A semiclassical study of collision-induced dissociation in \( \text{He} + \text{H}_2 \): The effect of molecular rotation

Kazuhiro Sakimoto

Institute of Space and Astronautical Science, Yoshinodai, Sagamihara 229-8510, Japan

(Received 25 January 1999; accepted 19 March 1999)

Dissociation processes in three-dimensional \( \text{He} + \text{H}_2 \) collisions are studied by using a semiclassical approach which treats the relative radial motion in classical mechanics and the other motions (vibration/dissociation and rotation) in quantum mechanics. Centrifugal sudden approximation is assumed to solve the semiclassical equation. The results are compared with previous full quantum mechanical calculations in which infinite order sudden approximation has been applied. The present study shows that the molecular rotation must be accurately taken into account in the dissociation process even at very high collision energies where the energy sudden assumption is usually expected to be satisfied for low molecular rotational states. © 1999 American Institute of Physics.

I. INTRODUCTION

Recently, it has become possible to carry out three-dimensional (3D) quantum mechanical calculations for collision-induced dissociation (CID),

\[ A + BC \rightarrow A + B + C. \]

A quantum mechanical treatment of the CID process is necessary at least in the following situations: (1) a quantum mechanical interference effect is seen in this process;

(2) the contribution of classically forbidden motion to the dissociation is significant for low vibrational states in nonreactive collision systems;

(3) the reverse process, i.e., three-body recombination (3BR), becomes more prominent at lower temperatures. The last is an especially important point. The quantum mechanical correlation effect becomes significant in three-body systems at very low temperatures, and the quantum mechanical consideration of 3BR has become just possible.

Since the theoretical methodology developed for CID is naturally available also in 3BR, the progress on the CID study can further promote an understanding of 3BR.

Previous quantum mechanical 3D studies for the CID process assumed an infinite order sudden (IOS) or vibrational sudden approximation. The use of the vibrational sudden approximation is limited to very high vibrational states for light molecules such as \( \text{H}_2 \). The applicability of the IOS approximation for the CID has not yet been examined sufficiently. To do that, we must consider the rotational degrees of freedom satisfactorily. However, since even the IOS approximation requires time consuming calculations for the CID process, the consideration of rotational motion becomes extremely troublesome in a fully quantum mechanical manner.

In a previous study (hereafter referred to as paper I), the present author has applied a semiclassical theory to the CID process in the \( \text{He} + \text{H}_2 \) system with restricted (collinear, T-shape,...) collision configurations. In the semiclassical method, the internal (vibration/dissociation) motion is treated in quantum mechanics, and the external (relative) motion is in classical mechanics. This type of treatment has been applied to several reactive collision processes. Paper I has shown that the semiclassical method provides a good agreement with a full quantum mechanical one for the CID process, and is very useful to gain the physical insight into the collision dynamics including some quantum mechanical natures. The present author has further solved accurately the CID problem for the coplanar \( \text{H} + \text{Ne}_2 \) system within the semiclassical framework, which treats the vibration/dissociation and rotation in quantum mechanics and the relative radial motion in classical mechanics. The IOS and centrifugal sudden (CS) approximations have also been examined for their applicability. It has been shown that the CS method gives a good agreement with the accurate one, whereas the IOS method is very poor. Inadequacy of the IOS approximation for \( \text{H} + \text{Ne}_2 \) originates in the fact that the collision energy is not sufficiently larger than the energy spacing of adjacent rotational levels related with the dissociation process, and the CID process occurs preferentially in the collinear configuration. The \( \text{H} + \text{Ne}_2 \) system might be rather unusual to discuss the applicability of the IOS approximation because \( \text{Ne}_2 \) has only two vibrational and a few rotational bound states.

The present paper carries out the 3D calculation for the CID in \( \text{He} + \text{H}_2 \) by using the semiclassical theory, and investigates the effect of the rotational motion on the CID process. To make the problem numerically solvable, the present study further assumes the CS approximation, which is expected to be reliable enough for the system with short range repulsive forces. The present results are compared with previous quantum mechanical IOS ones.

II. THEORY AND CALCULATIONS

A. Semiclassical equation

We denote the reduced masses of the total system \( \mu \) and of the molecule \( m \), and describe the system in Jacobi coor-

---

Electronic mail: sakimoto@pub.isas.ac.jp
coordinates \( \mathbf{R} \) and \( \mathbf{r} \), which are the intermolecular distance of He-H₂ and the internuclear distance of H₂, respectively. We choose the \( z \)-axis parallel to \( \mathbf{R} \). With an appropriate transformation, the Hamiltonian of the system in the CS approximation \(^{16}\) is given by

\[
H = \frac{1}{2 \mu} \left( \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{\hbar^2}{2\mu R^2} \right) + H_\alpha. \tag{1}
\]

Here, \( \hbar \) is the radial momentum of the intermolecular motion; \( \hbar \) is the effective orbital angular momentum quantum number; and

\[
H_\alpha = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial \gamma^2} + \frac{1}{r^2} \left( \frac{\partial^2}{\partial \gamma} \frac{\partial}{\partial \gamma} - \frac{\lambda^2}{\sin^2 \gamma} \right) \right) + V(R, r, \gamma), \tag{2}
\]

where \( \gamma \) is the angle between \( \mathbf{R} \) and \( \mathbf{r} \); \( \lambda \) is the azimuthal quantum number of the molecular rotation; and \( V(R, r, \gamma) \) is the potential energy surface (PES) of He+H₂. In the CS approximation, \( \lambda \) is conserved. Since the present study considers the initial rotational state of only \( j=0 \) \( (j \) being the molecular rotational quantum number), we assume \( \lambda=0 \) hereafter.

We employ the time dependent Schrödinger equation in which the vibration/dissociation and rotation are described in quantum mechanics, i.e.

\[
\frac{i\hbar}{\partial t} \psi(R, r, \gamma; t) = H\psi(R, r, \gamma; t). \tag{3}
\]

The variable \( R(t) \) in Eq. (3) is regarded as classical, and its time dependence is given by the expectation of the Hamiltonian \( H \) (i.e., energy conservation),

\[
E = \langle \psi | H | \psi \rangle = \frac{\mu}{2} \left( \frac{dR}{dt} \right)^2 + \frac{\hbar^2}{2\mu R^2} + \langle \psi | H_\alpha | \psi \rangle, \tag{4}
\]

where \( E \) is the total energy (hereafter, energies being measured from the bottom of the H₂ potential curve) and \( \langle \rangle \) means the integration over the quantum mechanical variables (i.e., \( \int dr \) or \( \int \sin \gamma d\gamma \)).

### B. Solution method

To solve Eq. (3) at energies above the dissociation limit \( D \), we employ a grid representation algorithm.\(^\text{17,18}\) We introduce a set of grid-based functions, \( u_\alpha(R) \) and \( v_\beta(\gamma) \), which are constructed from orthogonal polynomials associated with grid (quadrature) points, \( r_a \) \((a=0, 1, 2, ..., N)\) and \( \gamma_\beta \) \((\beta=1, 2, ..., M)\), respectively. As in paper I, we take

\[
u_a(r) = \frac{2 \omega_a^2}{r_{max} N} \sum_{n=1}^{N} \sin \left( \frac{n \pi r}{r_{max}} \right) \sin \left( \frac{n \pi r}{r_{max}} \right), \tag{5}
\]

where \( \omega_a = r_{max} \lambda N+1 = \Delta r \); \( r_a = \alpha \Delta r \); and \( r_{max} \) is taken large enough so that the vibrational continuum motion can be described with sufficient accuracy. It should be noted that the definition (5) is slightly different from that in Refs. 6 and 18, where the weights appear as \( \omega_a \) but not as \( \omega_a^2 \). The function \( u_a(r) \) satisfies the following properties:

\[
u_a(r) | u_a(r) \rangle = \omega_a^{-1/2} \delta_{\alpha, \alpha'}, \quad \langle u_a | u_{a'} \rangle = \delta_{\alpha, \alpha'}. \tag{6}
\]

Since H₂ is a homonuclear molecule, either even or odd values of the molecular rotational quantum number \( j \) are coupled in Eq. (3). Furthermore, the Hamiltonian \( H_\alpha \) is invariant under \( \gamma \rightarrow -\gamma \). Therefore, when the initial rotational state is \( j=0 \), the useful form of \( v_\beta(\gamma) \) is\(^\text{17(b)}\)

\[
v_\beta(\gamma) = w_\beta^{1/2} \sum_{n=0}^{M} P_{2n}(\cos \gamma) \tilde{P}_{2n}(\cos \gamma), \tag{7}
\]

where \( P_\beta(x) = (2n+1)^{-1/2} P_\beta(x) \) is the Legendre function; \( x = \cos \gamma \) is the zero point of \( P_{2n}(x) \); and \( \omega_\beta \) is the quadrature weight. In this case, the consideration of only the range \( 0 \leq \gamma \leq \pi/2 \) is sufficient, and hereafter the integration with respect to \( \gamma \) is taken over this range. The function \( \tilde{P}_{2n}(\cos \gamma) \) has the orthonormality relation,

\[
j_0^{1/2} \tilde{P}_{2n}(0) \tilde{P}_{2n}(\gamma) \sin \gamma d\gamma = \delta_{m,n}, \quad \text{and} \quad v_\beta(\gamma) \text{ satisfies}
\]

\[
v_\beta(\gamma_\beta') = w_\beta^{1/2} \delta_{\beta, \beta'}, \quad \langle v_\beta | v_\beta' \rangle = \tilde{\delta}_{\beta, \beta'}. \tag{8}
\]

Although only the case of \( \lambda=0 \) is considered here, the form (7) is very useful also for all the even numbers of \( \lambda^\text{19}\). In the case of odd \( \lambda^\text{'s}, the Jacobi (ultraspherical) polynomials \( P_{a-1}(\cos \gamma)^\text{20} \) can be employed to construct \( v_\beta(\gamma)^\text{19}\).

Using the grid-based functions \( u_a(r) \) and \( v_\beta(\gamma) \), we assume the wave packet \( \psi' \) in the form

\[
\psi'(R, \gamma, t) = \sum_{a', \beta'} \psi_{a', \beta'}(t) u_{a'}(r) v_\beta(\gamma), \tag{9}
\]

where we have put

\[
\psi_{a', \beta'}(t) = (\omega_{a'} w_\beta)^{1/2} \psi'(r_{a'}, \gamma_{\beta'}, t). \tag{10}
\]

Inserting this form into Eq. (3) and setting \( r=r_a \) and \( \gamma = \gamma_\beta \), we have a set of coupled linear differential equations with respect to \( \psi_{a', \beta'}(t) \),

\[
\frac{d\psi_{a', \beta'}(t)}{dt} = \frac{ih}{2m} \sum_{a'} \omega_{a'} \frac{d^2}{dr^2} u_{a'}(r_a) \psi_{a', \beta'}(t) - \frac{ih}{2mr_a^2} \sum_{\beta'} W_{\beta', \beta} \psi_{a', \beta'}(t) - \frac{i}{\hbar} V_{a', \beta'}(R(t)) \psi_{a', \beta'}(t), \tag{11}
\]

where \( V_{a', \beta'}(R) = V(R, r_a, \gamma_\beta) \), and

\[
W_{\beta', \beta} = (w_\beta w_\beta')^{1/2} \sum_{n=0}^{M} 2n(2n+1) \tilde{\tilde{P}}_{2n}(\cos \gamma_\beta') \tilde{P}_{2n}(\cos \gamma_{\beta'}). \tag{12}
\]

Owing to the definitions (5) and (7), the matrix elements \( \omega_{a'}^{1/2} \frac{d^2}{dr^2} u_{a'}(r_a) / dr^2 \) and \( W_{\beta', \beta} \) become symmetric. The numerical calculation is made in the same way as described in paper I.

For convenience, we define the following local distributions:

\[
\rho_{\alpha}(r, \gamma, t) = |\psi'(r, \gamma, t)|^2, \tag{13a}
\]

\[
\rho_r(r, t) = \int_{0}^{\pi} |\psi'(r, \gamma, t)|^2 \sin \gamma d\gamma, \tag{13b}
\]
\[
\rho_2(\gamma,t) = \int_0^{r_{\text{max}}} |\psi(r,\gamma,t)|^2 dr,
\]
(13c)
or in the grid representation
\[
\rho_1(r_a,t) = \omega_a^{-1} \sum_{\beta} |\psi_{a\beta}(t)|^2,
\]
\[
\rho_0(\gamma_\beta,t) = \omega_\beta^{-1} \sum_{\alpha} |\psi_{a\beta}(t)|^2,
\]
which are just equal to the Gauss quadrature rules for the integration.

C. Transition probabilities and cross sections

We take the initial condition of Eq. (11) as
\[
\psi_{a\beta}(t=0) = (\omega_a\omega_\beta)^{1/2} \chi^j_\alpha(0,0) \phi_{j0}(\gamma_\beta),
\]
where \(\chi^j_\alpha(r)\) is the vibrational bound wave function with the vibrational quantum number \(v\), and \(\phi_j(\gamma) = \tilde{P}_j(\cos \gamma)\) is the rotational wave function of molecules for \(\lambda = 0\). We can obtain the probability for the vibrational and rotational transition \((v,j=0)\rightarrow(v',j')\) in the form
\[
P^v(v,0\rightarrow v',j') = \left| \langle \chi^j_\alpha | \phi_{j'} | \psi(t=\infty) \rangle \right|^2
= \sum_{a\beta} (\omega_a\omega_\beta)^{1/2} \chi^j_\alpha(r_a) \tilde{P}_{j'}(\cos \gamma_\beta) \psi_{a\beta}(t=\infty)^2.
\]

Since the azimuthal quantum number \(\lambda\) is conserved and is equal to zero in the present case, the summation is unnecessary for the degenerate states in Eq. (15).

We define the transition probability for \(v\rightarrow v'\) (vibrational distribution) by
\[
P^v(v\rightarrow v') = \sum_{j' = 0}^{j_{\text{max}}} P^v(v,0\rightarrow v',j'),
\]
where \(j_{\text{max}}\) is the highest rotational quantum number for which the molecule is bound for the vibrational state \(v'\). We also define the rotational distribution of the bound molecule after the collision by
\[
P_v(j') = \sum_{v' = 0}^{v_{\text{max}}} P^v(v,0\rightarrow v',j'),
\]
where \(v_{\text{max}}\) is the highest vibrational quantum number for \(j'\). If the summation is taken over all the final bound and unbound vibrational states, the rotational distribution is given by
\[
\tilde{P}_v(j') = \int_0^{r_{\text{max}}} |\langle \phi_{j'} | \psi(r,\infty) \rangle|^2 dr.
\]
(18)

We can define the dissociation probability for \(v\) (and \(j = 0\)) as
\[
P^v(v\rightarrow\text{diss}) = 1 - \sum_{v' = 0}^{v_{\text{max}}} \sum_{j' = 0}^{j_{\text{max}}} P^v(v,0\rightarrow v',j')
= 1 - \sum_{v' = 0}^{v_{\text{max}}} P^v(v\rightarrow v')
= \sum_{j' = 0}^{j_{\text{max}}} [\tilde{P}_v(j') - P_v(j')].
\]
(19a)

Then, the cross section for the dissociation is obtained by
\[
\sigma(v) = \frac{\pi}{k_v} \sum_{j' = 0}^{j_{\text{max}}} (2j' + 1) P^v(v\rightarrow\text{diss}),
\]
where \(k_v\) is the wave number.

D. Relevant parameters

We use the \textit{ab initio} PES for He+H\textsubscript{2} given by Varandas and Brandão.\textsuperscript{21} This is the same as used in previous studies.\textsuperscript{2,3,5,6,14} The dissociation limit of H\textsubscript{2} is \(D = 4.748\) eV. For the values of \(v_{\text{max}}\) and \(j_{\text{max}}\), see Table I. Some features of the PES are shown in previous papers.\textsuperscript{3,5,6,14} We have carried out the calculations for the initial states \((v,j) = (0,0), (1,0), (2,0), \text{and} (3,0)\) at total energies \(E = 6 - 10\) eV. The transition probabilities have been evaluated at \(R = 8\) bohr. The value \(r_{\text{max}}\) must be chosen large enough such that the amplitude of the wave packet \(\psi'(r,\gamma,t)\) is always negligible at \(r > r_{\text{max}}\). (If a negative imaginary potential\textsuperscript{22} is applied at \(r = r_{\text{max}}\) we will be able to take \(r_{\text{max}}\) smaller.) We have set \(r_{\text{max}} = 10\) bohr, \(N = 80,\) and \(M = 15 - 25.\) The convergence has been checked by taking \(r_{\text{max}} = 15\) bohr, \(N = 200,\) and \(M = 30.\) The partial waves considered are \(j' \leq 70.\)

III. RESULTS AND DISCUSSION

A. Time evolution of local distributions

First, we see several snapshots of the local distribution \(\rho^{v=0}_{\gamma}(r,\gamma,t)\times\sin \gamma\) calculated at \(E = 10\) eV for \((v,j) = (0,0)\). Figure 1(a) is the snapshot taken at \(t = 100t_o\) (\(R\)

<table>
<thead>
<tr>
<th>(v)</th>
<th>(j_{\text{max}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>1</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>26</td>
</tr>
<tr>
<td>4</td>
<td>24</td>
</tr>
<tr>
<td>5</td>
<td>22</td>
</tr>
<tr>
<td>6</td>
<td>22</td>
</tr>
<tr>
<td>7</td>
<td>20</td>
</tr>
<tr>
<td>8</td>
<td>18</td>
</tr>
<tr>
<td>9</td>
<td>16</td>
</tr>
<tr>
<td>10</td>
<td>14</td>
</tr>
<tr>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>13</td>
<td>6</td>
</tr>
<tr>
<td>14</td>
<td>4</td>
</tr>
</tbody>
</table>
FIG. 1. Several snapshots of the local distribution $\rho^0_\psi(r,\gamma,t) \times \sin \gamma$ for the initial state $(v,j)=(0,0)$ at $E=10$ eV. (a) $t=100\tau_0$, $(t_\psi=2.4189 \times 10^{-17}$ s and $R=3.30$ bohr. (b) $t=240\tau_0$ and $R=1.50$ bohr. (c) $t=300\tau_0$ and $R=1.63$ bohr. (d) $t=360\tau_0$ and $R=2.21$ bohr. (e) $t=420\tau_0$ and $R=2.96$ bohr. (f) $t=480\tau_0$ and $R=3.76$ bohr. (g) $t=540\tau_0$ and $R=4.57$ bohr. (h) $t=600\tau_0$ and $R=5.38$ bohr. (i) $t=660\tau_0$ and $R=6.19$ bohr. (j) $t=720\tau_0$ and $R=7.00$ bohr. The turning point is $R_{TP}=1.47$ bohr at $t_{TP}=258\tau_0$, which is the time between the snapshots (b) and (e).

role for the collision dynamics than the incoming phase $(dR/dt<0)$ does. It should be noted that the turning point is $R_{TP}=1.47$ bohr at $t_{TP}=258\tau_0$, and a significant change in the wave packet is observed in the outgoing phase (c)–(e). At $t>450\tau_0$ ($R>3.5$ bohr), the He atom leaves sufficiently far away, and the molecule begins free rotation. The snapshots (f)–(h) show this behavior. In the final two snapshots (i) and (j), the redistribution of the wave packet occurs so as to localize it again in the molecular deep well. At the same time, some part of the wave packet for $\gamma \sim \pi/2$ still continues to expand and contributes to the dissociation.

Figure 1 suggests that the collision configurations around a T shape are essential to understand the collision nature in He+H$_2$. Figure 2, which plots the time evolution of the local distribution $\rho^0_\psi(\gamma,t) \times \sin \gamma$ at $E=10$ eV for $(v,j)=(0,0)$ and also $(2,0)$, shows more clearly to what extent the molecular orientation is restricted around $\gamma=\pi/2$ during the collision. At $t \sim 375\tau_0$ ($R \sim 2.4$ bohr), the peak of the local distribution at $\gamma=\pi/2$ becomes very sharp. When a long time has passed after the collision ($t>700\tau_0$), a complicated oscillatory structure is observed along the $\gamma$ coordinate. This indicates that the molecule is excited to high rotational states by these collisions.

When the molecular orientation $\gamma$ is assumed to be frozen during the collisions, previous studies$^{2,3,6,14,15}$ have indicated that the dissociation mechanism is classified into
Paper I shows that the nodal structure of the vibrational wave function is well preserved for a long time after the turning point when $\gamma$ is frozen, and further shows that only the outer part of the antinode can contribute to the dissociation. Since the number of the antinodes leading to the dissociation increases with energy, it produces undulation (the number of which is less than $v+1$) in the dissociation probability curve especially for high $v$. This is a quantum mechanical effect. Nobusada et al.\textsuperscript{5} already found that the interference of two classical trajectories made this undulation. Figure 3 shows that the preservation of the nodal structure along the $r$ coordinate is still present (at $t<600\tau_{\nu}$) even in the 3D collisions. Especially for $v=2$, we can find that the most outer antinode of the vibrational wave function mainly contributes to the dissociation. Unfortunately, the undulation structure is not seen so obviously in the 3D dissociation probability curve for $v\leq3$ (which is thereby not shown here). Nevertheless, for higher $v$ we can expect that the clear undulation will be present in the 3D collisions. The preservation of the nodal structure is tightly related to the fact that the system nearly keeps the T-shape configuration during the collision.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Time evolution (contour plot) of the local distribution $\rho^{(v=0)}(r,t)$ at $E=10\ eV$. The time is measured in atomic unit $\tau_{\nu}=2.4189\times10^{-13}\ s$. (a) The initial state is $(v,j)=(0,0)$. The time for the turning point is $t_{TP}=258\tau_{\nu}$. (b) $(v,j)=(2,0)$. $t_{TP}=282\tau_{\nu}$.}
\end{figure}

mainly two types in the nonreactive systems. One is the compression mechanism typically seen in the collinear collisions: that is, the internuclear distance $r$ is first contracted by the collision, and is then stretched so that the dissociation takes place. The other is the expansion mechanism typical in the T-shape collisions: in this case, the internuclear distance $r$ is always stretched for the dissociation. Figure 1 suggests that the expansion mechanism is important in He+H$_2$ when the rotational motion is taken into account. To see this more directly, Fig. 3 plots the time evolution of the local distribution $\rho^{(v=0)}(r,t)$ at $E=10\ eV$ for $(v,j)=(0,0)$ and $(2,0)$. The time evolution resembles very well the one for $\gamma=\pi/2$ of paper I, and shows that the dissociation occurs actually through the expansion mechanism.

In the case of H+Ne$_2$,\textsuperscript{13} however, the collinear configuration plays a much more essential role, and the compression mechanism is dominant for the dissociation. As suggested in previous studies,\textsuperscript{3,6,14,15,23} the difference between the He+H$_2$ and H+Ne$_2$ systems would be mainly due to the atomic mass combinations (i.e., heavy–light–light in He+H$_2$ and light–heavy–heavy in H+Ne$_2$). In the heavy–light–light system, the collinear collision is ineffective for the energy transfer such as vibrational excitation or dissociation.\textsuperscript{3,6,14,15} On the other hand, the energy transfer is always inefficient in the configurations around $\gamma=\pi/4$ regardless of the atomic mass combination.\textsuperscript{3,6,14,15} Consequently, the T-shape configuration becomes the most effective for the dissociation process in He+H$_2$. In the light–heavy–heavy or equal-mass systems, the collinear configuration is also effective for the energy transfer.\textsuperscript{3,6,14,15,23} Since the interaction range between an atom and a diatom is much longer for the collinear configuration than for the T-shape one, the importance of the collinear configuration would increase in H+Ne$_2$. Furthermore, it is not always possible to form the T-shape configuration for the H+Ne$_2$ collisions since the impact of the light H atom cannot cause a drastic movement of the heavy Ne atom. In the mass combination of He+H$_2$, the system immediately becomes the T-shape configuration by the close encounter.

Paper I shows that the nodal structure of the vibrational wave function is well preserved for a long time after the turning point when $\gamma$ is frozen, and further shows that only the outer part of the antinode can contribute to the dissociation. Since the number of the antinodes leading to the dissociation increases with energy, it produces undulation (the number of which is less than $v+1$) in the dissociation probability curve especially for high $v$. This is a quantum mechanical effect. Nobusada et al.\textsuperscript{5} already found that the interference of two classical trajectories made this undulation. Figure 3 shows that the preservation of the nodal structure along the $r$ coordinate is still present (at $t<600\tau_{\nu}$) even in the 3D collisions. Especially for $v=2$, we can find that the most outer antinode of the vibrational wave function mainly contributes to the dissociation. Unfortunately, the undulation structure is not seen so obviously in the 3D dissociation probability curve for $v\leq3$ (which is thereby not shown here). Nevertheless, for higher $v$ we can expect that the clear undulation will be present in the 3D collisions. The preservation of the nodal structure is tightly related to the fact that the system nearly keeps the T-shape configuration during the collision.

**B. Transition probabilities**

Figures 4–7 show the final vibrational distributions $P'(v\rightarrow v')$ at $E=8$ and 10 eV. Although the applicability of the present semiclassical theory was examined already in paper I, here we have checked it again by comparing the quantum mechanical IOS\textsuperscript{2} and presently calculated semiclassical IOS vibrational distributions. Figures 4 and 5(a) compare the two IOS results. We can obtain a fairly good agreement between the two methods. Hereafter, we thereby consider the IOS results only obtained by using the full quantum mechanical method. Furthermore, we can also expect that the semiclassical treatment is reasonably good for the CS calculations of He+H$_2$ collisions.

In Figs. 4, 5(a), and 6(a), the IOS vibrational distributions for $\gamma=0$ have only one conspicuous extremum for the...
vibrationally elastic \((v=v')\) transition. In the CS calculation, however, this is not true, and furthermore the vibrational distribution becomes more oscillatory with increasing \(v\). These results show that the IOS (essentially the rotational energy sudden) approximation is not reliable at all in the present case. Inadequacy of the IOS approximation is understandable from the fact that the important collisional action works preferentially around the T-shape configuration. Such a dynamical nature of the orientational preference can never be understood within the IOS approximation that assumes an equally oriented molecule. To confirm this fact more concretely, Fig. 5 shows the vibrational distributions for \(v=0, 1, 2\) calculated by freezing the orientations, i.e., \(\gamma=0, 0.393\pi, \pi/2\). We see that the predominance of the vibrational elastic transition in the IOS calculation comes from the contribution of the collinear collisions (in which the energy transfer is inefficient). However, the vibrational distribution for the collinear configuration no more resembles the CS result. The distribution for the T-shape configuration is somewhat (but not very) similar to the CS one. When we choose some intermediate orientation \((\gamma=0.393\pi)\), which should be close to \(\pi/2\), its vibrational distribution becomes most similar to the CS one. Figure 6 compares the final vibrational distributions also for \(v=1\) \((\gamma=0)\) and for \(v=2\) \((\gamma=30)\) obtained by freezing \(\gamma=0.393\pi\) and \(0.389\pi\), respectively. Good similarities to the CS distributions can be obtained. Also, in the case of \(\text{H}+\text{Ne}_2\) such preferential orientation is \(\gamma\approx 0\). The numerical labor would be drastically reduced if one could find the preferential orientation that could characterize the collision dynamics. However, this cannot be easily made in \(\text{He}+\text{H}_2\) because the \((\gamma\text{ frozen})\) transition probabilities are very sensitive to the orientation in the range \(\gamma\approx 0.35\pi - 0.45\pi\). Furthermore, since the local distribution \(\rho_{25}(\gamma, t)\) has a sharp maximum peak always at \(\gamma=\pi/2\) in the most important collisional duration \(t\approx 250t_o\) \(-500t_o\) (Fig. 2), probably the significance is only that the preferential orientation is just close to \(\gamma=\pi/2\). It will be difficult to obtain the preferential orientation from any simple kinematical or dynamical consideration.

Here, we criticize the rotational energy sudden approximation for the CID process. To see the characteristic of the \(\text{He}+\text{H}_2\) collisions, we compare the collision time \(\tau_{\text{coll}}\) and the characteristic time \(\tau_{\text{char}}=h/\Delta \epsilon\) where \(\Delta \epsilon\) is the energy spacing relevant to the transition. For the rotational transition \(j=0\rightarrow 2\) \((v=v')\) of \(\text{H}_2\), the characteristic time is \(\tau_{\text{char}}\)
We have \( \tau_{\text{coll}} \approx a/u \), where \( a \) is the interaction range and \( u \) is the initial velocity of the relative motion. When we take \( a = 1 \) bohr, which is a reasonable value for \( \text{He} + \text{H}_2 \), we have \( \tau_{\text{coll}} \approx 60t_o \) for \((v, j) = (0, 0)\) at \( E = 10 \text{ eV} \) (the highest energy considered in the present paper). In this estimate, the IOS approximation seems to work well for the rotational transition \( j = 0 \rightarrow 2 \). However, the definition of the collision time, \( t_{\text{coll}} = a/u \), is valid only for distant collisions, but is not so when hard direct encounters are important, such as in the present CID process. In the hard collisions, the relative velocity is not always nearly constant, and the interaction range strongly depends on the dynamical behavior of the molecule. This can be easily understood from Fig. 1, showing that the time duration for which the interaction works is different for the incoming and outgoing phases, and the collision time is totally \( \tau_{\text{coll}} \approx 200t_o \). The valid collision time is not so much shorter than (rather comparable to) the characteristic time \( (\tau_{\text{char}} \approx 600t_o) \) for \( j = 0 \rightarrow 2 \). Therefore, we cannot expect that the concept of the rotational energy sudden is a very good approximation. Furthermore, as seen in Fig. 8, the molecule is excited to high rotational states up to \( j' \approx 30 \rightarrow 40 \) in a large amount. If we consider the rotational transition \( j = 28 \rightarrow 30 \), we have \( \tau_{\text{char}} \approx 80t_o \), which is rather shorter than the collision time \( \tau_{\text{coll}} \approx 200t_o \). The IOS approximation becomes no more valid when such high rotational states are concerned with the collision dynamics. We can expect that as the orbital angular momentum \( \ell \) increases, the collision becomes a distant one and the excitation to high rotational states occurs less frequently. Figure 7 shows the final vibrational distribution at \( E = 10 \text{ eV} \) for \( \ell = 20, 40, \) and 60. We see that the IOS approximation becomes actually good when \( \ell = 60 \). In this case, the definition of \( \tau_{\text{coll}} = a/u \) is reasonable. However, as seen later (Figs. 9 and 10), such high partial waves have negligible contribution to the CID process.

Figure 8 shows the final rotational distributions (17) and (18) for \( \ell = 0 \) at \( E = 10 \text{ eV} \). Because of the hard collisions, we can see that the molecule is excited to very high rotational states. The difference of \( \mathcal{P}_v'(j') \) and \( \mathcal{P}_v''(j') \) is equal to the dissociation probability for the fragment having the angular momentum \( j' \). [See Eq. (19c).] When \( v = 0 \), most of the molecules with low \( j' (\leq 12) \) remain bound, and the dissociation occurs for \( 14 \leq j' \leq 28 \). Therefore, the excitation to the high rotational states is needed in the CID process for \( v = 0 \). As \( v \) increases, since the dissociation becomes prominent even for low \( j' \) and also for extremely high \( j' (j'_\text{max} = 30) \), the vibrational excitation (with \( \Delta j \sim 0 \)) and the rota-
tional excitation (to \( j' > j_{\text{max}} \)) can be both considered as the dissociation mechanism. In this case, the dissociation occurs almost equally for any possible \( j' \). As discussed just before, the IOS approximation poorly describes the excitation to very high rotational states. The fact that the contribution of the excitation to \( j > j_{\text{max}} \) is important directly suggests the inapplicability of the IOS approximation in the CID process.

We should pay attention here to the validity of the CS approximation in the present case. As seen in Eq. (1), the CS approximation neglects the conservation of the total angular momentum, and hence the orbital angular momentum \( \ell \) becomes constant during the collisions. Figure 8 shows that the maximum final angular momentum quantum numbers are 25–40 (for \( \ell = 0 \)). These values are close to the maximum \( \ell' (= \ell_{\text{max}}) \) that can contribute to dissociation (Figs. 9 and 10). A similar situation exists also in H+Ne\(_2\).\(^{15}\) For such high rotational excitation, i.e., \( j' \sim \ell_{\text{max}} \), can we assume that \( \ell' \) is constant, or do we have to consider the angular momentum conservation accurately? In H+Ne\(_2\), the CS approximation actually works satisfactorily.\(^{15}\) Unfortunately, the present study cannot examine the validity of the CS approximation. Nevertheless, from the success for H+Ne\(_2\), we expect that the CS approximation is satisfactory even for the CID process accompanied by the rotational excitation of \( \Delta j \sim \ell_{\text{max}} \).

C. Dissociation cross sections

The dissociation probabilities \( P(\nu \rightarrow \text{diss}) \) for \( \nu = 0–3 \) are plotted as a function of \( \ell \) in Figs. 9 and 10. As \( \nu \) increases, the difference between the CS and IOS results becomes more significant. For very high \( \ell \), the two results are close with each other when \( \nu = 0–2 \). This is because the collisions are distant ones and the IOS approximation eventually becomes reliable. When \( \nu = 3 \), since the geometrical size of the molecule is very large, the direct collisions are still possible even for very high \( \ell \), and the IOS approximation is poor for all the \( \ell' \)'s. When we consider the vibrational/rotational transition with only small changes of quantum numbers, the IOS approximation may be able to work well for the calculation of the cross section because very high partial waves (\( \ell' > 50 \) at \( E = 10 \text{ eV} \)) become non-negligible. However, the IOS approximation is no more valid in the partial waves that have an important contribution to the CID process.

Finally, Fig. 11 shows the energy dependence of the dissociation cross sections \( \sigma(\nu) \) for \( \nu = 0–3 \). The IOS method seems to agree well with the CS one at all the energies for \( \nu = 0 \) or at low energies for \( \nu = 1 \). However, from the detailed considerations for the transition probabilities in Sec. II B, this is merely accidental. For \( \nu = 2 \) and 3, the difference between the two methods is significant. The present study indicates that the IOS approximation largely underestimates the dissociation cross section for high \( \nu \). The same result was found by Nobusada and the present authors comparing the IOS and quasiclassical trajectory (QCT) calculations for \( \nu = 9 \). The reason for this is evident: i.e., the IOS approximation overestimates the contribution of the configurations around the collinear geometry and thereby gives a too
large probability for the vibrational elastic \((v=v')\) transition.

In most of the nonreactive systems, actual energy thresholds of the dissociation cross sections (called dynamical thresholds) are much higher than the dissociation limit \(D\) and shift to lower energies with increasing \(v\) as seen in Fig. 11. Nobusada and the present author found that the dynamical threshold obtained by the quantum mechanical IOS method was much lower than that of the QCT method for \((v,j)=(0,0)\). They mentioned that the difference between the IOS and QCT results occurred because the contribution of classically forbidden motion was dominant in the dynamical threshold region. Paper I shows that the present semiclassical method can take account of such a quantum mechanical effect, and that in the dynamical threshold region the contribution of the dissociation comes from the tail of the wave packet which contains a classically forbidden nature. Because the dissociation dynamics in the 3D collisions is well characterized by the collisions in the T-shape configuration, the discussion for \(\gamma = \pi/2\) in paper I would be still meaningful also in the present case. Furthermore, Fig. 11 shows that the CS and IOS cross sections agree well with each other for \((v,j)=(0,0)\) (though accidentally). Therefore, the present study also shows that the quantum mechanical effect is significant for the 3D CID process in the dynamical threshold region. For low vibrational/rotational states, a quantum mechanical or semiclassical treatment is required, especially at energies near the dynamical thresholds.

IV. SUMMARY

We have studied the CID process in 3DHe+H\(_2\) collisions by using the semiclassical theory. The comparison of the semiclassical IOS and the quantum mechanical IOS\(^2\) calculations shows that the semiclassical theory is sufficiently accurate in the present case. The rotation dynamics has been considered within the CS approximation, and we have found that the rotational energy sudden (and hence IOS) approxi-
mation is poor for the CID process in He$^+$H$_2$. The reason for the inadequacy of the IOS approximation is: (1) the CID process is caused by the hard direct collisions; (2) the CID process occurs preferentially around the T-shape configuration; (3) the CID process is accompanied by the excitation to very high rotational states. The present study shows that the accurate consideration of the rotational motion is necessary in the CID process. The IOS approximation would be also invalid for the vibrational/rotational transition with large changes of quantum numbers. Probably, the applicability of the IOS approximation will be limited to only the transition with small changes of quantum numbers. One should remember this point in trying to apply the IOS approximation.

The applicability of the CS approximation is not so evident for the CID process. The CID process in He$^+$H$_2$ is promoted by only a short-range repulsive force, and occurs mainly in hard direct (such as head on) collisions. These facts support the validity of the CS assumption. However, the high degree of rotational excitation by the hard collisions may require an accurate treatment of the orbital angular motion. In the case of H$^+$Ne$_2$,$^{15}$ which has a similar situation, the CS approximation is fairly good. Although the examination of the CS approximation for the CID process remains for future work, probably the CS approximation works satisfactorily even if the high degree of rotational excitation occurs.

By monitoring the time propagation of the wave packet, the semiclassical method is very useful to gain a deep insight into the collision dynamics. The method can also take some quantum mechanical effects into account, and enables us to understand the dissociation behavior near the dynamical threshold. Because an accurate quantum mechanical treatment is very difficult for molecular collisions at suprathermal energies, the semiclassical theory will be promising in that case. However, the present semiclassical theory has the de-
fect that open and closed channels cannot be defined accurately. This defect may be significant near the energy threshold of the transition; the semiclassical calculations sometimes (but not always) give an unusual behavior of the transition probability near the energy threshold. Some improvement may be required, e.g., when we apply the semiclassical theory to study the 3BR process at low energies.

ACKNOWLEDGMENT

The author would like to thank Dr. Kunizo Onda for reading the original manuscript and for some useful comments.