

Direct comparisons of rates for low temperature diffusion of hydrogen and deuterium on Cu(001) from quantum mechanical calculations and scanning tunneling microscopy experiments

Jeremy Kua

Materials and Process Simulation Center (139-74), California Institute of Technology, Pasadena, California 91125

Lincoln J. Lauhon

Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138

Wilson Ho

Department of Physics and Astronomy and Department of Chemistry, University of California, Irvine, California 92697

William A. Goddard III^{a)}

Materials and Process Simulation Center (139-74), California Institute of Technology, Pasadena, California 91125

(Received 22 January 2001; accepted 3 July 2001)

Recent experiments by Lauhon and Ho using scanning tunneling microscopy (STM) observed the direct hopping of H and D on Cu(001) as a function of temperature. They found nearly temperature independent tunneling for H below 60 K, but could not detect the tunneling threshold for D (it is at least 1000 times lower than for H). The availability of such direct and accurate measurements provides the opportunity for validating the level of theory required to predict the diffusion of adsorbates on surfaces. Thus, we carried out density functional theory (DFT) using the generalized gradient approximation (GGA-II) on periodic slabs. The calculated tunneling rate of $4.74 \times 10^{-4} \text{ s}^{-1}$ for H is in close agreement with the experimental value of $4.4 \times 10^{-4} \text{ s}^{-1}$. We predict $4.66 \times 10^{-9} \text{ s}^{-1}$ for the tunneling rate of D (one hop every 83 months!). Between 60 and 80 K, the calculated thermally activated diffusion rate of H is $10^{12.88} \exp(-0.181 \text{ eV/kT}) \text{ s}^{-1}$ in close agreement with the STM value: $10^{12.9 \pm 0.3} \exp(-0.197 \text{ eV/kT})$. For deuterium, between 50 and 80 K, the calculated rate is $10^{12.70} \exp(-0.175 \text{ eV/kT}) \text{ s}^{-1}$ in close agreement with the STM value: $10^{12.7 \pm 0.2} \exp(-0.194 \text{ eV/kT}) \text{ s}^{-1}$. These results validate that such first principles theory can be used to predict the diffusion (including tunneling) for adsorbates on surfaces, providing important data needed to unravel surface processes in catalysis and crystal growth. © 2001 American Institute of Physics. [DOI: 10.1063/1.1396815]

I. INTRODUCTION

The diffusion of adsorbates is an important elementary step in reactions on metal surfaces. Direct measurements are difficult, however, and the accuracy of calculated rates has not been established. The recent direct measurement of diffusional hopping rates for H and D on Cu(001) using scanning tunneling microscopy (STM) represents a breakthrough in experimental methods.¹ The observed rates differ by orders of magnitude from those of theory, suggesting that theoretical methods must be improved to be useful.

In this paper we use current state of the art methods for quantum calculations on periodic slabs and find results to be in excellent agreement with experiment, validating the use of theory to calculate diffusion processes on surfaces. This should be useful since diffusion processes are often affected by other factors involving coadsorbates and surface defects, making it difficult to extract direct rates from experiment.

Hydrogen chemisorption and diffusion are important in many applications in heterogeneous catalysis, fuel cell development, and hydrogen storage.²⁻⁴ In addition, they provide the simplest model system for validating theoretical and experimental methodologies.

In particular, the diffusion behavior changes dramatically at low temperatures. At higher temperatures, diffusion follows thermally activated Arrhenius behavior. However, at sufficiently low temperature, there is a crossover to a temperature-independent regime, where migration occurs via quantum tunneling. Previous experimental measurements of the diffusion of hydrogen on metal surfaces have been made by field emission microscopy (FEM),⁵⁻⁷ helium atom scattering (HAS),⁸ and a method based on laser optical diffraction (LOD).^{9,10}

There have been controversies regarding the experimental measurements for hydrogen diffusion on nickel. Gomer and co-workers⁷ found a transition from thermally activated to quantum tunneling at 120 K. However, Zhu and co-workers¹⁰ measured activated diffusion for temperatures as low as 65 K. Using a model potential based on density

^{a)} Author to whom correspondence should be addressed; electronic mail: wag@wag.caltech.edu

functional calculations with the generalized gradient approximation (GGA-II), Mattsson and co-workers^{11,12} calculated a transition temperature of ~ 63 K and a diffusion constant of $6.6 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ (or $3.5 \times 10^{-1} \text{ s}^{-1}$) for H on a rigid Ni(001) lattice.

Most recently, Lauhon and Ho¹ utilized scanning tunneling microscopy (STM) to directly measure hopping rates of individual hydrogen and deuterium atoms on Cu(001) surface at low temperatures and coverages. For hydrogen diffusion, their results led to a transition from thermal activation to quantum tunneling at 55 K. The hopping rate in the quantum tunneling regime is $v_{\text{hop,H}} = 4.4 \times 10^{-4} \text{ s}^{-1}$, corresponding to $D = 0.25 l^2 v_{\text{hop}} = 7.2 \times 10^{-20} \text{ cm}^2 \text{ s}^{-1}$ (where $l = 2.556 \text{ \AA}$ is the lattice constant). In the thermally activated regime, the rate is characterized by Arrhenius behavior. Between 60 and 80 K, they found the pre-exponential factor $A_{\text{H}} = 10^{12.9 \pm 0.3} \text{ s}^{-1}$ and the thermal barrier $E_{\text{H}} = 0.197 \text{ eV}$.

In comparison, our present calculations yield $v_{\text{hop,H}} = 4.74 \times 10^{-4} \text{ s}^{-1}$, $D_{\text{H}} = 7.74 \times 10^{-20} \text{ cm}^2 \text{ s}^{-1}$, $E_{\text{H}} = 0.181 \text{ eV}$, and $A_{\text{H}} = 10^{12.88}$ (for a mean temperature of 70 K). Our calculated transition temperature is 56.3 K. These results are in excellent agreement with experiment, validating the model being used.

For deuterium, Lauhon and Ho found that the thermal diffusion rate varied over seven orders of magnitude between 80 and 50 K with no transition to quantum tunneling down to a thermal hopping rate of $4 \times 10^{-7} \text{ s}^{-1}$ (one hop every 29 days). In the thermally activated regime from 50 to 80 K, they found $A_{\text{D}} = 10^{12.7 \pm 0.2} \text{ s}^{-1}$ and $E_{\text{D}} = 0.194 \text{ eV}$.

We calculate $E_{\text{D}} = 0.175 \text{ eV}$ and $A_{\text{D}} = 10^{12.70}$ (for a mean temperature of 65 K) in good agreement with experiment. In addition, for the quantum tunneling regime, we predict $v_{\text{hop,D}} = 4.66 \times 10^{-9} \text{ s}^{-1}$ (corresponding to $D_{\text{D}} = 7.62 \times 10^{-25} \text{ cm}^2 \text{ s}^{-1}$) and a transition temperature of 42.0 K. This suggests that the average hopping rate observed by experiment will be one hop every 83 months!

There have been many theoretical investigations of the diffusion of hydrogen on Cu(001) using flux-flux correlation functions,¹³ path integral quantum transition state theory (QTST)¹⁴ and other TST methods,^{15,16} transition wave packet approaches,¹⁷ and quantum kinetic approaches.¹⁸ Most of these studies investigated hydrogen diffusion in the 100–600 K range of temperatures where the transition to quantum tunneling would not have been observed. The barriers obtained were $\sim 0.5 \text{ eV}$, significantly higher than $\sim 0.2 \text{ eV}$ measured by Lauhon and Ho. The calculated diffusion rates for H at 120 K were of the order of 10^{-21} to $10^{-24} \text{ cm}^2 \text{ s}^{-1}$, orders of magnitude lower than measured. Some of these studies also report transition temperatures in the 100–125 K range.^{15,18}

Our present study examines hydrogen and deuterium diffusion at lower temperatures, 9 to 80 K, the same temperature range investigated by Lauhon and Ho. We use first principles nonlocal density functional theory to calculate the one-dimensional potential energy surface for H hopping from the four-fold cap site across a bridge site to an adjacent cap site. Section II describes the computational methods. The results are presented in Sec. III followed by some discussion in Sec. IV and concluding remarks in Sec. V.

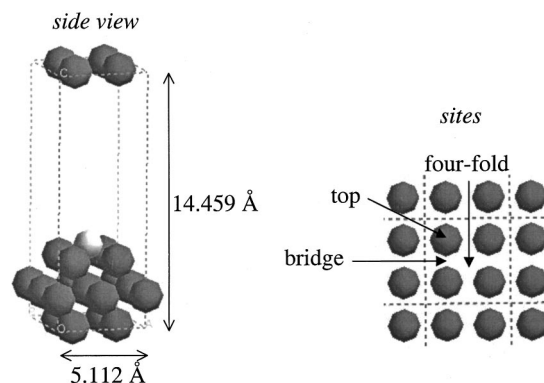


FIG. 1. Unit cell of Cu(001) used in slab calculations. The H is shown here in the four-fold cap site.

II. COMPUTATIONAL METHODS

All calculations used nonlocal density functional theory (DFT) with the generalized gradient approximation (GGA-II)¹⁹ and periodic boundary conditions. We used the norm-conserving plane wave pseudopotentials generated with the optimization scheme of Lin *et al.*²⁰ We found significant changes in relative energetics for cutoffs up to 600 eV, requiring a cutoff of 800 eV to obtain convergence. We found that a k -point sampling²¹ of $4 \times 4 \times 1$ was sufficient for convergence. A Fermi smearing range of 4.0 to 0.2 eV was applied with the broadening width halved every six steps. All energies were extrapolated to 0 K using the correction technique of Gillan and De Vita.²² All calculations were performed with the CASTEP code²³ in the CERIUS² software package.²⁴

We modeled the Cu(001) surface using a rigid three-layer slab with Cu–Cu distances frozen at the bulk distance of 2.556 Å. To model low surface coverage conditions we used a (2×2) unit cell size, leading to 12 Cu atoms per unit cell. Hydrogen was bound to one side of the slab. Slabs were separated by five layers of vacuum (see Fig. 1). Since we found that the calculated relative energy of H at the cap and bridge site on a four-layer slab was similar to the three-layer slab, we used the three-layer slab to calculate the energies of points along the reaction profile.

The one-dimensional reaction energy profile at several points along the x -coordinate connecting the cap and bridge sites was calculated by fixing the x and y coordinates of H and optimizing the height of H above the surface (the z -coordinate) as shown in Fig. 2. The points were fitted to a cosine curve [$y = a \cos(x/c) + b$, where $c = 0.406636$] to ensure that the derivative is zero at the minima and maxima. A least squares fit yielded $a = 0.212408$ and $b = 0.986203$ with an rms error of 0.025 Å. To calculate the zero point energy (ZPE), single point calculations were performed for each point perturbed in three directions: along the tangent of the fitted curve, and in the two perpendicular directions (see Fig. 3). Approximately four additional points at spacings of $\sim 0.02 \text{ \AA}$ were calculated in each of these three directions. These additional points, including the original point on the potential energy surface, were fit to a harmonic potential. All curves had the form $U = kQ^2$ where k is the force constant

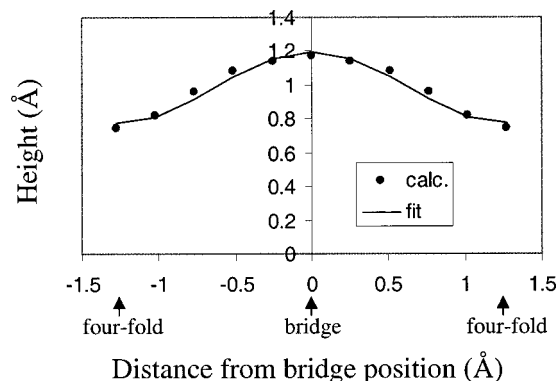


FIG. 2. Height of H above Cu(001) surface. The fitted curve is $y = 0.212\,408 \cos(x/0.406\,636) + 0.986\,203$.

corresponding to a three-dimensional harmonic potential. The frequency, ν , was then computed using

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (2)$$

The ZPE was calculated as the sum of $0.5 h\nu$ over these three modes except that the mode along the reaction path was ignored when its frequency was imaginary or below 10 cm^{-1} .²⁵ The calculated frequencies for H (D) are $740 (523) \text{ cm}^{-1}$ (\perp) and $539 (381) \text{ cm}^{-1}$ (two \parallel modes) for the four-fold cap site; $1142 (808) \text{ cm}^{-1}$ (\perp), $987 (698) \text{ cm}^{-1}$ (\parallel) and $i210 (i148) \text{ cm}^{-1}$ (\parallel) for the two-fold bridge saddle point. Excitation of the perpendicular vibrational mode for H in the four-fold cap site using the STM exhibits a peak at $565 (411) \text{ cm}^{-1}$.

III. RESULTS

The optimized heights of H/Cu(001) at the four-fold cap and two-fold bridge sites are 0.743 and 1.171 Å , respectively (see Fig. 2). There are no experimental measurements on the height of H above the surface. The relative electronic (non-ZPE corrected) energies along the reaction profile are shown in Fig. 4. The barrier height is 3.59 kcal/mol (0.156 eV). Including ZPE corrections (as described in the previous section), the barrier height is 4.04 kcal/mol (0.175 eV) at 0 K . There is one imaginary frequency for this transition state at $i210 \text{ cm}^{-1}$ corresponding to the direction along the reaction coordinate. The corresponding ZPE-corrected barrier height for D/Cu(001) at 0 K is 3.91 kcal/mol (0.170 eV). The ZPE-

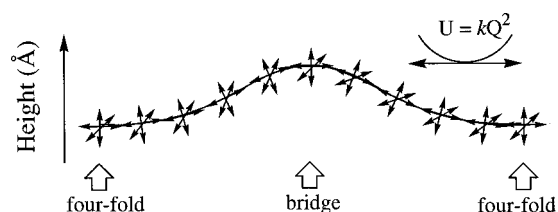


FIG. 3. Schematic showing calculation of zero point energy (ZPE). The calculated frequencies for H (D) are $740 (523) \text{ cm}^{-1}$ (\perp) and $539 (381) \text{ cm}^{-1}$ (two degenerate \parallel modes) for the four-fold cap site; $1142 (808) \text{ cm}^{-1}$ (\perp), $987 (698) \text{ cm}^{-1}$ (\parallel), $i210 (i148) \text{ cm}^{-1}$ (\parallel) for the two-fold bridge saddle point.

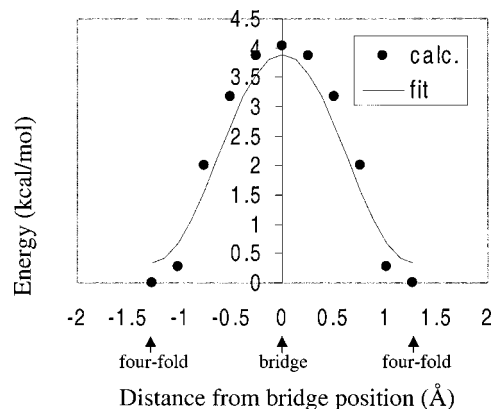


FIG. 4. Relative electronic (non-ZPE corrected) energies along reaction profile. The fitted curve is $y = 1.781\,070 \cos(x/0.406\,636) + 2.114\,365$.

corrected energies along the reaction profile are shown in Fig. 5. The fitted curve is $y = 2.135\,765 \cos(x/0.406\,636) + 2.251\,279$ with an rms error of 0.26 kcal/mol .

From STM measurements at low temperature, Lauhon and Ho¹ observed that hydrogen atoms diffuse across adjacent unit cells (across a bridge site) but never diagonally (across a top site). Our ZPE-corrected relative barrier for diffusing across the top site is 13.04 kcal/mol (0.57 eV) for hydrogen. Thus, the barrier to diffuse across the top site is more than three times higher than across the bridge site, explaining why this pathway is not observed at low temperature.

In the thermally activated regime, the hopping rate, v_{hop} , is characterized by the Arrhenius law, $v_{\text{hop}} = A \exp(-E/RT)$ where A is the pre-exponential factor and E is the activation energy. In simple transition state theory for a unimolecular process, this is rewritten as:

$$v_{\text{hop}} = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \quad (3)$$

Thus, the prefactor A and the activation energy E are given by

$$A = (ek_B T_m / h) \exp(\Delta S^\ddagger / R), \quad (4)$$

$$E = \Delta H^\ddagger + RT_m, \quad (5)$$

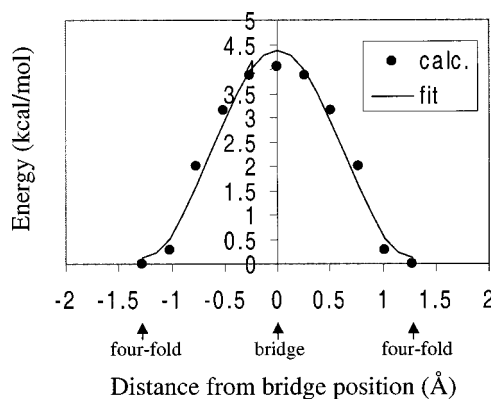


FIG. 5. ZPE-corrected relative energies along reaction profile for H. The fitted curve is $y = 2.135\,765 \cos(x/0.406\,636) + 2.251\,279$.

where T_m is the mean temperature at which the experiments have been carried out.

ΔH^\ddagger corresponds to our calculated ZPE-corrected relative barrier at 0 K. For a periodic one-dimensional system at low temperature, where no desorption of H takes place, there are only two contributions to ΔS^\ddagger :

- (i) $\Delta S_{\text{vib}}^\ddagger$ along the reaction coordinate
- (ii) A symmetry factor, $\sigma=2$, since hopping can take place either forward or backward along the reaction coordinate.

We calculated the vibrational entropy contribution from the difference in vibrational entropy between the transition state and the minima using

$$\Delta S_{\text{vib}}^\ddagger = R \ln q_{\text{vib}} - RT(d \ln q_{\text{vib}}/dT). \quad (6)$$

The vibrational partition function q_{vib} was calculated using

$$q_{\text{vib}} = \exp(-x/2)/(1 - \exp(-x)), \quad (7)$$

where $x = h\nu/k_B T_m$ and ν is the frequency at the minima along the reaction coordinate.

The contribution of the symmetry factor to ΔS^\ddagger is simply $R \ln 2$ for a periodic one-dimensional potential, since $\sigma=2$.

For hydrogen we chose $T_m = 70$ K since Lauhon and Ho measured the rate between 60 and 80 K in the thermally activated regime. From Eq. (6), we calculate $\Delta S^\ddagger = 1.29 \text{ cal mol}^{-1} \text{ K}^{-1}$, hence, from Eq. (4), $A_H = 10^{12.88} \text{ s}^{-1}$. Using Eq. (5) and $\Delta H^\ddagger = 4.04 \text{ kcal/mol}$, we calculate $E_H = 4.18 \text{ kcal/mol}$ (0.181 eV). These calculated values of A_H and E_H are in good agreement with the experimental values of $A_H = 10^{12.9}$ and $E_H = 0.197 \text{ eV}$ measured by Lauhon and Ho.

For deuterium we chose $T_m = 65$ K since Lauhon and Ho measured the rate between 50 and 80 K in the thermally activated regime. From Eq. (6), we calculate $\Delta S^\ddagger = 1.32 \text{ cal K}^{-1}$, hence, from Eq. (4), $A_D = 10^{12.70} \text{ s}^{-1}$. Using Eq. (5) and $\Delta H^\ddagger = 3.91 \text{ kcal/mol}$, we calculate $E_D = 4.04 \text{ kcal/mol}$ (0.175 eV). These calculated values of A_D and E_D are also in good agreement with the experimental values of $A_D = 10^{12.7} \text{ s}^{-1}$ and $E_D = 0.193 \text{ eV}$ measured by Lauhon and Ho.

To calculate the hopping rate in the quantum tunneling regime, we use the procedure of Mattsson *et al.*¹¹ A simple estimate for the hopping rate between two adjacent sites from perturbation theory is

$$v_{\text{hop}} = (4\pi^2/h)J^2\rho, \quad (8)$$

where ρ is the density of final states and J is the tunneling matrix element. In the Wentzel–Kramers–Brillouin (WKB) approximation, the tunneling matrix element can be written as

$$J = \left(\frac{h\nu}{4\pi^2} \right) \exp \left[-\frac{2\pi}{h} \int_{-x_0}^{+x_0} \sqrt{2m[V(x) - E]} dx \right], \quad (9)$$

where $V(x)$ is the potential along the minimum energy path, E is the ground-state energy, ν is the vibrational frequency at the potential minimum, and the turning points $\pm x_0$ are de-

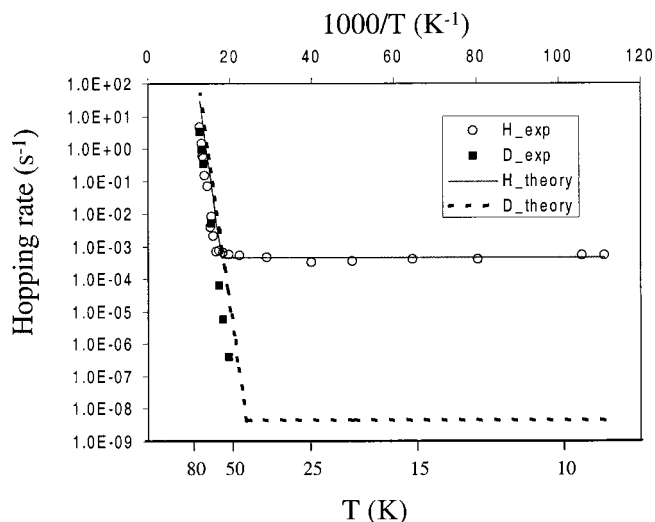


FIG. 6. Hopping rate vs temperature for H and D. The lines are from this work while the symbols are from experiment (Ref. 1).

termined by the condition that $V(x) = E$ at $x = \pm x_0$. Assuming that the motion is one-dimensional and using a single harmonic oscillator density of states $\rho = (2\pi/h\nu)$, the rate can be expressed as

$$v_{\text{hop}} = \left(\frac{\nu}{2\pi} \right) \exp \left[-\frac{4\pi^2}{h} \int_{-x_0}^{+x_0} \sqrt{2m[V(x) - E]} dx \right]. \quad (10)$$

Our ZPE calculations lead to, $\nu_H = 539 \text{ cm}^{-1} = 67 \text{ meV}$ and $\nu_D = 381 \text{ cm}^{-1} = 47 \text{ meV}$. To obtain the value of the integral in Eq. (10), we fitted the points from the calculated electronic energies without ZPE corrections (Fig. 4) to a cosine curve [$y = a \cos(x/c) + b$, where $c = 0.406636$] to ensure that the derivative is zero at the minima and maxima. A least squares fit yielded $a = 1.781070$ and $b = 2.114365$ with an rms error of 0.26 kcal/mol. The fitted curve was numerically integrated over 41 equally spaced points. This yields $v_{\text{hop}} = 4.74 \times 10^{-4} \text{ s}^{-1}$ (corresponding to $D = 7.74 \times 10^{-20} \text{ cm}^2 \text{ s}^{-1}$) for hydrogen,²⁶ and $v_{\text{hop}} = 4.66 \times 10^{-9} \text{ s}^{-1}$ (corresponding to $D = 7.62 \times 10^{-25} \text{ cm}^2 \text{ s}^{-1}$) for deuterium.

The transition temperature was calculated from the intersection of the extrapolated Arrhenius curve and the constant value of v_{hop} . This leads to quantum-classical transition temperatures of $T_{\text{qc}} = 56.3 \text{ K}$ for hydrogen and $T_{\text{qc}} = 42.0 \text{ K}$ for deuterium. The resulting calculated curves of hopping rate versus $1000/T$ for both isotopes are shown in Fig. 6 along with the experimental points measured by Lauhon and Ho. We find excellent agreement between both sets of results. In addition, our calculations predict the transition temperature and hopping rate for deuterium in the quantum-tunneling regime, not yet measured experimentally.

IV. DISCUSSION

Using a simple first principles approach, we calculated the hopping rate of hydrogen and deuterium on Cu(001) at low temperature, 9 to 80 K. We find a transition from the thermally activated regime to quantum tunneling at 56.3 K for H/Cu(001), in excellent agreement with the experimental value of $\sim 55 \text{ K}$. Our calculated hopping rates in both re-

gimes are in good agreement with the experimental measurements by Lauhon and Ho.¹ In addition, we predict the transition for D/Cu(001) to occur at 42.0 K with a temperature independent hopping rate of $4.66 \times 10^{-9} \text{ s}^{-1}$.

It is interesting that below 60 K, the experimentally observed hydrogen hopping rate is nearly temperature independent. The slight temperature dependence observed in the quantum-tunneling regime arises from lattice and electronic excitations that are not included in our calculations. These excitations induce rapid decoherence of the hydrogen atom wave function as was assumed in our expression for the hopping rate [Eq. (8)]. In addition, studies of quantum-tunneling in bulk have shown that the bare tunneling matrix element should be renormalized due to the static lattice distortion in the vicinity of the hydrogen and the nonadiabatic response of conduction electrons that screen the proton.²⁷ The weak temperature dependence observed in the surface diffusion data suggests a very small distortion, thus accounting for the excellent agreement with our static lattice calculations. This indicates that renormalization effects are relatively unimportant in this system.

Mattsson and co-workers^{11,12} carried out studies of diffusion for H/Ni(001) using a rigid lattice and the same level of DFT (GGA-II) as we use. Their calculations lead to a transition temperature of $T_{qc} \sim 63 \text{ K}$ and a diffusion constant of $6.6 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ for H/Ni(001). This is in good agreement with the experiments of Zhu and co-workers,¹⁰ who found activated diffusion for temperatures as low as 65 K. However, the experimental situation is controversial for H/Ni, with an earlier report⁷ of $T_{qc} = 120 \text{ K}$. The differences between our calculations and those of Mattsson are that they used:

- (1) a full monolayer (rather than 0.25 monolayers in our calculations),
- (2) the electronic energy from the DFT results at the cap and bridge sites were fitted to an embedded atom model (EAM), and
- (3) the energy curves and zero point energy were obtained from classical calculations using the EAM.

In contrast we used DFT to calculate a number of positions along the reaction coordinate from the cap to the bridge site. At each of these positions we optimized the axis perpendicular to the surface and calculated (also with DFT) a number of geometries perturbed from the equilibrium to obtain the local vibrational frequencies. It remains to be determined whether the large difference between the calculated H/Ni(001) diffusion constant and the H/Cu(001) diffusion constant calculated here is intrinsic to the metal surfaces or arises from differences in computational methods.

V. CONCLUSIONS

We find that first principles nonlocal density functional calculations on slabs of metal atoms leads to activated diffusion and tunneling rates in excellent agreement with experiment. These calculations use DFT for determining all parameters (the energy surface and the vibrational modes) but with a fixed subsurface. Such calculations are practical for H and other small organic and inorganic adsorbates on metals. Thus, we believe that it is practical to predict reliable values for these diffusional processes.

ACKNOWLEDGMENTS

This research was funded by the NSF [CHE 998557(wag), MRI 99-77872(wag), DMR-94-17866(wh)]. The facilities of the MSC are also supported by grants from DOE-ASCI, Chevron, 3M, ARO-MURI, Beckman Institute, Seiko-Epson, General Motors, Kellogg's, Dow Chemical, Avery Dennison, and Asahi Chemical.

- ¹L. J. Lauhon and W. Ho, Phys. Rev. Lett. **85**, 4566 (2000).
- ²K. Christmann, Surf. Sci. Rep. **9**, 1 (1988).
- ³*Hydrogen Effects in Catalysis*, edited by Z. Paal and P. G. Menon (Dekker, New York, 1988).
- ⁴Y. Fukai, *The Metal-Hydrogen System* (Springer, Berlin, 1993).
- ⁵R. Gomer, Rep. Prog. Phys. **53**, 971 (1990).
- ⁶R. DiFoggio and R. Gomer, Phys. Rev. B **25**, 3490 (1982).
- ⁷T.-S. Lin and R. Gomer, Surf. Sci. **336**, 245 (1991).
- ⁸A. P. Graham, A. Menzel, and J. P. Toennies, J. Chem. Phys. **111**, 1676 (1999).
- ⁹X. D. Zhu, A. Lee, A. Wong, and U. Linke, Phys. Rev. Lett. **68**, 1992 (1992).
- ¹⁰G. X. Cao, E. Nabighian, and X. D. Zhu, Phys. Rev. Lett. **79**, 3696 (1997).
- ¹¹T. R. Mattsson, G. Wahnström, L. Bengtsson, and B. Hammer, Phys. Rev. B **56**, 2258 (1997).
- ¹²T. R. Mattsson and G. Wahnström, Phys. Rev. B **56**, 14944 (1997).
- ¹³K. Haug, G. Wahnström, and H. Metiu, J. Chem. Phys. **92**, 2083 (1990).
- ¹⁴Y.-C. Sun and G. Voth, J. Chem. Phys. **98**, 7451 (1993).
- ¹⁵S. E. Wonchoba and D. G. Truhlar, J. Chem. Phys. **99**, 9637 (1993).
- ¹⁶S. M. Valone, A. F. Voter, and J. D. Doll, J. Chem. Phys. **85**, 7480 (1986).
- ¹⁷D. Zhang, J. C. Light, and S.-Y. Lee, J. Chem. Phys. **111**, 5741 (1999).
- ¹⁸V. Pouthier and J. C. Light, J. Chem. Phys. **113**, 1204 (2000).
- ¹⁹J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhals, Phys. Rev. B **46**, 6671 (1992).
- ²⁰J. S. Lin, A. Qteish, M. C. Payne, and V. Heine, Phys. Rev. B **47**, 4174 (1993).
- ²¹H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
- ²²A. De Vita and M. J. Gillan, J. Phys.: Condens. Matter **3**, 6225 (1991).
- ²³L. J. Clarke, I. Stich, and M. C. Payne, Comput. Phys. Commun. **72**, 14 (1992).
- ²⁴CERIUS² version 4.0, Molecular Simulations Inc., San Diego, 1999.
- ²⁵Except for the minimum, the ZPE is ill-defined along the reaction coordinate. Hence, the ZPE-corrected potential includes three modes at the minimum but two modes everywhere else along the reaction coordinate.
- ²⁶If instead the three-dimensional ZPE-corrected potential (Fig. 5) was used, the calculated tunneling rate is $4.54 \times 10^{-4} \text{ s}^{-1}$, slightly closer to the experimental measured value of $4.4 \times 10^{-4} \text{ s}^{-1}$.
- ²⁷E. B. Karlsson, *Solid State Phenomena as Seen by Muons, Protons and Excited Nuclei* (Oxford University Press, New York, 1995).