 069	0.013 480	0.026 053	0.019 239
	9	0.012 149	0.010 192	0.021 996	0.016 243
	10	0.008 816	0.007 396	0.018 451	0.013 626
	11	0.006 025	0.005 055	0.015 295	0.011 295
	12	0.003 789	0.003 178	0.012 435	0.009 183
	13	0.002 130	0.001 787	0.009 808	0.007 243
	14	0.001 033	0.000 866	0.007 374	0.005 446
	15	0.000 413	0.000 346	0.005 135	0.003 792
	16	0.000 127	0.000 107	0.003 154	0.002 329
	17	0.000 027	0.000 023	0.001 568	0.001 158
	18	0.000 003	0.000 003	0.000 532	0.000 393
	19	0.000 000	0.000 000	0.000 074	0.000 055
	T	1.192 050		1.354 155	

[a] The row labeled T contains the ratio of the total cross section to $\hat{\sigma}$ in the $\sigma_n/\hat{\sigma}$ column.

$\hat{\sigma}_0/\hat{\sigma}_c$, where

$$P_{0\to n}^{(i)} \equiv \sigma_n^{(i)}/\sigma_T^{(i)}. \tag{87}$$

The quantities $\sigma_n^{(i)}/\hat{\sigma}_i$, $\sigma_T^{(i)}/\hat{\sigma}_i$, and $P_{0\to n}^{(i)}$ do not depend upon $\hat{\sigma}_i$ and are listed in Table I for incident velocities in the km/sec range. The bounds on $P_{0\to n}$ ($P_{0\to n}^{(0)}$ and $P_{0\to n}^{(c)}$) are also plotted in Fig. 2 for transitions up to $n = 4$.

The probability per collision of vibrational excitation of carbon monoxide by oxygen in a shock wave for temperatures between 1800 and 4000 °K has been measured by Center[26] and found to be of the order of 10^{-2}. This agrees with our findings when we multiply our average probability per collision above threshold by the fraction of collisions

in an equilibrium gas of temperature T for which the relative energy is above the threshold energy E_t. This factor is[27]

$$e^{-x}(1 + x), \tag{88}$$

where $x = E_t/kT$ and lies between 0.48 and 0.82 for these temperatures.

V. SUMMARY

We have found that the assumptions leading to the impulse approximation are justified for atom–diatomic-molecule collisions provided the interaction is dominated by short-range forces. In the impulse approximation, the expression for the inelastic-scattering amplitude factors into a
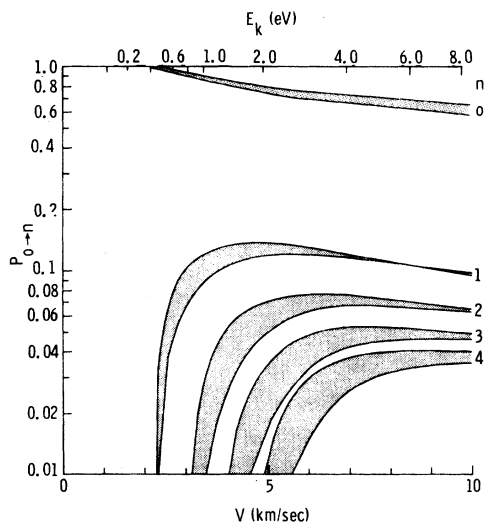
FIG. 2. Vibrational-excitation probabilities for collisions between carbon monoxide at rest in the lowest vibrational state and atomic oxygen with velocity V. The transition probability $P_{0 \to n}$ lies within the shaded region depending on the ratio δ_0/δ_c. The boundaries of the shaded regions are $P_0{}^{(c)}_{\to n}$ and $P_0{}^{(0)}_{\to n}$.

bound-state form factor and an atom-atom scattering amplitude that must be evaluated off the energy shell. We have found a closed-form expression for the bound-state form factor for vibrational

excitations by using a closure approximation to evaluate the sums over final angular momentum quantum numbers. We find that the vibrational inelastic-scattering cross sections do not depend on the initial angular momentum quantum number l_0.

Vibrational-transition probabilities evaluated using a fairly rough estimate for the atom-atom scattering amplitudes are in qualitative agreement with experiment. An improved estimate of the atom-atom scattering amplitude may be obtained semiclassically, quantum mechanically, or from atom-atom cross-section experiments.

We have found that the impulse approximation provides a rigorous tool for the calculation of atom–diatomic-molecule inelastic-scattering cross sections. We suggest that the application of the impulse approximation to diatomic–diatomic-molecule and various polyatomic collisions be investigated.

[1]K. F. Herzfeld and T. A. Litovitz, *Absorption and Dispersion of Ultrasonic Waves* (Academic, New York, 1959).

[2]K. Takayanagi, Progr. Theoret. Phys. (Kyoto) Suppl. 25, 1 (1963).

[3]D. Rapp and T. Kassal, Chem. Rev. 69, 61 (1969).

[4]H. S. W. Massey, *Electronic and Ionic Impact Phenomena*, 2nd ed. (Oxford U. P., London, England, 1971), Vol. III.

[5]D. J. Wilson and D. J. Locker, J. Chem. Phys. 57, 5393 (1972).

[6]G. F. Chew, Phys. Rev. 80, 196 (1950).

[7]W. L. Clinton, C. M. Cosgrove, and G. A. Henderson, Phys. Rev. A 2, 2357 (1970).

[8]P. Eckelt and H. J. Korsch, Chem. Phys. Lett. 11, 313 (1971).

[9]G. F. Chew and G. C. Wick, Phys. Rev. 85, 636 (1952).

[10]J. Ashkin and G. C. Wick, Phys. Rev. 85, 686 (1952).

[11]G. F. Chew and M. L. Goldberger, Phys. Rev. 87, 778 (1952).

[12]K. F. Herzfeld, *Thermodynamics and Physics of Matter* (Princeton U. P., Princeton, N. J., 1965), Sec. H.

[13]G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950).

[14]L. D. Landau and E. Teller, Z. Phys. Sowjet Union, 10, 34 (1936).

[15]G. Herzberg, *Electronic Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1966), pp. 430–432.

[16]Vibrational relaxation of N_2 arising from curve crossing in N_2O has been discussed by E. R. Fisher and E. Bauer [J. Chem. Phys. 57, 1966 (1972)] and by J. B. Delos [J. Chem. Phys. 59, 2365 (1973)].

[17]K. Alder and A. Winter, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. 32, 8 (1960); K. H. Kramer and R. B. Bernstein, J. Chem. Phys. 40, 200 (1964); J. Chem. Phys. 44, 4473 (1966).

[18]M. A. Wartell and R. J. Cross, Jr., J. Chem. Phys. 55, 4983 (1971); M. A. Wartell, J. Chem. Phys. 58, 4700 (1973).

[19]C. E. Treanor, J. Chem. Phys. 43, 532 (1965).

[20]L. S. Rodberg and R. M. Thaler, *Introduction to the Quantum Theory of Scattering* (Academic, New York, 1967).

[21]N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collision*, 3rd ed. (Oxford U. P., London, England, 1965).

[22]M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (U. S. GPO, Washington, D. C., 1964).

[23]E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis* 4th ed. (Cambridge U. P., Cambridge, England, 1965).

[24]A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton U. P., Princeton, N. J., 1957).

[25]P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), Vol. II, p. 1485.

[26]R. E. Center, J. Chem. Phys. **58**, 5230 (1973).

[27]S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases* (Cambridge U. P., Cambridge, England, 1961), p. 92.
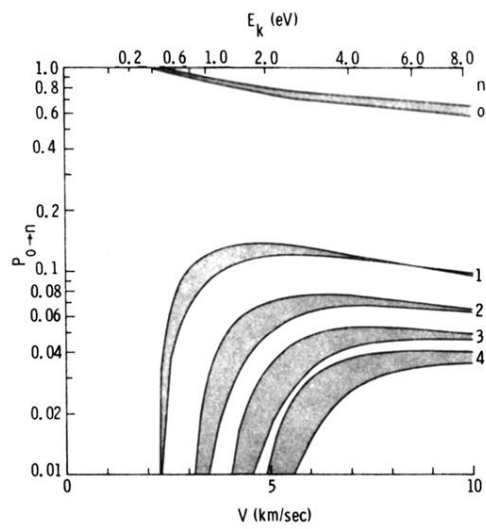
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