Quantum Diffusion of H on Pt(111): Step Effects

C. Z. Zheng, C. K. Yeung, M. M. T. Loy, and Xudong Xiao*

Department of Physics and Institute of Nano Science and Technology, Hong Kong University of Science & Technology, Hong Kong, China

(Received 22 May 2006; published 19 October 2006)

Using a linear optical diffraction technique, we have systematically investigated the defect effects on quantum surface diffusion of hydrogen on Pt(111) surfaces. The quantum tunneling effect was clearly observed for hydrogen diffusion at low temperatures as manifested by a leveling off of the diffusion coefficient on flat surfaces. The strong influence of surface defects on the quantum diffusion is in good agreement with the creation of an inhomogeneous surface with adsorption sites of different binding energies.

DOI: 10.1103/PhysRevLett.97.166101 PACS numbers: 68.35.Fx, 68.35.Dv, 68.43.Jk, 82.20.Xr

Because of the small mass of the hydrogen atom and the weakly corrugated potential energy surface, diffusion of hydrogen on metal surfaces may take both classical over-barrier hopping and quantum mechanical under-barrier tunneling. Quantum effects in surface diffusion are of broad interest and have been intensively studied both experimentally [1–15] and theoretically [16–26]. The first observation of a nearly temperature independent surface (chemical) diffusivity of H on W(110) in the low temperature regime by Gomer and coworkers [1] using field emission microscopy (FEM) has stimulated a great theoretical effort [16–26] because of the observed unexpected different behavior from the light atom diffusion in bulk metals, for which a much stronger temperature dependence was found [27]. Experimentally, while similar behaviors were observed by the same group using the same technique for H on a number of other metal surfaces [2–7], only one report using a different technique, scanning tunneling microscopy (STM), has confirmed the weak temperature dependence of surface (tracer) diffusivity for H on Cu(100) [13], but at a diffusion rate about 6–9 orders of magnitude slower ($\sim 10^{-19}$ cm^2/sec vs 10^{-10}–10^{-13} cm^2/sec). Using a linear optical diffraction (LOD) technique that probes diffusion over a length scale of microns, Zhu and his coworkers found an activated quantum diffusion with a strong temperature dependence for H on Ni(111) [11,12] and Ni(100) [8], drastically different from what has been observed by Gomer and his coworkers on the same systems [7]. These differing and apparently contradictory observations, using different techniques, need to be resolved in order to remove any doubts on the experimental observation of quantum surface diffusion.

Recognizing that different techniques detect different physical properties of a system, and that such properties might be influenced by different processes, we studied the quantum effects in surface diffusion using one of the above techniques, the linear optical diffraction technique [28–30]. The system we have chosen is H on Pt(111), because there is a theoretical prediction for this system [26], and we have extensively studied the over-barrier diffusion of this system [31]. Compared to FEM and STM, which detect the H diffusion only within a single well-ordered terrace, the linear optical diffraction technique probes diffusion over a length scale that includes many terraces. Thus, effects from steps between terraces must be considered. In this Letter, we report our findings on samples with varying defect (steps) densities. Our main results are (i) for nominally flat surfaces, a crossover from a strong temperature dependent classical diffusion at high temperatures to a rather weak temperature dependent quantum diffusion at low temperatures was observed for H atom; (ii) the crossover to the weak temperature dependent quantum diffusion was not observed for heavier particles, i.e., D or CO, on the same surface; (iii) quantum diffusion behaviors can differ for different nominally flat surfaces; and (iv) for stepped surfaces (nominally miscut of 1°), no quantum diffusion could be observed. These results unambiguously demonstrate for the first time that quantum diffusion with low activation energy can be observed over micron length scales with many terrace-step structures with a comparable magnitude as those obtained by FEM. Our results also demonstrate for the first time that defects, in particular, steps at high densities, suppress quantum tunneling. We argue that the suppression is due to creation of an inhomogeneous surface with adsorption sites of different energies, and not, as commonly believed, simply due to a high step barrier.

Our experiment was performed in an ultrahigh vacuum chamber with a base pressure of 2.0×10^{-10} Torr. Three single crystalline Pt(111) samples were used, two of which were flat with nominal miscut of 0.1° (but only guaranteed <0.25°), and one was stepped with miscut of 1° off the (111) plane along $[11\bar{2}]$ direction (all purchased from MaTeck GmbH, Germany). Extensive cycles of Ar$^+$ sputtering, oxygen treatment at 1000 K, and high temperature annealing at 1200 K were first employed to obtain clean Pt surfaces [32–34]. Routine cleaning with 30 minutes Ar$^+$ sputtering at room temperature and 5 minutes annealing at 1200 K was additionally applied each day before diffusion measurements. The cleanness and ordering of the sample surface were routinely checked by AES and LEED.

We used the linear optical diffraction technique [28–30] to measure the surface diffusion coefficient. H_2 gas was first dosed to the clean Pt surface at ~100 K to 0.4 monolayer (ML) by backfilling the chamber through a leak valve. Its coverage was controlled by the exposure whose corresponding coverage was evaluated from the thermal desorption spectra (TDS) [32–34], with the absolute calibration performed at 1 ML. Similar procedures were taken for D_2 in order to study the isotope effect [32]. Both H_2 and D_2 are known to dissociatively adsorb on the fcc type threefold hollow sites [35]. Subsequently, the sample temperature was raised or lowered to a diffusion temperature. By interfering two laser beams (Nd:YAG laser at 1.06 μm, 10 ns) at the surface via laser-induced thermal desorption, a one-dimensional grating of H (or D) was then created at the diffusion temperature. The grating periods were varied from 10.6 to 2.89 μm to cover a large dynamic range of measurement, and the depth of the coverage grating is about 0.02 ML. The smearing of the adsorbate grating via surface diffusion can now be detected by the decay of the first-order linear diffraction signal of a He-Ne laser beam [30]:

$$S(t) = S(0)\exp(-t/\tau), \quad \text{with} \quad \tau = s^2/8\pi^2 D, \qquad (1)$$

where D is the chemical diffusion coefficient and s is the grating period. In the present study, D was measured as a function of substrate temperature over a range of 68–150 K, below the uptake desorption temperature ~160 K [32] to avoid the influence of thermal desorption. The sample temperature was controlled by electron beam heating and liquid-nitrogen or liquid-helium cooling to within ±1 K and monitored by a K-type thermocouple spotwelded at the side of the samples.

In Fig. 1, we depict the surface diffusion results of H atoms on the two nominally flat surfaces and one stepped surface, where the diffusion coefficient is plotted as a function of reciprocal temperature in an Arrhenius form. While the typical experimental uncertainty in determining each diffusion coefficient is within a factor of 2, the data scattering in the low temperature region is considerably larger, possibly due to the inhomogeneous distribution of defects on the sample surface. The two nominally flat surfaces clearly exhibit a crossover from a high activation energy over-barrier diffusion to a low activation energy diffusion. The linear behavior at high temperatures for all the samples indicates a thermally activated diffusion process, $D^{\mathrm{cl}} = D_0^{\mathrm{cl}} \exp(-E^{\mathrm{cl}}/kT)$, with the deduced activation energy $E^{\mathrm{cl}} \sim 185 \pm 15$ meV and prefactor $D_0^{\mathrm{cl}} \sim 10^{-1.4\pm0.3}$ $\mathrm{cm}^2/\mathrm{sec}$ for the flat surfaces, and $E^{\mathrm{cl}} \sim 190 \pm 15$ meV and $D_0^{\mathrm{cl}} \sim 10^{-1.3\pm0.3}$ $\mathrm{cm}^2/\mathrm{sec}$ for the stepped surface. The leveling off to a rather weak temperature dependent diffusion at low temperatures on the nominally flat surfaces is commensurate with a mechanism due to quantum tunneling of H atoms between the adsorption sites. Between the two flat samples A and B, the diffusion coefficients coincide with each other at high temperatures, but display some difference at low temperatures. The transition temperature for the leveling off around 95 K is lower but comparable with those observed on nickel and tungsten surfaces by FEM and LOD [1–12], but significantly higher than the value on Cu(100) measured by STM [13]. Since quantum tunneling opens a new diffusion channel in addition to the classical one, the data shown in Fig. 1 should be fitted by [12,36]

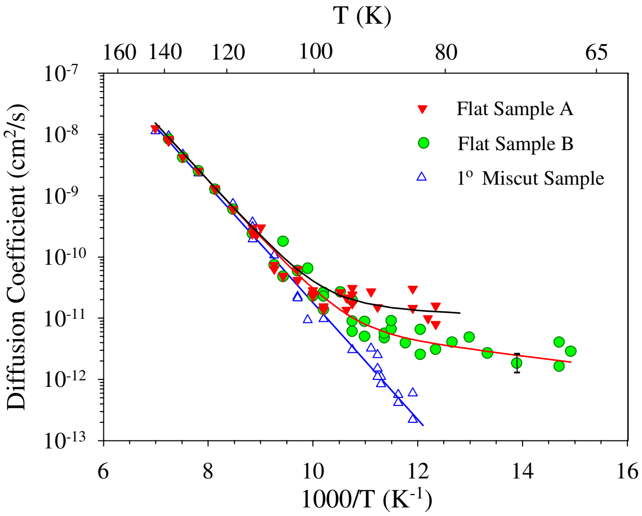

FIG. 1 (color online). H diffusion coefficient versus reciprocal temperature for three Pt(111) sample surfaces: two are nominal flat and one stepped with 1° miscut off the (111) plane along $[11\bar{2}]$ direction. The diffusion direction on the stepped surface is parallel to the steps. The solid lines are Arrhenius fits with either one or two activation processes.

$$\begin{aligned} D &= D^{\mathrm{cl}} + D^{\mathrm{qm}} \\ &= D_0^{\mathrm{cl}} \exp(-E^{\mathrm{cl}}/kT) + D_0^{\mathrm{qm}} \exp(-E^{\mathrm{qm}}/kT). \qquad (2) \end{aligned}$$

In addition to E^{cl} and D_0^{cl} given above, we obtain $D_0^{\mathrm{qm}} \sim 5 \times 10^{-11}$ $\mathrm{cm}^2/\mathrm{sec}$ and $E^{\mathrm{qm}} \sim 10$ meV for sample A, and $D_0^{\mathrm{qm}} \sim 8 \times 10^{-11}$ $\mathrm{cm}^2/\mathrm{sec}$ and $E^{\mathrm{qm}} \sim 20$ meV for sample B, as summarized in Table I. It is important to note for diffusion of more massive molecules such as CO on this surface, we have previously firmly established [37–39] that there is only one single thermally activated process within comparable diffusivity range.

We further strengthen the case here by measuring diffusion of deuterium on sample B, as shown in Fig. 2. Clearly, the diffusion of D atoms has a much slower diffusivity as compared to that of H atoms. The entire set of data can be

TABLE I. The fitted diffusion energies and prefactors by Eq. (2) for various surfaces.

Sample		E^{cl} (meV)	D_0^{cl} ($\mathrm{cm}^2/\mathrm{sec}$)	E^{qm} (meV)	D_0^{qm} ($\mathrm{cm}^2/\mathrm{sec}$)
Flat A		185 ± 15	$10^{-1.4\pm0.3}$	10 ± 5	5×10^{-11}
Flat B	H	185 ± 15	$10^{-1.4\pm0.3}$	20 ± 5	8×10^{-11}
	D	200 ± 18	$10^{-1.9\pm0.3}$	⋯	⋯
Stepped		190 ± 15	$10^{-1.3\pm0.3}$	⋯	⋯

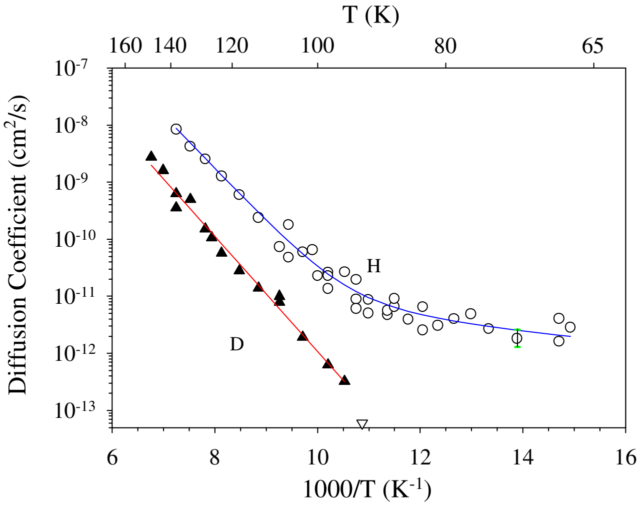

FIG. 2 (color online). Diffusion coefficient versus reciprocal temperature for H (replot) and D on sample B surface. The solid lines are Arrhenius fits with either one or two activation processes. The open triangle is an estimated diffusion coefficient value for deuterium at a lower temperature, representing the detection limit.

fitted by $D^{\rm cl} = D_0^{\rm cl} \exp(-E^{\rm cl}/kT)$, with $E^{\rm cl} \sim 200 \pm 18$ meV and $D_0^{\rm cl} \sim 10^{-1.9\pm0.3}$ cm^2/sec over the entire temperature range. The inverted open triangle indicates the limit of our detection capability, which appears to be higher than the quantum diffusion onset for D. The large difference between H and D is consistent with simple WKB estimate for the tunneling rate dependence on mass.

In contrast to the results on nominally flat surfaces, data shown in Fig. 1 for the 1° miscut sample displays only the over-barrier diffusion without showing any leveling off over the entire range of measurements even for H diffusion parallel to the steps, for which step effect is usually unimportant [39]. The quantum tunneling diffusion appeared to have been suppressed with the presence of steps. Below, we give a plausible explanation for this observation.

In general, quantum diffusion proceeds by incoherent sequence of tunneling through surface potential energy barriers, i.e., by uncorrelated tunneling events between nearest-neighboring adsorption sites [16–26]. Quantum tunneling can occur: (i) between two vibrational ground states that belong to two nearest neighbor adsorption sites or (ii) between two vibrational excited states that belong to two nearest neighbor adsorption sites through thermal activation. While the former may lead to a weak temperature dependence, the latter is a thermally activated tunneling process with an activation energy equal to the excitation energy of the vibrational excited state [25]. In the presence of defects, the surface is inhomogeneous with potential wells at the adsorption sites that are no longer identical. The nonequivalence of the adsorption sites can come from (i) small-polaron effect; (ii) adsorbate-adsorbate interaction; and (iii) surface defect-mediated adsorption energy changes. While the first two may occur even for perfect surfaces [11], the last one can create a large variety of nonequivalent sites depending on the defect density, the defect type, and the distance away from defects. As discussed in Ref. [31], the influence of defects can extend to a large area around the defect sites. Now, if the potential wells for a H atom in two neighboring sites are not the same, one expects that the vibrational states can no longer line up, and the quantum tunneling will be reduced [40]. With an effective energy difference ε between two vibrational ground states at the two neighboring adsorption sites, the tunneling diffusion rate assisted by phonons can be approximated by [41]

$$D^{\rm qm} = D_0^{\rm qm} \exp\left(-\frac{E_a}{kT} - \frac{\varepsilon}{2kT} - \frac{\varepsilon^2}{16E_a kT}\right), \qquad (3)$$

where E_a is the small-polaron activation energy on perfect surface and $D_0^{\rm qm}$ is a constant. Compared with Eq. (2), we have $E^{\rm qm} = E_a + \varepsilon/2 + \varepsilon^2/16E_a$. While it is difficult to determine E_a, we would assume that it dominates in sample A with $\varepsilon \sim 0$, which allows us to deduce $E_a \sim 10$ meV from the fitting parameter $E^{\rm qm} \sim 10$ meV. This value is in the high side of the reported polaron energy [13,25] and must be regarded as the upper bound because we ignored ε. For sample B, from the fitting result $E^{\rm qm} \sim 20$ meV, we deduce a value of $\varepsilon \sim 17$ meV, most likely arising from the different defect densities despite that both sample A and B are nominally flat. Our measured quantum diffusion coefficient around 10^{-11} cm^2/sec with a weak temperature dependence as compared with the thermally activated over-barrier diffusion seems to agree well with the estimated value of $10^{-9.2}$ cm^2/s by first principles calculation [26], although the latter predicted a much smaller diffusion barrier than we measured for the over-barrier diffusion.

Although the quantum diffusion was observed on both nominally flat surfaces, our results clearly show that even the uncontrolled defects, including steps from somewhat different miscuts, point defects, and laser pulse induced damages, have already manifested different quantum diffusion behaviors. For the 1° miscut sample with an average terrace of 48 atoms wide, even parallel to the step directions, the quantum diffusion is no longer observed within the temperature range measured. This is due to the step defects which affect adsorption sites even some distance away from the steps [31]. Assuming that the quantum tunneling diffusion will eventually set in at lower temperatures than ~84 K, the lowest temperature measured here, a lower bound of the effective ε can be estimated from Eqs. (2) and (3) to be ~34 meV by comparing data with those of sample A. The over-barrier diffusion for H perpendicular to the steps on this surface was observed to be faster than those parallel to steps and with an effective lower activation energy of ~150 meV [31]. In comparison with the flat surface activation energy (~185 meV), this appears to support our estimated ε value. The above discussion systematically and consistently demonstrated that the different diffusion behaviors at low temperatures on different samples come from different inhomogeneity of the surfaces created by defects.

We now discuss the isotope effect. The activation energy of D is found larger than that of H by ~15 meV, and the prefactor is roughly the same as that of H within the experimental uncertainty. According to theoretical calculations, the zero point energy difference between H and D on Pt(111) is about 45 meV [26,42]. Considering that there is a difference of zero point energy at the saddle point, our measured value is quite reasonable. The observed slower diffusivity for D is in agreement with many other observations [5–7,10,12], but with a significant difference that no leveling off is observed in the present case, similar to the recent study by STM [13]. The strong isotope effect is also consistent with the theoretically estimated value of $D(\mathrm{H})/D(\mathrm{D}) \approx 10^4$ obtained on Pt(111) surface [26]. A simple WKB estimate can further confirm the large difference. Thus, it is not surprising that we have not yet observed the weak temperature dependent diffusion coefficient for D at low temperatures.

In summary, we have measured the surface diffusion of H and D atoms on a number of Pt(111) surfaces by linear optical diffraction method. The observed weak temperature dependent diffusion coefficient of hydrogen at low temperatures can be attributed to quantum tunneling between the vibrational ground states instead of vibrational excited states of the nearest neighbor adsorption sites. For the first time, the defect effects as well as the weak temperature dependent quantum diffusion over a macroscopic size surface with steps and other uncharacterized defects have been unambiguously demonstrated, which may stimulate further theoretical investigations.

We wish to acknowledge financial support from the Research Grant Council of Hong Kong through Grant Nos. 603803 and HKUST6147/99P, the HKUST RIG Grant, and the William Mong Solid State Cluster Laboratory.

---

*To whom correspondence should be addressed.
Email: phxudong@ust.hk

[1] R. DiFoggio and R. Gomer, Phys. Rev. B **25**, 3490 (1982).
[2] C. Dharmadhikari and R. Gomer, Surf. Sci. **143**, 223 (1984).
[3] S. C. Wang and R. Gomer, J. Chem. Phys. **83**, 4193 (1985).
[4] E. A. Daniels, J. C. Lin, and R. Gomer, Surf. Sci. **204**, 129 (1988).
[5] T.-S. Lin and R. Gomer, Surf. Sci. **255**, 41 (1991).
[6] D.-S. Choi, C. Uebing, and R. Gomer, Surf. Sci. **259**, 139 (1991).
[7] E. A. Daniels and R. Gomer, Surf. Sci. **336**, 245 (1995).
[8] X. D. Zhu, A. Lee, A. Wong, and U. Linke, Phys. Rev. Lett. **68**, 1862 (1992).
[9] A. Lee, X. D. Zhu, L. Deng, and U. Linke, Phys. Rev. B **46**, 015472 (1992).
[10] A. Lee, X. D. Zhu, A. Wong, and L. Deng, Phys. Rev. B **48**, 011256 (1993).
[11] A. Wong, A. Lee, and X. D. Zhu, Phys. Rev. B **51**, 4418 (1995).
[12] G. X. Cao, E. Nabighian, and X. D. Zhu, Phys. Rev. Lett. **79**, 3696 (1997).
[13] L. J. Lauhon and W. Ho, Phys. Rev. Lett. **85**, 4566 (2000).
[14] A. J. Heinrich, C. P. Lutz, J. A. Gupta, and D. M. Eigler, Science **298**, 1381 (2002).
[15] J. Repp, G. Meyer, K.-H. Rieder, and P. Hyldgaard, Phys. Rev. Lett. **91**, 206102 (2003).
[16] M. J. Puska, R. M. Nieminen, M. Manninen, B. Chakraborty, S. Holloway, and J. K. Nørskov, Phys. Rev. Lett. **51**, 1081 (1983).
[17] K. A. Muttalib and J. Sethna, Phys. Rev. B **32**, 3462 (1985).
[18] I. C. da Cunha Lima, A. Troper, and S. C. Ying, Phys. Rev. B **41**, 011798 (1990).
[19] X. D. Zhu and L. Deng, Phys. Rev. B **48**, 17527 (1993).
[20] X. D. Zhu, Phys. Rev. B **50**, R011279 (1994).
[21] L. Y. Chen and S. C. Ying, Phys. Rev. Lett. **73**, 700 (1994).
[22] T. R. Mattsson and G. Wahnström, Phys. Rev. B **51**, 1885 (1995).
[23] T. R. Mattsson and G. Wahnström, Phys. Rev. B **56**, 014944 (1997).
[24] E. Pazy and B. Laikhtman, Phys. Rev. B **59**, 015854 (1999).
[25] S. C. Badescu, S. C. Ying, and T. Ala-Nissila, Phys. Rev. Lett. **86**, 5092 (2001).
[26] G. Källén and G. Wahnström, Phys. Rev. B **65**, 033406 (2002).
[27] I. S. Anderson, N. F. Berk, J. J. Rush, T. J. Udovic, R. G. Barnes, A. Magerl, and D. Richter, Phys. Rev. Lett. **65**, 1439 (1990).
[28] X. D. Xiao, Y. Xie, C. Jakobsen, H. Galloway, M. Salmeron, and Y. R. Shen, Phys. Rev. Lett. **74**, 3860 (1995).
[29] X. D. Xiao, Y. Xie, and Y. R. Shen, Phys. Rev. B **48**, 17452 (1993).
[30] X. D. Xiao, Y. Xie, and Y. R. Shen, Surf. Sci. **271**, 295 (1992).
[31] C. Z. Zheng, C. K. Yeung, M. M. T. Loy, and X. D. Xiao, Phys. Rev. B **70**, 205402 (2004).
[32] K. Christmann, G. Ertl, and T. Pignet, Surf. Sci. **54**, 365 (1976).
[33] K. Christmann and G. Ertl, Surf. Sci. **60**, 365 (1976).
[34] R. W. McCabe and L. D. Schmidt, Surf. Sci. **65**, 189 (1977).
[35] B. J. J. Koeleman, S. T. de Zwart, A. L. Boers, B. Poelsema, and L. K. Verheij, Phys. Rev. Lett. **56**, 1152 (1986).
[36] R. P. Bell, *The Tunnel Effect in Chemistry* (Chapman and Hall, London, 1980).
[37] J. W. Ma, X. D. Xiao, N. J. DiNardo, and M. M. T. Loy, Phys. Rev. B **58**, 4977 (1998).
[38] J. W. Ma, L. Cai, X. D. Xiao, and M. M. T. Loy, Surf. Sci. **425**, 131 (1999).
[39] J. W. Ma, X. D. Xiao, and M. M. T. Loy, Surf. Sci. **436**, L661 (1999).
[40] H. Grabert and U. Weiss, Phys. Rev. Lett. **54**, 1605 (1985).
[41] C. P. Flynn and A. M. Stoneham, Phys. Rev. B **1**, 3966 (1970).
[42] S. C. Badescu, P. Salo, T. Ala-Nissila, S. C. Ying, K. Jacobi, Y. Wang, K. Bedurftig, and G. Ertl, Phys. Rev. Lett. **88**, 136101 (2002).