Modeling of the Dissociative Adsorption Probability of the H₂-Pt(111) System Based on Molecular Dynamics

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Abstract. Molecular Dynamics (MD) was used to simulate dissociative adsorption of a hydrogen molecule on the Pt(111) surface considering the movement of the surface atoms and gas molecules. The Embedded Atom Method (EAM) was applied to represent the interaction potential. The parameters of the EAM potential were determined such that the values of the dissociation barrier at different sites estimated by the EAM potential agreed with that of DFT calculation results. A number of MD simulations of gas molecules impinging on a Pt(111) surface were carried out randomly changing initial orientations, incident azimuth angles, and impinging positions on the surface with fixed initial translational energy, initial rotational energy, and incident polar angle. The number of collisions in which the gas molecule was dissociated were counted to compute the dissociation probability. The dissociation probability was analyzed and expressed by a mathematical function involving the initial conditions of the impinging molecule, namely the translational energy, rotational energy, and incident polar angle. Furthermore, the utility of the model was verified by comparing its results with raw MD simulation results of molecular beam experiments.

Keywords: Molecular Dynamics, Hydrogen, Platinum, Dissociation, EAM
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INTRODUCTION

Dissociation of a hydrogen molecule on a platinum surface is a prototypical case of dissociative adsorption of a gas molecule on a metal surface. Studying this process is important not just for understanding the mechanism behind the fundamental phenomenon, but also because it could be the key to the industrial improvement of catalytic materials, such as the electrodes of a polymer electrolyte fuel cell (PEFC), and to achieve higher efficiency, to improve the stability, or to reduce the manufacturing cost. It might also lead to advanced catalyst designs, such as the utilization of nano-structured materials. To design such advanced catalysts, the development of a mathematical model of the reaction rate that considers nano-scale effects, that is, a multi-scale reaction rate model, is needed for design simulation purposes.

Recently, using density functional theory (DFT), information on the adsorption of H atoms on Pt(111) surfaces[1-7] has been reported and the dissociation barriers at various sites of the H₂-Pt(111) system[8] have been evaluated. Effective potentials between a gas molecule and various metal surfaces in six[9,10] dimensions of the gas orientation have been developed to accurately capture interactions. Even in the 6-D potential, since surface atoms were assumed to be fixed, the effects of atomic motion on dissociative adsorption could not be evaluated properly. A limited number of analyses that considered the thermal motion of surface atoms have been reported thus far[11-16] and the actual effects of thermal motion of surface atoms and the interaction between the motion of an impinging molecule and that of surface atoms have not been analyzed in detail. Although classical molecular dynamics, in which the interaction potential is assumed to be a function of the positions of the atoms in the system, is a suitable method to consider the motion of atoms, the conventional Lennard-Jones potential is not sufficient to simulate a dissociation process. Dissociation occurs as a result of a decrease in the bond strength between the atoms of a molecule, by filling antibonding orbitals of the gas molecule with free electrons from the surface. Therefore, the effect of electron

donation from the surface on the interaction potential must be considered in order to properly analyze the characteristics of dissociation phenomena.

The Embedded Atom Method (EAM) uses a potential that treats the interactions between gas atoms and a metal surface by considering the effects of the surface electrons.[17-24] In EAM, the form for the total potential energy, E_{tot}, of the system which consists of N Pt atoms and an H_2 molecule is given by

$$E_{\text{tot}} = \sum_{i=1}^{N} F_{\text{Pt}}(\rho_i) + \sum_{k=1}^{2} F_{\text{H}}(\rho_k) + \frac{1}{2} \sum_{i}^{N} \sum_{j(\neq i)}^{N} \phi_{\text{Pt-Pt}}(R_{ij}) + \phi_{\text{H-H}}(R_{12}) + \sum_{i=1}^{N} \sum_{k=1}^{2} \phi_{\text{Pt-H}}(R_{ik}), \qquad (1)$$

where subscripts i and j denote Pt atoms, k denotes an H atom, and R is the distance between atoms. The function, $F(\rho)$, is the energy of embedding an atom into the background electron density, and expresses the interaction between an atom and the electrons of the system. The functions, F_{Pt} and F_{H}, are the energies necessary to embed a Pt atom and an H atom, respectively. The function, $\phi(R)$, is the pair interaction potential between atoms separated by distance of R, and $\phi_{\text{Pt-Pt}}$, $\phi_{\text{Pt-H}}$, and $\phi_{\text{H-H}}$ are the pair interaction potentials between two Pt atoms, a Pt atom and an H atom, and two H atoms, respectively. The functions, ρ_i and ρ_k, are the electron densities contributed by the surrounding atoms at the position of Pt atom i and H atom k, respectively. In the EAM, the electron densities, ρ_i and ρ_k, are assumed to be the superposition of the electron density contributed by each surrounding atom.[21]

The authors have constructed the EAM potential of H_2-Pt(111) system by obtaining the functions, ϕ, ρ, and F.[25] These functions were determined such that the energy of the Pt crystal or that of an H_2 molecule, and the electron density around an H atom or that the on Pt(111) surface obtained by the EAM potential were consistent with those obtained by DFT. In addition, they were adjusted such that the dissociation barriers at specific sites on the Pt(111) surface obtained by the EAM were consistent with the results reported in Ref.8 obtained by DFT. Using the potential in a molecular dynamics (MD) approach, the authors analyzed the effect of thermal motions of atoms or molecules on the dissociation probability at several surface sites for the case that the incident angle is normal to the surface.[25] Recently the effect of incident angle on dissociation probability was also analyzed by the MD method.[26,27] The simulation results were averaged and compared to those obtained from molecular beam experiments[25] to check the validity of the simulations. The comparison showed that the MD based on the constructed EAM potential is capable of simulating molecular beam experiments to a certain degree.[26,27]

In this study, a number of MD simulations of gas molecules impinging on a Pt(111) surface are carried out, randomly changing the initial orientations, incident azimuth angles, and impinging positions on the surface with fixed initial translational energy, initial rotational energy, and incident polar angle. The number of collisions in which the gas molecule is dissociated is counted to compute the dissociation probability. The dissociation probability is analyzed and expressed by a mathematical function of the initial conditions of the impinging molecule, namely its translational energy, rotational energy, and incident polar angle. In addition, the model is compared with MD results that simulated molecular beam experiments.

COMPUTATIONAL CONDITIONS

In the simulations, H_2 molecules are incident on a Pt(111) surface consisting of 500 Pt atoms, which are aligned in five layers in the z direction, each of which consists of 10 Pt atoms (27.72 Å) in the x direction and 10 Pt atoms (24.00 Å) in the y direction, as shown in Fig. 1(a). Periodic boundary conditions are imposed in the x and y directions. Before simulating the dissociation of H_2 molecules, the relaxed Pt(111) surface temperature has been controlled to the target temperature T_s of 295 K. The method used to control the surface atoms is described in Ref. 25. Initial conditions of the simulations are as follows. The H_2 molecules approach the relaxed Pt(111) surface from a height of 5 Å. The collision location of the center of mass of H_2 molecules in the x and y axes are distributed at random in the rectangular area indicated in Fig. 1(b), instead of aiming at particular sites. The rectangular area in the figure is the minimum repeated unit surface area and is located at the center of the x-y domain of the computational region. An initial translational energy E_{tr} and an initial rotational energy E_{rot} are given to the impinging H_2 molecule. The orientations of the molecules are distributed in a random manner as described in Ref. 25. Simulations are performed for enough time steps for the H_2 molecule to reach the surface, depending upon the incidence energy. The configuration of the numerical experiment is shown in Fig. 1(a). The polar angle of incidence, θ_i, which is the angle between the line from the initial center of mass of the H_2 molecule to the collision point and the z axis, is a variable. The azimuthal angle of incident, ϕ_i, which is the angle between the line from the initial center of mass of the H_2

molecule to the collision point projected on the *x-y* plane and the *x* axis, is also chosen at random. Since the computational region in the *x-y* plane is small, the initial position of the molecule in *x* and *y* has to be outside of the computational region when the incident polar angle is large. This is avoided in this study by imposing periodic boundary conditions in the *x* and *y* directions. By doing this, the impinging molecule keeps interacting properly with the metal surface during the flight. Although the use of this method means that the molecule flies above the same surface more than once, it can be assumed that the effect on the surface molecules up to the moment of the collision is negligible since the impinging molecule is so light in comparison with the metal atoms. No vibrational energy is given to the molecule since almost all the H_2 molecules are in the vibrational ground state at 350 K, which is the typical operating temperature of a PEFC.


(a)   (b)
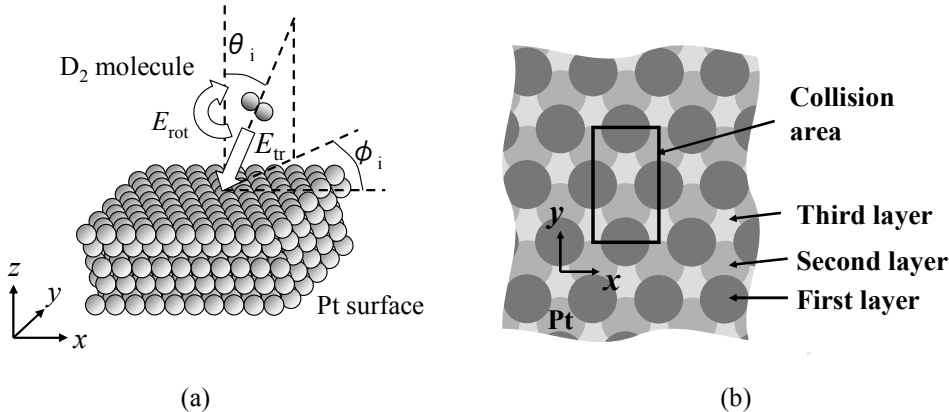
FIGURE 1. Configuration of H_2-Pt(111) system for MD simulations. (a). The angle, θ_i, denotes the polar angle of incidence. The angle, ϕ_i, denotes the azimuthal angle of incidence. (b). The collision area on the Pt(111) surface indicated by a rectangle located at the center of x-y domain of the computational region. Pt atoms of the upper layer are shown as a darker color.

The gas molecule is considered to be dissociated when the interatomic distance is larger than 3.5 Å. This criterion is the same as that used in Ref. 25. Each dissociation probability for a certain set of initial translational energy, initial rotational energy and the polar angle of incidence values is obtained as the fraction of dissociations found in 640 trials in which the orientation and collision position of the H_2 molecule, and the azimuth angle of incidence are all varied in a uniform random manner. The initial translational energy is varied from 0.0025 to 0.25 eV, and the initial rotational energy is varied from 0 to 0.16 eV. The polar angle of incidence, θ_i is varied from 0° (normal to the surface), 30°, 45°, or 60°. Detailed conditions and methods that are not described here can be found in Ref. 25. We have chosen three independent variables for the mathematical model of dissociation probability that will be established in the next section: the initial translational energy, rotational energy, and polar angle of incidence. The effect of azimuthal angle of incidence and the differences between sites are integrated in the model because it is assumed that the model will be used at macroscopic scale that cannot distinguish site differences and directions on the metal surface lattice. The initial energy ranges are chosen to cover the thermodynamic distribution at 350 K, which is the typical operating temperature of a PEFC, or less.

RESULTS

Figure 2 shows the variation of the dissociation probability as a function of initial translational energy and initial rotational energy when the polar angle of incidence is either $0°$, which is normal to the surface, 30°, 45°, or 60°. The following trends are apparent. The dissociation probability rises along with an increase in the initial translational energy, except for the region where both rotational energy and translational energy are very low. There seems to be no identifiable initial translational energy threshold for dissociation in the normal incidence polar angle case, but a threshold does appear gradually as the angle diverges from the normal direction. The dissociation probability rises with initial rotational energy up to a certain value when initial translational energy is not very low. On increasing the polar angle of incidence, or on keeping the initial translational energy constant and decreasing the effective translational energy normal towards the surface, $E_{tr,n} = E_{tr}\cos^2\theta_i$, the dissociation probability decreases, except for the region where both rotational energy and translational energy are very low. The rise at very low initial energy suggests that the "Steering Effect" at the top site described in our previous paper is operating.[25]

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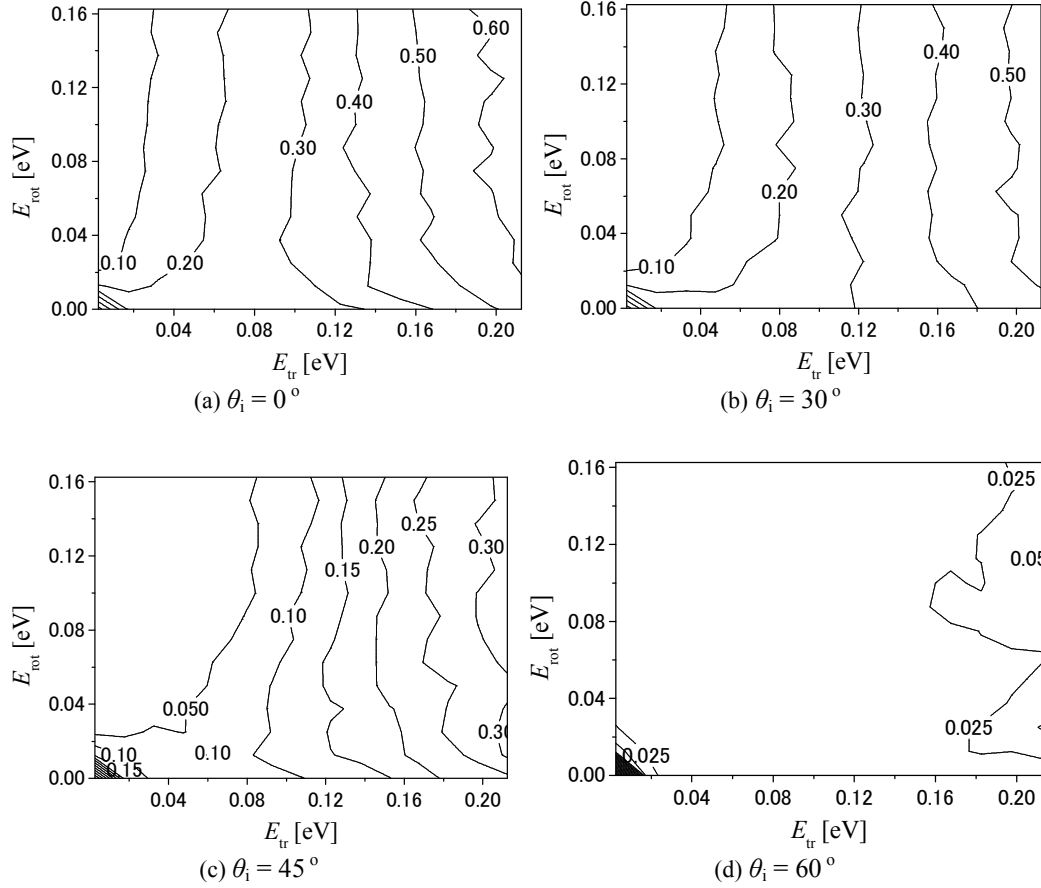
FIGURE 2. Contours of dissociation probability of H_2 on Pt(111) calculated by MD as a function of initial translational energy E_{tr} and initial rotational energy E_{rot}. Initial orientations of H_2 and azimuthal angle of incidence ϕ are chosen at random. Surface temperature, $T_s = 295$ K. Each panel shows the results for different polar angles of incidence θ_i. (a) $\theta_i = 0°$, (b) $\theta_i = 30°$, (c) $\theta_i = 45°$, and (d) $\theta_i = 60°$.

Considering the above phenomena, we propose the following mathematical form to express the dissociation probability of H_2 on a Pt(111) surface. The functional form consists of two terms. First term represents that the dissociation probability would be some value when normal incident energy exceeds the critical energy and zero otherwise. The critical energy corresponds to the barrier height between the physisorption region and the chemisorption region on the potential energy surface. The transition of the dissociation probability from zero to some value is smoothed by factors including the angle of incidence. The second term is for the steering effect which is apparent in the low kinetic energy region.

$$p\big(E_{tr,n}, E_{rot}, \theta\big) = A\big(E_{tr,n}, E_{rot}, \theta\big)/2 \cdot \big(1 + \tanh\big((E_{tr,n} - E_2)/W(\theta)\big)\big) + p'\big(E_{tr,n}, E_{rot}, \theta\big) \qquad (2)$$

Here A is a scaling factor that sets the maximum dissociation probability value. The factor W, which is the width of $E_{tr,n}$, is narrowed at large polar angles of incidence. The term p' is a correction term for the region where the initial rotational energy and translational energy are very low. The activation energy, E_i and the limiting parameters ψ_i are fitting parameters. The variable E_2 is the energy where the probability reaches a half of the maximum value. The scaling factor A increases with $E_{tr,n}$, and also increases with E_{rot} starting from ψ_2 when E_{rot} is 0. The value of p' rises to ψ_3 when both E_{rot} and E_{tr} approach 0, and is 0 elsewhere. It should be noted that E_2 is independent of the initial rotational energy, initial translational energy, and incidence angle. It can be said that Eqn. (2) is a refined version of the model proposed for H_2 on Cu(111) system by Harris[29], which emphasizes the effective translational energy normal towards the surface and the threshold in that value for the dissociation probability.

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$$A\left(E_{\mathrm{tr,n}}, E_{\mathrm{rot}}, \theta\right) = \left(1 - \exp\left(-E_{\mathrm{tr,n}}/E_1\right)\right)\left(1 - \left(1 - \psi_2\right)\exp\left(-E_{\mathrm{rot}}/E_3\right)\right) \tag{3}$$

$$W(\theta) = \psi_1 \cos^2\theta \tag{4}$$

$$p'\left(E_{\mathrm{tr,n}}, E_{\mathrm{rot}}, \theta\right) = \psi_3 \cos\theta \exp\left(-E_{\mathrm{rot}}/E_4\right)\exp\left(-E_{\mathrm{tr,n}}/\left(E_5 \cos^2\theta\right)\right) \tag{5}$$

Equation (2) is fitted to the MD simulation results by adjusting the fitting parameters as shown in Table 1.

TABLE 1. Fitted parameters for the proposed model of dissociation probability of H_2 on Pt(111), eqn. (2).

| Parameters	Values [eV]	Parameters	Values [-]
E_1	0.07905	ψ_1	0.2361
E_2	0.1200	ψ_2	0.8500
E_3	0.01043	ψ_3	0.3000
E_4	0.01009		
E_5	0.01729		

To verify this model, its results are compared to the dissociation probability predicted by our previous MD study[26,27] which simulated molecular beam experiments of D_2 dissociation on Pt(111).[28] It assumed that the impinging D_2 molecules have a rotational energy equivalent to thermal equilibrium at 1800 K. As reported in Luntz's experimental study,[28] no isotope effect was observed between D_2 and H_2[28], and we found that the simulation results could be represented by the proposed mathematical model, Eq. (2), constructed for H_2. With the thermal equilibrium assumption, the rotational energy obeys a Boltzmann distribution.

$$f\left(E_{\mathrm{rot}}\right) = 1/\left(k_{\mathrm{B}}T_{\mathrm{n}}\right)\exp\left(-E_{\mathrm{rot}}/\left(k_{\mathrm{B}}T_{\mathrm{n}}\right)\right) \tag{6}$$

where k_{B} is the Boltzmann constant and T_{n} is the nozzle temperature. The dissociation probability of the beam experiment can be estimated by multiplying the dissociation probability by the Boltzmann distribution and then integrating over the whole range of rotational energies.

$$p\left(E_{\mathrm{tr}}, \theta\right) = \int_0^\infty f\left(E_{\mathrm{rot}}\right)p\left(E_{\mathrm{tr}}, E_{\mathrm{rot}}, \theta\right)dE_{\mathrm{rot}} \tag{7}$$

Executing this integration analytically with Eqs. (2) and (6), the resulting expression is compared with MD results computed in our previous study[26,27] in Fig. 3. The MD results are represented well by the model developed here.
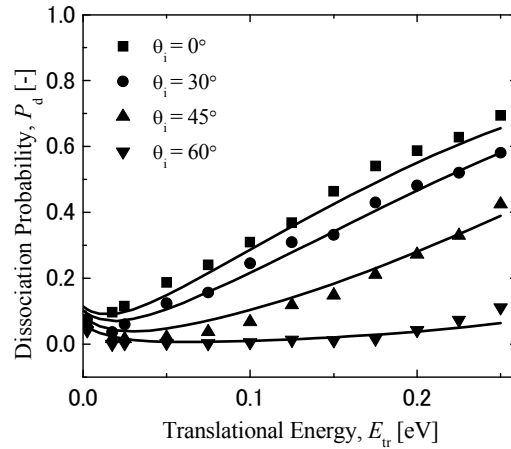
FIGURE 3. The dissociation probability of D_2 on Pt(111) predicted by the proposed mathematical model and by MD simulation as a function of initial translational energy E_{tr} and polar angle of incidence θ_{i} for a surface temperature, $T_{\mathrm{s}} = 295$ K and gas

temperature, $T_n = 1800$ K. The square, circle, and triangle symbols represent dissociation probabilities calculated from MD simulations.[26,27] The solid curves represent predictions from the proposed mathematical model, eqn. (7).

CONCLUSIONS

Using the Embedded Atom Method (EAM) potential, a number of MD simulations of gas molecules impinging on Pt(111) surface were carried out, changing the initial orientations, azimuthal angles of incidence, and collision locations on the surface in a random manner for fixed initial translational energy and initial rotational energy. The number of collisions in which the gas molecule was dissociated were counted to compute the dissociation probability. The dissociation probability was analyzed and expressed by a mathematical function of the initial conditions of the impinging molecule, namely its translational energy, rotational energy, and polar angle of incidence. The utility of the model was verified by comparing its predictions with raw MD simulation results of molecular beam experiments.

ACKNOWLEDGEMENTS

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