

## Theoretical Simulations of Grain-Surface Processes

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**Abstract.** Recent advances in theoretical simulations of grain-surface processes are reviewed. Classical molecular dynamics (MD) computer simulations were performed to investigate the whole process of H<sub>2</sub> formation on icy mantles of interstellar dust grains within a single model. Amorphous water ice slabs were generated at 10 K and 70 K as a realistic model surface of dust grains, and then two incident H atoms were successively thrown onto the surface to reproduce the H<sub>2</sub> formation process via  $H + H \rightarrow H_2$  on the dust surface. The following fundamental processes were studied in detail; 1) the sticking of H atom onto the grain surface, 2) the diffusion of H atom on the surface, 3) the reaction of two H atoms on the surface, 4) the ejection of H<sub>2</sub> from the surface. Then, the formation pumping mechanism of H<sub>2</sub> and the chemical desorption mechanism of frozen CO molecules in the vicinity of H<sub>2</sub> forming sites on dust grains were also studied.

### 1. Introduction

Grain-surface processes play important roles in astrochemistry. It is widely accepted that interstellar molecular hydrogen ought to be formed on the surface of cosmic dust grains, since exothermic bimolecular reactions cannot occur efficiently in gas phase under very low temperature and low pressure conditions. The H<sub>2</sub> formation via  $H + H \rightarrow H_2$  on dust grains involves the following fundamental processes; 1) sticking of incident H atoms onto the grain surface, 2) diffusion of H atoms over the surface, 3) reaction of two H atoms on the surface, and 4) ejection of product H<sub>2</sub> molecules from the surface back into the gas phase. It is considered that the H<sub>2</sub> emission spectrum in regions without a source of UV pumping or dynamical excitation originates from the formation pumping mechanism of H<sub>2</sub> produced on dust grains. Moreover, chemical desorption of frozen heavy molecules might occur in the vicinity of H<sub>2</sub>-forming sites on dust grains, if the release of H<sub>2</sub> formation energy could cause sufficient local heating.

Several authors have studied theoretically the processes and phenomena involving H<sub>2</sub> formation on dust grains (e.g. Hollenbach & Salpeter 1970; Leitch-Devlin & Williams 1985; Buch & Zhang 1991; Buch & Devlin 1993, 1994; Hunter & Watson 1978; Duley & Williams 1986, 1993; Williams 1993; Herbst 1995; Duley 1996; Parneix & Bréchnignac 1998; Forebrother et al. 2000). Recently, there have also been several experiments to reproduce the H<sub>2</sub> formation process on dust grain analogues (e.g. Pirronello et al. 1997, 1999). However, there have been

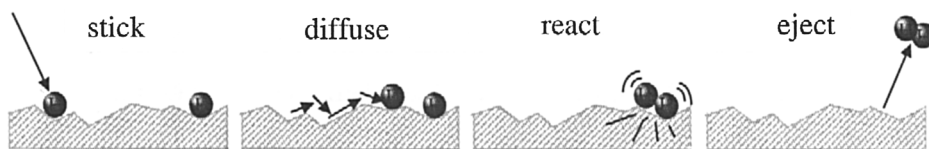


Figure 1. Fundamental processes of  $H_2$  formation on the surface of dust grains.

no theoretical studies which treat all processes and phenomena by a single model, and it is difficult to resolve the respective fundamental processes experimentally. On the other hand, recent theoretical studies by us (Takahashi et al. 1999a,b; Takahashi & Williams 2000) have attained the policy that the respective fundamental processes and the whole process and phenomena involving  $H_2$  formation on dust grains should be examined throughout in a single model, based on a classical molecular dynamics (MD) computational simulation. This paper focuses on reviewing advances in our theoretical simulations of grain-surface processes.

In the present theoretical model, a slab-shaped amorphous water ice was produced at 10 K and 70 K, as a realistic model surface of icy mantles of interstellar dust grains, and two H atoms were successively thrown onto the ice surface to reproduce the  $H_2$  formation process on dust grains, as is illustrated in Section 2. Four fundamental processes of  $H_2$  formation, the formation pumping mechanism of  $H_2$ , and the chemical desorption in the vicinity of  $H_2$  forming sites on the dust surface were investigated based on the above model, for which the results and discussion are shown in Sections 3, 4, and 5, respectively. The conclusions in this paper are summarized in Section 6.

## 2. Theoretical Model

### 2.1. MD simulation

Classical molecular dynamics (MD) simulation is a well established technique for studying molecular processes in the field of physical chemistry. In this simulation, Newtonian equations of motions are solved numerically to obtain positions, velocities, and forces as functions of time for all particles included in a many-body system. Despite the limitation of the classical treatment, this simulation can treat the real-time full-dynamics of the system and it has thus provided us with much realistic information about the molecular processes (see, e.g. Hansen & McDonald 1986). Our model, where the hydrogen atom or molecule is weakly physisorbed on the surface of icy mantles and motions are dominated by thermal dynamics, can be well treated by this technique (Masuda & Takahashi 1997; Masuda et al. 1998).

### 2.2. Computational details

For the first stage of this simulation, as a realistic model surface of icy mantles of interstellar dust grains, a slab-shaped amorphous water ice was generated under periodic boundary conditions. The size of the unit cell was about  $40 \text{ \AA} \times 40 \text{ \AA} \times 40 \text{ \AA}$ . As the initial conditions, 1000 water molecules were placed randomly

in the unit cell, and an equilibrium structure of amorphous water ice slab was obtained after 10 ps (picoseconds) ( $1 \text{ ps} = 10^{-12} \text{ s}$ ) run, where the time step was taken to be 1 fs (femtoseconds) ( $1 \text{ fs} = 10^{-15} \text{ s}$ ). The volume of the generated slab in the unit cell was about  $40 \text{ \AA} \times 40 \text{ \AA} \times 20 \text{ \AA}$ . For the second stage, the first incident H atom was thrown onto the amorphous water ice, and the sticking and diffusion processes of H atoms were mainly studied. Here, the time step was 1 fs. For the third stage, the second incident H atom was thrown onto the amorphous water ice, and the reaction and ejection processes of  $\text{H}_2$  molecules were mainly examined. Here, the time step was 0.1 fs. The temperatures of the amorphous water ice slab were kept at 10 K and 70 K by rescaling the velocities of water molecules at every time.

The total potential of the present system was approximately given as the sum of pair potentials. For the  $\text{H}_2\text{O}-\text{H}_2\text{O}$  pair, TIPS2 (Transferable Intermolecular Potential of the second version) by Jorgensen (1982) was employed. This potential function was modelled for rigid water molecules. For the  $\text{H}_2\text{O}-\text{H}$  pair, the Zhang-Sabelli-Buch potential function (1991) was employed. For the H-H pair, a Morse-type potential function with experimental parameters for a  $\text{H}_2$  molecule (Herzberg 1950) was used, where the dissociation energy of the  $\text{H}_2$  molecule is about 110 kcal/mol.

As for the MD algorithm, two methods were employed. In Method A, the  $\text{H}_2\text{O}$  molecules were treated as rigid and their intramolecular freedoms were constrained (hard ice model). On the other hand, in Method B, intramolecular vibrational modes of  $\text{H}_2\text{O}$  were taken into account by adding a spring-type potential to the TIPS2 potential (soft ice model). The latter model is, indeed, more realistic, but more time-consuming than the former model. As will be shown later, the hard ice model is sufficient to reproduce the water dynamics and there is little difference in the results between the two models.

### 2.3. Amorphous water ice

Experimentally, it is known that there are two forms of amorphous water ice, high-density one (about  $1.1 \text{ g cm}^{-3}$ ) below 38 K and low-density one (about  $0.94 \text{ g cm}^{-3}$ ) over 68 K (Jenniskens et al. 1995). It was found that the densities and the oxygen-oxygen distance radial distribution functions of 10 K and 70 K amorphous water ice slabs generated in the present MD simulation are in good agreement with those of high-density and low-density amorphous water ice, respectively. Thus, it is considered that these amorphous water ice slabs are good models for the real surface of icy mantles of interstellar dust grains.

## 3. Fundamental Processes of $\text{H}_2$ Formation on Dust Grains

### 3.1. Sticking process

As for the sticking process of incident H atoms onto the dust surface, two cases were found: the sticking case and the scattered one. It was found that the sticking probability depends on the kinetic temperature of incident H atoms. The results are shown in Table 1. Here, the sticking probability is unity when the hydrogen coverage is low. The sticking probability is almost unity when the temperature of incident H atoms is less than 70 K and it decreases with

increasing temperature. Since the present amorphous water ice is a slab-shaped one with infinite area, it is considered that its value of the sticking probability is larger than that for small ice clusters.

Table 1. The sticking probability of H atoms onto amorphous water ice (after Takahashi et al. 1999a).

Method	Temperature (K) Ice	H atom	Total number of simulations	Sticking probability
A	10	10	133	1.00
A	10	100	62	0.98
A	10	350	57	0.53
A	70	70	137	0.99
A	70	100	64	0.86
A	70	350	65	0.52
B	10	10	135	1.00
B	70	70	149	1.00

### 3.2. Diffusion process

In the sticking cases, it was found that the incident H atom diffused on the ice surface via thermal hopping for just a short time after sticking (1–3 ps) and then it became always trapped in one of the stable sites on the surface of amorphous water ice, because the incident H atom lost the excess energy during the hopping process and its total energy became small as it could not go up to the potential energy barrier of the well.

As a measure of the mobility of H atoms before trapping, the migration length and time were measured, and they were found to be, respectively, about 60 Å and 1700 fs for 10 K ice and 140 Å and 2600 fs for 70 K ice. It was found that the mobility of H atoms before trapping depends on the ice temperature.

As the mobility of H atoms after trapping, thermal desorption and diffusion time scales were estimated, respectively, by the following equations.

$$\tau_{des} = \nu^{-1} \exp(E_{des}/T_{ice}) \quad (1)$$

$$\tau_{dif} = \nu^{-1} \exp(E_{dif}/T_{ice}) \quad (2)$$

where  $\nu$  is the frequency of a classical oscillation in the potential well ( $\nu \approx 10^{13} \text{ s}^{-1}$ ),  $E_{des}$  is the adsorption potential well depth,  $E_{dif}$  is the height of the barrier to diffuse on the ice surface, and  $T_{ice}$  is the temperature of the amorphous water ice. According to the results of our MD simulation, it was found that  $E_{des}$  for H atoms trapped on the ice surface ranges from about 250 K to 2500 K. Since  $\tau_{des}$  strongly depends on the value of  $E_{des}$ , we assumed two cases:  $E_{des}=1250 \text{ K}$ , 500 K. For  $E_{dif}$ , we simply assumed two cases:  $E_{dif}=0.50 E_{des}$ ;  $E_{dif}=0.25 E_{des}$ . The resulting time scales are shown in Table 2. The desorption and diffusion time scales for 10 K ice were found to be rather too large for a larger value of

$E_{des}$ . In future work, we will estimate the thermal desorption and diffusion time scales more exactly based on detailed information about the potential energy surface of the amorphous water ice.

It is naturally expected that the quantum tunneling mechanism might dominate the H atom's diffusion process under such low temperatures. Since this problem cannot be treated by a classical MD simulation, we are studying the H atom's diffusion process including both thermal and quantum tunneling mechanisms by a quantum diffusion theory with a Monte-Carlo path-integral technique (Takahashi et al. 1998). We will also obtain the total diffusion constant including both mechanisms in future work.

Table 2. Thermal desorption and diffusion time scales of H atoms after they are trapped on the surface of amorphous water ice.

Temperature		Thermal desorption and diffusion time scales			
Ice (K)	H atom (K)	$E_{des}$ (K)	$\tau_{des}$	$\tau_{dif}$ $E_{dif}=0.50 E_{des}$	$\tau_{dif}$ $E_{dif}=0.25 E_{des}$
10	10	1250	$10^{34}$ years	$10^7$ years	$10^1$ s
10	10	500	$10^1$ years	$10^{-2}$ s	$10^{-8}$ s
70	70	1250	$10^{-5}$ s	$10^{-9}$ s	$10^{-11}$ s
70	70	500	$10^{-10}$ s	$10^{-12}$ s	$10^{-13}$ s

### 3.3. Reaction process

As for the reaction process of two H atoms on the dust surface, three reactive cases were found. The first is the Langmuir-Hinshelwood case (Fig. 2a), where two H atoms reacted with each other after they diffused on the dust surface. The second is the Eley-Rideal case (Fig. 2b), where the second incident H atom struck the first H atom that was trapped on the dust surface directly from the gas phase. The third is the almost elastic scattering case, where two H atoms once reacted but were immediately scattered from each other without an H<sub>2</sub> molecule being formed.

In our MD simulation, it was found that two H atoms began to react when they encountered at distances less than 3.5 Å, but in other cases they could not react. From this result, the effective reactive cross-section for H atoms on the ice surface was estimated about 40 Å<sup>2</sup>. The reaction probability, defined as the probability that H<sub>2</sub> is produced after two H atoms encountered each other on the ice surface, was found to be almost unity.

### 3.4. Ejection process

In the present MD simulation, it was found that the ejection process of the product H<sub>2</sub> molecule occurred subsequently after the two H atoms' reaction process via the direct ejection mechanism, in that part of the H<sub>2</sub> formation energy was used for the product H<sub>2</sub> itself to escape from the ice surface. It was also found that the product H<sub>2</sub> was ejected very rapidly after it was produced on the ice surface. The ejection time scale was measured, and it was found to be only about 500 fs.

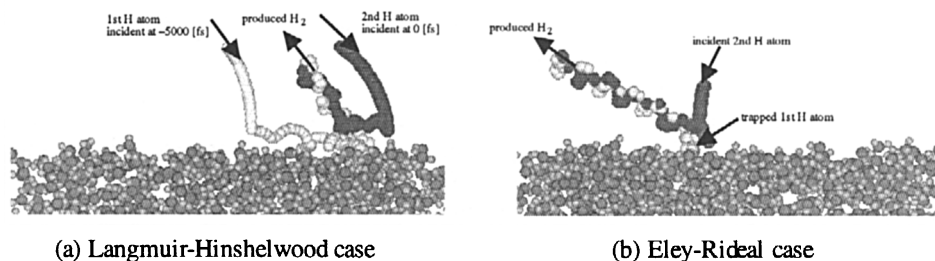


Figure 2. The reaction process of two H atoms on icy mantles of dust grains (after Takahashi et al. 1999a).

#### 4. Formation Pumping Mechanism of H<sub>2</sub> Produced on Dust Grains

The energy analysis of the H<sub>2</sub> molecules formed on the amorphous water ice surface was performed. The total energy of H<sub>2</sub> can be separated numerically into vibrational, rotational, and translational energies. Although vibrational energies obtained in this MD simulation are classical, it is possible to make them correspond approximately to quantum vibrational energy levels ( $v=0-14$ ). In the present work, it was regarded that if the classical energy lies between the quantum energy levels  $v$  and  $v+1$ , it is treated as being at the energy level  $v$ . The maximum error in this approximation is considered to be the extent of energy between two adjacent vibrational energy levels.

The resulting vibrational energy population is shown in Fig. 3. It has become clear that H<sub>2</sub> molecules formed on amorphous water ice are in high vibrationally excited states. The vibrational energy levels with the highest intensities are around  $v=8$ . The total averaged vibrational, rotational, and translational energies of the product H<sub>2</sub> molecule are shown in Table 3. More than 70% of the H<sub>2</sub> formation energy (about 110 kcal/mol) resides in the vibrational energy of H<sub>2</sub>, and another part is transferred into the rotational and translational energies of H<sub>2</sub>. The energy absorbed by the amorphous water ice can be approximately evaluated from the difference between the total energy of the ejected H<sub>2</sub> and the H<sub>2</sub> formation energy, and it was found to be only about 4%. These results are considered to be reasonable, because the H<sub>2</sub> molecule is a very light particle, the ejection time scale is very short, and H<sub>2</sub> is weakly physisorbed on the amorphous water ice.

It was found that there are only few differences in results between 10 K and 70 K ices and the hard ice model (Method A) and soft ice model (Method B). A small temperature dependence was caused by the fact that the surface of the 70 K ice has more randomness than that of the 10 K ice. There is some tendency that the H<sub>2</sub> formation energy could be transferred in more different ways in the soft ice model, because there is a stronger interaction between the H<sub>2</sub> and H<sub>2</sub>O molecules in the soft ice model where the intramolecular freedoms of H<sub>2</sub>O are taken into account than in the hard ice model where H<sub>2</sub>O is treated as rigid. It was found that there is little difference in the product energy distribution between the Langmuir-Hinshelwood and Eley-Rideal cases.

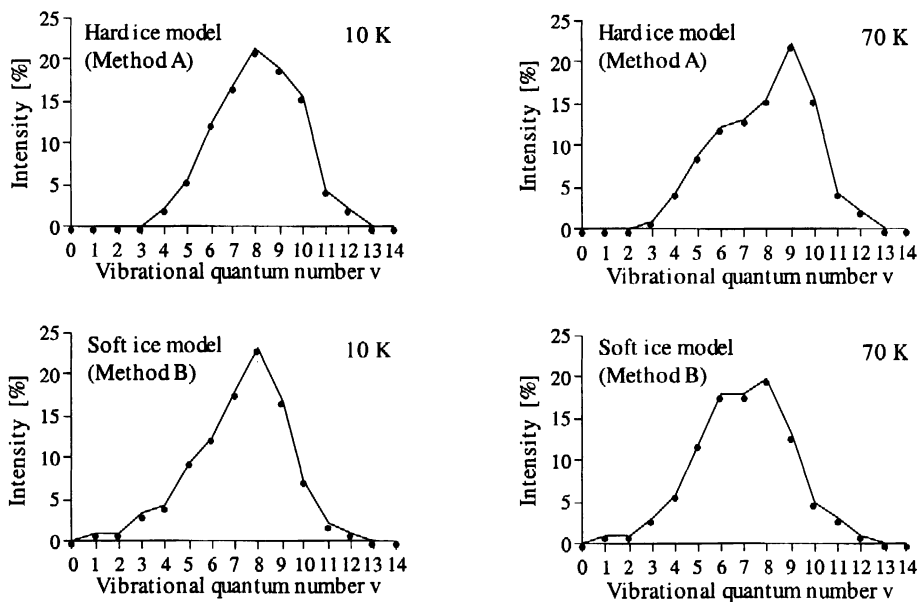


Figure 3. The vibrational energy population of  $H_2$  formed on the 10 K and 70 K amorphous water ice (after Takahashi et al. 1999b).

The present results reveal that interstellar molecular hydrogen newly formed on icy mantles of dust grains are highly vibrationally excited by the formation pumping mechanism. They are also highly excited rotationally and translationally. As was suggested by Duley & Williams (1993), this study shows that the rovibrational emission spectrum of  $H_2$  might be detectable in regions without a source of UV pumping or dynamical excitation.

## 5. Chemical Desorption around $H_2$ Forming Sites on Dust Grains

It is well known that heavy molecules exist in the gas phase of cold dense clouds, but the mechanism to eject them from the dust surface into the gas phase is poorly known. As one of the mechanisms which might be effective, it is considered that chemical desorption of weakly bound molecules such as carbon monoxide can occur in the vicinity of  $H_2$  forming sites on dust grains, if a small release of  $H_2$  formation energy is sufficient to heat dust locally.

In order to know whether the chemical desorption of a frozen CO molecule can occur or not, the time and space dependence of the local temperature of icy mantles of dust grains was examined by our MD simulation. The amorphous water ice slab was divided into several regions according to the distance from the  $H_2$  forming site, and further divided into the surface and bulk regions. The background temperature of the ice was initially set up at 10 K, and the temperature rescaling was switched off after two H atoms began to react.

Table 3. The average product energy distribution of H<sub>2</sub> formed on the 10 K and 70 K amorphous water ice. The numbers are the percentages divided by the H<sub>2</sub> formation energy, 110 kcal/mol (after Takahashi et al. 1999b).

Method	Temperature Ice (K)	H atom (K)	Average vibrational (%)	product rotational (%)	energies of H <sub>2</sub> translational (%)	Energy absorbed by ice (%)
A	10	10	78.5	9.9	7.4	4.0
A	70	70	76.7	10.7	8.5	3.9
B	10	10	72.4	12.2	11.6	3.8
B	70	70	70.4	14.3	10.6	4.5

It was found that the local temperature of the surface regions within 6 Å from the H<sub>2</sub> forming site increases up to about 20–30 K just after the two H atoms began to react, and then decreases gradually, because energy is dispersed into other regions. The lifetime of local heating was found to be about a few picoseconds.

The critical temperature for the CO desorption is defined as the temperature at which the sticking rate of CO onto dust grains and the desorption rate of CO from dust grains are comparable. This temperature was estimated under conditions in typical molecular clouds and it was found to be 20–30 K with various assumed binding energies. It might be seen that the result of the MD simulation supports the possibility of chemical desorption of CO. However, at such temperatures, the time scale for CO desorption is at least 10<sup>5</sup> years, while the lifetime of local heating caused by H<sub>2</sub> formation is just a few picoseconds. In addition, the time scale of H<sub>2</sub> formation in the vicinity of an adsorbed CO molecule on dust grains is estimated at most 10<sup>5</sup> years. Therefore, it is concluded that chemical desorption of frozen CO molecules in the vicinity of H<sub>2</sub> forming sites is negligible, at least, on large dust grains.

## 6. Conclusions

In the present work, it was shown that much information about grain-surface processes involving the H<sub>2</sub> formation process on icy mantles of interstellar dust grains could be obtained selfconsistently within a single theoretical model based on a MD simulation. The amorphous water ice slabs generated by our MD simulation were compared with those produced experimentally, and it was considered that they are good model surfaces of icy mantles of interstellar dust grains. Four fundamental processes of H<sub>2</sub> formation on dust grains were investigated in detail, for which the sticking probability, thermal mobilities of incident H atoms, three reaction patterns of two H atoms including Langmuir-Hinshelwood, Eley-Rideal, and elastic scattering cases, the reactive cross-section, the reaction probability, and the ejection lifetime of the product H<sub>2</sub> molecule were obtained. The product energy distribution of H<sub>2</sub> was examined, and it was found that H<sub>2</sub> molecules newly formed on icy mantles of dust grains are in highly vibrationally excited states by the formation pumping mechanism, which might suggest that the rovibrational emission would be detectable even in regions without a source of UV



pumping or collisional excitation. The chemical desorption in the vicinity of H<sub>2</sub> forming sites on dust grains was also examined based on the same model, and it was found that this mechanism is negligible, at least, on large dust grains.

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## References

- Buch, V. & Devlin, J.P. 1993, *J. Chem. Phys.*, 98, 4195  
——— 1994, *ApJ*, 431, L135  
Buch, V. & Zhang, Q. 1991, *ApJ*, 379, 647  
Duley, W.W. 1996, *MNRAS*, 279, 591  
Duley, W.W. & Williams, D.A. 1986, *MNRAS*, 223, 177  
——— 1993, *MNRAS*, 260, 37  
Forebrother, A., Fisher, A., & Clary, D.C. 2000, in preparation  
Hansen, J.P. & McDonald, I.R. 1986, *Theory of Simple Liquids* (2nd edition, Academic Press: New York)  
Herbst, E. 1995, *Annu. Rev. Phys. Chem.*, 46, 27  
Herzberg, G. 1950, *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules* (2nd edition, Van Nostrand: New York)  
Hollenbach, D. & Salpeter, E.E. 1970, *J. Chem. Phys.*, 53, 79  
Hunter, D.A. & Watson, W.D. 1978, *ApJ*, 226, 477  
Jenniskens, P., Blake, D.F., Wilson, M.A., & Pohorille, A. 1995, *ApJ*, 455, 389  
Jorgensen, W.L. 1982, *J. Chem. Phys.*, 77, 4156  
Leitch-Devlin, M.A. & Williams, D.A. 1985, *MNRAS*, 213, 295  
Masuda, K. & Takahashi, J. 1997, *Adv. Space Res.*, 19, 1019  
Masuda, K., Takahashi, J., & Mukai, T. 1998, *A&A*, 330, 773  
Parneix, P. & Bréchignac, Ph. 1998, *A&A*, 334, 363  
Pirronello, V., Biham, O., Liu, C., Shen, L., & Vidali, G. 1997, *ApJ*, 483, L131  
Pirronello, V., Liu, C., Roser, J. E., & Vidali, G. 1999, *A&A*, 344, 681  
Takahashi, J., Masuda, K., & Nagaoka, M. 1999a, *MNRAS*, 306, 22  
——— 1999b, *ApJ*, 520, 724  
Takahashi, J., Nagaoka, M., & Masuda K. 1998, *Int. J. Quantum Chem.*, 70, 379  
Takahashi, J. & Williams, D. A. 2000, *MNRAS*, in press  
Williams, D.A. 1993, in *Dust and Chemistry in Astronomy*, eds. T.J. Millar & D.A. Williams (Institute of Physics Publishing: Philadelphia), 143  
Zhang, Q., Sabelli, N., & Buch, V. 1991, *J. Chem. Phys.*, 95, 1080

## Discussion

*E. F. van Dishoeck:* Can you comment on the prospects for doing quantum mechanical calculations on the vibration-rotation distribution of H<sub>2</sub> upon formation?

*J. Takahashi:* Classical vibrational and rotational energies can be made to correspond to the quantum counterparts approximately. The maximum error in this

approximation is the extent of energy between two adjacent quantum energy levels. However, it is considered that this error can be cancelled out statistically by doing MD simulations many times.

*D. A. Williams:* A further comment in response to Ewine's question about the possibility of quantum mechanical treatments of H<sub>2</sub> formation on surfaces. It has not been done for amorphous ice, but a fully quantum mechanical calculation has been carried out for H<sub>2</sub> formation on a graphite surface by Farebrother, Fisher, & Clary, for a colinear system. The results of efficiency and of vibrational excitation for that system are similar to Junko's results for H<sub>2</sub> formation on ice.

*J. Takahashi:* I would like to comment on David Williams' comment. A fully quantum mechanical treatment is possible only for such a simple system as a colinear H<sub>2</sub> on a graphite surface, but it is much too time-consuming and impossible for such a complex system as the present one. Despite the limitations of the classical treatment, the present MD simulation has a strong point in that the full, real-time dynamics of the system can be taken into account and all fundamental processes can be studied throughout by a single model.

*P. Brechignac:* Since D. Williams mentioned the work by Clary's group on H<sub>2</sub>-formation on graphite surfaces, I wish to point out our previous work on graphite. The results are quite different, particularly in the vibrational distribution, and this should be cleared up in the near future. There are two possible sources for the discrepancy: (1) The quantum calculations are one-dimensional, our classical calculations (MD, as in your case) treat the full dimensionality of the problem. (2) The potential energy surface (PES) might be different. By the way, the reactive portion of your PES is very simple, so that it is not such a complicated system.

*J. Takahashi:* H<sub>2</sub> on a graphite surface is a chemisorption system. On the other hand, H<sub>2</sub> on amorphous water ice is a physisorption system, and the distortion of the PES in the H-H reactive region by H<sub>2</sub> - ice interaction is sufficiently small. Thus, the PES of the present system is well represented by adding pair potentials simply.

*J. M. Greenberg:* It is possible (as calculated by Li and myself) that the grain temperature in dark clouds is as low as 6–8 K. Would such a low temperature affect your results?

*J. Takahashi:* The effect of a grain temperature decrease from 10 K to 6–8 K will be revealed in the diffusion process of the H atoms. Time scales for thermal diffusion and desorption of H atoms will increase obviously with decreasing grain temperature.

*W. Schutte:* In interstellar ices CO is primarily found in apolar ices (CO, N<sub>2</sub>, O<sub>2</sub>; Tielens et al. 1991, ApJ, 381, 181; Chiar et al. 1995, ApJ, 455, 234). Could the formation of H<sub>2</sub> on the surface of such an ice lead to CO desorption?

*J. Takahashi:* This question is beyond the present study. However, it is supposed that the CO desorption from apolar ices would be easier than that from H<sub>2</sub>O ice, because the binding energy between CO and the former ices is less than between CO and the latter ice.