Influence of the Dipole Interaction on the Low-Energy Ion-Molecule Reactions

Kazuhiro Sakimoto and Kazuo Takayanagi

Institute of Space and Aeronautical Science, University of Tokyo, Komaba, Meguro-ku, Tokyo 153

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Collision dynamics of an ion-polar molecule system is influenced considerably by the dipole interaction. The recently-developed PRS (Perturbed Rotational State) approach is applied to the problem. It is found that the ion-polar molecule reaction rate is more than ten times larger in interstellar molecular clouds than the widely-used Langevin value. A scaling law holds approximately for the effective cross section as a function of the collision energy.

§ 1. Introduction

It is well known that for many ion-molecule reactions the rate constant is as large as $10^{-9}$ cm$^3$ s$^{-1}$ down to very low temperatures. Such a large rate constant is usually explained in terms of the Langevin theory,\textsuperscript{1)} where the polarization potential

$$V_{\text{pol}} = -\frac{a e^2}{2 R^4}$$  \hspace{1cm} (1)

is assumed to be the dominant interaction at large distances. In the above equation $a$ is the polarizability of the neutral molecule, $R$ is the intermolecular distance and $e$ is the elementary charge. The effective potential is given by the sum of the polarization potential and the centrifugal potential. The latter is a function of the impact parameter $b$. This effective potential has a barrier. If the collision energy is lower than the barrier height, the trajectory will be pushed away from the potential barrier and the collision will be a distant one. If the collision energy is higher than the barrier height, the collision pair approach each other with acceleration and come into close contact. There is a critical impact parameter $b_c$ for each energy $E$. The cross section $\pi b^2$ gives the Langevin cross section

$$\sigma_L = \pi \left( \frac{2 a e^2}{E} \right)^{1/2}.$$  \hspace{1cm} (2)

This kind of cross section is sometimes called the "orbiting" cross section because the collision pair move around many times (spiral motion) once the system passes the potential barrier. In some other papers, the cross section is called the "capture" cross section, which is somewhat misleading. The essential point is that such a collision leads to the collision pair coming into close contact with each other which is a necessary condition for a chemical reaction to take place. For this reason, we shall call the cross section of this nature the "hitting" cross section. This cross section gives a measure of the violent collision which leads to an exothermic reaction if there is such an exit channel. Thus we can predict the reaction rate constants.

When the neutral molecule is strongly polar, the observed reaction rate is sometimes larger than the Langevin value.\textsuperscript{2)} It is interesting, therefore, to study the influence of the dipole interaction on the ion-molecule reactions. Some approaches have been presented previously to calculate the hitting cross section for ion-polar molecule reactions. Dugan and his colleagues\textsuperscript{3), 4)} carried out a large amount of classical trajectory calculations. They could learn some features of the problem out of these calculations, but purely classical treatments are not suitable for studying collisions in very-low-temperature gases such as those in the interstellar molecular clouds. Dugan and Magee\textsuperscript{5)} and Hyatt and Stanton\textsuperscript{5)} applied the theory of the second-order Stark effect to obtain the adiabatic potential curves. They have not studied the possibility of transitions between different potential curves. Besides, the second-order calculations are not sufficiently accurate for close distances. In the so-called ADO (Average Dipole Orientation) theory proposed by Su and Bowers\textsuperscript{6), 7)} the molecular orientation is averaged with a classically-
determined probability. The ADO theory have successfully predicted the rate constants of many reactions at room temperature, but the predicted temperature dependence does not agree well with observation. The PRS (Perturbed Rotational State) method introduced and developed recently by the present authors is more suitable to study the topic.

§2. Outline of the PRS Theory

The details of the theory have been reported recently, so that only its outline will be given here. This is a semiclassical approach in the sense that the relative motion is described classically while the molecular rotation is treated quantum-mechanically. We assume for simplicity that the molecule is a linear rigid rotor and the incident ion is a point charge. Only the long-range dipole and the induced dipole (or polarization) potentials are taken into account.

In order to simplify the formulae and derive scaling laws, we introduce the reduced quantities which are dimensionless. For time $t$, internuclear distance $R$, impact parameter $b$, reduced mass of the collision pair $M$, incident velocity $v$, collision energy (initial kinetic energy) $E$, and the polarizability $\alpha$, we introduce the following reduced quantities:

\begin{align*}
\tau &= Bt/\hbar \\
x &= (B/D)e^{1/2}R \\
p &= (B/D)e^{1/2}b \\
\mu &= MDe/\hbar^2 \\
\beta &= \hbar e/(BDe)^{1/2} \\
K &= E/B = \mu\beta^2/2 \\
\alpha &= \alpha B/D^2,
\end{align*}

where $B$ is the rotational constant and $D$ is the dipole moment of the molecule.

The PRS functions are the eigenfunctions of the following eigenvalue problem for each fixed value of $x$:

\begin{align*}
H\chi_{jk}(\theta, \phi; x) &= u_{jk}(x)\chi_{jk}(\theta, \phi; x), \\
H &= \cos \theta x^{-1} + j^2,
\end{align*}

where $\theta$ and $\phi$ are the polar coordinates of the molecular axis in the coordinate system where $z$-axis is along the intermolecular distance vector $R$. In the collision problem, the direction of $R$ changes from time to time, so that we are using a rotating coordinate system. The angular velocity of this rotating frame relative to the space-fixed frame is denoted $\omega$ and its reduced (dimensionless) form will be $\Omega = h\omega/B$. In (5), $j^2$ is an operator such that $Bj^2$ is the Hamiltonian for the free rotation of the molecule. At large separations, $\chi_{jk}$ asymptotically tends to one of the spherical harmonics:

\begin{align*}
\chi_{jk}(\theta, \phi; x) \to \infty, Y_{jk}(\theta, \phi).
\end{align*}

In the same limit

\begin{align*}
\xi_{jk}(x) \to j(j + 1).
\end{align*}

This is the definition of the suffixes $j$, $\lambda$ of $\chi$ and $u$. In the limit of large separation, $j$ and $\lambda$ stand for the quantum numbers representing, respectively, the magnitude of the rotational angular momentum of the molecule and its $z$-component in the rotating coordinate system.

The time-dependent rotational wave function $\psi$ is determined by the time-dependent Schrödinger equation (in reduced unit)

\begin{align*}
i\frac{\partial}{\partial \tau} \psi(\tau) = H\psi(\tau),
\end{align*}

while the relative motion is determined by the energy and the angular momentum conservation laws:

\begin{align*}
U &= \text{total energy of the system divided by } B \\
&= \frac{\mu}{2} \left(\frac{dx}{dt}\right)^2 + \frac{\mu x^2}{2} (\Omega_x^2 + \Omega_y^2) - \frac{a}{2x^2} + \langle \psi(\tau) | H | \psi(\tau) \rangle, \\
J_x &= x - \text{component of the total angular momentum vector } J \\
&= \mu x^2 \Omega_x + \langle \psi(\tau) | j_x | \psi(\tau) \rangle, \\
J_y &= y - \text{component of the total angular momentum vector } J \\
&= \mu y^2 \Omega_y + \langle \psi(\tau) | j_y | \psi(\tau) \rangle.
\end{align*}

The energy conservation laws gives $U = \text{constant}$, but $J_x$ and $J_y$ are not constants of
motion because we are using the rotating frame of reference. The component $J_{x0}$, $J_{y0}$, $J_{z0}$ of $\mathbf{J}$ in the space-fixed frame are conserved. $J_x$ and $J_y$ are related to these components by

$$J_x = -J_{x0} \sin \beta + (J_{x0} \cos \alpha + J_{y0} \sin \alpha) \cos \beta$$

(12)

$$J_y = J_{y0} \cos \alpha - J_{x0} \sin \alpha,$$

(13)

where $(\alpha, \beta, 0)$ are the Euler angles of the rotation which transforms the space-fixed frame into the rotating frame.

The solution of (6) is now expanded in terms of the PRS functions:

$$\psi(\tau) = \sum_{j'j''} C_{j'j''}(\tau) \chi_{j'j''}(\theta, \phi; x(\tau)) \times \exp \left[-i \int_{\tau_0}^{\tau} \left\{ \mu_{j'j''}(x(\tau)) - \lambda' \Omega_z \right\} \mathrm{d}\tau \right].$$

(14)

It is shown\(^{10}\) that the coefficients $C$'s satisfy

$$\frac{\mathrm{d}C_{j'j''}}{\mathrm{d}\tau} = -\frac{\partial}{\partial x} \sum_{j'''} C_{j'j''} \chi_{j'} \frac{\partial}{\partial x} \chi_{j'''} \exp (i \eta_{j,j''})$$

$$-\Omega_z \sum_{j''} C_{j'j''} \chi_{j'} \chi_{j''} \exp (i \eta_{j,j''})$$

$$-\Omega_z \sum_{j''} C_{j'j''} \chi_{j'} \chi_{j''} \exp (i \eta_{j,j''}).$$

(15)

This set of equations and the eqs. (6), (7) and (8) are solved simultaneously to determine the rotational state of the molecule as well as the relative motion.

§3. Computations

In contrast to the simple Langevin theory or the ADO model, our theory can take account of the possibility of transitions between the adiabatic potential curves during collision. Because of this possibility, there is no single potential curve known at the beginning which we can use to calculate the barrier height. We thus adopt the following procedure. Let $b_1$ be an impact parameter for which the colliding pair reach at a distance less than a small value, say $x=0.045$ (2.7 Å for NH$_3$ and 9.9 Å for HCN). Furthermore, let $b_2$ ($>b_1$) be an impact parameter for which the system is reflected by the barrier. Then, the trajectory calculations are repeated with a new value of $b$ somewhat larger than the previous $b_1$ and also with another $b$ somewhat smaller than $b_2$. In this way, calculations are repeated until we have

$$b_2 - b_1 < 0.005 b_c,$$

(16)

where $b_c=(b_1+b_2)/2$. The hitting cross section $\sigma_{hit}$ is then given by

$$\sigma_{hit} = \pi b_c^2,$$

(17a)

$$\equiv (De/B)\pi p_c^2 = (De/B)\sigma_r,$$

(17b)

where $\sigma_r$ is the hitting cross section in reduced unit.

§4. Results and Discussion

4.1 Detailed calculations for a few lowest rotational states

We need only the minimum number of PRS functions to study the dynamics of ion-polar molecule collisions.\(^{9,10}\) We now study the cases where the molecule is initially at $j=0$ or $1$. Only the PRS functions up to $j=2$ are taken into calculations. The large angular-momentum transfer has a negligibly small probability in the low-energy distant collisions.\(^{10}\)

As examples, we take the following three reactions:

$$\text{NH}_3^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{NH}_2$$

(18a)

$$\text{H}^+ + \text{NH}_3 \rightarrow \text{NH}_3^+ + \text{H}$$

(18b)

$$\text{C}^+ + \text{HCN} \rightarrow \text{C}_2 \text{N}^+ + \text{H}.$$  

(18c)

The rate constant is fairly large for these reactions ($1.5 \sim 5 \times 10^{-9}$ cm$^3$ s$^{-1}$).\(^{11}\) The resonant charge transfer may be competitive with the reaction (18a), but the branching ratio is not known. There is only one exothermic channel for (18b) and (18c).

Figure 1 shows the hitting cross section for the system NH$_3^+$ + NH$_3$ as a function of the collision energy in reduced units. In the calculation by the ADO theory, the molecular rotational energy before collision is put to be zero. The Langevin cross section is too small at lower energies. This indicates clearly the importance of the dipole interaction. The ADO theory and the LD (Locked Dipole) model, where $\theta=0$ is assumed throughout collision, give cross sections comparable with the present calculations, but the difference is not negligible.

The effective ion-molecule interaction is affected by molecular rotation and thus by the angular-momentum transfer, so that the calculated hitting cross section (for the initial state $j=0$ as well as for $j=1$) as a function of
the collision energy has different slopes in the regions below and above the rotational excitation threshold. It is seen that the hitting cross section for the rotating molecule ($j=1$; the curve in Fig. 1 has been obtained by averaging over $\lambda=0, \pm 1$) is smaller than that of the nonrotating molecule ($j=0$), especially at low energies. This is because the dipole interaction is averaged out to give a smaller effective interaction when the molecule rotates more rapidly. For the state (1, 0), there is a small barrier with height of 0.6 reduced unit (see Fig. 1 in ref. 9). For this reason, the ion cannot come closer to the molecule at low energies and the hitting cross section goes to zero as is seen in Fig. 2.

It is remarkable that the LD cross section agrees fairly well with the PRS cross sections at higher energies. As the energy decreases, however, the difference becomes larger. Since the LD theory cannot take account of the molecular rotation, it overestimates the hitting cross section considerably especially when the actual molecule is in a rotating state. The good agreement with the LD theory found at higher energies can be explained as follows: As the collision energy increases, the critical distance $x_c$, the orbiting distance, becomes small. This is the distance, which, roughly speaking, separates the hitting region from that of reflection by the potential barrier. If the molecule is in a very low rotational state, the molecular rotation is considerably distorted as the ion approaches the molecule to a small distance and the molecular orientation is almost locked to the direction of the lowest potential energy (rotational hindrance). In fact, when $x_c$ is less than 0.05, the adiabatic potential $u_{jj}(x_c)$ for $j=0$ or 1 becomes fairly close to $-1/x_c^2$ which is the potential energy in the locked dipole configuration. The orbiting occurs at almost the same distance as the LD theory predicts. It must be noted, however, that when $x_c$ becomes comparable with size of the molecule, our treatment is no more applicable because there are strong short-range interactions which we have entirely neglected.

We can see in Fig. 2 that in the reduced units the hitting cross section as a function of the energy is very similar for the three reactions under consideration except at higher energies. This suggests a scaling law for the cross section. The curves for NH$_3^+$ + NH$_3$ and that for H$^+$ + NH$_3$ almost coincide. This suggests the $\mu$ (reduced mass)-independence of the hitting cross section. The curve for C$^+$ + HCN deviates from the other two at higher energies. This is probably due to the $a$(polarizability)-dependence of the cross section. In our calculations, the orbiting occurs at distances $x_c = 0.1 \sim 1$ when the energy $K$ is $10 \sim 20$ (0.012 $\sim$ 0.024 eV for NH$_3^+$ + NH$_3$) or less. If $a$ is much less than unity, the polarization interaction is much smaller in these distances than the dipole interaction, so that the orbiting is determined primarily by the dipole potential. For most of polar molecules, we have $a \leq 10^{-3}$. Thus the $a$-dependence of the hitting cross section is very small. At higher energies, however, $x_c$ becomes smaller and the polarization potential becomes comparable to the dipole potential and thus the $a$-dependence appears.
The $\mu$-independence can be explained as follows: According to the Massey's criterion, the rotational transition probability is very small when $\beta \ll 2.9$. This corresponds to $E \ll 21$ eV for NH$_3^+$ + NH$_3$. In this low-velocity region, we can approximately neglect changes of the quantum number $j$. For $j=1$, in contrast to the cases of higher $j$ (which will be discussed later), the adiabatic potential with $\lambda=0$ and those with $\lambda=\pm 1$ have a fairly large separation even at fairly large distances. Furthermore, there is no direct coupling between the adiabatic potential curves with $|\Delta \lambda|>1$. Therefore, at low velocity collisions, even $\lambda$ is a good quantum number. For $j=0$, there is only one potential curve. Thus for $j=0$ and $1$ we may consider only one $u_{j,\lambda}(x)$ at a time, so that the collision energy $K$ is given by

$$K = \frac{1}{2\mu} \left( \frac{dx}{d\tau} \right)^2 + \frac{(\mu \beta)^2}{2\mu x^2} - \frac{a}{2x} + u_{j,\lambda}(x) - j(j+1).$$

(19)

The last four terms on the right hand side as a whole give the effective potential in reduced units $V_{\text{eff}}$. We can also write this quantity as

$$V_{\text{eff}} = K \frac{p^2}{x^2} - \frac{a}{2x} + u_{j,\lambda}(x) - j(j+1).$$

(20)

For a given value of $K$, the critical values of $x$ and $p$ are determined by solving

$$\frac{\partial V_{\text{eff}}}{\partial x} = 0 \quad (21a)$$

and

$$V_{\text{eff}} = K. \quad (21b)$$

The reduced mass $\mu$ does not appear explicitly in these equations. Thus we can understand the $\mu$-independence of the hitting cross section.

Let us consider the rate constant $k(T)$ at temperature $T$. If we assume the $\mu$-independence of the cross section, $g(\kappa T/B) \equiv k(T)(BM)^{1/2}/eD$, where $\kappa$ is the Boltzmann constant, is a function of $a$ and $\kappa T/B$ only. $g(\zeta)$ is $\mu^{1/2}$ times the rate constant in reduced unit. Figure 3 shows $g(\zeta)$ as a function of $\zeta \equiv \kappa T/B$. It is seen that the $a$-dependence is fairly small in this temperature range. Therefore, we can apply the universal scaling law at least approximately. On the other hand, the $j$-dependence is considerable at very low temperatures, so that the rotational level population of the neutral molecule is important in determining the reaction rate.

![Fig. 3. Reduced rate constant times $\mu^{1/2}$ versus $\zeta \equiv \kappa T/B$ (temperature in reduced unit).](image)

### 4.2 Simplified calculations for higher rotational states

In the NH$_3$ gas at room temperature, the level population is largest at $j=4$. It is very laborious to calculate the hitting cross section by solving a set of coupled equations including all the appreciably populated states. We know, however, that the transitions between different-$j$ states have very small probabilities at low collision velocity under consideration. It is a reasonable approach to take account of coupling only between the channels with the same $j$ value.

Calculations are done for the NH$_3^+$ + NH$_3$ system. We neglect all the perturbed states except for $j=4$ ($j_z$-coupled calculation). Results are shown in Fig. 4, where circles, triangles, etc. are the $j_z$-coupled calculations, and the solid lines are calculations based on the eq. (19) ($j_z$-decoupled calculation). When the rotational energy of molecule is large, the molecular orientation is not locked as the ion and the molecule approach each other. Therefore, the

![Fig. 4. The hitting cross section in reduced unit for the rotational state $j=4$. ———: $j_z$-decoupled calculations; ○, △, □, +, *: $j_z$-coupled calculations.](image)
hitting cross section is smaller than that predicted by the LD theory even at higher energies.

The adiabatic potential $U_{44}$ except for $|\lambda|=4$ has a larger barrier as $|\lambda|$ becomes small. In the $J_z$-decoupled calculations the hitting cross section goes to zero, due to this barrier, at low energies as long as $|\lambda|$ is small. In the $J_z$-coupled calculations, however, the appearance of the hitting cross section is quite different. The energy-dependence of the hitting cross section with various initial $\lambda$'s in the $J_z$-coupled calculation are similar. The hitting cross section in the $J_z$-coupled calculation tends to become large as $|\lambda|$ is small in contradiction to the $J_z$-decoupled calculations. This difference indicates the defect of the $J_z$-decoupled calculations. This defect is partly understood by the following considerations. In Fig. 5, an ion-molecule collision is shown schematically. For simplicity we assume that the collision is a distant one and the molecular rotation remains unchanged during collision in the space-fixed frame and that the ion moves along a straight line. Let the molecule be in the $J_z=-4$ state at infinite separation before collision. As the ion approaches the molecule, $\lambda$ ($=j_z$ in the rotating frame) increases and at the nearest point $\lambda$ becomes zero. After collision $\lambda$ approaches $+4$. More or less the same behavior is observed even when the impact parameter is somewhat smaller. Thus, when the initial state is $\lambda=-4$, the adiabatic potential $U_{4,0}$ is the dominant potential at close distances. In Fig. 6, the distribution of the molecular rotation over various $\lambda$ values are shown as the function of the relative separation (approaching phase) for the case where the molecule is initially in the $\lambda=0$ state. It is seen that at the nearest point the rotational state is largely in the $\lambda=-4$ state. This shows that the $J_z$-decoupled approach is far from the real situation at least for relatively distant encounter. In the $J_z$-coupled calculations, on the other hand, due to the $\lambda$-transitions, the difference between the hitting cross sections for different initial $\lambda$'s is small.

In spite of these entirely different behaviors, our experience shows that the $J_z$-decoupled approach is still useful. In Table I, we show the hitting cross sections averaged over $\lambda$, both in the $J_z$-coupled and $J_z$-decoupled calculations. It is noticeable that on the average these two cross sections are very close to each other. This is a very encouraging result since it is much easier to calculate the hitting cross section in the $J_z$-decoupled method than in the $J_z$-coupled approach. As is shown in §4.1, we can expect the $\mu$-independence in the $J_z$-decoupled method. Thus the hitting cross section remains unchanged when the ion, as the collision partner of the polar molecule, is replaced by another ion.

If we assume the $\mu$-independence of the averaged hitting cross section, it can be shown that in reduced units $\beta\sigma_{\mu}^{1/2}$ is $\mu$-independent. In Fig. 7, we compare the present theory with experiment. The filled circles represent the $J_z$-coupled calculations for $\text{NH}_3 + \text{NH}_3$ sys-

![Fig. 5. Schematic illustration of apparent $\lambda$ transitions.](image)

![Fig. 6. The $\lambda$ distribution during collision (approaching phase). The initial rotational state is $\lambda=0$. Other parameters are $p=0.178$ and $K=20$.](image)

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tem. Agreement between experiment and theory is good at the collision energies below 200 reduced units (or below 0.25 eV for NH$_3^+$ + NH$_3$). At the collision energies above 200, the critical distance $x_c$ becomes comparable to the molecular size, where the simple dipole interaction cannot be applicable.

§5. Summary and Conclusions

A significant consequence of the present study is that we can expect the rate constant of some ion-polar molecule reactions in interstellar molecular clouds to be more than ten times larger than the Langevin value. In those clouds, the temperature is very low, say 20 K, and the density is also low, usually less than $10^5$ particles/cm$^3$. Therefore, most molecules are in the ground state of rotation. This is the case where the influence of the dipole moment upon the collision process is largest.

Table II shows some of our predictions obtained from Fig. 3 by reading graphs and values from other sources for comparison.

Another important result obtained is that the scaling law holds at least approximately for the hitting cross section as a function of collision energy, and for the rate constant as a function of temperature.

The present approach is based upon the semiclassical theory. In the extremely low-velocity collisions, the full wave-mechanical treatment is necessary.

For rotational states with high $j$ values, the calculations required in this approach become laborious, especially for obtaining the accurate adiabatic potential functions and also for evaluating the various matrix elements. If the $j_z$-decoupled approximation is always as good as in Table I, it is certainly very useful. Further tests are desirable.

One big defect of the present theory, and the Langevin theory for nonpolar molecules, is that we do not know exactly what will take place in the hitting collision. If there are more than one exothermic exit channels, we cannot tell the branching ratios between them. A study of reaction dynamics at close distances is necessary.

Numerical calculations have been made on FACOM 230-75 at the Institute of Space and

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Aeronautical Science, University of Tokyo.

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