PHYSICAL REVIEW VOLUME 71, NUMBER 2 JANUARY 15, 1947

Excitation of Molecular Vibrations by Electrons

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(Received October 14, 1946)

The cross section for the excitation of molecular vibration by electron impact is calculated for two cases: (1) On the assumption that a molecule interacts with an electron through the oscillating electric moment arising from the vibration, the cross sections of excitation and deexcitation are of the order $y^2\cdot 10^{-15}$ cm^2 where $y\cdot 10^{-18}$ c.g.s. unit is the matrix element of the electric moment associated with the vibrational transition. (2) For optically inactive vibration, an approximate estimate of the cross section in the case of the H_2 molecule is made by the method of distorted wave. The cross section is of the order $0.5\cdot 10^{-18}$ cm^2 for electrons of a few volts. These results are compared with the experimental results on the probability of electron energy transfer to molecular vibrations.

FROM many experiments on the energy loss of electrons in passing through a gas, there seems to be evidence for a considerable probability for the exchange of energy between an electron and the vibrational motion of a molecule.[1–3] Thus it was found by Harries that about 1 percent of the collisions of 5.2-volt electrons with nitrogen molecules results in the excitation of one vibrational quantum, while for carbon monoxide it is 3.3 percent.[1] Ramien found that about 2 percent of the collisions of 7-volt electrons with hydrogen molecules result in the excitation of one vibrational quantum.[2] While the theoretical method for the calculation of the probability of such energy transfers is well developed, no calculation seems to have been carried out. In an early paper, Massey has treated the problem of elastic scattering of fast electrons by H_2 molecules by Born's method,[4] and in a later paper the same author has calculated the cross section of the excitation of the rotational state of a symmetrical top having a permanent electric moment $\mathfrak{M}=x\cdot 10^{-18}$ c.g.s. unit.[5] It was found that this cross section is of the order $x^2\cdot 10^{-15}$ cm^2 for slow electrons. The result, however, is valid only when $\mathfrak{M}\ll h^2/8\pi^2me$ or $x\ll 1$, a condition not met by most actual molecules. The purpose of the present work is to make some estimates of the probabilities of excitation of molecular vibrations by electrons.

I. EXCITATION OF OPTICALLY ACTIVE VIBRATION

To calculate the probability of energy transfer between the vibration-rotational motion of a molecule and an electron, it is necessary to know the law of interaction between them. A rigorous theory should consider the interactions between the electron and the nuclei and electrons in the molecule; but such a theory would involve very complicated, if not unmanageable, calculations. As an approximation, we shall, following Massey,[5] replace the actual molecular field by one which is caused by the electric moment of the molecule. On this assumption, the interaction may be regarded as the sum of two parts, namely, the interaction between the electron and the permanent moment, and the interaction between the electron and the electric moment due to the vibration of the molecule. The Hamiltonian of the system: molecule+electron is, on neglecting the coupling between vibration and rotation,

$$H=H_v(X_1, X_2, \cdots)+H_r(\vartheta, \chi, \varphi)+H_e(R, \Theta, \Phi) + V(X_1, X_2, \cdots, \vartheta, \chi, \varphi, R, \Theta, \Phi),$$

where the X's are proportional to the normal coordinates of vibration, ϑ, χ, φ the Eulerian angles defining the orientation of the molecule, and R, Θ, Φ the polar coordinates of the electron. For definiteness, consider a symmetrical rotator and let χ be the angle defining rotation about the figure axis. If the molecule has a permanent moment $\mathfrak{M}$ along the figure axis and if we confine

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[1] W. Harries, Zeits. f. Physik **42**, 26 (1927).
[2] Ramien, Zeits. f. Physik **70**, 353 (1931).
[3] For references to the work of Bailey and others, see Mott and Massey, *Theory of Atomic Collisions* (Oxford University Press, New York, 1933), p. 217.
[4] H. S. W. Massey, Proc. Roy. Soc. **A129**, 616 (1930).
[5] H. S. W. Massey, Proc. Camb. Phil. Soc. **28**, 99 (1932).

ourselves to the excitation of a parallel vibration X_i, i.e., a vibration whose change of electric moment A_iX_i is along the figure axis, we have

$$\left.\begin{aligned} &V=V^I+V^{II},\\ &\text{where}\\ &V^I=\frac{\mathfrak{M}e}{R^2}\{\cos\vartheta\cos\Theta+\sin\vartheta\sin\Theta\cos(\varphi-\Phi)\},\\ &V^{II}=\textstyle\sum_i V_i^{II}=\sum_i \dfrac{A_iX_ie}{R^2}\{\cos\vartheta\cos\Theta\\ &\qquad\qquad\qquad+\sin\vartheta\sin\Theta\cos(\varphi-\Phi)\}.\end{aligned}\right\}(1)$$

This assumed form for the interaction V may perhaps be justifiable for large distance R but certainly becomes inadequate for close approach between the electron and the molecule.

The Schrödinger equation

$$H\Psi(X_1,X_2,\cdots,\vartheta,\chi,\varphi,R,\Theta,\Phi)=E\Psi \qquad (2)$$

can be solved by the usual method of expressing Ψ as a sum of products of the vibrational, rotational, and the electronic wave functions

$$\Psi=\sum_{v_1v_2\cdots JKM}\psi_{v_1v_2\cdots}(X_1,X_2,\cdots)\cdot\psi_{JKM}(\vartheta,\chi,\varphi)\cdot F_{v_1v_2\cdots JKM}(R,\Theta,\Phi), \qquad (3)$$

where the v's are the vibrational quantum numbers and $\psi_{v_1v_2}(X_1,X_2,\cdots)$ is the solution of

$$H_v\psi_{v_1v_2}\cdots(X_1,X_2,\cdots)=E_v\psi_{v_1v_2}\cdots, \qquad (4)$$

where E_v is the energy of vibration of the molecule. $\psi_{v_1v_2}\cdots(X_1,X_2,\cdots)$ is the product of the wave functions $\psi_{v_i}(X_i)$ of the normal vibrations. $\psi_{JKM}(\vartheta,\chi,\varphi)$ is the solution of the equation of a symmetrical top

$$H_r\psi_{JKM}(\vartheta,\chi,\varphi)=E_{JKM}\psi_{JKM} \qquad (5)$$

where

$$E_{JKM}=\frac{h^2}{8\pi^2A}\left\{J(J+1)-\left(\frac{A}{C}-1\right)K^2\right\}.$$

On substituting (3) into (2) and making use of (4) and (5), one obtains the following equations for the $F_{v_1v_2\cdots JKM}(R,\Theta,\Phi)$

$$\left[\nabla^2+\frac{8\pi^2m}{h^2}(E-E_v-E_{JKM})\right]F_{v_1v_2\cdots JKM}(R,\Theta,\Phi)$$
$$=\sum_{v_1'v_2'\cdots J'K'M'}\frac{8\pi^2m}{h^2}V(v_1v_2\cdots JKM;v_1'v_2'\cdots J'K'M')\cdot F_{v_1'v_2'\cdots J'K'M'}(R,\Theta,\Phi) \qquad (6)$$

where

$$V(v_1'v_2'\cdots,J'K'M';v_1v_2\cdots,JKM)=\int\overset{*}{\psi}_{v_1'v_2'}\cdots\overset{*}{\psi}_{J'K'M}(V^I+V^{II})\psi_{v_1v_2}\cdots\times\psi_{JKM}dX_1\cdots dX_nd\cos\vartheta d\chi d\varphi.$$

Now on account of the properties of the functions $\psi_{v_1v_2}\cdots(X_1,X_2,\cdots)$ and $\psi_{JKM}(\vartheta,\chi,\varphi)$, the matrix element $V^I(v_1'v_2'\cdots,J'K'M';v_1v_2\cdots,JKM)$ vanishes unless $v_1'=v_1$, $v_2'=v_2$, $\cdots v_n'=v_n$, $J'-J=0,\ \pm1$, $K'=K$, $M'-M=0,\ \pm1$. The matrix element $V^{II}(v_1'v_2'\cdots,J'K'M';v_1v_2\cdots,JKM)$ vanishes unless one, and only one, of the v_1', v_2', $\cdots v_n'$, say v_i', differs from v_i by ±1, and $J'-J=0,\ \pm1$, $K'-K=0$, $M'-M=0,\ \pm1$. In the following, we shall denote by v_i the vibrational state $v_1=0$, $v_2=0$, $\cdots v_{i-1}=0$, $v_i=v_i$, $v_{i+1}=0$, $\cdots$, $v_n=0$, and write

$$V(1_i,J'K'M';0_i,JKM)=V(0,0,\cdots,1_i,0,\cdots,J'K'M';0,0,\cdots0_i,\cdots0,JKM),$$

$$k^2_{v_iJKM}=(h^2/8\pi^2m)(E-E_{v_i}-E_{JKM}).$$

The system of Eqs. (6) becomes

$$\begin{aligned}[\nabla^2+k^2_{0_i000}]F_{0_i000}=\frac{8\pi^2m}{h^2}[&V^I(0_i000;0_i100)F_{0_i100}+V^I(0_i000;0_i101)F_{0_i101}\\ &+V^I(0_i000;0_i10-1)F_{0_i10-1}+\textstyle\sum_j\{V_i^{II}(0_i000;1_j100)F_{1_j100}\\ &+V_i^{II}(0_i000;1_i101)F_{1_i101}+V_j^{II}(0_i000;1_j10-1)F_{1_j10-1}\}],\end{aligned}$$

$$\begin{aligned}[\nabla^2+\overset{2}{k}_{0_i100}]F_{0_i100}=\frac{8\pi^2m}{h^2}[&V^{I}(0_i100;\,0_i000)F_{0_i000}+V^{I}(0_i100;\,0_i200)F_{0_i200}\\ &+V^{II}(0_i100;\,0201)F_{0_i201}+V^{II}(0_i100;\,0_i20-1)F_{0_i20-1}\\ &+\textstyle\sum_j\{V_j^{II}(0_i100;\,1_j000)F_{1_i000}+V_j^{II}(0_i100;\,1_j200)F_{1_j200}\\ &\qquad+V_j^{II}(0_i100;\,1_j201)F_{1_j201}+V_j^{II}(0_i100;\,1_j20-1)F_{1_j20-1}\}],\end{aligned}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \tag{7}$$

$$\begin{aligned}[\nabla^2+\overset{2}{k}_{1_i000}]F_{1_i000}=\frac{8\pi^2m}{h^2}[&V^{I}(1_i000;\,1_i100)F_{1_i100}+V^{I}(1_i000;\,1_i101)F_{1_i101}\\ &+V^{I}(1_i000;\,1_i10-1)F_{1_i10-1}+V_i^{II}(1_i000;\,0_i100)F_{0_i100}\\ &\qquad+V_i^{II}(1_i000;\,0_i101)F_{0_i101}+V_i^{II}(1_i000;\,0_i10-1)F_{0_i10-1}]\end{aligned}$$

$$\begin{aligned}[\nabla^2+\overset{2}{k}_{1_i100}]F_{1_i100}=\frac{8\pi^2m}{h^2}[&V^{I}(1_i100;\,1_i000)F_{1_i000}+V^{I}(1_i100;\,1_i200)F_{1_i200}\\ &+V^{I}(1_i100;\,1_i20-1)F_{1_i201}+V^{I}(1_i100;\,1_i20-1)F_{1_i20-1}\\ &+V_i^{II}(1_i100;\,0_i000)F_{0_i000}+V_i^{II}(1_i100;\,0_i200)F_{0_i200}\\ &\qquad+V_i^{II}(1_i100;\,0_i201)F_{0_i201}+V_i^{II}(1_i100;\,0_i20-1)F_{0_i20-1}].\end{aligned}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

We shall now assume that

$$\begin{aligned}\alpha&\equiv 8\pi^2me\mathfrak{M}/h^2\ll 1,\\ \beta_i&\equiv 8\pi^2meA_iX_i(0,\,1)/h^2\ll 1,\end{aligned}\tag{8}$$

where $A_iX_i(0,\,1)$ is the matrix element of the electric moment associated with the vibrational transition $v_i=0\leftrightarrow v_i=1$. On writing $\mathfrak{M}=x\cdot 10^{-18}$ and $A_iX_i(0,\,1)=y_i\cdot 10^{-18}$ c.g.s. unit, the relations (8) become

$$x\ll 1,\quad y_i\ll 1. \tag{8$'$}$$

On this assumption, the system of Eqs. (7) can be solved by successive approximation. For definiteness, consider an electron impinging on the molecule in the ground state $(0,\,0,\,\cdots,\,0,\,0,\,0)$ so that the wave function of the electron is F_{0_i000}. It is seen from (7) that F_{0_i100} would be of the order αF_{0_i000}; F_{1_i100} of the order $\beta_iF_{0_i000}$ and F_{1_i000} of the order $\alpha\beta_iF_{0_i000}$. Thus

$$\begin{aligned}&[\nabla^2+\overset{2}{k}_{1_i100}]F_{1_i100}=\frac{8\pi^2m}{h^2}[V_i^{II}(1_i100;0_i000)F_{0_i000}]\\ &+\text{terms of the order } \alpha^2\beta F_{0_i000} \text{ and } \alpha\beta^2F_{0_i000},\end{aligned}\tag{9}$$

which reduces, on neglecting small quantities of higher order, to

$$\begin{aligned}[\nabla^2+\overset{2}{k}_{1_i100}]F_{1_i100}=(8\pi^2m/h^2)&\\ \times V_i^{II}(1_i100;\,0_i000)F_{0_i000}.&\end{aligned}\tag{9$'$}$$

Now

$$\begin{aligned}V_i^{II}(1_i,\,100;\,0_i,\,000)(R',\,\Theta',\,\Phi')&\\ =eA_iX_i(0,\,1)\cos\Theta'/\sqrt{3}R'^2.&\end{aligned}$$

If in the zeroth approximation we represent F_{0_i000} of the incoming electron by a plane wave $F_{0_i000}(R,\,\Theta,\,\Phi)=\exp(ikn\cdot R)$, the asymptotic expression of $F_{1_i100}(R,\,\Theta,\,\Phi)$ is

$$\begin{aligned}F_{1_i100}(R,\,\Theta,\,\Phi)\sim\frac{2\pi meA_iX_i(0,\,1)}{\sqrt{3}h^2}\cdot\frac{e^{ik_{1100}R}}{R}&\\ \times\int e^{i(kn-k_{1_i100}n_1)\cdot R'}dR'\cos\Theta'd\cos\Theta'd\Phi',&\end{aligned}$$

where n, n_1 are the unit vectors along the direction of the incoming and the scattered electron, respectively. A little calculation gives for the total cross section for the simultaneous excitation of the vibrational and the rotational state the expression

$$Q_{1_i100}(k)=\frac{2\pi\beta_i^2}{3}\cdot\frac{1}{k^2}\ln\frac{k+k_{1100}}{k-k_{1100}} \tag{10}$$

as a function of the initial kinetic energy $E=h^2k^2/8\pi^2m$ of the electron.

For the de-excitation or quenching process $(1_i, 100)\rightarrow(0_i, 000)$, we represent the incoming electron by a plane wave $F_{1_i100}=\exp(ikn\cdot R)$ and calculate F_{0_i000} in (7). The cross section can be shown to be

$$Q_{0_i000}(k)=\frac{2\pi\beta_i^2}{3}\cdot\frac{1}{k^2}\ln\frac{k_1+k}{k_1-k} \tag{11}$$

where $(h^2/8^2\pi^2m)(k_1^2-k^2)=\epsilon$ is the energy transferred to the electron. It is seen that $Q_{1_i100}(k)$ and $Q_{0_i000}(k)$ satisfy the relation

$$e^{-\epsilon/kT}\int_0^\infty vQ_{0_i000}(v)\cdot f(v)dv=\int_{(2\epsilon/m)^{\frac{1}{2}}}^\infty vQ_{1_i100}(v)\cdot f(v)dv,$$

as required by the principle of detailed balancing. v is the velocity of the electron and $f(v)$ is the Maxwell velocity distribution function.

For the excitation process $v_i, J, K, M\rightarrow v_i+1, J+1, K, M$, a little consideration shows that the same expression (10) holds, except for a numerical factor of the order unity. The cross section for the excitation of the vibrational state alone would be of the order $\alpha^2\beta_i^2$ times $Q_{1_i100}(k)$. This is rather a consequence of the special form (1) which we have assumed for the interaction V, and perhaps not much weight should be attached to it.

For a linear molecule, a little calculation shows that entirely similar results hold. Thus for the simultaneous excitation of a parallel active vibration and rotation $v, J, M=0, 0, 0 \rightarrow 1, 1, 0$, the total cross section is given by (10) with the subscripts 1_i100 replaced by

$$v_i, J, M=1_i, 1, 0.$$

In Fig. 1, Q_{1_i100} and Q_{0_i000} are plotted as functions of the initial kinetic energy of the electron in units of $y^2\cdot 10^{-15}$ cm^2 for a vibration-rotational transition for which the energy transfer is 0.1 volt, corresponding to a frequency of $\sim$800 cm^{-1}. For a vibration with $A_iX_i(0, 1)\sim 0.1\times 10^{-18}$ c.g.s. unit, the cross sections are of the order 10^{-17} cm^2 for slow electrons.

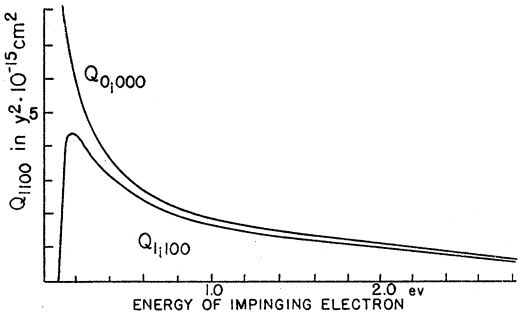

FIG. 1. Cross sections as functions of the energy of impinging electron.

A few words may be said concerning the validity of (10). For molecules having no permanent moment such as CO_2, CS_2, C_2H_2, C_3O_2, CH_4, CCl_4, etc., $V^I=0$ and the condition for the validity of (10) is $\beta_i\ll 1$ or $A_iX_i(0, 1)\ll 10^{-18}$. From absorption coefficient and infra-red dispersion measurements for such molecules as CO_2, estimates of the effective charge in the relation $A_iX_i(0, 1)=$ effective charge$\times$change in nuclear distances lead to values which are of the order of one electronic charge.[6] As the change in nuclear distances is small compared with the interatomic distances and hence $\ll 10^{-8}$ cm, it follows that $A_iX_i(1, 0)\ll 10^{-18}$, although accurate values for $A_iX_i(1, 0)$ are not readily available.

For molecules with a permanent electric moment, the condition for the validity of (10) is seen from (9) to be $y\ll 1$ and $x^2\sim y$. Thus (10) will be a good approximation when applied to CO for which $x=0.11$. As the gas kinetic cross section for electrons in CO is $\sim 3\times 10^{-16}$ cm^2, Harries'[1] observation mentioned before would lead to a value $\sim 1\times 10^{-17}$ for Q_{110}. On the assumption (1), this value of Q_{110} would correspond to a value 0.1×10^{-18} for the change of the electric moment due to the vibration of CO. This value is entirely reasonable, although it must be pointed out that the assumption (1) fails to account for the observed excitation of vibration of such molecules as H_2 and N_2, since for optically inactive vibrations, the above theory would predict zero cross section. In dealing with these cases, the assumed form (1) for V is obviously inadequate. Also, for most molecules,

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[6] Cf. J. H. Van Vleck, *Quantum Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1931), §15.

x is of the order unity and the approximation made in obtaining (10) can no longer be justified.

II. EXCITATION OF OPTICALLY INACTIVE VIBRATION

In treating the problem without the assumption (1), it is necessary to solve the Schrödinger equation of the electron in the field of the nuclei and the electrons of the molecule. It is at once obvious that the mathematical calculations involved would be very lengthy even for the simplest of molecules, namely, hydrogen. In the following, we shall make some rough estimates in the case of hydrogen. It is reasonable to suppose that for other molecules, the essential feature is the same and results of similar order of magnitude would be obtained, although there is a great difference in mathematical complexity.

Let us denote the coordinates of the impinging electron by the subscript 1 and those of the molecular electrons by 2 and 3. Let r, p be the distances of an electron from the nuclei a and b, ρ be the nuclear separation, and ϑ, φ be the polar angles of the line of nuclei. The Hamiltonian of the system: molecule+electron is

$$H=H_e(r_2,\,p_2,\,r_3,\,p_3)+H_v(\rho)+H_r(\vartheta,\,\varphi)$$
$$+H(r_1)+V(r_1,\,p_1,\,r_{12},\,r_{13})$$

where H_e is the Hamiltonian of the molecular electrons in the field of the fixed nuclei; $H_v(\rho)$ is the Hamiltonian corresponding to the vibrational motion of the nuclei; $H_r(\vartheta,\varphi)$ is the Hamiltonian of the rotational motion of the molecule; $H(r_1)$ is the kinetic energy part of the impinging electron, and V is the interaction

$$V=e^2\left(-\frac{1}{r_1}-\frac{1}{\rho_1}+\frac{1}{r_{12}}+\frac{1}{r_{13}}\right). \tag{12}$$

The solution of the equation

$$(H_e+H_v+H_r)\Psi^0=E^0\Psi^0$$

may be approximated by

$$\Psi^0(r_2,\,p_2,\,r_3,\,p_3,\,\rho,\,\vartheta,\,\varphi)$$
$$=\psi_n(r_2,\,p_2,\,r_3,\,p_3)\cdot\psi_v(\rho)\cdot\psi_{JM}(\vartheta,\,\varphi)$$

where $\psi_{JM}(\vartheta,\varphi)$ is the rotational wave function of a linear molecule; $\psi_v(\rho)$ the vibrational wave function; and ψ_n is the electronic wave function containing the nuclear distance ρ as a parameter. For the normal $^1\Sigma$ state, ψ_n can be taken to be that given by Wang

$$\psi_0=C^2\exp[-\tfrac{1}{2}\mu(r_2+p_3)]+\exp[-\tfrac{1}{2}\mu(r_3+p_2)],$$
$$C=(\tfrac{1}{2}\mu)^6[2\pi(1+S)]^{-1},$$
$$S=(1+\tfrac{1}{2}\mu\rho+\mu^2\rho^2/12)^2e^{-\mu\rho},$$
$$\mu=2Z/a_0,\quad Z=1.166.$$

To solve the equation

$$(H_e+H_v+H_r+H(r_1)+V)\Psi=E\Psi,$$

we proceed by the usual method of expressing Ψ as a sum of products

$$\Psi=\sum_{nvJM}\psi_n(r_2,\,p_2,\,r_3,\,p_3)$$
$$\cdot\psi_v(\rho)\cdot\psi_{JM}(\vartheta,\,\varphi)\cdot F_{nvJM}(r_1), \tag{13}$$

the sum being taken over all the electronic, vibrational, and rotational states n, v, JM. On writing

$$k^2_{nvJM}=(8\pi^2m/h^2)(E-E_n-E_v-E_{JM}), \tag{14}$$

the equations for the $F_{nvJM}(r_1)$ are

$$[\nabla^2+k^2_{nvJM}]F_{nvJM}(r_1)=(8\pi^2m/h^2)$$
$$\sum_{n'v'J'M'}V(n'v'J'M';\,nvJM)(r_1)\cdot F_{n'v'J'M'} \tag{15}$$

where

$$V(n',\,v',\,J'M';\,n,\,v,\,JM)=\int\psi_{n'}{}^*\psi_{v'}{}^*\psi_{J'M'}{}^*$$
$$\times V\psi_n\psi_v\psi_{JM}dr_2dr_3d\rho d\cos\vartheta d\varphi.$$

The equation for F_{0000} is, for example,

$$[\nabla^2+k^2_{0000}]F_{0000}(r_1)=(8\pi^2m/h^2)$$
$$\times[V(0000;\,0000)(r_1)\cdot F_{0000}(r_1)$$
$$+V(0000;\,0010)(r_1)F_{0010}(r_1)+\cdots$$
$$+V(0000;\,0100)(r_1)F_{0100}(r_1)$$
$$+V(0000;\,1000)(r_1)F_{1000}(r_1)+\cdots] \tag{16}$$

where the F_{0010}, F_{0100}, etc., are given by similar equations. The possibility of solving this system of equations by successive approximation depends on the smallness of certain matrix elements of V compared with others. Consider first

$$V_1=\int \psi_0{}^*(r_2p_2r_3p_3)\,V\psi_0(r_2p_2r_3p_3)dr_2dr_3$$

$$=-\frac{e^2}{1+S}\left\{\frac{e^{-\mu r_1}}{r_1}\left(1+\frac{\mu r_1}{2}\right)+\frac{e^{-\mu p_1}}{p_1}\left(1+\frac{\mu p_1}{2}\right)\right\}$$

$$-\frac{16\pi e^2C^2\sqrt{S}}{\mu^3}\int\left(\frac{1}{r_1}+\frac{1}{p_1}-\frac{2}{r_{12}}\right)$$

$$\times e^{-\mu(r_2+p_2)/2}dr_2. \quad (17)$$

Evaluation of the integral on the right leads to a very lengthy function in r_1 and p_1. Reference to Massey's work shows that the contribution of this term to the elastic scattering cross section is small in the limiting cases of fast electrons and of zero scattering angle.[4] For the purpose of making a rough estimate only, we shall neglect this term in the following.

For matrix elements of V with respect to the normal and an excited electronic state, general considerations lead one to expect

$$V(0,\, v,\, JM;\, n,\, v,\, JM)$$

$$\ll V(0,\, v,\, JM;\, 0,\, v,\, JM). \quad (18)$$

To calculate the matrix elements of V with respect to the rotational states

$$V_2=V(0,\, J'M';\, 0,\, JM)$$

$$=\int \overset{*}{\psi}_{J'M'}(\vartheta,\, \varphi)\,V_1\psi_{JM}(\vartheta,\, \varphi)d\cos\vartheta d\varphi, \quad (19)$$

let us take the direction of the impinging electron as the polar axis of the angles ϑ and φ so that

$$\begin{aligned} r_1{}^2&=r^2+(\tfrac{1}{2}\rho)^2+r\rho\cos\vartheta,\\ p_1{}^2&=r^2+(\tfrac{1}{2}\rho)^2-r\rho\cos\vartheta, \end{aligned} \quad (20)$$

where r is the distance of the colliding electron from the center of the molecule. Since V_1 does not depend on φ, and since the transformation of ϑ into $\pi-\vartheta$ leaves V_1 unchanged, it follows that

$$V_2(0,\, J'M';\, 0,\, JM)=0 \text{ unless } M'=M$$

and

$$J'-1=0,\ \pm2,\ \pm4,\ \cdots. \quad (21)$$

Integration over ϑ in (19), when V_2 does not vanish, will be very complicated on account of the dependence of r_1 and p_1 on ϑ in (20); but again as an approximation, we shall replace this averaging of V_1 over all orientations of the molecule by taking a central field

$$V_2(0,\, 00;\, 0,\, 00)=-\frac{2e^2}{1+S}\frac{e^{-\mu r}}{r}\left(1+\frac{\mu r}{2}\right). \quad (22)$$

Finally, consider the matrix element

$$V(n',\, v',\, J'M';\, n,\, v,\, J,\, M)$$

appearing in (15). On writing $\rho=\rho_0+\xi$ where $\xi/\rho_0\ll1$, one has

$$V_2(\rho)=V_2(\rho_0)+\left(\frac{\partial V_2}{\partial\rho}\right)_{\rho_0}\xi+\cdots$$

so that

$$V(0,\, 1,\, 00;\, 0,\, 0,\, 00)$$

$$=\rho_0\left(\frac{\partial V_2}{\partial\rho}\right)_{\rho_0}\cdot\int\psi_1{}^*(\xi)\frac{\xi}{\rho_0}\psi_0(\xi)d\xi$$

$$=\rho_0\left(\frac{\partial V_2}{\partial\rho}\right)_{\rho_0}\cdot\frac{1}{\rho_0}\cdot\left(\frac{h}{4\pi^2M\nu}\right)^{\frac{1}{2}}.$$

Now for hydrogen, $\rho_0=0.75\times10^{-8}$ cm, $\nu=4270$ cm^{-1} so that

$$\rho_0\left(\frac{\partial V_2}{\partial\rho}\right)_{\rho_0}=0.42\,V(0,\, 0,\, 00;\, 0,\, 0,\, 00),$$

$$\frac{1}{\rho_0}\left(\frac{h}{4\pi^2M\nu}\right)^{\frac{1}{2}}=1/9$$

and

$$V(0,1,00;0,0,00)\simeq0.05\,V(0,0,00;0,0,00). \quad (23)$$

In general,

$$V(n,\, v',\, JM;\, n,\, v,\, LM)$$

$$\ll V(n,\, v,\, JM;\, n,\, v,\, JM), \quad v'\neq v. \quad (24)$$

On considerations of (18), (21) and (24), we need only consider terms containing F_{0000}, F_{0020}, F_{0042}, etc., in (16). The term

$$V(0,\, 0,\, 00;\, 0,\, 0,\, 00)F_{0000}$$

represents the distortion of the electron wave by the molecular field, while the terms in F_{0020}, F_{0040}, etc., represent the effect of the inelastically scattered waves on the elastically scattered wave. As a further approximation, we shall neglect the latter effect and (16) becomes

$$[\nabla^2+k_{0000}^2]F_{0000}(r)=(8\pi^2m/h^2)\times V(0,0,00;0,0,00)(r)F_{0000}(r). \quad (25)$$

The equation for $F_{0100}(r)$ is

$$[\nabla^2+k_{0100}^2]F_{0100}(r)=(8\pi^2m/h^2)\times[V(0,1,00;0,0,00)F_{0000}(r)+V(0,1,00;0,1,00)F_{0,1,00}(r)+\cdots] \quad (26)$$

in which we have neglected again terms containing $V(0,1,00;0,1,J0)$ where $J=2,4,6,\cdots$. The method of solving these equations is well known.[7] Thus

$$F_{0000}(r)=\sum_{n=0}^{\infty}(2n+1)i^n e^{i\eta_n}L_n(r)P_n(\cos\vartheta) \quad (27)$$

where $L_n(r)$ is that solution of

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dLn}{dr}\right)+\left[k_{0000}^2-\frac{8\pi^2m}{h^2}\times V(0,0,00;0,000)(r)-\frac{n(n+1)}{r^2}\right]L_n=0 \quad (28)$$

which is finite at the origin, and η_n is determined by $V(0,0,00;0,0,00)$ and k^2 and is given approximately by

$$\eta_n=-\frac{4\pi^3m}{h^2}\int_0^\infty V(0,0,00;0,0,00)(r)\times\left(\frac{2kr}{\pi}\right)^{\frac{1}{2}}L_n(r)J_{n+\frac{1}{2}}(kr)rdr$$

$$\simeq-\frac{4\pi^3m}{h^2}\int_0^\infty V(0,0,00;0,0,00)(r)\times[J_{n+\frac{1}{2}}(kr)]^2rdr \quad (29)$$

which is valid if η_n is small. Calculation gives

$$\eta_0=\frac{4\pi^2me^2}{h^2(1+S)k}\left\{\ln\left[1+\left(\frac{2k}{\mu}\right)^2\right]+\frac{1}{1+(\mu/2k)^2}\right\}, \quad (30)$$

and for electron energy of 2.5, 5, 10 volts,

$$\eta_0=0.43,\ 0.53,\ 0.65,$$

respectively. For these low energies, η_1 is negligibly small.

The solution of (26), which can be put, on account of (23) and the expansion of V_2 about ρ_0 given before, in the form

$$[\nabla^2+k_{0100}^2-(8\pi^2m/h^2)V(0,0,00;0,0,00)]F_{0100}(r)=(8\pi^2m/h^2)0.05V(0,0,00;0,0,00)F_{0000}(r), \quad (31)$$

has the asymptotic form

$$F_{0100}(r)\sim\frac{0.05\times2\pi m}{h^2}\cdot\frac{e^{ik_{0100}r}}{r}\int\mathfrak{F}(r',\pi-\Theta)\cdot V(0,0,00;0,0,00)(r')F_{0000}(r')dr' \quad (32)$$

where

$$\mathfrak{F}(r,\vartheta)=\sum_{l=0}^{\infty}(2l+1)i^l e^{i\zeta_l}\mathfrak{L}_l(r)P_l(\cos\vartheta) \quad (33)$$

is the solution of the homogeneous equation obtained from (31) by equating the left-hand side to zero, and

$$\cos\Theta=\cos\vartheta\cos\vartheta'+\sin\vartheta\sin\vartheta'\cos(\varphi-\varphi').$$

On carrying out the integration in (32), one obtains

$$F_{0100}(r)\sim\frac{e^{ik_{0100}r}}{r}\left[\frac{0.05\times2\pi m}{h^2}4\pi\sum_{n=r}^{\infty}(-1)^n(2n+1)\times e^{i(\eta_n+\zeta_n)}P_n(\cos\vartheta)\int_0^\infty V(0,0,00;0,0,00)(r')\times L_n(r')\mathfrak{L}_n(r')r'^2dr'\right].$$

As the η_n are small according to (29), the contribution to the cross section from these harmonics is small so that the differential cross section for the excitation of the vibrational state by one quantum is

$$\left|\frac{0.05\times8\pi^2m}{h^2}\int_0^\infty V(0,0,00;0,0,00)(r)\times L_0(r)\mathfrak{L}_0(r)r^2dr\right|^2.$$

Now for electrons of about 10 volts and vibra-

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[7] Mott and Massey, reference 3, Chaps. II and VI.

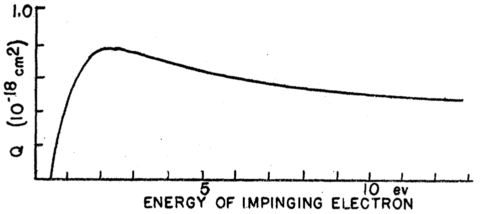

FIG. 2. Total cross section as a function of the energy of impinging electron.

tional quantum $h\nu \simeq 0.5$ volt, $k^2 \equiv k_{0000}{}^2 \simeq k_{0100}{}^2$ so that $L_0(r)\,\mathfrak{L}_0(r)$ can be replaced approximately by $|L_0(r)|^2$. By (29),

$$-\frac{8\pi^2 mk}{h^2}\int_0^\infty V(0,0,00;0,0,00)(r)L_0(r)\,\mathfrak{L}_0(r)r^2dr$$

$$\simeq -\frac{4\pi^3 m}{h^2}\int_0^\infty V(0,0,00;0,0,00)$$

$$\times |J_{\frac{1}{2}}(kr)|^2 r dr = \eta_0(k).$$

The total cross section is then

$$Q_{0100}(k) = 4\pi\left(\frac{0.05}{k}\right)^2 \frac{k_{0100}}{k}\eta_0{}^2(k). \qquad (34)$$

In Fig. 2, Q_{0100} is plotted against the energy of the impinging electron.

According to the calculated cross section, since the gas-kinetic cross section for electrons in H_2 is about 10^{-16} cm^2, one would expect about $\frac{1}{2}$ of a percent of the collisions between electrons of a few volts and H_2 to be inelastic, resulting in the excitation of one vibrational quantum. This is to be compared with the value ~2 percent found by Ramien for 7-volt electrons.[2] Considering the many simplifying approximations made in the calculation, one may perhaps feel that the calculation does give the correct order of magnitude for the cross section of such processes.

PHYSICAL REVIEW VOLUME 71, NUMBER 2 JANUARY 15, 1947

The Relation between the Force Constant and the Interatomic Distance of a Diatomic Linkage

II. A Modified Huggins Relation

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(Received October 14, 1946)

1. Huggins' relation between the force constant and the interatomic distance is modified so that the constants are now characteristic of the molecular period. 2. The new relation predicts the interatomic distance from the force constants of a diatomic linkage with an accuracy slightly better than Huggins' original relation. 3. Various aspects of the new relation are discussed.

HUGGINS[1] has shown that by assuming a modified Morse potential function for a diatomic linkage in the form

$$U = e^{-a(R-R_{12})} - C'e^{-a'(R-R_e)}, \qquad (1)$$

he was able to obtain a relation between the interatomic distance R_e and the force constant K_e as

$$R_e = R_{12} - \frac{2.303}{a}\log\frac{K_e}{a^2 - aa'}. \qquad (2)$$

He then determined the constants a and R_{12} semi-emperically, so that for certain groups of molecules a is a group constant and R_{12} an

TABLE I. Values of A, B, and a for various molecular periods.

Molecular period	A in 108 cm^{-1}	B	Relation K_e in dynes/cm R_e in 10^{-8} cm	a in 108 cm^{-1}
00	−1.78	7.11	$\log K_e = -1.78R_e + 7.11$	4.10
01	−1.356	7.17	$\log K_e = -1.356R_e + 7.17$	3.12
02	−1.17	7.16	$\log K_e = -1.17R_e + 7.16$	2.69
11	−1.83	8.28	$\log K_e = -1.83R_e + 8.28$	4.21
12	−2.00	8.97	$\log K_e = -2.00R_e + 8.97$	4.61
22	−1.10	7.71	$\log K_e = -1.10R_e + 7.71$	2.53

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[1] M. L. Huggins, J. Chem. Phys. 3, 473 (1935); 4, 308 (1936).