

Anomalous isotope dependence of hydrogen diffusion rates on tungsten (110) surfaces: Implications for lattice–hydrogen interactions

Assa Auerbach, Karl F. Freed, and R. Gomer

The James Franck Institute, The University of Chicago, Chicago, Illinois 60637

(Received 8 September 1986; accepted 13 November 1986)

A theoretical analysis is provided of the anomalous isotope effects observed for the diffusion of hydrogen on the W(110) surface in the limit of zero coverage. Low temperature tunneling diffusion shows an isotope effect several orders of magnitude smaller than predicted by simple rigid lattice models, while the higher temperature activated diffusion displays an *inverse* isotope effect several orders of magnitude larger than the rigid lattice predictions. It is shown here that both effects can be explained consistently by a single model of hydrogen–tungsten interactions in which there is a large separation in time scales between the hydrogen and tungsten motions. Tunneling is described with a small polaron model. Large phonon overlap factors are found to diminish the role of the tunneling matrix element and thereby to decrease the isotope effect. Activated diffusion is described as a many-phonon process in which the vibron is thermally excited as a result of phonon–vibron coupling. The same coupling parameter explains both the tunneling and activated diffusion results. This coupling parameter is shown to be dependent on adsorbate mass.

I. INTRODUCTION

The dynamics of adsorbed atoms on metal surfaces is a subject of great theoretical interest to which relatively little experimental effort has been devoted. A very sensitive probe of the details of the adsorbate–substrate interactions is provided by the adsorbate diffusion coefficient $D(T)$. Recent measurements of $D(T)$ as a function of temperature have been made by the field-emission-fluctuation spectroscopy¹ technique. Here we examine the low coverage results for hydrogen diffusion on the tungsten (110) surface, summarized in Figs. 1 and 2, and show how it is possible to extract from the *unusual* isotope dependence of $D(T)$ several important features of the hydrogen–tungsten interactions which are involved in the diffusion process.

The unusual experimental findings involve the following observations:

(1) Classical theories of the high temperature D yield the Arrhenius form

$$D_{\text{high } T} \cong l^2 \omega_H m_H^{-1/2} \exp(-\bar{V}/k_B T), \quad (1.1)$$

where \bar{V} is the barrier height for diffusion, l the jump length (i.e., lattice spacing), and $\omega_H/2\pi$ the attempt frequency for ¹H. However, as seen in Fig. 1, the Arrhenius prefactor in the activated regime increases dramatically with increasing hydrogen mass m_H . Freed² has shown that the huge inverse isotope dependence can be explained as a purely quantum mechanical effect to be expected in this system as a consequence of strong coupling between a local low energy phonon and a much higher energy hydrogen vibron.

(2) At low temperatures, D becomes very weakly temperature dependent (see Fig. 2) and tunneling dominates. The frozen lattice approximation implies that the only mass scale in the problem is m_H and therefore that the diffusion coefficient should have the form

$$D_j = l^2 \omega_H \exp[-S_1(m_j/m_1)^{1/2}], \quad j = 1, 2, 3. \quad (1.2)$$

When the tunneling does not occur near the barrier maxi-

mum, it is permissible to use a WKB approximation, and S_1 is the WKB exponent for H₁ tunneling. Equation (1.2) is inconsistent with experiment, which shows a much weaker dependence of tunneling rate on hydrogen mass: If the value of S_1 is estimated from Eq. (1.2) and if the experimental values of D_1 , D_2 , and D_3 are inserted in Eq. (1.2), the resulting values of D are many orders of magnitude too large, unless the prefactor $l^2 \omega_H$ is considerably smaller than the expected value of $\sim 10^{-3} \text{ cm}^2 \text{ s}^{-1}$. Thus in order to reduce this prefactor, either there is strong “mass renormalization” as suggested by Muttalib and Sethna,³ or, as we prefer to

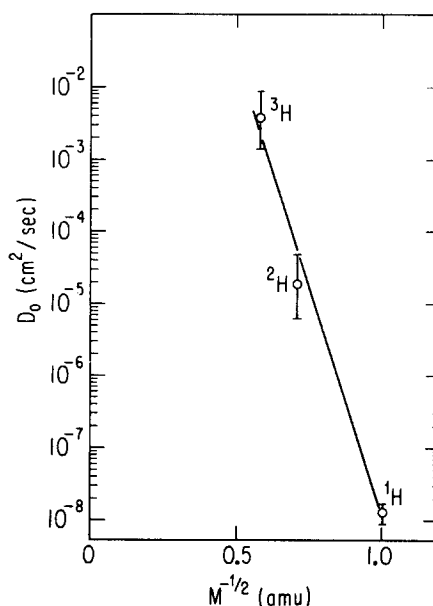


FIG. 1. Prefactors D_0 for hydrogen diffusion on W(110) in the thermally activated regime vs $M^{-1/2}$ extrapolated to zero coverage. D_0 is defined by $D = D_0 e^{-\bar{V}/k_B T}$ where \bar{V} is the activation energy. M is the isotope mass in amu. [From Ref. 1(b).]

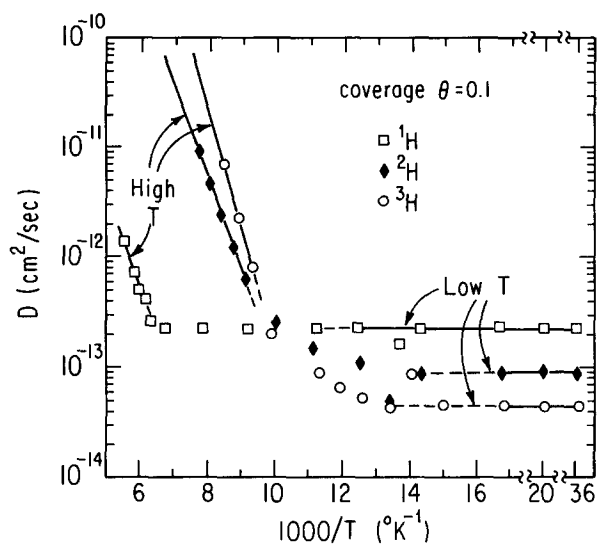


FIG. 2. Log D vs inverse temperature for the three isotopes at low coverage. Solid lines are fitted by Eqs. (3.9) and (4.2) for the low and high temperature regimes, respectively.

describe it, large lattice overlap factors must contribute to the tunneling matrix elements because the lattice must distort to accommodate the hydrogen tunneling.

Since phonon-hydrogen coupling appears to be important in determining the diffusion rates, it should be possible to explain diffusion in both the high and low temperature regimes by the same microscopic model of hydrogen-tungsten interactions. The purpose of this paper is to demonstrate that this can be done and to use the experimental data to deduce some general features of the potential which describes the phonon-hydrogen interactions. Section II discusses the single-well problem which governs the coupled dynamics of the hydrogen and the local lattice distortions within a single potential well for the hydrogen atom on W(110). Sections II and III briefly review the theories of small polaron hopping (SPH) and nonadiabatic activation (NAA), respectively, and show them to be applicable to this system in the tunneling and activated regions, respectively. The crucial parameter, which justifies both approaches, is the large ratio of the frequencies of the hydrogen vibration to that of the phonons. We analyze the data in terms of the SPH and NAA models and find that a novel feature of the interaction emerges, namely that the lattice distortion (polaron) appears to have a sizeable dependence on the hydrogen mass. This conclusion has also been reached independently by Emin who has proposed a simple explicit model potential exhibiting this behavior.⁴ This result has important implications for any *ab initio* or semiempirical calculations of the potential, i.e., it is necessary to calculate the hydrogen wave function self-consistently in order to determine the effective potential which it feels. We also deduce that relatively few localized phonons within a narrow spectral range are probably relevant in the coupling to the hydrogen motion.

II. THE SINGLE WELL PROBLEM

Since the sublimation energy of W is 9.3 eV and since the binding energy of H on W(110) is 2.8 eV, the energies

per W-W and per H-W bond are comparable. Thus, it seems reasonable to assume that the H-W and W-W force constants are of the same order of magnitude. The large ratio of tungsten to hydrogen masses $m_W/m_H \gg 1$ therefore implies a clear separation of time scales between the vibron and local phonon frequencies ω_H and ω_L , respectively, namely that $\omega_H \gg \omega_L$. This assumption is confirmed by the direct measurements of ω_H (96 and 160 meV) and by the surface Debye temperature [~ 27 meV for W(110)].⁵ We also assume that the interatomic forces are not of long range, and therefore the dynamics of an H atom at a given surface adsorption site α is most strongly coupled to only a few localized lattice modes, denoted by q_i^α , $i = 1, 2, \dots$. This results in considerable simplification of the analysis of the coupled hydrogen-lattice problem in the experimental temperature regime $273 \text{ K} > T > 27 \text{ K}$. Additional coupling of hydrogen to the lower lying excitations of the lattice provides a thermal heat bath and source of dissipation which is discussed in the following sections. Here we first treat the single well problem, which does not involve intersite tunneling, as the starting point for understanding the diffusion process in both the activated and tunneling regimes.

We begin by expanding the total potential energy V for the hydrogen coordinate r about \bar{r} , where \bar{r} is the equilibrium interstitial position in the distorted surface adsorption site. The single well Hamiltonian H^{SW} is written as

$$H^{\text{SW}} = T_H + T_W + V(r, \{q_i\}), \quad (2.1a)$$

where q_i is the i th phonon coordinate and where the kinetic energy operators are

$$T_H = -\frac{\hbar^2}{2m_H} \partial_r^2, \quad T_W = -\frac{\hbar^2}{2m_W} \sum_i \partial_{q_i}^2. \quad (2.1b)$$

Because of the time scale separation, an adiabatic (or Born-Oppenheimer) approximation allows the single well eigenstates to be written as the product $\psi_{m,n}(\{q_i\})\phi(r; \{q_i\})$ where the site index α is dropped for convenience. The vibron and phonon wave functions obey, respectively, the Schrödinger equations

$$[T_H + V(r, \{q_i\})]\phi_n = U_n(\{q_i\})\phi_n, \quad (2.2a)$$

$$[T_W + U_n(\{q_i\})]\psi_{m,n} = E_{m,n}\psi_{m,n}. \quad (2.2b)$$

Expanding U_n to quadratic order around its minimum $\bar{q}_i(n)$ gives

$$U_n(\{q_i\}) = U_n(\{\bar{q}_i(n)\}) + \frac{1}{2} m_W \sum_i \omega_{L,i}^2 [q_i - \bar{q}_i(n)]^2 + \mathcal{O}[q - \bar{q}(n)]^3, \quad (2.3)$$

where $\omega_{L,i}$ defines the local phonon frequency, and $\bar{q}_i(n)$ is the polaron distortion due to the occupation of the n th vibron state in the surface ad site. In general, Eq. (2.2a) implies that $U_n(\{q_i\})$ and hence both $\omega_{L,i}$ and $\bar{q}_i(n)$ depend on hydrogen mass and vibron quantum number. When the potential V is smooth, U_n in Eq. (2.2a) is well approximated by the harmonic oscillator eigenvalues $(n + \frac{1}{2})\hbar\omega_H$ for the vibron levels, where $\omega_H = \omega_H(\{q_i\})$. As a result the mini-

mum positions $\bar{q}_i(n)$ in Eq. (2.3) satisfy

$$\bar{q}_i(n) \equiv \bar{q}_i(n, m_H) = \bar{q}_i \left[(n + \frac{1}{2}) m_H^{-1/2} \right]. \quad (2.4)$$

Equation (2.4) leads to a useful relation between the isotope dependence of the polaron distortions and their variations with the vibron quantum number. This relation is obtained in terms of the finite difference approximation

$$\frac{d\bar{q}_i(n)}{dm_H} \simeq -\frac{1}{2} (n + \frac{1}{2}) m_H^{-1} [\bar{q}_i(n+1) - \bar{q}_i(n)], \quad (2.5)$$

which is used later for semiquantitative comparisons between tunneling and activated diffusion.

III. THE SMALL POLARON HOPPING

At approximately 100 K the measured high temperature diffusion coefficients $D(T)$ exhibit a relatively sharp transition from activated behavior $D \approx \exp(-\bar{V}/T)$ to a very weak temperature dependence at lower temperatures (Fig. 2). This suggests that at these lower temperatures quantum tunneling processes dominate over thermal activation over the intersite barriers. The small polaron hopping (SPH) theory, which has been specifically developed to treat electron motions in metals in the presence of strong electron-phonon coupling,^{6,7} provides a natural framework for treating the hydrogen tunneling. The common feature of the electron-phonon and vibron-phonon problems is that a large separation exists between the electron and phonon time scales as well as between the hydrogen and lattice characteristic time scales.

We assume for now, and return later to justify this assumption, that the hydrogen motion for $100 \text{ K} > T > 27 \text{ K}$ is described by incoherent tunneling hops between neighboring wells. This breaking of coherence is produced either by slight disorder or by a heat bath with a continuum of low energy ($\ll 27 \text{ K}$), bosonic excitations which may involve acoustic phonons, hole-particle excitations, etc. Disorder can arise from lattice strain, from impurities and from the fact that experiments must be made at nonzero coverage. The lack of coherence implies that at the measured temperatures above 27 K the tunneling is dominated by nondiagonal transitions which do not conserve the heat bath quantum numbers, so that coherent diagonal transitions are unimportant. Thus, the diffusion coefficient is given by the Fermi golden rule expression for incoherent hopping,

$$D = \frac{2\pi}{\hbar} l^2 J^2 \rho(T), \quad (3.1)$$

where J is the tunneling matrix element, which we discuss shortly, and in the heat bath model ρ is the weakly temperature dependent density of inelastic boson excitations contributing to the nondiagonal transitions. If the breaking of coherence between tunneling events is due to static disorder, ρ in Eq. (3.1) is replaced by $(\Delta_{ei})^{-1}$, where Δ_{ei} is the mean energy mismatch between the neighboring intersite configurations. The magnitude of Δ_{ei} depends on the strength of the disorder. This disorder mechanism would also yield a weak temperature dependence in Eq. (3.1).

Flynn and Stoneham⁸ (FS) have explicitly calculated $\rho(T)$ for two distinct microscopic models of the heat bath.

FS use phonons as the heat bath, but here their work can straightforwardly be generalized to include low lying acoustic phonons and electron-hole excitations.) We quote two of their main results for $\rho(T)$ for different coupling symmetries between the tunneling coordinate and heat bath boson coordinates in order to justify our contention that the heat bath could produce incoherent hydrogen hopping and that the prefactor of Eq. (3.1) is weakly temperature dependent.

First FS show that a set of antisymmetrically coupled (e.g., linear in both tunneling and boson coordinates) oscillators yields

$$\rho_a(T) = \left[\frac{\pi}{4\Delta_a K_B T} \right]^{1/2} \exp(-\Delta_a/K_B T), \quad (3.2)$$

where Δ_a is the associated heat bath relaxation energy, released by shifting the oscillator coordinates (distorting the adsorption site) to minimize the total hydrogen-environment potential. When both symmetric and antisymmetric couplings are present, FS show that $\rho(T)$ may be expressed as

$$\rho_{a,s}(T) = \left[\frac{1}{4\Delta_a \Delta_s} \right]^{1/2} \exp\left[-\frac{(\Delta_a + \Delta_s)}{K_B T} \right], \quad (3.3)$$

where Δ_s is the symmetric distortion energy for the most probable tunneling path. These model expressions are useful to justify the contention that at temperatures high compared to $\Delta_{s,a}$ the density $\rho(T)$ is expected to vary only slowly with temperature. Because of the relatively large region of flat temperature dependence observed for $100 \text{ K} > T > 27 \text{ K}$, these inelastic bosonic processes have an upper cutoff $\bar{\Delta} \ll 27 \text{ K}$ which is well below the excitation energies of the vibron and of the local phonons $\hbar\omega_H$ and $\hbar\omega_L$, respectively, that contribute to the diagonal ground-state to ground-state transitions in the tunneling matrix element J . If such a separation did not exist, the transition to activated behavior would be gradual and over a large temperature range instead of the fairly sharp behavior observed. Knowledge of $\bar{\Delta}$ would also allow us to estimate ρ at $T \gg 27 \text{ K}$, since Eqs. (3.2) and (3.3) give $\rho \approx (\hbar\bar{\Delta})^{-1}$ in this limit.

The lowest temperature regime of the SPH model occurs where there is coherent band motion. Whaley *et al.*⁹ use a band-like transport equation to explain the low temperature data of Ref. 1. Here we argue, however, that even at the lowest accessible temperatures, this regime is unattainable because of the extreme narrowness of the expected hydrogen bandwidth J . The criterion for coherent propagation over more than one lattice constant is that $\bar{\Delta} \ll J$. We estimate an upper bound for J from the observed D_T at 27 K, which is taken for the purposes of this estimate as equal to $D_{T=0}$. Thus we have

$$J \leq \hbar D_{T=27 \text{ K}} l^{-2} \approx 10^{-12} \text{ eV}, \quad (3.4)$$

where $l \approx 3 \text{ \AA}$ is the nearest neighbor hopping distance. It is therefore quite unlikely that $\bar{\Delta}$ could be as much as nine orders of magnitude below the experimental temperatures of 10^{-3} eV in order to satisfy the condition $\bar{\Delta} \ll J$ for the existence of coherent band motion for the hydrogen at 27 K. If the incoherence is induced by static disorder, then the above arguments proceed using $\bar{\Delta} = \Delta_{ei}$ as a measure of the random energies involved.

J is the multidimensional tunneling matrix element between localized vibron-phonon states at neighboring sites. The formalism of the path decomposition expansion¹⁰ (PDX) allows us to evaluate J by simultaneously using the semiclassical approximation and the fast-flip or Franck-Condon approximation. The first is asymptotically exact in the limit of small $\hbar\omega_H/\bar{V}$, and the second is accurate in the limit of large ω_H/ω_L . The latter condition is consistent with our Born-Oppenheimer-type separation, while corrections due to a finite barrier height are easily appended but do not change the general conclusions. The PDX involves separating configuration space into disjoint regions where the wave functions are independently determined. Thus, we use the single-well Born-Oppenheimer wave functions ψ^α , $\alpha = 1, 2$, for the local phonons, where α denotes the site occupied by the hydrogen. The ground state diagonal tunneling matrix element is then given by

$$J = \hbar\omega_H \left(\frac{2m\omega_H}{\pi\hbar l_t} \right)^{1/2} \langle \Psi_{0,0}^1 | \Psi_{0,0}^2 \rangle \exp(-S_H), \quad (3.5)$$

where the action under the tunneling barrier is evaluated semiclassically as

$$S_H = -\frac{2}{3\hbar} (2m_H \bar{V}_t)^{1/2} l_t, \quad (3.6)$$

and where a quartic double-well potential for the hydrogen tunneling coordinate r_1 is parametrized as

$$V(r_1) = \bar{V}_t \left[\left(\frac{r_1}{l_t/2} \right)^2 - 1 \right]^2. \quad (3.7)$$

The subscripts in Eq. (3.5) designate that both wells have the local phonons in their ground states. In principle, \bar{V}_t can be larger than the measured activation energy \bar{V} since the activation process chooses the minimal barrier height needed to cross over to the neighboring well and since the energy \bar{V}_t , on the other hand, is the height of the barrier along the minimum action path between the two wells. Here we set $\bar{V} = \bar{V}_t$ and lump our ignorance of the exact tunneling path and potential into the uncertainty in the tunneling distance l_t . The form of Eq. (3.6) is then valid for more general potentials than Eq. (3.7) where l_t is on the order of the actual tunneling distance.

The overlap factor can be evaluated using the Gaussian eigenfunctions associated with the potential in Eq. (2.3). Ignoring changes in phonon frequencies between a well which is occupied by a hydrogen or is not, this overlap is

$$\begin{aligned} \langle \psi_{0,0}^1 | \psi_{0,0}^2 \rangle &\equiv \exp(-S_w) \\ &= \exp \left\{ -\frac{m_w}{\hbar} \sum_i \omega_{L,i} [q_i(0) - \bar{q}_i^\infty]^2 \right\}, \end{aligned} \quad (3.8)$$

where \bar{q}^∞ is the mean phonon position when there is no hydrogen at the site. It is straightforward to include phonon frequency changes, but there is presently insufficient information to provide any information on these changes. Thus, we employ the standard model of Eq. (3.8), which should be of sufficient accuracy for our order of magnitude-type calculations. The overlap action S_w can in general reduce the diffusion coefficients by a sizeable amount, even for relative-

ly small polaronic distortions. Note that S_w contains two identical contributions from the two wells in ψ^1 and ψ^2 ; hence, there is no factor of 1/2 in front of the summation over modes in Eq. (3.8).

As shown in Ref. 10, when large changes of curvatures in the transverse components of hydrogen coordinates r_2 and r_3 are coupled to the tunneling coordinate r_1 , the effective barrier height \bar{V} is expected to be strongly isotope dependent through a quantum renormalization of the tunneling barrier with the shift $\delta V \sim m_H^{-1/2}$. This barrier renormalization results from the "squeezing" of the transverse zero point motion near the barrier top and is discussed in the solution of such model problems as in Ref. 10, Sec. IV. Although such anomalous isotope dependences have been observed in bulk diffusion, the values of \bar{V} determined here from the data in the activated regime appear to be only weakly isotope dependent. Thus, we disregard the transverse hydrogen coordinates as irrelevant for the tunneling analysis.

We therefore fit the low temperature, low coverage data for $D(m_H)$ to our final theoretical expression for the tunneling diffusion,

$$\begin{aligned} D &= \omega_H \left(\frac{2m\omega_H}{\pi\hbar l_t} \right)^{1/2} (\hbar\omega_H/\tilde{\Delta}) \\ &\times \exp \left\{ -2 \left(\frac{m_H}{m_1} \right)^{1/2} S_1 - 2S_w - 2(m_H - m_1) \right. \\ &\left. \times \frac{dS_w}{dm_H} \Big|_{m_1} \right\}, \end{aligned} \quad (3.9)$$

where a Taylor expansion of S_w and $m_H = m_1$ is introduced to simplify the form of m_H dependence. We estimate $l_t \approx 0.5-0.8$ Å from the geometry of the surface and take $\hbar\omega_H = 100$ meV from Ref. 5. Unfortunately, we do not have a way to independently determine a lower bound on the heat bath or disorder scale $\tilde{\Delta}$. Thus, we choose it to be in the wide range of 0.1-2 meV. Substitution of these quantities into Eq. (3.9) and use of the experimental data¹ for D yields

$$S_1 = 3.7 \pm 0.6, \quad S_w = 14 \pm 2, \quad (3.10a)$$

$$\frac{dS_w}{dm_H} = -1.5 \pm 0.3, \quad (3.10b)$$

where the range of values in Eq. (3.10) comes from the range of possible $\tilde{\Delta}$.

Equation (3.10b) implies the data for D can only be fit with an isotope dependent factor $S_w(m_H)!$ (Choosing higher values for l_t and \bar{V}_t would lead to even a larger value of dS_w/dm_H .) This is one of our main results: The low temperature diffusion data are shown here to require a sizeable isotope dependence of the hydrogen-lattice force constants that determine the phonon overlap factor through $\omega_{L,i}$ and \bar{q}_i .

As noted above, the work of Muttalib and Sethna³ invokes the opposite time scale separation, namely, the hydrogen tunneling time is argued to be long compared to phonon inverse frequencies. Although the resulting "mass renormalization" also yields a large contribution to the tunneling action, thus reducing the relative hydrogen mass dependence of D , it is inconsistent with measurements of vibron and phonon frequencies.⁵ As mentioned earlier, the smallness of

ω_L/ω_H is essential in explaining both isotope dependence in S_w and the inverse isotope dependence of the activation prefactor. We now discuss the latter behavior.

IV. NONADIABATIC ACTIVATION

Consider now the thermally activated regime. The principal contribution to the diffusion coefficient is assumed to come from barrier climbing by H atoms, rather than from activated polaron hopping. This assumption is based on the experimentally observed *strong inverse* isotope effect, namely that the activation energies vary only slightly with adsorbate mass but that the prefactors vary as $D_0 \sim \exp(-cm_H^{-1/2})$ (see Fig. 1). If activated polaron hopping were involved, the prefactor would go as $D_0 \sim \exp(-c'm_H^{+1/2})$ since the hydrogen tunneling would introduce a tunneling exponent *strongly decreasing* with increasing mass.

The quantum theory of thermal activation above a barrier has been formulated in Ref. 4. It involves solving the master equation for the Markovian probabilities of occupying the ladder of vibron states in a given single potential well. Freed² has applied this theory to the present system by using H^{SW} of Sec. II, where the role of the local phonons is to "promote" the hydrogen up the vibronic ladder of states until it passes the barrier of energy \bar{V} and hops to a neighboring well. The intrawell transitions are generated by the nonadiabatic correction to the Born–Oppenheimer approximation and are induced by the operator P ,

$$P\phi(\mathbf{r}, \{q\}) \equiv [T_w, \phi(\mathbf{r}, \{q_i\})], \quad (4.1)$$

where T_w is defined in Eq. (2.1b), and where the rates of the interwell transitions are dependent on the shifts in the phonon equilibrium positions $\bar{q}(n+1) - \bar{q}(n)$. The resulting expression for D is given by

$$D_{\text{high } T} = D_0 \exp(-\bar{V}/T), \quad (4.2)$$

where D_0 is proportional to the average nonadiabatic matrix element between consecutive vibron levels. In practice only about 2–3 vibron levels exist below the barrier, so here we study only the $0 \rightarrow 1$ transition as this may very well be the rate limiting transition for the activation process.

The Golden Rule expression for D_0 is consequently given by

$$D_0 = \frac{2\pi}{\hbar} l^2 \sum_{\{m_i\}} |\langle \Psi_{\{m_i\},0} | P | \Psi_{\{0\},1} \rangle|^2 \delta(\sum_i m_i \hbar \omega_{L,i} - \hbar \omega_H), \quad (4.3)$$

where the second quantum numbers on Ψ are those of the vibron. The matrix element of P cannot depend exponentially on the hydrogen mass since it is evaluated between vibron wave functions in the same well. Thus, we factor Eq. (4.3) into the vibron matrix element $|P_{01}|^2$ and the phonon overlap factors. The overlap factor of a single phonon mode between its ground state and its N_i th excited state is

$$|\langle 0 | R_L \rangle|^2 = \exp(-X_{01}) X_{01}^{N_i/R_L}, \quad (4.4)$$

where $R_L = \hbar \omega_H / \hbar \omega_L$ is the number of phonon quanta required to promote the vibron from its ground state to its first excited state, and X_{01} is the dimensionless shift

$$X_{01} = \frac{m_w \omega_L}{2\hbar} [\bar{q}(1) - \bar{q}(0)]^2. \quad (4.5)$$

For a set of Einstein phonons of the same frequency ω_L , the total overlap factor is given by Eq. (4.5) with X_{01} replaced by the sum

$$X_{01} = \frac{m_w \omega_L}{2\hbar} \sum_i [\bar{q}_i(1) - \bar{q}_i(0)]^2. \quad (4.6)$$

Thus, in this case the behavior of Eq. (4.3) for large R_L becomes²

$$D_0 = \frac{2\pi}{\hbar} |P_{01}|^2 \exp\{-X_{01} - R_L [\log(R_L/X_{01}) - 1]\}. \quad (4.7)$$

When R_L is large, the isotope dependence in Eq. (4.7) is dominated by the second argument in the exponential which goes as $-m_H^{-1/2}$. If additional lower frequency modes ω'_L are involved where $R'_L > R_L$ it can be shown using a two frequencies model (see Ref. 2) that their contribution to Eq. (4.7) is suppressed provided that are not coupled very strongly, i.e., they do not yield an exponentially larger contribution to X_{01} , such that $X'_{01} \approx \exp(R'_L/R_L) X_{01}$. Thus the effective $R_L \sim m_H^{-1/2}$ dependence is given by the primarily higher frequencies ω_L . This assumption is compatible with any microscopic approach involving short range or pairwise interactions, where the strongly coupled lattice modes are primarily the local optical modes. In principle, X_{01} is expected⁴ to be inversely proportional to $(m_H)^{-1}$ as shown in Sec. II for the scaling of $\bar{q}(n, m_H)$ in Eq. (2.4).

We estimate the magnitude of X_{01} by fitting Eq. (4.7) to the experimental D_0 values shown in Fig. 1. Using $\omega_H/\omega_L \approx (m_w/m_H)^{1/2} = 13.5$ it is found that X_{01} is roughly of $O(1)$.

The consistency of this result is checked by relating X_{01} to the isotope dependence of the overlap factor dS_w/dm_H which is determined from the tunneling data in the previous section. Using Eqs. (3.8), (4.6), and (2.5) we write

$$\begin{aligned} \left(\frac{dS_w}{dm_H}\right)^2 &= \left\{ \frac{2m_w}{\hbar} \sum_i \omega_L [\bar{q}_i(0) - \bar{q}_i^\infty] \frac{dq_i}{dm_H} \right\}^2 \\ &\approx \left\{ \frac{m_w}{\hbar} \sum \omega_{L,i} (\bar{q}_i - \bar{q}_i^\infty) \frac{3}{2} m_H^{-1} [\bar{q}_i(1) - \bar{q}_i(0)] \right\}^2 \\ &\approx 3 S_w m_H^{-2} X_{01}. \end{aligned} \quad (4.8)$$

Substituting the values determined in Eq. (3.10) into Eq. (4.8) in turn yields $X_{01} \approx 0.3$ – 2.0 .

Although the isotope dependence observed in activated diffusion argues against activated polaron hopping, as already noted, it is worthwhile to ask why this should be so, since hydrogen diffusion in the bulk of metals is usually taken to proceed by polaron hopping.⁸ The short answer seems to be that in the bulk the barrier for hydrogen motion is rather high, so that activation over it is never competitive with polaron hopping at accessible temperatures. It is intuitively reasonable that the opposite should be true in surface diffusion, but it is worthwhile to attempt a more quantitative

answer. If activated polaron hopping were to occur, D would be given approximately by

$$D \approx l^2 \omega_H \exp(-S_W \hbar\omega_L/kT) \exp(-2S_H). \quad (4.9)$$

The strain energy is $S_W \hbar\omega_L$ and may be evaluated using the value of S_W deduced from the tunneling data. If we take $S_W \sim 14$ from Eq. (3.10a) and $\hbar\omega_L \sim 100 \text{ cm}^{-1} = 0.012 \text{ eV}$ as an average phonon frequency,⁵ we find $S_W \hbar\omega_L \sim 0.17 \text{ eV} = 4 \text{ kcal/mol}$. This value is comparable to the observed activation energy, and the smallness of the prefactor for ¹H could arise from the hydrogen tunneling term $\exp(-2S_H)$ in Eq. (4.9). However, in that case we would expect a substantial increase in activation energy and D_0 as T increases, since tunneling would then be replaced by barrier climbing. This is not observed over the accessible range of activated diffusion, as shown by Fig. 2. The estimate of strain energy is of course very rough. However, even if it were substantially less than 4 kcal, appreciable tunneling in the activated regime would lead to a much more gradual crossover between tunneling and fully activated behavior than is seen for ¹H. Furthermore, Eq. (4.9) cannot account for D_0 of ²H and ³H in any case since the observed values of D_0 are much larger than predicted by inclusion of $\exp(-2S_H)$ if the smallness of D_0 for ¹H is attributed to this factor. Finally, as coverage increases small changes in ω_L can account for the observed increases in D_0 via the Freed NAA mechanism.² No comparable explanation in terms of activated polaron hopping comes to mind.

V. DISCUSSION

The preceding sections have shown that substrate phonons play a vital part in hydrogen diffusion on W(110) and that both activated and nonactivated diffusion can be explained consistently in terms of adsorbate-phonon interactions if a large separation in time scales for hydrogen and tungsten motions is assumed. This adiabatic separation also leads in a natural way to an isotope dependence of effective hydrogen-lattice force constants. The isotope dependence has been invoked in the activated regime to explain the ratio of D_0 values for the three isotopes and in the tunneling regime to explain the fact that S_W has some dependence on hydrogen mass. The present analysis is consistent with assuming that only a small number of neighboring tungsten coordinates, i.e., local phonons, are involved. Thus, a micro-

scopic approach, using pairwise potentials of short range, is justifiable.

This paper deals only with the very low coverage limit. Reference 1 shows that D is significantly coverage dependent in the tunneling regime, but that the D vs θ curves remain essentially parallel, i.e., that the isotope effects remain constant, except for a difference between ¹H and ³H on the one hand and ²H on the other at $\theta > 0.7$. Speculations on the coverage dependence of D have been given elsewhere.^{1(b),11} For present purposes it suffices that the isotope effect is almost coverage independent (with the exception of ²H at high coverage). Thus the considerations of this paper probably apply at higher coverage as well. D_0 in the activated regime also shows strong coverage effects,^{1(b)} which are different for each isotope. It has been speculated^{1(b)} that these have to do with small changes in phonon (and/or adsorbate) frequencies with increasing coverage. A detailed discussion would go beyond the scope of this paper, but it seems quite reasonable that very small changes of this kind can account for the observed behavior within the framework of the present model.

ACKNOWLEDGMENTS

This work is supported by the Materials Research Laboratory of the National Science Foundation at the University of Chicago. A preliminary account of this work was presented at the 19th Jerusalem Symposium.¹²

¹(a) R. DiFoggio and R. Gomer, *Phys. Rev. B* **25**, 3490 (1982); (b) S. C. Wang and R. Gomer, *J. Chem. Phys.* **83**, 4193 (1985).

²K. F. Freed, *J. Chem. Phys.* **82**, 5264 (1984); *Top. Appl. Phys.* **15**, 23 (1976).

³K. Muttalib and J. Sethna, *Phys. Rev. B* **32**, 3462 (1985).

⁴D. Emin (private communication).

⁵G. B. Blanchet, N. J. Dinardo, and E. W. Plummer, *Surf. Sci.* **118**, 496 (1982).

⁶T. Holstein, *Ann. Phys.* **8**, 343 (1959).

⁷*Many Particle Physics*, edited by Gerald D. Mahan (Plenum, New York, 1983), Sect. VI B.

⁸C. P. Flynn and A. N. Stoneham, *Phys. Rev. B* **10**, 396 (1970).

⁹B. Whaley, A. Nitzan, and B. Gerber, *J. Chem. Phys.* **84**, 5181 (1986); A. Nitzan (private communication).

¹⁰A. Auerbach and S. Kievelson, *Nucl. Phys. B* **257** FS14 (1985).

¹¹M. Tringides and R. Gomer, *Surf. Sci.* **166**, 440 (1986).

¹²A. Auerbach, K. F. Freed, and R. Gomer, in *Tunneling*, edited by J. Jortner and B. Pullman (Reidel, Dordrecht, in press).