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INTERCHANGE OF TRANSLATIONAL, ROTATIONAL AND VIBRATIONAL ENERGY IN MOLECULAR COLLISIONS

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Abstract

The change in internal energy of molecules upon collisions has been analysed. Formulae, (26) to (27-C), for the effective cross section of inelastic collisions have been obtained as functions of known properties of the molecules, subject to certain conditions. These conditions are: the atoms which come into contact during collision must belong to the first row of the periodic table; the vibrational quantum numbers which suffer a change must be small.

Vibrational quantum numbers have a marked reluctance to change during collisions at room temperature. The probability that a N_2 molecule in its first excited vibrational state transfer its energy to He in a head on collision is 0.0^76. The probability that another N_2 molecule absorb this energy is 0.0^44. A lack of resonance of 0.01 volt can decrease the effective cross section by a factor of 0.02.

Rotational quantum numbers change readily except in unusual cases.

I. Introduction

In a gaseous system we often wish to know the effective cross section of a collision between two systems in which one or both suffer a change of quantum numbers. If this change involves electron jumps, as in the quenching of resonance radiation, it is not limited to collisions in which the systems would be said classically to come into contact. Such transitions have been observed to take place when the closest distance of approach is many times the classical diameter of the systems.[1] In this type of collision the changes in the motion of the two systems as a whole may be relatively unimportant in comparison to the change of quantum numbers.

In another interesting type of collision the electronic states remain unaltered, and the vibrational and rotational states are changed. The experimental data have been discussed by Oldenberg.[2] In many cases the probability of a transfer is very small even in head-on collisions. In such collisions changes in the internal molecular quantum numbers are unimportant in comparison to changes in the motion of the two systems as a whole. A study of the latter change must thus precede a study of the former. Such a procedure is adopted in this paper. The exact motion of the centers of gravity of the two colliding systems is found when the internal coordinates are replaced

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[1] Baxter, J.A.C.S. **52**, 3920 (1930); Boeckner, Bureau Stand. **5**, 13 (1930).

[2] Oldenberg, Phys. Rev. **37**, 194 (1931).

by their averaged values. This motion corresponds to an elastic collision. The internal motions of the systems are then treated as perturbations that give rise to changes in the internal quantum numbers during collision.

The discussion of collision phenomena is preceded by an examination of inter-molecular forces (II). The principles of energy interchange may be most clearly analyzed in systems so idealized that all irrelevent difficulties are absent. Thus the interchange of vibrational and translational energy is investigated in the simplified collision of an atom and a diatomic molecule where all motion is confined to a line (III). Similarly the interchange of rotational and translational energy is examined first for the collision of an atom with a rigid symmetrical molecule, all motion being limited to a plane (IV). The results of the investigation of these idealized collisions are then combined in such a way as to give definite numerical information about collisions in an actual gaseous system (V).

II. INTER-MOLECULAR FORCES

In ordinary collisions the inter-molecular forces need be known only for those inter-molecular distances in which the overlapping of electrons is slight. At these collision distances the mutual energy may be split to a good approximation into three parts: that due to van der Waal's attraction, the negative coulomb energy arising from interpenetration of electrons, and the repulsive resonance energy. The mutual energy between two molecules is approximately the sum of the mutual energies between the constituent atoms, provided the resonance forces are taken to be repulsive.

London and Eisenschitz[3] have shown that the repulsive resonance energy between two H atoms dominates the attractive energies. This may safely be considered to be true for all atoms in the first row of the periodic table. However, this resonance energy becomes smaller both with an increase of the total quantum number n[4] and of the azimuthal quantum number l[5]. Hence the following considerations will be confined to atoms in the first row.

In the outer region of an atom, i.e., the region that overlaps in ordinary thermal collisions, the electronic density varies approximately[6] as r^{n^*} exp-$(-2\alpha s)$. Here s is the distance from the nucleus, and α is the square root of the ionization potential.[7] The asymptotic expansion of the resonance energy[8] between two atoms will contain the factor exp-$(\alpha_1+\alpha_2)R$, where α_1 and α_2 refer

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[3] E. Eisenschitz and F. London, Zeits. f. Physik **60**, 491 (1930).

[4] W. Heisenberg, Zeits. f. Physik **49**, 619 (1928).

[5] M. Delbruck, Proc. Roy. Soc. **129**, 686 (1930).

[6] D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89 (1928).

[7] Energy, length, mass will in this paper be expressed in the atomic units 13.53 volts, 0.528×10^{-8} cm, m_e, unless otherwise specified.

[8] This may be verified by examining the general type of integral that arises in calculating the resonance energy. See Zener and Guillemin, Phys. **34**, 999 (1929), Eqs. (28) and (29). When the integral logarithms are replaced by their asymptotic expansions all terms will have the factor exp-$(\alpha_1+\alpha_2)r$. This opportunity is taken for pointing out that $m-v+1$ should replace $m-v$ in Eq. (25), and $m!/(m-v)!\cdot v+1$ should replace $e^{-\alpha}A_v(1, \alpha)$ in (26) and (30) of this reference.

to the two atoms, and R is their nuclear separation. The mutual potential between atoms or symmetrical diatomic molecules, averaged over all internal molecular coordinates, will contain the factor exp-$(\alpha_1+\alpha_2)r$, where r is the distance between the centers of gravity of the two systems. An approximation to the actual potential may thus be written as

$$V(r) = E''e^{(\alpha_1+\alpha_2)(r_{E''}-r)}. \tag{1}$$

The constants E'', $r_{E''}$ are to be experimentally determined. They have the relation $V(r_{E''}) = E''$. If $E'' = E_{300}$ denotes the average energy of a gas molecule at room temperature, then r_{300} will be the classical average closest distance of approach.

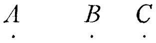
It is desirable to compare the theoretical formula (1) with experimental data. The data on inter-molecular forces have been thoroughly reviewed by Lennard-Jones.[9] If the constants c, α are determined to make $c\ \exp(-\alpha r)$ join smoothly to the repulsive energy formulae of Lennard-Jones at r_{300}, then α should be considered as the experimental value of $\alpha_1+\alpha_2$. A comparison of these constants is given in Table I.

TABLE I. *Energy constants.*

	Lennard-Jones	Spectroscopic
H_2	2.08	2.12
He	3.50	2.68
Ne	2.2	2.5

III. VIBRATION-TRANSLATION

The interchange of vibrational and translational energy will be investigated in the collision of atom A with the molecule $B-C$, the atoms A, B, C being confined to a line.



This interchange will be a function of the various physical parameters, such as the force beinding B and C, the repulsive force begween A and B, the initial translational and vibrational energies, and the relative masses.

If the atoms were sufficiently massive, and if the translational and vibrational energies were sufficiently great, only an investigation by classical mechanics would be necessary. But these conditions are not satisfied in the interesting cases where only the first vibrational states are excited. Nevertheless, it is profitable to consider the classical picture, as in general the same qualitative dependence upon the physical parameters will be present in the mechanics of the classical and quantum theory.

The classical picture will now be used in finding the conditions of maximum transfer of energy from vibration to translation with the optimum phase relation between the vibrational and translational motion. The system is first simplified by assuming the impact between A and B to be instantane-

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[9] R. H. Fowler, Statistical Mechanics, Chap. X (1929).

ous. Then if the mean vibration velocity of B is comparable to the relative velocity of A and the molecule $B-C$, with an optimum phase relation, the impact between A and B will occur when the molecule has all its internal energy in the form of kinetic energy. The energy transfer will then be a maximum when the masses of A and B are nearly equal. However, the vibrational energy of light molecules is much larger than the mean translational energy at room temperatures. Hence in order that A strike B while the latter has a maximum velocity, A must be lighter than B.

The effect of the finite time of impact between A and B is now examined. If this time is small in comparison to the period of oscillation of the molecule B-C, the impact may be regarded as instantaneous. As it becomes large in comparison to the period of oscillation, the atom will tend to act only upon the center of gravity of the molecule. The interchange of vibrational and translational energy then becomes small. With a fixed initial translational energy, a decrease in the mass of A will lessen this time of impact, and thus increase this interchange irrespective of the mass of B.

It is of interest to compare this time of impact with the period of oscillation in collisions between actual molecules. If r is the distance between A and B, their mutual energy may be taken to be

$$V(r) = E''e^{-\alpha(r-r_{E''})} \tag{1'}$$

as was seen in II. If E'' is set equal to the mutual energy E, then a reasonable value for the time of impact is the time τ_i during which $r<r_0$. Here, r_0, together with F, is determined to make the parabola

$$U(r) = F(r - r_0)^2 \tag{2}$$

join smoothly to $V(r)$ at $r=r_E$. Thus (1′) has been replaced by the potential

$$W(r) = \begin{array}{ll} F(r - r_0)^2, & r < r_0. \\ 0 & , r > r_0. \end{array} \tag{3}$$

The ratio of τ_i to the period of vibration of B-C, τ_v, is one half the ratio of the frequency of vibration of the molecule to the frequency of vibration of a particle of mass

$$\mu = \frac{M_A(M_B + M_C)}{M_A + M_B + M_C} \tag{4}$$

in the potential (2). This ratio is

$$\beta = \frac{40}{\alpha} \frac{\omega_0}{8106}\left(\frac{\mu}{E}\right)^{1/2}$$

where ω_0 is the wave number of the molecule, μ is expressed in units of atomic hydrogen, and E is in units of the mean energy of a gas molecule at room temperature, E_{300}. A numerical example shows this ratio to be relatively large. For instance, in the collision of He with N_2 at room temperature, $\alpha=2.4$, $\omega_0=2345$, $\mu=3.5$ $E \simeq 1$, giving $\beta=9$.

The above considerations lead to the following classical conclusions for light molecules. Since the intra-molecular binding forces are large in comparison to the inter-molecular repulsive forces at collision distances, and since the internal energy of these molecules is large in comparison to their temperature equilibrium translational energy, the interchange of vibrational and translational energy will be small. H_2 will absorb more readily than any other molecule translational energy not only from a C-H bond but from any light molecule.

A precise quantitative theory for the one dimensional collision is developed by the following quantum mechanical analysis.

The coordinates will be taken to be: the center of gravity of the complete system, X; the nuclear separation of molecule B-C, x; and the distance between the atom A and the center of gravity of the molecule, r. This choice has been made in order that the kinetic energy may be written as

$$T = T_x + T_x + T_r.$$

The wave equation, after eliminating the center of gravity of the complete system, then becomes[7]

$$\left\{\frac{1}{\mu_m}\frac{d^2}{dx^2} + \frac{1}{\mu}\frac{d^2}{dr^2} - V(x) - V(x, r) + E\right\}\Psi = 0 \tag{5}$$

Here

$$\mu_m = \frac{M_B M_C}{M_B + M_C}$$

and μ is given by (4). The energy $V(x)$ is the potential energy of the isolated molecule B-C, and $V(x, r)$ is the mutual energy of atom A and the molecule. The energy E has a continuous range of values. If E_i is the energy of the isolated molecule, then $p_i = \mu^{1/2}(E - E_i)^{1/2}$ is proportional to the momentum associated with the translational motion.

Let the normalized function $\psi_i(x)$ be a solution of the wave equation for the isolated molecule, namely

$$\left\{\frac{1}{\mu_m}\frac{d^2}{dx^2} - V(x) + E_i\right\}\Psi_i(x) = 0.$$

Corresponding to the physical requirement that before collision the molecule be in the vibrational state v_0, a solution of (5) is to be found of the form

$$\Psi \overset{r\to\infty}{=} \frac{(e^{ip_{v_0}r} + e^{-ip_{v_0}r})}{(p_{v_0})^{1/2}} + \sum_v \gamma_{v_0}{}^{v} \frac{e^{-ip_v r}}{(p_v)^{1/2}} \Psi_v(x) \tag{6}$$

The summation is over all indices for which p_v is real. The probability that the molecule has changed its vibrational quantum number from v_0 to v will be $|\gamma_{v_0}{}^{v}|.^2$

In order to obtain the coefficients $\gamma_{v_0}{}^{v}$, ψ is expanded as follows:

$$\Psi = \sum_v Q_v(r)\Psi_v(x). \tag{7}$$

The Q_v's are undetermined functions. Substitution of this expansion into (5) gives

$$\sum_v \left\{ \frac{d^2}{dr^2} - \mu V(x, r) + p_v^2 \right\} Q_v(r) \Psi_v(x) = 0.$$

Multiply by $\Psi_v(x)$ and integrate with respect to x.

$$\left\{ \frac{d^2}{dr^2} - \mu V_v^{v}(r) + p_v^2 \right\} Q_v(r) = \mu \sum_{v' \neq v} Q_{v'}(r) V_v^{v'}(r) \tag{8}$$

where

$$V_v^{v'}(r) = \int \Psi_v(x) V(x, r) \Psi_{v'}(x) dx.$$

By neglecting the right member an equation for the zeroth approximation, $Q_v^0(r)$, is obtained.

$$\left\{ \frac{d^2}{dr^2} - \mu V_v^{v}(r) + p_v^2 \right\} Q_v^0(r) = 0.$$

Since $V_v^v(\infty) \to 0$, $Q_v^0(r)$ becomes sinusoidal for large r. Denote that particular solution that vanishes at $r=0$ by $U(p_v/r)$. Let this solution be so normalised that

$$U(p_v/r) \overset{r \to \infty}{=} \frac{\sin (p_v r + \theta_v)}{p_v^{1/2}}. \tag{9}$$

Choose another particular solution by its asymptotic behavior

$$X(p_v/r) \overset{r \to \infty}{=} \frac{e^{-i(p_v r + \theta_v)}}{p_v^{1/2}}. \tag{9'}$$

The zeroth approximation to $Q_v(r)$ corresponds to an elastic collision in which the molecule has the quantum number v. Hence

$$Q_v^0(r) = \begin{matrix} U(p_v/r), & v = v_0. \\ 0 \quad , & v \neq v_0. \end{matrix} \tag{10}$$

The first approximation to $Q_v(r)$ is obtained by substituting this zeroth approximation into the right member of (8).

$$\left\{ \frac{d^2}{dr^2} - \mu V_v^{v}(r) + p_v^2 \right\} Q_v^1(r) = \begin{matrix} \mu U(p_{v_0}/r) V_{v/0}^{v}, & v \neq v_0 \\ 0 \qquad\qquad\quad , & v = v_0. \end{matrix} \tag{11}$$

The solution of these equations that satisfies the boundary condition (6) is

$$\begin{aligned} -Q_v^1(r) = {} & \mu X(p_v/r) \int_0^r U(p_v/r') V_{v_0}^{v}(r') U(p_{v_0}/r') dr' \\ & + \mu U(p_v/r) \int_r^\infty X(p_v/r') V_{v_0}^{v}(r') U(p_{v_0}/r') dr' \end{aligned} \tag{12}$$

$$Q_{v_0}^1(r) = C_1 X(p_{v_0}/r). \tag{12'}$$

The validity of (12) may be verified by direct substitution into (11). The left member vaishes identically except for the term

$$-\mu U(p_{v_0}/r)V_{v_0}{}^{v}\{X'(p_v/r)U(p_v/r) - X(p_v/r)U'(p_v/r)\}.$$

Now the subtraction of

$$X\left(\frac{d^2}{dr^2} - \mu V_v{}^v + p_v{}^2\right)U = 0$$

from

$$U\left(\frac{d^2}{dr^2} - \mu V_v{}^v + p_v{}^2\right)X = 0$$

gives

$$\frac{d}{dr}(X'U - XU') = 0.$$

Hence

$$X'U - XU' = C.$$

But from (9), (9′), $C = -1$. Hence (12) satisfies (11) identically.

C_1 is to be determined from the equation of continuity,—

$$\int\left(\Psi\frac{d}{dr}\overset{*}{\Psi} - \overset{*}{\Psi}\frac{d}{dr}\Psi\right)dx = 0.$$

Since the second integral in (12) vanishes as r becomes infinitely large, the first two approximations to the coefficients in the expansion (7) gives a ψ of the form (6) with

$$\begin{aligned}\gamma_{v_0}{}^{v} = \mu\int_0^\infty dr\int_{-\infty}^{\infty} dx\,U(p_v/r)\Psi_v(x)V(x, r)&\\ \cdot U(p_{v_0}/r)\Psi_{v_0}(x),\ \ v \neq v_0.&\\ \gamma_{v_0}{}^{v_0} = C_1.&\end{aligned}\tag{13}$$

The conditions under which this first approximation is valid will now be investigated. In general the successive approximations of the Born collision method do not converge. However, if the first terms become smaller, they may form a semi-convergent series that has a physical meaning. The relative magnitude of successive approximations will depend upon the physical parameters of the system. The application of (13) is thus limited to those systems with parameters such that the first successive approximations to the solutions of (8) which vanish at $r = 0$ become smaller. It will be found that all systems examined in this study satisfy this condition.

An approximation to the probability is obtained by assuming a simplified potential of the form

$$V(x, r) = E''e^{-\alpha(r - r_{E''})}(1 + qz)$$

where z is the displacement of x from its equilibrium value. A reasonable value for q is the coefficient in the first term of the expansion of $e^{-\lambda\alpha z}$, where

$$\lambda = \frac{M_C}{M_B + M_C} \cdot \tag{14}$$

Neglecting the higher powers of z limits this analysis to molecules in which the amplitudes of vibration are relatively small. With this potential $\gamma_{v_0}{}^{v}$ may be factored as

$$\gamma^{v}{}_{0} = \xi_{v_0}{}^{v}\eta_{pv_0}{}^{pv}$$

where

$$\xi_{v_0} = q\int_{-\infty}^{\infty} \Psi_v(z) z \Psi_{v_0}(z) dz \tag{15}$$

and

$$\eta_{pv_0}{}^{pv} = \mu E'' \int_{0}^{\infty} U(p_v/r) e^{-\alpha(r-r_{E''})} U(p_{v_0}/r) dr. \tag{15'}$$

The U's are solutions of

$$\left(\frac{d^2}{dr^2} - \mu E'' e^{-\alpha(r-r_{E''})} + p^2\right) U(p/r) = 0 \tag{16}$$

and are normalised to satisfy (9).

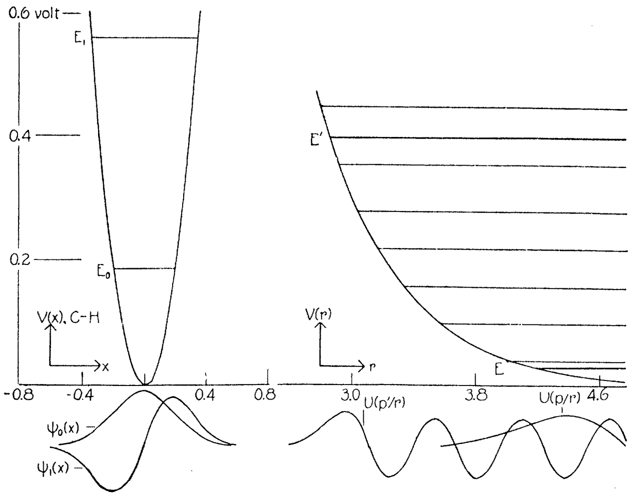

Fig. 1.

Since only a very rough approximation to $\eta_{p'}{}^{p}$ can be obtained without great analytical difficulties, it is profitable to consider first the qualitative dependence of $\eta_{p'}{}^{p}$ upon the physical parameters.

In Fig. 1 are drawn the potentials and pertinent wave functions. The energy levels to $V(r)$ are drawn for energy values whose $U(p/r)$ have nodes at

$r=r_0$, where r_0 is chosen arbitrarily at a point where $V(r)$ first becomes appreciable. Here E, E' refer to the initial and final translational energies, with $E<E'$, and p, p' to the corresponding momenta.

An increase of the molecular binding force $-dV(z)/dz$ relative to the repulsive force $-dV(r)/dr$ will increase the number of energy levels between E' and E, thus increasing the fluctuations in sign of the integrand of (17), and thus decreasing $\eta_{p'}{}^{p}$. An increase in the reduced mass μ will have a similar effect.

An increase of E and E' by similar amounts will increase $\eta_{p'}{}^{p}$ by lessening the number of energy levels between E and E'.

An examination shows that in ordinary thermal collisions between molecules whose atoms belong to the first row of the periodic table, the first maximum of $g(p/r)$ lies in the region $r<r_0$, and that several "energy levels" always lie between E and E'. The qualitative results of the classical and the quantum mechanical treatment are thus similar in such collisions. In the language of the former a decrease in the slope of $V(r)$ or an increase of the reduced mass μ results in an increase of the time of collision. In the language of the latter, similar changes result in an increased fluctuation of sign in the integrand of (17).

An analytical approximation to $\eta_{p'}^{p}$ is obtained by replacing the exponential potential by a potential which renders Eq. (16) soluble in known functions. Such a potential is

$$V_a = \frac{A}{(r-B)^2}, \quad r > B$$

$$V_a = \infty\,, \quad r < B.$$

The constants A, B are adjusted to make V_a as similar as possible to the potential (1′) in the important range of r. With the choice

$$V_a = \frac{4E''/\alpha^2}{(r - r_{E''} + 2/\alpha)^2} \tag{17}$$

the two potentials join smoothly at $r=r_{E''}$. A reasonable value of E'' is $(E\,E')^{1/2}$.

The differential equation (16) now becomes

$$\left\{\frac{d^2}{dx^2} - \frac{4\mu E''/\alpha^2}{x^2} + p^2\right\} U(p/x) = 0$$

where $x=r-r_{E''}+2/\alpha$. Its solution is the Bessel function

$$U(p/x) = \left(\frac{\pi}{2}\right)^{1/2} x^{1/2} J_v(px) \tag{18}$$

with

$$v = (4\mu E''/\alpha^2 + 1/4)^{1/2} \simeq 2(\mu E'')^{1/2}/\alpha.$$

This solution is normalized to satisfy (9).

The expression (15′) for $\eta^{p}{}_{p'}$ now becomes

$$\eta^{p}{}_{p'} = 2\pi \frac{\mu E''}{\alpha^2} \int_0^\infty \frac{J_v(px)J_v(p'x)dx}{x}.$$

The substitution of

$$\int_0^\infty \frac{J_v(px)J_v(p'x)}{x} dx = (p/p')^v/2v, \quad p < p'$$

(Watson, Theory of Bessel Functions, p. 401) reduces this to

$$\eta^{p}{}_{p'} = \frac{\pi(\mu E'')^{1/2}}{2\alpha}(E/E')^{(\mu E'')^{1/2}/\alpha}. \tag{19}$$

If the molecule is assumed to be vibrating as a linear oscillator, then (15) reduces to

$$\xi^{\,v}_{v-1} = \frac{\alpha}{2}\left(\frac{v}{\mu_m(E_v - E_{v-1})}\right)^{1/2}, \tag{20}$$

all the other integrals vanishing.

As a numerical example, consider the one dimensional collision at room temperature of He with N_2, in which N_2 is deactivated from the first excited vibrational state to the normal state. Here $\alpha = 2.14$, $E/E' = 1/8$, $\mu E'' = 58$, $\mu_m(E_1 - E_0) = 274$. The probability for this deactivation is thus given by

$$(\gamma_0{}^1)^2 = (\xi_0{}^1)^2(\eta_{p'}{}^{p})^2 = 0.004 \times 0.0^4 15 = 0.0^7 6. \tag{21}$$

IV. Rotation-Translation

The principles involved in the interchange of rotational and translational energy are most readily studied in the collision of a rigid diatomic molecule and an atom, all motion being confined to a plane. This collision will first be discussed from the classical standpoint.

The symmetry of the molecule limits the energy transfer in a single impact. If an electron is excited to such a state that its time average distribution is nearly spherical, then the energy interchange in a collision will become small. Hence the energy transferred during a collision will be very dependent upon the electronic state of the molecule. This has been empirically observed.[10] Comparison of the time of collision with periods of rotation is not important, since the latter is usually the larger.

In order to treat this collision problem by quantum mechanics, a suitable mutual potential must be found. If the analysis is limited to symmetrical diatomic molecules, a simple potential having the necessary properties is

$$V(r, \epsilon) = V(r)\left\{1 + h(\cos^2 \epsilon - \tfrac{1}{2})\right\}. \tag{22}$$

Here r has the same meaning as in the previous section, and ϵ is the angle between the molecular axis and the line joining the atom with the center of the molecule. The potential $V(r)$ is taken to be (1′). A reasonable value for h

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[10] R. Rompe, Zeit. f. Physik 65, 428 (1930).

is obtained by requiring that the ratio $V(r,\ 0)/V(r,\ \pi/2)$ equal the ratio $V(r+x_0/2)+V(r-x_0/2)/2V([r^2+x_0^2/4]^{1/2})$, where x_0 is the nuclear separation in the molecule, and where r is set equal to r_{300}. This condition gives

$$h=\frac{2\left[e^{\alpha x_0/2}+e^{-\alpha x_0/2}-2e^{-\alpha([r_{300}2+x_0^2/4]^{1/2}-r_{300})}\right]}{\left[e^{\alpha x_0/2}+e^{-\alpha x_0/2}+2e^{-\alpha([r_{300}2+x_0^2/4]^{1/2}-r_{300})}\right]}\ . \tag{23}$$

By considerations similar to those leading to (5), the following wave equation of our two dimension system of a rotator and an atom may be obtained:

$$\left\{\frac{1}{I}\frac{d^2}{d\phi_1^2}+\frac{1}{\mu}\frac{1}{r}\frac{d}{dr}r\frac{d}{dr}+\frac{1}{\mu}\frac{1}{r^2}\frac{d^2}{d\phi^2}-V(r,\epsilon)+E\right\}\Psi=0.$$

Here ϕ_1, ϕ are the azimuthal angles associated with the molecule and the line joining the atom to the center of the molecule.

A solution of this equation corresponding to the molecule being in a definite rotational state before collision, and having a probability of being in several after the collision, is obtained by a method closely analogous to that of the previous section. The zeroth approximation is of the form

$$\Psi=e^{im_1\phi_1}\sum_{m=-\infty}^{\infty}e^{i\delta_m}e^{im\phi}U_m(p_{m1}/r).$$

The phase factor δ_m[11] is arbitrary. The function $U_m(p_{m_1}/r)$ is the solution of

$$\left\{\frac{1}{\mu}\frac{1}{r}\frac{d}{dr}r\frac{d}{dr}-\frac{1}{\mu}\frac{m^2}{r^2}-V(r)+E-\frac{m_1^2}{I}\right\}U_m(p_{m1}/r)=0$$

that vanishes[12] at $r=0$ and is normalised to satisfy

$$U_m(p_{m_1}/r)^{r\to\infty}=\frac{\sin(p_{m1}r+\beta_{m1})}{(p_{m1}r)^{1/2}}\ .$$

The only allowable transitions are $m=\pm 2$. The probability that the quantum numbers change from m_1, m to m_1-2, $m+2$ is

$$\left(\gamma\begin{matrix}m_1-2, & m+2\\ m_1, & m\end{matrix}\right)^2=\frac{h^2}{16}\left\{\int_0^\infty U_m(p_{m_1}/r)V(r)U_{m+2}(p_{m_1-2}/r)rdr)\right\}^2$$

or

$$\left(\gamma\begin{matrix}m_1-2, & m+2\\ m_1 & m\end{matrix}\right)^2\leqq\frac{h^2}{16}\left\{\int_0^\infty U_0(p_{m_1}/r)V(r)U_0(p_{m_1-2}/r)rdr\right\}^2. \tag{24}$$

However, these individual probabilities are not of primary interest, but only the effective cross section of such a collision. If

$$\gamma\begin{matrix}m_1-2 & m+2\\ m_1 & m\end{matrix}=\begin{matrix}1, & m<m_0\\ 0, & m>m_0\end{matrix}$$

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[11] W. Pauli, Probleme der Modernen Physik p. 42. (Hirzel, Leipzig, 1928.)

[12] The formulation of this boundary condition is rather arbitrary, as an equally justifiable condition would be to require that $U(p/r)$ have a zero slope at $r=0$. However, as long as the probability remains negligibly small that the atom pass through the molecule, both boundary conditions will give the same result.

this effective cross section would be equal to the kinetic theory cross section, σ_{KT}. Here, m_0 is the largest m for which the molecule and atom would classically come into contact. An upper limit to the effective cross section σ_{eff} is obtained by using the equality sign in (24) when $m < m_0$, and setting the left member equal to zero when $m > m_0$. This gives

$$\sigma_{\text{eff}} < \frac{h^2}{16}\left\{ \int U_0(p/r)V(r)U_0(p'/r)rdr \right\}^2 \sigma_{KT},$$

in which p_{m_1}, p_{m_1-2} have been replaced by p, p'.

An approximation to this integral is obtained in a manner identical to that used in the previous section. The only difference is that here the relation $v = 2(\mu E'')^{1/2}/\alpha$ is exact. An upper limit to the cross section is then

$$\sigma_{\text{eff}} < \frac{h^2}{16}(\eta_{p'}^{p})^2\sigma_{KT}$$

in which $\eta_{p'}{}^{p}$ is given by (19).

As a numerical example, consider the probability that a N_2 molecule, considered as non-vibrating, give two quanta of rotational energy to a He atom in a two dimensional collision at room temperature. In this example $h = 1.3$, $(\eta_{p'}{}^{p})^2 = 11$, resulting in

$$\sigma_{\text{eff}} < 1.2\,\sigma_{KT}.$$

V. General Collisions

In the previous sections discussion has been restricted to a one-dimensional collision of an atom and a vibrating molecule, and to a two-dimensional collision of an atom and a rotating molecule. The analysis is now extended to three-dimensional collisions between two molecules both of which vibrate and rotate.

The quantum mechanical treatment of such a collision in three dimensions is difficult, since the equation whose solution corresponds to an elastic collision is not in general separable in the mutual coordinates. However, in the classical theory collisions of the second kind are most probable between an atom and vibrator when all motion is confined to a line, and between an atom and rotator when all motion is confined to a plane. We may expect a similar relation in quantum mechanics, so the previous inequalities obtained for one and two dimensional collisions may be taken to be valid for three-dimensional collisions.

Provided the amplitude of vibrations are relatively small, the mutual potential may be approximated by the product of functions of individual coordinates. Thus when both molecules are diatomic, a simple potential is

$$V = V(r)(1 + a_1z_1)(1 + a_2z_2)(1 + f_1(\epsilon_1)(1 + f_2(\epsilon_2)) \tag{25}$$

where $V(r)$ is taken to be (1′); z_1 and z_2 are the displacements of the internuclear separations of the two molecules from their equilibrium values; ϵ_1 and ϵ_2 are the mutual angles between the line joining the centers of gravity of the two molecules and the axes of the two molecules; and f_1, f_2 are arbitrary functions.

When the mutual potential is so factorable, the probability of an inelastic collision will also be expressible as a product. One factor of this product will be a function of the constants of translational motion. Denote this factor by $P_{E,E'}$. Each of the other factors will be associated with a change of one quantum number. These factors will be independent of one another. For example, in a collision in which the vibrational quantum number v changes to $v-1$, the associated probability factor $P_{v,v-1}$ will not be influenced by changes of other quantum numbers.

Hence if σ_{KT} is the kinetic theory cross section of a collision, the effective cross section of a collision in which the quantum numbers $v_1, l_1, \cdots$ change to $v_1', l_1', \cdots$ will be

$$\sigma_{\text{eff}} < \sigma_{KT} P_{E,E'} P_{v_1,v_1'} P_{l_1,ll'} \cdots . \tag{26}$$

In the following description of these factors, atomic units[7] are used.

When μ refers to the reduced mass of the two systems, α to the sum of the square roots of the ionization energies (in units of 13.53 volts) of the two atoms which become adjacent during collision, $E(E')$ to the smaller (greater) of the initial and final mutual energies of translation, and $E''=(E\,E')^{1/2}$, reference to (19) shows that for sub-elastic collisions

$$P_{E,E'} = \frac{\mu E''\pi^2}{4\alpha^2} . (E/E')^{2(\mu E'')^{1/2}/\alpha}. \tag{27a}$$

In super-elastic collisions[13] $P_{E,E'}$ is to be multiplied by the factor $(E/E')^{1/2}$.

When the mutual potential contains only the first power of the displacement of a vibrator from its equilibrium position, the vibrational quantum number can change only by unity. Reference to (20) shows that the factor $P_{v,v-1}$ associated with a change of vibrational quantum number $v \rightarrow v-1$ or $v-1 \rightarrow v$ is

$$P_{v,v-1} = \frac{\lambda^2\alpha^2 v}{4\mu_m(E_v - E_{v-1})} \tag{27-b}$$

where the difference in energy between the two states is $E_v - E_{v-1}$, where λ is given by (14), and μ_m is the reduced mass of the vibrator.

If one of the colliding systems is a symmetrical diatomic molecule, the dependence of the interaction energy upon the mutual angle ϵ is approximately expressed by the factor $1+h(\cos^2\epsilon-\frac{1}{2})$, corresponding to (22). The constant h, determined from (23), varies from 1 to 1.5 for diatomic symmetrical molecules whose electronic states are normal. If the electronic states are highly excited, h may approach zero. Insofar as this approximation is valid, the molecule can change its rotational quantum number l by only ± 2. The corresponding probability factor is

$$P_{l,l\pm 2} = h^2/16. \tag{27-c}$$

The statistical factor[13] relating the probability of the transition $l \rightarrow l+2$ to that of $l+2 \rightarrow l$ is neglected.

A few general observations will be drawn from the above formulae.

The molecules to which this analysis applies change a few rotational quantum numbers freely.

The transfer of vibrational energy may be difficult even in cases of exact resonance,[14] e.g. the cross section for the transfer of vibrational energy from a N_2 molecule in its first excited state to a normal N_2 at room temperature is $0.0^4 4 \times$ kinetic theory cross section. This resonance cross section increases both with the reduced mass of the two molecules, and with temperature. However, the effects of a lack of resonance are most marked in heavy molecules. If the reduced mass is 30 m_H, the effective cross section is reduced by a factor of 0.025 if the translational energy must change by 0.01 volt at room temperature.

The efficiency of H_2 as contrasted to He in deactivating molecules[15] cannot be explained as due to their difference in mass. It is to be ascribed to the much greater facility with which H_2 can absorb a considerable amount of energy by a change of a few rotational quantum numbers, than by a change of translational energy.

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