JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 33, No. 4, OCTOBER, 1972

Reactions of Highly Excited Atoms with Molecules $\mathrm{A}^{**}+\mathrm{BC}\rightarrow\mathrm{A}^{+}+\mathrm{B}+\mathrm{C}^{-}$

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(Received February 28, 1972; revised manuscript received April 6, 1972)

Reactions of highly excited atoms (A^{**}) with molecules (BC)

$$\mathrm{A}^{**}+\mathrm{BC}\rightarrow\mathrm{A}^{+}+\mathrm{B}+\mathrm{C}^{-}\,, \qquad (1)$$

are studied. It is theoretically shown that the cross section for (1) can be approximately expressed in terms of that for dissociative attachment of electrons to molecules BC, namely,

$$\mathrm{e}+\mathrm{BC}\rightarrow\mathrm{B}+\mathrm{C}^{-}\,.$$

The rate constants and the angular distributions of the products for some reactions including

$$\mathrm{K_r}^{**}+\mathrm{CCl_4}\rightarrow\mathrm{K_r}^{+}+\mathrm{CCl_3}+\mathrm{Cl}^{-}\,, \qquad (2)$$

are predicted. The rate constant for reaction (2) is found to be of the order of the magnitude 10^{-7} cm^3/sec. Together with the results of the previous papers (M. Matsuzawa: J. chem. Phys. **55** (1971) 2685; J. Phys. Soc. Japan **32** (1972) 1088) it is pointed out that the measurements of reactions of highly excited atoms with molecules give useful information on the inelastic scattering of a slow electron by the molecules.

§ 1. Introduction

Recently reactions of highly excited atoms with molecules have been experimentally studied by several workers.[1–7]

A high Rydberg electron (say, principal quantum number $n\gtrsim 10$) in atoms and molecules is loosely bound and is distant from an ion core. Therefore, this electron can be regarded as an almost free slow one. Taking into account this feature of the Rydberg electron, Fermi[8] theoretically showed that the pressure shift of the Rydberg state can be understood in terms of knowledge of elastic scattering of a slow electron by a perturbing atom. Later Sobel'man and other Russian workers[9] made more detailed studies including the width of the Rydberg state based on the same idea.

In our previous papers[10,11] we have theoretically shown that knowledge of inelastic scattering of the slow electron by the molecule is very useful for the understanding of the mechanism of some kinds of reactions of the highly excited atoms with the molecules. Namely, in our first paper[10] (to be referred to as I), we have treated the ionization of the highly excited atoms (A^{**}) by collision with polar molecules (B)

$$\mathrm{A}^{**}+\mathrm{B}\rightarrow\mathrm{A}^{+}+\mathrm{B}+\mathrm{e}\,.$$

At room temperature, the molecule B is usually in a rotationally excited state. We assume that the Rydberg electron is ionized as a result of its energy gain from the molecule B by the rotational de-excitation. Using knowledge of the rotational de-excitation of the polar molecule by the slow electron impact, we have obtained the calculated cross sections for the above mentioned ionization process in reasonable agreement with experimental data.[10]

In our second paper[11] (to be referred to as II hereafter), we have theoretically studied electron transfer process from the highly excited atoms A^{**} to the molecules B

$$\mathrm{A}^{**}+\mathrm{B}\rightarrow\mathrm{A}^{+}+\mathrm{B}^{-}\,.$$

We have shown that the rate constant for this process is equal to that of the non-dissociative thermal electron capture by the molecule B namely

$$\mathrm{e}+\mathrm{B}\rightarrow\mathrm{B}^{-}\,.$$

This result is in reasonable agreement with the data on the electron transfer from the highly excited argon atom to the $\mathrm{SF_6}$ molecule. This theory, however, fails to explain the observed electron transfer to $\mathrm{CH_3CN}$[6] and $\mathrm{CS_2}$[7] molecules, which do not capture thermal electrons.

Melton and Hamill[12] experimentally gave the evidence for the reaction,

$$\mathrm{Kr}^{**}+\mathrm{CCl_4}\rightarrow\mathrm{Kr}^{+}+\mathrm{CCl_3}+\mathrm{Cl}^{-}\,.$$

In the present paper, we theoretically treat this type of reactions of the highly excited atoms (A**) with the diatomic or polyatomic molecules (BC),

$$\mathrm{A^{**}+BC \to A^{+}+B+C^{-}} \tag{1.1}$$

based on the same idea as that used in our previous papers. Namely, we show that experimental and theoretical knowledge of dissociative attachment (DA) of the slow electrons to the molecules BC

$$\mathrm{e+BC \to B+C^{-}}\ , \tag{1.2}$$

is very useful for the understanding of the mechanism of reaction (1.1). Using the experi mental and theoretical data of DA, we evaluate rate constants of reaction (1.1) for some halogen-containing molecules, and predict angular distributions of final products formed in this reaction.

§ 2. Theoretical Treatment

In reaction (1.1), we must consider a collision in which one highly excited Rydberg electron and three heavy particles namely the ion core A^{+} the atoms B and C are involved.* At first sight, this process seems to be a very complicated one (see Fig. 1). However, we can show that this reaction is considered as a combination of two simpler processes if we take advantage of some features of the highly excited atom.

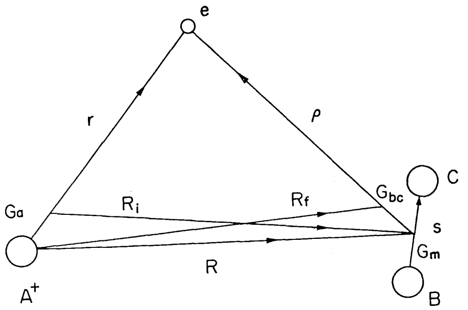

Fig. 1. Ga is the center of mass of the electron and the ion core A^{+} and G_{bc} that of the electron and the molecule BC. For simplicity the polyatomic molecule is depicted as if it were a diatomic molecule and G_m is the center of mass of the molecule BC.

Based on the idea similar to that used in I and II, we can consider that mainly the interaction between the Rydberg electron and the molecule BC is responsible for the reaction (1.1). This interaction is the same one in the reaction (1.2), namely, DA of the slow electrons to the molecules BC.

There are some theoretical treatments on DA, which give the results consistent with existing experimental data.[13–18] The DA process (1.2) is understood as an electronic transition from a continuum to a discrete electronic state, which then dissociates.[13,15] That is to say, the DA process is separated into two simpler processes,

$$\mathrm{e+BC \to BC^{-}}\ , \tag{1.2a}$$
$$\mathrm{BC^{-} \to B+C^{-}}\ . \tag{1.2b}$$

The final electronic discrete state in process (1.2a) is degenerate with a continuum and is necessarily a resonance. It is experimentally known that there are two kinds of temporary negative ions, namely, the long-lived (lifetime $\sim 10^{-6}-10^{-3}$ sec) and the short-lived (lifetime $\sim 10^{-15}-10^{-13}$ sec) ones.[19] In our previous paper II on the electron transfer process from the highly excited atom A** to the molecule B, we have treated the long-lived negative ions, which can be observed in a conventional mass spectrometer. Contrary to the process treated in II, the negative ion formed in process (1.2a) is the short-lived one because it dissociates during the time of the order of a vibrational period.

Analogously to DA, reaction (1.1) is understood as the electron transfer process from the highly excited atom (A**) to the molecule (BC) followed by dissociation of the temporary negative ion BC^{-} formed, namely,

$$\mathrm{A^{**}+BC \to A^{+}+BC^{-}}\ , \tag{1.1a}$$
$$\mathrm{BC^{-} \to B+C^{-}}\ . \tag{1.1b}$$

This separation is a good approximation because the electronic transition (1.1a) is a very rapid process compared with the dissociation of the negative ion.

We assume that the negative ion formed in process (1.1a) is the same species as that formed in process (1.2a). Then we can understand the mechanism of reaction (1.1) in terms of the knowledge of the DA process (1.2). Further it should be noted that the electron transfer process (1.1a) is almost the same process as that treated in II. Therefore, we can treat reaction (1.1a) using the procedures employed in II with some slight modifications, namely, we can use the expression (II-2.15) as the scattering amplitude g in scattering direction Ω for reaction (1.1a),**

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* In some cases, B may be a polyatomic radical. For simplicity, we shall call B "an atom" in this section.

** Equations quoted from paper II are prefixd with the symbol II.

$$g(\Omega)=-\frac{\mu_f}{2\pi}(2\pi)^{3/2}G(\alpha|Q)\langle\psi_\gamma|H_{QP}|\Phi^+_{q\beta}\rangle^*\,, \qquad (2.1)$$

where $H_{QP}=QHP$ and H is the Hamiltonian of the system for the molecule BC plus electron, $G(\alpha|Q)$ is the wave function in the momentum space for the electron, in the Rydberg state $\alpha(=(n,l,m))$, and μ_f is the reduced mass of the outgoing particles in (1.1a). Further, ψ_γ is the wave functions of the negative ion BC^- and $\Phi^+_{q\beta}$ is the wave function which describes the scattering state for the system of the molecule BC plus electron.** Here Q and P are the projection operators which project out the resonance state of the negative ion BC^- and the potential scattering state (BC+e) respectively, and $\boldsymbol{Q}$ is the momentum transfer, that is to say

$$\boldsymbol{Q}=\boldsymbol{K}'-\boldsymbol{K}=\boldsymbol{q}^{***}\,. \qquad (2.2)$$

The negative ion formed in (1.1a) is the short-lived one and the resonance state is defined relative to the electronic motion only.[13,15] Therefore, we define the Q operator

$$Q=|\psi_{\mathrm{res}}\rangle\langle\psi_{\mathrm{res}}|^{****} \qquad (2.3)$$

instead of eq. (II-2.5). This Q operator projects out only the electronic component ψ_{res} of the wave function ψ_γ for the negative ion BC^-. Here we have assumed that the colliding system (BC+e) has only one open channel, namely, the potential scattering and only one closed channel relative to the electronic motion, namely the DA process. This is quite a realistic situation for some cases of the DA of the thermal electrons to the molecules BC.[20]

So far we have considered that the relative motion between the atom B and the negative ion C^- is clamped. In order to take into account process (1.1b), we have only to relax this restriction. If we denote the separation between B and C^- by $\boldsymbol{s}$***** (see Fig. 1), we can write the wavefunction ψ_γ of the negative ion in the following form

$$\psi_\gamma=\psi_{\mathrm{res}}\xi_{\varepsilon\omega}(\boldsymbol{s})\,, \qquad (2.4)$$

where ξ is the wavefunction for the relative motion between B and C^- which is normalized with respect to the energy ε and the direction ω of the relative motion between B and C^-. If we substitute the wavefunction (2.4) into eq. (2.1), we obtain the amplitude for reaction (1.1) per unit energy ε and unit solid angle ω of the relative motion of the dissociation between B and C^-

$$g(\Omega,\varepsilon,\omega)=-\frac{\mu_f}{2\pi}(2\pi)^{3/2}G(\alpha|Q)$$
$$\times\langle\psi_{\mathrm{res}}\xi_{\varepsilon\omega}|H_{QP}|\Phi^+_{q\beta}\rangle\,, \qquad (2.1a)$$

where $\boldsymbol{K}'$ in eq. (2.2) should be considered to be the wave vector of relative motion between the A^+ ion and the center of mass $\boldsymbol{G}_m$ of the dissociating negative ions BC^- and γ specifies ε and ω besides the internal states of B and C^-. Here, the directions Ω and ω are defined relative to the $\boldsymbol{K}$ and $\boldsymbol{Q}$ axes respectively. For the present time, the theoretical evaluation of the matrix element $\langle\psi_{\mathrm{res}}\xi_{\varepsilon\omega}|H_{QP}|\Phi^+_{q\beta}\rangle$ is a very difficult task for such a polyatomic molecule as the carbon tetrachloride molecule. However, we can show that this matrix element is related to that for DA. This enables us to evaluate this matrix element using the experimental data on DA.

The scattering amplitude $g_{da}(\omega)$ for DA

$$g_{da}(\omega)=-\frac{\mu_d}{2\pi}\langle\psi_{\mathrm{res}}\xi_{\boldsymbol{k}}|H_{QP}|\Phi^+_{q\beta}\rangle\,, \qquad (2.5)$$

where $\boldsymbol{q}$ is the wave vector of the incident electron in process (1.2) and is equal to the momentum transfer $\boldsymbol{Q}$ in reaction (1.1a), $\boldsymbol{k}$ the wave vector for the relative motion between B and C^- and μ_d is the reduced mass for the dissociation, namely,

$$\mu_d=\frac{M_b(M_c+1)}{M+M_c+1}\,.$$

The wavefunction $\xi_{\boldsymbol{k}}$ is normalized with respect to wave vector $\boldsymbol{k}$ according to the usual boundary condition for scattering, so that we have

$$\xi_{\varepsilon\omega}(\boldsymbol{s})=\frac{\sqrt{k\mu_d}}{(2\pi)^{3/2}}\xi_{\boldsymbol{k}}(\boldsymbol{s})\,.$$

After some mathematical manipulations using this relation, eq. (2.1a) and eq. (2.5), we obtain

$$\sigma(\alpha,\beta\to\gamma,\Omega,\varepsilon,\omega)=\frac{\mu_i\mu_f}{m_f}\frac{K'Q}{K}|G(\alpha|Q)|^2$$
$$\times\sigma_{da}(\boldsymbol{q},\omega)^\dagger\,, \qquad (2.6)$$

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* In the following atomic units, in which $e=\hbar=m=1$, are used unless otherwise stated.

** The same notations as those in II are used except that the quantities on the molecule B are replaced by those on the molecule BC, for example, M_{bc} instead of M_b etc.

*** The absolute value of the momentum transfer $\boldsymbol{Q}$ should not be confused with the projection operator Q. In the following, the projection operator Q appears only as the subscript, namely, in the form H_{QP}, H_{PQ} etc.

**** We assume an isolated resonance.

***** The situation in Fig. 1 is depicted for the initial channel. Exactly speaking, $\boldsymbol{s}$ should be the separation between B and C^- after the capture of the Rydberg electron by the molecule BC.

† In the following, the quantum numbers α, β, γ are not written explicitly, if not necessary.

where m_f is the reduced mass between the electron and the molecule BC. Here it should be noted from eq. (2.2) that the wave number of the electron $\boldsymbol{q}$ is equal to the momentum transfer $\boldsymbol{Q}$ in reaction (1.1a), namely $\boldsymbol{Q}=\boldsymbol{K}'-\boldsymbol{K}$. These wave vectors $\boldsymbol{K}$, $\boldsymbol{K}'$ should satisfy

$$\frac{K^2}{2\mu_i}-\frac{1}{2n^2}+\varepsilon_\beta=\frac{K'^2}{2\mu_f}+\varepsilon_\gamma\ , \tag{2.7}$$

which is the conservation law of energy. Here ε_β is the internal energy of the molecule BC and ε_γ is that of the negative ion BC^- including the relative motion between B and C^- namely

$$\varepsilon_\gamma=\varepsilon+\varepsilon_B+\varepsilon_{C^-}\ ,$$

where ε_B and ε_{C^-} are the internal energies of the atom B and the negative ion C^- and $\varepsilon(=k^2/2\mu_d)$ is the energy of the motion for the dissociation. The expression (2.6) is the main result in the present paper. We can easily see that eq. (2.6) can give us all knowledge of reaction (1.1), namely, rate constant and angular distribution of the final products, if there is sufficient data on the DA process (1.2).

§ 3. Evaluation of the Rate Constant for Reaction (1.1)

In this section we evaluate the rate constant for reaction (1.1). The angular distribution of the final products in this reaction will be discussed in the next section. For some halogen-containing molecules, such as, CCl_4, I_2 etc., the DA processes occur with large cross sections at thermal energies.[20,21,22] For these molecules, reaction (1.1) can take place. This arises from the fact that a bound electron in a high Rydberg state can be regarded as a free electron with the momentum distribution given by $|G(\alpha|q)|^2$.

In order to evaluate the total cross section, we must integrate the differential cross section over Ω, ε, ω. Integration of eq. (2.6) over ω yields the differential cross section for reaction (1.1) per unit solid angle Ω for the scattering direction and per unit energy ε for the motion for dissociation, namely

$$\begin{aligned}\sigma(\Omega,\varepsilon)&=\int\sigma(\Omega,\varepsilon,\omega)\mathrm{d}\omega\\&=\frac{\mu^2K'Q}{K}|G(\alpha|Q)|^2\sigma_{da}(Q)\ ,\end{aligned} \tag{3.1}$$

where $\sigma_{da}(Q)$ is the total cross section for DA. We assume that $\sigma_{da}(Q)$ has been averaged over the molecular orientations. Here we have neglected the electron mass 1 compared with those of the heavy particles. Namely we have used $m_f\sim 1$ and

$$\mu_i\simeq\mu_f\simeq\mu\simeq\frac{M_aM_{bc}}{M_a+M_{bc}}\ .$$

Further we integrate the expression (3.1) over Ω using the relation

$$\mathrm{d}\Omega=2\pi\sin\Theta\mathrm{d}\Theta=\frac{2\pi}{KK'}Q\mathrm{d}Q\ ,$$

where Θ is the scattering angle in reaction (1.1a). Then we find as the differential cross section per unit energy ε for the motion of the dissociation,

$$\sigma(\varepsilon)=\frac{2\pi\mu^2}{K^2}\int_{|K-K'|}^{K+K'}Q|G(\alpha|Q)|^2\sigma_{da}(Q)Q\mathrm{d}Q\ . \tag{3.2}$$

Now we need the explicit dependence of σ_{da} on the wave number of the incident electron. There are some experimental studies on this dependence over the energy range from the thermal energy to about 0.8 eV.[21–27] We cannot safely extrapolate these experimental data to lower energy region. For this purpose the quantum-mechanical threshold law can be used.[28–30] It is theoretically shown that σ_{da} is a product of the cross section for resonance formation σ_c and a survival factor S[13–18]

$$\sigma_{da}=\sigma_cS\ .$$

For DA of the thermal electrons to the molecule BC, the negative ion state is purely repulsive in Franck Condon region and the potential curve for the negative ion crosses that for the molecule BC near the minimum of the latter as illustrated in Fig. 2. In this case the magnitude of σ_{da} is mainly determined by the capture cross section σ_c.[20] In other words, for DA of the thermal electrons to these molecules, autoionization is relatively unimportant. Thus, the survival factor S is expected to be almost equal to unity. Therefore, the DA cross section can be approximately written in the form[13–16]

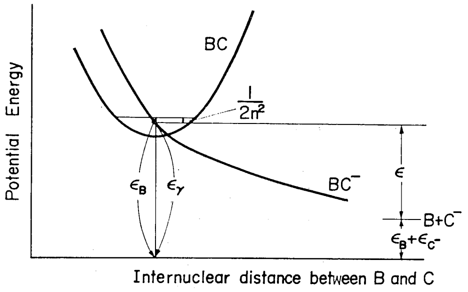

Fig. 2. The potential energy curves appropriate to the dissociative attachment of the thermal electrons to the molecules.

$$\sigma_{da} \simeq \sigma_c \propto \frac{\Gamma}{q^2} , \tag{3.3}$$

where Γ is the width for autoionization given by[13]

$$\Gamma = 2\pi |\langle \psi_{\text{res}} | H_{QP} | \Phi^{+}_{q\beta} \rangle |^2 . \tag{3.4}$$

The quantum-mechanical threshold law yields[28,29]

$$\Gamma \propto q^{2L+1} , \tag{3.5}$$

where L is the lowest angular momentum of the incident electron.* Substitution of eq. (3.5) into eq. (3.3) leads to the expressions

$$\sigma_{da} = c q^{2L-1} , \tag{3.6}$$

where c is a constant.[28,29] When this expression is substituted into eq. (3.2) we find as the expression for the differential cross section per unit energy ε for the dissociation,

$$\sigma(\varepsilon) = \frac{2\pi\mu^2}{K^2} c \int_{|K-K'|}^{K+K'} Q^{2L+1} \frac{1}{n^2} \times \sum_{l,m} |G(n,l,m|Q)|^2 \mathrm{d}Q . \tag{3.7}$$

Here, for simplicity, we have averaged over the quantum numbers l, m of the Rydberg electron of the initial states, namely

$$\frac{1}{n^2} \sum_{l,m} |G(nlm|Q)|^2 = \frac{8}{\pi^2 n^5} \frac{1}{\left(Q^2 + \dfrac{1}{n^2}\right)^4} .^{31)} \tag{3.8}$$

The integral over Q converges so rapidly that the integration can be extended to infinity without any great error. Therefore, we have been using the expression (3.8)

$$\sigma(\varepsilon) = \frac{8\mu^2 c}{\pi K^2 n^{2L-1}} f(n^2 |K-K'|^2) , \tag{3.9}$$

where

$$f(t) = \int_t^\infty \frac{t^L}{(t+1)^4} \mathrm{d}t .$$

In order to obtain the cross section for reaction (1.1) of the n-th excited atom with the molecule we must calculate the integral

$$\sigma_n(v) = \int \sigma(\varepsilon) \mathrm{d}\varepsilon , \tag{3.10}$$

where v is the velocity of the relative motion between A** and BC. We can see that the transition for $|K-K'| \lesssim 1/n$ give the main contribution to the integral (3.10) based on the same argument on the integration (II-2.25). These transitions can take place for the molecules to which DA of the thermal electrons is possible. We find, using the conservation law of the energy (2.17),

$$\begin{aligned} K-K' &\simeq \frac{\mu}{K}\left(\frac{1}{2n^2} - \varepsilon_\beta + \varepsilon_r\right) \\ &\simeq \frac{\mu}{K}\left(\frac{1}{2n^2} - \varepsilon_\beta + \varepsilon + \varepsilon_{\mathrm{B}} + \varepsilon_{\mathrm{C}^-}\right) . \end{aligned} \tag{3.11}$$

There is one different point from the usual situation of the DA process, namely, the energy of the electron is negative because the Rydberg electron is bound. However, this binding energy is at most of the comparable order of the magnitude of the vibrational energy spacing of the molecule BC. For example, this binding energy is less than 3×10^{-2} eV for $n \gtrsim 20$. There can occur transitions which satisfy the condition $|K-K'| \lesssim 1/n$. These transitions give the main contribution to the integral (3.10). Using the relation (3.11) we have

$$\sigma_n(v) = \begin{cases} \dfrac{c}{v} & \text{for } s \text{ wave} \quad (3.12\text{a}) \\[2ex] \dfrac{c}{n^2 v} & \text{for } p \text{ wave} \quad (3.12\text{b}) \\[2ex] \dfrac{5c}{n^4 v} & \text{for } d \text{ wave} \quad (3.12\text{c}) \end{cases}$$

If we denote the rate constant for reaction (1.1) of the n-th excited atom with molecule by k_n, we have

$$k_n = \langle v \sigma_n(v) \rangle = \begin{cases} c & \text{for } s \text{ wave} \quad (3.13\text{a}) \\[2ex] \dfrac{c}{n^2} & \text{for } p \text{ wave} \quad (3.13\text{b}) \\[2ex] \dfrac{5c}{n^4} & \text{for } d \text{ wave} \quad (3.13\text{c}) \end{cases}$$

where bracket $\langle \cdots \rangle$ means the average over Boltzman distribution. Namely, the rate constant for (1.1) is independent of the velocity of the relative motion within our approximation. If we use the low energy limiting form (3.6) for σ_{da}, the rate constant k_{da} for DA is given for s wave capture.

$$k_{da} = \langle q \sigma_{da}(q) \rangle = c . \tag{3.14}$$

In this case, we obtain the simple result

$$k_n = k_{da} . \tag{3.15}$$

This is the same result as that derived in II, because the capture of the electron is a dominant factor for the DA process of the thermal electrons to the molecules. From the experimental results of DA on the molecules CCl_4 the DA cross section is increased with the decrease of the electron energy. Then it is reasonable to assume that s wave capture take place for the CCl_4 molecule. Thus using the experimental data we can easily obtain the value of rate constant for reaction

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* As to the relation between L and the states of BC and BC$^-$, see next sections (eq. (4.7) (4.8) etc.).

(1.1), which is given in Table I. For other molecules to which DA occurs at thermal velocities the rate constants based on the assumption of s wave capture are also given in Table I. So far we have adopted the hydrogen-like model and have ignored the individuality of the highly excited atom. Further in expressions (3.13), the parameters do not appear, which characterise the individual atom, for example, reduced mass etc. Thus these values take the same ones for all the highly excited atoms within our approximation.

Table I. Rate constants for $A^{**}+BC\to A^{+}+B+C^{-}$ at room temperature (300 K).

molecule (BC)	ion (C^{-})	rate constant (cm^3/sec)
CCl_4	Cl^{-}	1.9×10^{-7} [a,b,d]
HI	I^{-}	2.7×10^{-7} [b]
DI	I^{-}	1.6×10^{-7} [b]
CCl_3F	F^{-}	1.1×10^{-7} [b]
n-$C_{10}H_{21}Br$	Br^{-}	3.9×10^{-9} [a]
I_2	I^{-}	7.5×10^{-10} [c] (p wave) 2.0×10^{-9} [c] (d wave)

a The cross sections at 300 K are calculated using data and eq. (1) in ref. 21.

b The maximum cross sections listed in Table I of ref. 20 are adopted as the values of σ_{da} at 300 K.

c These values correspond to principal quantum number 30 and see text.

d There are two values listed for CCl_4 in Table I of ref. 20. The smaller one is not adopted because it does not agree with the recent experimental data in ref. 21.

For I_2 molecule, there are some experimental data[23-27] on the energy dependence for the process

$$e+I_2\to I+I^{-}\ . \tag{3.16}$$

Truby[27] showed that the rate constant for (3.16) decreases with the decrease of the electron energy, which gives the possibility that the s wave is not the lowest allowed one. Person[32] has thought that the negative ion states responsible for DA of the thermal electron to the I_2 molecule is either ${}^2\Pi_{g(1/2)}$ or ${}^2\Pi_{g(3/2)}$. If this assignment is correct, the lowest allowed partial wave of the incident electron is the d wave due to conservation of nuclear symmetry. Shipsey[33,34] has considered that attachment to form a Π_u state is more likely at low electron energies to explain the experimental data on the energy dependence of σ_{da} by Truby.* In this case, p wave should be adopted as the lowest allowed partial wave. From the existing experimental data, we cannot definitely determine which of p or d wave should be adopted.** Therefore, we evaluate the rate constants for both p and d wave capture. There is, however, the discrepancy between two experimental data[23,26,27] for the absolute value of the cross section averaged with a Maxwellian distribution at 300 K. We can easily obtain the maximum cross section, using the new data by Truby[27] combined with the procedure employed by Biondi and Fox.[24,25] Namely, we have $\sigma_{da}^{\max}=1.4\times10^{-16}$ cm^2. We fit this value to the formula (3.6) assuming that σ_{da} takes the maximum at thermal energy $\varepsilon_{\max}\sim0.03$ eV. The calculated results for p and d wave capture are shown in Table I. These values are less reliable than in the case of s wave capture because c in eq. (3.6) sensitively depends on the choice of the value $\varepsilon_{\max}$.

§ 4. Angular Distribution of the Final Products

In this section, we predict the angular distribution of the products formed in reaction (1.1) based on eq. (2.6). Using the momentum distribution (3.8) of the Rydberg electron averaged over l, m the differential cross section for reaction (1.1) is given by

$$\sigma(\Omega,\varepsilon,\omega)=\frac{\mu^2K'Q}{K}\frac{1}{n^2}\sum_{l,m}|G(n,l,m|Q)|^2\sigma_{da}(q,\omega)\ . \tag{4.1}$$

Here, we assume that σ_{da} has been averaged over the molecular orientations. Integration of σ over ε gives the angular distribution of the final products for reaction (1.1) namely

$$\sigma(\Omega,\omega)=\int\sigma(\Omega,\varepsilon,\omega)d\varepsilon\ , \tag{4.2}$$

where ε is determined by the conservation law of energy (2.7). Further, if we are concerned with the angular distribution of A^{+} ion, we must integrate $\sigma(\Omega,\omega)$ over ω

$$\sigma(\Omega)=\int\sigma(\Omega,\omega)d\omega$$

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* In ref. 33, it is stated that ${}^2\Pi_{g(1/2\cdot3/2)}$ states are responsible for DA to the I_2 molecule, which requires d wave capture. However, recently he has written to us that he was really considering forming a Π_u state and made a mistake in writing his paper (ref. 33).[34]

** Another useful information comes from the angular distribution of the products, which will be discussed in the next section.

$$=\frac{\mu^2}{K}\int K'Q\,\frac{1}{n^2}\sum_{l,m}|G(n,l,m|Q)|^2\sigma_{da}(q)\mathrm{d}\varepsilon\ , \tag{4.3}$$

where $\sigma_{da}(q)$ is the total cross section for DA of the electrons with momentum $\boldsymbol{q}$ to the molecules BC. Now, eq. (3.6) can be used as the explicit expression for σ_{da}. At room temperature, we approximately obtain

$$K\sim 14\,\mathrm{au}\ ,$$

for Kr+CCl$_4$ system at thermal energies. Thus we have $|K-K'|\lesssim 1/n \ll K$. This means that a transfer energy between relative motion and the internal energy is small. In this case, from the conservation law of energy

$$\Delta E=\varepsilon+\varepsilon_{\mathrm{B}}+\varepsilon_{\mathrm{C}^-}-\varepsilon_\beta+\frac{1}{2n^2}$$
$$=\frac{K^2-K'^2}{2\mu}\simeq\frac{K}{\mu}(K-K')\ ,$$

and the relation

$$Q^2=K^2+K'^2-2KK'\cos\Theta$$
$$\simeq(K-K')^2+(K\Theta)^2\ ,$$

we find

$$Q^2\simeq\left(\frac{\mu}{K}\Delta E\right)^2+(K\Theta)^2\ , \tag{4.4}$$

where Θ is the scattering angle between A$^+$ and the center of mass G_m of B and C$^-$. (see Fig. 3)

Substitution of expressions (3.6) and (4.4) into eq. (4.3) leads to the following expressions

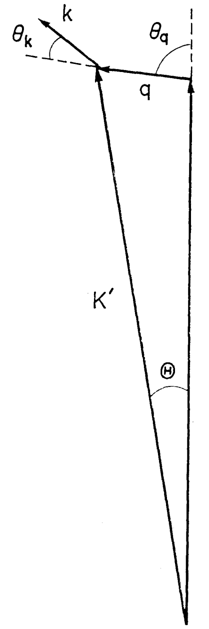

Fig. 3. Relations between wave vectors $\boldsymbol{K}$, $\boldsymbol{K'}$, $\boldsymbol{q}$ and $\boldsymbol{k}$ and scattering angles Θ, θ_q and θ_k.

$$\sigma_L(\Theta)=\frac{8\mu cK}{\pi^2n^5}\int_{-\infty}^{\infty}\frac{(t^2+K^2\Theta^2)^L}{\left(t^2+K^2\Theta^2+\dfrac{1}{n^2}\right)^4}\mathrm{dt}$$
$$=\frac{5\mu c}{2\pi n^5K^6}\frac{1}{(\Theta^2+\Theta_0{}^2)^{3.5}}\quad\text{for } L=0\ , \tag{4.5a}$$
$$=\frac{3\mu c}{\pi n^5K^4}\frac{\Theta^2+\dfrac{1}{6}\Theta_0{}^2}{(\Theta^2+\Theta_0{}^2)^{3.5}}\quad\text{for } L=1\ , \tag{4.5b}$$
$$\left.\begin{aligned}&=\frac{4\mu c}{\pi n^5K^2}\frac{\Theta^4+\dfrac{1}{2}\Theta_0{}^2\Theta^2+\dfrac{1}{8}\Theta_0{}^4}{(\Theta^2+\Theta_0{}^2)^{3.5}}\\ &\qquad\text{for}\quad L=2\ ,\end{aligned}\right\} \tag{4.5c}$$

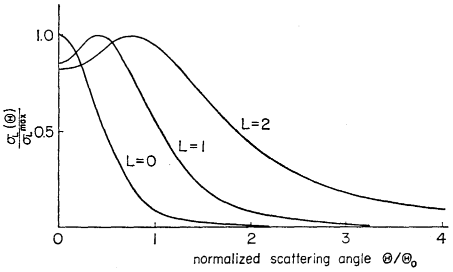

Fig. 4. Normalized angular distribution of the ion A+: as to the notation, see text.

where $t=(\mu/K)\{\varepsilon+\varepsilon_{\mathrm{B}}+\varepsilon_{\mathrm{C}^-}-\varepsilon_\beta+(1/2n^2)\}$ and $\Theta_0=1/Kn$. These angular distributions are shown in Fig. 4. Integration of expressions (4.5) over Θ, namely

$$\sigma=2\pi\int\sigma(\Theta)\sin\Theta\mathrm{d}\Theta\simeq 2\pi\int\sigma(\Theta)\Theta\mathrm{d}\Theta\ ,$$

leads to the total cross sections given by (3.12). We can easily see from these results that scattering between A$^+$ and BC$^-$ occurs at very small angles namely $\Theta\lesssim\Theta_0$. In the case of the krypton atom colliding with the carbon tetrachloride molecule we have $\Theta_0\simeq 3\times10^{-3}$ rad for $n=20$.

To obtain the angular distribution of B or C$^-$, we have only to know the angular dependence of DA of the electrons with momentum $\boldsymbol{q}$ to the molecules BC. This problem has already been treated by O'Malley and Taylor.[18] They have used the approximation of the local complex potential for the dissociating motion between B and C$^-$, which is not applicable to our case, namely DA of the thermal electrons to the molecules. This arises from the fact that the energy of the incident electron is not large compared with the vibrational spacing of the molecule.[14,17,18] However, other approximations, namely the slow rotation of the molecule, the lowest angular momentum (or one-center) approximation for the slow incident electron, and others stated in ref. 18

are applicable to our case. If we assume the conservation of the angular momentum for the relative motion between B and C$^-$, we can use the approximate angular distribution by O'Malley and Taylor, namely ref. 18 eq. (14) with a slight modification, namely

$$\sigma_{da}(q,\omega)=\sigma_{da}(q)|Y_{L\lambda}(\theta_k)|^2\ , \qquad (4.6)$$

where $Y_{L\lambda}$ is the spherical harmonics and θ_k is the angle between vectors $\boldsymbol{q}$ and $\boldsymbol{k}$. (see Fig. 3) Further, L, λ are determined by the following relations

$$\lambda=|\Lambda_{\rm res}-\Lambda_{\rm m}|\ , \qquad (4.7)$$

$$L\geq\lambda\ , \qquad (4.8)$$

where L is the lowest allowed angular momentum of the incident electron. Here $\Lambda_{\rm res}$ and $\Lambda_{\rm m}$ are the axial orbital angular momentum of the negative ion BC$^-$ and the molecule BC. In homonuclear diatomic molecules, due to nuclear symmetry, L is further restricted to even or odd according as the states of the molecule and the negative ion have the same or opposite parity.

In eq. (4.6), an expression $\sigma_{da}(q)$ without the local complex approximation should be adopted. We can use the quantum mechanical threshold law for the thermal energy electron, for the present purpose. Substitution of eq. (3.6) and eq. (4.6) into eq. (4.2) gives

$$\sigma_{L\lambda}(\Omega,\omega)=\frac{8\mu^2c}{\pi^2n^5K}\times\int d\varepsilon K'\frac{Q^{2L}}{\left(Q^2+\dfrac{1}{n^2}\right)^4}|Y_{L\lambda}(\theta_k)|^2\ . \qquad (4.9)$$

If we denote the directions of vectors $\boldsymbol{K}'$, $\boldsymbol{q}(=\boldsymbol{Q})$ and $\boldsymbol{k}$ by $(\Theta,\Phi)(\theta_q,\phi_q)$ and (θ,ϕ) with respect to $\boldsymbol{K}$ axis, we find relations

$$\cos\theta_k=\cos\theta\cos\theta_q+\sin\theta\sin\theta_q\cos(\phi-\phi_q)\ , \qquad (4.10)$$

and

$$\cos\theta_q=\frac{K'^2-K^2-Q^2}{2KQ}\ , \qquad \phi_q=\Phi\ . \qquad (4.11)$$

Until now, we have fixed the direction of the wave vector $\boldsymbol{q}$, which can take all directions around $\boldsymbol{K}$ axis. Therefore, we must average the cross section $\sigma_{L\lambda}(\Omega,\omega)$ over the azimuthal angle ϕ_q of the vector $\boldsymbol{q}$, namely

$$\sigma_{L\lambda}(\Theta,\theta)=\frac{1}{2\pi}\int d\phi_q\sigma_{L\lambda}(\Omega,\omega)\ , \qquad (4.12)$$

which one can measure experimentally. Using expressions (2.7) and (4.4), we obtain

$$\cos\theta_q\simeq-\frac{\dfrac{\mu\Delta E}{K}}{\sqrt{\left(\dfrac{\mu\Delta E}{K}\right)^2+(K\Theta)^2}}\ . \qquad (4.11a)$$

Here we have neglected Q^2 compared with K'^2-K^2 because $Q^2\lesssim1/n^2\ll K'^2-K^2$. Substitution of eqs. (4.9) (4.10) and (4.11a) into eq. (4.12) yields the expressions shown in Table II. Integration of $\sigma_{L\lambda}(\Theta,\theta)$ over all angles θ, namely

$$2\pi\int_0^\pi\sigma_{L\lambda}(\Theta,\theta)\sin\theta d\theta\ ,$$

leads to the expressions of $\sigma_L(\Theta)$ given by eqs. (4.5a, b, c). Further if we are concerned only with the angular distribution of B atom or C$^-$ negative ion, we must integrate $\sigma_{L\lambda}(\Theta,\theta)$ over all angles Θ, namely

$$\sigma_{L\lambda}(\theta)=2\pi\int_0^\pi\sigma_{L\lambda}(\Theta,\theta)\sin\Theta d\Theta$$
$$\simeq2\pi\int_0^\infty\sigma_{L\lambda}(\Theta,\theta)\Theta d\Theta\ .$$

As shown in appendix, this integration gives the

Table II. Explicit formulas for $\sigma_{L\lambda}(\Theta\ \theta)$.

L	λ	$\sigma_{L\lambda}(\Theta\ \theta)$
0	0	$\frac{1}{4\pi}\sigma_0$
1	0	$\frac{3}{4\pi}[\sigma_1(P_1)^2-K^2\Theta^2\sigma_0P_2]$
	1	$\frac{3}{8\pi}[\sigma_1(P_1{}^1)^2+K^2\Theta^2\sigma_0P_2]$
2	1	$\frac{15}{8\pi}\left[\frac{1}{9}\sigma_2(P_2{}^1)^2-K^2\Theta^2\sigma_1(P_2-2P_3P_1)-K^4\Theta^4\sigma_0P_4)\right]$
	2	$\frac{15}{32\pi}\left[\frac{1}{9}\sigma_2(P_2{}^2)^2+2K^2\Theta^2\sigma_1(P_2-P_3P_1)+K^4\Theta^4\sigma_0P_4)\right]$

$\sigma_L=\sigma_L(\Theta)$ are defined by eqs. (4.5 a, b, c) and $P_l{}^m=P_l{}^m(\cos\theta)$ are the Legendre polynomials.

isotropic distribution, that is to say,

$$\sigma_{L\lambda}(\theta)=\frac{1}{4\pi}\sigma_n{}^L(v)\ , \tag{4.13}$$

where $\sigma_n{}^L(v)$ is the total cross section for reaction (1.1) of the n-th highly excited atom A** with the molecule BC given by eq. (3.12). This isotropy comes from the fact that the dissociation starts after the formation of the negative ion BC^-.

In this section we have, so far, implicitly assumed that BC is a diatomic molecule. However, Christodoulides and Christophorou[21] have analyzed the experimental data on DA to the n-C_NH_{2N+1}-Br molecules based on the assumption that these molecules can be considered as diatomic-like molecule $R(=C_NH_{2N+1})$-Br and obtained the results consistent with the theory of O'Mally[13] as far as the production of Br^- is concerned. Therefore, there may be the possibility that the derived expression is useful for some polyatomic molecule for which the diatomic picture is valid.

In the rest of this section, we apply our results to the reaction of the highly excited atoms A** with the molecules CCl_4 and I_2.

For the CCl_4 molecule based on the same assumption of s wave capture as in the preceding section, the angular distribution of A^+ ion is given by eq. (4.5a). (see Fig. 4) We have $\Theta_0=10'$ or 1.5°, for $n=20$ and at thermal velocities according as an atom A is a krypton atom or a hydrogen atom. Further if the diatomic-like picture as CCl_3-Cl is valid, the angular distribution of Cl^- formed is isotropic as given by eq. (4.13). In this case even if the scattering angle Θ is fixed, the angular distribution of B or C^- is also isotropic because we have $L=0$, $\lambda=0$. (see Table II)

For I_2 molecule, if Person's assignment

$$^2\Pi_{g(1/2),(3/2)}\ ,$$

for the negative ion state is correct, we have $L=2$ and $\lambda=1$ for the attachment $\Sigma_g-\Pi_g$, namely d wave capture occurs in DA of the thermal electrons to the I_2 molecules.[32] If we adopt the capture to give a $^2\Pi_u$ state by Shipsey,[33,34] we obtain $L=1$ and $\lambda=1$, namely, p wave capture. Dunn[35] derived the selection rules for the cases of the direction of incident electrons parallel and perpendicular to the molecular axis for a class of reactions including DA. Under the approximation of the slow rotation which O'Malley and Taylor[18] employed, only those molecules contribute to DA at angle θ_k which are initially oriented along the direction ω. Then Dunn's selection rules apply only to the cases for $\theta_k=0°$ and 90°. According to the Dunn's selection rule $\Sigma_g-\Pi_g$ capture is forbidden. However, this does not mean that this capture is forbidden at angles θ_k except for 0° and 90°. It seems that there is no experimental data to directly determine which partial wave p or d should be adopted as mentioned in the preceding section.

Consequently, the angular distribution of A^+ ion is given by (4.5b) for p wave capture or by (4.5c) for d wave capture. (see Fig. 4) Here we have $\Theta_0=10'$ and 1.5° for $n=20$ and at thermal velocities between A** and BC according as the highly excited atom is a krypton or a hydrogen atom. The angular distribution of I^- or I is isotropic as given by eq. (4.13). However, if the scattering angle Θ is fixed, the angular distribution of I^- or I becomes somewhat complicated as shown in Table II because we have $L=1$, $\lambda=1$ or $L=2$, $\lambda=1$ according as p or d wave capture takes place. For example, if Θ is fixed at zero angle, the angular distribution of I or I^- is given by

$$\sigma_{11}(0,\theta)\propto\sin^2\theta \quad \text{for } p \text{ wave capture}$$

or

$$\sigma_{21}(0,\theta)\propto\sin^2 2\theta \quad \text{for } d \text{ wave capture}\ .$$

§5. Discussions

The rate constants for reaction (1.1) are of order of the magnitude 10^{-7} cm³/sec for some halogen-containing molecules based on s wave capture. (see also Table I) The angular distributions of the products in reaction (1.1) are predicted in terms of eqs. (4.5) (4.12) (4.13) and Table II. Some results have been derived from the assumed assignment of the negative ion states. Further in our procedures we assume the plane-wave approximation for the relative motion between A^+ and BC^- ion after electron transfer has taken place. The deviation from the plane wave may not be negligible because of Coulomb attractive force in close collisions. This effect may modify the angular distributions predicted by our theory. However, it is very difficult to estimate this effect due to loss of simplicity of our theory without plane-wave approximation for relative motion. Therefore, our results obtained should be experimentally tested. Unfortunately there is no quantitative experimental data, which can be compared with our results. However, from eq. (2.6), it is shown that the knowledge of DA is very useful for the understanding of reaction (1.1). Generally speaking, together with the theoretical results obtained here and in the two previous papers[10,11] we can safely say that if there is one inelastic scattering of the slow electron by the molecule, there must exist the reaction of the highly excited atom with the molecules corresponding to this inelastic scattering of the slow electron by this molecule.

So far we have emphasized that we can understand the mechanism of the reactions of the highly excited atoms with the molecules in terms of the knowledge of the thermal electron scattering by the molecules. However, we have often very few and less reliable data on this thermal electron scattering. Inversely we can use the experimental results on the reaction of the highly excited atoms with the molecules to obtain the knowledge of the electron-molecule scattering. The measurement of the dependence of k_n on the principal quantum number n is effectively equivalent to the more direct measurement of cross sections for the thermal electron DA. Using eqs. (3.13a, b, c) we can obtain the information on what partial wave plays an important role in the DA process at the very low electron energy. From this we get information on the temporary negative ion state.

In the previous paper II, we have implicitly assumed s wave capture for other molecules than the SF_6 molecule for which there is the experimental evidence.[36,37] However, these assumptions should be experimentally tested. The above-mentioned discussions on DA can be also applied to the electron transfer process treated in II. This is because the theoretical results obtained in the preceding sections are derived under the condition that DA of the thermal electrons to the molecules results since the negative ion thus formed has a small probability for autodetachment.

Further if our approximations are sufficiently good, it should be noted that the measurements of the angular distributions for reactions (1.1) inversely yield informations on DA. We can easily see from the expressions (2.6) that the measurements of the angular distribution on reactions (1.1) yields the information on the cross sections for DA (1.2) if the initial Rydberg state of the electron is specified experimentally. In other words, if all the parameters Ω, ε, ω are simultaneously determined with a good accuracy, the angular distribution of reaction (1.1) yields the same information as that obtained in the experiment where the electron beam with a very low energy exactly equal to $Q^2/2$ impinges on the molecule BC. This arises from the relation (2.2). However, to determine Q experimentally, we must measure Θ and ε. If we take into account the condition $Q\lesssim 1/n$, we find from eq. (4.4)

$$|\Delta E|<\frac{K}{\mu n}\sim 3\times 10^{-3}\,\mathrm{eV}\quad\text{or}\quad 3\times 10^{-2}\,\mathrm{eV}\ , \tag{5.1}$$

for $Kr^{**}+I_2$ system or $H^{**}+I_2$ system, respectively. For the present time, it is experimentally a very difficult task to measure the energy distribution of the products formed in (1.1) with a good accuracy in such a narrow energy range as (5.1). On the other hand, the condition $Q\lesssim 1/n$ gives the relation

$$\Theta\lesssim\Theta_0=\frac{1}{Kn}\ . \tag{5.2}$$

For the lighter atom, for example, a hydrogen atom, we obtain $\Theta_0\sim 1.5°$ for $n\simeq 20$ and at thermal velocities. In this case, we can measure the angular distribution experimentally. We must, therefore, integrate the cross sections (2.6) over ε and obtain the expressions (4.5) and (4.12). (see also Table II) The measurements of the angular distributions of the final products in reaction (1.1) give the possibility to obtain the more direct information on the low energy electron scattering by the molecules and the information on the temporary negative ion formed in reaction (1.1). Namely the measurement of the angular distribution of the A^+ ion yields the information on the total cross section σ_{da} for DA. On the other hand, the measurement of the angular distribution of the C^- ion at a fixed scattering angle Θ gives the information on the angular distribution of DA. For these measurements, the lighter atom is suitable which is scattered at larger angles because it is easy to determine the angular distribution of A^+ ion.

The same discussions on the angular distribution of the A^+ ion eqs. (4.5) are applicable to the electron transfer process treated in II as shown in the case of rate constants.

So far we have discussed reactions (1.1) and (II-1.1) in which the Rydberg electron temporarily attaches to the molecule to form a compound state, namely a short-lived or long-lived negative ion. We call this type of reaction case a hereafter. However, there is another type of reactions of the highly excited atoms with the molecules B in which the Rydberg electron does not form the compound state with the molecule B, namely,

$$A(\alpha)+B(\beta)\to A(\alpha')+B(\beta')\ , \tag{5.3}$$

where α, α' and β, β' specify the states of the highly excited atoms and of the molecules. In the following, we call this type of reaction case b. In this case the scattering amplitude $f(\alpha, \beta, \boldsymbol{K}\to$

$\alpha', \beta', \boldsymbol{K}')$ as given by eq. (11) of I is written in terms of the scattering amplitude $f_{el}(\beta\boldsymbol{q}\rightarrow\beta\boldsymbol{q}')$ on the inelastic scattering of the slow electron by the molecule B

$$\mathrm{e}+\mathrm{B}(\beta)\rightarrow\mathrm{e}+\mathrm{B}(\beta') \,. \tag{5.4}$$

That is to say, we have

$$f(\alpha\beta\boldsymbol{K}\rightarrow\alpha'\beta'\boldsymbol{K}) = \mu\int G(\alpha'|\boldsymbol{q}')^{*}G(\alpha|\boldsymbol{q})f_{el}(\beta\boldsymbol{q}\rightarrow\beta'\boldsymbol{q}')\mathrm{d}\boldsymbol{q} \,, \tag{5.5}$$

where

$$\boldsymbol{q}'-\boldsymbol{q}=\boldsymbol{K}-\boldsymbol{K}'=\boldsymbol{Q} \,. \tag{5.6}$$

In paper I, we have treated the case where $\alpha\rightarrow\alpha'$ and $\beta\rightarrow\beta'$ transitions are the ionization of the highly excited atom and the rotational de-excitation of the molecule respectively.

Anyway, we can obtain the angular distribution and other necessary information on the inelastic scattering of the slow electron by the molecule B (5.4) from the measurement on reaction (5.3) if the initial state of the Rydberg electron is selectively produced. In case b, the situation is less clear-cut than that in case a, as shown in eq. (5.5), because there exists the relation (5.6) instead of (2.2). However, if $f_{el}(\beta\boldsymbol{q}\rightarrow\beta'\boldsymbol{q}')$ depends strongly on the momentum transfer $\boldsymbol{Q}$ and the dependence of f_{el} on $\boldsymbol{q}$ and $\boldsymbol{q}'$ individually is weak or if the Born approximation is valid for the inelastic scattering of the slow electron, we find

$$f(\alpha\beta\boldsymbol{K}\rightarrow\alpha'\beta'\boldsymbol{K})=\mu\langle\alpha|e^{i\boldsymbol{Q}r}|\alpha'\rangle f_{el}(\beta\rightarrow\beta'\boldsymbol{Q}) \,. \tag{5.7}$$

This is the usual expression for scattering amplitude by the impulse approximation.[38] The measurement of the angular distribution of the reaction (5.3) yields information on the angular distribution of the inelastic scattering of the low energy electron by the molecule (5.4). Thus, there is the possibility that one can use the relation (5.7), for example, for the experimental studies of the forward scattering of the rotational transition of the polyatomic molecule, for which Born approximation is considered to be a good approximation.

Finally we summarize our main theoretical results as follows: Reaction (1.1) is understood as the electron transfer process from the highly excited atom A** to the molecule BC followed by the dissociation of the temporary negative ion BC⁻ into B and C⁻. Then the differential cross section for reaction (1.1) can be written in terms of that for the dissociative attachment of the thermal electrons to the molecules (1.2). (see (2.6)) The rate constants for reactions (1.1) are evaluated to be of the order of magnitude $10^{-7}\,\mathrm{cm}^3/\mathrm{sec}$ at room temperature for some halogen-containing molecules. (see Table I) The angular distributions of the final products formed in reaction (1.1) are given by eqs. (4.5) (4.12) and (4.13) and the explicit expressions shown in Table II, which are determined by the state of the molecule BC and of the negative ion BC⁻. The angular distribution of A⁺ ion after integration of the scattering angles θ of B or C⁻ shows that scattering of A⁺ ion takes place at very small angles. On the other hand, the distribution of B or C⁻ is isotropic if the integration is carried out over the scattering angles Θ between A** and BC. This isotropy arises from the mechanism in which the motion of the dissociation between B and C⁻ starts after the formation of the negative ion BC⁻. It is shown that the measurements of the reaction of the highly excited atoms with the molecules can give the reliable information on the inelastic scattering of the thermal electrons by the molecules

Acknowledgements

The author greatly appreciates helpful discussions with Professor Tsutomu Watanabe of the University of Tokyo and the members of seminar held at Watanabe's laboratory.

Appendix: Isotropy of $\sigma_{L\lambda}(\theta)$

In this appendix, we show that the angular distribution

$$\sigma_{L\lambda}(\theta)=2\pi\int_0^\infty\sigma_{L\lambda}(\Theta\,\theta)\Theta\mathrm{d}\Theta \,, \tag{A·1}$$

is isotropic. Using eqs. (4.9) and (4.12) we have

$$\sigma_{L\lambda}(\theta)=\frac{16\mu^2c}{\pi n^5}\int_0^\infty\Theta\mathrm{d}\Theta\int\mathrm{d}\varepsilon\frac{Q^{2L}}{\left(Q^2+\dfrac{1}{n^2}\right)^4}I_{L\lambda} \,, \tag{A·2}$$

where

$$I_{L\lambda}=\frac{1}{2\pi}\int|Y_{L\lambda}(\theta_k)|^2\mathrm{d}\phi_q \,. \tag{A·3}$$

Here the functions $|Y_{L\lambda}(\theta_k)|^2$ are the polynomials of $\cos\theta_k$. Then these functions can be expanded in terms of Legendre polynomials $P_n(\cos\theta_k)$, namely

$$|Y_{L\lambda}(\theta_k)|^2=\sum_{n=0}^{2L}C_n{}^{L\lambda}P_n(\cos\theta_k) \,. \tag{A·4}$$

Substituting the addition theorem for the Legendre polynomial

$$P_n(\cos\theta_k)=P_n(\cos\theta)P_n(\cos\theta_q) +2\sum_{m=1}^{n}\frac{(n-m)!}{(n+m)!}P_n{}^m(\cos\theta)P_n{}^m(\cos\theta_q)$$

$$\times\cos m(\phi-\phi_q)$$

into the integral (A·3), we find

$$I_{L\lambda}=\sum_{n=0}^{2L}C_n{}^{L\lambda}P_n(\cos\theta)P_n(\cos\theta_q)\ . \qquad (\mathrm{A}\cdot5)$$

Substitution of eq. (A·5) into (A·2) gives

$$\sigma_{L\lambda}(\theta)=\frac{16\mu^2c}{\pi n^5}\sum_n C_n{}^{L\lambda}J_n{}^LP_n(\cos\theta)\ , \qquad (\mathrm{A}\cdot6)$$

where

$$J_n{}^L=\frac{K}{\mu}\int_0^\infty \Theta\mathrm{d}\Theta\int_{-\infty}^{\infty}\mathrm{d}t\ \frac{Q^{2L}}{\left(Q^2+\dfrac{1}{n^2}\right)^4}P_n(\cos\theta_q)\ , \qquad (\mathrm{A}\cdot7)$$

and

$$t=\frac{\mu}{K}\left(\varepsilon+\varepsilon_{\mathrm{B}}+\varepsilon_{\mathrm{C}^-}-\varepsilon_\beta+\frac{1}{2n^2}\right)\ .$$

If we transform the variables Θ and ε to Q and θ_q using the relations (4.4), (4.11a) and

$$K\Theta=Q\sin\theta_q\ ,$$

we find

$$J_n{}^L=\frac{1}{K\mu}\int_0^\infty Q\mathrm{d}Q\int_0^\pi \mathrm{d}\theta_q\, Q\sin\theta_q\,\frac{Q^{2L}}{\left(Q^2+\dfrac{1}{n^2}\right)^4}$$
$$\times P_n(\cos\theta_q)$$
$$=\frac{1}{K\mu}\int_0^\infty\frac{Q^{2L+2}}{\left(Q^2+\dfrac{1}{n^2}\right)^4}\mathrm{d}Q\int_0^\pi P_n(\cos\theta_q)$$
$$\times\sin\theta_q\mathrm{d}\theta_q=0 \quad \text{for} \quad n>0\ .$$

Then $\sigma_{L\lambda}(\theta)$ is independent of angle θ and this angular distribution is isotropic.

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