Slow-Electron Scattering by Strongly Polar Molecules

By

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Summary. The cross section for electron scattering by a polar molecule is calculated with taking account of temporary capture of the electron in the dipole field of the molecule. The calculation is based on the second-order time-dependent perturbation theory in which a temporary captured state is to be regarded as an intermediate one. If the dipole moment D of the molecule is relatively large (the numerical example is given for $D=2.50 \times 10^{-18}$ esu cm), the scattering cross section is enhanced due to the process of electron capture.

1. INTRODUCTION

In a recent paper Turner [1] has suggested that in scattering of electrons by polar molecules a temporary capture of the electron by the target molecule occurs and this gives rise to an enhancement of the total scattering cross section. The possibility of a bound state of an electron in the field of a dipole has been investigated by Wallis et al [2]. With numerical calculation they have concluded that there is a bound state for a dipole moment larger than 2.14×10^{-18} esu cm. On the other hand it is shown experimentally that the momentum-transfer cross sections for electron scattering by some polar molecules, such as H_2O , D_2O , H_2S , are appreciably large and do not agree with the results in the usual theory [3]. Considering these facts Turner has estimated the effect of the electron capture on the scattering cross section.

According to Turner's theory, a passing electron can exert a torque on the molecular dipole and might excite the molecule to a higher rotational state. The electron might lose enough energy to form a bound state in the field of the dipole. If this state has a finite lifetime, the decay into molecule and electron occurs promptly and this process contributes to the total scattering cross-section.

Turner has calculated the capture rate and the lifetime of the captured state. He has shown that the lifetime is comparable to the period of rotation of the molecule. This short lifetime implies that it is not a good approximation to treat the capture process and the decay process separately and that they must be considered simultaneously. In the present paper we calculate the cross section for electron scattering by a polar molecule with taking account of temporary capture of the electron by the target. In doing this, we treat the capture process and the decay process in a unified manner; *i.e.*, we apply the second-order perturbation theory in which the

captured state is to be regarded as an intermediate state. It is assumed that the intermediate state has a finite lifetime.

The following calculation is based on the adiabatic approximation and the rotational energy operator of the molecule in the total Hamiltonian is treated as a perturbation. This treatment is a good approximation in slow-electron scattering.

In 2 the general formula for the scattering cross-section is derived with taking account of the temporary capture. In 3 the wave functions are given and with use of them the matrix elements are calculated. Finally, numerical estimation and discussion are given in 4.

2. SCATTERING CROSS SECTION

Let us investigate scattering of an electron by a polar molecule which is assumed to be represented by a rigid rotator having a dipole moment. The total Hamiltonian of the system is

$$H = H_M(\mu, \nu) + H_e(\mathbf{r}; \mu, \nu) . \quad (2.1)$$

Here H_M is the Hamiltonian of the rigid rotator with a dipole whose polar and azimuthal angles are (μ, ν) , and H_e is the Hamiltonian of the electron in the field of the dipole, $\mathbf{r}$ being the coordinate of the electron.

It is assumed that the rotational motion of the molecule is so much slow compared with the motion of the electron that the two motions are coupled adiabatically. Therefore, an eigenfunction of the total Hamiltonian H can be expressed by a product of an eigenfunction of H_e calculated for fixed dipole coordinate (μ, ν) and an angular momentum eigenfunction of H_M . Furthermore, the Hamiltonian H_M , representing the rotation of the molecule, can be treated as a perturbation which couples the motions of the molecule and the electron.

Denoting an eigenfunction of H_M by $Y(JM|\mu, \nu)$, we have

$$H_M Y(JM|\mu, \nu) = E(J) Y(JM|\mu, \nu) . \quad (2.2)$$

If there exist both continuous and discrete states for the operator H_e , we write

$$H_e(\mathbf{r}; \mu, \nu) f(\mathbf{k}|\mathbf{r}; \mu, \nu) = E(k) f(\mathbf{k}|\mathbf{r}; \mu, \nu) \quad (2.3)$$

for a continuous state and

$$H_e(\mathbf{r}; \mu, \nu) f(\alpha|\mathbf{r}; \mu, \nu) = E(\alpha) f(\alpha|\mathbf{r}; \mu, \nu) \quad (2.4)$$

for a discrete state. The eigenfunction $f(\mathbf{k}|\mathbf{r}; \mu, \nu)$ represents a free electron with momentum $\hbar\mathbf{k}$ in the field of the dipole whose coordinates (μ, ν) are fixed; $f(\alpha|\mathbf{r}; \mu, \nu)$ represents a bound electron in the dipole field.

In the following we calculate the probability of the transition from the initial state $(J_i M_i k_i)$ to the final state $(J_f M_f k_f)$ with use of the time-dependent perturbation theory. As usual, we put the eigenfunction of H as

$$\begin{aligned}
\Psi = & \sum_{J M k} a(J M k | t) Y(J M | \mu, \nu) f(\mathbf{k} | \mathbf{r}; \mu, \nu) \exp \left\{ -\frac{i}{\hbar} E(J) t - \frac{i}{\hbar} E(k) t \right\} \\
& + \sum_{J' M' \alpha} b(J' M' \alpha | t) Y(J' M' | \mu, \nu) f(\alpha | \mathbf{r}; \mu, \nu) \exp \left\{ -\frac{i}{\hbar} E(J') t - \frac{i}{\hbar} E(\alpha) t \right. \\
& \quad \left. - \frac{t}{2\tau(J' M' \alpha)} \right\}, \quad (2.5)
\end{aligned}$$

where the quantity $\tau(J' M' \alpha)$ is the lifetime of the state $(J' M' \alpha)$ which is assumed to be finite.

Substituting this function into the Schrödinger eq.

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \quad (2.6)$$

and following the usual second-order perturbation theory, we obtain the amplitude a_f of the final state $(J_f M_f k_f)$ after the transition from the initial state $(J_i M_i k_i)$ as follows:

$$\begin{aligned}
a_f = & \left\{ \sum_{J M k} \frac{\langle J_f M_f k_f | H_M - E(J) | J M k \rangle \langle J M k | H_M - E(J_i) | J_i M_i k_i \rangle}{E(J) + E(k) - E(J_i) - E(k_i)} \right. \\
& \left. + \sum_{J' M' \alpha} \frac{\langle J_f M_f k_f | H_M | J' M' \alpha \rangle \langle J' M' \alpha | H_M | J_i M_i k_i \rangle}{E(J') + E(\alpha) - E(J_i) - E(k_i) - \frac{i\hbar}{2\tau(J' M' \alpha)}} \right\} \\
& \times \frac{\exp \left[i \{ E(J_f) + E(k_f) - E(J_i) - E(k_i) \} \frac{t}{\hbar} - 1 \right]}{E(J_f) + E(k_f) - E(J_i) - E(k_i)}, \quad (2.7)
\end{aligned}$$

and thus

$$\begin{aligned}
|a_f|^2 = & \left\{ \left| \sum_{J M k} \frac{\langle J_f M_f k_f | H_M - E(J) | J M k \rangle \langle J M k | H_M - E(J_i) | J_i M_i k_i \rangle}{E(J) + E(k) - E(J_i) - E(k_i)} \right|^2 \right. \\
& + \left| \sum_{J' M' \alpha} \frac{\langle J_f M_f k_f | H_M | J' M' \alpha \rangle \langle J' M' \alpha | H_M | J_i M_i k_i \rangle}{E(J') + E(\alpha) - E(J_i) - E(k_i) - \frac{i\hbar}{2\tau(J' M' \alpha)}} \right|^2 \\
& \left. + (\text{interference term}) \right\} \frac{2 \left[1 - \cos \frac{t}{\hbar} \{ E(J_f) + E(k_f) - E(J_i) - E(k_i) \} \right]}{\{ E(J_f) + E(k_f) - E(J_i) - E(k_i) \}^2}. \quad (2.8)
\end{aligned}$$

Here the first term in the wavy brackets in (2.8) corresponds to the transition through a free-electron state as an intermediate one and this transition may occur even if there exist no captured states. On the other hand the second term represents the transition through a bound state and we are now interested in only this term. Besides these two terms there is in (2.8) a term representing an interference be-

tween the above two transition processes. For simplicity we here neglect the effect of such an interference on the scattering cross section.

Now the probability of the transition through a captured state can be calculated from (2.8) to be

$$w(J_i M_i k_i \rightarrow J_f M_f k_f) = \frac{2\pi}{h} \rho(J_f M_f k_f) \left| \sum_{J' M' \alpha} \frac{\langle J_f M_f k_f | H_M | J' M' \alpha \rangle \langle J' M' \alpha | H_M | J_i M_i k_i \rangle}{E(J') + E(\alpha) - E(J_i) - E(K_i) - \frac{i\hbar}{2\tau(J' M' \alpha)}} \right|^2. \quad (2.9)$$

The final state $(J_f M_f k_f)$ consists of the molecule in the state $(J_f M_f)$ and a free electron having momentum $\hbar k_f$, so that the state density $\rho(J_f M_f k_f)$ is

$$\rho(J_f M_f k_f) = \frac{V}{(2\pi)^3} \frac{m_e k_f}{\hbar^2} d\hat{k}_f, \quad (2.10)$$

where $\hat{k}_f$ is the unit vector along k_f , $d\hat{k}_f$ is the angular part of dk_f , V is the volume in which the wave function is normalized, and m_e is the mass of electron.

With use of (2.9) and (2.10), the differential cross section for the scattering of an electron by a polar molecule with taking account of temporary capture of the electron around the molecule is written as

$$\sigma^r(\hat{k}_f) d\hat{k}_f = \frac{V^2}{4\pi^2} d\hat{k}_f \frac{m_e^2}{\hbar^4} \frac{k_f}{k_i} \left| \sum_{J' M' \alpha} \frac{\langle J_f M_f k_f | H_M | J' M' \alpha \rangle \langle J' M' \alpha | H_M | J_i M_i k_i \rangle}{E(J') + E(\alpha) - E(J_i) - E(k_i) - \frac{i\hbar}{2\tau(J' M' \alpha)}} \right|^2. \quad (2.11)$$

This cross section has a form of resonance-type, as it should have. The superscript r stands for resonance-type scattering.

3. WAVE FUNCTIONS AND THE MATRIX ELEMENTS

To evaluate the cross section (2.11), we must know the wave functions $f(\mathbf{k} | \mathbf{r}; \mu, \nu)$, $f(\alpha, | \mathbf{r}; \mu, \nu)$ and, with use of them, calculate the matrix elements $\langle J_f M_f k_f | H_M | J' M' \alpha \rangle$ and $\langle J' M' \alpha | H_M | J_i M_i k_i \rangle$.

In the following the polar molecule is assumed to be a point dipole so that the Hamiltonian H_e is

$$H_e = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{De}{r^2} \cos \bar{\theta} \quad (3.1)$$

where D is the dipole moment of the molecule and $\bar{\theta}$ is the polar angle of the electron relative to the dipole.

As in Turner's paper, we determine the eigenfunctions of H_e as follows:

i) *Initial state*

The initial electron state is to be regarded as consisting of the sum of an incident plane-wave $\exp(i\mathbf{k}_i \cdot \mathbf{r})$ and an outgoing spherical-wave determined in the first Born approximation, *i.e.*

$$\begin{aligned} f(\mathbf{k}_i | \mathbf{r}; \mu, \nu) &= \frac{1}{\sqrt{V}} \exp(i\mathbf{k}_i \cdot \mathbf{r}) + \frac{Dem_e}{2\pi\hbar^2\sqrt{V}} \frac{\exp(i\mathbf{k}_i r)}{r} \int \frac{\cos \theta'}{r'^2} \exp(i\mathbf{K} \cdot \mathbf{r}') d\mathbf{r}' \\ &= \frac{1}{\sqrt{V}} \exp(i\mathbf{k}_i \cdot \mathbf{r}) + \frac{2iDem_e}{\sqrt{V}\hbar^2} \frac{\eta}{K} \frac{\exp(i\mathbf{k}_i r)}{r}. \end{aligned} \quad (3.2)$$

Here $\mathbf{K} = \mathbf{k}_i - k_i \hat{\mathbf{r}}$, $\hat{\mathbf{r}}$ being the unit vector along $\mathbf{r}$, and η is the angle between $\mathbf{K}$ and the dipole.

In the polar coordinate system where the polar axis is along the vector $\mathbf{k}_i$, the term η/K is written in form

$$\frac{\eta}{K} = \frac{1}{4k_i} \frac{-\sin \mu \cos \nu \sin \theta \cos \varphi - \sin \mu \sin \nu \sin \theta \sin \varphi + \cos \mu (1 - \cos \theta)}{\sin^2\left(\frac{1}{2}\theta\right)}, \quad (3.3)$$

where (μ, ν) and (θ, φ) are the polar and azimuthal angles relative to $\mathbf{k}_i$ of the dipole and $\mathbf{r}$, respectively.

ii) *Final state*

As in the case of the initial state, the final state is to be regarded as consisting of the sum of an outgoing plane-wave $\exp(i\mathbf{k}_f \cdot \mathbf{r})$ and an incoming spherical-wave. Thus, we have

$$f(\mathbf{k}_f | \mathbf{r}; \mu, \nu) = \frac{1}{\sqrt{V}} \exp(i\mathbf{k}_f \cdot \mathbf{r}) + \frac{2iDem_e}{\sqrt{V}\hbar^2} \frac{\eta'}{K'} \frac{\exp(-i\mathbf{k}_f r)}{r}, \quad (3.4)$$

where $\mathbf{K}' = \mathbf{k}_f + k_f \hat{\mathbf{r}}$ and η' is the angle between $\mathbf{K}'$ and the dipole.

In the coordinate system where the polar axis is along the vector $\mathbf{k}_f$, the term η'/K' is written as

$$\frac{\eta'}{K'} = \frac{1}{4k_f} \frac{\sin \mu' \cos \nu' \sin \theta' \cos \varphi' + \sin \mu' \sin \nu' \sin \theta' \sin \varphi' + \cos \mu' (1 + \cos \theta')}{\cos^2\left(\frac{1}{2}\theta'\right)}, \quad (3.5)$$

where (μ', ν') and (θ', φ') are the angles relative to $\mathbf{k}_f$ of the dipole and $\mathbf{r}$, respectively.

iii) *Intermediate bound-state*

In the derivation of the bound state of H_e , Turner has used a variational method. He has set the wave function in the form

$$f(\alpha | \mathbf{r}; \mu, \nu) = 2 \left(\frac{z}{a_0} \right)^{3/2} \exp\left(-\frac{zr}{a_0}\right) [C_0 Y(00 | \bar{\theta}, \bar{\varphi}) + C_1 Y(10 | \bar{\theta}, \bar{\varphi})]. \quad (3.6)$$

Here $Y(00|\bar{\theta}, \bar{\varphi})$ and $Y(10|\bar{\theta}, \bar{\varphi})$ are the spherical harmonics depending on the electron coordinates relative to the dipole, and $a_0 = \hbar^2/m_e e^2$ is the Bohr radius. The numerical coefficients C_0 , C_1 , and z are to be determined by the variational method.

Here we adopt also the form (3.6) and determine the coefficients C_0 , C_1 , and z in the following way.

For the normalization it is required that

$$|C_0|^2 + |C_1|^2 = 1, \quad (3.7)$$

and without loss of generality C_0 and C_1 may be taken to be real numbers, so that

$$C_0^2 = 1 - C_1^2. \quad (3.6)$$

By using (3.6) the expectation value of the electron energy $\langle H_e \rangle$ is calculated to be

$$\langle H_e \rangle = z^2 \left[\frac{e^2}{2a_0} (1 + 4C_1^2) - \frac{4De}{\sqrt{3} a_0^2} C_1 (1 - C_1^2)^{1/2} \right]. \quad (3.9)$$

We minimize $\langle H_e \rangle$ with respect to C_1 and get*

$$\langle H_e \rangle_{\min} = z^2 \frac{e^2}{2a_0} \left\{ 3 - 2 \sqrt{1 + \frac{4}{3} \frac{D^2}{e^2 a_0^2}} \right\} \quad (3.10)$$

at

$$C_1^2 = \frac{1}{2} - \frac{1}{2} \left(1 + \frac{4}{3} \frac{D^2}{e^2 a_0^2} \right)^{-1/2}.$$

From (3.10) it is shown that the electron energy becomes negative for a dipole moment $D > (\sqrt{15}/4)ea_0 = 2.46 \times 10^{-18}$ esu cm. There exist, therefore, some bound states for an electron in the field of a dipole the moment of which is larger than 2.46×10^{-18} esu cm.

Finally, the coefficient z is to be determined by comparing the above $\langle H_e \rangle_{\min}$ with the electron binding energy calculated numerically for a finite dipole [2].

Thus, we can estimate the matrix elements with use of the wave functions (3.2), (3.4) and (3.6). The calculation is straightforward but lengthy, so that only the results are given here.

For $k_i a_0 \ll 1$, which is the case of practical importance,

$$\begin{aligned} \langle J'M' \alpha | H_M | J_i M_i k_i \rangle &= \frac{i}{\sqrt{V} I} \left(\frac{a_0}{z} \right)^{1/2} \frac{D e m_e}{k_i} \left\{ 2 \sqrt{\pi} C_0 S^{(1)}(J'M'; J_i M_i) \right. \\ &\quad \left. + \frac{\sqrt{3\pi}}{2} C_1 S^{(3)}(J'M'; J_i M_i) \right\}, \end{aligned} \quad (3.11)$$

* Turner has not minimized the energy (3.9) but he has minimized the dipole moment D under the condition $\langle H_e \rangle = 0$. His procedure, therefore, gives the value of D for which $\langle H_e \rangle_{\min} < 0$, but not the exact values of C_1 , C_0 for which $\langle H_e \rangle$ has its minimum value.

where I is the moment of inertia of the polar molecule and

$$\begin{aligned}
S^{(1)}(J'M'; JM) &= J'(J'+1)\{\alpha(JM)\delta_{J', J+1} + \beta(JM)\delta_{J', J-1}\}\delta_{M'M}, \\
S^{(3)}(J'M'; JM) &= [(J+1)(J+2)\{\varepsilon(JM)\zeta(J'M') + \gamma(JM)\eta(J'M')\}\delta_{J+1, J'-1} \\
&\quad + J(J-1)\{\varepsilon(J'M')\zeta(JM) + \gamma(J'M')\eta(JM)\}\delta_{J-1, J'+1}]\delta_{M'M} \\
&\quad - [(J+1)(J+2)\{\varepsilon^2(JM) + \gamma^2(JM)\} \\
&\quad + J(J-1)\{\zeta^2(JM) + \eta^2(JM)\}]\delta_{J,J'}\delta_{M'M}; \\
\alpha(JM) &= \beta(J+1, M) = \left[\frac{(J+M+1)(J-M+1)}{(2J+1)(2J+3)} \right]^{1/2}, \\
\gamma(JM) &= \eta(J+1, -M+1) = \left[\frac{(J-M+1)(J-M+2)}{(2J+1)(2J+3)} \right]^{1/2}, \\
\varepsilon(JM) &= \zeta(J+1, -M-1) = \left[\frac{(J+M+1)(J+M+2)}{(2J+1)(2J+3)} \right]^{1/2}.
\end{aligned}$$

In the calculation of $\langle J_f M_f k_f | H_M | J' M' \alpha \rangle$, it is necessary to transform the molecular wave function $Y(J_f M_f | \mu, \nu)$ which is represented in the polar coordinate system with the axis along the initial momentum k_i , into the representation in the coordinate with the axis along the final momentum k_f . In general the relation

$$Y(JM | \mu, \nu) = \sum_{m=-J}^J A_J(Mm | \Theta) Y(Jm | \mu', \nu') \quad (3.12)$$

holds, where (μ, ν) are the polar and azimuthal angles of the molecular dipole relative to k_i , (μ', ν') are those relative to k_f , and Θ is the angle between k_i and k_f . The coefficient $A_J(Mm | \Theta)$ is given by [4]

$$\begin{aligned}
A_J(Mm | \Theta) &= \sum_n \frac{(-1)^n \{(J+M)!(J-M)!(J+m)!(J-m)!\}^{1/2}}{n! (J+M-n)! (J-m-n)! (n+m-M)!} \\
&\quad \times \left(\cos \frac{\Theta}{2} \right)^{2J-2n-m+M} \left(\sin \frac{\Theta}{2} \right)^{2n+m-M}, \quad (3.13)
\end{aligned}$$

the summation running over all values of n for which the denominator is finite.

Using the wave functions (3.4) and (3.6), and relation (3.12), we obtain, for $k_f a_0 \ll 1$,

$$\begin{aligned}
\langle J_f M_f k_f | H_M | J' M' \alpha \rangle &= -\frac{i}{\sqrt{V} I} \left(\frac{a_0}{z} \right)^{1/2} \frac{Dem_e}{k_f} \sum_{m'} \sum_m A_{J'}(M'm' | \Theta) A_{J_f}(M_f m | \Theta) \\
&\quad \times \left\{ 2\sqrt{\pi} C_0 S^{(1)}(J'm'; J_f m) - \frac{\sqrt{3\pi}}{2} C_1 S^{(3)}(J'm'; J_f m) \right\}. \quad (3.14)
\end{aligned}$$

4. NUMERICAL RESULTS AND DISCUSSION

To illustrate the results numerically, we investigate the case satisfying the

conditions:

- i) The incident electron is scattered elastically, *i.e.* $k_i = k_f$ and $J_i = J_f$.
- ii) There exists only one bound-state α .
- iii) When we estimate the lifetime of the intermediate state, it is assumed that the state decays into the energy state of J_i -level. Namely, we can estimate the lifetime in the form

$$\frac{1}{\tau(J'M'\alpha)} = \frac{Vm_e k_0}{(2\pi)^2 \hbar^3} \sum_M \int d\hat{k}_0 |\langle J'M'\alpha | H_M | J_i M k_0 \rangle|^2, \quad (4.1)$$

where

$$\frac{\hbar^2 k_0^2}{2m_e} = E(J') + E(\alpha) - E(J_i).$$

These conditions are set for simplification of the numerical calculation. More general cases may be treated analogously.

As is shown in (3.11), the matrix element is not zero only for $J' = J_i \pm 1$ or $J_i \pm 2$, and $M' = M_i$. Here we consider only the case of $J' = J_i + 1$ and $M' = M_i$, where the differential cross-section is given in the form

$$\begin{aligned} & \sigma^r(J_i M_i k_i \rightarrow J_i M_f k_f | \hat{k}_f) \\ &= \frac{V^2}{4\pi^2} \frac{m_e^2}{\hbar^4} \left| \frac{\langle J_i M_f k_f | H_M | J_i + 1, M_i, \alpha \rangle \langle J_i + 1, M_i, \alpha | H_M | J_i M_i k_i \rangle}{E(J_i + 1) + E(\alpha) - E(J_i) - E(k_i) - \frac{i\hbar}{2\tau(J_i + 1, M_i, \alpha)}} \right|^2. \end{aligned} \quad (4.2)$$

From (3.11) and (3.14), we get

$$\begin{aligned} & \langle J_i + 1, M_i, \alpha | H_M | J_i M_i k_i \rangle \\ &= \frac{i}{\sqrt{V I}} \left(\frac{a_0}{z} \right)^{1/2} \frac{Dem_e}{k_i} 2\sqrt{\pi} C_0(J_i + 1)(J_i + 2) \alpha(J_i M_i), \end{aligned} \quad (4.3)$$

and

$$\begin{aligned} & \langle J_i M_f k_f | H_M | J_i + 1, M_i, \alpha \rangle \\ &= \frac{-i}{\sqrt{V I}} \left(\frac{a_0}{z} \right)^{1/2} \frac{Dem_e}{k_i} 2\sqrt{\pi} C_0(J_i + 1)(J_i + 2) F_{J_i}(M_f M_i | \Theta), \end{aligned} \quad (4.4)$$

where

$$\begin{aligned} F_{J_i}(M_f M_i | \Theta) &= \sum_m A_{J_i+1}(M_i m | \Theta) A_{J_i}(M_f m | \Theta) \alpha(J_i m) \\ &= \begin{cases} \alpha(J_i M_f) \cos \Theta & \text{for } M_f = M_i \\ -\frac{1}{2} \varepsilon(J_i M_f) \sin \Theta & \text{for } M_f = M_i - 1 \\ \frac{1}{2} \gamma(J_i M_f) \sin \Theta & \text{for } M_f = M_i + 1 \\ 0 & \text{otherwise} \end{cases}. \end{aligned}$$

Similarly $\tau(J_i + 1, M_i, \alpha)$ is calculated to be

$$\begin{aligned} \frac{1}{\tau(J_i + 1, M_i, \alpha)} &= \frac{Vm_e k_0}{(2\pi)^2 \hbar^3} \int d\hat{k}_0 \sum_M |\langle J_i + 1, M_i, \alpha | H_M | J_i M k_0 \rangle|^2 \\ &= \frac{m_e k_0}{(2\pi)^2 \hbar^3} \left\{ \frac{1}{I} \left(\frac{a_0}{z} \right)^{1/2} \frac{Dem_e}{k_0} \right\}^2 4\pi C_0^2 (J_i + 1)^2 (J_i + 2)^2 \\ &\quad \times \int d\hat{k}_0 \sum_M \{F_{J_i}(MM_i | \theta_0)\}^2. \end{aligned} \quad (4.5)$$

Substituting (4.3), (4.4) and (4.5) into (4.2) and using the relation

$$\sigma_m^r(J_i k_i) = \frac{1}{2J_i + 1} \sum_{M_i} \sum_{M_f} \int (1 - \cos \Theta) \sigma^r(J_i M_i k_i \rightarrow J_f M_f k_f | \hat{k}_f) d\hat{k}_f, \quad (4.6)$$

we get the momentum-transfer cross section as follows:

$$\sigma_m^r(J_i k_i) = \frac{L(J_i) \epsilon^2 (a_0 k_i)^{-4} a_0^2}{[\Delta E(J_i) - E(k_i)]^2 + K(J_i) \epsilon^2 (a_0 k_0)^{-2}}, \quad (4.7)$$

where

$$\Delta E(J_i) = E(J_i + 1) + E(\alpha) - E(J_i)$$

$$\epsilon = \frac{C_0^2}{z} \left(\frac{D}{ea_0} \right)^2 \left(\frac{m_e a_0^2}{I} \right)^2 \frac{e^2}{a_0}$$

$$K(J_i) = \frac{4}{9} \frac{(J_i + 1)^6 (J_i + 2)^4}{(2J_i + 3)^2}$$

$$L(J_i) = \frac{16\pi}{9} \frac{(J_i + 1)^6 (J_i + 2)^4}{(2J_i + 1)(2J_i + 3)},$$

and the relation

$$\begin{aligned} &\sum_m \int_{-1}^1 d \cos \theta \{F_J(mM | \theta)\}^2 \\ &= \frac{1}{3} \{2\alpha^2(JM) + \epsilon^2(J, M - 1) + \gamma^2(J, M + 1)\} \\ &= \frac{2}{3} \frac{J + 1}{2J + 3} \end{aligned}$$

has been used. Here the summation over M_f and the average over M_i have been taken because we are not interested in the values of M_i and M_f .

In particular, $\sigma_m^r(J_i k_i)$ is simplified for $k_i = k_0$ (i.e. $\Delta E(J_i) = E(k_i)$) and it becomes

$$\sigma_m^r(J_i k_0) = 4\pi \frac{2J_i + 3}{2J_i + 1} \frac{a_0^2}{(a_0 k_0)^2}. \quad (4.8)$$

As a typical example, we consider a polar molecule which has a dipole moment $D=2.50 \times 10^{-18}$ esu cm and a moment of inertia $I=10^{-40}$ gcm². This molecule has rotational eigenstates with energy $(\hbar^2/2I)J(J+1)$. As is shown in (4.7), the cross section becomes large for $\Delta E(J_i)=E(k_i)$. Taking as $E(k_i)$ the thermal energy ($E(k_i) \sim 0.02$ eV) and considering the energy difference between the successive rotational states, we are most interested in the scattering by a molecule in the state $J_i=5$.

For $D=2.50 \times 10^{-18}$ esu cm, there exists a bound state for an electron in the dipole field and the wave function (3.6) can be adopted for the bound state. The coefficients in (3.6) are taken such that $C_0^2=0.831$ and $z=0.3$. In this case the binding energy $E(\alpha)$ is estimated from the paper of Wallis *et al.*[2] to be -2.19×10^{-2} eV. Substituting these data into (4.7), we obtain the momentum-transfer cross section in the atomic unit,

$$\sigma_m^r(J_i=5, k_i) = \frac{1.32 \times 10^{-7} k_i^{-4}}{\left(7.31 \times 10^{-4} - \frac{k_i^2}{2}\right)^2 + 6.12 \times 10^{-6}}. \quad (4.9)$$

From (4.9) it is shown that in this case the width of the resonance is very large. This fact means that the lifetime of the captured state is shorter than the period of rotation of the target molecule. The magnitude of the cross section, however, is comparable to the one obtained for direct scattering by the usual calculation in the Born approximation. Hence this process of temporary capture may enhance the total cross section for electron scattering by a polar molecule.

When the above result is compared with the one obtained experimentally, there remain some problems. First, real polar molecules, such as H₂O, NH₃, *etc.*, have smaller dipole moments than 2.46×10^{-18} esu cm, so that the wave function (3.6) for a bound state cannot be used and some other methods of determination of the wave function must be introduced.

Fox and Turner [5] have improved the wave function for the bound state and, instead of (3.6), given a function in the form

$$f(\alpha | \mathbf{r}; \mu, \nu) = K_0 \exp \left\{ -z \left(\frac{r}{a_0} \right)^t \right\} \left[C_0 Y(00 | \bar{\theta}, \varphi) + C_1 Y(10 | \bar{\theta}, \varphi) \right]$$

where K_0 is the normalization constant and the coefficients C_0 , C_1 , z and t are to be determined by the variational principle. They have shown that this type of function can be used for a dipole moment as small as 1.65×10^{-18} esu cm. If we use this bound-state wave function for H₂O, of which dipole moment is 1.85×10^{-18} esu cm, a similar result to the above is obtained except that the width of the resonance becomes larger. This shorter lifetime of the bound state made by a smaller dipole moment is due to a larger spatial extension of the bound-state wave function for a smaller dipole moment.

The next problem is concerned with the assumption that the polar molecule can be regarded as a point dipole. It is not clearly known how much error is involved

in such an approximation.

Furthermore, there is another problem in the case of a small dipole moment. It is clear that the binding energy becomes smaller for a smaller dipole. This implies classically that a bound electron moves around the dipole very slowly. In this case, therefore, the period of circulation of a bound electron may become comparable to or longer than the period of rotation of the polar molecule so that the bound state obtained in the approximation of the fixed dipole becomes practically meaningless. Hence those minimum values of the dipole moment making some bound state for electrons which have been estimated recently by Lévy-Leblond [6] and others [7] have less physical meanings. If the rotational motion of the molecule is taken into consideration, it might happen that there are no bound states in the field of a dipole whose moment is somewhat larger than such minimum values as estimated in the approximation of the fixed dipole; if so, the capture process might become less effective except for a very large dipole moment.

Although these problems must be solved, the result of the present paper seems to show the possibility of enhancement of the cross section for electron scattering by polar molecules, at least by strongly polar molecules, if taking into consideration temporary capture of electrons by the dipole. For relatively smaller dipole moments, the present treatment is somewhat doubtful and more detailed treatment is necessary to be done later.

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