Direct Observation of the Quantum Tunneling of Single Hydrogen Atoms with a Scanning Tunneling Microscope

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Single hydrogen atoms were imaged on the Cu(001) surface by scanning tunneling microscopy (STM). The vibrations of individual H and D atoms against the surface were excited and detected by inelastic electron tunneling spectroscopy (STM-IETS). Variable temperature measurements of H atom diffusion showed a transition from thermally activated diffusion to quantum tunneling at 60 K. Regimes of phonon-assisted and electron-limited quantum tunneling were observed. The thermal diffusion rate of D atoms varied over 7 orders of magnitude between 80 and 50 K with no transition to quantum tunneling down to a thermal hopping rate of 4×10^{-7} s^{-1}.

Pioneering measurements of the diffusion of hydrogen atoms on metal surfaces were made by field emission microscopy (FEM) [1–4]. Other methods were subsequently applied, including helium atom scattering (HAS) [5] and various optical techniques [6–8]. Clear transitions from activated diffusion to apparently temperature independent diffusion were deduced from FEM data on Ni and W surfaces and attributed to the onset of quantum tunneling. The tunneling, or quantum diffusion, of muons, protons, and deuterons in bulk metals, insulators, and superconductors is a well developed field [9–11], and tunneling on metal surfaces is to be expected given the relatively small potential barriers between adsorption sites. The nature of the low temperature diffusion observed on Ni and W surfaces, however, remains unclear due to difficulties arising from, among other things, the possible effects of steps, defects, and adsorbate-adsorbate interactions, as well as difficulties in establishing absolute values for the diffusion rate [4]. Substantial disagreements between experimental methods, including the actual existence of a temperature independent regime on Ni(111) [3,8], compound the difficulty of comparing experiments with theory. Theoretical work [12–18] has in general resulted in semiquantitative agreement for diffusion at high temperatures [13,14], and transitions to quantum diffusion have been found [13–16,18], but the agreement with low temperature diffusion data is qualitative at best. One outstanding puzzle is the unexpectedly small difference in H and D diffusion rates in the nonactivated regime measured by FEM [3,4].

Scanning tunneling microscopy (STM) is a logical tool to choose for surface diffusion studies. Significant advantages include the ability to work at very low coverages, thereby eliminating adsorbate-adsorbate interactions, and the ability to observe the local environment of each individual diffusing adsorbate. In addition, a large range of event rates can be measured with the implementation of atom-tracking [19] and direct imaging of a selected population of diffusing species. With judicious choices of imaging conditions and control experiments, the effects of the tip on adsorbate motion can be minimized and distinguished from the intrinsic properties of the adsorbate-surface system.

To achieve quantum tunneling rates that are observable with a STM, small mass adsorbates and a weakly corrugated potential are required. The obvious candidate for such studies is the hydrogen atom which has so far eluded observation on metal surfaces [20]. Hydrogen has been extensively studied on semiconductor surfaces, but the large potential corrugations present significant barriers to surface diffusion [21]. Here we report the first STM images of isolated hydrogen atoms on a metal surface. By varying the temperature of the Cu(001) surface and observing the motion of individual hydrogen atoms, regimes of classical thermally activated diffusion, phonon-assisted quantum tunneling, and electron-limited quantum tunneling were discovered.

Experiments were performed using a homemade variable temperature STM housed in an ultrahigh vacuum chamber with a base pressure of 2×10^{-11} Torr [22]. The preparation of the Cu(001) sample and tungsten tips has been described previously [19]. Acetylene molecules were dosed from gaseous sources to coverages of ~0.01 monolayer via a capillary array doser attached to a variable leak valve. Hydrogen and deuterium atoms were adsorbed on the surface of Cu(001) by breaking C—H and C—D bonds of adsorbed acetylene (HCCH) and its isotopes (HCCD, DCCD) [23]. Dissociation of HCCH resulted in isolated atomic hydrogen and molecular dicarbon (C_2).

Atomic hydrogen appeared as a small depression in STM constant current images at low bias [Fig. 1(a)]. The corrugation varied from 0.02–0.2 Å depending on the tip end shape, the tunneling current, and the sample bias. High resolution images of H on the Cu(001) lattice show that it occupies the fourfold hollow site in agreement with the site of minimum binding energy determined by density functional theory calculations [24]. The perpendicular vibrational mode of H against the surface was excited and
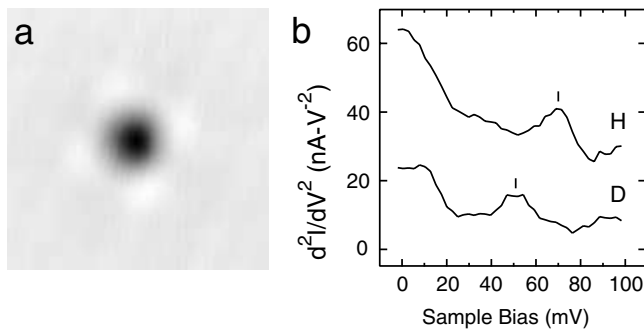
FIG. 1. STM image and vibrational spectra of H and D on Cu(001) at 9 K. (a) 15×15 Å^2 STM image of an isolated hydrogen atom taken at 0.1 nA tunneling current and 20 mV sample bias. (b) STM-IETS spectra of H and D. A background spectrum taken over the bare copper surface has been subtracted. The indicated peaks are due to the excitation of the H-Cu and D-Cu stretch modes. The rms bias modulation was 7 mV and the tunneling gap was set at 0.1 nA, 50 mV. Signal averaging times were 14 and 28 min for these H and D spectra, respectively. The image and spectra were acquired at 9 K.

detected by inelastic electron tunneling spectroscopy (STM-IETS) [25]. Vibrational spectra of H(D) atoms taken by STM-IETS exhibited a peak at 70(51) meV [Fig. 1(b)], in agreement with the location of the H—Cu(D—Cu) stretch determined by electron energy loss spectroscopy (EELS) [26]. This observation confirms the identity of the depression in Fig. 1(a) as a single H atom. A relative change in conductance as large as 1.1(0.7)% was measured upon excitation of the H—Cu(D—Cu) stretch mode. This quantity is directly proportional to the inelastic tunneling cross section [25]. The parallel vibrational mode was not observed.

For substrate temperatures of 65 to 80 K, the thermally diffusive motion of individual H and D atoms was followed using an atom-tracking method previously employed to measure the thermal diffusion of acetylene molecules [19]. Tracking was performed with a tunneling current of 0.1 nA and a sample bias of 40 mV. Single hop events corresponded to a change in tip position of one nearest neighbor distance (2.55 Å) as the tip followed the individual diffusing atoms. The hopping rate corresponds to the inverse of the average residence time. The minimum resolvable residence time was subtracted from the average to correct for undercounting at very short residence times. Multiple hops did not influence the event rate.

Below 65 K, the hopping rate was low enough to follow the diffusive motions of individual atoms by repeated imaging. Successive images of ~100 atoms were taken every ~15 min over the course of several hours and the distances they traveled were measured. Only atoms in impurity-free regions of the surface were monitored. Atoms which came within ~10 Å (4 lattice sites) of an impurity or C_2 molecule were no longer measured. For uncorrelated single hopping events on a two dimensional lattice, the mean-square value of the distance d traveled

in time t is related to the hopping rate ν by the expression $\langle d^2(t) \rangle = 2l^2 \nu t$, where $l = 2.55$ Å is the distance between adjacent lattice sites. d^2 for each particle was determined by adding the squares of the distances traveled in the x and y directions. The H and D hopping rates measured by atom tracking and repeated imaging from 9 to 80 K are shown in Fig. 2(a). Expanded views of the regions measured by single atom tracking and multiple imaging are shown in Figs. 2(b) and 2(c), respectively [27].

In the repeated imaging mode, the tip spent ~50 ms within 1 Å of any given H atom every 2500 s, which is the average residence time in the low temperature regime (<60 K). Under the imaging conditions of 0.1 nA and 40 mV at 9 K, the tip was held directly over a single H atom for 30 min. No hopping was observed. Histograms of the diffusion distances showed no systematic bias with respect to the direction of tip motion used to acquire the images. From this we conclude that the diffusion observed by multiple imaging was not induced by the presence of the tip.
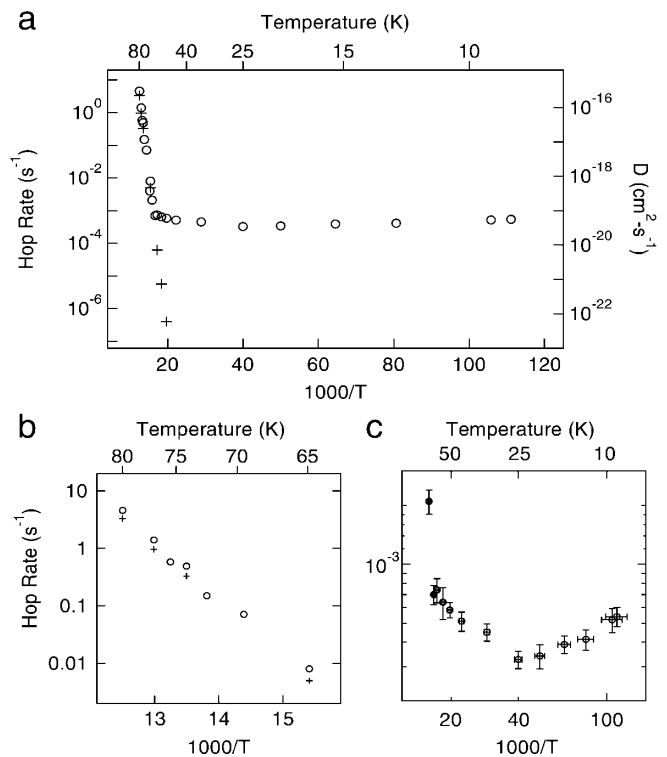

FIG. 2. Classical and quantum diffusion of H and D on Cu(001). (a) Arrhenius plot of the hopping rate of H(∘) and D(+) between 80 and 9 K measured by single-atom tracking (80–65 K) and repeated imaging (63–9 K). The right axis gives the equivalent single particle diffusion constant, D, which is related to the hop frequency ν by the expression $D = 1/4l^2\nu$, where the lattice constant $l = 2.55$ Å. (b) Arrhenius plot of the hopping rate of H(∘) and D(+) atoms determined by single-atom tracking between 65 and 80 K. (c) Log-log plot of the H hopping rate between 63 and 9 K determined by repeated imaging.

In the higher temperature region for which atom tracking was employed, the presence of the tip directly over an H atom increased the hopping rate. By measuring the hopping rate using different tips, tunneling currents, sample biases, and tracking parameters [28], we estimated that the hopping rate between 65 and 80 K was at most $1.5\times$ the hopping rate that would be measured without the tip influence under the standard measurement conditions of 0.1 nA and 40 meV. As an additional check, the H hopping rate at 63 K was measured by both methods and found to be $2\times$ higher for the atom-tracking method. Because the time spent over the H atom per hop is negatively correlated with the hopping rate, and thus temperature, this represents an upper bound on the tip-assisted diffusion that is consistent with our estimated error of 1.5 for higher temperatures.

The salient features of the data presented in Fig. 2 are the following. First, the D hop rate, R_D, follows an Arrhenius law over the entire range of measured rates. This is in contrast to the hopping rate of H which abruptly levels off at 60 K. The consistently Arrhenius-law behavior of D atoms, measured using the two different methods, suggests that the crossover to nearly temperature independent diffusion seen for H atoms does not originate with a change in measurement method. The ratio of H and D diffusion rates at 50 K is greater than 10^3. Measurements of H and D diffusion on Ni and W by FEM have not observed such a large difference in rates. Second, the quantum diffusion of H exhibits two distinct regimes. The H hop rate, R_H, decreases weakly with decreasing T from 60 to 25 K and increases with decreasing T from 25 to 9 K. We note that the striking discontinuity in the H diffusion rate at 25 K provides further evidence that the rate variations do not arise due to tip effects; H diffusion rates below 60 K were measured over several separate experimental runs with separate tip and sample preparations. Discussion of the physical mechanisms which produce these varied behaviors will begin with the quantum regime of coherent tunneling at zero temperature and proceed to the classical regime of thermally activated over-barrier hopping.

The overlap of H atom ground-state wave functions between neighboring potential minima can be significant due to the small mass of the proton [29]. If the potential corrugation is made sufficiently small, the H atom is essentially delocalized and is best described in terms of bandlike states, analogous to the Bloch states of electrons. At finite temperatures, electron and phonon scattering lead to decoherence of the H atom wave function and particle localization. Successive hops become uncorrelated when the phase-correlation damping rate becomes comparable to the tunneling rate between potential minima [11,30]. The H atom then hops between adjacent lattice sites at a reduced rate in a process known as incoherent tunneling. An additional reduction in the tunneling rate arises from the static distortion of the lattice in response to hydrogen adsorption; the distortion takes the ground states of neighboring potential minima out of resonance.

The diffusion of H on Cu(001) for $9 \leq T \leq 60$ K, shown in Fig. 2(c), is therefore described as incoherent tunneling in the presence of lattice and electronic excitations. Kondo calculated that the diffusion rate of a particle in the presence of electrons should scale as T^{2K-1}, where K is a dimensionless particle-electron coupling constant [30]. The temperature dependence arises from the non-adiabatic response of the thermally excited electron-hole pairs to the diffusing particle. Fitting our data below 25 K to this expression gives $K = 0.25 \pm 0.05$. For comparison, the value obtained from muon diffusion in bulk copper is 0.226 [31]. Zhu has discussed the change in K that might be expected for surface diffusion [32]; lower densities of conduction electrons in the vicinity of adsorbed H are expected to lead to $K_{surf} > K_{bulk}$. We note that the present report is the first definitive observation of electron-limited surface diffusion and clearly demonstrates the quantum nature of the process.

As the temperate increases, lattice vibrations assist the H in overcoming the barrier induced by the static lattice distortion (polaron). The hopping rate increases with temperature as the ground state levels of the occupied and nearest neighbor sites are brought into resonance by lattice fluctuations. The weak temperature dependence of the rate between 25 and 60 K [Fig. 2(c)] suggests a phonon-assisted tunneling process with relatively small activation energy. A fit to our data between 45 and 60 K using the high temperature expression for small polaron tunneling [9] yields an activation energy of ~ 3 meV [33]. This agrees with the calculated lattice distortion energy of H on Ni(001) [14]. A calculation including both electronic and lattice excitations is necessary to quantitatively determine the relative importance of electronic and phononic processes in the transition region of 25 to 60 K.

At sufficiently high temperatures, the H atom readily acquires enough energy to surmount the classical barrier to diffusion. In this regime, the rate is characterized by the well known Arrhenius law $R = \nu \exp(-E_a/kT)$, where the prefactor ν is a classical attempt frequency and E_a an activation energy [34]. R_H between 60 and 80 K and R_D between 50 and 80 K are well described by this relation [Fig. 2(a)], yielding: $\nu_H = 10^{12.9\pm0.3}$; $E_H = 197 \pm 4$ meV; $\nu_D = 10^{12.7\pm0.2}$; $E_D = 194 \pm 3$ meV. The H prefactor of $10^{12.9}$ s^{-1} is comparable to the vibrational frequency and the prefactor ratio, $\nu_H/\nu_D = 1.35 \approx \sqrt{2}$, is consistent with the expected value for a classical oscillator in a harmonic potential.

An abrupt transition for classical to quantum diffusion has also been obtained in calculations of H diffusion on Ni(001) [13–16]. These authors have pointed out that the width of the transition region is sensitive to the shape of the barrier potential. Given the density of data in the vicinity of the transition region, a proper theoretical treatment of the tunneling process should provide a good description of the potential seen by the tunneling proton. This potential will also affect the calculated ratio of H and D tunneling

rates; a value of $R_H/R_D \simeq 5 \times 10^5$ was obtained for H on Ni(001) [14]. For Cu(001), if we assume a square barrier of height E_H and width $l = 2.55$ Å in the WKB approximation, we obtain $R_H/R_D \simeq 10^3$. The apparently classical behavior of the D hop rate in the measured range is therefore not surprising.

Should H prove to be observable on other metal surfaces, the methods described here could be applied to systems where current experimental data are in conflict. In particular, the latest data for H diffusion on Ni(111) [8], unlike previous FEM data [3], do not show a crossover to a temperature independent regime and the diffusion rates are within the range of a variable temperature STM.

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[27] At 50.7 K, the D hopping rate was determined by observing individual hop events within the scan areas of higher resolution images. 145 D atoms were monitored by repeated imaging over 92 hours and 19 single hop events were observed, giving a rate of 4×10^{-7} s^{-1}. We know of no other method capable of measuring rates this low.

[28] The search algorithm, described in Ref. [19], involves circling around the location of the adsorbate. The time the tip spends directly over the H can be made arbitrarily small.

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[33] The high temperature form assumes that multiphonon processes are important. This is justified for temperatures near the onset of classical diffusion (60 K).

[34] The onset of apparently classical behavior corresponds to the dominance of transitions between vibrational excited states; the tunneling rate increases rapidly with the vibrational quantum number.