The formation mechanism of molecular hydrogen on icy mantles of interstellar dust

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ABSTRACT
The fundamental processes of H2 formation via H + H → H2 on the surfaces of icy mantles of interstellar dust have been investigated consistently within a single model based on a classical molecular dynamics (MD) computational simulation. As a model surface for icy mantles of dust grains, an amorphous water ice slab was generated at 10 and 70 K under periodic boundary conditions. The first and second incident H atoms were then ‘thrown’ on to the model surface. Two MD procedures were employed: (i) the H2O molecules were treated as rigid (hard ice model); (ii) the intramolecular vibrational modes of H2O were included (soft ice model). The amorphous water ice slabs produced by our MD simulations are found to be good models for the surfaces of icy mantles of dust grains. For the various fundamental processes of H2 formation on the dust surface, the following results emerge. (1) For the sticking of an H atom on to the surface, a sticking probability that depends on the temperature of the incident H atom is obtained. (2) For the diffusion of an H atom on the surface, it is found that the first incident H atom diffuses via the thermal hopping mechanism at the first stage, and then it is always trapped in one of the stable sites on the amorphous ice. The migration length and time have been calculated for the mobility of the incident H atom before it is trapped. The time-scales of thermal diffusion and desorption of H atoms after trapping have also been estimated. (3) For the reaction of two H atoms on the surface, the following three reaction patterns are observed: (i) H2 is produced via the Langmuir–Hinshelwood mechanism; (ii) H2 is produced via the Eley–Rideal mechanism; (iii) the almost elastic collision of two H atoms occurs without H2 being formed. The effective reactive cross-section is estimated at about 40 Å2. The reaction probabilities are found to be near unity. (4) For the ejection of H2 from the ice surface, the product H2 is subsequently ejected after the reaction process, using part of the excess energy derived from the H2 formation. The average lifetime of ejection is about 400–600 fs. Most of the ejected H2 molecules are found to be in vibrationally and rotationally excited states.

Key words: atomic processes – molecular processes – ISM: atoms – dust, extinction – ISM: molecules.

1 INTRODUCTION
The molecules in interstellar space are considered to be produced in two ways. One of these is via gas-phase reactions, and the other is via surface reactions on dust grains. Most of the observed gas-phase interstellar molecules can be produced via gas-phase reactions. However, exothermic bimolecular reactions, such as the formation of molecular hydrogen from two hydrogen atoms, H + H → H2, cannot occur efficiently in the gas phase under low-pressure conditions, and H2 formation is believed to occur predominantly on the surfaces of dust grains (see e.g. Williams 1993; Herbst 1995).

Interstellar dust grains may have icy mantles, predominantly of H2O, which accumulate on solid particles inside dark clouds. Astronomical observations tell us that icy mantles are expected to be composed of amorphous water ice rather than crystalline (see e.g. Hagen, Tielens & Greenberg 1981). High-density amorphous water ice was first discovered by Narten, Venkatesh & Rice (1976), and Jenniskens et al. (1995) identified it in electron diffraction experiments and modelled its structure. It is said that there are two
forms of amorphous water ice: the low-density form above 68 K and the high-density form below 38 K (Jenniskens & Blake 1994).

The fundamental processes of H2 formation on the surfaces of dust grains are considered to be as follows: (1) the sticking of incident H atoms on to the grain surface; (2) the diffusion of H atoms over the surface; (3) the reaction of two H atoms on the surface; and (4) the ejection of the H2 molecule from the surface back into the gas phase (see e.g. Williams 1993; Herbst 1995).

The sticking of H atoms and the adsorption of H2 on the icy mantles of dust grains have been studied theoretically by several workers. Hollenbach & Salpeter (1970) represented the surface systems of a dust grain by a harmonic oscillator driven at a single characteristic frequency. Leitch-Devlin & Williams (1985) calculated the sticking coefficients and the mobilities of additional atoms (H, H2, etc.) on the surfaces of crystalline solids with full quantum mechanical treatment. The dynamics and structure of amorphous clusters including 116 water molecules were studied by Zhang & Buch (1990) and by Buch (1990) using a computational simulation technique via the classical molecular dynamics (MD) method. The sticking probability of H and D atoms on an amorphous cluster of 115 water molecules was studied by Buch & Zhang (1991). Buch & Devlin (1993, 1994) further studied the adsorption of H2 on an amorphous cluster of 450 water molecules for the purpose of interpretation of the ortho/para ratio of H2 and interstellar infrared spectra of H2/H2O.

The production and ejection processes of surface molecules on dust grains have been also studied theoretically by several workers. It has been considered that the reactive processes occur between adsorbed species on the grain surface via a diffusive mechanism (Williams 1993; Herbst 1995). The desorption processes have been considered to involve the excitation of product molecules, which might have been frozen-out, by photons or cosmic rays or by coupling with heated dust particles (Williams 1993; Herbst 1995; Dzugilenko & Herbst 1995). There is another possibility: that the exothermic reactions between adsorbed species (the Langmuir–Hinshelwood mechanism) can lead directly to the ejection of product molecules (Williams 1993; Herbst 1995). The Eley–Rideal mechanism, in which a gas-phase atom directly strikes an adsorbed one and leads to the reaction and ejection processes, has been also considered to be efficient (Herbst 1995; Duley 1996). There is a possibility that H2 molecules formed on the dust grains are in vibrationally excited states (Hunter & Watson 1978; Duley & Williams 1986, 1993; Duley 1996).

Recently, as a realistic model for the surfaces of the icy mantles of dust grains, slab-shaped amorphous water ice with infinite area was produced by MD simulation under periodic boundary conditions with 1000 water molecules in a unit cell. The sticking probability and mobility of a hydrogen atom were studied in detail on the surface using the MD simulation technique (Masuda & Takahashi 1997; Masuda, Takahashi & Mukai 1998).

Classical MD simulation is a well-established technique for studying molecular processes in the field of physical chemistry. This technique is based on the numerical solutions of Newton’s equations of motion for a many-body system. Despite the limitation of the classical treatment of motion, it has provided us with much realistic information about molecular processes when they are dominated by thermal dynamics (see e.g. Hansen & McDonald 1986). Our model, in which the hydrogen atom or molecule is physisorbed on the surface of the icy mantle and has excess thermal energy during most of the processes, could be well treated by this technique (Masuda & Takahashi 1997; Masuda et al. 1998). The quantum treatment is necessary only for the diffusion process of the H atom after it loses the excess thermal energy and becomes trapped on the surface of the dust grain (Takahashi, Nagaoka & Masuda 1998).

In interstellar chemistry, the determination of the rate constant for H2 formation on the grain surface is a very significant problem. For this purpose, the formation mechanism of H2 on grain surfaces, which consists of sticking, diffusion, reaction and ejection processes, should be investigated from an overall point of view. Furthermore, it is preferable to obtain the sticking probability, diffusion constant, reaction probability, ejection rate etc. self-consistently within a single model. However, there have been very few studies so far that follow this prescription. Therefore the present study is aimed at following this procedure by using an MD computer simulation technique (Masuda & Takahashi 1997; Masuda et al. 1998; Takahashi, Masuda & Nagaoka 1999).

In the present work, the slab-shaped amorphous water ice was produced by MD simulation, as a realistic model for the surfaces of icy mantles of dust grains. Then two H atoms were successively ‘thrown’ on to the surface, and their dynamical behaviours were investigated by MD simulation for the sticking, diffusion, reaction and ejection processes: i.e. whether and how they lead to H2 formation on the ice surface. In Section 2, the computational procedure of the simulation is described. The results and discussion are presented in Section 3, and the conclusions are summarized in Section 4.

2 COMPUTATIONAL PROCEDURE

In MD computer simulations, positions, velocities and forces of the molecules are obtained as functions of time by numerically solving the Newtonian equations of motion for the many-body system. The total potential of the system is generally given as a sum of pair potentials. We employed this technique to model the surfaces of icy mantles of interstellar dust grains and to study the formation process of H2 on these surfaces.

First, the slab-shaped amorphous water ice was generated by MD simulation using periodic boundary conditions. The volume of the slab in the unit cell was about 40 × 40 × 20 Å3, containing 1000 water molecules. Then the MD simulation was performed for the system consisting of both the amorphous water ice slab and the first incident H atom ‘thrown’ on to the surface. Next the second incident H atom was thrown on to the surface. The temperatures assumed here were 10 and 70 K. In these simulations, the full dynamics was treated for all of the atoms and molecules in the system, and thus the energy transfer from H atoms and H2 to the ice surface was directly taken into account.

The potential model used for a pair of H2O molecules was TIP52 (Transferable Intermolecular Potential, second version) by Jorgensen (1982):

\[
V_{H2O-H2O} = \frac{A}{r_{ij}^{12}} - \frac{C}{r_{ij}^{6}} + \sum_{i} \sum_{j} \frac{q_{i} q_{j} e^{2}}{r_{ij}}.
\]

In this model, two positive charges \(q_{i}\) are located on H atoms and one negative charge \(q_{M}\) is at a distance of 0.15 Å from the oxygen atom on the bisection of the H–O–H angle. In this equation, the first and second terms are the Lennard–Jones parts and the third is the Coulomb part; \(i, j\) indicate the positions of three charges of H2O and H2O, respectively; \(i, j = H, M\); \(r_{0}^{6}\) is the distance between the two oxygen atoms; \(r_{ij}\) is the distance between the positions \(i\) and \(j\); \(e\) is the unit electric charge; \(A, C, q_{M}\) and \(q_{H}\) are the empirical parameters \((A = 695.000 \text{ kcal} \cdot \text{Å}^{12} \cdot \text{mol}^{-1}, C = 600 \text{ kcal} \cdot \text{Å}^{6} \cdot \text{mol}^{-1}, q_{H} = 0.535, q_{M} = -2q_{H})\). This potential function was modelled for the rigid water molecules. As the equilibrium geometry of H2O,
For an $H_2$ molecule (Herzberg 1989) was used as the interaction potential between the two $H$ atoms:

$$V_{H-H} = 2\sum_{j=1}^{4} 4\epsilon_{ijm} \left[\left(\frac{\sigma_{ijm}}{r}\right)^6 - \left(\frac{\sigma_{ijm}}{r}\right)^2\right] Y_{ijm}(\theta, \phi).$$  

(2)

In this model, the origin is placed on the oxygen atom of $H_2O$, $r$ is the distance between the incident $H$ atom and the oxygen atom, and $\theta$ and $\phi$ are the spherical angles. The potential parameters were prepared using the results of \textit{ab initio} molecular orbital calculations, and consist of two factors: the Lennard–Jones part and the spherical harmonics $Y_{ijm}(\theta, \phi)$. The values of the parameters $\epsilon_{ijm}$ and $\sigma_{ijm}$ were taken from Zhang et al. (1991). The maximum potential well depth was 53 cm$^{-1}$ at about $r = 3.3$ Å.

A Morse-type potential function with experimental parameters for an $H_2$ molecule (Herzberg 1989) was used as the interaction potential between the two $H$ atoms:

$$V_{H-H} = D_e \left[1 - \exp\left(-\beta(r - r_e)\right)\right]^2 - D_e,$$  

(3)

$$\beta = \left(\frac{2\pi^2 e^2 \omega_e}{\hbar^2 \mu}\right)^{1/2},$$  

(4)

where $r$ is the distance between the two $H$ atoms; $r_e$ is its equilibrium value ($r_e = 0.74166$ Å); $D_e$ is the dissociation energy ($D_e = D_0 + 0.5\omega_e = 109.5$ kcal mol$^{-1}$); $D_0$ is the dissociation energy with a zero-point energy correction ($D_0 = 4.476$ eV); $\omega_e$ is the harmonic frequency ($\omega_e = 4395.24$ cm$^{-1}$); and $\mu$ is the reduced mass of $H_2$.

For the present system, intermolecular potentials were simply given by the above pair potentials for $H_2O$–$H_2O$, $H$–$H_2O$, and $H$–$H$. The interaction potential for $H_2$–$H_2O$ in the reactive region was assumed to be given by the sum of $H$–$H_2O$ potentials. This approximation is considered to be reasonable because the interaction energy for $H$–$H$ (109.5 kcal mol$^{-1}$) is far larger than that for $H$–$H_2O$ (0.3 kcal mol$^{-1}$).

For the algorithm of the MD simulation, two procedures were employed. (i) The $H_2O$ molecules were treated as rigid and the SHAKE–Verlet algorithm was used for integration with the quaternion formalism (hard ice model). (ii) The intramolecular vibrational modes of $H_2O$ were taken into account (soft ice model). In the latter case, the following intramolecular potential was added to the TIPS2 intermolecular terms (Zhang & Buch 1990):

$$\Delta V_{H_2O} = \sum_{i,j} 0.5k_{ij} \left[r_{ij} - r_{ij}(eq)\right]^2,$$  

(5)

where $i$ and $j$ denote the atoms in a water molecule; $k_{OH}$ and $k_{HH}$ are the force constants for the $O$–$H$ and $H$–$H$ bonds, respectively; $r_{ij}$ denotes the distance between $i$ and $j$; and $r_{ij}(eq)$ is $r_{ij}$ for the equilibrium geometry of $H_2O$. In the present work, the force constants were set to moderate numbers, $k_{OH} = 78$ mdyn Å$^{-1}$ and $k_{HH} = 18.7$ mdyn Å$^{-1}$. These intramolecular terms are regarded as a model for the molecular vibration, including $O$–$H$ stretching and $H$–$O$–$H$ bending motions.

For the first stage of our simulation, the amorphous water ice slab was generated by MD simulations using method (i) under the three-dimensional boundary condition. As the initial conditions, 1000 water molecules were placed randomly in the range $-15 < z < +15$ Å in a unit cell of about $40 \times 40 \times 40$ Å$^3$ volume, where $z = 0$ was taken at the plane including the centre of the cell. The time-step for the MD simulation was taken to be 1 fs (femtosecond) (1 fs = $10^{-15}$ s). After a 10–ps (picoseconds) (1 ps = $10^{-12}$ s) run, an amorphous water ice slab with a thickness of about 20 Å, which corresponds to about seven layers of ice, was generated and its structure was considered to be in equilibrium. The choice of the number of $H_2O$ molecules was based on the stability of the slab-shaped amorphous water ice with a sufficiently large surface area and bulkiness to represent the icy mantles of dust grains. The surfaces of the slab were located at $z = \pm 10$ Å. Thus the resulting slab was found to have a two-dimensional periodicity in the $x$- and $y$-directions. We assumed that one of the surfaces, at $z = +10$ Å, was the model surface of the icy mantles of the dust grains.

For the second stage, under the two-dimensional periodic boundary condition, MD simulations using method (i) were performed for both the slab and the first incident $H$ atom thrown on to the model surface. The coordinates and velocities of the water molecules at the first stage were used as the initial conditions for the amorphous ice. In contrast, the initial velocity of the incident $H$ atom was designed to correspond to thermal velocities of 70 and 10 K, reflecting the 10- and 70-K amorphous water ice. For the initial position of the incident $H$ atom, the value of $z$ was kept at 20 Å and those of $x$ and $y$ were randomly selected. Furthermore, the direction of the $H$ atom thrown on to the slab surface was randomly selected. The time-step of the MD simulation was taken to be 1 fs and the duration of the run was 5 ps. The MD simulation at this stage was performed mainly to study the sticking and diffusion processes of $H_2$ formation.

For the third stage, the second incident $H$ atom was thrown on to the model surface on which the first $H$ atom was stuck. The MD simulation was performed by using both methods (i) and (ii). As the initial conditions for the water molecules and the first incident $H$ atom, the coordinates and velocities generated at the last step of the second stage were used. The initial position and velocity of the second incident $H$ atom were selected in the same way as for the first incident $H$ atom. The time-step of the MD simulation was taken to be 0.1 fs and the duration of the run was 2 ps. The MD simulation at this stage was performed mainly to study the reaction and ejection processes of $H_2$ formation, but also to study the sticking and diffusion processes of the second incident $H$ atom.

The temperatures of the amorphous water ice slab were kept at 10 and 70 K by rescaling the velocities of the $H_2O$ molecules at every time-step. This procedure was based on the simple assumption that the relaxation of the excitation of $H_2O$ and the radiative cooling could be simultaneously taken into account through the temperature scaling. This procedure was also carried out to mimic the canonical ensemble at a given thermodynamical temperature for $H_2O$ molecules.

3 RESULTS AND DISCUSSION

3.1 Amorphous water ice

It is known that amorphous water ice has a high-density structure (about 1.1 g cm$^{-3}$) below 38 K and a low-density structure (about 0.94 g cm$^{-3}$) above 68 K (Jenniskens & Blake 1994). By MD simulations using method (i), in which $H_2O$ molecules were treated as rigid (hard ice model), the densities of the amorphous water ice slabs at 10 and 70 K were found to be about 1.07 and about 0.93 g cm$^{-3}$, respectively. As was discussed previously (Masuda & Takahashi 1997; Masuda et al. 1998), the $O$–$O$ distance radial distribution functions at 10 and 70 K were also found to be in good agreement with the experimental measurements.
agreement with those of high-density and low-density amorphous water ice produced experimentally (Jenniskens et al. 1995). Thus we consider that the present amorphous water ice slabs are good models for the surfaces of icy mantles of dust grains.

In order to perform MD simulations using method (ii), in which the intramolecular vibrations of H$_2$O were taken into account (soft ice model), the structures of the amorphous water ice slabs produced by method (i) were used as the initial structures. It was found that the structures became modified gradually after the simulation started, but that they remained almost constant for about 2 ps when the MD simulation via method (ii) was performed.

### 3.2 Sticking process of a hydrogen atom

The behaviours of an H atom thrown on to amorphous water ice are classified into the sticking case and the scattered case. In the former case, part of the energy of the incident H atom is absorbed by the amorphous water ice during the collision process on the surface, and the H atom finally becomes stuck. In the latter case, the incident H atom rebounds from the surface immediately after the encounter, without adequate energy transfer from the incident H atom to the ice.

The dependence of the sticking probability on the kinetic temperature of the incident H atom was examined by using method (i) in previous work (Masuda et al. 1998). In contrast, the sticking probability of the incident H atom on the amorphous water ice has been obtained by using both methods (i) and (ii) in the present work. The results are shown in Table 1, where the data for 10- and 70-K H atoms are from the present work, while those for 100- and 350-K H atoms are taken from the previous work (Masuda et al. 1998). It was found that there is a small difference between the results from methods (i) and (ii) for 10- and 70-K H atoms. A clear tendency is seen for the sticking probability to become smaller as the kinetic temperature of the incident H atom becomes larger. The sticking probability as a function of the kinetic temperature of the incident H atom was found to be well fitted by an analytical expression from Hollenbach & Salpeter (1970) and Buch & Zhang (1991), where the average attractive adsorption potential well depth was estimated at 2.5 kcal mol$^{-1}$ ($= 1250$ K) (Masuda et al. 1998).

### 3.3 Diffusion process of a hydrogen atom

In the sticking cases, the incident H atoms diffuse on to the surface of amorphous water ice via the thermal hopping mechanism at the first stage (for 1–3 ps), and then become trapped in one of the stable sites: that is, physisorbed at the sites corresponding to the local minima of the potential energy surface. The average total energy of the impinging H atom gradually decreases, because part of the energy is absorbed by amorphous water ice during the hopping process of the H atom. After the incident H atom is trapped in a potential well, its average total energy is so small that it can never overcome the potential energy barrier of the well. Thus it is difficult for the trapped H atom to rediffuse from one stable site to another via the thermal hopping mechanism. In fact, no trapped H atoms were found to restart diffusing within the computational time in our MD simulation (5 ps).

The mobilities of the incident H atom on the amorphous water ice in the diffusion process are classified into the mobility before the H atom is trapped and that after trapping. In previous work (Masuda et al. 1998), by using method (i), the average migration length and time of the impinging H atom during the surface hopping process at the first stage were calculated as measures of the mobility before trapping, and were found to depend only on the slab temperature. The results are shown in Table 2. The mobility for method (ii) was not estimated quantitatively, because the simulation time with this method was as small as 2 ps. It is considered that the results are of the same order.

For the mobility after the H atom is trapped, we estimated the time-scales for the trapped H atom to rediffuse via thermal hopping ($\tau_{\text{dif}}$) and to be desorbed from the ice surface thermally ($\tau_{\text{des}}$), by the following equations (Herbst 1995):

\[ \tau_{\text{dif}} = \frac{1}{v} \exp(E_{\text{dif}}/k_BT_{\text{ice}}). \]  
\[ \tau_{\text{des}} = \frac{1}{v} \exp(E_{\text{des}}/k_BT_{\text{ice}}). \]

Table 1. Sticking probability of H atom on to the amorphous water ice.

<table>
<thead>
<tr>
<th>Method</th>
<th>Temperature (K)</th>
<th>Number of simulations</th>
<th>Sticking probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice</td>
<td>H atom</td>
<td>Number</td>
<td></td>
</tr>
<tr>
<td>(i)</td>
<td>10</td>
<td>133</td>
<td>133</td>
</tr>
<tr>
<td>(i)</td>
<td>10</td>
<td>61</td>
<td>62</td>
</tr>
<tr>
<td>(i)</td>
<td>10</td>
<td>30</td>
<td>57</td>
</tr>
<tr>
<td>(i)</td>
<td>70</td>
<td>136</td>
<td>137</td>
</tr>
<tr>
<td>(i)</td>
<td>70</td>
<td>55</td>
<td>64</td>
</tr>
<tr>
<td>(i)</td>
<td>70</td>
<td>34</td>
<td>65</td>
</tr>
<tr>
<td>(i)</td>
<td>10</td>
<td>135</td>
<td>135</td>
</tr>
<tr>
<td>(i)</td>
<td>70</td>
<td>149</td>
<td>149</td>
</tr>
</tbody>
</table>

Table 2. Mobility of an H atom before and after it is trapped on the amorphous water ice.

<table>
<thead>
<tr>
<th>Method</th>
<th>Temperature (K)</th>
<th>Mobility before trapping</th>
<th>Mobility after trapping</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice</td>
<td>H atom</td>
<td>Migration length</td>
<td>Migration time</td>
</tr>
<tr>
<td>(i)</td>
<td>10</td>
<td>60 Å</td>
<td>1.7 ps</td>
</tr>
<tr>
<td>(i)</td>
<td>70</td>
<td>140 Å</td>
<td>2.7 ps</td>
</tr>
</tbody>
</table>

\[ \tau_{\text{des}} = \frac{1}{v} \exp(E_{\text{des}}/k_BT_{\text{ice}}). \]
where $\nu$ is the frequency of classical oscillation on the ice surface, $E_{\text{diff}}$ is the height of the barrier to rediffusion, $E_{\text{des}}$ is the average adsorption potential well depth, $k_B$ is the Boltzmann constant, and $T_{\text{ice}}$ is the temperature of the amorphous water ice. In our MD simulation, it was found that $\nu \approx 10^{13} \text{ s}^{-1}$ and $E_{\text{des}} \approx 2.5 \text{ kcal mol}^{-1}$ (see Section 3.2). Although we have performed no analysis for the value of $E_{\text{diff}}$, it is generally considered that $E_{\text{diff}}$ is less than $E_{\text{des}}$. In the present work, we have simply assumed two cases: $E_{\text{diff}} = 0.25E_{\text{des}}$ and $E_{\text{diff}} = 0.50E_{\text{des}}$. The resulting time-scales are shown in Table 2. We admit that the present results are very rough estimates. In future work, we will perform a more exact estimation of the thermal diffusion and desorption time-scales based on all of the information about the potential energy surface of the amorphous water ice.

Naturally, at such low temperatures as 10 and 70 K, the quantum mechanical effect might be very important in the diffusion process of an H atom, since it could diffuse further via the quantum tunnelling mechanism even after it is trapped thermally. In order to estimate the diffusion constant including the quantum tunnelling effect, a new formalism using the differential diffusion constant was recently developed (Takahashi et al. 1998). A rate calculation was performed for an H atom diffusing from one trapped site to another on the amorphous water ice slab. The numerical value was compared with the hopping rate constant of classical thermal diffusion, and a large quantum effect was found. In future work, the quantum mechanical diffusion constant will be calculated for the diffusion of an H atom over the whole surface of the amorphous water ice.

### 3.4 Reaction process of two hydrogen atoms

There are two mechanisms by which two hydrogen atoms can meet on the grain surface. One is the Langmuir–Hinshelwood mechanism, in which the second incident H atom sticks on to the grain surface and then diffuses into the vicinity of the site where the first H atom is trapped. The other is the Eley–Rideal mechanism, in which the second H atom in the gas phase strikes directly the first H atom adsorbed on the grain surface (see e.g. Williams 1993; Herbst 1995; Duley 1996). Which is more effective depends on the collision rate of H atoms on the surface and the time-scale from the sticking of the H atom to its ejection. In the present MD simulations, the second H atom was intentionally thrown into the vicinity of the first H atom trapped on the surface of the amorphous water ice, because the observation of the reaction process of two H atoms was the main aim. Therefore, the meeting of the the two H atoms consists of a combination of the above two mechanisms.

There were many MD trajectories for which the two H atoms could not react during the limited simulation time. It was found that the two H atoms could not encounter each other and diffused away if the minimum distance between them was more than about 3.5 Å.

In other words, they recombined when they approached each other within that critical distance, where the attractive potential between two H atoms $V_{\text{H–H}} = -1.0 \text{ kcal mol}^{-1}$. Thus the effective reactive cross-section was evaluated at about 40 Å$^2$.

The trajectories for which two H atoms could encounter each other and react are classified into three cases: I, II and III. Fig. 1 shows an example of the case in which $H_2$ was produced via the Langmuir–Hinshelwood mechanism (case I). The MD trajectories of the first and second incident H atoms on the amorphous water ice are shown in the top picture. The time dependences of the H–H distance and the height of each H atom are shown in the middle graph. The time origin was taken at the time when the second H atom was thrown on to the surface. The H height (along the $z$-axis) was measured from the plane including the centre of the amorphous water ice slab. The location of the rough surface of the amorphous water ice slab was about $z = 8–12$ Å. It was found that the second incident H atom stuck on to the surface at about 1260 fs, then diffused on to the surface, and met with the first H atom at about 1330 fs, when the minimum H–H distance was about 0.40 Å. The time dependence of the sum of kinetic energies of the two H atoms is shown in the bottom graph. The potential energy between the H atoms was transferred to the kinetic energy of the two reacting H atoms. Their maximum kinetic energy was found to be about 108 kcal mol$^{-1}$ at the equilibrium H–H distance. The intense oscillation of the H–H distance and the total kinetic energy represent the product $H_2$ molecule in a vibrationally excited state.

Fig. 2 shows an example of the Eley–Rideal case (case II). It was seen that the second H atom never diffused on to the surface of the amorphous water ice, but struck the first H atom directly at about 400 fs, and then an H$_2$ molecule was produced and ejected from the surface at about 460 fs. In contrast, Fig. 3 shows an example of an almost elastically scattered case (case III). It was seen that the two H atoms met and reacted at about 640 fs, but immediately scattered each other without $H_2$ being stabilized.

The excess energy released when an $H_2$ molecule is formed mainly originates from the $H_2$ formation energy, which is equal to the recombination energy of the two H atoms, 109.5 kcal mol$^{-1}$, corresponding to the well depth of the Morse-type H–H potential function $V_{\text{H–H}}$. A very small part of the excess energy might be supplied as the rotational energy arising from the torque of the two H atoms. Compared with the interaction energy between two $H_2O$ molecules (6.2 kcal mol$^{-1}$) and that between $H$ and $H_2O$ (0.3 kcal mol$^{-1}$), the $H_2$ formation energy is very large. In MD simulations using method (i) where $H_2O$ was treated as rigid (hard ice model), the excess energy from $H_2$ formation can be absorbed by the amorphous water ice through the coupling of the $H_2$–$H_2O$ libration with the intermolecular vibrational modes of $H_2O$ molecules in the ice. In method (ii) where the intramolecular vibrational motions of $H_2O$ were taken into account (soft ice model), the excess energy can be absorbed as both the intermolecular and intramolecular vibrational energies of $H_2O$ molecules. When part of the excess energy was effectively absorbed by the amorphous water ice during the reaction of the two H atoms, $H_2$ could be formed (cases I and II). When this did not happen, an almost elastic collision of the two H atoms occurred (case III).

The results for cases I, II and III are shown in Table 3. As was mentioned in the first paragraph of this section, since the second H atom was intentionally thrown into the vicinity of the first H atom in the present simulations, there might be little significance in the ratios of cases I and II. The reaction probability of the two incident H atoms on the amorphous water ice is defined as the sum of probabilities of cases I and II. The present definition of the reaction probability is not a global one, but a microscopic one. The results are also shown in Table 2. The reaction probability on the soft ice (method ii) is almost unity. In contrast, the reaction probability on the hard ice (method i) was found to be less than unity. It is considered that it was more difficult for the two reacting H atoms to couple with $H_2O$ molecules in the hard ice and to lose part of their excess energy for $H_2$ formation, since there are only intermolecular vibrational modes of the $H_2O$ molecules.

The geometrical character of the two reacting H atoms on the amorphous water ice is as follows. Before the two H atoms reacted, the first H atom was physisorbed in one of the stable sites on the ice, where the distance between the H atom and the nearest $H_2O$ was about 3 Å. Then the second incident H atom
attached itself on to the head of the first H atom. H2 was physisorbed in the head-on configuration and vibrated at the bottom of the potential well. The orientations of H2O molecules in the vicinity of the H atom or the H2 molecule could be slightly rearranged so as to stabilize it.

3.5 Ejection process of molecular hydrogen

The desorption mechanism has been considered to involve the excitation of product molecules, which might be frozen-out after they are produced, by photons or cosmic rays. There is another possibility: that the exothermic reactions between adsorbed species can lead directly to the ejection of product molecules (Williams 1993; Herbst 1995).

In the present simulation, it has become apparent that the ejection of the product H2 occurred successively after the reaction of two H atoms via the direct ejection mechanism. In this mechanism, part of the excess energy derived from H2 formation was absorbed by ice, and then part of the remaining excess energy was used to eject the product H2 from the ice surface.

The ejection rate can be evaluated from the time-scale for the H2 molecule to escape from the grain surface. The time-scales of ejection were measured for those H2 molecules that were formed in both case I (Langmuir–Hinshelwood case) and case II (Eley–Rideal case). For
about half of the trajectories in those cases, the product H₂ molecules stayed on the amorphous water ice only for a very short time (less than 100 fs), and they were subsequently ejected from the ice surface. For the other half, the product H₂ stayed for a relatively longer time (about 100–200 fs), hopping on the ice surface before its ejection. The average time-scales for cases I and II and also the averages as a whole are shown in Table 4. It was found that there was a small difference between them. Because of the small number of trajectories, the temperature dependence and the difference between methods (i) and (ii) could not be seen clearly. It was proved that the average time-scale as a whole is very short, only about 400–600 fs.

According to the oscillation of time dependences of the H–H distance and the total kinetic energies in Figs 1–3, most of the ejected H₂ molecules were found to be in vibrationally excited states. Since the librational mode of H₂ on the ice could lead to the rotational mode as well as the vibrational one of H₂, the ejected H₂ could also be in rotationally excited states. Actually, according to the time dependences of the heights of the first and second H atoms shown in Figs 1–3, it can be seen that the ejected H₂ molecules were rotating. An analysis of the energy distribution of the ejected H₂ molecules is performed in another paper (Takahashi et al. 1999).

4 CONCLUSIONS

In the present work, we have studied the formation mechanism of
H$_2$ on the surfaces of icy mantles of interstellar dust by a theoretical procedure based on a classical molecular dynamics (MD) computational simulation. The following fundamental processes of H$_2$ formation on the dust surface have been examined in detail: (1) sticking of the incident H atom on to the grain surface; (2) diffusion of the H atom over the surface; (3) reaction of two H atoms on the surface; and (4) ejection of the product H$_2$ molecule from the surface back into the gas phase. All of the information, including the sticking probability of the H atom, the migration length and time of the H atom, the diffusion and desorption timescales of the H atom, the reactive cross-section and reaction probability of the two H atoms, and the ejection time-scale of the product H$_2$ molecule, was obtained for the above processes consistently within a single model.

In future work, we will perform an analysis of the energy distribution in the formation process of H$_2$ on icy mantles of dust grains. We will also perform a spectral analysis of the amorphous water ice itself, to study the energy transfer mechanism between the H atom or H$_2$ molecule and the H$_2$O molecules in the ice. In addition, the thermal diffusion and desorption rates of the H atom on icy mantles will be calculated, based on all of the information about the potential energy surface of the amorphous water ice. Since quantum tunnelling effects should be taken into account under low-temperature conditions in interstellar space, the quantum mechanical diffusion rate constants will be calculated for the diffusion of the H atom on to the amorphous water ice. Then we will calculate the chemical reaction rate for the H$_2$ formation process on the grain surface as a whole.
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REFERENCES


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