On The Inelastic Collision between Molecules, I

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The energy transfer between the vibration and the translation in the molecular collision is investigated for the linear configuration of two diatomic molecules. The method of calculation is completely parallel to that of Jackson and Mott. The results are applied to the interpretation of the experimental facts for the anomalous supersonic dispersion and the qualitative successes are obtained.

§ 1. Introduction

As is well known, quantum mechanics has been established firmly in the region of atoms or molecules. However, the theory of molecular collisions (especially of inelastic ones) presents so large mathematical difficulty that it has been studied only rarely. But the molecular collisions play the important role in the various phenomena, e.g. the discharge in gas, the phenomena in the ionosphere, the chemical reaction in general, the anomalous supersonic dispersion, and so on. Thus it is desirable to investigate more closely the various elementary processes in the molecular collisions.

In this paper we treat the energy transfer between the vibrational and the translational degrees of freedom in the collision of simple molecules with each other, and apply the results to explain the experimental facts relating to the anomalous supersonic dispersion. Problems of this kind were examined twenty years ago by Zener, who discussed the coupling of the translation with the vibration or the rotation. Subsequently a more mathematically refined treatment was proposed by Jackson and Mott in connection with the calculation of the accommodation coefficient. These authors, however, did not consider the possibility that the vibrational energy of the one molecule may be transferred not only to the translation but also to the vibration of the other molecule by the collision. Such a process is studied in this paper. The method of the calculation is completely parallel to that used by Jackson and Mott.

Now the influence of the collision partner for the deactivation of the molecule considered may be classified as follows:

1. the effect of the molecule as a whole (dependence on mass and size).
2. the effect of the rotation (possibility of taking off a part of the excess energy by the rotational degrees of freedom).
3. the effect of the vibration (effect similar to the above, by the vibrational degrees of freedom).
4. the electronic effect (dependence on the form of the intermolecular force. If the
collision partners can (at least in principle) react chemically with each other, then the intermolecular force potential will have very different feature from the other cases. The possibility of the excitation of electronic states will play no important role in the thermal collision at ordinary temperature.

In this paper, we touch the effects 1 and 2 only briefly, and do not enter into the effect 4. For the estimation of the vibrational effect, we furthermore restrict ourselves to the linear configuration of two diatomic molecules without rotation, as shown in Fig. 1(a). More generally, if the transition probabilities for the configurations of Fig. 1(a), (b) and (c) are \( p_a, p_b \) and \( p_c \) respectively, we may assume that the transition probability for the case of the collision in the general configuration of Fig. 1(d) is given by a suitable interpolation, e.g.

\[
p_a = p_a \left( \cos^2 \theta_1 + \frac{P_b}{P_a} \sin^2 \theta_1 \right) \left( \cos^2 \theta_2 + \frac{P_c}{P_a} \sin^2 \theta_2 \right),
\]

without any serious error.

Now for the vibration-vibration coupling the transition probability will be comparatively large for the configuration of Fig. 1(a), and for other configurations it will be very much smaller. Thus we may put roughly

\[
p_a \cong p_a \cos^2 \theta_1 \cos^2 \theta_2,
\]

and by averaging over the angles \( \theta_1 \) and \( \theta_2 \) we have

\[
\bar{p}_a \cong p_a / 9.
\]

Therefore, if we write the average transition probability as \( p_a \bar{p}_0 \), then \( \bar{p}_0 \) is order of magnitude of \( 10^{-1} \) and when we are interested in the relative probability only, it is sufficient to know the factor \( p_a \), i.e., the transition probability for the special configuration (a).

The results of our calculations show that the final result is very sensitive to the choice of the parameter contained in the perturbation potential. (See Fig. 3 and 4.) Thus we have to investigate the potential curve for each special case. This problem, as well as several related problems will be considered in subsequent papers.

§ 2. Effect of a molecules as a whole*

First of all, the difference in geometrical extension will necessarily cause the difference in the effective cross section for the transition investigated, although these two cross sections are not always proportional to each other.

* Atomic units are used throughout this paper. Thus, for example, electron mass=1, \( \hbar = 1 \), and the energy quantum \( \hbar \nu = \hbar \omega \) has the same numerical value as the angular frequency \( \omega \).
In the second place, the difference of the mass of the collision partner causes the change of the reduced mass ($\mu$) for the total system. If the energy transferred from the vibrational to the translational degrees of freedom is equal to $\Delta E$, then

$$E = \frac{k^2}{2\mu}; \quad \Delta E = \frac{(k+\Delta k)^2 - k^2}{2\mu} = \sqrt{2E} \left(\frac{\Delta k}{\sqrt{\mu}}\right) + \frac{1}{2} \left(\frac{\Delta k}{\sqrt{\mu}}\right)^2.$$

Now the average relative translational energy for each collision, which is derived from the Maxwellian velocity distribution, is $\bar{E} = 2kT$, independent of the reduced mass. Thus, for the fixed value of $\Delta E$, we have $\Delta k \propto \sqrt{\mu}$. Since the large change of the wave number $k$ means the small overlapping between the initial and the final translational wave functions, the smallness of the reduced mass is in favor of the large transition probability (provided the other conditions unchanged). From the experimental evidence for the anomalous supersonic dispersion, we know that the He-atom, though it has neither vibrational nor rotational degrees of freedom, is more effective for the deactivation of $O_2$ compared with $O_2$ itself. This will be explained by the fact that the ratio of reduced masses for the two systems $O_2$ and $O_2$He is $9:2$. As another example, the experimental fact that the ratio of the effectiveness (transition probability per collision) of $H_2$ and $D_2$ for the deactivation of the vibration of $CO_2$ is $3:1$ can be explained only by taking the difference of the reduced mass into account.

§ 3. Effect of the rotation

Generally, the rotational level spacings are much smaller than the vibrational ones. Therefore, in order that the rotational degrees of freedom may take off the great part of excess energy after vibrational deactivation, a large change of the rotational quantum number must necessarily occur which is improbable. However, if the rotational level spacings are comparatively large (as in the case of $H_2$ and $HCl$ etc.), the rotation may have appreciable effects on the deactivation of vibration. The experimental fact that $HCl$ is considerably effective for the vibrational deactivation of $CO_2$, $Cl_2$ etc., may be explained by the large rotational level spacings of $HCl$, though the explanation that this effectiveness is due to the special form of the intermolecular force is also possible. The large rotational level spacing, on the other hand, gives rise to the rotational supersonic dispersion. The treatment of this problem will be postponed to a later article.

§ 4. Effect of the vibration

It is well known that Born approximation is not valid for the slow atomic collisions. However, the transition probability between the vibration of one molecule and the vibration of another molecule is known experimentally to be very small. Therefore, the method of distorted wave may be applied.

As stated in the introduction, we consider
the special configuration which is illustrated by Fig. 2. The independent variables are $x_1$, $x_2$ and $x$ as shown in Fig. 2. The Schrödinger's wave equation for the whole system is as follows

$$[-H^{(1)} - H^{(2)} + (1/2\mu) \frac{\partial^2}{\partial x^2} + (W-V)]\Psi(x; z_1, z_2) = 0,$$

where

$$H^{(i)} = -(1/2\mu_i) \frac{\partial^2}{\partial z_i^2} + 2\pi^2 \mu_i z_i^2,$$

and

$$\mu_1 = m_1 m_2 / (m_1 + m_2), \quad \mu_2 = m_3 m_4 / (m_3 + m_4),$$
$$\mu = (m_1 + m_2) (m_3 + m_4) / (m_1 + m_2 + m_3 + m_4).$$

Here, we adopt the exponential form for the potential energy:

$$V = C_0 \exp\left\{-ax - \lambda_1 x_1 - \lambda_2 x_2 \right\}$$
$$= C \exp(-ax) \exp(\lambda_1 z_1) \exp(\lambda_2 z_2),$$

where

$$\lambda_1 = m_1 / (m_1 + m_2), \quad \lambda_2 = m_4 / (m_3 + m_4).$$

$H^{(i)}$ is the well-known Hamiltonian operator for the harmonic oscillator and we represent its normalized eigenfunctions by $\phi_{n}^{(i)}(z_i)$, which satisfy

$$H^{(i)} \phi_{n}^{(i)}(z_i) = (n + \frac{1}{2}) \omega \phi_{n}^{(i)}(z_i).$$

Now we seek for the solution of the form:

$$\Psi = \sum_{n,m} f_{n,m}(x) \phi_{n}^{(1)}(z_1) \phi_{m}^{(2)}(z_2).$$

If the molecule 1 is in the first excited state before collision, then we must impose the asymptotic conditions

$$f_{1,0} \xrightarrow{x \to \infty} \exp(-i k_{1,0} x) + A_{1,0} \exp(i k_{1,0} x),$$
$$f_{n,m} \xrightarrow{x \to \infty} A_{n,m} \exp(i k_{n,m} x), \quad (n, m) \neq (1,0).$$

Then the transition probability per collision is given by

$$p_{1,0}^{n,m} = (k_{n,m} / k_{1,0}) |A_{n,m}|^2.$$

The method used for the determination of $A_{n,m}$ is similar to that of Jackson and Mott\(^{(2)}\) who considered the collision problem between a harmonic oscillator and an inert gas atom. Completely parallel calculations give the following result which corresponds to the Eq. (19) of these authors,

$$p_{1,0}^{n,m} = \frac{4 (V_{1,0}^{(1)})^2 (V_{0,0}^{(2)})^2}{k_{1,0} k_{n,m}^2} \left[2 \mu C \int_{-\infty}^{\infty} F_{1,0} F_{n,m} \exp(-ax) dx \right]^2,$$
where

\[ Y_{s,t}^{(i)} = \int_{-\infty}^{\infty} \phi_{s}^{(i)}(\varepsilon_i) \phi_{t}^{(i)}(\varepsilon_t) \exp(a \lambda \varepsilon_s) d\varepsilon_s, \]

and \( F \) is the solution of

\[ \left[ d^2/dx^2 + k_{n,m}^2 - 2\mu C \cdot \exp(-a x) \right] F_{n,m}(x) = 0, \]

which approaches zero for \( x \to -\infty \) and behaves asymptotically as \( \cos(k_{n,m}x + \gamma) \) for \( x \to +\infty \). The explicit form of this \( F \)-function and the integral containing this function were obtained by Jackson and Mott, and the use of their results gives the final expression for the transition probability

\[ \rho_{n,m} = \frac{\pi^2}{4} \left( Y_{1,n}^{(i)} \right)^2 \left( Y_{0,m}^{(i)} \right)^2 \left[ \frac{q_{n,m}^2 - q_{1,0}^2}{\cosh \pi q_{n,m} - \cosh \pi q_{1,0}} \right]^2 \sinh \pi q_{n,m} \sinh \pi q_{1,0}. \]

(1)

where \( q_{n,m} = 2k_{n,m}/\alpha \). The vibrational matrix elements \( Y_{s,t} \) are easily calculated for small \( s, t \) and are as follows:

\[ Y_{0,0}^{(i)} = \exp(a^2 \lambda_i^2/4\mu_i) \approx 1, \]

\[ \lambda_i = \mu_i \omega_i, \]

(2)

\[ Y_{1,0}^{(i)} = a \lambda_i / (2\mu_i)^{1/2} \times \exp(a^2 \lambda_i^2/4\mu_i). \]

Numerical examples for the case of \( \lambda = 1/2 \) (homonuclear diatomic molecule) and \( \alpha = 1, 3, 5 \) are shown in Fig. 3.

Next, we consider the remaining important factor

\[ I_{n,m} = \left( \frac{q_{n,m}^2 - q_{1,0}^2}{\cosh \pi q_{n,m} - \cosh \pi q_{1,0}} \right)^2 \sinh \pi q_{n,m} \sinh \pi q_{1,0}. \]

(3)

Usually \( q \) is much larger than unity and in this case we may put

\[ I_{n,m} = \left( \frac{q_{n,m}^2 - q_{1,0}^2}{\exp(\pi q_{n,m}) - \exp(\pi q_{1,0})} \right)^2 \exp(\pi q_{n,m}) \exp(\pi q_{1,0}). \]

(3a)

Moreover, if \( \exp(\pi q_{n,m}) \gg \exp(\pi q_{1,0}) \), we have

\[ I_{n,m} = (q_{n,m}^2 - q_{1,0}^2)^2 \exp(\pi q_{1,0})/\exp(\pi q_{n,m}). \]

(3b)

In this last approximation, we obtain, using the definition of \( q \), that
\[ I_{n,m} \propto \Delta E \cdot \exp \left\{ -\text{const} \cdot \Delta E / (k_{n,m} + k_{1,0}) \right\}. \] (4)

Thus, if the initial translational energy becomes large, also the transition probability becomes large.

Now the energy conservation relation is expressed by

\[ k_{n,m}^2 + 2\mu(n\omega_1 + m\omega_2) = k_{1,0}^2 + 2\mu\omega_1. \]

If we fix the initial wave number \( k_{1,0} \), the matrix element \( I_{n,m} \) is a function of energy change \( \Omega = (k_{n,m}^2 - k_{1,0}^2) / 2\mu \) and is independent of \( n \) and \( m \). Numerical examples for \( I(\Omega) \) for the case of \( k_{1,0} = 10 \), which corresponds to \( \text{O}_2, \text{N}_2 \) etc., at room temperature, are illustrated by Fig. 4.

Now we may expect that the exact resonance case \( (\Omega = 0) \) is the maximum point of the function \( I(\Omega) \). But it is only approximately true. Since the expansion of this function near \( \Omega = 0 \) gives

\[ I = \frac{4}{\pi^2} q_1 \beta + \frac{4}{\pi^2} q_1(\gamma_{n,m} - \gamma_{1,0}) + O((\gamma_{n,m} - \gamma_{1,0})^2), \] (5)

the maximum point of this function is shifted to a positive value of \( \Omega (\gamma_{n,m} > \gamma_{1,0}) \).

A characteristic feature of the function \( I \) is the very rapid decrease for the increase of its argument \( \Omega \), which is a marked contrast to the comparatively slow variation of \( Y_s,t \). As a result, the two quanta process \((1,0) \rightarrow (0,1)\) may become much more probable than the one quantum process \((1,0) \rightarrow (0,0)\) which explains the various effects for the anomalous supersonic dispersion in gases. (See the next section.)

§ 5. Some applications

The numerical values shown in Fig. 3 and 4 correspond to the special choice of the parameters. For the simple molecules consisting of atoms with nearly equal masses such as \( \text{O}_2, \text{N}_2, \text{CO}, \text{CO}_2, \text{NO}, \text{N}_2\text{O} \) etc., these figures may be used to make qualitative discussions, because the difference of the vibrational frequencies will be the most dominant factor there.

\( \text{O}_2 \ldots \ldots (\omega = 7.2 \times 10^{-3} \text{ atomic units}) \) The transfer of the vibrational energy of \( \text{O}_2 \) to the vibrational...

\[ k_{\text{initial}} = 10, \quad 2M = 5 \times 10^{14}. \]
energy of another O₂ is an example of the exact resonance, and therefore has a comparatively large probability. But such transfer can not be detected experimentally. On the other hand the probability of energy transfer to the translation is $3 \times 10^{-8}$ (using the values from Fig. 3 and 4, provided $a = 3$). Since it is not the vibration-vibration coupling, the extra factor $\rho_0$ discussed in the introduction may be put as 1/3 instead of 1/10. Thus the average number $Z$ of collisions occuring before the deactivation of vibrational excitation is about $10^8$ which is compared with the experimental value $Z > 5 \times 10^6$.

From the experimental evidences we know that the molecules such as N₂O, CO etc. are more effective than O₂ itself, though they have large vibrational frequencies. This may be ascribed to the difference of potential curves for the individual cases. In fact, the transition probability varies over a comparatively wide range for a small variation of the parameter $a$. (See Fig. 3 and 4.)

$N_2O$......This molecule has the following three modes of vibration:
1. deformation vibration: $\omega_1 = 2.7 \times 10^{-3}$,
2. valence vibration (symmetrical): $\omega_2 = 5.9 \times 10^{-3}$,
3. valence vibration (antisymmetrical): $\omega_3 = 10.2 \times 10^{-3}$.

When two $N_2O$ molecules collide with each other, a possible process is that the valence vibration of the one $N_2O$ is deactivated while the deformation vibration of the other $N_2O$ is activated. In this way, the three modes of vibration are not independent of each other. The transition probabilities (however, only relative) between various levels of $N_2O$ are shown in Fig. 5. Here we have used the approximate relations:

$$P_{n\to(n-1)} = 2n - 1,$$
$$P_{n\to1} = (P_{2\to1})^{n-1}.$$ 

From this diagram we can see that the deactivation probability of the symmetric valence vibration increases by factor of 500 by coupling with the 2nd excited state of the deformation vibration, and very much approaches to the deactivation probability of the deformation vibration itself. Thus we may hope that the experimental evidence of Eucken-Nümann can be explained by this coupling effect. (They found that the relaxation times for the deformation and the valence vibration are not so different as by factor 10 with each other.)

From Fig. 5, we can also see that the deactivation probability of the antisymmetric valence vibration is much different from that of the other two modes of vibration. However, the antisymmetric valence vibration contributes only a little to the dispersion phenomena in the room temperature and the separation of the two maxima of dispersion can not be tested. Thus, it is desirable to investigate experimentally the supersonic dispersion at higher temperature (for example 300°C or more).

$CO_2$......The behavior of CO₂ is completely analogous to that of $N_2O$ and, therefore, only the transition diagram is shown (Fig. 6).
§ 6. Conclusions

Since the calculations performed in this paper are accompanied with many simplifications, we cannot obtain the quantitative conclusions from them. However, it is not so unreasonable to believe that the general principle explaining the experimental facts has been obtained. In other words, the ordinary method of distorted wave seems to give a satisfactory way of calculation.

The main articles which will be investigated in the following papers are:

1) More quantitative calculations for some special cases (The intermolecular force potential has to be calculated for each case quantummechanically. The general geometrical configuration (Fig. 1(d)), the rotational effect must be considered.).
2) The rotational supersonic dispersion for \( \text{H}_2 \).
3) The use of the average energy of the thermal collisions will be replaced by the averaging procedure over the Maxwellian distribution etc.

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Note added in proof:
Recently, we calculated the rotational dispersion of the supersonic wave in the hydrogen gas (see § 3).
A satisfactory result was obtained. The detailed report will be published soon.