State-specific dissociative recombination at low energy

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Abstract. The vibrationally and rotationally specific cross section is investigated for the dissociative recombination (DR) of H$_2^+$ and HeH$^+$ using the multi-channel quantum defect theory. In order to give the zero energy cross section, a convolution formula is introduced. A systematics in the vibrational dependence of DR is made clear. The rotational motion plays an important role in the DR at energies lower than 0.1 eV, causing large enhancement in some cases and rotational sensitivity. The state-specific investigation indicates a possibility of a non-thermal distribution of the initial rotational states in storage-ring experiments on HD$^+$.

1. Introduction
Understanding the initial state dependence is indispensable in the study of dissociative recombination (DR) between molecular ions and electrons. The vibrational-state dependence has been systematically measured by some storage-ring experiments for the DR of hydrogen molecular ions [1, 2]. The DR cross section measured at zero collision-energy essentially depends on the energy resolution of the measurement. Thus, a theoretical investigation is necessary to obtain the real values of the cross section. The rotational motion largely affects the DR at low collision energy [3] and is crucial in the cold Coulombic dynamics. In this report, we shall demonstrate the importance of the state-specific analysis of the DR of HeH$^+$ and H$_2^+$.

2. Method
We used multi-channel quantum defect theory (MQDT) for the calculations on DR presented in this report. MQDT is a powerful theoretical tool to represent the non-adiabatic interaction (NAI) uniformly both in the Rydberg states and in the low-energy electronic continuum states. The basic idea of MQDT consists of a transformation relation between two good representations of an inner and an outer region. In the inner region, the incident electron interacts with the molecular ion, where the adiabatic approximation is a good representation because of the Coulombic acceleration. In the outer region, particles must satisfy the boundary conditions, where a target-states expansion is a good representation. Besides the vibrational motion, the rotational motion is naturally included in the MQDT calculation. The MQDT approach succeeded in the analysis of Rydberg state spectroscopy and also of dynamical processes, such as ionization [4]. An extension of MQDT to dissociative processes was achieved by introducing discretized dissociative basis functions beside usual vibrational functions [3, 5].

MQDT is applicable only to systems where (1) the electronic states consist of Rydberg states or low-energy continuum states and (2) a good representation exists for each of the regions mentioned. The DR of HeH$^+$ below 1 eV satisfies those conditions. On the other hand, for H$_2^+$, since here valence electronic states of two-electron excited configurations contribute to the DR, we need to hybridize...
MQDT with another method which is applicable to non-Rydberg states. The interaction between the initial, one-electron excited state and the two-electron excited state is configuration interaction (CI), which is distinguished from the NAI. The so called ‘two-step method’ where CI and NAI are solved stepwise was established [6]: first, the basis functions diagonalizing the CI are generated, and next, these functions are used as the basis of the inner region of the MQDT. In the first step, we need to solve the scattering problem induced by the CI. First order perturbation theory on the CI has been adopted in many calculations. An algebraic method for evaluating the spectrally resolved Lippmann-Schwinger equation of the CI scattering gives a more reliable result [7]. Adopting Chebyshev quadrature, we could solve this algebraic equation in an accurate and stable way [5, 8].

There are generally many two-electron excited states of different symmetries. Each of the symmetries creates a Rydberg manifold. These Rydberg manifolds of two-electron excited states could be taken into account by utilizing discretized dissociative functions [9]. Highly excited two-electron excited states affect DR if the initial vibrational state is higher than \( v = 3 \) or if the collision energy is higher than several eV [10]. The contribution brought by those highly excited states makes it difficult to study DR with rotational motion and with accurate CI scattering states, since the electronic information on the highly excited states is not available in sufficient detail.

3. Observed rate coefficient

In order to analyze the zero-energy experiment, we must know the relation between the observed rate coefficient and the calculated cross section. In a merged beams experiment as performed at storage rings, the energy fluctuations in the longitudinal (indicated by \( \parallel \)) and transverse (\( \perp \)) direction with respect to the beam axis are different because of the kinematics. We use \( v \) and \( T \) for the velocity and the temperature related to the fluctuation, respectively, and denote the Boltzmann constant as \( k \). The observed rate coefficient \( Y_{\text{obs}} \) at the collision energy \( E_0 \) is represented using the cross section \( \sigma(E) \) at the collision energy \( E \) as

\[
Y_{\text{obs}}(E_0) = \int_{-\infty}^{\infty} dv_\parallel \int_{0}^{\infty} dv_\perp v \sigma(E) \frac{m}{kT_\perp} \exp \left( -\frac{mv_\perp^2}{2kT_\perp} \right) \sqrt{\frac{m}{2\pi kT_\parallel}} \exp \left( -\frac{mv_\parallel^2}{2kT_\parallel} \right),
\]

where the relative velocity between the electron and molecular ion is \( v = \sqrt{(v_0 + v_\parallel)^2 + v_\perp^2} \) with \( v_0 = \sqrt{2E_0/m} \). This is equivalent to equation (3) of Mowat et al. [11] and our starting point.

In order to separate the variables in the integration, we transform the variable of \((v_\parallel, v_\perp)\) to \((v, \theta)\),

\[
v^2 = (v_0 + v_\parallel)^2 + v_\perp^2,
\]

\[
\tan \theta = \frac{v_\perp}{v_0 + v_\parallel}.
\]

Because the Jacobian of this transformation is \(-v\), the observed yield becomes

\[
Y_{\text{obs}} = \frac{m}{kT_\perp} \sqrt{\frac{m}{2\pi kT_\parallel}} \int_{0}^{\infty} dv \, v \sigma(E) \int_{0}^{\pi} d\theta \exp \left\{ -\frac{m}{2k} \left( \frac{v^2}{T_\perp} \sin^2 \theta + \frac{1}{T_\parallel} (v \cos \theta - v_0)^2 \right) \right\}.
\]

After rewriting \( v \) by \( E = \frac{1}{2}mv^2 \), the integration over \( \theta \) is transformed from \( \theta \) to \( t = \cos \theta \). The result is

\[
Y_{\text{obs}} = Y_{\text{obs}}(E_0) = \sqrt{\frac{2}{\pi m kT_\perp}} \sqrt{\frac{1}{kT_\parallel}} \int_{0}^{\infty} dE \, E \sigma(E) I(E, E_0),
\]
where
\[
I(E, E_0) = \int_{-1}^{1} dt \exp \left\{ - \left( -\frac{E}{kT_\perp} + \frac{E_0}{kT_\parallel} \right) t^2 + 2\sqrt{\frac{EE_0}{kT_\parallel}} t - \frac{E}{kT_\perp} - \frac{E_0}{kT_\parallel} \right\}.
\]

(6)

When \( T_\parallel < T_\perp \), that means the coefficient of \( t^2 \) being negative, \( I(E, E_0) \) can be represented by using the error function
\[
\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_{0}^{x} \exp \left( -s^2 \right) ds
\]

(7)

as
\[
I(E, E_0) = \frac{1}{2} \sqrt{\frac{\pi kT_\perp}{E(T_\perp - T_\parallel)}} \exp \left\{ \frac{E_0}{k(T_\perp - T_\parallel)} - \frac{E}{kT_\perp} \right\} \left\{ \text{erf}(\beta) - \text{erf}(\alpha) \right\},
\]

(8)

where
\[
(\alpha, \beta) = \pm \sqrt{\frac{E}{k}} \left( \frac{1}{T_\parallel} - \frac{1}{T_\perp} \right) - \sqrt{\frac{E_0}{kT_\parallel}} \sqrt{\frac{T_\perp}{T_\parallel - T_\parallel}}.
\]

(9)

Finally we obtain the relation between the observed cross section \( \sigma_{\text{obs}}(E_0) \), usually defined as \( Y_{\text{obs}}(E_0)/v_0 \), and the calculated real cross section \( \sigma(E) \) by considering
\[
\sigma_{\text{obs}}(E_0) = \sqrt{\frac{1}{\pi} \frac{1}{kT_\perp}} \sqrt{\frac{1}{kT_\parallel}} \frac{1}{\sqrt{E_0}} \int_{0}^{\infty} dE \sigma(E) I(E, E_0).
\]

(10)

If the cross section is sharply distributed at the energy \( E = E_r \), that is \( \sigma(E) = \sigma_0 \delta(E - E_r) \), the above equation naturally becomes equation (7) from the paper of Danared [12]. This condition is not valid for molecular DR, unlike for dielectric recombination of atomic ions. The Equations (5) and (8)–(10) are adopted to the analysis hereafter.

In the absence of any resonance structure the cross section is inversely proportional to the collision energy, i.e., \( \sigma(E) = \sigma_0/E \) with a constant value \( \sigma_0 \). In this case, the observed rate coefficient at zero energy is given by Equations (5) and (6) as
\[
Y_{\text{obs}}(E_0 = 0) = \sqrt{\frac{2}{\pi m}} 2\sigma_0 \sqrt{\frac{1}{k(T_\perp - T_\parallel)}} \arctan \sqrt{\frac{T_\perp - T_\parallel}{T_\parallel}}.
\]

(11)

**Figure 1.** Convoluted DR rate coefficient of \(^4\text{HeH}^+\). The dependence of transversal fluctuation temperature is shown: \( T_\perp = 1\text{ meV } (---) \), 100 meV (- - - - ), 10 meV (······). The longitudinal temperature is 0.1 meV and the initial rotational state is assumed the thermal distribution of 300 K. The rate coefficient without convolution is shown by the solid curve with dots.
For $T_{\perp} \gg T_{\parallel}$, the observed zero energy rate coefficient $Y_{\text{obs}}(E_0 = 0)$ is proportional to $T_{\perp}^{-0.5}$.

Figure 1 shows an example of convoluted rate coefficient with various temperatures of transversal fluctuation. We can see that the zero energy rate coefficient becomes small with the fluctuation temperature being large.

4. Rotational motion in HeH$^+$

Figure 2 shows a comparison between the calculated reduced cross section and the observed one for four isotopes of the helium hydride molecular ion. The reduced cross section here is defined by the cross section multiplied with the collision energy. A thermal distribution of 800 K was assumed for the initial rotational states in the calculation. The calculated result is convoluted with the thermal fluctuations of electron velocities for a temperature of 10 meV in transversal and 0.1 meV in longitudinal direction. The experiment has been performed by Tanabe et al. using the storage ring TARN II [13] and gave relative values for the cross section. This figure presents the same data as the previous work [13] except for showing the reduced cross section in a linear instead of a logarithmic scale in order to verify in more detail the agreement between the calculation and the experiment. There are many resonance structures owing to rotationally and vibrationally excited Rydberg state and a reasonable agreement in the overall shape is found.

The rotational-state specific cross section is shown in figure 3. We see the clear dependence of the cross section on the rotational state at the energies below 0.2 eV. Comparing the results where rotations

![Figure 2](image-url)
Figure 3. DR cross sections of $^4$HeH$^+$ for the initial vibrational ground state. The rotational-state dependence is shown for $N^+ = 0$–3 by a solid curve. The dotted curve indicates the cross section that ignored the rotational transition.

are included or ignored, respectively, we can see that the rotational motion enhances the DR cross section by one or two orders of magnitude at these low energies.

5. Vibrational dependence at zero energy

As was seen in the previous sections, the temperature of electron velocity fluctuations is important to determine the observed DR rate coefficient in molecular ions. After a suitable convolution of calculated cross sections for the hydrogen ion H$_2^+$, figure 4 shows that the rotational motion strongly affects the DR at energies below 0.1 eV. We could not perform a calculation including the rotational motion for the higher two-electron excited states; these were found [5] to affect strongly the DR for higher vibrational states $v > 3$. Thus we should compare the present calculation with the experiment at relatively high energy, where the rotational effect is small.

Figure 5 shows the vibrational state dependence of the DR rate coefficients of H$_2^+$ for different values of the collision energy $E_0$. The rotational motion is ignored in this calculation. Although the absolute values change with $E_0$, the qualitative behavior of the vibrational dependence is common to the rate coefficients at three different energies. The experiment is qualitatively represented by the present calculation. The large change between the $v = 4$ and $v = 5$ is induced by the opening of the dissociative
Figure 4. DR rate coefficient of H$_2^+$ for the initial vibrational ground state. The rotational-state dependence is shown for $N^+=0$–3. The curve with 'No rotation' show the result of calculation ignored rotational motion, and the curve with 'Lowest only' means the calculation taking into account the lowest two-electron excited state only besides ignoring the rotational motion. The calculated values are convoluted by $T_\perp = 11.8$ meV and $T_\parallel = 0.1$ meV of energy fluctuation.

Figure 5. DR rate coefficient of H$_2^+$ as a function of the initial vibrational state $v$. The fluctuation temperature is the same as figure 4. The rate coefficient is taken at energies of 10 meV (——), 1 meV (- - -) and 0.2 meV (······). The experiment [2] is shown by ■ (relative rate coefficients scaled by an arbitrary constant).
channels due to the $n = 3$ Rydberg states. The higher two-electron excited states play an essential, important role in the vibrational state dependence.

6. Low energy DR cross section of HD$^+$

The calculated DR cross section for HD$^+$ turned out previously [5] to be two to three times larger than the experimental value [5]. In this earlier calculation, we assumed a thermal distribution of the initial rotational populations for temperatures of 300 K and 800 K, respectively. By investigating the rotationally specific cross section, we found that the results for rotational states $N < 4$ are generally more than three times larger than those for the higher rotational states, $N = 4$ and 5. As is seen in figure 6, not only the magnitude, but also the profile of the calculated cross section for $N = 4$ is similar in character to the observed cross section. We would point out the possibility that the distribution of initial rotational states might not be thermal under the experimental conditions, but considerably concentrated in $N = 4$ or higher rotational states.

References

[1] Zajfman D et al. 2000 Dissociative Recombination: Theory, Experiment and Applications IV ed M Lasson J B A Mitchell and I F Schneider (Singapore: World Scientific) pp 146–59
[2] Krohn S et al. 2003 Dissociative Recombination of Molecular Ions with Electrons ed S L Guberman (Kluwer Academic / Plenum Publishers) pp 127–38
[3] Takagi H 2004 Phys. Rev. A 70 022709
[4] Jungen Ch and Atabek O 1977 J. Chem. Phys. 66 5584
[5] Takagi H 2000 Dissociative Recombination: Theory, Experiment and Applications IV ed M Lasson, J B A Mitchell and I F Schneider (Singapore: World Scientific) pp 180–9
[6] Giusti A 1980 J. Phys. B 12 3867
[7] Takagi H 1993 Dissociative Recombination: Theory, Experiment and Applications ed B R Rowe, J B A Mitchell and I A Canosa (Plenum Press) pp 75–85
[8] Pichl L and Horáček J 1996 J. Phys. A 29 L405
[9] Takagi H 2002 Physica Scripta T96 52
[10] Takagi H 2003 Dissociative Recombination of Molecular Ions with Electrons ed S L Guberman (Kluwer Academic / Plenum Publishers) pp 177–86
[11] Mowat J R et al. 1995 Phys. Rev. Lett. 74 50
[12] Danared H 1995 Physica Scripta T59 121
[13] Tanabe T et al. 1998 J. Phys. B 31 L297; Corrigendum: 1999 ibid. 32 5221