

Determination of the Quantum Contribution to the Activated Motion of Hydrogen on a Metal Surface: H/Pt(111)

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Measurements of the atomic-scale motion of H and D atoms on the Pt(111) surface, above the crossover temperature to deep tunneling, are presented. The results indicate that quantum effects are significant up to the highest temperature studied (250 K). The motion is shown to correspond to nearest neighbor hopping diffusion on a well defined fcc (111) lattice. The measurements provide information on the adiabatic potential of both the adsorption site and the transition state and give strong empirical support for a dissipative transition-state theory description of the quantum contribution to the motion.

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The physics of hydrogen dynamics on surfaces is both fundamentally and technologically important. Hydrogen processes are crucial to a wide range of chemical reactions, ranging from heterogeneous chemical synthesis to the modern challenges of batteries and hydrogen fuel cells. In each case, when rational design methods are applied, understanding the dynamics of adsorbed hydrogen will play a crucial role. More fundamentally, hydrogen is unique as the smallest possible atomic adsorbate. Its low mass means that even at moderate temperatures, classical mechanics can become insufficient to describe H dynamics and quantum processes dominate [1–3]. Hence, studying H motion provides an unusual opportunity to test quantum rate theories. There have been a number of experimental studies, which have stimulated a substantial body of theoretical work. However, light atoms provide an extreme challenge to experiment, partly due to the limited sensitivity that many techniques have to H atoms. Methods differ in the length scales they explore and in the coverage required to observe the motion so that there are contradictions in the evidence (e.g., [4,5]). The isotopic variation and temperature dependence in other experiments cannot be explained using existing theory (see, for example, [6]). In the present work we describe an extensive set of new measurements giving both the rate and the mechanism for activated motion of H (or D) on Pt(111). Our results agree with a simple quantum transition-state model, including isotopic scaling laws, and provide a consistent and quantitative picture for diffusion in this system. Motion is observed at low coverages and occurs on the extended atomic terraces of the surface, with observations that include the region of transition between classical diffusion and quantum tunneling.

We use helium spin-echo (HeSE), which is particularly sensitive to surface hydrogen and gives uniquely detailed dynamical information [7]. Adsorbed hydrogen atoms at a metal surface have a significant cross section for scattering helium atoms so that the diffraction pattern from a periodic

array of static adsorbates can be analyzed to provide detailed structural information [8]. The helium spin-echo technique exploits the same strong scattering in the context of dynamic structures. It is now a well established method [7,9,10] and provides a direct measure of dynamical correlations on an atomic scale in both position and time. An individual measurement gives the decay with time, t , of the correlation function, $I(\Delta\mathbf{K}, t)$, for different momentum transfers, $\Delta\mathbf{K}$, of the scattered particles. $I(\Delta\mathbf{K}, t)$ is the well known intermediate scattering function (ISF) [11,12] and represents the rate of correlation loss with time t (ps range) and with $\Delta\mathbf{K}$. The latter bears a reciprocal relationship ($2\pi/\Delta K$) with periods in real space (typically nm). In the present experiment $I(\Delta\mathbf{K}, t)$ decays exponentially in both high-symmetry directions. By examining the variation of the exponential decay or “dephasing” rate, α over a range of experimental conditions (temperature, $\Delta\mathbf{K}$, etc.), we can build up a detailed, microscopic picture of motion on the surface. In particular, jump diffusion gives a sinusoidal dependence of α on $\Delta\mathbf{K}$ at low to intermediate $\Delta\mathbf{K}$ [7].

A Pt(111) sample (Surface Prep. Lab., NL) was installed in the Cambridge HeSE spectrometer [13] (base pressure 3×10^{-11} mbar), prepared by repeated cycles of argon ion sputtering (800 eV, 450 K) and annealing (1100 K), and its quality checked by helium reflectivity. A high quality surface with low step density is confirmed by the exceptionally strong helium reflectivity we observe. Hydrogen was dosed onto the clean surface by backfilling the sample chamber with H_2 and monitoring the dissociative uptake using the helium beam. From the reflectivity changes, adsorbate coverages could be determined quantitatively using cross section information in [14]. HeSE measurements were carried out over a range of momentum transfers, corresponding to different periodic scales in real space, at temperatures between 80 and 220 K for H and D, in turn, at a coverage of 0.1 ML. Figure 1 shows typical measurements at $\Delta\mathbf{K} = 0.86 \text{ \AA}^{-1}$ along [11 $\bar{2}$]. In the ps range each measurement is dominated by a single

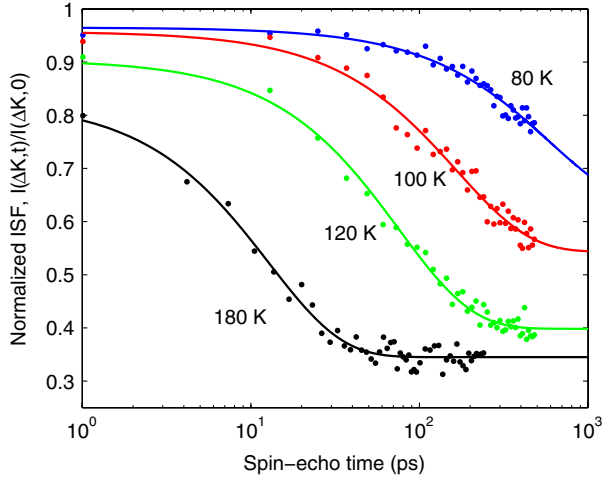


FIG. 1 (color online). Typical HeSE surface correlation measurements, for 0.1 ML atomic H on Pt(111) (points). The data were obtained at a momentum transfer of 0.86 \AA^{-1} along $[11\bar{2}]$ (a periodic scale of 7.3 \AA in real space). In each case the time variation is dominated by a single exponential decay (solid lines). The varying initial levels relate to differing phonon contributions to the ISF.

exponential decay. Since these decays are absent on the clean surface, we attribute them to diffusing H. The exponential form is consistent with hopping diffusion, while the decay rate indicates motion occurs freely over sub-ns time scales. The remaining portion of $I(\Delta\mathbf{K}, t)$ does not decay and is due to helium atoms scattered from static features on the substrate.

The dephasing rate, α , was extracted from each measurement using $I(\Delta\mathbf{K}, t) = A \exp(-\alpha t) + C$ as shown in Fig. 1. The magnitude of α scales with the hopping rate, while the form of $\alpha(\Delta\mathbf{K})$ enables the mechanism of motion to be determined. $\alpha(\Delta\mathbf{K})$ is shown in Fig. 2 for several different conditions (points), corresponding to as wide a measurement range as possible given our available experimental resolution and intensity. When motion occurs in idealized (instantaneous) jumps on a Bravais lattice, the expected form for the dephasing rate is given by the established Chudley & Elliott model [15], $\alpha(\Delta\mathbf{K}) = 2\sum_j \nu_j \sin^2(\Delta\mathbf{K} \cdot \mathbf{j}/2)$ where the sum is over the possible jump vectors, \mathbf{j} , and ν_j is the hopping rate associated with that jump. The solid lines in Fig. 2 show this model applied to nearest neighbor jumps between fcc hollow sites on the Pt(111) surface. Agreement with the model indicates that H (or D) atoms perform nearest neighbor random jumps and the motion is diffusive [7]. Deviations from nearest neighbor jumps would show up as additional Fourier components. Since these are minimal, we conclude that multiple jumps may be neglected and that H dynamics and D dynamics both take place in the “moderate to high” friction regime [16].

Having established that the motion is dominated by single hops, we can derive the microscopic tracer diffusion coefficients without assumptions. The relationship is well

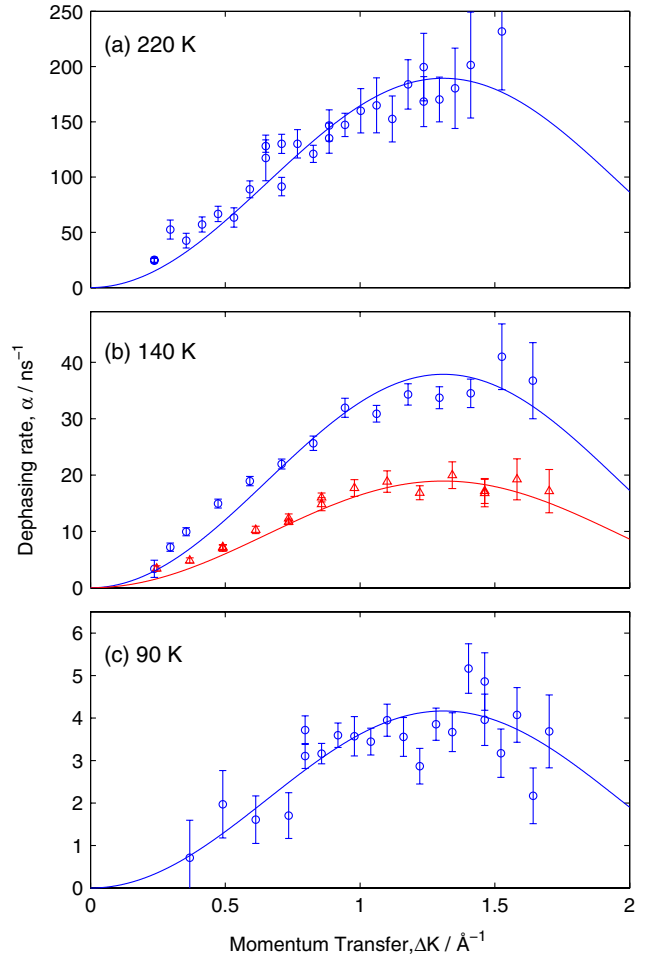


FIG. 2 (color online). Plots of the dephasing rate, α , obtained from HeSE measurements of H diffusion (blue circles) and D diffusion (red triangles) for temperatures of (a) 220, (b) 140, and (c) 90 K and momentum transfers along the $[11\bar{2}]$ direction. The results are in excellent agreement with the sinusoidal form expected for diffusive hopping between adjacent fcc hollow sites (solid line).

known [2,3], and for nearest neighbor hopping gives the diffusion constant, $D^* = a^2\Gamma/4$, where Γ is the total hopping rate ($\Gamma = \sum_j \nu_j$) and $a = 2.77 \text{ \AA}$ is the jump length. The temperature dependence of Γ and D^* are shown as an Arrhenius plot in Fig. 3 for both isotopes. Neither isotope shows the simple, straight-line behavior characteristic of classical Transition-State Theory (TST) as described by the usual expression for the rate, $\Gamma = \Gamma_0 \exp(-E_a/k_B T)$. The curvature of the Arrhenius plots indicates a quantum contribution to the overall rate.

Although the measurements reached as low as $T = 80 \text{ K}$, we do not observe the flattening out of the Arrhenius plot that is characteristic of deep tunneling [16,17]. It is therefore sufficient to apply the quantum theory of dissipative tunneling for temperatures above the crossover temperature between tunneling and thermal activation [16,18,19]. The expression for the rate we then use [16,20] is

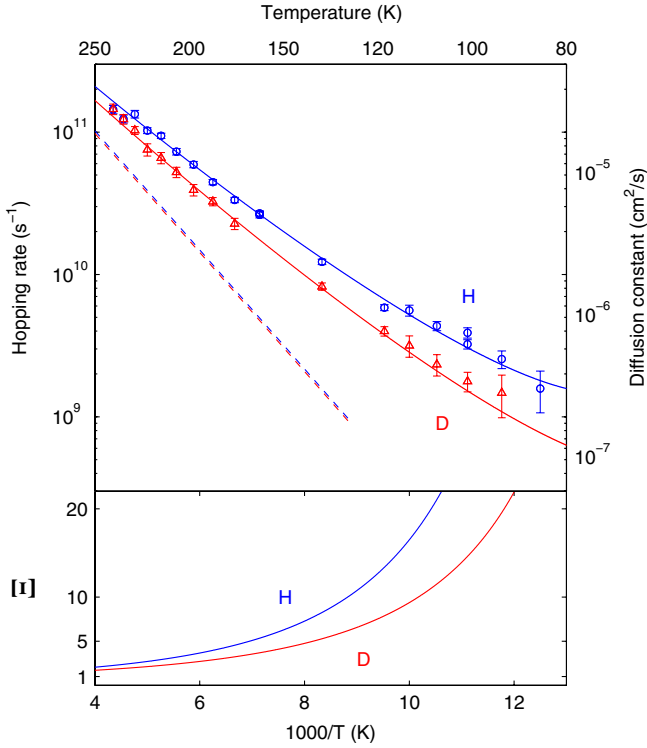


FIG. 3 (color online). Arrhenius plots of the temperature dependence of the hopping rate for H diffusion (blue circles) and D diffusion (red triangles) at a momentum transfer of 0.86 \AA^{-1} along the $[11\bar{2}]$ direction and a coverage of 0.1 ML. A change in gradient for both H and D is evident. The increased rate of diffusion for both isotopes at low temperatures corresponds to the rate contribution due to quantum tunneling. The solid lines show the quantum-TST model described in the text, while the dashed lines show the corresponding classical rates alone, i.e., $\Xi = 1$. The lower panel shows the quantum rate correction, Ξ , also described in the text. Quantum effects dominate when Ξ is much larger than 1, but are important over the entire temperature range.

$$\Gamma = \frac{3\omega_0}{2\pi} \Xi x_b \exp(-E_a/(k_B T)), \quad (1)$$

where ω_0 is the angular frequency of vibration at the adsorption site and the factor of 3 reflects the number of possible jump directions. For Ohmic damping with friction coefficient γ , the friction-dependent barrier frequency, $x_b \omega_b$, is given, in terms of the friction coefficient, as $2x_b \omega_b = -\gamma + \sqrt{4\omega_b^2 + \gamma^2}$, where x_b is the dimensionless Kramers factor and ω_b gives the curvature of the inverted potential at the transition state as an effective frequency. Finally, Ξ is the quantum correction, which includes tunneling through the parabolic barrier. Its frictional dependence has been derived by Wolynes [20],

$$\Xi = \prod_{n=1}^{\infty} \frac{\omega_0^2 + n^2 \nu^2 + n\nu\gamma}{-\omega_b^2 + n^2 \nu^2 + n\nu\gamma} \quad (2)$$

as given in Eq. 9.32 of Ref. [16], where $\nu = 2\pi k_B T/\hbar$ is the fundamental Matsubara frequency.

In this theory, there are four parameters that describe the motion of a given species: the well and barrier frequencies, the friction coefficient and the barrier height. However, apart from the activation energy, the scaling of these parameters with the mass, m , of the diffusing atom is known. The barrier and well frequencies scale as $m^{-1/2}$, while the friction coefficient scales as m^{-1} [16]. The well frequency for H, $\omega_0 = 31 \text{ meV}$, has been measured using HREELS [21], leaving us with a four parameter theory that should describe both the H and D diffusion data, requiring values of E_a for both H and D, plus x_b and ω_b for one isotope. The results of the analysis are presented in Fig. 3. The solid lines show the quantum result, while the dashed lines give the classical rates ($\Xi = 1$) for both isotopes. The parameters are $\omega_b/\omega_0 = 5.4 \pm 0.4$, $x_b = 0.21 \pm 0.02$ for H and $x_b = 0.29 \pm 0.03$ for D. The activation energy $E_a = 83 \pm 2 \text{ meV}$, was taken to be the same for both H and D diffusion (a difference of $\pm 2 \text{ meV}$ caused substantial degradation of the fit). The resulting estimate for the crossover temperature [16], $T_c = \hbar\omega_b x_b/(2\pi k_B) = 66 \text{ K}$ for H and $T_c = 63 \text{ K}$ for D, is consistent with our original assumption that all the data presented here are at temperatures which are above the crossover temperature. From the inset to Fig. 3, which gives the quantum correction, $\Xi(1/T)$, it is evident that the hopping of the H and D atoms is dominated by tunneling at low temperatures and that the quantum correction remains substantial as we approach room temperature.

The model and data are in extraordinarily good agreement indicating that a simple, 1D quantum tunneling picture captures the essence of the physics involved in this system. The correct isotopic scaling of the barrier, the quantum contribution and the friction are all reproduced accurately, which to our knowledge has not been achieved before. The factors E_a and x_b are constrained mainly by the data at high temperatures, while ω_b/ω_0 is sensitive to the tunneling rate. Hence, while the model does not provide, or require, a complete potential, it gives a unique parameterization of the key features of the system, such as the effective width of the tunneling barrier. The absolute values of the friction obtained from the analysis are much higher than those observed in systems involving heavier atoms or larger molecular species [7]. However, the inverse mass scaling of γ expected for any particles coupled to a heat bath [16], such as the substrate electrons, indicates that large values might be expected for light species. The gradual nature of the transition to the regime dominated by tunneling, which is evident from our data, is in sharp contrast with observations on Cu(001) [22] where the transition to deep tunneling appears to occur over a narrow temperature range near 65 K [17].

It is also possible to describe the data using an additive model [5,23], which combines the activated classical rate with an activated quantum rate, assuming one or more states in either the H or D vibrational band structure provides the dominant quantum contribution. Such an approach would require at least 8 independent parameters to model both the classical and quantum regimes for the

two adsorbates. The proton band-energies calculated by Ying and co-workers [21] offer plausible candidates for a dominant contribution ($n = 1 \rightarrow n = 3 \oplus 4$ or $n = 7 \oplus 8$, respectively, for low and high temperatures); however, there is no such simple choice in the case of D [24] and it is unclear why certain bands should be preferred. In fact, our data suggest that the behavior of H and D does not depend on the band structures in a detailed way. The theoretical curves presented in Fig. 3 give a natural description of the observations with a minimum of assumptions. Quantum-TST uses the key features of the potential to obtain the hopping rate directly, and implicitly includes a range of energy levels, all of which contribute to the tunneling. The resulting picture is rather appealing and allows the experimental data to be described within a simple activated tunneling model, which behaves correctly as the temperature is reduced. All states are important, but in terms of diffusion, the ensemble is most important, rather than the details of the potential and band structure.

At 140 K and above, our observed hopping rates are consistent with the earlier quasielastic helium scattering (QHAS) study by Graham *et al.* [4] but cannot be reconciled with the much slower diffusion processes observed by Zheng *et al.* [5]. The latter measurements rely on the linear optical diffraction technique and are made over a micron length scale so that rates are sensitive to surface preparation and the presence of surface steps [5] as well as to the effects of subsequent laser treatment [25]. In the present work, we have demonstrated (Fig. 2) that the measured rates correspond to single hops on an fcc (111) lattice and, therefore, correspond to motion on well defined atomic terraces. Deviations from Arrhenius form have also been noted in some studies of H in bulk materials [26,27]. Phonon frequencies are generally much higher in the bulk and lattice distortions play a greater role [27]. In addition bulk systems have multiple interstitial sites so the phenomenology, while apparently similar, is not directly comparable with the present work.

In summary, we have presented a comprehensive new set of data for H diffusion on Pt(111) and the first quasielastic helium scattering measurements of tunneling mediated diffusion. Our results are qualitatively different from optical studies of the same system; however, they represent a true measure of motion at an atomic scale on the terraces of an ideal surface. This point has particularly wide consequences, given the ongoing efforts to model these prototypical hydrogenic systems. Our data are consistent with a surface potential whose curvature at the inverted transition site is significantly greater than at the adsorption site, giving a narrow barrier and a large quantum contribution to the motion. We obtain remarkable agreement with the established picture of dissipative tunneling in the presence of Ohmic friction, demonstrating that quantum-TST models provide an appropriate approach to the dynamics of light atoms on surfaces. The detailed picture that we describe offers a quantitative and fully consistent description of the transition from classical behavior at high temperatures to a regime dominated by quantum tunneling.

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