Effects of Molecular Rovibrational States and Surface Topologies for Molecule-Surface Interaction: Chemisorption Dynamics of D_2 Collision with Rigid Ni Surfaces

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A quasiclassical and micro-canonical molecular dynamic simulation techniques have been applied for $D_2(v,j)+Ni$-surface collision systems. Dissociative adsorptions of a D_2 molecule on the rigid low index $(100),(110)$ and (111), surfaces of the nickel are investigated to understand the effects of the different surfaces, impact sites and the initial rovibrational states of the molecule on molecule-surface collisions. Interactions between the molecule and the Ni surfaces are mimicked by a LEPS potential. Dissociative chemisorption probabilities of the $D_2(v,j)$ Molecule (for the vibrational $(v)=0$ and rotational $(j)=0,1,3,10$, and for the $v=1, j=0$ states on different impact sites of the surfaces) are presented for the translation energies between 0.001 and 1.0 eV. The probabilities obtained at each collision site have unique behavior for the colliding molecule which is moving along the surface normal direction. It has been observed that at the low collision energies the indirect processes (steering effects) enhance the reactivity on the surfaces. The results are compared to the related studies in the literature.

Keywords: Chemisorption; Diatomic molecule; Deuterium molecule; Nickel surface

I. INTRODUCTION

One of the most active research areas, in surface science studies within the last several decades, is the interaction of small molecules with metals [1-17]. Due to their role as catalyst, particularly, the transition-metal systems have been subjects of the primary considerable interest and extensively studied for developing detailed microscopic pictures and understanding the dynamical processes occurring on solid and cluster surfaces. The characteristic behavior of the simplest molecule H_2 (dissociation on the surfaces of the metals and their alloys) is a typical and an important model for heterogeneous catalysis [7]. Determination of the sticking coefficients is the main traditional approach to the problem for different experimental conditions [8, 9]. In our earlier works, at three different sites on the $Ni(100)$ surface, the reaction dynamics of the $H_2(v,j)$ [10] and $D_2(v,j)$ [11] molecules (including the inelastic channels of the D_2) were considered. Moreover, we have reported a detailed molecular dynamic (MD) analysis of the reactive channels of the ground state case, $D_2(v=0,j=0)$, for the collisions at different sites of the low-index $(100),(110)$ and (111) surfaces of the nickel [12]. This type of analysis is important to understand better the effects of potential energy surface (PES), the crystal surface and topologically different impact sites on the dissociative chemisorption (DC), and also it is a test for the validity of the PES used. This present work extends our earlier works to cover the DC dynamics of the $D_2(v,j)$ molecule, for the $v=0, j=0,1,3,10$ and for the $v=1, j=0$, on various impact sites of these surfaces for the translation energies from 0.001 to 1.0 eV. This will add new dimensions to our understanding of the effect of the rovibrational excitations at different impact locations. The DC probabilities are calculated by averaging over all dissociation pathways for each of the collision energy of the molecule. The significance of the incident energy of the molecule can be shown by determining the steering or rotational to translational (R-T) energy transfer factors. There is a strong dependence on the crystal surface, impact sites, PES, collision energies, and the initial rovibrational states of the molecule of the reactive probabilities. These points will be discussed in the following Sections.

In our studies the surface atoms are kept as rigid and the interactions between the molecule and the Ni surfaces are described by a LEPS (London-Eyring-Polani-Sato)[13,14] potential. In Ref. [14] two sets of parameters (denoted as LEPS-I and LEPS-II) of this PES were considered for the same collision system. The first set is much less reactive and forms much higher dissociation barriers compared to the second one (therefore the second set is employed in our present study). In that study (Ref. [14]), furthermore, the averaged DC probabilities were calculated by running at least 100 trajectories (sometimes 200 or 300) to sample the aiming points on the unit cell of the surface. A convergence test on the DC probabilities was applied, as discussed in one of the previous studies (Ref. [12]), and it was observed that these numbers of the trajectories were not sufficient to reach converged DC probabilities. Therefore, the DC probabilities are calculated by using 1000 trajectories per set of initial conditions in the present work.

The effects of phonons and surface motion would result in a small increase in the width of the peak of the DC probabilities at low collision energy region for the D_2 compared to that of the H_2 [15]. Due to the rigidity of the surfaces in our present work this difference between the isotopes of the hydrogen molecules has been reduced. Furthermore, the magnitudes of the DCs would be slightly smaller if one assumes a non-rigid surface since a small amount of the energy of the molecule is transferred to the non-rigid surface during

the collision. Therefore, there is a less energy for the molecule to break its bond. On the other hand, the quantum effects for the deuterium molecule is less than the hydrogen molecule because the D_2 is heavier then the H_2. Even though the quantum effect does not change the general trend of the results presented in this study, we want to minimize this effect for the calculations of the DCs. Therefore, the D_2 isotope has been selected for the analysis. In addition, the D_2 has a smaller zero-point energy compared to the H_2, and smaller energy spacing between the rovibrational states. Therefore the H_2, for the same state, has higher internal energy. As a result, it would have slightly higher DC values in general compared to the D_2 molecule. In a recent study of Vincent et al. [15] the isotope effects for the H_2/D_2 and rotational excitation effects for the H_2 on Pt(111) are investigated. It is reported that there is a small difference in the dissociation probabilities of the H_2 and D_2.

Rotational hindering, in general, is dominant for the low rotational states, $j < 5$ values, because at the higher j values the rotating molecule cannot be easily re-oriented to a more favorable geometry for the reaction [15]. In order to present this effect clearly some rotational states in this region ($j = 0, 1, 3$) have been chosen. In addition, the vibrational excitation has been considered to see the effects on the DC mechanism. Moreover, calculations have been carried out for the $v = 0, j = 10$ and $v = 1, j = 0$ states to show the mode effect on the DC (the molecule with $v = 0, j = 10$ has slightly higher energy than that of the $v = 1, j = 0$ state). As seen, the $v = 1, j = 0$ state is much more reactive then the former state. This shows that there is a strong mode dependence of the DC.

II. COMPUTATIONAL BACKGROUNDS

Although the computational details in this work are the same as in Refs. [11, 12], repeating the most relevant parts here is necessary for the clearness of the report. In this work the $D_2(v, j)$ bombardment of the sites on the surfaces at normal incidence has been performed using a constant energy MD simulation. Hamilton's equations of motion were solved using Hamming's modified 4^{th} order predictor-corrector propagator with a step size of 5×10^{-16} s for the deuterium atoms. The nickel crystal surfaces are formed by the rigid atoms; the atoms are held fixed at their equilibrium positions. The surfaces are large and thick enough, therefore, the edge effects are negligibly small on the "decision" of the molecule up to the time of falling into the DC or scattering channels. The sizes of the low index surfaces are determined by considering the interaction distances. The atoms of the molecule begin to interact with the surface more strongly when the center-of-mass (c.m.) of the molecule is 2 $\AA$ above the surface (contour graphs of Ref. [12]). If the height of the c.m. is more than this value, then, $D-D$ interaction is stronger compared to the D_2 - surface interaction. Furthermore, when the $D-D$ separation distance is 1.5 $\AA$ or more, it can be said that the molecule is in the dissociation channel. In our simulation, however, 2.2 $\AA$ *D-D* distance is used as the dissociation criteria in order to eliminate errors on counting of the trajectories in the DC channel. The molecule at the higher collision energies (above 0.1 eV) dissociates or leaves the surface almost immediately.

The PES used in this simulation was formed by a four-body LEPS function which accounts for the $D-D$ and $D-Ni$ interactions (for details see Refs. [14]). The initial states of the molecule (v, j, coordinates and momenta) were prepared by using Porter-Raff-Miller method [18]. At the beginning of each trajectory the molecule starts moving from the asymptotic region, a distance of 7.0 $\AA$ above the surface, towards the crystal along the surface normal. The molecule collides with the specific target sites of the crystal surface with defined collision energies within $0.001 - 1.0$ eV. Each trajectory has a different phase of the D_2 oscillator and different orientation of the molecule with respect to the surface. For each of the collisions three displacements are monitored which are i) the distance between the deuterium atoms ($D-D$), ii) the distance between the deuterium and the target site (*D*-surface), and iii) the distance of the center of mass of the molecule from the target (D_2-surface). The trajectory is terminated either when the *D-D* distance exceeds three times the equilibrium bond distance of the D_2 molecule, or when the back-scattered molecule reaches again to the asymptotic region. The former one is counted as a reactive trajectory, and the later one represents a nonreactive collision with the surface. The DC probability is obtained from

$$P(E_{tr}) = \widetilde{N}(E_{tr})/N, \tag{1}$$

where $N = 1000$, and $\widetilde{N}$ is the number of reactive trajectories at collision energy E_{tr}.

III. RESULTS AND DISCUSSIONS

In our recent publication [10] the DC probabilities of the $H_2(v, j) + Ni(100)$ collision system for some rovibrational states of the molecule are presented as a function of the collision energy on the atop, center, and bridge sites of the surface. For these sites the ground state deuterium was also considered for all the rigid low index nickel crystal surfaces. The $Ni(110)$ surface (with the atop, center, short and the long bridge sites) has more sites then the other surfaces. Therefore, it is a more open surface. This feature of the surface certainly affects the reactivity differently for each of the initial conditions. In Fig. 1 effects of the initial rotational excitations and the surface topology are shown in detail for the vibrational ground state of the D_2, with the incident energies from 0.001 to 1.0 eV on the $Ni(110)$. The open regions on the surface are more reactive and the long- bridge site is the most suitable one for the dissociation of the molecule. As shown, the DC probabilities at the atop-site have threshold energies (about 0.25 eV) for the $j = 0, 1$ and 3.

This means that the molecule (for the $v = 0$) should have at least the threshold amount of the energy to be able to break its bond at the atop-site of the surface. The surface reactivity rapidly increases at the atop-site by increasing the collision energy of the molecule. As it has been pointed out by the contour graph of the atop site of Ni(110) in Ref. [12], there is an energy barrier and its hight is of 0.47 eV. On the other hand,

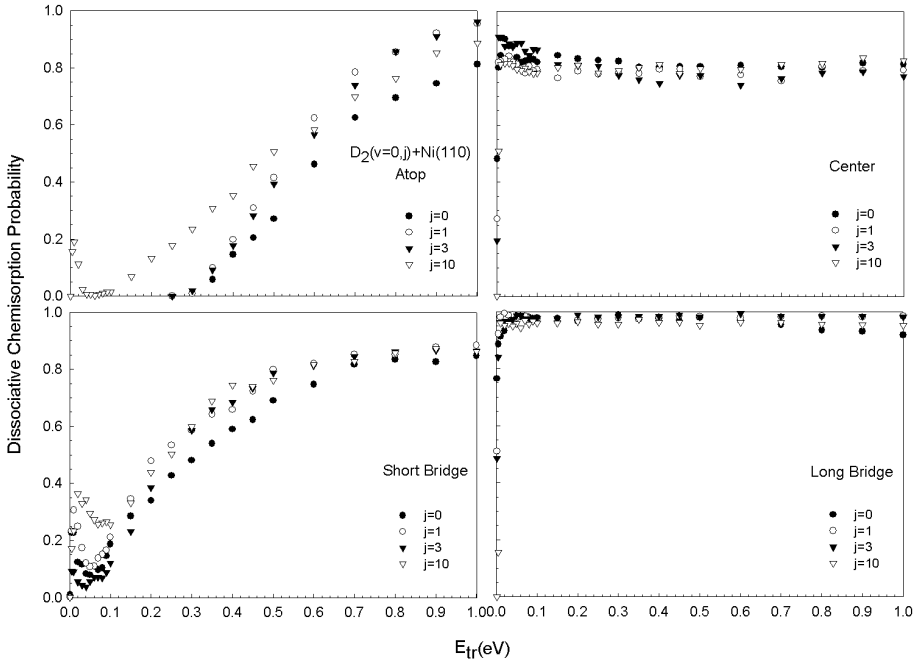

FIG. 1: The DC probabilities on the low index $Ni(110)$ surface at the topologically different impact sites as a function of the translational energy for the $D_2(v,j)$ molecule for various initial rotational states, $j = 0, 1, 3$ and 10 at $v = 0$.

for the $j = 10$ there is no threshold energy to observe the reactivity at this site because the molecule has sufficient internal energy to pass the energy barriers to break its bond on the surface. Furthermore, peaks are observed within the $0.01 - 0.05$ eV energy range because the steering of the molecule to a more favorable orientation is effective in the low collision energy region [19,20]. The energy barrier hight for the short bridge site is of 0.18 eV, but there is no barrier for the center and the long bridge sites [12] on this surface. More specifically, the molecule can steer from the atop or short-bridge site to a more open center site or to a long-bridge site. In the low collision energy region, the D_2 has to follow the lower energy parts of the PES, "valley", which directs the molecule towards to surface. Hence, the D_2 has a chance to find the suitable orientation with respect to the surface as approaches slowly to the impact site. At the lower collision energies and j values, the steering to a more favorable orientation is much easier (for the details see Ref. [10] and related references therein). This reorientation to a more favorable geometry is the source of the indirect mechanism [12]. Therefore, at the lower collision energy regions the DC probabilities, in general, are higher, e.g., the indirect mechanism dominates the reactivity, especially, on the short-bridge site of the Surface and for all the lower rotational states of the molecule. At the higher collision energies the steering effect becomes less effective, however, increase in the collision energy yields higher DC. The rovibrational effects are gradually losing their identity at the higher collision energies for the short-bridge site (the DC probability for the short-bridge site gradually increases, and reaches to a threshold value of near 0.8 eV). As the collision energy increases towards 1.0 eV the DC probabilities are merging to their highest values at each site except the center site.

The rotational hindering of the DC is determined particularly for the collision energies below 0.1 eV for all the sites of the $Ni(110)$ surface. The hindering process is a well known effect (especially $j < 5$) in the dissociation process of the H_2 on metal surfaces [19]. In addition, as shown in the graph for the center-site of the $Ni(110)$, when the molecule collides the surface with the higher collision energies, a slight decrease in the trends of the DC probabilities is observed. This is the result of the higher repulsive force on the molecule from the surface atoms at the center-site compared to those of the other sites. As a result, at the higher energies, the D_2 as a molecule can come closer to the surface layer on this site, and therefore, it has somewhat higher chance to be repelled. Because of the symmetric configurations of the nickel atoms around the target sites, they push the D atoms backwards (the inelastic scattering channel). Therefore, the DC probabilities are decreasing slowly as the collision energy increases almost up to 0.6 eV at the center-site (the probability of back scattering from the surface increases). On the other hand, on the long-bridge site the potential energy valley is wider and deeper in the exit channel compared to the other sites (as the atoms separate, their c.m. comes closer to the surface). As a result, the long-bridge site is always more reactive than the other three sites. These results are consistent with the contour plots of these sites [12]. As seen, the collision energy of the molecule and the topology of the surfaces have significant influence on the reactivity.

In Fig. 2 the calculated DC probabilities, for the three different rovibrational states of the molecule, $(v = 0, j = 0), (v =$

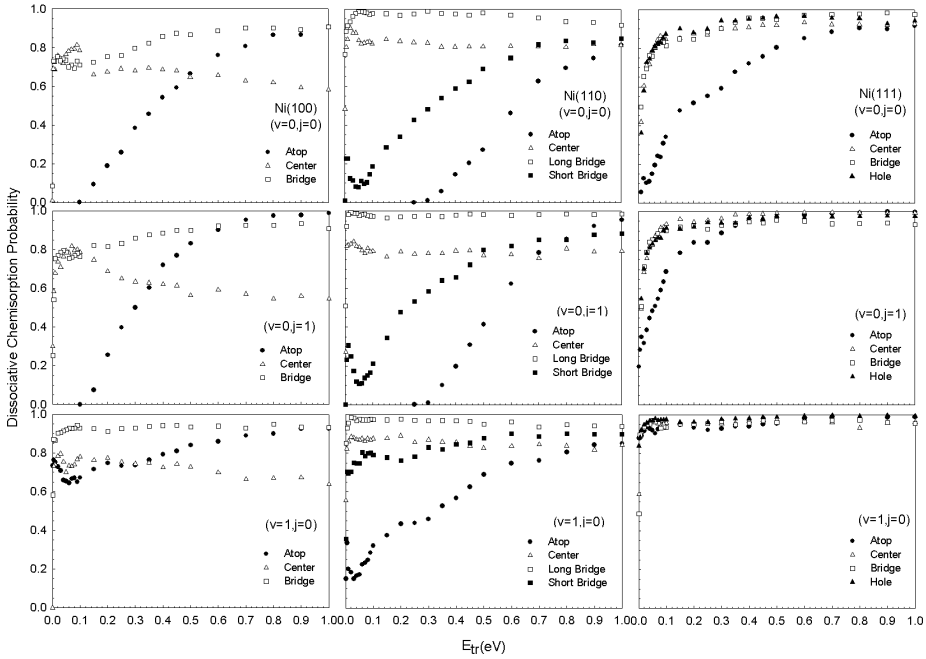

FIG. 2: The DC probabilities on the topologically different impact sites of the low index $(100),(110)$ and (111) surfaces as a function of the translational energy for the $D_2(v,j)$ molecule for three different initial rovibrational states, $(v=0,j=0),(v=0,j=1)$ and $(v=1,j=0)$. The first row is taken from Ref. [12].

$0, j=1)$ and $(v=1,j=0)$, are compared for all the topologically different sites of the $(100),(110)$ and (111) surfaces. It is obvious that the surface topology, in general, has a dominant influence on the reactivity. However, this influence, especially by the rovibrational excitation, is being loosed for the (111) due to the closer similarities of the impact sites on this surface (it is a closed-pack surface). Therefore, the DC probabilities are less sensitive to the surface sites on the (111). In contrast, the DCs on the (100) and (110) have strong dependence on the surface topology as seen in Fig. 2. One of the prominent features of this figure is that (for all the cases on all the surfaces) the DC increases at the lower collision energy region because of the indirect mechanism: the molecule searches for the suitable orientation with respect to the surface to break its bond. The time duration of the molecular adsorption strongly depends on the collision energy. Therefore, the longer lifetime enhances the reactivity which is highly effective in the low collision energy region for the *Ni*-surfaces. As discussed above two opposing factors, the steering and R-T energy transfer [21, 22], are working for and against the dissociation process. The steering enhances the DC when the impinging molecule does not have sufficient rotational energy even for the ground state case as shown in the first row of Fig. 2 (taken from Ref. [12]). Experimental [9, 23] (H_2 on *Ni* and *Pd* surfaces) and theoretical [24, 25] evidences of this indirect mechanism were observed when the molecule hits to the surface with the low energy (less than 0.1 eV). This mechanism was also observed in the simulations of D_2+Ni_{13} collision system [26-30]. For the higher collision energies, the effect of the indirect mechanism is negligibly small [26-32]. The R-T energy transfer originates from the strong coupling between the rotational and translational degrees of freedom which pertains to the effective transfer of the rotational energy to the translational energy. The R-T energy transfer dominates when the impinging molecule has sufficient rotational energy to assist in its adsorption. The vibrational excitation of the impinging D_2 molecule always promotes dissociation on the low index *Ni* surfaces, and the DC probabilities are higher almost at all energies than those of the rotationally exited molecule as seen in Fig. 2. The site effects become almost indistinguishable for the $(v=1,j=0)$ state at the (111) surface.

All these show that the surface topology plays important role, and also coupling between the modes of the molecule makes the dynamics of the DC more difficult to explain. In order to understand those effects it requires more detailed analysis. The analysis we have given above computationally demanding calculations. Therefore, the surface is treated rigid which leads to a remarkable savings of the computing time. Assumption of the rigidity artificially somewhat increases the DC probabilities. However, the trends of the DC processes are not affected by this rigidity.

IV. CONCLUDING REMARK

As a result with model potentials one cannot expect a quantitative agreement with all the experimental results for all the $Ni(100),Ni(110)$ and $Ni(111)$ surfaces. However, these

model calculations are important to find some of the answers for the dynamics of the DC process. Vibrational excitation of molecule is more effective for the reactivity than the rotational excitation of the molecule. The most of the impact sites on the *Ni*-surface display indirect process for the DC. The open sites such as the long-bridge and the center site of the (110) are more reactive. At the lower collision energies effects of the surface sites are more visible. As the collision energy increases, overlapping of the curves is observed among the different rotational excitations. This shows that strong coupling exists between the rotational and the translational modes of the molecule. In general, the $Ni(110)$ surface is relatively more reactive than the other nickel surfaces.

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