ION–MOLECULE REACTIONS AT EXTREMELY LOW ENERGIES:
$H^- + H \rightarrow H_2 + e$

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Ion–molecule reactions at very low energies (<10^-2 eV) are investigated quantum-mechanically, taking the reaction $H^- + H \rightarrow H_2 + e$ as an example. Quantum effects, the zero-energy limit of the cross section, and the validity of an orbiting model are examined. The orbiting model is found to be satisfactory. However, since the potential is much more attractive than the polarization force, the orbiting cross section is larger than the Langevin value. When the strength of the reactive interaction is artificially reduced, resonance effects become important.

1. Introduction

Ion–molecule reactions are a very important process for molecular formation in interstellar clouds and in the upper atmosphere of the earth. Recently, many experimental studies have been done on ion-molecule reactions at temperatures much lower than 100 K (see ref. [11] and references therein).

For exothermic ion–molecule reactions, the reaction cross section may be given by $P_r \sigma_{orb}$, where $\sigma_{orb} = \pi b_{orb}^2$ (b_{orb} being the orbiting impact parameter), and $P_r$ is the reaction probability. This is based on classical mechanics. At very low energies, however, the classical model would not be appropriate to describe the reaction process, because only a small number of partial waves contribute to the reaction.

It would be very interesting, therefore, to investigate the quantum dynamics of the low energy ion–molecule reaction. To do this, one must know the details of the interaction potential. This is not readily achieved for a complex system. In the present study, accordingly, we take up the following simple associative detachment process,

$H^- + H \rightarrow H_2 + e $  

This system has a small reduced mass, and is thereby a good candidate to investigate quantum mechanical effects.

A quantum mechanical calculation for process (1) was carried out by Mizuno and Chen [2] and by Bieniek and Dalgarno [3,4]. However, no attention was paid to very low energy collisions. Furthermore, an accurate ab initio calculation showed recently that, at large internuclear distances $R$, the potential energy curve for $H^- + H$ is more attractive than those used previously [5]. It is expected that this attractive force significantly influences low energy collisions. The system $H^- + H$ is unstable against electron detachment at small distances. This gives rise to an imaginary part of the potential energy curve. This imaginary part is regarded as the interaction for reaction (1). The system $H^- + H$ has an unusual large imaginary part, not necessary so for other systems. Hence, it is interesting to know how the reaction probability $P_r$ depends on the magnitude of the reactive interaction. To see this, we also examine a model case by artificially varying the magnitude of the imaginary part. The energy range studied is 10^{-6}-10^{-2} eV. Atomic units are used throughout unless otherwise stated.

2. Interaction potential

By using a Born–Oppenheimer approximation, one can define a local complex potential for $H^- + H$, i.e.

$W(R) = V(R) - \frac{1}{2}i F(R)$.

(2)
Fig. 1 shows the complex potential energy curve for the \( ^2\Sigma^+_u \) state used in the present calculation. There is another potential curve with \( ^2\Sigma^+_g \) symmetry which is asymptotically degenerate with the \( ^2\Sigma^+_u \) state. However, the \( ^2\Sigma^+_g \) potential is repulsive so that it does not contribute to low energy collisions.

The potential energy curve for \( H^+ + H^- \) crosses with the \( H^+ + H \) potential at \( R = 3 \) au. The negative ion \( H^- \) exists only as a resonance state with an energy width \( \Gamma \) (i.e. an imaginary part of the potential) at a distance smaller than the crossing point. Since the energy width is very large for \( H^- + H \), it is difficult to determine the complex potential accurately [6]. Furthermore, non-locality of the potential may be important [6]. We adopt a semiempirical complex (local) potential determined by Bardsley and Wadehra [7] for \( R < 3 \) au, but shifted it uniformly to connect at \( R = 3 \) au with the long-range part of the potential described below. The semiempirical potential differs somewhat from recent ab initio calculations [6,8,9]. For low energy collisions, however, we will show that the detachment cross section (summed over final states) does not depend on the details of the short-range part of the complex potential.

Beyond the crossing point, the negative ion \( H^- \) is electronically stable. We employ the accurate ab initio potential energy determined by Scnekowitz et al. [5], fitting their results by the following form at \( R > 6 \) au,

\[
V(R) = -AR \exp(-BR) - \frac{\alpha}{2R^4} - \frac{C}{R^6}.
\]

Here \( A = 0.012316 \) au, \( B = 0.3848 \) au, \( \alpha = 4.5 \) au is the polarizability of \( H \), and \( C = 89 \) au is taken from Dalgarno and Kingston [10]. The potential is much more attractive than the asymptotic polarization potential \(-\alpha/2R^4\) even at distances as large as 20 au.

3. Calculations

The imaginary part of the potential absorbs a flux of the elastic collision of \( H^- + H \). We can regard the loss of flux as due to detachment. In low energy collisions, detachment always leads to formation of molecular hydrogen.

The radial wavefunction for the collision by the complex potential \( W(R) \) is determined by solving the equation

\[
\left( \frac{d^2}{dR^2} + \frac{J(J+1)}{R^2} - 2\mu [E - W(R)] \right) F_J(R) = 0,
\]

where \( E \) is the collision energy, \( J \) is the orbital angular momentum of relative motion, and \( \mu \) is the reduced mass. By fitting \( F_J(R) \) to the asymptotic form

\[
F_J(R) \xrightarrow{R \to \infty} D [\exp(-i(kR - \frac{1}{2}J\pi))]^{-S_J} \exp[i(kR - \frac{1}{2}J\pi)],
\]

we obtain an \( S \)-matrix element \( S_J \). In eq. (5), \( D \) is a constant, and \( k \) is the wavenumber. We use a logarithmic derivative propagation method to solve (4) [11]. If we neglect nuclear symmetry, the cross section for absorption due to the imaginary part of the potential is given by [12]

\[
\sigma_{ab} = \frac{\pi}{k^2} \sum_J (2J+1) (1 - |S_J|^2).
\]

The wavefunction must be properly symmetrized for nuclear exchange [13]. Then we have the cross section for the associative detachment (1) in the form...
$$\sigma_{\text{ab}} = \frac{\pi}{k^2} \sum_J w_J (2J+1)(1-|S_J|^2),$$  \hfill (7)

where \( w_J = 3/4 \) for even \( J \) and \( w_J = 1/4 \) for odd \( J \).

4. Results and discussion

First, let us neglect the nuclear symmetry to see the essence of the dynamics more clearly. Fig. 2 shows the orbiting cross section \( \sigma_{\text{orb}} = \pi b_{\text{orb}}^2 \), the Langevin cross section \( \sigma_L = \pi (2\alpha/E)^{1/2} \), and the absorption cross section (6). The orbiting impact parameter \( b_{\text{orb}} \) is estimated by use of the real part of the potential (2). Furthermore, we carried calculations by using complex potentials in which the imaginary part of the potential is reduced to be \( \Gamma = \Gamma_0/10, \Gamma_0/100, \text{ and } \Gamma_0/1000 \), respectively (\( \Gamma_0 \) being the potential imaginary part given by Bardsley and Wadehra [7]).

As mentioned previously, the potential \( V(R) \) is much more attractive than the polarization potential at intermediate distances. As a result, the orbiting cross section is larger than the Langevin value at higher energies. However, as the energy decreases, the orbiting occurs at very large distances, and consequently the difference between the two cross sections becomes negligible.

We find that the absorption cross section with the normal \( \Gamma \) coincides fairly well with the orbiting cross section. Fig. 3 shows the absorption probability \( P_J = 1 - |S_J|^2 \) for each partial wave. The probability \( P_J(E) \) is nearly a step function taking two values of zero and unity except for partial waves with small \( J \). This means that reaction occurs whenever the colliding particles overcome the centrifugal barrier, and furthermore tunneling or resonance effects are negligible. At very low energies, only a few partial waves contribute to the reaction. However, the deviation of \( \sigma_{\text{ab}} \) from \( \sigma_{\text{orb}} \) is small.

It is very interesting that the cross section remains unchanged even if the imaginary part \( \Gamma \) is reduced to \( 1/10 \). This is a very important finding. The complex potential cannot be determined well at \( R < 3 \) au because of large \( \Gamma \). However, the present result shows that the reaction cross section is independent of \( \Gamma \) as long as \( \Gamma \) is large. Furthermore, the reaction cross section is equal to the orbiting one, to which only the long-range part of the potential contributes. Thus, the cross section for process (1) can be determined accurately in spite of the ambiguity of the potential at \( R < 3 \) au. We should note however that the short-range part of the potential is important when the fi-
nal state of $\text{H}_2$ is specified. In this case, the local approximation itself may be poor [4,6].

When we reduce $\Gamma$ further, the cross section becomes smaller than $\sigma_{\text{orb}}$. However, the cross section for $\Gamma_0/100$ is larger than $\sigma_{\text{orb}}$ at $E<10^{-3}$ eV. There, since only s and p waves contribute to the collision, the orbiting cross section has no meaning. Furthermore, the energy dependence of the absorption cross sections is quite different from $E^{-1/2}$ at low energies when $\Gamma$ is reduced. The zero-energy limit of elastic cross sections in the presence of the polarization potential was discussed by O'Malley et al. [14]. By replacing their short-range potential with a complex-valued one, and by using the formula (6), it can be shown that the absorption cross section approaches the limit

$$\sigma_{\text{ab}} \rightarrow \sigma_L 2\text{Im}(B_0^{-1}),$$  

(8)

where a constant $B_0$ is defined by eq. (4.2) of ref. [14]. The quantity $B_0$ is determined by the short-range part of the potential (2) that deviates from $-\alpha/2R^4$. In the present case, since the potential is a complex value, $B_0$ has an imaginary part. From (8), we can see that the absorption cross section has the same energy dependence as $\sigma_L$ (i.e. $E^{-1/2}$) at extremely low energies. This is consistent with the fact that the cross sections for "exothermic reactions" generally have the energy dependence $E^{-1/2}$ as $E \to 0$ [15].

We find that the absorption cross sections for $\Gamma_0/100$ and $\Gamma_0/1000$ have noticeable structures at $E>10^{-4}$ eV. This is due to resonances. Fig. 4 shows the probability $P_J(E)$ for the imaginary part of $\Gamma_0/1000$. We can clearly see which partial wave is responsible for a resonance. For the imaginary part of $\Gamma_0/100$, the background (off resonance) probability is about 0.5 except at lower energies. Even if we take the resonances into account, the average probability does not so much differ from 0.5. However, for the imaginary part of $\Gamma_0/1000$, the resonances enhance the average probability from the background value 0.06. The resonance effect becomes more important as the magnitude of the imaginary part $\Gamma$ decreases. The importance of the resonance effect in the case of small $\Gamma$ has been pointed out also for radiative charge transfer [16,17].

Fig. 5 shows cross section (7) taking the nuclear symmetry into account. Owing to the statistical factor $W_J$, the cross section is about half of the orbiting value. This is easily verified. If it is assumed that $P_J=1$ for $J<J_{\text{orb}} (=k_{\text{orb}})$ and $P_J=0$ for $J>J_{\text{orb}}$ in eq. (7), one can show
\[ \sigma_{ad} = \frac{\kappa}{4k^2} (J_{\text{orb}} + 1)(2J_{\text{orb}} + 1). \]  

When \( J_{\text{orb}} \gg 1 \), this becomes \( \sigma_{ad} = \frac{1}{2} \sigma_{\text{orb}} \).

For comparison we show the results obtained by Mizuno and Chen [2] (case C in their paper). Bieniek [4] also calculated the cross section at \( E = 0.0129 \) eV. He obtained \( \sigma_{ad} = 321 \) au while the present result is 772 au. Since the long-range parts of the potential used by Mizuno and Chen and by Bieniek are not accurate, their cross sections are too small.

Table 1 shows the rate constant for associative detachment (1). The orbiting rate constant is larger than the Langevin value \( 2\pi(\alpha/\mu)^{1/2} (= 2.69 \times 10^{-9} \text{ cm}^3/\text{s}) \). The reaction rate constant has a temperature \( (T) \) dependence, and its value is about half of the orbiting rate constant. Since the cross section has the energy dependence \( E^{-1/2} \) as \( E \to 0 \), the rate constant is finite in the limit of \( T \to 0 \).

Experimental studies have been made only at \( E > 0.05 \) eV [18]. The present results cannot be compared with the experiments because the contribution of the \( 2^3\Sigma_g^+ \) state is important in this energy region. At \( E \approx 0.01 \) eV, the present reaction rate constant is about \( 5 \times 10^{-9} \text{ cm}^3/\text{s} \). It seems that this value is larger than those extrapolated from the experimental data. Since the theoretical reaction rate constant depends only on the long-range part of the potential, accurate measurements at low energies would provide evidence for the validity of the potential (3).

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<th>Temp. (K)</th>
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\(^{a)} \text{The Langevin value is } 2.69 \times 10^{-9} \text{ cm}^3/\text{s} \).

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References