

Dissociative Chemisorptions of H₂/D₂ on the Pd₁₃ (295K) Cluster as Function of Translation Energy

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Abstract

In this study, the kinetics the reaction of Pd clusters with Hydrogen molecular was used study quasiclassical molecular dynamics simulation. The structure of the clusters was obtained by the thermal quenching techniques. The potential energy of the H₂ /D₂ molecules was obtained by an embedded-atom potential also the reaction between the H₂ /D₂ and Pd is modeled by LEPS (London-Eyring-Polanyi-Sato) function. The chemisorption probability has calculated the function of impact parameters, collision energies, and rovibrational initial state. The dissociative probability of the H₂/D₂ isotopic effect was studied.

Keywords: Molecular Dynamics Simulation, Palladium clusters, Dissociative chemisorption, Hydrogen, Deuterium.

1. Introduction

Understanding the process involved in the chemisorption probability of molecules on the surface of small clusters has been of great interest for many years and was considered as a fertile research area. The properties of small metal clusters can be highly dependent on cluster sizes and are different from the bulk metal ^[1,5,7]. Palladium (Pd) cluster has a great ability to adsorb hydrogen, a good catalyst and is used to speed up hydrogenation and dehydrogenation reaction ^[2,3]. In this work, we have conducted a study of quasi-classical trajectory reaction of H₂/D₂ rovibrational initial state (v=0, j=0) molecule with the Pd (13) clusters. The results pertaining to the reactive channel are presented. The dissociative chemisorption probability is calculated as functions of the impact parameters and molecules collision energy.

2-Theoretical and mathematical calculations

The total potential energy surface defining the forces acting on each H₂ /D₂+Pd_n collision system is represented as:

$$V = V_{EAM} + V_{LEPS} \quad (1)$$

Where V_{EAM} is embedded Atom potential describing the interactions between the atoms in Pd-cluster and the V_{LEPS} is a LEPS potential (London-Eyring-Polanyi-Sato) describe the interaction between the clusters and molecule ^[1,4,6].

To study the probability of dissociation chemisorption of the H₂/D₂ molecule, with specified energy and impact parameters on clusters, we have run N=500 trajectories for each set of initial conditions. These trajectories correspond to different initial relative orientations of the molecule and of the clusters are calculated as:

$$P_{v,j,T}(b, E_{tr}) = \frac{\bar{N}_{v,j,T}(b, E_{tr})}{N} \quad (2)$$

Where $\bar{N}_{v,j,T}(b, E_{tr})$ is the number of effective trajectories? The calculations were repeated by increasing the impact parameter b with $\Delta b=0.25\text{\AA}$, and the intervals of translation energy are from 0.01- 1.05eV with intervals $\Delta E_{tr}= 0.05\text{eV}$.

Reaction cross section of the dissociation chemisorption is calculated in accordance with

$$\sigma_{v,j,T}(E_{tr}) = 2\pi \int_0^{b_{\max}} P(b, E_{tr}) b db \quad (3)$$

Where b_{\max} is the longest impact parameter at which $P_{v,j,T}(b, E_{tr}) = 0$
 The Boltzmann equation used to evaluate temperature of the cluster.

$$T(k) = \frac{2\langle E_k \rangle}{(3n - 6)k} \quad (4)$$

Where E_K the total kinetic energy of the cluster (k) is the Boltzmann constant and (n) is the number of atoms in clusters. □

The reaction rate constants of the systems are calculated by:

$$k_{v,j,T}(T) = \left(\frac{2}{\pi \mu k T} \right)^{3/2} \int_0^{\infty} \sigma_{v,j,T}(E_{tr}) E_{tr} \times \exp\left(-\frac{E_{tr}}{kT}\right) dE \quad (5)$$

In this work the palladium clusters Pd(13,17) is prepared at desired temperature T(0k) and the H₂/D₂ molecule is prepared at specific initial vibrational and initial rotational states (v=0,j=0) state.

At the beginning of each trajectory the time is set to zero. The molecule is sent towards the cluster starting from distance 8.5Å away from the center of mass of the Pd cluster with specified collision energy E_{tr} and an impact parameter, b. The H-H and H-cluster distances are monitored for each collision. The trajectory is terminated either when the H-H distance exceeds 2.223Å or when departing from the cluster^[5].

3-Result and discussion

The dissociation probability of the molecule on the cluster was studied in the present work a function of the translation energy from $E_{tr}= 0.0$ to 1.05 eV with $\Delta E=0.05$ eV and a small range of impact parameters from $b= 0$ to 6 Å with $\Delta b=0.25$ Å.

For the rovibrational state (v=0,j=0) as shown in Fig (1) and impact parameters ranging from $b=0.25$ Å to $b=2.5$ Å the dissociation probability decreases and reaches its minimum value at $E_{tr}=0.2$ eV and start to increase again with the translation energy increment. At impact parameters 4 Å and 5 Å the probability decrease with increasing the translation energy and at $b=6$ Å the dissociation probability was zero for all translation energies.

For the rovibrational state ($v=0, j=3$) as shown in Fig.(2) there is no significant change in the results from that reported at ($v=0, j=0$) rovibrational state, and still, the dissociation probability keeps lowering before the 0.2 eV after which it starts to increase. For 4 Å and 5 Å impact parameter there the slight existence of dissociation probability at lower range translational energies and at 6 Å there is no interaction detected.

At rovibrational state ($v=0, j=10$) the dissociation probability was higher than other rovibrational state ($v=0, j=0$) and ($v=0, j=3$) as presented in Fig.(3). Moreover and following the same consistency: at impact, parameters range 0.25Å-2.5Å the dissociation probability increases with increasing of translation energy and decrease as increases of the impact parameter. At impact parameter $b=4$ Å the dissociation probability shows some increase before 0.3 eV, but again starts to decrease with the increase in translation energy. However, at this impact parameter, there is a dissociation probability reported for all translation energies which is completely different from the previous cases.

As expected, there is no change in of $b = 6$ Å from before and the reaction cross section reported zero values for all translation energy states. At rovibrational state ($v=3, j=0$) and at impact parameters 0.25Å, 1Å, 2.5Å, 4Å the dissociation probability increase with increasing translation energy and have a greater probability compared to other rovibrational states. At impact parameter, 5Å the probability was increasing at low translation energy region near 0.25 eV beyond which the probability start to decrease till it reaches zero values at 0.7eV. Again for $b= 6$ Å, their dissociation probability vanishes.

The isotopic effect on the dissociation probability of D_2 molecule with pd_n cluster a function of translation energy and the small range of impact parameters $b = 0$ to $b = 6$ Å was investigated and the results were plotted in Fig.(5).

This result is in a good correspondence with $Ni+D_2$ dissociation probability studies^[1].

Summary

These results achieve that the interaction probability is as higher as much when the molecule collides the cluster near the center of mass and it is as lower as much when it collides away from the center of mass. Moreover, it was found that the increase in the rovibrational states enhances the reaction probability even at larger impact parameters.

From the results, it is clear that the dissociation probability for D_2 is lower than that of H_2 and this is true for all different translation energies and different impact parameters. Moreover, the

deuterium dissociation probability vanishes starting from $b=4 \text{ \AA}$ while hydrogen dissociation probability vanishes $b=6 \text{ \AA}$. Furthermore, It is very clear that from the monitored and plotted data, the cross section increase monotonically with increase of rovibrational state v_i, j_i .and that the vibrational effect exerting more influence than that of the rotational in increasing of the reaction cross section.

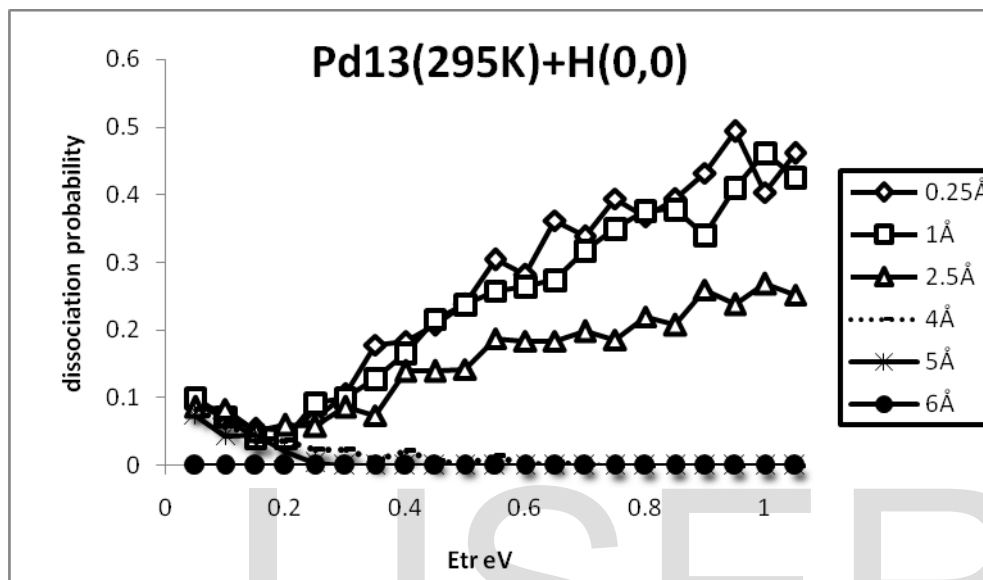


Fig.(1) Dissociation probability as a function of the translation energy for different values of impact parameters; for rovibrational state ($v=0, j=0$).

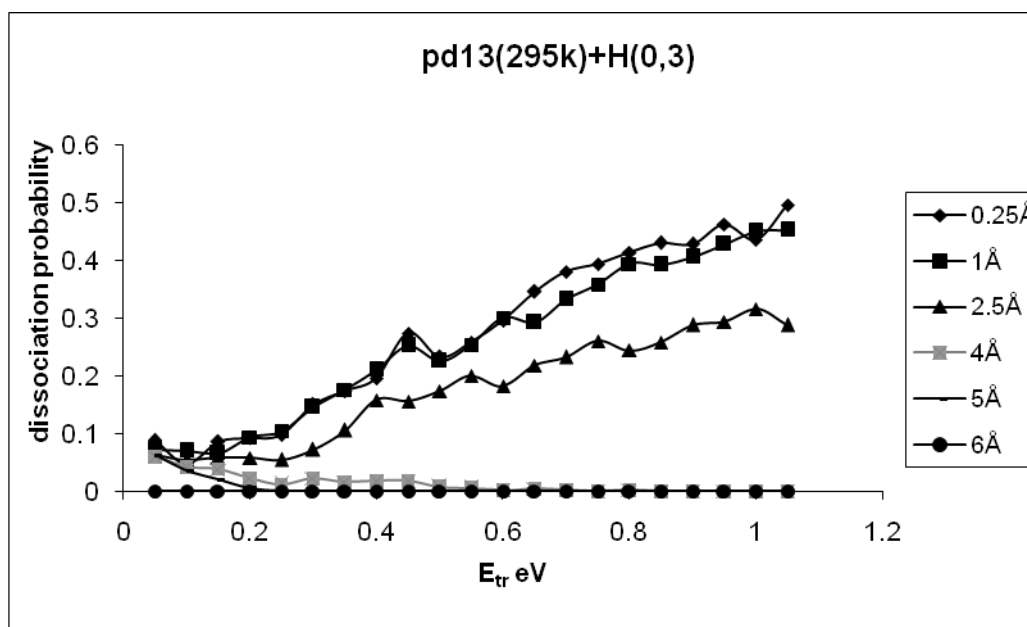


Fig.(2) Dissociation probability as a function of the translation energy for different values of impact parameters; for rovibrational state ($v=0, j=3$). □

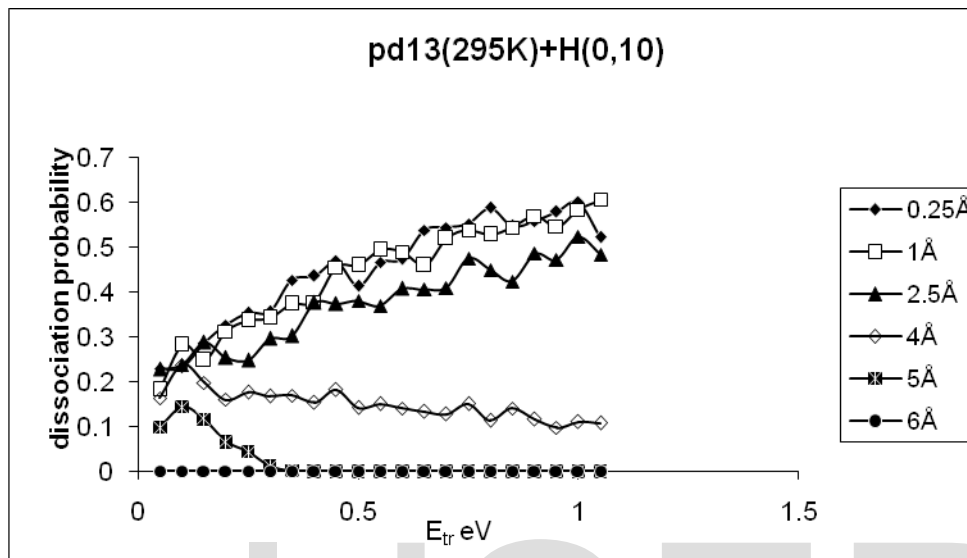


Fig.(3) Dissociation probability as a function of the translation energy for different values of impact parameters; for rovibrational state ($v=0, j=10$). □

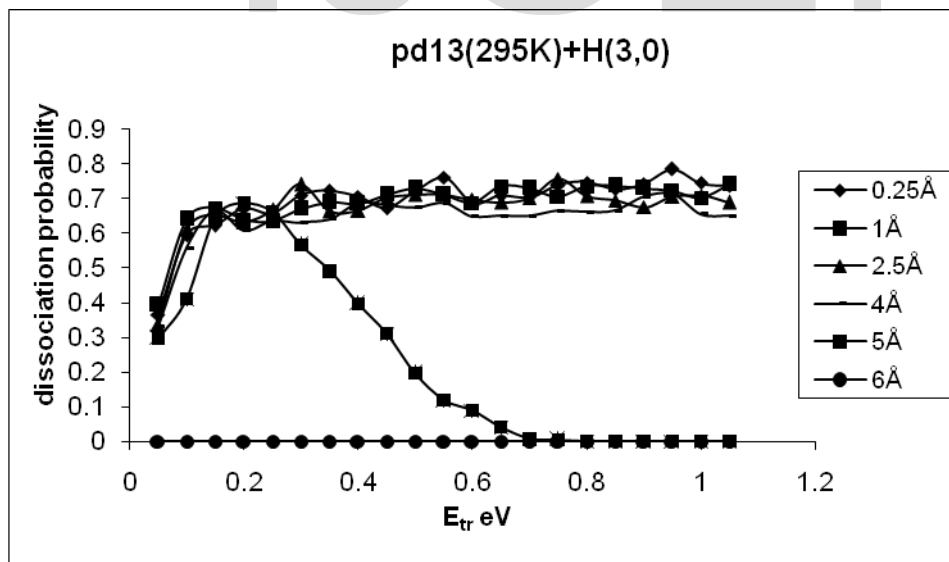


Fig.(4) Dissociation probability as a function of the translation energy for different values of impact parameters; for rovibrational state ($v=3, j=0$). □

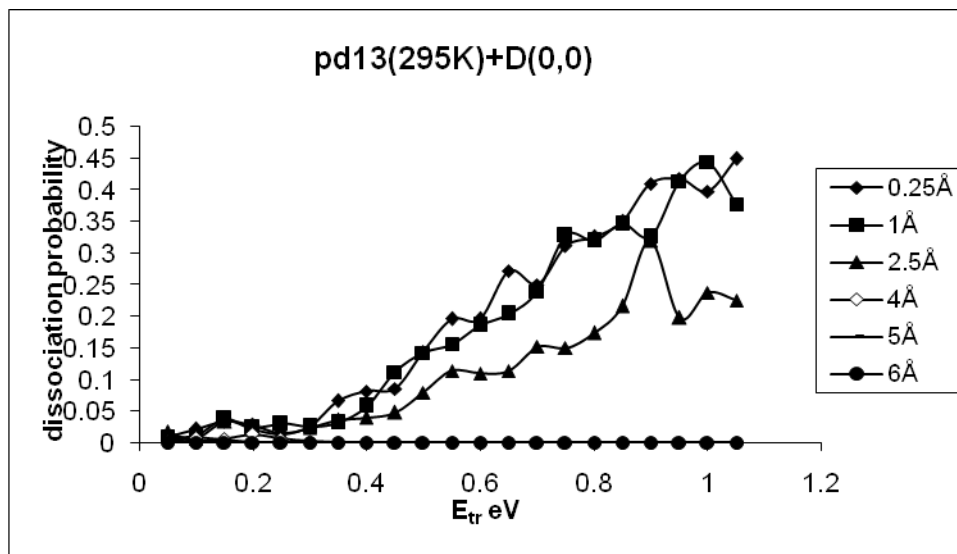


Fig.(5) Dissociation probability as a function of the translation energy for different values of impact parameters in the D₂ molecule at rovibrational state (v=0, j=0).

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