A semiclassical study of vibrational and rotational transition in He + H₂ at suprathermal energies

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Abstract

Vibrational and rotational transition in suprathermal (> a few eV) He + H₂ collisions is studied by using a semiclassical method in which one degree of freedom (i.e., relative radial motion) is described by classical mechanics and the others by quantum mechanics. The present study solves the semiclassical equation in a numerically accurate manner. That is, the vibration and orbital/molecular rotation are treated without employing any decoupled approximations. Also carried out are the semiclassical calculations using a centrifugal sudden (CS) and infinite order sudden (IOS) approximations. The comparison with the accurate semiclassical calculation shows that the CS approximation is always satisfactory, but the IOS approximation is not so good as one expected. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

A recent theoretical progress has become possible to carry out a fully converged quantum mechanical calculation of energy transfer processes in suprathermal (> a few eV) molecular collisions [1–6]. In performing such numerical calculations, an infinite order sudden (IOS) or centrifugal sudden (CS) approximation has been frequently applied, and has been expected to be satisfactory at higher collision energies. However, a critical examination of such decoupled approximation has not yet been sufficiently made in the suprathermal energy region because an accurate calculation has been quite difficult. Hence, the applicability of the IOS and CS approximations at high energies is still uncertain.

The present paper considers He + H₂, which is the simplest nonreactive system, and is a prototype for the study of molecular energy transfer. The rotational energy spacing of the \( j = 0 \) and 2 levels \( j \) being the rotational quantum number) is about 0.04 eV, which is two orders of magnitude smaller than the collision energy of a few eV. Accordingly, one may expect that the rotational energy sudden (ES) or IOS approximation (if the CS assumption is good) works in He + H₂ at suprathermal energies. However, the present author [7] (hereafter referred to as paper I) has shown that the ES approximation is no more valid for the dissociation process in He + H₂. This is because the dissociation process occurs preferentially around a T-shape configuration, and is...
accompanied by the excitation to very high rotational states. (The ES approximation assumes an equally oriented molecule, and becomes worse for very high rotational states.) Paper I has suggested that the applicability of the IOS approximation may be limited to the transition with only small changes of quantum numbers. The same conclusion for the inapplicability of the IOS approximation has been also obtained in the coplanar study of H + Ne$_2$ [8].

The collision processes in He + H$_2$ are dominated by a short-range repulsive force. Thereby, one expects the validity of the CS approximation. However, owing to the high degree of rotational excitation during the collisions as mentioned above [7], the CS assumption might be a failure; that is, although the large angular momentum transfer might affect the orbital motion, such a dynamical effect is ignored in the CS approximation. In any way, the applicability of the IOS approximation has been also limited to the transition with only small changes of rotational states. Paper I has suggested that the applicability of the IOS approximation may be limited to the vibrational transition but also for the dissociation. Furthermore, the semiclassical method is very useful to gain the physical insight into the collision dynamics including some quantum mechanical natures. Therefore, we can believe that the semiclassical method is very powerful to study the suprathermal collision dynamics.

The present paper investigates the vibrational and rotational transition in three dimensional He + H$_2$ collisions at energies 1–10 eV by using the semiclassical methodology. The relative radial motion is treated in classical mechanics, and the vibration and orbital/molecular rotations are in quantum mechanics. The present paper considers the latter quantum motions accurately without introducing any decoupled approximations, and also carries out the calculations further introducing the CS and IOS approximations to examine their reliability.

2. Theory and calculations

2.1. Semiclassical equation

We consider He + H$_2$ with the reduced masses of the total system $\mu$ and of the molecule $m$. We describe the system in Jacobi coordinates $\mathbf{R}$ and $\mathbf{r}$, which are the intermolecular distance of He–H$_2$ and the internuclear distance of H$_2$, respectively. We choose a body-fixed (BF) frame in which the $z$-axis is parallel to $\mathbf{R}$. The rotation from a space-fixed (SF) frame to the BF frame are given by the Euler angles ($\alpha, \beta, \gamma$).

With an appropriate transformation [10–15], the Hamiltonian of the system can be written as

$$ H = \frac{1}{2\mu} P_R^2 + H_0. $$

Here, $P_R$ is the radial momentum of the intermolecular motion, and

$$ H_0 = \frac{(\mathbf{J} - \mathbf{j})^2}{2MR^2} + \frac{\mathbf{j}^2}{2m_r^2} - \frac{\hbar^2}{2m_r} \frac{\partial^2}{\partial r^2} + V(\mathbf{R}, r, \theta), $$

where $\mathbf{J}$ and $\mathbf{j}$ are the total and molecular angular momentum vectors, respectively; $\theta$ is the polar angle of $\mathbf{r}$; $V(\mathbf{R}, r, \theta)$ is the potential energy surface (PES) of He + H$_2$; and the operator $(\mathbf{J} - \mathbf{j})^2$ is given by [17]

$$(\mathbf{J} - \mathbf{j})^2 = \mathbf{J}^2 + \mathbf{j}^2 - 2 J_z j_z - J_z j_z - j_z J_z. $$

We solve the time dependent Schrödinger equation in which the vibrational ($r$) and rotational ($\mathbf{R}, \mathbf{r}$) variables are described in quantum mechanics, i.e.,

$$ i\hbar \frac{\partial}{\partial t} \Psi^{JM}(\hat{\mathbf{R}}, \mathbf{r}, t) = H_0 \Psi^{JM}(\hat{\mathbf{R}}, \mathbf{r}, t), $$

where $J$ and $M$ are the total angular momentum quantum number and its azimuthal component in the SF frame, respectively. The wavefunction $\Psi^{JM}$ can be expanded as [18]

$$ \Psi^{JM}(\hat{\mathbf{R}}, \mathbf{r}, t) = \sum_{\lambda} \bar{D}_{M\lambda}(\alpha, \beta, \gamma) \psi^{JM}(\mathbf{r}, t), $$

where $\gamma$ is the azimuthal angle of $\mathbf{r}$, and

$$ \bar{D}_{M\lambda} = \left( \frac{2J + 1}{8\pi^2} \right)^{1/2} (D_{M\lambda}^*)^{\ast} $$

(5)
is the normalized Wigner $D$ function [19]. The number of coupled channels can be reduced by considering the parity conservation. We introduce the parity-adopted $D$ function ($p = \pm$) [20,21], i.e.,

$$
\tilde{D}_{M}^{J}(p) = [2(1 + \delta_{\alpha,\beta})]^{-1/2} \left[ D_{Mb}^{J} + p(1 - 1)^{J+\lambda} D_{M}^{J-\lambda} \right].
$$

(6)

Then, Eq. (4) is decomposed into

$$
\Psi_{JM} = \Psi_{JM(+)} + \Psi_{JM(-)}
$$

where

$$
\Psi_{JM(p)} = \sum_{\lambda \geq 0} \tilde{D}_{M}^{J(p)} \psi_{JM(p)},
$$

(7)

with

$$
\psi_{JM(p)} = [2(1 + \delta_{\alpha,\beta})]^{-1/2} \left[ \psi_{J+\lambda} + p(1 - 1)^{J+\lambda} \psi_{J-\lambda} \right].
$$

(8)

The wavefunction $\Psi_{JM(p)}$ satisfies Eq. (3) for each $p = +$ or $-$, and only nonnegative $\lambda$'s are coupled in the expansion (7). The parity-adopted $D$ function satisfies the following property, which is the origin of the BF Coriolis coupling [17,20]

$$(j_+ j_- + j_- j_+) \tilde{D}_{M}^{J(p)} = \hbar^{2}(1 + \delta_{\alpha,\beta})^{1/2} \Gamma(J, -\lambda) \tilde{D}_{M-1}^{J(p)}$$

$$
\times \left( \frac{\partial}{\partial \theta} - \lambda \cot \theta \right) + \hbar^{2}(1 + \delta_{\alpha,\beta})^{1/2} \Gamma(J, \lambda)$$

$$
\times \tilde{D}_{M+1}^{J(p)} \left( \frac{\partial}{\partial \theta} - \lambda \cot \theta \right),
$$

(9)

where

$$
\Gamma(J, \lambda) = [J(J+1) - \lambda(\lambda+1)]^{1/2}.
$$

The variable $R(t)$ in Eq. (1) or Eq. (3) is regarded as classical, and its time dependence is given by the expectation value of the Hamiltonian $H$ (i.e., energy conservation),

$$
E = \frac{\langle \Psi_{JM(p)} | H | \Psi_{JM(p)} \rangle}{\langle \Psi_{JM(p)} | \Psi_{JM(p)} \rangle}
$$

$$
= \frac{\mu}{2} \left( \frac{dR}{dt} \right)^{2} + \frac{\langle \Psi_{JM(p)} | H_{0} | \Psi_{JM(p)} \rangle}{\langle \Psi_{JM(p)} | \Psi_{JM(p)} \rangle},
$$

(11)

where $E$ is the total energy (hereafter, energies being measured from the bottom of the $H_2$ potential curve) and $\langle \rangle$ means the integration over the quantum mechanical variables.

### 2.2. Numerical method

We employ a grid representation algorithm [22–25] to solve Eq. (3). We introduce a set of grid-based functions, $u_{k}(r)$ and $\psi_{k}(\theta)$, which are constructed from orthogonal polynomials associated with grid points, $r_{k}$ ($k = 0,1,2, \cdots ,N$) and $\theta_{l}$ ($l = 1,2, \cdots ,M$), respectively.

As in paper I, we take Chebyshev polynomials for $u_{k}(r)$, i.e.,

$$
u_{k}(r) = \frac{2w_{k}^{1/2}}{r_{\text{max}}} \sum_{n=1}^{N} \sin \left( \frac{n\pi r_{k}}{r_{\text{max}}} \right) \sin \left( \frac{n\pi r}{r_{\text{max}}} \right),$$

(12)

where $w_{k} = r_{\text{max}}/(N + 1) \equiv \Delta r$; $r_{k} = k\Delta r$; and $r_{\text{max}}$ is taken large enough so that the calculated transition probabilities are not dependent on $r_{\text{max}}$. The function $\nu_{k}(r)$ satisfies the following properties

$$u_{k}(r_{k}) = w_{k}^{-1/2} \delta_{k,k'}, \langle u_{k} | u_{k'} \rangle = \delta_{k,k'}.$$  

(13)

For a homonuclear molecule, either even or odd molecular rotational quantum numbers $j$ are coupled in Eq. (3). Owing to this fact, the integration for $\theta$ can be taken only in the range $0 \leq \theta \leq \pi/2$. We hereafter consider the case of even $j$. Paper I shows that if only even $\lambda$ can be assumed in the expansion (7), the useful form of $\psi_{k}(\theta)$ is

$$
u_{k}^{(j)}(\theta) = w_{k}^{1/2} \sum_{n=0}^{M} \bar{P}_{2n}(\cos \theta) \bar{P}_{2n}(\cos \theta),$$

(14)

where $\bar{P}_{2n}(x) = (2n+1)^{1/2}P_{2n}(x)$ is the normalized Legendre polynomial; $x_{i} = \cos \theta_{i}$ is the zero point of $\bar{P}_{2n}(x)$; and $w_{k}^{(j)}$ is the quadrature weight. The function $\psi_{k}^{(j)}(\theta)$ satisfies

$$\psi_{k}^{(j)}(\theta) = w_{k}^{(j)}^{-1/2} \delta_{k,k'}, \langle \psi_{k}^{(j)} | \psi_{k'}^{(j)} \rangle = \delta_{k,k'}.$$  

(15)

When $\lambda$ is odd, however the form (14) is no more appropriate. This is easily understood by seeing the wavefunction of free rotation; that is, since the associated Legendre function with $\lambda = \text{odd}$ is always given by $P_{n}^{\lambda}(x) = (1 - x^{2})^{1/2} \times \text{(polynomials of } x)$,
the quadrature representation with a finite number of polynomials like Eq. (14) is inaccurate [26]. Instead of Eq. (14), we can find that the following form is very efficient for odd $\lambda$

$$v_{\ell}^\theta(\theta) = (w_{\ell}^\theta)^{1/2} \sin \theta \sum_{n=1}^{M+1} \overline{Q}_{2n}(\cos \theta) \overline{Q}_{2n}(\cos \theta),$$

(16)

where $\overline{Q}_{2n}(x) = [(2n + 1)(n + 1)/4n]^{1/2} p_{n}^{(1,1)}(x)$ is the normalized Jacobi (Gegenbauer) polynomial [27]; and $x = \cos \theta$ and $w_{\ell}^\theta$ are, respectively, the zero point and weight of $\overline{Q}_{2n}(x)$. It should be noted that $\sin \theta \times \overline{Q}_{2n}(\cos \theta)$ is just equal to the normalized associated Legendre function $P_{n}^{\ell+1}(\cos \theta)$. Eq. (16) satisfies

$$v_{\ell}^\theta(\theta) = (w_{\ell}^\theta)^{-1/2} \sin \theta \delta_{\ell,r}, \quad \langle v_{\ell}^\theta | v_{\ell'}^\theta \rangle = \delta_{\ell,r}. $$

(17)

Some workers constructed the grid-based function $v_{\ell}^\theta(\theta)$ for each $\lambda$ from the associated Legendre function $P_{n}^{\ell}(\cos \theta)$ [28–30]. This requires different grid points depending on each $\lambda$ for the $\theta$ coordinate. In the present study, the two sets of grid points, i.e., $\theta_{\ell}^e$ and $\theta_{\ell}^o$, are only needed.

Using the grid-based functions $u_{\ell}(r)$ and $v_{\ell}^\theta(\theta)$, and noticing the properties (13), (15), and (17), we can assume the wavefunction $\psi_{\ell}^{M}(r, \theta)$ in Eq. (7) as

$$\psi_{\ell}^{M}(r, \theta, t) = \sum_{k\ell r} \psi_{k\ell r}^{M}(r, \theta, t) u_{\ell}(r) v_{\ell}^\theta(\theta) ,$$

(18)

where we have put

$$\psi_{k\ell r}^{M}(r, \theta, t) = (w_{k}^{\ell} w_{r}^{\theta})^{1/2} \psi_{k\ell r}^{M}(r, \theta, t) \quad \text{for even } \lambda $$

(19a)

$$\psi_{k\ell r}^{M}(r, \theta, t) = (w_{k}^{\ell} w_{r}^{\theta})^{1/2} \psi_{k\ell r}^{M}(r, \theta, t) / \sin \theta_{\ell} \quad \text{for odd } \lambda $$

(19b)

Using Eqs. (7) and (18) and setting $r = r_{l}$ and $\theta = \theta_{l}^{e, o}$ in Eq. (3), we have a set of coupled linear differential equations with respect to $\psi_{k\ell r}^{M}(r, \theta)$,

$$\frac{d\psi_{k\ell r}^{M}(r, \theta, t)}{dt} = -i\hbar \left[ J(J+1) - 2\lambda^2 \left(\frac{1}{2\mu R^2} + \frac{1}{2mr_{l}^2}\right) \right] \times \sin^2 \theta_{l}^{e, o} \left( \frac{V(R, r_{l}, \theta_{l}^{e, o})}{h^2} \right) \psi_{k\ell r}^{M}(r, \theta, t) + \frac{i\hbar}{2\mu R^2} \left( \sum_{r} A_{l}^{r} \psi_{k\ell r}^{M}(r, \theta, t) \right)

+ \frac{i\hbar}{2\mu R^2} \left( 1 + \delta_{l, o} \right)^{1/2} \Gamma(J, -\lambda)

\times \left( \sum_{r} B_{l}^{r} \psi_{k\ell r}^{M-1}(r, \theta, t) + \frac{i\hbar}{2\mu R^2} \left( 1 + \delta_{l, o} \right)^{1/2} \Gamma(J, \lambda) \sum_{r} B_{l}^{r} \psi_{k\ell r}^{M+1}(r, \theta, t) \right)

(20)

where

$$A_{l}^{r} = \left( w_{k}^{\ell} w_{r}^{\theta} \right)^{1/2} \sum_{n=0}^{M} 2n(2n + 1)

\times \overline{Q}_{2n}(\cos \theta_{l}^{e}) \overline{Q}_{2n}(\cos \theta_{l}^{o}) \quad \text{for even } \lambda $$

(21a)

$$A_{l}^{r} = \left( w_{k}^{\ell} w_{r}^{\theta} \right)^{1/2} \sum_{n=1}^{M+1} 2n(2n + 1)

\times \overline{Q}_{2n}(\cos \theta_{l}^{e}) \overline{Q}_{2n}(\cos \theta_{l}^{o})

- \frac{1}{\sin^2 \theta_{l}^{e, o}} \delta_{l, o} \quad \text{for odd } \lambda, $$

(21b)

and

$$B_{l}^{r} = \left( w_{k}^{\ell} w_{r}^{\theta} \right)^{1/2} \sum_{n=1}^{M} \left[ 2n(2n + 1) \right]^{1/2}

\times \overline{Q}_{2n}(\cos \theta_{l}^{e}) \overline{Q}_{2n}(\cos \theta_{l}^{o})

- \lambda \cos \theta_{l}^{e, o} \left( w_{k}^{\ell} w_{r}^{\theta} \right)^{1/2} \sum_{n=1}^{M+1} \overline{Q}_{2n}(\cos \theta_{l}^{e}) \overline{Q}_{2n}(\cos \theta_{l}^{o})

\times \overline{Q}_{2n}(\cos \theta_{l}^{e, o}) \quad \text{for even } \lambda $$

(22a)
$$B_{i,j}^{+\pm} = \pm (w_i^0 w_j^\mp)^{1/2} \sum_{n=1}^{M} \left[ 2n(2n+1) \right]^{1/2} \left( \cos \theta_i^p \right) \left( \cos \theta_j^\mp \right) \left( \sin \theta_i^p \right) \left( \sin \theta_j^\mp \right) \times P_{2n}^c(\cos \theta_i^p) P_{2n}^c(\cos \theta_j^\mp)$$

From Eqs. (6) and (8), the mixing in Eq. (20) occurs among $\lambda = 0, 1, \ldots$ for $p = (1)^j$ and only among $\lambda = 1, 2, \ldots$ for $p = (1)^j$. The energy conservation (11) is explicitly given by

$$E = \frac{\mu}{2} \left( \frac{dR}{dt} \right)^2 - \text{Im} \left[ \hbar \sum_{\alpha k l} \left( \psi_{k l}^{(r)}(r, \theta, t) \right)^* \frac{\partial \psi_{k l}^{(r)}(r, \theta, t)}{\partial t} \right] \sum_{\alpha k l} |\psi_{k l}^{(r)}(r, \theta, t)|^2,$$

(23)

2.3. Transition probabilities and cross sections

As the initial condition, we can introduce

$$\psi^{(r)}(r, \theta, t = 0) = \chi_{i,j}^{r}(r) P_{J_j}^{\lambda_j}(\cos \theta) \delta_{\lambda_i \lambda_j},$$

(24)

where $\chi_{i,j}^{r}(r)$ is the vibrational wavefunction with the vibrational quantum number $v_i$ and $P_{J_j}^{\lambda_j}(\cos \theta)$ is the normalized associated Legendre function. From Eq. (24), Eq. (8) gives for $\lambda_i \geq 0$

$$\psi_{k l}^{(r)}(r, \theta, t = 0) = \left[ (1 + \delta_{k,0})/2 \right]^{1/2} \chi_{i,j}^{r}(r) P_{J_j}^{\lambda_j}(\cos \theta) \delta_{\lambda_i \lambda_j},$$

(25)

In this choice, we obtain $\sum_{\alpha k l} |\psi_{k l}^{(r)}(r, \theta, t)|^2 = (1 + \delta_{k,0})/2$ in Eq. (23).

It is convenient to define the following probability amplitude at $t = \infty$

$$C_{i,j}^{H}(t = \infty) = \left[ (1 + \delta_{k,0})/2 \right]^{1/2} \left\langle \psi_{k l}^{H}(r) \left| \psi_{k l}^{(r)}(r, \theta, t) \right\rangle \right\rangle(t = \infty).$$

(26)

Then, we can obtain from Eq. (8)

$$C_{i,j}^{(+)} = C_{i,j}^{(+)} + C_{i,j}^{(-)}(t = \infty),$$

(27a)

and

$$C_{i,j}^{(+)} = C_{i,j}^{(+)} - C_{i,j}^{(-)}(t = \infty).$$

(27b)

The relation

$$C_{i,j}^{(+)} = C_{i,j}^{(+)}(t = \infty)$$

is convenient to calculate the probability amplitude for $\lambda_i < 0$.

The probability for vibrational and rotational transition $v_i, J_i \rightarrow v_f, J_f$ is given by

$$P_f(v_i, J_i \rightarrow v_f, J_f) = \sum_{\lambda_i \lambda_f} \left| C_{i,j}^{(\pm)} \right|^2.$$}

(29)

We further define the rotationally summed transition probability $(v_i, J_i \rightarrow v_f)$ as

$$P_f(v_i, J_i \rightarrow v_f) = \sum_{J_f = 0}^{j_{\text{max}}} P_f(v_i, J_i \rightarrow v_f, J_f),$$

(30)

where $j_{\text{max}}$ is the highest rotational quantum number for which the molecule is bound for the vibrational state $v_f$. The cross-sections for transitions $v_i, J_i \rightarrow v_f, J_f$ and $v_i, J_i \rightarrow v_f$ are obtained by, respectively

$$\sigma(v_i, J_i \rightarrow v_f, J_f) = \frac{2J + 1}{k_{i,j}} \sum_{J_f = 0}^{j_{\text{max}}} P_f(v_i, J_i \rightarrow v_f, J_f),$$

(31a)

and

$$\sigma(v_i, J_i \rightarrow v_f) = \sum_{J_f = 0}^{j_{\text{max}}} \sigma(v_i, J_i \rightarrow v_f, J_f).$$

(31b)

where the wavenumber is given by $k_{i,j} = \sqrt{2\mu (E - e_{i,j})}/\hbar$ with $e_{i,j}$ being the vibrational/rotational energy of the molecule.

2.4. Decoupled approximations

We have also carried out the calculations by using the CS and IOS approximations. The CS approximation is obtained by neglecting the BF Coriolis coupling (9) and by setting $(\mathbf{J - j})^2 = J(J+1)$ in Eq.
The choice of the effective value for \((J - j)^2\) sometimes requires some attention for calculating a certain physical quantity [34]. However, no such worry is needed in the present case. In the CS approximation, \(\Lambda\) becomes conserved. This approximation has been used to study the dissociation process in paper I, and the details of the numerical method are given therein.

The IOS approximation assumes \((J - j)^2 = J(J + 1)\) and further \(j^2 = 0\) in Eq. (2) [35–37]. In the IOS approximation, the Hamiltonian \(H_0\) depends on the angle \(\theta\) only parametrically through the PES, and the rotational degrees of freedom are fully decoupled. The numerical calculation in this case is carried out in the same way as described in Ref. [9]. A detailed comparison between the semiclassical IOS and quan-

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**Fig. 1.** Rotational transition probabilities \(P(^v_i = 0, j_i = 0 \rightarrow ^v_f = 0, j_f)\) for \(J = 0, 40, 80, 100\) at \(E = 5\) eV, calculated by the accurate (AC), CS, IOS, and energy corrected (EC) IOS methods.
tum mechanical IOS calculations has been also made in paper I, and has shown the reliability of the semiclassical methodology.

2.5. Relevant numerical parameters

We use the ab initio PES for He + H₂ given by Varandas and Brandão [38]. This is the same as used in paper I. The calculation is carried out for the initial state \((v_i, j_i) = (0,0)\) at the total energies \(1 \leq E \leq 10\) eV. The transition probabilities have been evaluated at \(R = 8\) bohr. We have set \(r_{\text{max}} = 4\) bohr, \(N = 32\), \(M = 10\), and \(\lambda = 0.1,2\) are coupled in Eq. (20). For these choices, the probabilities are converged within a few percent for the transition to \(v_f < 5\). The calculation for the transition to very high vibrational states or for the dissociation requires

Fig. 2. Time dependence of the average molecular orientation \(\langle \theta \rangle\) in radian and of the average molecular distance \(\langle r \rangle\) in bohr (see text) for \((v_i, j_i) = (0,0)\) at \(E = 5\) eV. The calculations are carried out for \(J = 20\) and 40 by the accurate (AC) and CS methods. The time for the turning point is \(t_{\text{TP}} \sim 320\ \tau_0\). The time is measured in atomic unit \(\tau_0 = 2.42 \times 10^{-17}\) s.
much more computational time, and will be reported in the next study. The partial waves considered are $J \leq 200$.

3. Results and discussion

First, we consider the pure rotational excitation. Fig. 1 shows the probabilities for $v_i = 0, j_i = 0 \rightarrow v_f = 0, j_f$ at $E = 5$ eV. Comparison is made among the results of the accurate (AC), CS, and IOS calculations for partial waves $J = 0, 40, 80, 100$. We can see that the CS approximation is fairly good for all the partial waves, and the IOS approximation is not valid for low partial waves ($J \leq 40$). The present accurate calculation shows that most of the molecules are excited to high rotational states for low $J$. The

Fig. 3. Cross sections $\sigma(v_i = 0, j_i = 0, j_f = 0 \rightarrow v_f, j_f)$ in bohr$^2$ for $v_f = 0, 1, 2, 3$ at $E = 3$ eV, calculated by the accurate (AC), CS, and IOS methods.
IOS approximation cannot describe well such high rotational excitation. This is because the ES assumption is worse when higher rotational states are concerned [7]. To avoid this defect, energy correction is sometimes introduced in the IOS approximation. We have also calculated the energy corrected (EC) IOS method for $J = 0$, in which the collision energy is set to $E = \epsilon_{ij}$. Fig. 1 however shows that this correction is ineffective in the present case. As $J$ increases, the transition probabilities to high rotational states become small. Therefore, the ES assumption becomes valid for high $J$ although the excitation itself is less important. As a result, it is concluded that the IOS approximation is poor for the

Fig. 4. The same as Fig. 3 except for $E = 5$ eV.
calculation of the He + H₂ collisions whenever large angular momentum transfer occurs.

Paper I, based on the CS approximation, has shown that the dissociation in He + H₂ occurs through a certain specific (i.e., T-shape) configuration. To see how the T-shape configuration plays an important role in the mechanism of the vibrational excitation, we introduce the average molecular orientation \( \langle \theta \rangle \) and the average distance \( \langle r \rangle \), respectively defined by

\[
\langle \theta(t) \rangle = \sum_\lambda \langle \psi^{J\lambda}(t) | \theta | \psi^{J\lambda}(t) \rangle,
\]

\[
\langle r(t) \rangle = \sum_\lambda \langle \psi^{J\lambda}(t) | r | \psi^{J\lambda}(t) \rangle.
\]
In the IOS approximation, all the molecular orientations are equally possible, and hence we have always $\langle \theta \rangle = 1$. Fig. 2 plots the time dependence of $\langle \theta \rangle$ and $\langle r \rangle$ in the collisions with $J = 20$ and 40 at $E = 5$ eV. Both the accurate and CS results show that the molecular orientation is biased to $\pi/2$ at $t = 300 \sim 450 \ t_0$ ($t_0 = 2.4189 \times 10^{-17}$ s being the atomic unit of time). During this time duration, the He atom is present in the neighborhood of the molecule (i.e., $R \sim \langle r \rangle$), and the molecular distance $\langle r \rangle$ is stretched more and more as $\langle \theta \rangle$ approaches to $\pi/2$. At $t > 500 \ t_0$, the He atom is sufficiently far.

Fig. 6. Opacities $(2J+1)P^J(\nu_i = 0, j_i = 0 \rightarrow v_f)$ as a function of $J$ for $v_f = 1, 2, 3, 4$ at $E = 5$ eV, calculated by the accurate (AC), CS, and IOS methods.
away from the molecule, and \( \langle r \rangle \) begins oscillation, which means that the molecule is vibrationally excited. Thus, we can see that the important impulse leading to the vibrational excitation works around the T-shape configuration. We find that the CS approximation cannot reproduce very well the accurate \( \langle \theta \rangle \). However, it is interesting that the CS result is very good for \( \langle r \rangle \). In any way, the present accurate calculation also shows the importance of the T-shape configuration in the excitation mechanism.

Fig. 7. Energy dependence of the cross sections \( \sigma(v_i = 0, j_i = 0 \rightarrow v_f) \) in bohr\(^2\) for \( v_f = 1, 2, 3, 4 \), calculated by the accurate (AC), CS, and IOS methods.
Fig. 2 indicates that the orientational preference is stronger for lower \( J \). This fact also suggests that the IOS approximation is worse for lower \( J \).

Figs. 3–5 show the cross-sections for \( 0,0 \to v_f, j_f \) as a function of the final rotational quantum number \( j_f \) for each \( v_f \) (i.e., the rotational distribution) at \( E = 3, 5, \) and \( 8 \) eV, respectively. The CS results are slightly larger than the accurate values when \( v_f = v_i (=0) \), and are smaller (except for high \( j_f \)) when \( v_f > v_i \). Regardless of the collision energies, the CS results are almost satisfactory both qualitatively and quantitatively. At the high energy (\( E = 8 \) eV), the molecule is excited to very high rotational states especially for \( v_f > v_i \). Such large angular momentum transfer might affect the orbital motion, and the CS method might be a failure because the conservation of the total angular momentum is not accurately taken into account in this approximation. However, an agreement between the CS and accurate results is good at the high energy. Therefore, the present study shows that the CS approximation works satisfactory even for the collisions with large angular momentum transfer. On the other hand, Figs. 3–5 show that the IOS cross sections are poor in most cases. When \( v_f > v_i \), in particular, the IOS rotational distributions become even qualitatively different from the accurate ones at higher energies: the IOS distribution has the maximum value always at \( j_f = 0 \) though the accurate and CS ones do not. For \( v_f = v_i \), however, the IOS method becomes better with increasing energy. We expect that the IOS cross sections for \( v_f = v_i \) become accurate when the energy is sufficiently high. Green et al. [1] found the same result that the IOS cross-sections were good for \( v_f = v_i \), but not so for \( v_f \neq v_i \) by comparing the quantum mechanical CS and IOS calculations for H + CO at collision energies of 0.7–1.9 eV. For \( v_f = v_i \), the contribution to the cross section comes from very high partial waves, where the IOS approximation is better as mentioned previously.

Fig. 6 shows the opacities, defined by \( (2J + 1)^2 P_f (00 \to v_f) \), as a function of \( J \) for \( v_f > v_i \) at \( E = 5 \) eV. With increasing \( v_i \), higher partial waves become less important. The CS result shows somewhat large deviation from the accurate one for \( J > 50 \). When the angular momentum \( J \) is high, the CS assumption is not expected valid because the Coriolis coupling (9) becomes important. Nevertheless, as seen in the figure, such high partial waves have only small contribution to the cross section. Therefore, the defect of the CS approximation is not significant in the present case. It should be noted, however, that the CS approximation is good even for very high partial waves (\( J \geq 80 \)) when the \( v_f = v_i \) transition is considered (Fig. 1). Finally, we consider the rotationally summed vibrational excitation cross section. Fig. 7 summarizes the energy dependence of the cross sections \( \sigma (00 \to v_f) \) for \( v_f = 1, 2, 3 \) and 4. Figs. 3–5 show that the IOS approximation cannot describe well the rotational distribution. As seen in Figs. 6 and 7, when we consider the rotationally summed opacities or cross sections, the IOS approximation seems to be not so bad for low \( v_f \). Table 1 shows the relative deviation of the rotationally summed CS and IOS cross-sections from the accurate value. The IOS approximation is no more valid for \( v_f = 3 \) and 4 at the low energy, and becomes somewhat tolerable for \( v_f = 1–4 \) at the high energy. On the other hand, as expected, the CS cross-sections agree well with the accurate results for all \( v_f \)’s in the whole energy range considered here.

### Table 1

Percent errors of the rotationally summed vibrational excitation cross sections in the CS and IOS approximations, \( 100 \times (\sigma_{\text{CS,IOS}} - \sigma_{\text{AC}}) / \sigma_{\text{AC}} \), where \( \sigma_{\text{AC}}, \sigma_{\text{CS}}, \) and \( \sigma_{\text{IOS}} \) are the accurate, CS, and IOS results, respectively. The transitions are \( v_f = 0, j_f = 0 \to v_f = 1, 2, 3, 4 \); and the energies are \( E = 5 \) and \( 10 \) eV.

<table>
<thead>
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<th>( v_f )</th>
<th>( E = 5 ) eV</th>
<th>( E = 10 ) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>IOS</td>
</tr>
<tr>
<td>( v_f = 1 )</td>
<td>-15.2</td>
<td>-30.2</td>
</tr>
<tr>
<td>( v_f = 2 )</td>
<td>-23.3</td>
<td>-7.3</td>
</tr>
<tr>
<td>( v_f = 3 )</td>
<td>-25.8</td>
<td>43.2</td>
</tr>
<tr>
<td>( v_f = 4 )</td>
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<td>127.6</td>
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4. Summary

We have studied the vibrational and rotational excitation in He + H\(_2\) at energies \( 1 \leq E \leq 10 \) eV by employing the semiclassical theory. The present numerical technique enables us to consider all the rotational degrees of freedom accurately. The present
A semiclassical method is very useful in the study of high energy molecular collisions where reliable quantum mechanical calculations are impossible.

As far as the rotationally summed excitation cross-section is concerned, the IOS approximation may be tolerable for small changes \( |v_f - v_i| \). However, the IOS method gives poor results for the rotational distribution, and is not useful to understand the details of the collision dynamics. On the whole, the present study and paper I together reveal that the IOS approximation is no more applicable in the collisions where large energy transfer or molecular dissociation takes place. The IOS approximation is less reliable than one expected.

On the other hand, the CS approximation is almost satisfactory not only for rotationally summed vibrational excitation but also for rotational distribution. This result is true without regard to the amount of transferred energy or of transferred angular momentum. Therefore, we can expect that the CS approximation is reliable enough also for dissociation processes. The conclusions of paper I based on the CS approximation would be valid. The CS approximation is very powerful to investigate the collision dynamics in the suprathermal energy region.

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References