Energetics and Vibrational States for Hydrogen on Pt(111)

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We present a combination of theoretical calculations and experiments for the low-lying vibrational excitations of H and D atoms adsorbed on the Pt(111) surface. The vibrational band states are calculated based on the full three-dimensional adiabatic potential energy surface obtained from first-principles calculations. For coverages less than three quarters of a monolayer, the observed experimental high-resolution electron peaks at 31 and 68 meV are in excellent agreement with the theoretical transitions between selected bands. Our results convincingly demonstrate the need to go beyond the local harmonic oscillator picture to understand the dynamics of this system.

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Hydrogen on metal surfaces, and in particular on Pt(111), has received considerable experimental [1–7] and theoretical [8–15] attention. Together with Pd, Pt is the most important material for heterogeneous catalysis of hydrogenation reactions. On the fundamental side, hydrogen on metal surfaces provides a unique opportunity to observe the crossover from classical to quantum dynamics at relatively elevated temperatures [16–19].

For the vibrational excitations of H/Pt(111), Baró *et al.* [4] applied high-resolution electron energy-loss spectroscopy (HREELS) and observed for H (D) at coverages up to 0.7 monolayer (ML) two peaks at 68 (50) meV (assigned to the symmetric stretch mode SS), and 153 (112) meV (assigned to the asymmetric stretch mode AS). On the other hand, Richter and Ho [5] found three peaks at 67 (51) meV, 112 (84) meV and 153 (108) meV in their HREELS measurements for a full ML of H (D). They assigned these to the AS mode, the SS mode, and the unresolved overtone and combination losses, respectively. To date, the disagreement between these observations is not resolved. In addition, recent measurement of the diffusion barrier for this system [6] yielded a very low value of about 70 meV, considerably less than a previous value of about 200 meV. All these discrepancies emphasize our lack of understanding of this important system.

On the theoretical side, an earlier first-principles (FP) study [8] at a full ML coverage has shown that H adsorbs in the threefold hollow fcc site. More recent FP calculations [10–13] at lower coverages indicate that unlike for H/Ni(111) and H/Pd(111) [20–23], the top site for H/Pt(111) is also a local minimum only slightly higher in energy than the fcc site. In addition, the energy barrier for the fcc-hcp-fcc path is only about 70 meV. In these calculations the main focus has been on adiabatic potential energy surface (APES). The curvatures determined at the potential minima [8,10,11] could not account quantitatively for the observed vibrational excitation energies. Given the recent results of the shallow barrier between the fcc and hcp sites, it is clear that quantum effects are essential in understanding the dynamics of this system, and the vibrational spectroscopy needs to be interpreted in terms of excitations between vibrational band states as proposed earlier [16,17].

In this Letter we investigate the energetics and vibrational properties of H and D adatoms on the Pt(111) surface. The experiments consist of HREELS investigations of H and D adsorption on Pt(111) and its dependence on coverage. The experiments were performed in an ultrahigh vacuum (UHV) apparatus with a base pressure of 3×10^{-11} mbar as described elsewhere including sample preparation [24]. The HREEL spectrometer was of the latest commercial Ibach design (Delta 0.5, SPECS, Germany). The H_2 exposure was performed by backfilling the preparation chamber while the sample was cooled to 85 K with liquid N2. The exposure was varied between 0.1 and 500 L (1 L $= 1.33 \times 10^{-6}$ mbar $\times$ s). The coverage θ was determined from thermal desorption (TD) assuming $\theta = 1$ at saturation. The TD spectra of Christmann *et al.* [3] were well reproduced. We focus on the spectrum for the low coverage interval $\theta \leq 0.75$ ML, within which the HREEL spectra are qualitatively the same [25].

The spectra for H and D for $\theta \leq 0.75$ for specular geometry are shown in Fig. 1. It is well known that the loss intensity for vibrations of atomic H on transition metal surfaces is quite low since it is mainly caused by impact scattering. In spite of these intensity problems (note the magnifications in Fig. 1) the spectra clearly indicate the two H derived losses at 31 and 68 meV. Note that these new observations are quite different from previous results obtained at a full ML [4,5]. In particular, the previously reported peaks at 112 and 153 meV are not observed at these lower coverages. In Fig. 2, we also show the results for off-specular geometry where the 31 meV peak disappears while the 68 meV remains, indicating that the former is mostly of dipole character. For deuterium, there is a clear loss peak at 23.5 meV, corresponding to the 31 meV peak

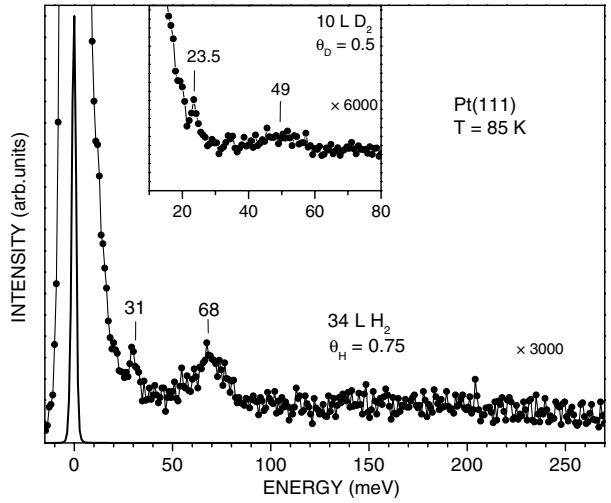


FIG. 1. HREEL spectra for H on Pt(111) at $\theta = 0.75$ ML (H) and 0.5 ML (D) for specular geometry. The spectrum for D is in the inset, with the low-energy features displayed on a smaller scale. The primary electron energy is $E_0 = 2.0$ eV. The exposure is given in Langmuir (L) (1 L $\approx 1.33 \times 10^{-6}$ mbar $\times$ s).

for hydrogen with an isotope down-shift. There is a very broad higher mode between 40 and 60 meV not very well resolved from the noise background.

We now turn to the theoretical calculations for the vibrational excitations. The FP calculations for 3D APES were done self-consistently with a parallel plane-wave code [26] based on density functional theory with the generalized gradient approximation [27]. The Troullier-Martins pseudopotential [28] was used for Pt and the Vanderbilt nonlocal ultrasoft pseudopotential [29] for H. Electronic wave functions were expanded in a plane-wave basis with a kinetic energy cutoff at 35 Ry. For the irreducible Brillouin-zone integration eight special $\vec{k}$ points [30] were used, together with a Fermi smearing of 0.2 eV. The calculated lattice constant for bulk Pt was $a = 7.568$ a.u. (experimentally $a = 7.415$ a.u. [31]). The supercell ($2 \times 2 \times 4$) has 16 Pt atoms and one H atom, corresponding to a quarter

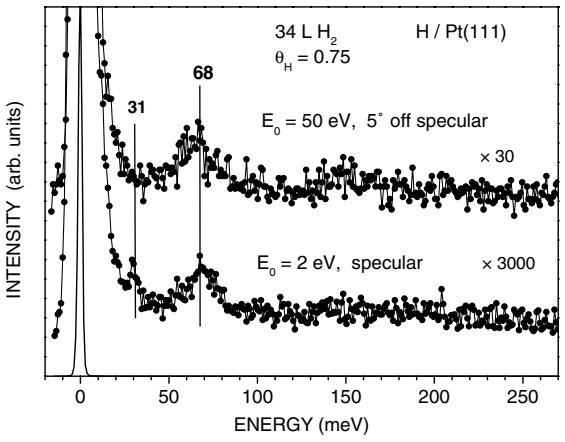


FIG. 2. Comparison of HREEL spectra for H on Pt(111) for specular and off-specular geometries.

monolayer coverage. The z axis is oriented towards the vacuum which was 14 Å thick. The coordinates of the Pt atoms were relaxed before adding the H. Only the vertical coordinate of the H atom was relaxed during the calculations for each (x, y) position of the APES. We also checked the effects of the relaxation of Pt surface atoms. We found that the potential energy differences between the fcc, bridge, and hcp sites change less than 5 meV [32].

We first present results for the 3D APES as shown in Fig. 3. The 2D minimum APES is shown in the inset. The top site is metastable and only 25 meV above the lowest energy adsorption fcc site and is surrounded by large energy barriers. Along the fcc-hcp-fcc path, there is a shallow barrier of 78.9 meV. At all sites the H (D) is chemisorbed with an electronic charge transfer from the substrate toward the adatom, similar to that reported for H/Ni(111) [21]. These results agree well with other recent calculations [10–13,15]. In particular, the approach of Källén and Wahnström [15] is closest to the present work and the resultant APES are very similar. However, there are quantitative differences particularly concerning the curvature and anharmonicity at the fcc sites. These will lead to substantial differences for the vibrational band excitations as detailed below.

To study the vibrational modes of the H and D adatoms, we calculated the band states for the single particle Hamiltonian with the FP 3D APES. The Hamiltonian is diagonalized in a basis set $\{|\vec{G}, n\rangle\}$ given by a direct product between 595 in-plane plane waves $\langle \vec{r} \,|\, \vec{G} \rangle$ and 14 harmonic-oscillator states $\langle z \,|\, \Psi_n \rangle$ for the z coordinate. The lower branches $n = 1$–16 for H are shown schematically in Fig. 4, along with the corresponding centers $\vec{r}_0$ of

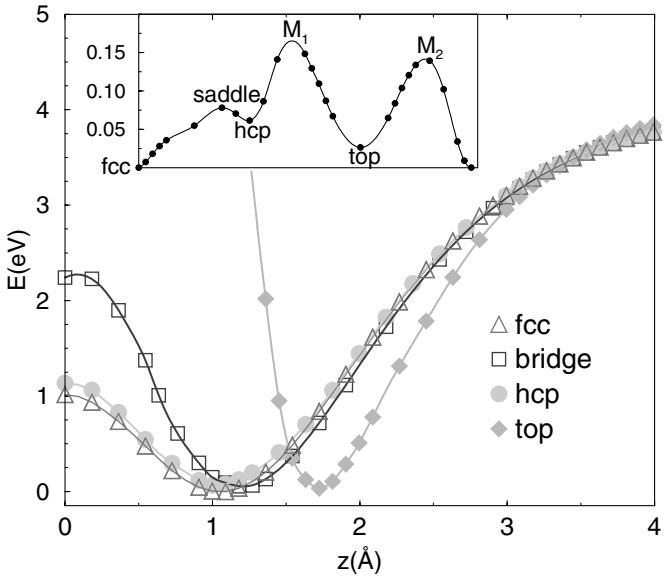
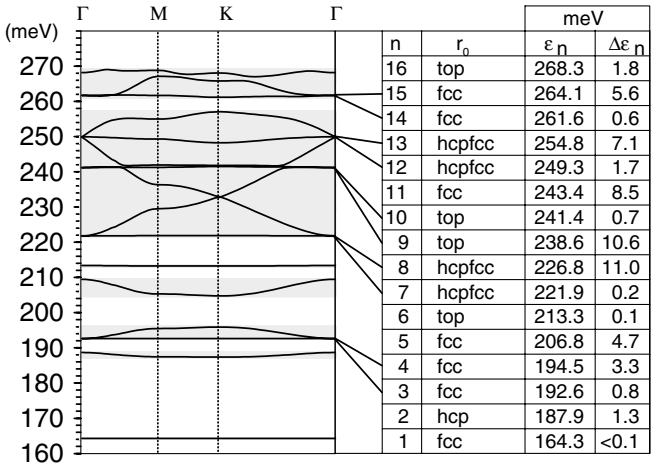


FIG. 3. Vertical cuts in the 3D APES at high-symmetry sites. The topmost atomic plane is at $z = 0$, and the vacuum is at $z > 0$. The inset shows the 2D minimum APES along the path fcc-bridge-hcp-top-fcc.



		meV	
n	r_0	ε_n	$\Delta\varepsilon_n$
16	top	268.3	1.8
15	fcc	264.1	5.6
14	fcc	261.6	0.6
13	hcpfcc	254.8	7.1
12	hcpfcc	249.3	1.7
11	fcc	243.4	8.5
10	top	241.4	0.7
9	top	238.6	10.6
8	hcpfcc	226.8	11.0
7	hcpfcc	221.9	0.2
6	top	213.3	0.1
5	fcc	206.8	4.7
4	fcc	194.5	3.3
3	fcc	192.6	0.8
2	hcp	187.9	1.3
1	fcc	164.3	<0.1

FIG. 4. The lowest vibrational branches for H/Pt(111). ε_n denotes the band center, $\Delta\varepsilon_n$ the bandwidth, and r_0 the center of the BS with $\vec{k} = 0$.

the probability distributions for the $\vec{k} = 0$ states, the band centers ε_n, and the widths $\Delta\varepsilon_n$. In addition, many modes have mixed in-plane and vertical character and cannot be described in conventional AS or SS terms. Also, the intervals between the band centers do not match with the local harmonic oscillator model based on the curvatures at the potential minimum. Finally, the higher bands have considerable bandwidth, reflecting the delocalized nature of the adsorbed H through tunneling processes [16,17].

The first band $n = 1$ localized at the fcc site is very narrow ($\Delta\varepsilon_1 < 0.1$ meV). The next band $n = 2$ is localized at the hcp site. Its center is at $\varepsilon_2 = 23.6$ meV above the center of the lowest band and it has a bandwidth of $\Delta\varepsilon_2 = 1.3$ meV. The difference $\varepsilon_2 - \varepsilon_1$ confirms that even with the zero point energies taken into account, adsorption at low temperatures is confined to the fcc sites. To analyze the vibrational excitation energies arising from transitions starting from the lowest band $n = 1$, we will focus only on those excited band states with finite amplitudes at the fcc site. The first excitations are toward the composite band $3 \oplus 4$, which has a total bandwidth of 4.1 meV. The two subbands are degenerate at $\vec{k} = 0$, with E symmetry. The excitation to these bands, calculated as the difference between the band centers $\varepsilon_{3\oplus4} - \varepsilon_1$, occurs at 29.1 meV. Taking into account the bandwidths, this is in excellent agreement with the new mode at 31 meV observed in the present experiment. Moreover, this mode has mixed in-plane and vertical character with sizable dipole elements in the normal direction. This is confirmed by the fading of the 31 meV peak in the off-specular direction (see Fig. 2).

The next excitation is to the band $n = 5$, and to the $7 \oplus 8$ pair of bands. The former is of A symmetry has a bandwith of 4.7 meV, while the latter has two subbands degenerate at $\vec{k} = 0$ (with E symmetry) and a total bandwidth of 11.2 meV. The excitation energies are 42 and 60 meV, respectively. These bands have mainly an in-plane character. We suggest that the observed peak centered at 68 meV could be a composite of these unresolved transitions. Another point to note about the higher bands $7 \oplus 8$ is that they have considerable weight at both the fcc and hcp sites. The states in these excited bands have high mobility throughout the surface. The excitation energy 60 meV needed to reach these bands is close to the activation energy observed in the quasielastic helium scattering experiment by Graham *et al.* [6]. Thus, our band state results support the picture that the diffusion of H on Pt(111) happens not through classical hopping but rather via the activated tunneling mechanism as recently proposed [18] to account for the similar behavior observed for H/Ni(111). The results give a direct confirmation of the protonic band picture introduced in [16,17].

When D is substituted for H in the calculations, the lower bands have a one-to-one correspondence with the H case with a down-shift of frequency approximately by a factor of $1/\sqrt{2}$ as expected. For deuterium, the first excitation energy is at 23.2 meV toward a composite band of width 0.2 meV, in excellent agreement with the experimental observation for D as shown in Fig. 1. There are transitions to higher bands at excitation energies between 30 and 60 meV: an excitation to an A band at 30.8 meV (bandwidth 0.8 meV), one to an E composite band at 46 meV (bandwidth 3.4 meV), and another to an E composite band at 59.8 meV (bandwidth 2.9 meV). These could account for the broad peak centered at 49 meV observed in the experiment.

There are many more excitations to the higher bands that we have not addressed here. Experimentally, they are not observed at low coverages ($\theta \leq 0.75$ ML). Qualitatively, one can understand this by noting that the higher bands are much more extended than the ground states and thus the matrix elements should be much smaller. As such, the resultant weak and broad peaks are hard to observe. The picture changes at full ML because then the tunneling of the H atom would be suppressed by on-site exclusion and effectively the H atoms are localized again. Interestingly, at a full ML, the 31 meV peak disappears from the observations and two additional peaks appear at 110 and 153 meV [7] in the present experiment. These loss peaks agree nicely with the earlier results of Richter and Ho [5].

In summary, we have presented a combination of theoretical calculations and experiments on the energetics and vibrational properties of H and D adatoms on Pt(111). The experimental data for the loss peaks at low coverages ($\theta \leq 0.75$ ML) differ significantly from previous studies at full H coverage. There is good agreement between the observed HREELS loss peaks and the protonic band structure calculations derived from a full 3D APES. This demonstrates that the vibrational spectroscopy of H adsorbed on metals and in particular for H/Pt(111) cannot be understood simply in terms of localized AS and SS oscillation modes at the adsorption sites, as often assumed in

the literature. This picture is also crucial for a proper understanding of the recent diffusion data for H/Pt(111) [6]. Finally, we emphasize that the dynamical behavior of this system at full ML is quite different from that at low coverages. There is also a possibility of change of adsorption sites. Further studies for the full ML case are in progress.

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