

## H(D) → D(H) + Cu(111) collision system: Molecular dynamics study of surface temperature effects

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All the channels of the reaction dynamics of gas-phase H (or D) atoms with D (or H) atoms adsorbed onto a Cu(111) surface have been studied by quasiclassical constant energy molecular dynamics simulations. The surface is flexible and is prepared at different temperature values, such as 30 K, 94 K, and 160 K. The adsorbates were distributed randomly on the surface to create 0.18 ML, 0.28 ML, and 0.50 ML of coverages. The multi-layer slab is mimicked by a many-body embedded-atom potential energy function. The slab atoms can move according to the exerted external forces. Treating the slab atoms non-rigid has an important effect on the dynamics of the projectile atom and adsorbates. Significant energy transfer from the projectile atom to the surface lattice atoms takes place especially during the first impact that modifies significantly the details of the dynamics of the collisions. Effects of the different temperatures of the slab are investigated in this study. Interaction between the surface atoms and the adsorbates is modeled by a modified London–Eyring–Polanyi–Sato (LEPS) function. The LEPS parameters are determined by using the total energy values which were calculated by a density functional theory and a generalized gradient approximation for an exchange–correlation energy for many different orientations, and locations of one- and two-hydrogen atoms on the Cu(111) surface. The rms value of the fitting procedure is about 0.16 eV. Many different channels of the processes on the surface have been examined, such as inelastic reflection of the incident hydrogen, subsurface penetration of the incident projectile and adsorbates, sticking of the incident atom on the surface. In addition, hot-atom and Eley-Rideal direct processes are investigated. The hot-atom process is found to be more significant than the Eley-Rideal process. Furthermore, the rate of subsurface penetration is larger than the sticking rate on the surface. In addition, these results are compared and analyzed as a function of the surface temperatures. © 2011 American Institute of Physics. [doi:10.1063/1.3583811]

### I. INTRODUCTION

Hydrogen reactions on the metal surfaces are still on the focus of many studies.<sup>1–29</sup> Theoretical investigation of different reaction channels of such collision systems is very difficult because of the large number of particles involved in this system, and for the computer simulation type of work one needs to develop accurate potential energy surfaces for all different interactions existing in the collision system. Here we will investigate H(D) → D(H) + Cu(111) collision system formed by the incident gas-phase H (or D) atom and D (or H) atoms adsorbed on Cu(111) surface as a function of the surface temperatures. There are three molecule-production channels, such as formations of HD, D<sub>2</sub>, and H<sub>2</sub> molecules depending on the initial coverage and type of the incident projectile atom. These products may be observed via Eley-Rideal (ER), near ER, or hot-atom (HA) mechanisms. In the ER mechanism, an incident H (or D) atom takes out an adsorbate D (or H) atom in a direct collision to form a product of the HD molecule. Only one type of molecule (HD) forms in this pro-

cess. On the other hand, an incoming atom may move up and down over the surface after the primary collision and becomes a HA. This HA may spend some time on the surface and knocks off some adsorbates. After that it may take an adsorbate from the surface and then they leave in the form of one of the diatomic molecules (HD or D<sub>2</sub>/H<sub>2</sub>). Near ER is in between ER and HA type of processes, i.e., molecule formation on the surface takes relatively shorter time compared to the HA. In addition to the molecular formation, in the HA mechanism, the incoming projectile due to the dissipation of its energy via interactions with the adsorbed atoms and the surface atoms may be trapped on the surface. In addition to the later HA pathway, a HA or an adsorbate which is kicked off from its site because of a collision with the HA, or an adsorbate kicked off from its site by another adsorbate may penetrate into the subsurface site. In this present study all these possible pathways are investigated in detail. Therefore our present study fills the important gap in the literature on this collision system.

The adsorption energy of a hydrogen atom, as well known, is about 2–3 eV for some number of metal surfaces. On the other hand, the binding energies of the product molecules are almost twice of this adsorption energy.

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Therefore, as expected, the molecular desorption processes are obviously exothermic by more than 2 eV. There are a number of theoretical and experimental studies of these types on Cu,<sup>1–18</sup> and on different metal surfaces, such as Ni,<sup>19–24</sup> Pt,<sup>25–27</sup> Al,<sup>28</sup> Si.<sup>29</sup> These studies and our present work suggest that rates of all the reaction channels and their mechanisms can differ from metal to metal and also vary on different faces of the same metal.

For the sake of readers we will review below the related literature as discussed in Ref. 14. In the theoretical studies,<sup>1–3</sup> reaction dynamics of a gas phase H(D) atom with a D(H) atom adsorbed on a flat and rigid Cu(111) surface were examined by the implementation of 2D and 3D quantum calculations. Computational studies of the same interaction<sup>4–6</sup> system were carried out by utilizing quasiclassical methods and a potential energy surface (PES), allowing surface corrugation which initiates the formation of HA mechanisms. Moreover, strong isotope effects on the translational energy and ro-vibrational distributions of the HD product<sup>2,4</sup> were observed. In the other quasiclassical molecular dynamics studies,<sup>4,6</sup> the Cu surface was kept rigid. Therefore, the energy transfer to the surface Cu atoms is ignored. Strong isotope effects were also found on the HD/H<sub>2</sub>(D<sub>2</sub>) product formation probabilities.<sup>4</sup> In these studies, penetration of H(D) atom to the subsurface was not analyzed because of the rigid flat/corrugated surface approximations.

Dai and Light,<sup>7</sup> using four-dimensional planar model for gas phase H(D) atom adsorbed D(H) atom on Cu(111), studied quantum dynamics of the gas-surface reaction. The rigid surface corrugation was used in this research. They found isotope effect on the energy distributions of the product molecules.<sup>7</sup> Yoshia and co-workers<sup>8</sup> investigated isotope effects on hydrogen abstraction from Cu(111) by performing quantum dynamics calculations. They found out that abstraction reaction probability for the interaction of a gas phase H atom with the adsorbed D atom on the Cu(111) surface (H-on-D) is larger than that for the D-on-H. Furthermore, they showed that the mean normal translational and vibrational energies for the H-on-D are bigger than those for the D-on-H. They calculated reaction cross sections, such as 5.91 Å<sup>2</sup> and 4.92 Å<sup>2</sup> for H-on-D and D-on-H, respectively.

Rettner and co-workers<sup>9–12</sup> studied experimentally the dynamics of the formation of HD product molecules for the same interaction system, mentioned above. They reported that the reaction cross section was calculated approximately as 5 Å<sup>2</sup> and almost half of the incident atoms may initiate to form the HD product molecules for the coverage of half a monolayer (ML). Besides, a small number of inelastic back scatterings of H(D) take place within 10° of the incident angle at 0.07 eV of the incident energy. In these studies, isotope effects were also reported for all the degrees of freedom, i.e., in the vibrational, rotational, and translational excitations of the product molecules. Furthermore, a considerably smaller isotope effect in the rate of formation of the product molecules was reported. The HD product molecules have a high degree of rotational and vibrational excitations as they leave the surface. In addition they reported that the mechanism of the HD products is nearly at the ER limit.

In another experimental study, the interaction of gaseous H(D) atoms with D(H) adsorbed on Cu(111) was also worked out by Kammler and Küppers,<sup>13</sup> where 0.34 H(D) surface coverage was considered at 80 K. All three types of the product molecules, HD and D<sub>2</sub>(H<sub>2</sub>) formations were reported. The only way to form the D<sub>2</sub>(H<sub>2</sub>) molecules is the HA pathway; indirect formation of the molecule. It was reported that the formation probability of the product D<sub>2</sub>(H<sub>2</sub>) molecules was observed almost as 0.01 of all the product formations. For the H and D adsorbates the abstraction cross sections were reported to be 2.0 Å<sup>2</sup>, in addition, they reported that the abstraction does not depend on the temperature. Probabilities of the abstraction for the adsorbed D and H on Cu(111) were 0.36 per incoming atom. What they also revealed is that the rate of HD formation was directly correlated to the surface coverages.

In this study, using scientific computer simulations techniques, the ER and HA reactions of H-on-D and D-on-H processes on the Cu(111) surface at different temperatures of the surface were analyzed. Since the Cu(111) crystal surface was considered to be a non-rigid slab, besides the other reaction channels mentioned in the other theoretical works above, the effect of the energy transfer from the incoming H(D) atom to the surface atoms on the reaction dynamics is examined here. In our previous paper, the reaction rates were analyzed as a function of the surface coverage at 94 K of Cu(111).<sup>14</sup> Here we have extended the investigation to the reaction dynamics of the product molecules at different surface temperatures and coverages. Some of our earlier results<sup>14,15</sup> are also presented here to help the readers.

Furthermore, our simulation model is more realistic than the models used in the other theoretical studies because of the choice of the PES described briefly in the text, and much better description of the Cu surface. LEPS form suggested by DePristo and co-workers<sup>30</sup> has been used as the building block of the PES in this study, and this was necessary to describe all the interactions in the system. Thus, interactions among the hydrogen atoms and between the hydrogen atoms and the surface atoms are taken into account for analyzing the reaction dynamics simultaneously. The parameters of this LEPS form were adjusted to simulate the H(D) → D(H) + Cu(111) system in our previous papers.<sup>14,15</sup> Now, we have analyzed the collision system whether there is a temperature effect on the reaction dynamics or not at different surface coverages. Some of our related results have been compared to those of the earlier theoretical and experimental studies. The dynamics of the HA and ER processes have been discussed also for different temperatures of the surface in this study. In Sec. II, the theoretical model is summarized, and the results of the quasiclassical simulations are presented in Sec. III. Lastly, we conclude with a short summary.

## II. THEORETICAL MODEL

In our study, interactions of the incident gaseous H(D) atoms with adsorbed D(H) atoms on Cu(111) surface have been studied with quasiclassical molecular dynamics (MD) method. The earlier studies<sup>1–4,16</sup> on the same system did not

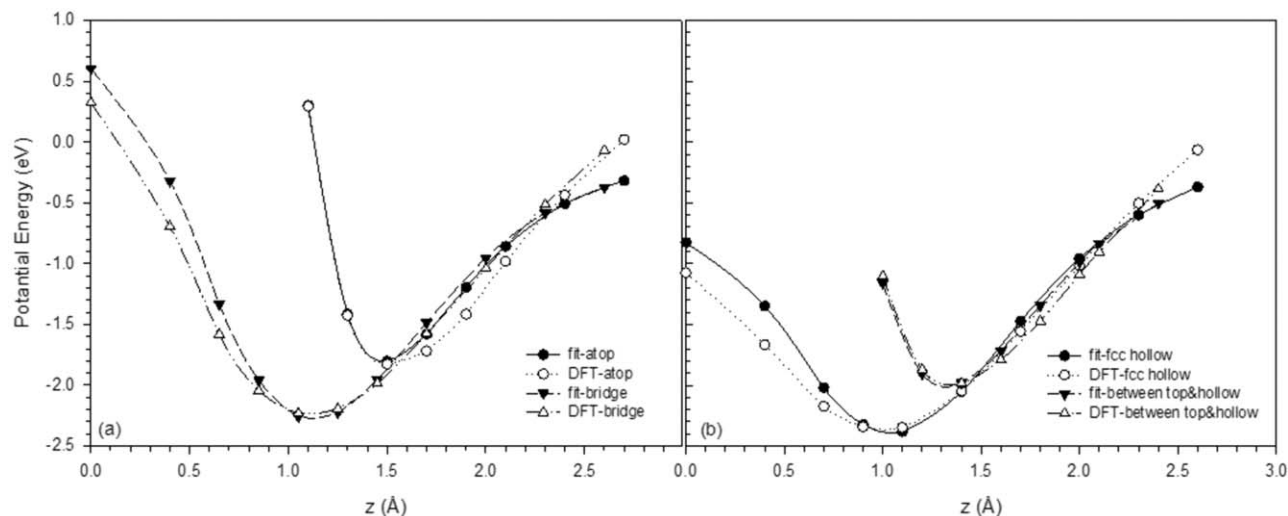


FIG. 1. Curves display the potential energies of a single H atom over the four high-symmetry sites on a Cu(111) surface. (a) atop and bridge, (b) fcc hollow and a site located half way between the hollow and atop sites are plotted as a function of  $z$  which is the distance of the H atom above the surface. Calculated energy points (taken from Ref. 16) and fitted model  $V_L$  potential values described in the text are presented. (This figure is taken from Refs. 14 and 15, see for details).

consider the penetration of hydrogen atoms to the subsurface. They mentioned that subsurface penetrations were possible, but did not consider it in their work. Their model did not allow this process. However, in our simulation it is possible to study all the reaction channels of the system because of the model (modified LEPS function and the  $V_{\text{EAM}}$  PES used to mimic the Cu(111) surface) used in our simulation. We have considered a model  $V_T$  PES which carries the information of the instantaneous positions of the metal atoms in the slab as well as the positions of the hydrogen atoms. This PES contains two major components, i.e.,  $V_T = V_{\text{EAM}} + \text{LEPS}$  ( $V_L$ ), where  $V_{\text{EAM}}$  is the many-body embedding atom potential for the Cu slab; represents the interactions between the Cu atoms. On the other hand, the LEPS potential is used for defining the interactions among the H(D) atoms and H(D)-Cu atoms. Classic form of the four-body  $V_L$  function cannot describe the many-body interactions on the surface, therefore somewhat modified LEPS PES is designed for the surface reactions in Refs. 19, 21, and 22. For the sake of readers we briefly review the model below.

The modified LEPS for the  $j$ th H atom interaction with all the Cu atoms ( $\{\vec{r}_{\text{Cu}}\}$  represents Cu atom positions in the slab) within the H-Cu interaction cut-off radius and with the other H atoms in the vicinity is approximated in the following manner:

$$V_H(\vec{r}_j) = \sum_{\substack{i=1 \\ i \neq j}}^N V_L(\vec{r}_j, \vec{r}_i, \vec{r}_{\text{Cu}}) - (N-1) V_a(\vec{r}_j), \quad (1)$$

i.e., is the total interaction energy of the  $j$ th H atom on the surface where the adsorbate atoms are placed at the positions of  $\vec{r}_j$ . Here,  $V_a(\vec{r}_j)$  describes the interaction of a single adsorbate (the  $j$ th atom) with the Cu atoms. The  $V_L$  is the LEPS function which takes into account the interactions of the H-H and H-surface atoms simultaneously (see for details in Refs. 15, 19, 21, and 30). Here,  $N$  is the number of the adsorbates within the H-H interaction cut-off radius of the LEPS

function for the  $j$ th hydrogen. When  $N = 1$ , the  $V_L$  function is reduced to the form  $V_a(\vec{r}_j)$ .  $V_{\text{EAM}}$  is represented as

$$V_{\text{EAM}} = \sum_i \left[ F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{j \neq i} \phi(r_{ij}) \right], \quad (2)$$

where  $\phi(r_{ij})$  is a pair potential as a function of the distance  $r_{ij}$  between the  $i$ th and  $j$ th slab atoms,  $F$  (many-body term) is the embedding energy (following Foiles,<sup>31</sup>  $F(\bar{\rho})$  is defined by requiring the universal energy form of Rose *et al.*,<sup>32</sup> and  $\bar{\rho}$  is the total host electron density at the position of the Cu atom  $i$  (see for details in Ref. 33).

We have used the calculated total energy points<sup>16</sup> for different configurations of one and two hydrogen atoms on the Cu(111) surface to parameterize the  $V_L$  form<sup>15,30</sup> in our simulation. To our knowledge there are no any other study calculated H-Cu and 2H-Cu energies on the same surface with the same method. This study gives the necessary amount of data on different parts of the surface and orientation of the molecule (2H). These calculations are important for the fitting of the LEPS function and the accuracy of the PES especially for the reactive channels. There are some studies<sup>17,34</sup> that provide H-Cu(111), but they do not have 2H-Cu interaction energies. Persson and co-workers<sup>16</sup> performed calculations within the density-functional theory method using the generalized gradient approximation for the exchange-correlation energy to determine those energy points. In these calculations they placed single H atom at different symmetry sites of the surface to calculate the total energies as a function of the height of a hydrogen atom from the surface. In addition they calculated the total energies of 2H-surface interactions on many different parts of the surface, and for different orientation of the 2H atoms; collinear and quasi-collinear configurations. For the parameterization of the  $V_L$ , firstly 37 total energy values of H-Cu interactions are considered. These energy points are selected from four high symmetry sites; atop, fcc hollow, the bridge, and a site located half way between the hollow and atop sites.<sup>16</sup> In Fig. 1, the fitted total energy values are

TABLE I. The fitted parameters of LEPS ( $V_L$ ) function (Set-2 in Refs. 14 and 15).

$\Delta_{H,H} = 0.0$	$D_2 = 0.148$ eV	$\Delta_{H,Cu} = 0.01$
$D_e = 4.740$ eV	$D_H = 2.0$ eV	$R_H = 2.74$ Å
$\alpha_e = 1.9$ Å <sup>-1</sup>	$\alpha_2 = 1.48$ Å <sup>-1</sup>	$R_2 = 2.26$ Å
$R_e = 0.733$ Å	$\alpha_H = 0.9$ Å <sup>-1</sup>	$N_{4s} = 0.2$

plotted as a function of  $z$ , the distance of a H atom above the surface. The binding energies calculated for a H, on the fcc hollow, bridge, atop sites, and a site located half way between the hollow and atop sites, are  $-2.39$ ,  $-2.28$ ,  $-1.80$ , and  $-2.0$  eV, respectively, and the corresponding heights of these adsorption sites above the surface are 1.04, 1.13, 1.5, and 1.33 Å, respectively. These binding energies and heights comply with the theoretical work<sup>16</sup> as seen in Fig. 1 (see for details Ref. 15).

After this first step, the  $V_L$  parameters were tuned further by using the 218 total energy values of the 2H-surface taken out from Fig. 4 of Ref. 16 (energy counter graphs of collinear and quasi-collinear configurations of 2H-Cu surface interactions). The final values of  $V_L$  parameters used in our simulations are given in Table I using the notation of Refs. 15 and 30, and these parameters yield root-mean-square (rms) errors of 0.182 and 0.161 eV with regard to all of the 2H-Cu(111) and H-Cu(111) total energy points, respectively.

The Cu(111) surface (in the  $x$ - $y$  plane, and  $z$  is the surface normal) is realistically constructed and contains 1092 Cu atoms (the dimensions of the surface area are about  $35$  Å  $\times$   $26$  Å). The lattice constant is  $3.615$  Å.<sup>33</sup> There are six atomic layers in an ABCA massing. The zero point energies (ZPE) of the adsorbates, H (or D), at their binding sites are calculated in the harmonic approximation. These ZPE val-

ues are 42.14, 42.29, and 80.42 meV, respectively; vibrational energies of H atom along the  $x$ ,  $y$ , and  $z$  directions. The calculated ZPE values are 29.81, 29.91, and 56.89 meV, respectively, for the D atom. At the initial step, the adsorbates have random energies and phases depending on the amount of the ZPEs. The temperature of the surface is calculated from

$$T(K) = \frac{2 \langle E_{kin} \rangle}{(3n - 6)k}, \quad (3)$$

where  $\langle \rangle$  signifies the time average, calculated over the equilibration run.  $E_{kin}$  is the total kinetic energy of the Cu atoms,  $n$  and  $k$  are the number of atoms in the surface and the Boltzmann constant, respectively, and  $(3n-6)$  is the internal degrees of freedom of the Cu(111).

In our numerical computation we used a fourth-order predictor-corrector variable step-size propagator to solve Hamilton's equations of motion for all the particles in the entire system. For each of the collisions, at time  $t = 0$  the projectile atom is placed initially at  $7$  Å above the surface, and is sent towards the surface parallel to the surface normal. The initial kinetic energy of the projectile is the same as that of the Rettner and co-workers' experiments,<sup>9-12</sup> 0.07 eV. For all initial conditions which are determined by the isotopic state and initial coverage of the surface, 4000 trajectories are sent to a half unit cell area in the center of the slab. Each of the trajectories is different in terms of the locations of the adsorbates which are randomly placed over the 72 fcc hollow sites and of the randomly determined phases on the surface to create 0.50, 0.28, and 0.18 ML of coverages. The standard periodic boundary conditions have been implemented in the simulation. Each of the trajectories is evolved for up to 2.0 ps and/or until one of the following events is observed; (i) reflection of the incident projectile, (ii) HD or D<sub>2</sub>/H<sub>2</sub> molecular formation and after that leaving the surface up to

TABLE II. Probabilities of all different events take place on the surface for the various channels obtained among all the trajectories run for each isotopic combination and different temperature. D-on-H hints that a gas phase incident D atom on H-covered Cu(111) surface at the coverage is indicated, and so on. Descriptions of these various channels are given in the text. (Probabilities are calculated from 4000 collision events). For the sake of convenience, results of 94 K are taken from Ref. 14.

Temperature (K)	Collision System	Coverage (ML)	HD Formation	H <sub>2</sub> /D <sub>2</sub> Formation	Sticking	Subsurface	Reflection
30	D-on-H	0.50	0.398	0.096	0.004	0.438	0.065
	D-on-H	0.28	0.229	0.026	0.045	0.685	0.016
	D-on-H	0.18	0.151	0.009	0.037	0.799	0.005
	H-on-D	0.50	0.446	0.057	0.010	0.405	0.083
	H-on-D	0.28	0.261	0.013	0.054	0.646	0.027
	H-on-D	0.18	0.175	0.004	0.047	0.760	0.014
94	D-on-H	0.50	0.423	0.113	0.005	0.387	0.073
	D-on-H	0.28	0.245	0.035	0.042	0.662	0.017
	D-on-H	0.18	0.159	0.016	0.044	0.776	0.006
	H-on-D	0.50	0.502	0.066	0.005	0.352	0.075
	H-on-D	0.28	0.288	0.019	0.053	0.611	0.029
	H-on-D	0.18	0.186	0.008	0.039	0.753	0.015
160	D-on-H	0.50	0.379	0.137	0.000	0.423	0.061
	D-on-H	0.28	0.236	0.034	0.013	0.707	0.010
	D-on-H	0.18	0.163	0.017	0.017	0.801	0.003
	H-on-D	0.50	0.499	0.106	0.000	0.359	0.037
	H-on-D	0.28	0.310	0.019	0.017	0.640	0.016
	H-on-D	0.18	0.211	0.009	0.020	0.746	0.014



the asymptotic level, (iii) trapping of the incoming atom, (iv) subsurface penetration of an adsorbate or the incident atom. The final ro-vibrational ( $j$  and  $v$ ) states distributions of the product molecules are analyzed following the prescription of Porter and co-workers.<sup>35</sup>

### III. RESULTS

In Table II we demonstrate the probabilities of all the possible channels for each of the isotopic replacements and the initial coverages (at 30 K, 94 K, and 160 K). These listed channels briefly are; the incident atom reacts with an adsorbate, HD formation may occur via an ER or a HA pathway. The incoming atom or HA strikes an adsorbate and thus this adsorbate escapes from its original binding site of the surface and travels some distance over and/or under the surface. During this time, it may react with another adsorbate

to form H<sub>2</sub> (or D<sub>2</sub>) product molecule. This is called secondary reaction since this event occurs after the initial impact and as an indirect way. If a H (D) atom goes into the subsurface and stays there until the end of 2.0 ps, we record this event as a “subsurface” trajectory. If the incident atom does not cause any product formation until the end of 2.0 ps or it does neither reflect nor stays in the subsurface, then this event is labeled as “sticking.” We label the inelastic back scattering of the incoming projectile atom as “reflection.” These are the orders in Table II.

As seen from Table II, although the rate of D<sub>2</sub> formation for the H-on-D is less than the rate of H<sub>2</sub> formation for the D-on-H, the rate of HD formation for the H-on-D is more than that for the D-on-H. This has resulted from the isotopic effect. Our probability for the HD product formation is consistent with the experimental results of Rettner and co-workers<sup>9–12</sup> for the 0.5 ML coverage at 94 K. Their incident angle was

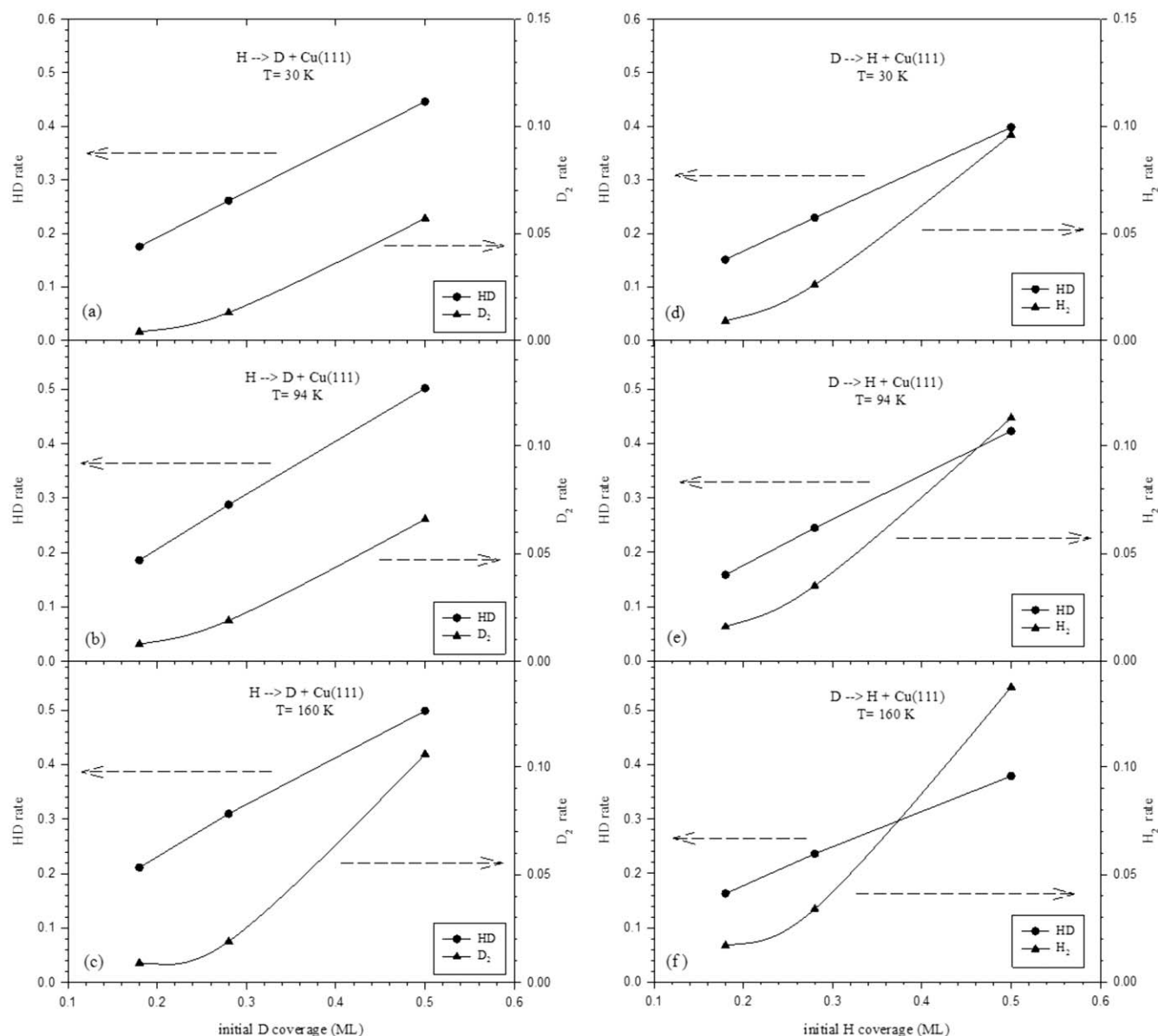


FIG. 2. (a)–(c) HD and D<sub>2</sub> formation rates are shown for the H-on-D collision systems as functions of the surface coverage and temperatures. (d)–(f) HD and H<sub>2</sub> formation rates are shown also for D-on-H collision systems. Linear behaviors are for the HD formations, and nonlinear curves for the D<sub>2</sub>(H<sub>2</sub>) products. (T = 94 K is taken from Ref. 14).

within  $10^\circ$  in the experiment. In our study, we have taken the normal incidence to the surface. Results show that a small angular difference does not play any significant role. Main reason for the incident atom to become a HA is the surface corrugation. After the initial impact its momentum vector becomes nearly parallel to the surface, and this atom may hop several times on the surface as it moves and dissipates its energy to the surface and other adsorbates. As a result a HA is formed. This process (forming HA) is the main mediator of all the channels except the reflection event. The reflection rate of the incident atom was found to be very small, between 0.005 and 0.083 which is consistent with the theoretical<sup>4</sup> and experimental studies.<sup>11</sup> The other reaction pathways play an effective role as seen from Table II. We observed that the probability of the reflection was found to

be correlated with the initial coverage of the surface at 30 K, 94 K, and 160 K temperatures, i.e., the higher the coverage the higher the rate of reflection. The temperature effect seems to be rather weak at these coverages. Rather weak isotopic effect was observed on the reflection rate at all coverages at these temperatures.

A detailed examination of the trajectories confirms that the incident atom is trapped in a hollow site. The rate of subsurface penetration is larger than the sticking rate onto the surface, as seen. The subsurface penetration takes place in the following way. After the initial collision, the incoming atom or the knocked off adsorbate may bounce several times on the surface. If one bounces into an fcc-hollow site, it may penetrate into the slab. The fcc-hollow site where there is not any Cu atom in between the first and the third layer, on the other

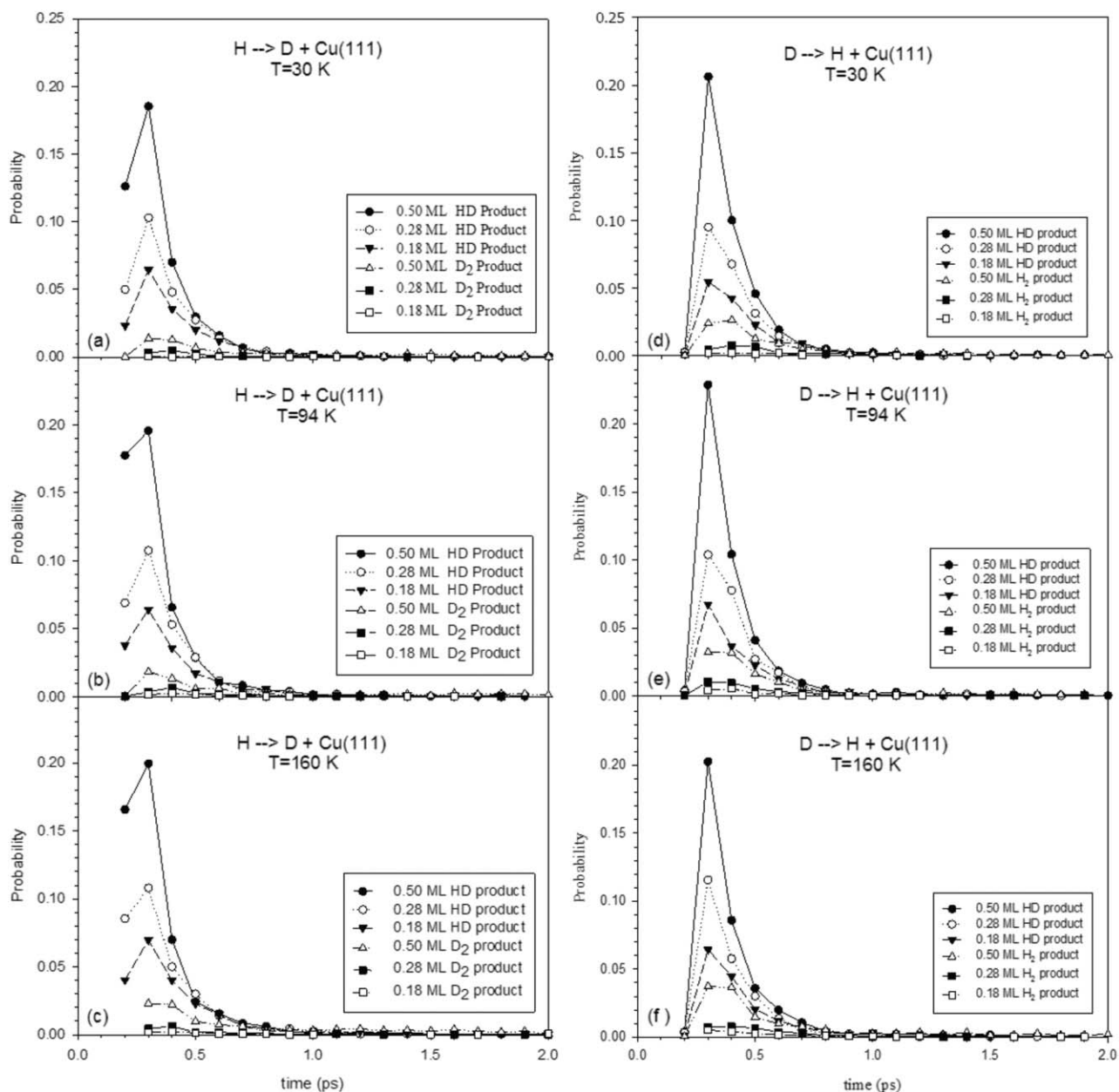


FIG. 3. Probability distributions of reaction times of the formation of products at 30 K, 94 K, and 160 K of the surface temperatures; (a), (b), and (c) for H on D-covered Cu(111) surface for the initial D coverages of 0.18, 0.28, and 0.5 ML. (d), (e), and (f) for D on H-covered Cu(111) surface for the initial H coverages of 0.18, 0.28, and 0.5 ML.

hand, the hcp-hollow site has a Cu atom in the second layer. Therefore, a hydrogen atom can enter easily to the subsurface site through the fcc-hollow site. Activation barriers are not observed over these hollow sites for the penetration of H(D) atoms.<sup>13–15,17,18,34</sup> After the penetration, a HA moves into the subsurface, and dissipates its energies via multiple collisions with the surface atoms. Eventually it may be trapped below the surface layer at one of the subsurface sites. Sometimes some of the incoming atoms or adsorbates which were penetrated into the subsurface may rise again above the surface layer.

At high coverages, because of the many adsorbates on the surface, the energy barriers of these sites are affected, therefore, the incoming atom or knocked off adsorbates are prevented from penetrating into the subsurface, i.e., the more

the coverage the less the rate of subsurface penetration is observed in Table II. This event is almost not affected by the temperature increase in this range either. The isotopic effect is very weak on the subsurface events.

On the other hand, the sticking events are hindered by the temperature as seen. For the H-on-D processes the sticking is decreasing with the temperature increase. On the other hand this similar trend for the D-on-H processes is observed clearly only from 94 K to 160 K. Furthermore, the sticking process is increasing with the decreasing surface coverage. There is almost no isotopic effect on this process.

When the temperature of the surface is increased, the rates of H<sub>2</sub>(D<sub>2</sub>) secondary molecular formations are increasing with a nonlinear behavior. This is due to the fact that increasing the temperature of the surface enhances the

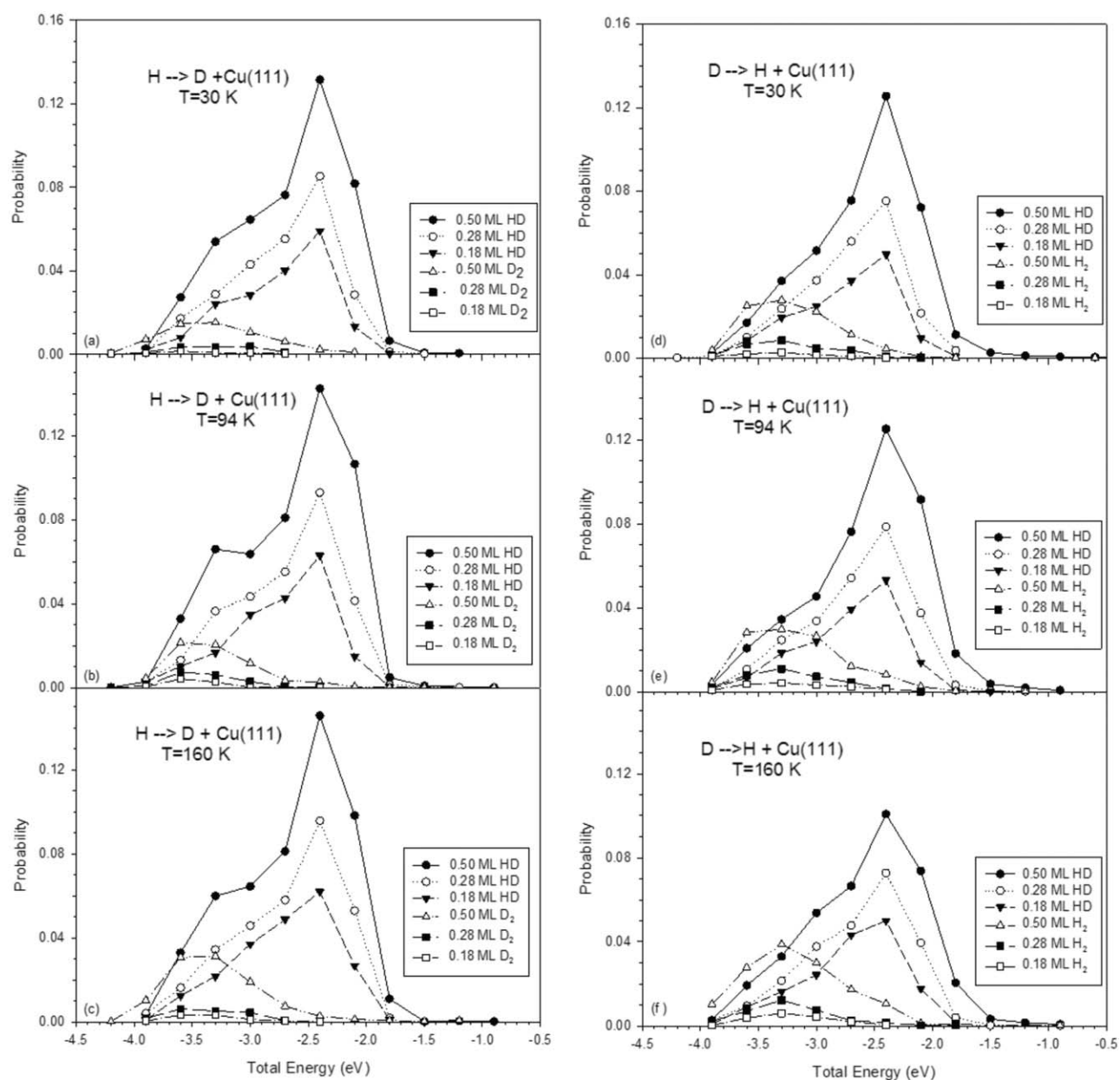


FIG. 4. Probability distributions of the total energies of the product molecules at 30 K, 94 K, and 160 K of surface temperatures; (a), (b), and (c) for D on H-covered Cu(111) surface for the initial H coverages of 0.18, 0.28, and 0.5 ML. (d), (e), and (f) for H on D-covered Cu(111) surface for the initial D coverages of 0.18, 0.28, and 0.5 ML.

adsorbates mobility, and this increases the surface corrugation compared to that of the low temperature. This causes a higher rate of formation of the HA atoms, and therefore enhances the reaction channels. This is highly visible for the 0.5 ML of surface coverage, which is near the saturation level.<sup>14</sup> As a result, the surface corrugation plays a very important role for all the reaction channels. This event is highly correlated with the surface coverage, i.e., the higher the coverage the higher the secondary molecular formation. There is a strong isotopic effect on this channel.

Furthermore, present results show that the HD formation rates are directly proportional to the surface coverage for each of the surface temperatures. This result is also consistent with the experiment.<sup>13</sup> At lower coverages the temperature depen-

dence is visible, the rate increases with the increasing temperature. There is a strong isotopic effect on the rate of HD formation, i.e., the H-on-D collision system has a higher rate of HD formation compared to the D-on-H system.

Kammler and Küppers<sup>13</sup> also observed  $H_2(D_2)$  products whose percentages were found to be about 1%. Our rates of these formations are slightly higher compared to 1% for the 0.5 ML at 94 K and 160 K. This may be due to the relatively small number of trajectories (4000) used in the simulation. One has to consider many more trajectories to have better converged values for these low rate events. This will off course reduce the errors, but it requires much more computational time. However, our rates of the  $H_2(D_2)$  products are sensibly consistent with the experimental study.<sup>13</sup>

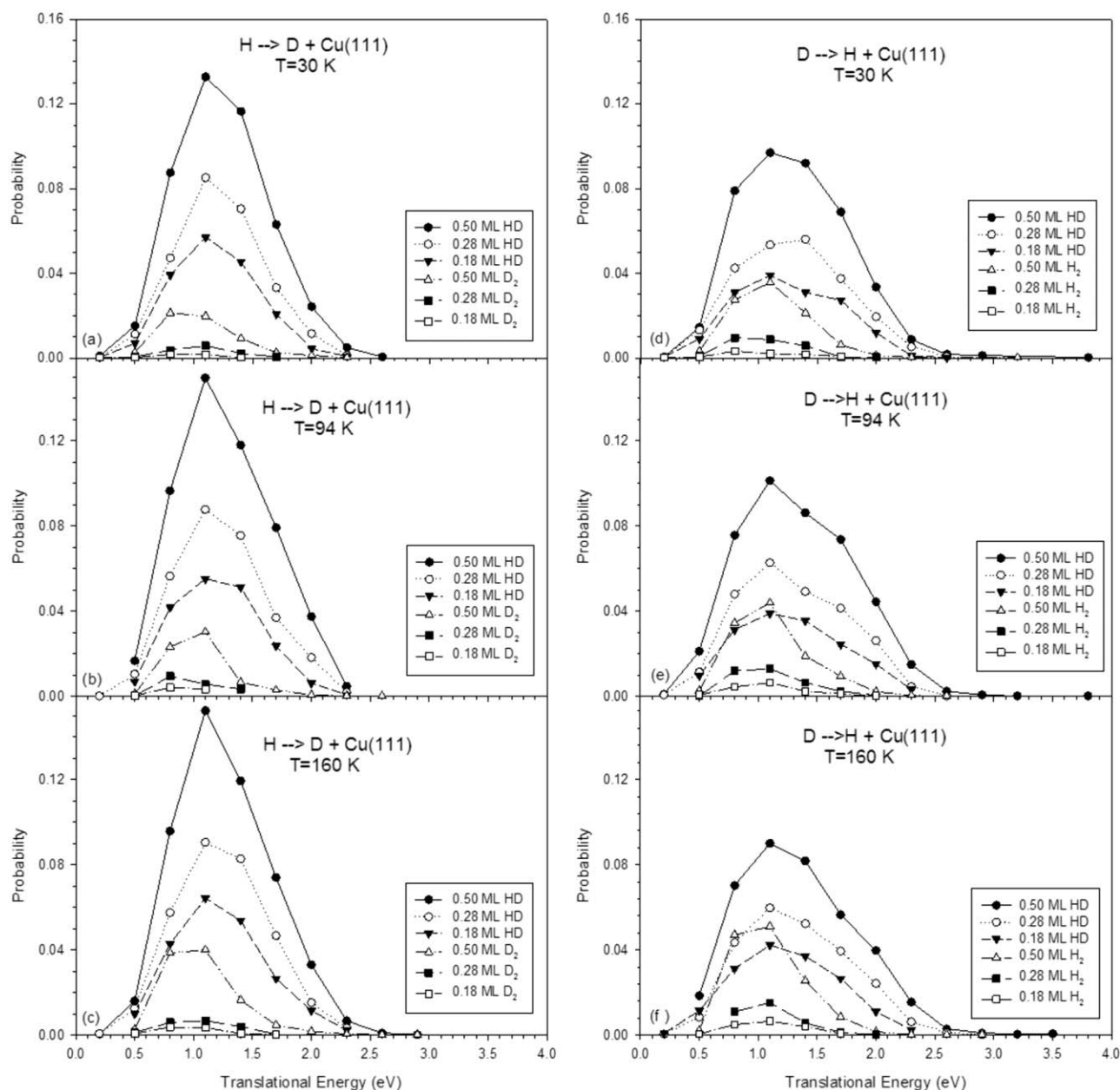


FIG. 5. Probability distributions of translational energies of formation of the products at 30 K, 94 K, and 160 K of surface temperatures; (a), (b), and (c) for H on D-covered Cu(111) surface for the initial H coverages of 0.18, 0.28, and 0.5 ML. (d), (e), and (f) for D on H-covered Cu(111) surface for the initial D coverages of 0.18, 0.28, and 0.5 ML.



We plotted the linear behaviors of the HD formation rate and quadratic dependences of  $H_2(D_2)$  formation rates (as a function of the surface coverage) in Fig. 2 (result for 94 K of the Cu(111) surface is taken from our previous paper<sup>14</sup>). These results are compatible with the results of Ref. 13. Besides, the same behaviors of the product formation rates have been observed for Ni surface<sup>20,22,23</sup> and Pt surface<sup>25,26</sup> as well.

In Fig. 3, probability distributions of reaction times are illustrated at 30 K, 94 K, and 160 K for both H-on-D and D-on-H collision systems. Reaction times start with the beginning of the trajectories which are 7 Å above the surface, and finishes with the formation of the product molecules. The reaction times for the formation of HD molecules are within 0.2 ps–0.3 ps range, corresponding to either direct ER or

short-time HA mechanisms. In this short time, the incident atom can jump only one or two times on the surface before reacting with an adsorbate atom, and then it forms a HD product. In Fig. 3, it is clearly seen that probability of the HD formation, occurring via either direct ER or short-time HA mechanisms, for the H-on-D collision system is more than that for the D-on-H collision system at each of the surface temperature. As mentioned earlier, this difference depends on isotopic replacement. Reaction times from about 0.4 ps to 2.0 ps can be attributed to the HA reactions. Secondary products also occur via HA pathways. HA reactions play more important role on the HD formation. This shows that the incident atom, approaching to the surface, travels over the surface for a longer time and dissipates some of its energy to the slab and adsorbates before forming a HD molecule. The HD molecule

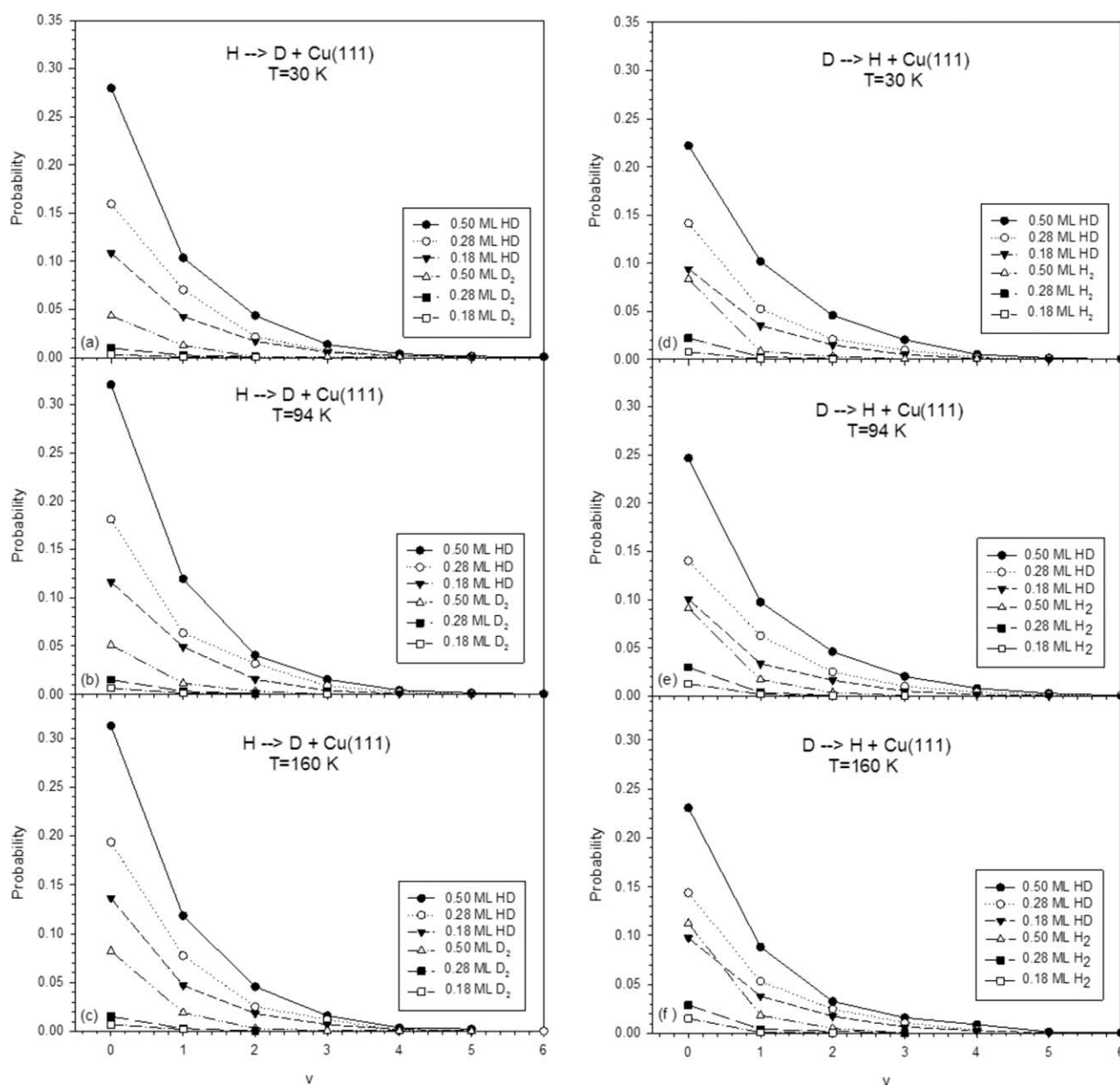


FIG. 6. Probability of vibrational distributions of formation of the products at 30 K, 94 K, and 160 K of surface temperatures; (a), (b), and (c) for H on D-covered Cu(111) surface for the initial H coverages of 0.18, 0.28, and 0.5 ML. (d), (e), and (f) for D on H-covered Cu(111) surface for the initial D coverages of 0.18, 0.28, and 0.5 ML.

instantly leaves from the surface after forming. Moreover, any important effect based on the temperature was not observed on the probability distributions of reaction times.

In Fig. 4, probability distributions of the total energies which are sum of the potential, rotational, vibrational, and translational energies of the product molecule are exhibited at 30 K, 94 K, and 160 K for both H-on-D and D-on-H collision systems. In this graphics, curves of the total energies are normalized.

The HD products which have total energy values around the peak energies,  $-2.4$  eV, are occurred by the ER or short-time HA since their reaction times are shorter than the other events. Similar results for the Ni(100) surface have been observed in Ref. 19.

Strong isotopic effects were observed on the probability distributions of the total energies because of differences of the rate of HD formations between the collision systems. This effect shows that the rate of HD occurrence via ER or very short-time HA mechanism of the H-on-D collision system is larger than that of the D-on-H collision system. The same effect was also observed in the Fig. 3. The rest of the total energy distributions for the HD, smaller than  $-2.4$  eV, can be attributed to the HA reactions. This shows that the incident atom is trapped, and travels over/under the surface and loses its energy by colliding with the adsorbates and surface atoms for longer times before reacting with an adsorbate. So, these HD products have lower kinetic energies. In the total energy graphics, it is easily observed that the HA reaction pathways dominate the formation of HD products as in Fig. 3.

As discussed before the HA(s) are also responsible for the secondary products ( $D_2$  or  $H_2$ ). In Fig. 4, their observed peak values are shifted towards the lower total energies ( $-3.6$  eV and  $-3.3$  eV). Therefore, they have less internal and translational kinetic energies. Their probabilities are much smaller than those of the HD formations. All curves show rather weak isotopic effects, but, they display very strong coverage dependence.

In Fig. 5, probability distributions of the translational energies of the HD and  $H_2/D_2$  products were compared with each other for both of the isotopic combinations at 30 K, 94 K, and 160 K, and at all coverages. All curves have peak values at near 1 eV of the translational energy. For the H-on-D collisions the probabilities of HD(s) are larger than those of the D-on-H system. They are also sensitive to the surface coverages. There are slight differences among the distributions for the formations of the secondary products ( $D_2$  or  $H_2$ ) between the different collision systems, coverages, and the temperatures, as seen. Our results comply with the results of Rettner and co-workers.<sup>9-12</sup>

In Fig. 6 probability distributions of the vibrational states of the HD and  $H_2/D_2$  products were compared with each other for both of the isotopic replacements at 30 K, 94 K, and 160 K. Most of the product molecules are in the vibrational ground state. This shows that molecules, in general, have rotational and translational kinetic energies. There are some isotopic effects on the vibrational distributions. However, effects of the surface temperatures are negligible since these temperatures are much smaller than the vibrational temperatures (kinetic energies).

#### IV. CONCLUSION

In this study, we have theoretically performed the ER and HA reactions of H-on-D and D-on-H processes on the Cu(111) surface at different temperatures of the surface. Since the Cu(111) crystal surface was taken as a non-rigid slab, in addition to the various reaction channels mentioned in Sec. III, effect of the energy transfer from the incoming H(D) atom to the surface atoms on the reaction dynamics is examined. Here we have centered our attention to the reaction dynamics of the product molecules at different surface temperatures and coverages. Isotopic effects play an important role for the rates of HD,  $H_2$ , and  $D_2$  formation. Surface corrugation is an important mediator for the incident atom to become a HA. Reflection rate of the incoming atom was obtained to be very small, between 0.005 and 0.083 which is consistent with the theoretical<sup>4</sup> and experimental studies.<sup>11</sup> The probability of the reflection was found to be correlated with the initial coverage of the surface at 30 K, 94 K, and 160 K temperatures, i.e., the higher the coverage the higher the rate of reflection. Rather weak isotopic effect was observed on the reflection rate at all coverages at these temperatures.

A comprehensive analysis of the trajectories approves that the incident atom may be trapped in a hollow site. The rate of subsurface events is larger than the sticking rate onto the surface. Our results show that fcc-hollow sites are the main penetration sites of the incident atom to the subsurface. Activation barriers are not noticed over these hollow sites for the penetration of the incident atoms.<sup>13-15,17,18,34</sup> Effects of the temperature and isotopic difference are very weak on the subsurface events. The sticking events are hindered by the temperature. This process is increasing with the decreasing surface coverage. There is more or less no isotopic effect on this process.

Linear behaviors are obtained for the HD formations while nonlinear behaviors are observed for the  $D_2(H_2)$  products. These behaviors are functions of the surface coverage for each of the surface temperatures. As a result, the surface corrugation plays a very important role for all the reaction channels. Besides, the reaction channels are highly correlated with the surface coverage. Isotopic replacement plays important roles on some of the channels.

<sup>1</sup>B. Jackson and M. Persson, *J. Chem. Phys.* **103**, 6257 (1995).

<sup>2</sup>M. Persson and B. Jackson, *Chem. Phys. Lett.* **237**, 468 (1995).

<sup>3</sup>M. Persson and B. Jackson, *J. Chem. Phys.* **102**, 1078 (1995).

<sup>4</sup>D. V. Shalashilin, B. Jackson, and M. Persson, *Faraday Discuss.* **110**, 287 (1998).

<sup>5</sup>S. Caratzoulas, B. Jackson, and M. Persson, *J. Chem. Phys.* **107**, 6420 (1997).

<sup>6</sup>D. V. Shalashilin, B. Jackson, and M. Persson, *J. Chem. Phys.* **110**, 11038 (1999).

<sup>7</sup>J. Dai and J. C. Light, *J. Chem. Phys.* **110**, 6511 (1999).

<sup>8</sup>Y. Miura, H. Kasai, and W. A. Dino, *J. Phys.: Condens. Matter* **14**, 4345 (2002).

<sup>9</sup>C. T. Rettner, *Phys. Rev. Lett.* **69-2**, 383 (1992).

<sup>10</sup>C. T. Rettner and D. J. Auerbach, *Phys. Rev. Lett.* **74-22**, 4551 (1995).

<sup>11</sup>C. T. Rettner and D. J. Auerbach, *J. Chem. Phys.* **104**, 2732 (1996) and references therein.

<sup>12</sup>C. T. Rettner and D. J. Auerbach, *Surf. Sci.* **357-358**, 602 (1996).

<sup>13</sup>T. Kammler and J. Küppers, *J. Chem. Phys.* **111**, 8115 (1999).

<sup>14</sup>C. D. Vurdu, S. Özçelik, and Z. B. Güvenç, *Surf. Sci.* **601**, 3745 (2007).

- <sup>15</sup>Can D. Vurdu and Ziya B. Güvenç, *Commun. Nonlinear Sci. Numer. Simul.* **15**, 648 (2010).
- <sup>16</sup>M. Persson, J. Strömquist, L. Bengtsson, B. Jackson, D. V. Shalashilin, and B. Hammer, *J. Chem. Phys.* **110**, 2240 (1999).
- <sup>17</sup>J. Strömquist, L. Bengtsson, M. Persson, and B. Hammer, *Surf. Sci.* **397**, 382 (1998).
- <sup>18</sup>M. F. Luo and G. R. Hu, *Surf. Sci.* **603**, 1081 (2009).
- <sup>19</sup>Z. B. Güvenç, X. Sha, and B. Jackson, *J. Chem. Phys.* **115**, 9018 (2001).
- <sup>20</sup>B. Jackson, X. Sha, and Z. B. Güvenç, *J. Chem. Phys.* **116**, 2599 (2002).
- <sup>21</sup>Z. B. Güvenç, X. Sha, and B. Jackson, *J. Phys. Chem. B* **106**, 8342 (2002).
- <sup>22</sup>Z. B. Güvenç and D. Güvenç, *Surf. Sci.* **529**, 11 (2003).
- <sup>23</sup>T. Kammler, J. Lee, and J. Küppers, *J. Chem. Phys.* **106**, 7362 (1997).
- <sup>24</sup>R. Martinazzo, S. Assoni, G. Marinoni, and G. F. Tantardini, *J. Chem. Phys.* **120**, 8761 (2004).
- <sup>25</sup>S. Wehner and J. Küppers, *J. Chem. Phys.* **108**, 3353 (1998).
- <sup>26</sup>S. Wehner and J. Küppers, *Surf. Sci.* **411**, 46 (1998).
- <sup>27</sup>J.-Y. Kim and J. Lee, *J. Chem. Phys.* **113**, 2856 (2000).
- <sup>28</sup>J. Boh, G. Eilmsteiner, K. D. Rendulic, and A. Winkler, *Surf. Sci.* **395**, 98 (1998).
- <sup>29</sup>S. A. Buntin, *J. Chem. Phys.* **108**, 1601 (1998).
- <sup>30</sup>K. Raghavan, M. S. Stave, and A. E. DePristo, *J. Chem. Phys.* **91**, 1904 (1989).
- <sup>31</sup>S. M. Foiles, *Phys. Rev. B* **32**, 7685 (1985).
- <sup>32</sup>J. H. Rose, J. R. Smith, F. Guinea, and J. Ferrande, *Phys. Rev. B* **29**, 2963 (1984).
- <sup>33</sup>A. F. Voter, Los Alamos Unclassified Technical Report No. LA-UR 933901, 1993.
- <sup>34</sup>K. Nobuhara, H. Nakanishi, H. Kasai, and A. Okiji, *J. Appl. Phys.* **88**, 6897 (2000).
- <sup>35</sup>R. N. Porter, L. M. Raff, and W. H. Miller, *J. Chem. Phys.* **63**, 2214 (1975).

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