Isotope effect of quantum mechanical collinear He + H₂⁺ reaction at energies below and above the dissociation threshold

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Accurate time-independent quantum mechanical calculations have been carried out for collinear He + XH⁺, HX⁺, X⁺ (X = Mu, H, D, T) collisions on a realistic potential-energy surface at total energies of 1–6 eV. The present paper provides an entire view of the reaction features over a wide range of energies both below and above the dissociation threshold. At energies below the dissociation threshold, the resonance structure seen in the exchange reaction is studied for the isotope combinations mentioned above. At energies above the dissociation threshold, the effect of isotope variations on the competition between the exchange and dissociation reactions is discussed.

1 Introduction

Recent theoretical progress has made it practicable to perform accurate three-dimensional (3D) quantum mechanical calculations of atom–diatom reaction processes. Nevertheless, such calculations have been limited to low-energy reactions, and extension of the procedure to the high-energy region still requires further effort. At high energies, the inelastic, exchange and dissociation processes

$$A + BC(v) \rightarrow A + BC(v')$$

$$\rightarrow AB(v'') + C$$

$$\rightarrow A + B + C$$

become equally important. (Here, v, v' and v'' are vibrational quantum numbers, and we neglect the electronically non-adiabatic transition.) In the commonly employed quantum mechanical methods, like the close-coupled approach, description of the dissociation process is difficult compared with that of the inelastic or exchange process. However, investigation of the reaction dynamics over a wide range of energies is very important. It will be of particular interest to see how the exchange process is influenced by the absence or the presence of the dissociation channel. For this purpose, the reaction processes must be calculated with the same, sufficient accuracy at energies both below and above the dissociation threshold. Developing an accurate quantum mechanical approach for the high-energy reaction is also a challenging problem.

As far as collinear dissociation collisions are concerned, many quantum mechanical studies have been carried out. However, most of them considered simplified model systems. Recently, an accurate quantum mechanical calculation has become possible for non-reactive and reactive systems on realistic potential-energy surfaces (PES). Some interesting quantum mechanical effects have been found in the dissociation process. Very recently, quantum mechanical 3D calculations of non-reactive dissociation collisions have been carried out by using an infinite order sudden (IOS) approximation. However, IOS calculations are extremely expensive, and furthermore, the application of the IOS approximation to a reactive system is not so simple as that to a non-reactive system. At the present time, therefore, only in collinear calculations can we study the reactive collisions quantum mechanically over a wide range of energies both below and above the dissociation threshold.

Low-energy collinear He + H₂⁺ collisions are of interest for observing the effect of resonance on the exchange reaction. Recently, while making an accurate time-independent quantum mechanical calculation, Sakimoto and Onda have shown that the exchange reaction is very rich in resonances even at energies just below the dissociation threshold and even for very high initial vibrational states, v. This result was confirmed later by Balakrishnan and Sathyamurthy employing the time-dependent wavepacket propagation approach. Very recently, most of the He + H₂⁺ resonances have been assigned in terms of periodic classical trajectories. Several quantum mechanical 3D studies have been carried out for He + H₂⁺. Resonances are found also in the 3D collisions with the total angular momentum J = 0. On the other hand, for collinear He + H₂⁺ collisions at energies above the dissociation threshold, an accurate quantum mechanical calculation has been performed using the same method as that used in ref. 31. From the results of ref. 24 and 31, we have a complete picture of the He + H₂⁺ reaction over a wide range of energies (E ≤ 7 eV), with the same accuracy.

To study how the combination of system masses characterizes the reaction process is very helpful for obtaining a better understanding of the reaction dynamics. In the present work, we focus attention on the isotope effect on the collinear He + H₂⁺ reaction. We consider the resonances and also the competition between the exchange and dissociation processes. The resonance process will be affected markedly by the replacement of the atomic constituents with their isotopes. So far, the isotope effect has not been studied in detail for the He + H₂⁺ resonances. In dissociation on the whole, several collinear quantum mechanical calculations have been carried out to study the mass effect. These studies have shown that the mass kinematical factor plays a significant role in dissociation. However, these studies have assumed simplified model PESs or fictitious mass combinations. In ref. 24, the dissociation process for variations of isotopes were also investigated. The isotope combinations of ⁴He + ¹H₂⁺, ³He + XT⁺ (X = Mu, H, T) were considered. Of these, the ³He + T₂⁺ system is especially interesting since it realizes equal-mass constituents (the mass of ³He being identical to that of T). In the normal ⁴He + H₂⁺ case, the exchange reaction always dominates the dissociation. However, ref. 24 shows a strikingly different feature for the equal-mass combination. This suggests that a very interesting mass effect can be

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observed experimentally. In ref. 24, to show the mass effect more impressively, the isotope combination of \(^3\)He and T was taken into account. However, this is a somewhat special case. The present work considers the collisions for extensive isotope variations, i.e. \(^4\)He + XH, \(^4\)He, \(^4\)X, \(^4\)X, \(^4\)X (X = Mu, H, D, T) and \(^3\)He + T, at total energies of 1–6 eV (below and above the dissociation threshold).

In this work, the time-independent quantum mechanical approach developed by Sakimoto and Onda\(^{19}\) is employed. This numerical method can be applied without any difficulties to collisions at energies both below and above the dissociation threshold, and the results obtained are numerically accurate without regard to the energy region. The present paper provides an accurate description of the collision process over a wide energy range in a unified quantum mechanical method.

2 Theory

We consider a collinear triatomic system A–B–C with masses \(m_A, m_B, m_C\), respectively. Let \(R_{AB}\) and \(R_{AC}\) be the Jacobi coordinates corresponding to the A + BC arrangement (A channel), and let \(R_{AB}\) and \(R_{BC}\) be the Jacobi coordinates corresponding to the AB + C arrangement (C channel). Defining the mass-scaled coordinates by

\[
R_i = \frac{a_iR_{i,j,k}}{r_i}, \quad \mu_i = \frac{m_i m_j}{m_i + m_j}, \quad a_i = (\mu_{i,j,\mu})^{1/4}
\]

where \((i, j, k)\) is the cyclic permutation of \((A, B, C)\), and

\[
\mu = \left[\frac{m_A m_B m_C}{m_A + m_B + m_C}\right]^{1/2}
\]

we obtain the time-independent Schrödinger equation as

\[
\left\{-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r_i^2} + \frac{\partial^2}{\partial \theta_i^2}\right) + V(R_i, r) - E\right\}\psi = 0
\]

where

\[
\mu = \left[\frac{m_A m_B m_C}{m_A + m_B + m_C}\right]^{1/2}
\]

is the characteristic mass of the system; \((R, r)\) is \((R_A, r_A)\) or \((R_C, r_C)\); \(V(R, r)\) is the PES, and \(E\) is the total energy measured from the lowest minimum of the diatomic well.

The hyperspherical coordinate system has great advantages for the description of both the exchange and the dissociation process.\(^{15,16}\) The hyperspherical coordinates \((\rho, \omega)\) are defined by \(\rho = \sqrt{R^2 + r^2}\)\(^{1/2}\), \(\omega = \tan^{-1}(r/R)\). The hyperspherical angle \(\omega\) is a natural variable between 0 and the skew angle \(\omega_{\text{max}} = \tan^{-1}(m_j/\mu)\). Using these coordinates, and inserting \(\Psi(\rho, \omega) = \rho^{-1/2}\psi(\rho, \omega)\) into eqn. (3), we have the partial differential equation

\[
\rho^2 \frac{\partial^2 \psi}{\partial \rho^2} + \frac{\partial^2 \psi}{\partial \omega^2} + W(\rho, \omega) = 0
\]

where \(W(\rho, \omega) = 2\mu^2(E - V(\rho, \omega))/\hbar^2 + 1/4\). 

2.1 Scattering boundary conditions

When the dissociation channel is open, the imposition of an accurate scattering boundary condition becomes quite difficult in numerical calculations.\(^8\) Previous workers,\(^8\)–\(^20\) employing the time-dependent wavepacket method, were able to obtain a total dissociation probability. They first calculated the bound-to-bound (b–b) transition probabilities, and defined the dissociation probability by subtracting the total b–b transition probability from unity. However, the S matrix elements are evidently of physical importance, rather than the total probabilities. In fact, the information from the S matrix elements is required to calculate the energy distribution of the dissociative fragments.\(^17\)\(^,\)\(^20\) In the previous wavepacket studies, the derivation of the S matrix elements corresponding to the dissociation channels was not discussed. One might expect that the use of hyperspherical coordinates would provide the solution to this problem. However, the hyperspherical coordinate system is not suitable for the description of the asymptotic channels because the Hamiltonian of the total system is not separable in these coordinates for finite \(\rho\). A forced use of hyperspherical coordinates to obtain the S matrix elements produces a fictitious \(\rho\) dependence in the calculated transition probabilities.\(^{16,19,40}\) Recently, one approximation to solve this problem was suggested by Sakimoto and Onda.\(^{19}\) Their method is numerically efficient, and is sufficiently accurate for most purposes.\(^{20,23,24}\) Hence, in the present work, this method is invoked for the imposition of the scattering boundary condition.

Note that at sufficiently large \(\rho \gg \rho_0\), the total Hamiltonians for \(\omega \approx 0\) and for \(\omega \approx \omega_{\text{max}}\) are separable in the A + BC and AB + C Jacobi coordinates, respectively. Accordingly, as in Fig. 1, setting a boundary points at \(\rho = \rho_0\) and \(\omega = \omega_0\), we assume that the motion of the dissociative fragments is confined to the box of \(0 \leq r_A \leq \rho_0\) at \(\rho = \rho_0\), \(\omega_0\) for the BC molecule, and to the box of \(0 \leq r_C \leq \rho_0\) \(\sin \omega_{\text{max}} - \omega_0\) for the AB molecule. In this way, the dissociation continuum is discretized and the continuum channels are all classified into either the A or the C channel. Furthermore, all the bound and continuum channels together make an orthonormal complete set \(\{\phi_i(r); r_A = 0, 1, 2, \text{ etc.}; i = \text{A}, \text{C}\}\). Previous studies\(^{19,20,23}\) have shown that this procedure does not cause a serious error if the boundary point \((\rho_0, \omega_0)\) is sufficiently far from the region where the bound wavefunctions of the molecules have finite amplitudes.

We assume that the total wavefunction, \(\Psi_s\), is matched to the following asymptotic form at \(\rho \gg \rho_0\)

\[
\Psi_v = \sum_{a} \phi_a^s(r_A)[\delta_{a,v}R_A^s + c_{a,v}^sR_C^s]
\]

where the radial functions, \(s_A(r_A)\) and \(c_A(r_A)\), are given by

\[
\begin{align*}
\psi_A(\rho) & = k_{\text{vii}}^{-1/2}\cos(k_{\text{vii}}R_A) \\
\psi_C(\rho) & = k_{\text{vii}}^{-1/2}\cos(k_{\text{vii}}R_C)
\end{align*}
\]

Fig. 1 Schematic diagram for matching the total wavefunction to the asymptotic form
asymptotic states necessarily and non-artificially belong to either the A or the C channel.

2.2 Numerical method

In order to solve eqn. (5) from \( \rho = 0 \) to \( \rho = \rho_b \) accurately, a direct numerical method proposed by Sakimoto and Onda\(^{19}\) was employed. This method is based on the discrete variable representation (DVR) algorithm.\(^{41,42}\) A two-dimensional (equally spaced) grid in the configuration space represented by hyperspherical coordinates is defined

\[
\rho_a = x A \rho (x = 0, \ldots, N),
\]

\[
\omega_b = \beta A \rho (\beta = 0, \ldots, M)
\]

where \( \rho_o = \rho_a \) and \( \omega = \omega_{\text{max}} \). The DVR basis functions, \( u_v(\rho) \) and \( v_p(\omega) \), which are constructed from orthogonal polynomials with quadrature points of \( \rho_o \) and \( \omega_o \), respectively are introduced and the Kronecker delta properties, \( v_p(\omega_o) = \delta_{\omega_o}, \)

\( v_p(\omega_o) = \delta_{\omega_o} \), are satisfied. A Lagrange polynomial of the third degree for \( u_v(\rho) \) and a linear combination of Chevyshev polynomials for \( v_p(\omega_o) \) are selected, i.e.

\[
v_p(\omega_o) = \frac{2}{M + 1} \sum_{m=1}^{M} \sin \left( \frac{\pi m}{M + 1} \omega_o \right) \sin \left( \frac{\pi \omega_o}{(M + 1) \omega_o} \right) \quad (8)
\]

The choice for \( u_v(\rho) \) corresponds to the use of the three-point finite difference algorithm.

Using these DVR basis functions, the wavefunction is expanded in the form

\[
\Psi(\rho, \omega) = \sum_{\rho \in \rho_a} \sum_{\omega \in \omega_b} \psi_{\rho, \omega} u_v(\rho) v_p(\omega)
\]

\( \Psi(\rho, \omega) = \sum_{\rho \in \rho_a} \sum_{\omega \in \omega_b} \psi_{\rho, \omega} u_v(\rho) v_p(\omega) \quad (9) \)

where \( \psi_{\rho, \omega} = \psi(\rho, \omega) \). Inserting this into eqn. (5) and setting \( \rho = \rho_a \) and \( \omega = \omega_o \) gives a set of coupled linear equations with respect to \( \psi_{\rho, \omega} \),

\[
x^2(\psi_{\rho, \omega} - \psi_{\rho+1, \omega}) + \sum_{\rho} \frac{d^2}{d\omega^2} \omega_{\rho, \omega} \psi_{\rho, \omega} + W(\rho, \omega) \psi_{\rho, \omega} = 0 \quad (10)
\]

Solving these equations with the proper boundary [eqn. (6)], we can determine the K matrix elements. For the details of the numerical algorithm, see ref. 19. This numerical scheme has the great advantage that changing the system masses and the PESs is very simple and straightforward.

3 Calculation

In Table 1, the skew angles, \( \omega_{\text{max}} \), the characteristic masses, \( \mu \), and the lowest \( (v = 0) \) vibrational energies of the isolated reagent (BC) and product (AB) molecules are summarized for the systems considered here. The A + B\(_2\), heavy–heavy–light (HHL) and heavy–light–heavy (HLH) systems are shown. In all the systems, the atom A (\(^4\)He or \(^3\)He) has the largest mass. The HHL systems have \( m_A \geq m_o \geq m_c \). Since the skew angle ranges from 20.8 to 73.4°, the present study covers various cases. The PES of the He + H\(_2^+\) system, given by Joseph and Sathyamurthy\(^{43}\) who fitted the ab initio energies of McLaughlin and Thompson\(^{44}\), was employed. The dissociation limit is 2.787 eV, measured from the lowest minimum of the diatomic well.

The scattering boundary condition is imposed at \( \rho_b = 15–25a_0 \). For the system with the smaller skew angle, the larger value of \( \rho_b \) is needed. The present values for \( \rho_b \) are sufficient to obtain accurate exchange and dissociation probabilities in all the cases considered here. The number of grid points is taken to be \( M = 200–300 \) for \( \alpha \) and \( N = 2000–3000 \) for \( \rho \). The probabilities are converged within a few percent with respect to these choices. The calculation was carried out at total energies \( E = 1–6 \) eV (below and above the dissociation threshold). In particular, to study resonance structures, the calculations are carried out in the energy range 1–2 eV with a mesh interval \( \leq 0.01 \) eV. Although a mesh interval of 0.01 eV is not always sufficiently small to analyse the details of the resonance structure, it is sufficient to obtain an overall view of the resonances.

4 Results and Discussion

At energies below the dissociation threshold, the reaction probabilities in the present systems have a complicated energy dependence due to the resonances. On the other hand, at energies above the dissociation threshold, the energy dependence of the probability becomes simple. Therefore, the reaction dynamics are discussed by dividing the energy region into \( E = 1–2 \) eV and \( E = 2–6 \) eV. Furthermore, the results for the present isotope combinations are shown by classification into three types A + B\(_2\), HHL and HLH (as summarized in Table 1). This classification is probably the most useful to obtain a clear view of the systematics in the reaction processes.

4.1 Exchange reaction at energies below the dissociation threshold \((E = 1–2 \text{eV})\)

First, the exchange processes in the normal He + H\(_2^+\) and the equal-mass \(^3\)He + T\(_2^+\) systems for the A + B\(_2\) iso- tope combination are compared. The two systems show quite distinct reaction features at energies above the dissociation threshold.\(^{44}\) Fig. 2 displays the total exchange probabilities for the initial vibrational states \( v = 0 \) and 1 at \( E = 1–2 \) eV. The total exchange probability is obtained by summing the

<table>
<thead>
<tr>
<th>Table 1</th>
<th>System properties of A + BC for different isotope combinations</th>
</tr>
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<tbody>
<tr>
<td>A + B(_2):</td>
<td>He + MuH(_2^+)</td>
</tr>
<tr>
<td>skew angle/degrees</td>
<td>45.8</td>
</tr>
<tr>
<td>( \mu )</td>
<td>0.111</td>
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<tr>
<td>B(_2) ((v = 0))</td>
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</tr>
<tr>
<td>AB ((v = 0))</td>
<td>1.266</td>
</tr>
<tr>
<td>HHL:</td>
<td>He + DH(_+)</td>
</tr>
<tr>
<td>skew angle/degrees</td>
<td>61.9</td>
</tr>
<tr>
<td>( \mu )</td>
<td>1.076</td>
</tr>
<tr>
<td>BC ((v = 0))</td>
<td>0.125</td>
</tr>
<tr>
<td>AB ((v = 0))</td>
<td>0.912</td>
</tr>
<tr>
<td>HLH:</td>
<td>He + MuH(_+)</td>
</tr>
<tr>
<td>skew angle/degrees</td>
<td>20.8</td>
</tr>
<tr>
<td>( \mu )</td>
<td>0.299</td>
</tr>
<tr>
<td>BC ((v = 0))</td>
<td>0.316</td>
</tr>
<tr>
<td>AB ((v = 0))</td>
<td>1.266</td>
</tr>
</tbody>
</table>

\(^a\) Characteristic mass in u \((1 \text{u} = 1.661 \times 10^{-27} \text{kg})\). \(^b\) Energy (in eV) of the vibrational ground state \((v = 0)\) measured from the lowest minimum of the diatomic well.
state-to-state exchange probabilities over all the final states. The results for He + H$_2^+$ are taken from ref. 31. The two systems are both very rich in resonances. In He + H$_2^+$, the resonance becomes less evident at higher energies, and a stepwise increase in the probability is present at the threshold energy of the new product, HeH$^+$ ($v'$ + 1) + H channel. The overall probability becomes larger at higher energies (see also Fig. 6, later). In $^3$He + T$_2^+$, the probability is much smaller than that in He + H$_2^+$, and does not become so large even at high energies. Therefore, prominent resonance structures always remain over the 1–2 eV energy range. Also for this reason, a stepwise increase in the probability is not clear in $^1$He + T$_2^+$. Previous studies$^{24,31}$ show that in He + H$_2^+$ the largest exchange probability is almost for the $v = 0$ vibrational state at $E > 1.4$ eV. However, in $^3$He + T$_2^+$ and also in most of the other systems shown later, the exchange reaction becomes more efficient for higher vibrational states (vibrational enhancement). The mass combination of the normal He + H$_2^+$ system is favoured by the exchange process for $v = 0$.

As shown in Fig. 3, the HHL systems are almost inactive for the exchange process except for resonances. The resonance effect plays a dominant role in the HHL-type isotope combination. In He + TH$^+$, however, even the resonances are negligible for $v = 0$ and 1. The total exchange probabilities for $v = 2$ and 3 in this system are also plotted, and the resonance is found to become more significant for higher vibrational states. The overall resonance structure in He + DH$^+$ is somewhat similar to that in $^3$He + T$_2^+$. Note that the skew angles of the two systems are very similar (Table 1). In He + HMu$^+$, the resonances for $v = 1$ are remarkably sharp and strong at low energies. However, at high energies, the magnitude of the resonance peak becomes very small.

Adiabatic potential-energy curves in hyperspherical coordinates are sometimes useful to analyse the resonance position.$^{45–47}$ In the case of He + H$_2^+$, the resonances cannot always be classified as the quasi-bound states of the adiabatic potential-energy curves because the non-adiabatic coupling is not negligible.$^{29,33,34}$ However, since the energy separation of the HMu$^+$ vibrational states is large, the adiabatic picture may be expected to improve for He + HMu$^+$. The adiabatic potential energies are shown in Fig. 4. These curves can support several quasi-bound states. If these states have energy levels above the threshold of the HeH$^+$ ($v' = 0$) + Mu channel, they may correspond to the resonances in the exchange reaction. Such energy levels are also shown in Fig. 4. Consider the exchange reaction for $v = 1$. Since the He + HMu$^+$ system has very small exchange probabilities except for resonances, the most efficient non-adiabatic transition from the $v = 1$ adiabatic state would be that to $v = 2$ (or $v = 0$). The $v = 2$ energy curve supports four quasi-bound levels at $E = 1.07, 1.22, 1.31$ and 1.37 eV. (The diagonal part of the non-adiabatic coupling is not taken into account in calculating the quasi-bound energy levels.) These states can support resonances at least in the elastic process. An avoided crossing between the $v = 2$ and $v' = 1$ curves at $p = 6.2a_0$ works efficiently to produce the exchange product for the quasi-bound states at $E = 1.22, 1.31$ and 1.37 eV. Furthermore, since the two quasi-bound energy levels of the $v' = 1$ curve are very close to the lower two ($E = 1.07$ and 1.22 eV) of the $v = 2$ curve, the transition between the nearly degenerate states is very fast. Therefore, the four quasi-bound states of the $v = 2$ adiabatic potential-energy curve can be related closely to the four pronounced resonances at $E \approx 1.12, 1.18, 1.28$ and 1.35 eV shown in Fig. 3. Nevertheless, the characterization of the He + HMu$^+$ resonance states seems to be somewhat complicated in the adiabatic picture. This is because the He + HMu$^+$ system has a very large skew angle. At energies $E > 1.4$ eV, since the contribution to the resonances comes from the quasi-bound levels of the $v' \geq 3$ states, the resonance peak height becomes much smaller. The situation in He + HMu$^+$ at high energies becomes rather similar to that in He + DH$^+$ and TH$^+$.

Fig. 5 shows the results for the HLH-type combination. The three systems He + MuH$^+$, HT$^+$ and HD$^+$ have quite different reaction features. First, we consider He + MuH$^+$. This system has only a small number of resonances at $E \approx 1.34,
1.58, 1.67, 1.74, 1.80, 1.90, 1.96 and 2.0 eV. This is because the small skew angle (and the light characteristic mass) makes the number of possible resonance states very small. The small skew angle (and the light characteristic mass) makes the resonance effect less significant in He + HD$^\ddagger$. Stepwise increases of the probability are seen clearly in He + HD$^\ddagger$, and less clearly in He + HT$^\ddagger$. The stepwise structure is absent in He + MuH$^\ddagger$ because the threshold energy of the $v' \geq 1$ product channel is larger than $E = 2$ eV.

For the HLH-type combination, when the skew angle is large, as in He + HT$^\ddagger$, many resonances are clearly visible. However, in He + HD$^\ddagger$, there are no remarkable resonances except at $E \approx 1.05$ eV in the present scale of Fig. 5. (If the scale is enlarged, the resonances make an undulation in the probabilities for $v = 0$ with an amplitude of ca. 0.01.) It is rather surprising that the resonance effect is less significant in He + HD$^\ddagger$. Stepwise increases of the probability are seen clearly in He + HD$^\ddagger$, and less clearly in He + HT$^\ddagger$. The stepwise structure is absent in He + MuH$^\ddagger$ because the threshold energy of the $v' \geq 1$ product channel is larger than $E = 2$ eV. It is interesting that some similarities are present in the He + HD$^\ddagger$ and H$_2^+$ reactions, i.e. the two systems have clear stepwise structures, and furthermore the magnitudes of the probabilities averaged over the resonances in He + H$_2^+$ are almost the same as in the He + HD$^\ddagger$.

### 4.2 Exchange and dissociation reaction at $E = 2–6$ eV

For the A + B$_2$-type combination, we consider He + Mu$_2^+$, H$_2^+$, D$_2^+$, T$_2^+$ and $^3$He + T$_2^+$, $^{24}$ which are listed in order of increasing skew angles. Fig. 6 displays the total exchange and total dissociation probabilities for $v = 0$ at $E = 2–6$ eV. The equal-mass $^3$He + T$_2^+$ system has the smallest exchange and the largest dissociation probabilities at high energies. On the other hand, the normal He + H$_2^+$ system has the largest exchange and the smallest dissociation probabilities. The former result confirms the finding of ref. 23 and 24 that the dissociation becomes very efficient when the system has equal-mass constituents. If the case of He + Mu$_2^+$ is excluded, the present study further shows the simple pattern that the exchange probabilities decrease and the dissociation probabilities almost all increase as the skew angle increases. (As shown later in Fig. 11, however, the He + Mu$_2^+$ system is not an

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Fig. 4 Adiabatic potential-energy curves in hyperspherical coordinates for He + HMu$^\ddagger$ and MuH$^\ddagger$. The solid and dashed curves show the adiabatic energies for the reagent and product channels, respectively. The horizontal lines indicate the quasi-bound energy levels supported by the adiabatic energy curves.

Fig. 5 Total exchange probabilities for the initial vibrational quantum numbers $v = 0$ and 1 at the total energies $E = 1–2$ eV in the HLH systems of He + HMu$^\ddagger$, HT$^\ddagger$ and HD$^\ddagger$. The arrows show the position of the threshold energy for the new product channel AB$^\ddagger$ + C.

For the HLH-type combination, when the skew angle is large, as in He + HT$^\ddagger$, many resonances are clearly visible. However, in He + HD$^\ddagger$, there are no remarkable resonances except at $E \approx 1.05$ eV in the present scale of Fig. 5. (If the scale is enlarged, the resonances make an undulation in the probabilities for $v = 0$ with an amplitude of ca. 0.01.) It is rather surprising that the resonance effect is less significant in He + HD$^\ddagger$. Stepwise increases of the probability are seen clearly in He + HD$^\ddagger$, and less clearly in He + HT$^\ddagger$. The stepwise structure is absent in He + MuH$^\ddagger$ because the threshold energy of the $v' \geq 1$ product channel is larger than $E = 2$ eV. It is interesting that some similarities are present in the He + HD$^\ddagger$ and H$_2^+$ reactions, i.e. the two systems have clear stepwise structures, and furthermore the magnitudes of the probabilities averaged over the resonances in He + H$_2^+$ are almost the same as in the He + HD$^\ddagger$.

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exception to the pattern.) In high-energy collisions for all the A + B₂ systems, the sum of the exchange and dissociation probabilities is close to unity, and hence the reagent homonuclear molecule is mostly broken up after collisions.

Fig. 6 shows the results for the HH-L-type combination of He + DH⁺, ³He + TH⁺ 24 and He + HMu⁺. In most cases, the exchange and dissociation probabilities are very small. The reagent molecule in the HH-L system usually survives after collisions at energies both below and above the dissociation threshold. An interesting exception is He + DH⁺, which has large dissociation probabilities. The important point to understand is that the skew angle of He + DH⁺ is very close to ωₘₐₓ = 60° of the equal-mass ³He + T₂⁻ system (Table 1). From Fig. 6-8, furthermore, only the ³He + T₂⁻ and He + DH⁺ systems both exhibit the peculiar characteristic that the dissociation probability is much larger than the exchange probability. As noted above, the similarity between the two systems is present also in the overall resonance structure at energies below the dissociation threshold.

However, it should be noted that the He:D:H mass ratio 4:2:1 is very different from the equal-mass ratio. Thus, the result for He + DH⁺ suggests that the skew angle is essential to understand the similarity and furthermore that the dissociation always becomes efficient when the system has ωₘₐₓ ≈ 60°.

Fig. 8 displays the total exchange and total dissociation probabilities for the HH-L systems of He + MuH⁺, HT⁺, ³He + HT⁺ 24 and He + HD⁺ (in increasing order of skew angle). As in the A + B₂-type combination, the probabilities have non-negligible values. However, unlike the A + B₂-type system the exchange probability is always larger than the dissociation one in the present energy range. Although the He + HD⁺ and H₂⁺ systems show some similarities at E = 1-2 eV, the manner of the competition between the exchange and dissociation processes appears to be different in the two systems at energies above the dissociation threshold. The presence of the dissociation channel affects the reaction dynamics differently in He + HD⁺ and H₂⁺. The high-energy behaviour in the He + HD⁺ reaction is rather similar to that in the He + MuH⁺ reaction. This can be understood because the skew angles of the two systems are very similar (Table 1). If the typical HH-L-type system He + MuH⁺ is excluded, a clear pattern that the exchange and dissociation process both become more efficient as the skew angle increases is again found. In He + MuH⁺, the exchange probability has an energy dependence different from the others. Perhaps the exchange probability for He + MuH⁺ will reach the maximum value at a much higher energy. The He + MuH⁺ reaction mechanism in the present energy range would be different from the other HH-L ones.

To investigate more details of the reaction dynamics, Fig. 9 and 10 display the probability distributions of the final vibrational states in the inelastic and the exchange processes, respectively. For the A + B₂-type system, high vibrational states have large populations both in the inelastic and the exchange processes. This result is related to the fact that the A + B₂-type combination always has large dissociation probabilities. Furthermore, as the skew angle increases, the maximum peaks in the inelastic and the exchange distributions move towards relatively higher vibrational states. Therefore, in collisions of larger skew angles, the final state is preferentially the continuum one rather than the bound one.
the dissociation probability at the total energy initial vibrational quantum number \( v \). Inelastic and exchange probabilities and the components of Table 2 is more important for dissociation. However, in He large as the \( A \)-channel component. The exchange mechanism channel component of the dissociation probability is twice as large as the \( A \)-channel component. Therefore, the inelastic mechanism is more efficient for dissociation. However, it is interesting that the \( C \)-channel component is twice as large as the \( C \)-channel component. The exchange mechanism is more important for dissociation. However, in He + \( T_2^+ \), which has large dissociation probabilities, the two dissociation components have similar magnitudes. Hence, both the inelastic and the exchange mechanisms contribute equally to dissociation in this case.

In the present calculation, as shown in eqn. (6), we can discriminate the \( A \)- and \( C \)-channel components of the dissociation probability. We may regard the dissociative transition to the \( A \) channel as the vibrational excitation to the continuum, and that to the \( C \) channel as the exchange to the continuum. Table 2 shows the inelastic and exchange probabilities and the two components of the dissociation probability. In He + \( D_2^+ \), which has large exchange probabilities, the \( C \)-channel component of the dissociation probability is twice as large as the \( A \)-channel component. The exchange mechanism is more important for dissociation. However, in He + \( T_2^+ \), which has large dissociation probabilities, the two dissociation components have similar magnitudes. Hence, both the inelastic and the exchange mechanisms contribute equally to dissociation in this case.

Table 2 Inelastic and exchange probabilities and the components of the dissociation probability at the total energy \( E = 5 \text{ eV} \)

<table>
<thead>
<tr>
<th>dissociation</th>
<th>inelastic</th>
<th>exchange</th>
<th>( A ) channel</th>
<th>( C ) channel</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{He} + \text{B}_2^+ )</td>
<td>0.044</td>
<td>0.827</td>
<td>0.044</td>
<td>0.085</td>
</tr>
<tr>
<td>( \text{He} + \text{D}_2^+ )</td>
<td>0.187</td>
<td>0.374</td>
<td>0.231</td>
<td>0.207</td>
</tr>
<tr>
<td>( \text{HLHL type:} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{He} + \text{DH}^+ )</td>
<td>0.930</td>
<td>0.005</td>
<td>0.044</td>
<td>0.021</td>
</tr>
<tr>
<td>( \text{He} + \text{TH}^+ )</td>
<td>1.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>( \text{HLHL type:} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{He} + \text{HT}^+ )</td>
<td>0.996</td>
<td>0.003</td>
<td>0.000</td>
<td>0.001</td>
</tr>
<tr>
<td>( \text{He} + \text{HD}^+ )</td>
<td>0.490</td>
<td>0.445</td>
<td>0.012</td>
<td>0.053</td>
</tr>
</tbody>
</table>

Fig. 8 Total exchange and total dissociation probabilities for the initial vibrational quantum number \( v = 0 \) at the total energies \( E = 5 \text{ eV} \) for the HLH systems of \( \text{He} + \text{MuH}^+, \text{HT}^+ \) and \( \text{HD}^+ \). The results for \( ^3\text{He} + \text{HT}^+ \) are also shown. The skew angle increases in the order \( \text{MuH}^+, \text{HT}^+, ^3\text{He} + \text{HT}^+ \) and \( \text{HD}^+ \).

Fig. 9 Transition probabilities for the inelastic collision \( \text{A} + \text{BC}(0) \rightarrow \text{A} + \text{BC}(v) \) at the total energy \( E = 5 \text{ eV} \). (a) The \( \text{A} + \text{B}_2 \) systems of \( \text{He} + \text{MuH}^+, \text{H}_2^+, \text{D}_2^+, \text{T}_2^+ \) and \( ^3\text{He} + \text{T}_2^+ \). (b) The HLH systems of \( \text{He} + \text{DH}^+, \text{TH}^+, \text{HMu}^+ \) and \( ^3\text{He} + \text{TH}^+ \). (c) The HLH systems of \( \text{He} + \text{MuH}^+, \text{HT}^+ \), \( \text{HD}^+ \) and \( ^3\text{He} + \text{HT}^+ \).

Fig. 9 shows that the degree of vibrational excitation in the HLH-type system is small compared with that in the other types. Therefore, the HLH-type combination is mostly inefficient for the inelastic process as well as for exchange and dissociation processes. This characteristic is expected to be due to the mass combination of \( m_A \gg m_B \gg m_C \), and as exemplified in \( \text{He} + \text{HMu}^+ \) [Fig. 9(b)], only the elastic process will be dominant in the limit of \( m_B/m_C \rightarrow \infty \) (i.e. \( \alpha_{\text{max}} \rightarrow 90^\circ \)). The \( \text{He} + \text{DH}^+ \) system has only a moderate mass difference \( (m_B/m_C = 2:1) \). In this case, excitation to higher vibrational states is possible, and dissociation can take place to some extent. For the dissociation in \( \text{He} + \text{DH}^+ \), Table 2 shows that the \( A \)-channel component is twice as large as the \( C \)-channel component. Therefore, the inelastic mechanism is more important for dissociation. However, it is interesting that the \( C \)-channel component of the dissociation probability is much larger than the exchange one. This means that the exchange transition leads mainly to dissociation in \( \text{He} + \text{DH}^+ \).

In HLH systems, the exchange mechanism is expected to be generally important because round-trip motion along the \( \omega \) coordinate during a close encounter is active for small skew angles. In fact, Table 2 shows that the \( C \)-channel component is larger than the \( A \)-channel component in the HLH-type system. However, Fig. 8 shows that round-trip motion does not lead to dissociation when the skew angle is very small. In \( \text{He} + \text{HD}^+ \), the skew angle is probably still large enough for the exchange mechanism to work efficiently for dissociation.

The characteristic mass, \( \mu \), is very small (\( < 1 \text{ au} \)) in the systems containing the Mu atom (Table 1). Therefore, as seen in Fig. 9 and 10, these systems have populations only at very
low vibrational states. One may consider that the systems containing Mu are always distinct from the other isotope combinations. However, in both A + B₂ and HHL systems, the distributions for all the isotope combinations vary rather smoothly with the skew angle. The exception to this smooth variation is the He + MuH⁺ exchange distribution in the HHL-type combination. As expected, this fact can be related to the exchange mechanism peculiar to the typical HHL system.

The magnitudes of the transition probabilities can be arranged almost in the order of the skew angle for the A + B₂ and HHL-type systems. Fig. 11 presents the total exchange and total dissociation probabilities vs. the skew angle for all three types together in one diagram. Surprisingly, the probability curves for both the exchange and the dissociation processes can be connected with no discontinuity over all the skew angles. The skew angle characterizes the reaction dynamics universally, regardless of the type of mass combinations. The exchange probability reaches a maximum at ω_max ≈ 50°, which corresponds to He + H₂⁺. It is uncertain why the mass ratio of 4:1:1 is so efficient for the exchange process. Anyway, this accidental mass combination for the normal He + H₂⁺ system results in the unique behaviour that the exchange probability is almost unity at high energies and that the v = 0 state has in most cases the largest exchange probability at E > 1.4 eV. In Fig. 6, it seems that the He + Mu₂⁺ system is an exception to the expected systematic arrangement. However, since a smooth curve can be drawn in the region ω_max = 40–50°, it can be seen that the He + Mu₂⁺ system (ω_max = 45.8°) is not the exception. There are two important skew angles, ca. 45 and 60°, at which the dissociation probability gives maxima. The dissociation becomes most efficient at ω_max ≈ 60°, which corresponds to the equal-mass system. As discussed before, for the peak at ω_max ≈ 45°, the exchange mechanism is more important in the dissociation. As ω_max increases, the inelastic mechanism also becomes important, and for the peak at ω_max ≈ 60°, the inelastic and exchange mechanisms have equal contributions. At ω_max > 60°, the inelastic mechanism becomes rather dominant in the dissociation. Especially in the range 45 ≤ ω_max/degrees ≤ 60 (A + B₂ type), the exchange and dissociation probabilities clearly have opposite dependences on the skew angle. The two processes compete strongly with each other in this range. When the skew angle is large (>65°), no reaction processes occur. The exchange reaction is prominent also at ω_max = 20.8°. However, as mentioned already, this case is the typical HHL system in which the middle constituent is the Mu atom. The other A + B₂ and HHL systems containing the Mu atom do not show such a distinct feature. Therefore, if we exclude the typical HHL reaction as an exception, it can be concluded that either the exchange or the dissociation reaction occurs only in a narrow range 40 ≤ ω_max/degrees ≤ 65.

5 Further discussion and conclusions
The isotope effect is significant in collinear collisions at energies both below and above the dissociation threshold. The reaction dynamics for the present isotope variation are well characterized by classifying the systems into the A + B₂, HHL and HHL types, and can be rather universally classified by the skew angle, ω_max, at energies above the dissociation threshold. Because of the complicated resonance structures, extracting a pattern such as that shown in Fig. 11 is difficult at energies below the dissociation threshold. It is very important to know to what extent a single parameter of the skew angle can characterize the reaction dynamics at energies above the dissociation threshold. The three systems A + B₂, HHL and HHL principally cover the skew angles of 45–90, 45–90, and 0–60°, respectively. Of particular interest is the case in which the different types have the same skew angle, i.e. do the different types exhibit similar reaction features? Unfortunately, the use of isotopes cannot realize such combinations in the He + H₂⁺ study. However, we may consider other rare-gas elements instead of using the isotope of He, since we expect that the PES of He + H₂⁺ is not so different from that of a rare-gas atom + H₂⁺. The study of a heavy rare-gas atom + DH⁺ and TH⁺ (HHL) is especially encouraging.
because the two systems have skew angles of ca. 55 and ca. 60°, respectively.

Kaye and Kuppermann 18 studied the exchange and dissociation processes in H + H2, HHL, and HLH systems by using a simplified model H + H2 PES. Their results in the equal-mass and the HLH (ωmax = 24.5°) systems were qualitatively the same as in the present study. The isotope combinations of HeH2+ cannot cover the LHL-type combination. The typical LHL-type (mH > mH2, mH3) has a very large skew angle (ca. 90°). Kaye and Kuppermann found that the exchange and dissociation probabilities were both large in the H + H2+ PES, another peak may appear at ωmax ≥ 90° in Fig. 11. However, the present study for the HHL-type system shows that neither of the exchange and the dissociation processes takes place at ωmax → 90° (mH/mH2 → ∞). The mass combinations of the typical HHL and LHL systems are so different that we cannot characterize the reaction features only in terms of the skew angle. As far as the real isotope variations of He and H are concerned, we can use the simple systematics for reactions at energies above the dissociation threshold.

From Fig. 7 and 8, we can consider dissociation on the collision site, i.e., He + BC vs. He + CB. When BC = HMu+ or HT+, dissociation takes place far more frequently when the He atom collides with the lighter atom of the BC molecule. This suggests that the dissociation process is strongly dependent on the molecular orientation when we consider the 3D collisions of He + HMu+ and HT+. In He + HD+ dissociation, the present result shows that the probability for collisions with the heavier D atom is larger, but the probability for the opposite collision site is hardly changed. Therefore, the orientation dependence of the 3D He + HD+ dissociation will not be so large as those of the 3D He + HMu+ and HT+ dissociation processes.

Dissociation will be less efficient in the 3D He + H2+ collisions because the collinear dissociation probability is very small. If the H2+ molecule is replaced by the isotope HD+, DT2+ or T2+, the collinear dissociation probability becomes large. Therefore, we expect that their 3D dissociation also becomes much more frequent. In fact, experimental 51, 52 and quasiclassical trajectory (QCT)53–56 studies have shown that the dissociation cross-section is larger for He + HD+ than for He + H2+. This can be partly understood in terms of the collinear reaction dynamics.

In the 3D collisions of A + BC (B ≠ C), we have two product molecules, AB and AC. In the present isotope combinations, since the HHL system always has much larger exchange probabilities than the HHL system (Fig. 3 and 5), we may expect that the molecule with the lighter mass is much more plausible as the exchange product in the 3D collisions. However, the 3D QCT calculation of Kumar et al. 57 using the same PES has shown that in He + HD+, the exchange cross-section is larger for the HeD+ + H channel than for the HeH+ + D channel. Even if only the collisions at the zero impact parameter are considered in their QCT calculation, the HeD+ formation dominates the HeH+ one. This result is in conflict with the present expectation. As discussed by Kumar et al., the 3D perspective of the PES is needed to understand the isotope effect in this 3D reaction. Also, to check the difference between the collinear and 3D reaction dynamics, a 3D study of He + HT+ is interesting because the exchange reaction hardly occurs in the collinear He + TH+ collisions. In the collinear He + HMu+ collisions, the resonance is pronounced and the exchange probability is very small except for the resonances. In the collisions with the opposite site, i.e., He + MuH+, although the exchange probability is large, the product channel HeMu+ + H is energetically forbidden at E < 1.266 eV. Therefore, in the 3D He + HMu+ exchange reaction at E < 1.266 eV, the collinear He + HMu+ config-

The author would like to thank Drs. F. Koike and K. Onda for reading the original manuscript. This work is partially supported by a Grant-in-aid for Scientific Research on Priority Area ‘Theory of Chemical Reactions’ from the Ministry of Education, Science and Culture of Japan

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*Paper 6/04770J; Received 8th July, 1996*