



Diffusion of Xe on Ni(111)

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Abstract

We have measured the diffusion rate $D(T)$ for Xe on Ni(111) from 30 to 60 K at coverages of $\theta = 0.04$ and $\theta = 0.16$. By fitting $D(T)$ to Arrhenius forms $D_0 \exp(-E_d/RT)$, we found the diffusion to be characterized by small activation energy and unusually small diffusivity: $E_d = 0.33 \pm 0.02$ kcal/mol and $D_0 = 2 \times 10^{-9 \pm 0.2}$ cm²/s at $\theta = 0.04$, and $E_d = 0.40 \pm 0.04$ kcal/mol and $D_0 = 3 \times 10^{-8 \pm 0.3}$ cm²/s at $\theta = 0.16$. We discuss the significance of our result in the light of similar observation of small diffusion barriers and *unusually* small diffusivities for Xe on W(110) and for Al diffusion on Al(111) and on Au(111) reported recently. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Diffusion of atoms and molecules on a solid surface continues to be one of the topics at the forefront of surface science and condensed matter physics. With the vast improvement of experimental techniques in recent years, new data are being reported and accumulated rapidly and they have enriched the detailed as well as the general understanding of surface diffusion and its impact on other aspects of surface science and material physics [1].

One of the standing issues in surface diffusion research is understanding the observation in some systems of *unusually* small pre-exponential factors or diffusivities D_0 . Small diffusivities are usually accompanied by small activation energy barriers. Experimental observations of small diffusivities have been reported by different groups using very different experimental techniques. In a field-emission cur-

rent fluctuation study of Xe diffusion on W(110), Chen and Gomer observed a small activation energy barrier of 1.1 kcal/mol and a diffusivity of 10^{-8} cm²/s [2]. In a scanning tunneling microscopy study of the saturation nucleation density [3–5] of aluminum (Al), Barth and coworkers recently found that the diffusion of Al on Al(111) and on Au(111) was characterized also by small activation energy barriers (1.0 kcal/mol and 0.7 kcal/mol, respectively) and small diffusivities in the range of $10^{-7} \sim 10^{-9}$ cm²/s [6,7]. The experimentally measured activation barrier for Al on Al(111) agrees well with the reliable ab initio calculation [8–10]. The value of the diffusivity is, however, far below the expected value of $10^{-3} \sim 10^{-4}$ cm²/s based upon the transition-state theory [11,12]. The value of $10^{-3} \sim 10^{-4}$ cm²/s has been seen in many other surface diffusion processes [1].

In this Letter, we show that the diffusion of Xe on Ni(111) is another case characterized by a small activation energy barrier and a very small diffusivity. The relative simplicity of the interaction between an

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inert gas atom with a metal surface will stimulate a more thorough theoretical investigation that hopefully can shed a new light into the issue of small diffusivities [13]. In a study of Xe adsorption on Pt(111), Müller showed that an ab initio calculation based on the local-density-approximation (LDA) should be good enough to qualitatively and semi-quantitatively reproduce the experimentally observed binding energy of a Xe adatom on a transition metal surface such as Ni(111) and the binding energy of an adsorbed Xe dimer [13]. However, it remains a theoretical challenge to explain the small diffusivity even for such a relatively simple system as Xe on Ni(111).

2. Experimental

We measure the diffusion rate of Xe on Ni(111) by monitoring the first-order linear optical diffraction from Xe submonolayer density gratings on Ni(111). The optical diffraction method has been described previously [14,15]. The first-order optical diffraction signal $S(t)$ decays as $S(t) = S(0) \exp(-2\pi^2 Dt/b^2)$, where b is the half period of the Xe density grating. We extract the diffusion rate D or $D(T)$ from the decay exponent of $S(t)$. The optical setup for preparation and detection of Xe density gratings is the same as in Ref. [15]. The experiment is conducted in an ultrahigh vacuum chamber with a base pressure less than 2×10^{-11} torr during the experiment. A 1.2-cm diameter Ni(111) disc is used as the substrate. The substrate is cleaned by Ne ion sputtering at room temperature for 20 min followed by annealing at 1000 K for a few seconds. A retarding-field Auger electron spectrum of the cleaned Ni(111) surface reveals no traces of sulfur and carbon. The temperature of the Ni substrate is variable from 28 to 1200 K, and is measured directly with a chromel–alumel thermo-couple spot-welded to the side of the Ni disc.

At the saturation coverage of $\theta_s = 0.33$, Xe adatoms forms a $(\sqrt{3} \times \sqrt{3}) R30^\circ$ structure that is commensurate with the underlying Ni(111) lattice [16]. The Xe–Xe separation at the saturation coverage equals the van der Waals diameter of Xe to within 1%. In a recent LEED study of Xe adsorption on Cu(111), Seyller and coworkers found that ad-

sorbed Xe atoms also form a $(\sqrt{3} \times \sqrt{3}) R30^\circ$ over-layer structure [17]. Based upon their analysis of the LEED intensity versus electron beam energy, these authors suggested that Xe adatoms reside on on-top sites instead of 3-fold hollow sites. Since Ni(111) and Cu(111) have very similar lattice constants and many adsorbates behave similarly on these two surfaces, it is possible that Xe adatoms occupy on-top sites on Ni(111) as well, although we can not rule out 3-fold hollow sites as actual adsorption sites.

3. Results and discussion

In Fig. 1, we show the Arrhenius plots of the measured diffusion rate $D(T)$ from 30 to 60 K at a coverage of $\theta = 0.04$ and $\theta = 0.16$. At a given temperature, $D(T)$ at $\theta = 0.16$ is always larger than the rate at $\theta = 0.04$ by a factor of 4 to 6. At both coverages $D(T)$ increases by roughly a factor of 8 as the temperature increases from 30 to 60 K. By fitting $D(T)$ with an Arrhenius form $D_0 \exp(-E_d/RT)$, we arrive at an activation energy barrier $E_d = 0.33 \pm 0.02$ kcal/mol and a diffusivity $D_0 = 2 \times 10^{-9 \pm 0.2}$ cm²/s at $\theta = 0.04$, and $E_d = 0.40 \pm 0.04$ kcal/mol and $D_0 = 3 \times 10^{-8 \pm 0.3}$ cm²/s at $\theta = 0.16$. For

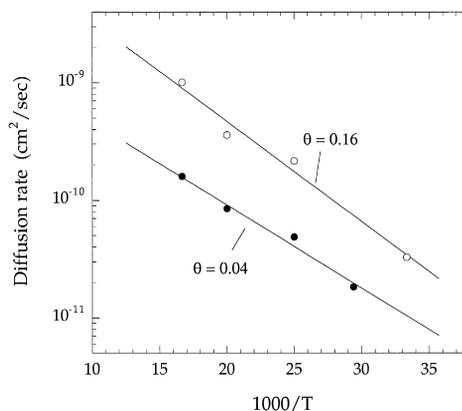


Fig. 1. Arrhenius plots of measured diffusion rate of Xe on Ni(111) from 30 to 60 K at coverages of $\theta = 0.04$ (solid circles) and $\theta = 0.16$ (open circles). The solid lines are fits to Arrhenius forms $D_0 \exp(-E_d/RT)$. At $\theta = 0.04$, the fit yields $D_0 = 2 \times 10^{-9}$ cm²/s and $E_d = 0.33$ kcal/mol. At $\theta = 0.16$, the fit yields $E_d = 0.4$ kcal/mol and $D_0 = 3 \times 10^{-8}$ cm²/s.

comparison, the diffusion of hydrogen on the same Ni(111) surface is characterized by an energy barrier of 4.5 kcal/mol and a typical diffusivity of 3×10^{-3} cm²/s [14].

The diffusion activation energy barrier $E_d = 0.33$ kcal/mol or 14 meV is less than 1/10 of the heat of desorption $E_a = 4.4$ kcal/mol for Xe on Ni(111) [16], indicating that Xe moves on a weakly corrugated potential. For comparison, the heat of desorption for Xe on Pt(111) is 6.4 kcal/mol [18], slightly larger than that on Ni(111); while the activation energy barrier for diffusion is 1.2 kcal/mol [19], more than 3 times as large as that on Ni(111). Based on an LDA calculation, Müller suggests that on Pt(111) Xe adatoms prefer on-top sites for adsorption and the diffusion occurs by hopping over two-fold bridge sites [13]. If Xe adatoms on Ni(111) also prefer on-top sites for adsorption as on Pt(111) and Cu(111), the over-barrier hopping diffusion is expected to take place between on-top sites over 2-fold bridge sites with an activation energy of $E_d = 0.33$ kcal/mol. If instead Xe adatoms prefer high-coordination sites for adsorption as do hydrogen and CO, we should expect Xe to hop between 3-fold hollow sites and over 2-fold bridge sites. An ab initio calculation of the binding energy of a Xe adatom on Ni(111) will help to distinguish these two possibilities [13].

We should point out that the observed activation energy is very close to the energy to break up a Xe dimer on Ni(111) so that the dimer break-up may dominate the energetics of surface diffusion instead of the usual site-to-site hopping. In this case, a Xe adatom moves more or less *freely* on Ni(111) except for occasional collisions with other Xe adatoms; as a result of collision, the Xe adatom forms a dimer with its collision partner. Since Xe dimers are expected to be much less mobile, the break-up of these Xe dimers can be the rate-limiting process in the surface diffusion. As shown by Müller for Xe on Pt(111) [13], the Xe 5p orbital hybridizes with the unfilled d-band of a transition metal and the hybridization causes a net electron transfer from adsorbed Xe to the metal surface. The resultant charging of Xe adatoms leads to additional Coulomb repulsion that in turn weakens the Xe–Xe interaction. As a result the binding energy of a Xe dimer decreases from 0.54 kcal/mol in gas-phase to 0.32 kcal/mol on

Pt(111). Since the Xe–Ni binding energy is similar to Xe–Pt binding energy, we expect the charge transfer from adsorbed Xe to the Ni surface to be comparable and thus the Xe dimer binding energy on Ni(111) is likely to be also around 0.32 kcal/mol. This is very close to our measured activation barrier. Again an ab initio calculation of binding energies of Xe dimers as well as monomers on Ni(111) will help to settle whether or not the dimer break-up dominates the diffusion energetics.

The most notable of our measurements is the small diffusivity $D_0 = 2 \times 10^{-9} \sim 3 \times 10^{-8}$ cm²/s for Xe on Ni(111), as opposed to 10^{-3} cm²/s for hydrogen on the same surface. The value of 10^{-3} cm²/s for diffusivity is generally considered ‘typical’ based on the transition-state theory. On the other hand unusually small diffusivities have been reported by Chen and Gomer for Xe on W(110) [2] and very recently by Barth and coworkers for Al on Al(111) and on Au(111) [6,7]. Barth et al. observed the empirical association of small diffusivities of Al on Al(111) and on Au(111) with simultaneously small activation barriers. Xe diffusion on Ni(111) in our present study can be considered as another example of a small diffusivity accompanied by a small activation barrier. We should caution that the exact physical nature of this empirical association is not clear at this moment. Thus it is not obvious that the mechanism responsible for the small diffusivity for Al on Al(111) and on Au(111) is also responsible for the similar behavior for Xe on Ni(111). Unlike the diffusion of hydrogen on Ni(111) that crosses over from a classical over-barrier hopping to a quantum under-barrier tunneling with a smaller coincidence energy barrier and a significantly reduced diffusivity [15], Al and Xe in the investigated temperature ranges (above 30 K) are expected to behave classically.

Considering that the diffusion of hydrogen atom on Ni(111) is characterized by a ‘typical’ diffusivity of 10^{-3} cm²/s and a much larger energy barrier of 4.5 kcal/mol, it is tempting to attribute the observed small diffusivity for Xe on Ni(111) to the compensation effect or Meyer–Neldel rule [20]. The Meyer–Neldel rule refers to the observation in many activated processes that pre-exponential factors increase with increasing activation energy barriers. In a recent embedded-atom-method molecular-dynamics study of self diffusion on a number of metals, Boisvert,

Lewis, and Yelon found that the Meyer–Neldel rule seemed to hold with the activation energy barrier ranging from 0.3 to 23 kcal/mol [21]. However even for the smallest activation barrier of 0.3 kcal/mol, the diffusivity computed by Boisvert et al. is still in the range of $10^{-3} \sim 10^{-4}$ cm²/s, 4 orders of magnitude larger than the diffusivity for Xe on Ni(111). The inadequacy of the compensation effect or the Meyer–Neldel rule to account for the small diffusivities for Al on Al(111) and on Au(111) has also been pointed out by Barth and coworkers [7]. In fact based upon the molecular-dynamics simulation, Boisvert, Lewis, and Yelon argued that the Meyer–Neldel rule applies under the condition when diffusion activation barriers E_d are a few times larger than the Debye energies of the substrates. This condition is not satisfied for Xe on Ni(111) and W(110) nor for Al on Al(111) and Au(111). As a result it may not be surprising that the Meyer–Neldel rule as revisited by Boisvert and coworkers does not apply to these cases.

4. Conclusions

In summary, we found that the diffusion of Xe on Ni(111) is characterized by a small activation barrier of $E_d = 0.33$ kcal/mol and an unusually small diffusivity $D_0 = 2 \times 10^{-9} \sim 3 \times 10^{-8}$ cm²/s. The energetics of the diffusion is dominated either by that of site–site hopping or by the energy to break up a Xe dimer on Ni(111). The diffusion of Xe on Ni(111) represents a case of classical activated rate processes that are characterized by unusually small pre-exponential factors. Since only for a few activated rate processes can the pre-exponential factors be ascertained experimentally, ‘typical’ values of pre-exponential factors are routinely assumed in the analysis and simulation of complex surface processes such as epitaxy and surface reactions. It is thus an important theoretical challenge to understand the origin of small pre-exponential factors. In some cases

they may profoundly change the expected outcome of complex surface processes.

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