

A quantum mechanical study of $\text{He} + \text{H}_2 \rightarrow \text{He} + \text{H} + \text{H}$ in the energy range 5–10 eV

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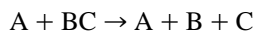
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Abstract

The collision-induced dissociation process in $\text{He} + \text{H}_2$ is studied quantum mechanically using the infinite-order sudden approximation. The dissociation cross sections for the initial vibrational states $v = 0-9$ are reported in a wide range of the total energy 5–10 eV and the rate constants are calculated in the temperature range 1000–10000 K. The dissociation cross sections are strongly dependent on v . It is found that the details of interaction potential strongly affect the dissociation dynamics for low v . The reliability of the classical trajectory method is discussed. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Collision-induced dissociation (CID)



is an important process in various fields of research such as shock-wave experiments [1], astrophysics [2], tandem mass spectrometry [3] and atom-surface scattering processes [4]. Furthermore, since CID is a reverse process of three-body recombination [5] which has not yet been well studied, a detailed investigation of CID would be helpful to understand the dynamics of three-body recombination.

Almost all the previous quantum mechanical studies of CID have assumed some particular collision configurations such as collinear or T shape [6–13]. Thus we cannot claim that the quantum mechanical CID dynamics has been satisfactorily clarified. A lot of three-dimensional (3D) quasi-classical trajectory (QCT) calculations have also been carried out [14–19]. However, in the collinear and T-shape colli-

sions, the quantum mechanical and semiclassical studies have shown that the QCT method does not work well near the dissociation threshold, especially for low vibrational states [6,20–22]. Therefore, it is important to carry out accurate 3D quantum mechanical calculations of CID, not only for understanding the dynamics correctly, but also for examining the reliability of the QCT method.

Unfortunately, however, it is still not possible to carry out an exact 3D quantum mechanical calculation for CID. This was also true even if one introduces the decoupling methods such as centrifugal sudden (CS) [23] or infinite-order-sudden (IOS) [24] approximations. Recently, however, Pan and Bowman [25] and the present authors [26] (hereafter referred to as I) succeeded in making the 3D calculations of CID using the IOS approximation. Particularly in paper I, the direct numerical method to solve the Schrödinger equation developed by Sakimoto and Onda [8] was successfully utilized to clarify the

dynamics. This method is much more powerful than the standard close-coupling techniques [11,12,25].

In paper I, the dissociation cross section was calculated only at the total energy $E = 8$ eV. In this work, we have extended the calculation to a wider energy range $E = 5$ –10 eV, although the dissociation cross sections are reported only for v (vibrational quantum number) = 0–9. The calculations still require a lot of computational time for high vibrational states. It should also be noted that one of the present authors [27,28] has introduced a vibrational sudden approximation for CID, which is suitable for studying the CID for high vibrational states. The dissociation rate constants are also evaluated in the temperature range $T = 1000$ –10000 K.

2. Method of calculations

Since the present numerical method is the same as that of I, only a brief outline is given below. In the IOS approximation [24], the Coriolis coupling is neglected and the rotation of the diatomic molecule is frozen during the collision and the Schrödinger equation is given by

$$\left[-\frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R - \frac{\hbar^2}{2\mu_{H_2} r} \frac{\partial^2}{\partial r^2} r + \frac{\tilde{l}(\tilde{l}+1)}{2\mu R^2} + \frac{\tilde{j}(\tilde{j}+1)}{2\mu_{H_2} r^2} + V(R, r, \gamma) \right] \Psi(R, r) = E\Psi(R, r), \quad (1)$$

where R is the intermolecular distance between He and the center-of-mass of H_2 , r is the internuclear distance of H_2 , μ is the atom-molecule reduced mass, μ_{H_2} is the reduced mass of H_2 and E is the total energy measured from the bottom of the potential well of H_2 . The quantities \tilde{l} and \tilde{j} represent the effective orbital and molecular rotational angular momentum quantum numbers, respectively. We employ the potential energy surface (PES), $V(R, r, \gamma)$, obtained by Varandas and Brandao [29], where γ is the molecular orientation angle between \mathbf{R} and \mathbf{r} . We have assumed $\tilde{l} = l$ (the initial one) and $\tilde{j} = 0$. The numerical method used here to solve Eq. (1) is described in detail in I. Once we obtain the scattering matrix elements $S_{v'v}^l(\gamma)$ for the transition $v \rightarrow v'$ as a

function of γ , the state-to-state cross section is evaluated from [24]

$$\sigma(j'v' \leftarrow jv) = \frac{\pi}{k_{jv}^2} \frac{1}{2j+1} \sum_l \sum_{m_j} (2l+1) |\langle j'm_j | \delta_{v'v}^l(\gamma) | jm_j \rangle|^2, \quad (2)$$

where k_{jv} is the channel wave number and j and j' are the initial and the final rotational quantum number, respectively. Here, for simplicity, we have used the notation v to represent not only the vibrational state but also the vibrational continuum. The total cross section is given by

$$\begin{aligned} \sigma_{jv}^T &= \sum_{v'}^{\text{all}} \sum_{j'}^{\infty} \sigma(j'v' \leftarrow jv) \\ &= \sum_{v'}^{\text{all}} \frac{\pi}{2k_{jv}^2} \int_0^\pi d\gamma \sin\gamma \sum_l (2l+1) \\ &\quad \times |\delta_{v'v}^l - S_{v'v}^l(\gamma)|^2, \end{aligned} \quad (3)$$

where the summation with respect to v' is taken over all the final bound and continuum vibrational states. Furthermore, we define the total cross section for the bound to bound transitions by

$$\begin{aligned} \sigma_{jv}^B &= \sum_{v'}^{14} \sum_{j'}^{\infty} \sigma(j'v' \leftarrow jv) \\ &= \sum_{v'}^{14} \frac{\pi}{2k_{jv}^2} \int_0^\pi d\gamma \sin\gamma \sum_l (2l+1) \\ &\quad \times |\delta_{v'v}^l - S_{v'v}^l(\gamma)|^2. \end{aligned} \quad (4)$$

Here, we have assumed that all j' 's are allowed as the bound states for $v' = 0$ –14. Then, the dissociation cross section for the initial vibrational state v may be defined by

$$\begin{aligned} \sigma_{\text{diss},jv} &= \sigma_{jv}^T - \sigma_{jv}^B \\ &= \frac{\pi}{2k_{jv}^2} \int_0^\pi d\gamma \sin\gamma \sum_l (2l+1) P_{\text{diss},v}^l(\gamma), \end{aligned} \quad (5)$$

where $P_{\text{diss},v}^l(\gamma)$ is the γ -dependent dissociation probability given by

$$P_{\text{diss},v}^l(\gamma) = 1 - \sum_{v'=0}^{14} |S_{v'v}^l(\gamma)|^2. \quad (6)$$

It should be noted that Eqs. (3)–(5) are actually independent of the initial rotational state j . However,

since $\tilde{j}=0$ is assumed in Eq. (1), the present results will be valid only for low j . The initial-state specified dissociation rate constant can be calculated from

$$k_{\text{diss},jv}(T) = \sqrt{\frac{8\kappa T}{\pi\mu}} (\kappa T)^{-2} \times \int_0^\infty dE_{\text{tr}} \sigma_{\text{diss},jv}(E_{\text{tr}}) E_{\text{tr}} \exp\left(\frac{-E_{\text{tr}}}{\kappa T}\right), \quad (7)$$

where T is temperature, κ is the Boltzmann constant and E_{tr} is the translational energy.

3. Results and discussion

Fig. 1 shows the dissociation cross sections for $v = 0-9$ as a function of the total energy E . The arrow in the figure indicates the dissociation limit D ($= 4.75$ eV), above which the CID is energetically possible for all vibrational states. The dissociation cross sections increase with increasing v for a fixed total energy E (i.e. vibrational enhancement). The

vibrational enhancement has been pointed out in early studies [6,14–16,18–22]. In our previous calculation of $\text{He} + \text{H}_2$ with $l=0$ [13], the dissociation probability shows the vibrational enhancement at $E \leq 10$ eV for $\gamma=0$, but does not for $\gamma=\pi/4$ and $\pi/2$. However, the present IOS study confirms that the vibrational enhancement always occurs in the total dissociation cross section over a wide energy range.

Fig. 1 also indicates that actual thresholds i.e. dynamical thresholds, are much higher than the dissociation limit D and shift to higher energies with decreasing v . These dynamical thresholds $E_{\text{dyn}}(v)$ can be defined unambiguously by fitting the cross sections to an analytical function proposed by Parks et al. [30] i.e.

$$\sigma_{\text{diss},v} = A_v (E - E_{\text{dyn}}(v))^{n_v} / E_{\text{tr}}, \quad (8)$$

where A_v and n_v are v -dependent adjusting parameters. The fitting parameters and the dynamical thresholds are listed in Table 1. The dynamical threshold for $v = 9$ is almost the same as the

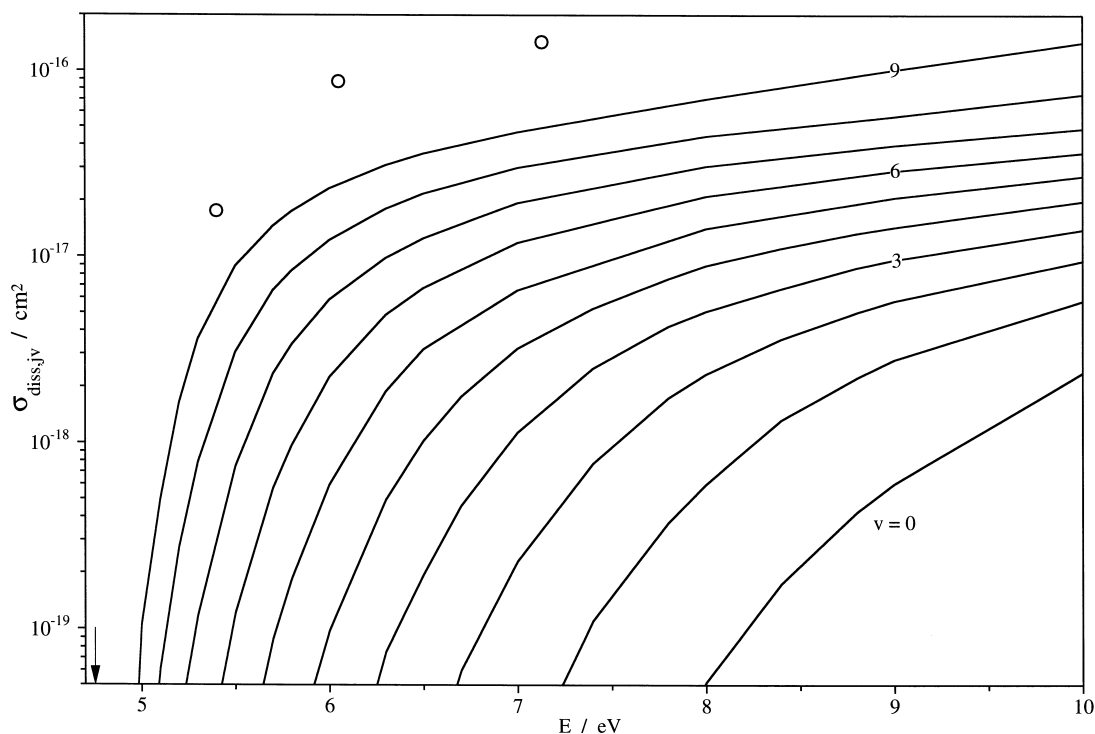


Fig. 1. Dissociation cross sections for $v = 0-9$ as a function of total energy. The arrow indicates the dissociation limit (4.75 eV). Open circles are the results of the classical trajectory calculation by Dove and Raynor [16].

Table 1

Fitting parameters and the dynamical thresholds for $v=0-9$. ${}^{\text{QCT}}E_{\text{dyn}}(v)$ means the classical dynamical thresholds for $(v,j)=(0,0)$ and $(9,0)$ obtained by Dove and co-workers [16,17]

v	A_v	n_v	$E_{\text{dyn}}(v)$ (eV)	${}^{\text{QCT}}E_{\text{dyn}}(v)$ (eV)
0	1.55(-18) ^a	2.8	7.4	11.4
1	3.05(-18)	2.47	6.82	—
2	4.6(-18)	2.26	6.38	—
3	7.5(-18)	2.05	6.08	—
4	8.8(-18)	2.07	5.78	—
5	1.05(-17)	2.05	5.5	—
6	1.5(-17)	1.95	5.35	—
7	2.1(-17)	1.86	5.2	—
8	2.8(-17)	1.85	5.07	—
9	4.2(-17)	1.83	4.97	4.96

^a Numbers in parentheses are multiplicative power of 10.

dissociation limit, but that for $v=0$ is higher than D by 2.65 eV. The dynamical threshold for $(v,j)=(0,0)$ evaluated from the QCT calculation is also much higher than the dissociation limit in $\text{He} + \text{H}_2$ [17], but the result is quite different from the present IOS value as shown in Table 1. The QCT estimate for high vibrational state (and $j=0$) [16], however, seems to be all right (see the case of $v=9$ in Table 1). This is basically due to the fact that the QCT method cannot be reliable for low vibrational states. This will be discussed later more deeply. It would be worthwhile to note that when the collision system has a rearrangement channel i.e. reactive channel, the dynamical threshold mostly coincides with the dissociation limit even for $v=0$ [7,17,18]. Whether the system has a rearrangement channel or not is an important factor in the CID dynamics especially for low vibrational states. The studies of collinear dynamics have revealed that the existence of a rearrangement channel can promote the dissociation at energies just above the dissociation limit [7,18,31]. In most of the non-reactive systems, the interaction between an atom and a diatomic molecule is simply repulsive and hence the CID rarely occurs at energies just above the dissociation limit, especially in the case of low vibrational states.

Using the QCT method, Dove and co-workers reported the CID cross sections for the $\text{He} + \text{H}_2$ system for various high rotational and vibrational states [16,17]. However, in the case of low rotational states ($j \sim 0$), they showed the cross sections only for a few vibrational states. In Fig. 1, the results of

Dove and co-workers are also plotted for $(v,j)=(9,0)$. The dissociation cross sections obtained by the present IOS and their QCT calculations do not agree well with each other, although the corresponding dynamical thresholds are in good agreement with each other as mentioned above. The QCT result is available for $(v,j)=(0,0)$. However, its dynamical threshold is too high (Table 1) and the QCT cross

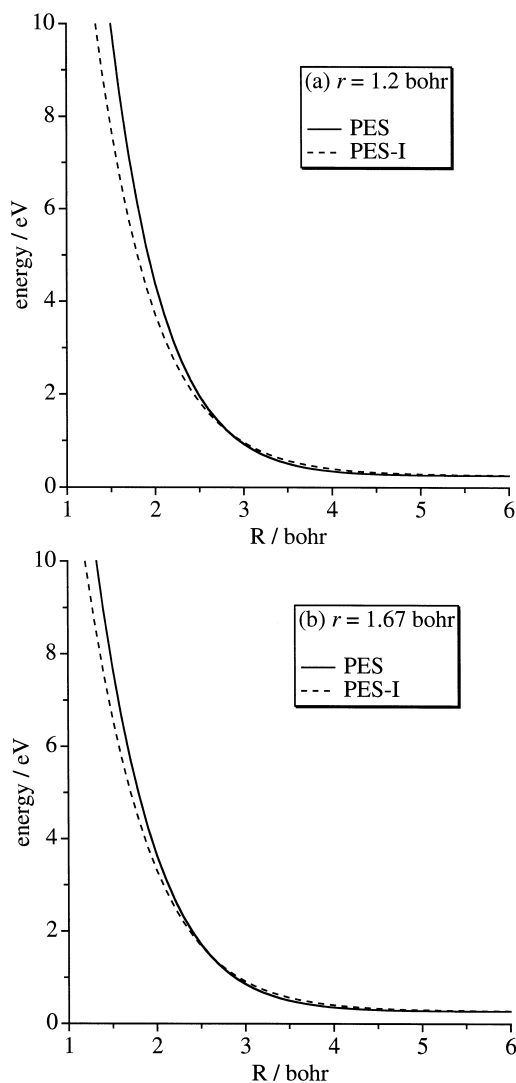


Fig. 2. $\text{He}-\text{H}_2$ interaction energy of the original PES (solid line) and the PES-I (broken line) as a function of R . The internuclear distance of H_2 is fixed at (a) 1.2 bohr (inner classical turning point of the $v=0$ vibrational state) and at (b) 1.67 bohr (outer turning point).

section is more different from the present results for $(v, j) = (0, 0)$.

Let us consider the reason for the disagreement between the IOS and QCT results. First of all, it should be noted that the presently used PES is different from that used by Dove and co-workers. Unfortunately, we could not reproduce exactly the same PES as that of Dove and co-workers because they did not give an explicit equation form of the two body term for H–H. Therefore, we have carried

out an IOS calculation by using a PES similar to theirs (referred to as PES-I), in which the two-body term for H–H is the same as the present one but the two-body He–H and the three body terms are replaced by those of Dove and Raynor [16]. Fig. 2 shows the He–H₂ interaction energy of the original PES and the PES-I as a function of R , where the H₂ distance is fixed at the inner ($r = 1.2$ bohr) and outer ($r = 1.67$ bohr) classical turning points of the $v = 0$ vibrational state. No big difference exists be-

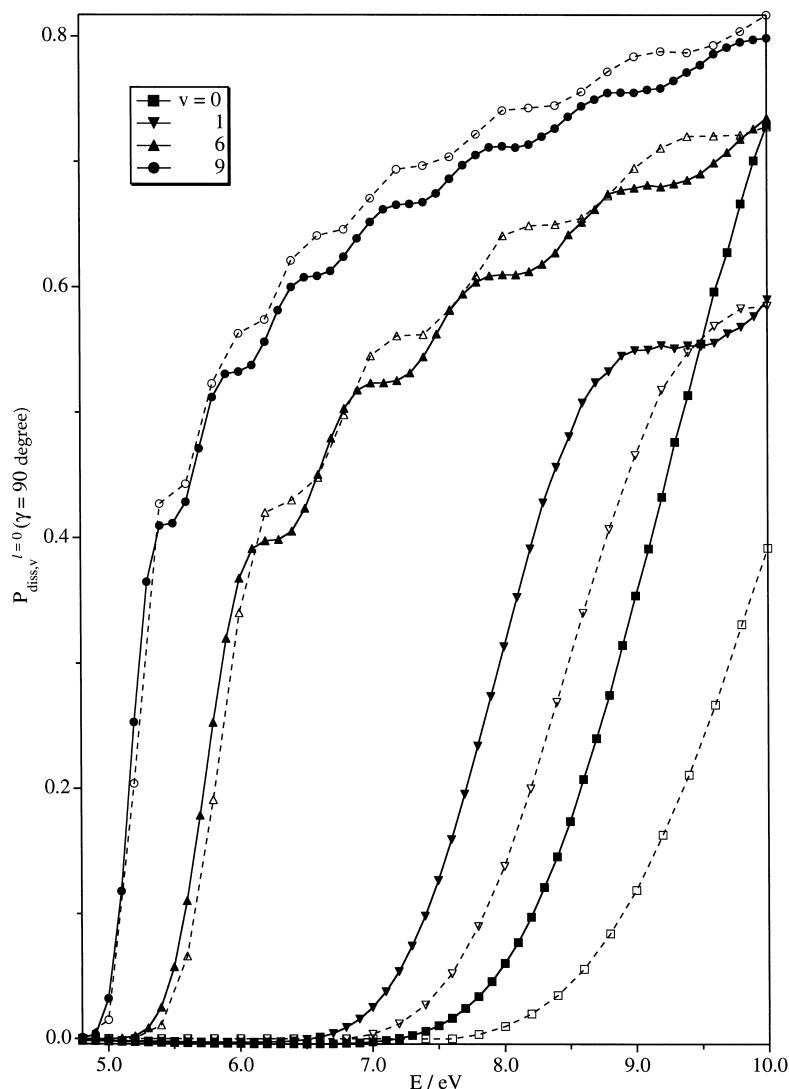


Fig. 3. Dissociation probabilities for $v = 0, 1, 6$ and 9 at $\gamma = 90^\circ$ as a function of total energy (solid lines). The broken lines are corresponding dissociation probabilities obtained by using PES-I (see, text).

tween the two PESs except that the present one is slightly more repulsive. Since in paper I the CID was confirmed to mainly occur at $\gamma \sim 90^\circ$ except for extremely high vibrational states, we have made the IOS calculations at $\gamma = 90^\circ$ and $l = 0$. The results for $v = 0, 1, 6$ and 9 are shown in Fig. 3. The two results are quite similar for the high vibrational states $v = 6$ and 9 , but are different in the case of the low vibrational states $v = 0$ and 1 . As v decreases, PES-I gives much smaller dissociation probabilities

than the original PES. This is in accord with the 3D results mentioned above. Since the original PES is more repulsive than the PES-I, the dissociation would occur more frequently on the original PES. Nevertheless, it is rather surprising that only a slight difference in PES largely affects the dissociation dynamics. In the case of low vibrational states, we thus come to the natural conventional conclusion that a high accuracy of PES is needed. For high vibrational states, as shown by one of the present authors [27,28],

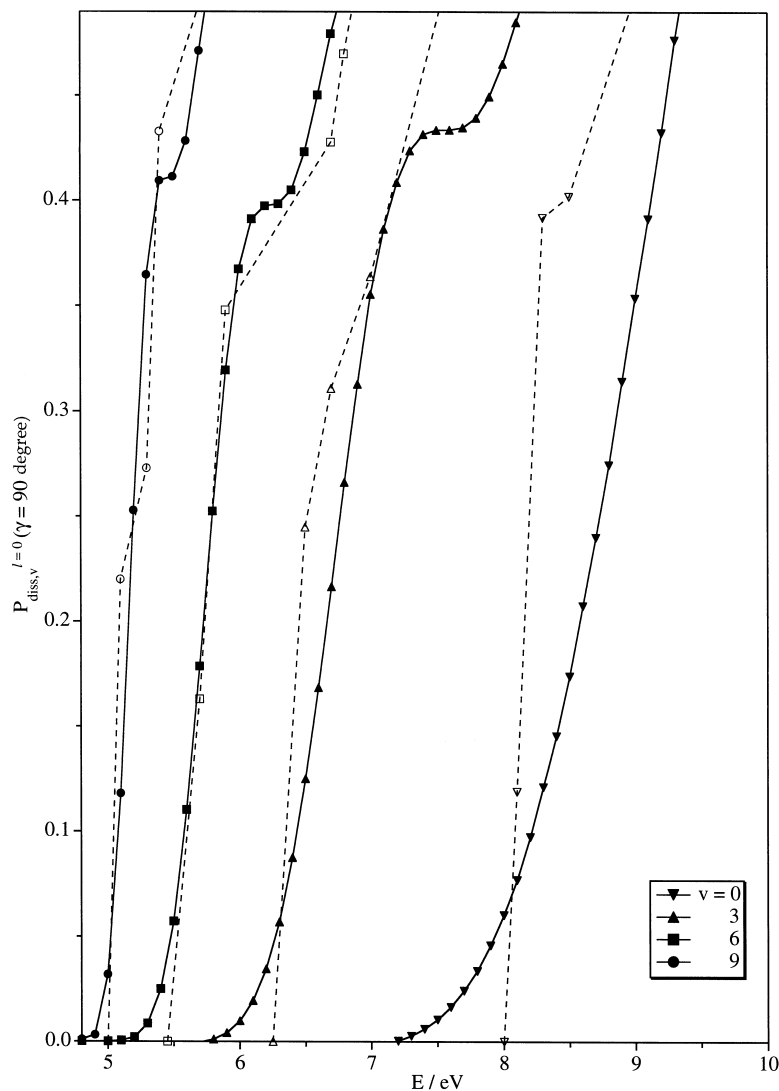


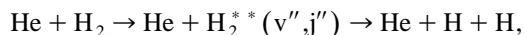
Fig. 4. Dissociation probabilities for $v = 0, 3, 6$ and 9 at $\gamma = 90^\circ$ as a function of total energy (solid lines). The broken lines are the corresponding dissociation probabilities of a classical trajectory calculation.

the CID dynamics is roughly determined by the geometrical size of a molecule. This implies that the CID is rather insensitive to the details of the PES.

Secondly, we have to check the reliability of the QCT method, especially for low vibrational states. In fact, the collinear and T-shape studies indicated that the QCT method was not valid for small v at energies near dissociation threshold [6,20–22], where the contribution of the classically forbidden motion is significant. In order to further confirm this, we have done a QCT calculation using the original PES for $v = 0, 3, 6$ and 9 at $\gamma = 90^\circ$ and $l = 0$. Fig. 4 depicts a comparison between this QCT calculation and the present IOS result. The agreement is relatively good for $v = 9$, but poor for $v = 0$. Since the angle region $\gamma \sim 90^\circ$ gives a large contribution to the 3D cross section, we can expect a similar discrepancy in the total dissociation cross section.

The last question is the accuracy of the present IOS method. We expect that the approximation is not so bad for the study of CID, because the short range interaction plays a dominant role and the kinetic energy is usually much higher than the rotational energy spacing unless the total energy is very close to the dissociation limit. Furthermore, the validity of the approximation becomes better for low vibrational states because the kinetic energy is higher. For high vibrational states, however, we should reconsider the definition of the dissociation cross section in the present IOS formalism. To derive the dissociation cross section Eq. (5), we have made the summation over all, actually an infinite number of, final rotational states (see, Eqs. (3) and (4)). In reality, the number $N_j(v)$ of rotational states which support bound states is finite [32]. When v is low, this number N_j is sufficiently large so that the above summation would probably be quite accurate. When v is high, however, only a small number of rotational states are allowed as bound states (e.g. $N_j(v = 14) = 4$). Consequently, the present method based on Eq. (5) may largely underestimate the dissociation cross section. This might be the main reason why the IOS cross section is smaller than that of the QCT calculation for $v = 9$.

Another problem is that we did not consider the indirect dissociation process;



where $\text{H}_2^*(v'', j'')$ represents a quasibound state supported by the centrifugal barrier. This indirect process was taken into account in the QCT study and was found to enhance the dissociation cross section for high rotational states [16]. It is not certain how much these indirect processes contribute to the over all CID in the case of low rotational states. In any case, the present IOS calculation somewhat underestimates the dissociation cross section by neglecting these indirect processes.

4. Concluding remarks

We have made quantum mechanical calculations of the CID in $\text{He} + \text{H}_2$ at total energies 5–10 eV by using the IOS approximation. The vibrational enhancement i.e. the increase of cross section with increasing vibrational quantum number v , was confirmed in the energy range considered here. The dynamical threshold for $v = 0$ is much smaller than that of the QCT calculations obtained by Dove and co-workers [16,17]. This causes a significant difference in the dissociation rate constants at low temperatures for low vibrational states. In Table 2, the dissociation rate constants based on the present results are shown for $T = 1000, 2000, 3000, 6000$ and 10000 K.

The present study implies that the previous QCT results for low vibrational states should be reconsidered more carefully, especially at energies near the

Table 2
Dissociation rate constants ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for $v = 0-9$

v	T (K)				
	1000	2000	3000	6000	10000
0				1.61(–18)	6.73(–16)
1				2.94(–17)	5.91(–15)
2				2.60(–16)	2.64(–14)
3			1.25(–19)	1.68(–15)	9.19(–14)
4			2.67(–18)	8.84(–15)	2.77(–13)
5			4.20(–17)	4.03(–14)	7.59(–13)
6		2.54(–18)	5.12(–16)	1.59(–13)	1.90(–12)
7		6.46(–17)	4.93(–15)	5.52(–13)	4.38(–12)
8		1.20(–15)	3.85(–14)	1.74(–12)	9.61(–12)
9	1.03(–17)	1.66(–14)	2.47(–13)	5.06(–12)	2.11(–11)

^a Numbers in parentheses are multiplicative power of 10.

dynamical thresholds. The QCT calculation may give a too high dynamical threshold. This is because the classically forbidden motion is important in the dynamical threshold region. When v is high, the explicit consideration of the molecular rotational states is needed because the number of rotationally bound states becomes small and furthermore the indirect dissociation processes become non-negligible. The effect of the rotational states has been ignored in the present calculation, and will be studied in the future work.

Finally, a conventional but interesting question is how sensitive are the dissociation dynamics to the details of the PES? The present study has confirmed that a high accuracy is required for PES when low vibrational states are considered. When v increases, however, the dynamics becomes rather insensitive to the details of the PES.

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