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Isotope effect in hydrogen surface diffusion

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The isotope effect in quantum diffusion of H on Ni(001) is thoroughly treated using the path-centroid method for the transition rate combined with a potential fitted to first-principles calculations. Around room temperature, our results are in quantitative agreement with experimental results. At low temperatures, we find a transition to temperature-independent diffusion, but no signs of an anomalous isotope dependence. [S0163-1829(97)05247-8]

I. INTRODUCTION

Hydrogen interacting with metals has attracted a great deal of experimental and theoretical interest, in basic as well as in applied research areas. One challenging issue is the possibility of quantum tunneling as a migration mechanism, and its consequences. It is well established that tunneling influences the diffusion of hydrogen in metals.[1] For hydrogen adsorbed on metal surfaces, the experimental information is more scarce. At low temperatures only two techniques have been used: field-emission-fluctuation microscopy (FEM),[2] and a method based on laser optical diffraction (LOD).[3] Theoretical treatments have been advanced in great detail,[4,5] but despite these conceptual developments the applicability of the different theoretical methods for analysis of experimental data has been limited by the lack of accurate descriptions of the hydrogen-metal interaction.

Measurements by Gomer and co-workers using FEM have been in focus for many years. For H adsorbed on both W (Ref. 6) and Ni (Ref. 7) surfaces, they found a transition from activated diffusion to an almost temperature-independent behavior when lowering the temperature. The diffusion rate at low temperatures was found to be of the same order of magnitude for both hydrogen and deuterium, which cannot be understood in terms of a simple one-dimensional model of tunneling. The progress achieved with the FEM technique was slow for diffusion measurements at low temperatures, and the recent utilization of an experimental method in this field, LOD,[3] is therefore very promising. The first studies using LOD appeared to support the FEM data,[3] but later refinement of the measurements produced data that strongly contradict the FEM results. For H on Ni (111), Zhu and co-workers found activated diffusion for temperatures as low as 65 K (Ref. 8) for both hydrogen and deuterium. They did not observe any signs of a leveling off around 100 K.

In view of the uncertain experimental situation, it has become important to perform quantitative calculations in the quantum tunneling regime. The development of electron-structure calculations using density-functional theory has been rapid during the last few years,[9] and it has now become feasible to determine the interatomic interaction energies for various configurations of the nuclei. In a previous paper,[10] we have presented results for H on Ni(001) which show that the potential-energy surface for that system can now be determined with quite a high accuracy.

In this paper we present extensive quantitative path-centroid rate calculations using a potential based on first-principles calculations. We will discuss hydrogen quantum diffusion in general, and the isotope effect in the low-temperature region in particular. In a previous study Auerbach, Freed, and Gomer[11] concluded that the low-temperature diffusion data by Gomer and co-workers for H on W(110) (Ref. 6) can only be understood if the hydrogen-lattice force constants have a sizable isotope dependence, while Muttalib and Sethna[12] in an earlier study used the so-called slow-flip approximation for the path integrals to explain the unusual isotope effect. Here we find no support for either of these two mechanisms. The hydrogen-lattice force constants are found to be weak, and show essentially no isotope dependence. By including the lattice motion quantum mechanically, we show that by incorporating the proper time scale for the lattice motion no significant change is obtained for the magnitude of the diffusion constant, either for H or D, and the conjecture by Muttalib and Sethna cannot explain the unusual isotope effect seen by Gomer and co-workers.

II. METHOD

We treat the diffusion process as uncorrelated jumps between nearest-neighboring sites. At high temperatures the motion is more classical in character, while at lower temperatures it becomes dominated by tunneling transition between vibrational ground states for the hydrogen atom. Due to the extremely small bandwidth for hydrogen on a rigid Ni (001) surface ($\sim 10^{-7}$ eV (Ref. 10)), we disregarded any coherent band motion. Coupling to medium excitations, electron-hole pairs, and phonons will destroy the phase coherence at finite temperatures, and the appropriate description becomes incoherent tunneling.[4] The measurements are also always performed at finite coverages, in the range 0.1–0.6 of a monolayer, and hydrogen-hydrogen interaction is always present.

A particularly powerful method for determining the thermally averaged transition rate between two localized states is the path-centroid formulation, introduced by Gillan.[13,14] The main computational advantage is that the method only requires evaluation of quantum-mechanical partition functions, which can be carried out for general many-atom potentials

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using the Monte Carlo technique. The rate coefficient is written in the form

$$k=\tfrac{1}{2}\overline{v}\,P(x^{*}), \qquad (1)$$

where $P(x^{*})$ is an equilibrium factor, the probability of finding the centroid for the hydrogen quantum path at the dividing surface (the transition state) between two stable minima, and the prefactor $\overline{v}$ is dynamic in origin and has to be approximated. At high temperatures it is given by the thermal velocity $\sqrt{2/(\pi\beta m)}$, and in that limit the path-centroid formulation reproduces the well-known classical transition state theory. At low temperatures the dominant contributions to the transition rate come from paths which are located at two stable minima at the same time, the so-called instantons,[15,16] and in that limit Eq. (1) correctly reproduces the Flynn-Stoneham formula for the transition rate.[17] The prefactor $\overline{v}$ is then equal to $2\sqrt{\pi}\Delta x/(\beta\hbar)$, where Δx is the width of the centroid density at the transition state[14] and is determined by the curvature of the potential barrier. The probability $P(x)$ is given by

$$P(x)\equiv Q^{-1}\int \mathcal{D}[x(\tau)]\,\delta(x-\overline{x})\exp\left\{-\frac{1}{\hbar}S[x(\tau)]\right\}, \qquad (2)$$

where Q is the partition function, and $S[x(\tau)]$ is the action.

Voth, Chandler, and Miller made a more rigorous derivation of Eq. (1), using time-correlation functions, including the behavior of the prefactor.[18] The path-centroid formula was also derived recently from the imaginary-free-energy method.[5] Its validity at very low temperatures and for asymmetric barrier problems has been questioned.[19] However, the path-centroid formula gives accurate results for symmetric barrier problems and for $T>\frac{1}{2}T_c$, where T_c denotes the crossover temperature where tunneling transitions between vibrational ground states for hydrogen start to dominate the overall diffusion process. Here we consider here a symmetric barrier problem and restrict ourselves to $T>\frac{1}{2}T_c$. The method was applied by several groups of researchers to various activated rate processes, for example, hydrogen diffusion in and on metals,[13,20,21] hydrogen dissociation,[22] electron-transfer reactions,[18,23,24] and proton-transfer reactions.[25] Reviews of the method and its applications were given by Voth.[26]

We used a potential-energy surface described recently.[10] It makes use of first principles calculations for the H-Ni interaction, together with the embedded-atom-method (EAM) description for the Ni-Ni interaction.[27] In the region of interest, between the hollow and bridge sites, the model potential accurately interpolates between the first-principles data. The potential is very different from the original EAM potential[28] which we used in our earlier work,[21] but rather similar to the potentials by Rice *et al.*[29] and Wonchoba, Hu, and Truhler.[30]

III. RESULTS

First we discuss the result for a rigid lattice, and then present data for the diffusion constant both when the metal atoms are treated as a classical bath and when they are treated fully quantum mechanically. All calculations are performed with a single hydrogen atom adsorbed on a six-layered slab with 108 Ni atoms, 18 in each layer. For the slab we use periodic boundary conditions in the lateral direction, and a fixed bottom layer in the normal direction. This corresponds to a hydrogen coverage of 0.056, compared with a full monolayer. The experimental measurements by Lin and Gomer[7] are performed at several different coverages, ranging from 0.15 to 0.63, but no strong or systematic coverage dependence is observed for the isotope effect at low temperatures. Our present calculations at low coverages should therefore be sufficient for elucidating the unusual isotope dependence.

Our previous first-principles calculations for the potential-energy surface[10] are performed for a monolayer of hydrogen, and the potential parameters for the H-Ni interaction, derived from those calculations, would therefore change slightly at lower coverages due to the reduced H-H interaction. This would lead to some small qualitative changes of the potential-energy surface, but no major effect for the overall temperature dependence of the diffusion constant.

A. Rigid lattice

Even in the absence of lattice motion, unconventional isotope effects can be obtained due to the three-dimensional character of the potential-energy surface. If the curvature of the potential perpendicular to the tunneling path increases when moving from the center to the bridge position, the isotope effect will be less pronounced compared with the usual square-root dependence in the WKB exponent. A large effect of this kind could explain the absence of a pronounced isotope effect at low temperatures. However, if that was the case, one would expect to find a clear difference in the activation energy for diffusion at room temperature for the two isotopes, but this has not been experimentally observed.[31]

Our previous first-principles calculations of the potential-energy surface do not support this explanation either.[10] We find that our calculated numbers for the bandwidths, which are directly related to the tunneling matrix elements, differ substantially for hydrogen and deuterium, and that this difference can be rationalized using an effective one-dimensional potential. The curvature of the potential around the barrier top is found to be somewhat larger compared with the stable site, but this effect is far too small to explain the unusual isotope effect. *We therefore conclude that diffusion on the rigid lattice can not explain the unusual isotope effect found by Lin and Gomer.*[7]

B. Dynamic but classical lattice

We first consider a classical bath. All Ni atoms are treated as point particles while for hydrogen a quantum path is used. The latter is discretized into P parts, with P in the range 24–48 depending on the temperature. The convergence has been tested with up to $P=96$. For the metal we use 108 Ni atoms in a six-layered slab with periodic boundary conditions in the lateral directions, and a fixed bottom layer in the normal direction.

We solve the integrals entering Eq. (2) using the Monte Carlo (MC) technique. All MC moves for the hydrogen path are made in pairs to preserve the position of the centroid along the tunneling direction. The centroid is allowed to move in a plane orthogonal to the transition direction, and

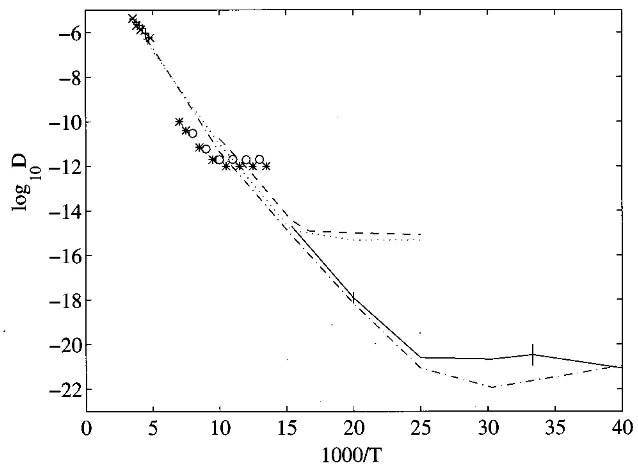

FIG. 1. The diffusion coefficient D (cm^2/s), one logarithmic scale, as a function of the inverse temperature (1000/K). Present work: hydrogen, classical lattice (dotted line); hydrogen, quantum-mechanical lattice (dashed line); deuterium, classical lattice (dot-dashed line); and deuterium, quantum-mechanical lattice (full line with error marks corresponding to two standard deviations). Experimental results: hydrogen: Mullins *et al.* (Ref. 31) (+), George, De Santolo, and Hall (Ref. 37) (×), and Lin and Gomer (Ref. 7) (○); deuterium: Lin and Gomer (Ref. 7) (*).

the mean force acting on the centroid is evaluated. The centroid probability is found by integrating along the transition direction, and for this integration we evaluate the force at a sufficient number of points to enable integration over a smooth function. The prefactor is determined by measuring the width of the centroid probability at the bridge position, following the discussion by Gillan.[14] At the lowest temperature (around 30 K), the probability distribution for hydrogen starts to deviate from a Gaussian distribution, and the determination of the transition rate becomes somewhat uncertain. This and other deficiencies of the path-centroid formulation have been discussed by Stuchebrukov[32] and Makarov and Topaler.[19]

In Fig. 1 we show our results. The result for the diffusion constant at low temperatures is surprisingly close to the result obtained from the calculated numbers of the bandwidth for a rigid lattice:[10] $D^H = 6.6\times 10^{-16}$ cm^2/s and $D^D = 1.4\times 10^{-21}$ cm^2/s, for hydrogen and deuterium, respectively. The effect of the coupling to the lattice motion is hence small.

To clarify this, we determined the distortion of the lattice when hydrogen is adsorbed. We first allowed the surface to relax in the absence of hydrogen. We then solved the Schrödinger equation for a single hydrogen or deuterium adsorbed on the frozen lattice. The energy eigenvalues for these configurations are denoted E_{fix}. The corresponding wave functions were used to calculate the forces on the metal atoms, which are given in Table I. We then iteratively calculated the relaxation energies: we allowed the lattice to relax, and solved the Schrödinger equation again, using the potential from the relaxed configuration, and repeated the procedure until the energy was converged. It usually took 5–6 iterations. The corresponding energy eigenvalues are denoted E_{rel}, which includes the energy stored in the distorted lattice. The magnitudes of the displacements of the nearest metal atoms as well as the ''localization energies'' $E_{\text{loc}} = E_{\text{fix}} - E_{\text{rel}}$ are also given in Table I.

We find that the forces and the subsequent displacement of the lattice atoms are all small. This explains the very similar results for the diffusion constant on the rigid and dynamic lattices, respectively. *We find no large isotope dependent hydrogen-lattice force constants.*

In our previous study,[21] we found a larger distortion of the metal atoms for the same system. The localization energy was then $E_{loc} = 48$ meV. In that case the hydrogen was located in the surface plane, and the distortion was larger. First-principles calculations[10] and experiments by Stensgaard and Jakobsen[33] show, however, that the hydrogen atom is located about 0.5 Å away from the surface, and that the model potential used in our previous study is too crude. Our findings confirm the statement by Puska *et al.*[34] that the lattice distortions are very weak for hydrogen chemisorbed on Ni surfaces.

C. Dynamic lattice

We now turn to a more correct description where the metal atoms are also treated quantum mechanically. For quantum paths for Ni atoms we use 4–16 discrete points, with the largest value for the Ni atoms closest to the hydrogen atom. We show our results in Fig. 1.

The diffusion constant becomes somewhat larger compared with the classical lattice. The increase is larger for deuterium compared with hydrogen, *but the change cannot account for the anomalous isotope effect*. In view of the

TABLE I. Localization energy, vibrational excitation energies perpendicular to the surface, and displacements of and forces on neighboring metal atoms, for hydrogen and deuterium on frozen (frozen) and fully relaxed surfaces (relaxed). The difference in localization energy is very small between hydrogen and deuterium, and the shift in excitation energy after relaxation is negligible. The closest neighboring nickel atoms are the four atoms in the surface plane surrounding the hollow site, denoted A, and the atom immediately below the hollow site, denoted B. The magnitudes of the displacements and forces are denoted $|\Delta r|_A$, $|F|_A$, and $|\Delta r|_B$, $|F|_B$ for A and B atoms, respectively.

	E_{loc}, meV	$\hbar\omega_\perp$, meV	$\|\Delta r\|_A$, Å	$\|\Delta r\|_B$, Å	$\|F\|_A$, eV/Å	$\|F\|_B$, eV/Å
Hydrogen, frozen		87			0.091	0.064
Hydrogen, relaxed	2.72	86	0.014	0.008		
Deuterium, frozen		63			0.086	0.063
Deuterium, relaxed	2.47	62	0.013	0.007		

small hydrogen-lattice force constants, there is no reason to expect a large change compared with the classical lattice.

IV. CONCLUSIONS

We find good agreement with diffusion measurements around room temperature for H/Ni(001) using first-principles data for the interaction potential, but our findings for the isotope effect at low-temperatures do not support the FEM data.[7] The experimental situation is, however, unclear. The very recent low-temperature diffusion data for H/Ni(111) by Zhu and co-workers,[8] based on LOD, show activated diffusion for temperatures as low as 65 K, whereas the FEM data show an abrupt change of the temperature dependence at $T = 120$ K.[7] The two different experimental techniques give diffusion constants which differ by up to five orders of magnitude at low temperatures.

We use the path-centroid formulation for the transition rate, and include the lattice degrees of freedom fully quantum mechanically. Coherent band motion is disregarded based on the very small bandwidth, $\sim 10^{-7}$ eV, determined on a rigid lattice.[10] We also neglected electronic excitations. This is not fully justified for diffusion on a metal surface.[35,36] However, we regard it unlikely that the adatom-electron coupling constant would be markedly different for hydrogen and deuterium, respectively, such that the magnitude for the diffusion constant would become similar for the two different isotopes.

In conclusion, we have shown that the diffusion rate at low temperatures for hydrogen adatoms on the Ni(001) is quite distinct from the rates for deuterium, the difference being about five orders of magnitude. We find no evidence of the anomalous isotope effect found at low temperatures in the FEM experiments.[7] LOD measurments on H/Ni(001) are highly desirable in order to resolve the question of a possible anomalous isotope dependence in hydrogen diffusion on metal surfaces at low temperatures.

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[1] Y. Fukai, *The Metal-Hydrogen System* (Springer-Verlag, Berlin, 1993).

[2] R. Gomer, Rep. Prog. Phys. **53**, 917 (1990).

[3] X. D. Zhu, A. Lee, A. Wong, and U. Linke, Phys. Rev. Lett. **68**, 1862 (1992).

[4] Y. Kagan and A. J. Legget, in *Quantum Tunneling in Condensed Media*, Modern Problems in Condensed Matter Science, Vol. 34 (North-Holland, Amsterdam, 1992).

[5] V. A. Benderskii, V. I. Goldanskii, and D. E. Makarov, Phys. Rep. **233**, 195 (1993).

[6] R. DiFoggio and R. Gomer, Phys. Rev. B **25**, 3490 (1982).

[7] T. S. Lin and R. Gomer, Surf. Sci. **255**, 41 (1991).

[8] G. X. Cao, A. Wong, and X. D. Zhu, *Bulletin of the American Physical Society* (American Physical Society, New York, 1996), Vol. 41, p. 421; G. X. Cao and X. D. Zhu, in *Surface Diffusion: Atomistic and Collective Processes*, Vol. 360 of *NATO Advanced Study Institute, Series B: Physics*, edited by M. Tringides (Plenum, New York, 1997).

[9] M. C. Payne *et al.*, Rev. Mod. Phys. **64**, 1045 (1992).

[10] T. R. Mattsson, G. Wahnström, L. Bengtsson, and B. Hammer, Phys. Rev. B **56**, 2258 (1997).

[11] A. Auerbach, K. F. Freed, and R. Gomer, J. Chem. Phys. **86**, 2356 (1987).

[12] K. A. Muttalib and J. Sethna, Phys. Rev. B **32**, 3462 (1985).

[13] M. J. Gillan, Phys. Rev. Lett. **58**, 563 (1987).

[14] M. J. Gillan, J. Phys. C **20**, 3621 (1987).

[15] W. Miller, J. Chem. Phys. **62**, 1899 (1975).

[16] S. Coleman, in *The Whys of Subnuclear Physics*, edited by A. Zichichi, The Subnuclear Series, Vol. 15, (Plenum, New York, 1979), p. 805.

[17] C. P. Flynn and A. M. Stoneham, Phys. Rev. B **1**, 3966 (1970).

[18] G. A. Voth, D. Chandler, and W. H. Miller, J. Chem. Phys. **91**, 7749 (1989); J. Phys. Chem. **93**, 7009 (1989).

[19] D. E. Makarov and M. Topaler, Phys. Rev. E **52**, 178 (1995).

[20] F. Christodoulos and M. J. Gillan, Philos. Mag. B **63**, 641 (1991); M. J. Gillan and F. Christodoulos, Int. J. Mod. Phys. C **4**, 287 (1993); Y. C. Sun and G. A. Voth, J. Chem. Phys. **83**, 7451 (1993); S. W. Rick, D. L. Lynch, and J. D. Doll, *ibid.* **99**, 8183 (1993).

[21] T. R. Mattsson, U. Engberg, and G. Wahnström, Phys. Rev. Lett. **71**, 2615 (1993); T. R. Mattsson and G. Wahnström, Phys. Rev. B **51**, 1885 (1995).

[22] G. Mills and H. Jónsson, Phys. Rev. Lett. **72**, 1124 (1994).

[23] R. Egger and C. H. Mak, J. Chem. Phys. **99**, 2541 (1993).

[24] C. H. Mak and J. N. Gehlen, Chem. Phys. Lett. **206**, 130 (1993).

[25] D. Li and G. A. Voth, J. Phys. Chem. **95**, 10 425 (1991).

[26] G. A. Voth, J. Phys. Chem. **97**, 8365 (1993); Adv. Chem. Phys. **93**, 135 (1996).

[27] S. M. Foiles, M. I. Baskes, and M. S. Daw, Phys. Rev. B **33**, 7983 (1986).

[28] M. S. Daw and M. I. Baskes, Phys. Rev. B **29**, 6443 (1984).

[29] B. M. Rice *et al.*, Chem. Phys. **92**, 775 (1990).

[30] S. E. Wonchoba, W.-P. Hu, and D. G. Truhlar, Phys. Rev. B **51**, 9985 (1995).

[31] D. R. Mullins *et al.*, Surf. Sci. **186**, 67 (1987).

[32] A. A. Stuchebrukhov, J. Chem. Phys. **95**, 4258 (1991).

[33] I. Stensgaard and F. Jakobsen, Phys. Rev. Lett. **54**, 711 (1985).

[34] M. J. Puska *et al.*, Phys. Rev. Lett. **51**, 1081 (1983).

[35] J. Kondo, Physica B **126**, 377 (1984).

[36] X. D. Zhu, Phys. Rev. B **50**, 11 279 (1994).

[37] S. M. George, A. M. DeSantolo, and R. B. Hall, Surf. Sci. **159**, L425 (1985).