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Quantum treatment of H adsorbed on a Pt(111) surface

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A static potential energy surface for 1/4 of a monolayer of adsorbed hydrogen atoms on a Pt(111) surface has been calculated using first-principles density-functional theory calculations. The Schrödinger equation is solved for the hydrogen atoms in this potential. The results agree well with stable site, vibrational spectroscopy, and diffusion measurements, and resolve the conflicting interpretations of those experiments.

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Considerable effort has been devoted to the study of the interaction of hydrogen with transition metal surfaces during the last decades.[1] Experimental, theoretical, and computational methods are being used and applications such as catalytic reactions and hydrogen storage are in focus. The hydrogen atom is the simplest chemisorption species and it provides an ideal model system for testing theoretical models and dynamical concepts. It is especially interesting due to its small mass and the possibility of quantum-mechanical effects. Platinum is of particular importance as catalyst for various reactions involving hydrogen, one example being the water formation reaction.[2]

Despite extensive investigations the properties of the H/Pt(111) system are incompletely known and understood. No definite consensus has been achieved concerning the stable site from theoretical calculations,[3–5] the interpretation of the measured vibrational modes is unsettled,[6–8] and very high diffusivities have been observed in quasielastic helium atom scattering (QHAS) experiments[9] in contrast to previous macroscopic laser induced desorption experiments.[10]

In this letter we address and resolve all these issues by treating the hydrogen motion quantum-mechanically in a potential mapped out by careful first-principles electronic-structure calculations. We find a flat and very anharmonic potential energy surface for H on Pt(111) and show that a quantum-mechanical treatment of the H motion becomes essential.

The first-principles electronic-structure calculations are done in the framework of the density-functional theory (DFT)[11,12] with the exchange-correlation treated at the generalized gradient approximation level, version Perdew-Wang 91.[13] We use the DACAPO 1.31 code,[14] which is an implementation of the plane-wave pseudopotential method. The ion cores are described by the Vanderbilt ultrasoft pseudopotentials[15] and for the expansion of the one-electron wave functions we use a cutoff energy of 25 Ry. The Brillouin-zone is sampled in $6\times6\times1$ points using the Monkhorst–Pack scheme[16] and to improve the convergence the Fermi discontinuity is smeared according to the Gillan scheme.[17] The atomic structure relaxation is performed with the BFGS quasi-Newton method.[18] The slab supercell approach with periodic boundaries is employed to model the surface. In most calculations a $2\times2\times5$ atom supercell is used with 13 Å vacuum and a 1/4 monolayer of H put on one side of the slab. Unless stated, the Pt atoms are held fix at the positions of a relaxed clean Pt(111) surface.

To decide the number of layers in the Pt slab we have determined the adsorption energy for H as a function of the thickness of the slab. Our results are given in Table I. In the calculations we keep the platinum atoms fix at the positions of a relaxed clean Pt(111) surface. When relaxing the clean Pt(111) surface, the two layers in the bottom are held fix. We find that the adsorption energies for the fcc, bridge, and hcp sites are well converged at five layers. The top position is less well converged but that position is of minor importance in the present study. Our results compare well with previous calculations using only three layers,[19] but this is not enough to achieve the accuracy needed to compare with experiments. Based on this we use a five layer thick slab.

We have also tested the effect of relaxation in the presence of 1/4 monolayer of adsorbed H. For five Pt layers the adsorption energy for hydrogen in the different sites show that the fcc site is favored by approximately 40 meV. This result is essentially unchanged if the three uppermost Pt atoms are allowed to relax. The relaxation just shifts the energy values down as seen in Table II. Geometrically the Pt surface atoms relax toward the bulk.

The motion of H is treated quantum mechanically. Due to the mass difference between H and Pt we use the adiabatic approximation for a separation of the motion of light H atom and the heavier Pt atoms. Furthermore, we assume that the Pt atoms can be held fix in the positions of a relaxed clean Pt(111) surface based on the comparatively small effect of relaxation illustrated in Table II. The 3D potential energy surface is then mapped out by calculating the adsorption energy for a 1/4 monolayer of adsorbed H at different positions in a periodic 1×1 cell. All together 75 energy points are calculated in five planes parallel to the surface. The distance between the points in the surface plane is 0.41 Å and perpendicular to the plane 0.35 Å.

TABLE I. DFT values for the adsorption energy for a 1/4 monolayer of H adsorbed on Pt(111). The adsorption energy is calculated as $E_{\mathrm{ads}_\mathrm{H}}=E_{\mathrm{PtH}}-\frac{1}{2}E_{\mathrm{H}_2}-E_{\mathrm{Pt}}$, i.e., the difference in energy for one hydrogen atom on the surface as compared to one hydrogen atom in a hydrogen molecule. All values are in eV.

	Top	fcc	Bridge	hcp
3 layers of Pt	−0.457	−0.461	−0.434	−0.441
5 layers of Pt	−0.410	−0.455	−0.407	−0.418
7 layers of Pt	−0.393	−0.460	−0.405	−0.420

TABLE II. DFT values for the adsorption energy of a 1/4 monolayer of H with a slab of five layers when all the Pt atoms are fixed, and when the first three Pt layers are allowed to fully relax in the presence adsorbed H. The effect of the relaxation of the Pt atoms is an approximately equal energy shift for all sites. All values are in eV.

	Top	fcc	Bridge	hcp
Pt fixed	−0.410	−0.455	−0.407	−0.418
Pt relaxed	−0.439	−0.492	−0.442	−0.455

The Schrödinger equation for the H motion is solved numerically using the finite difference approximation. The lowest lying eigenvalues are efficiently extracted using the Lanczos algorithm. Since the potential is periodic in two dimensions the Bloch theorem applies for the wave function in the plane of the surface. The energy eigenstates are characterized by a band index and a two-dimensional wave vector. The width of the energy bands is obtained by evaluating the difference in the eigenstate energy at the center and at the boundary of the Brillouin zone.[20]

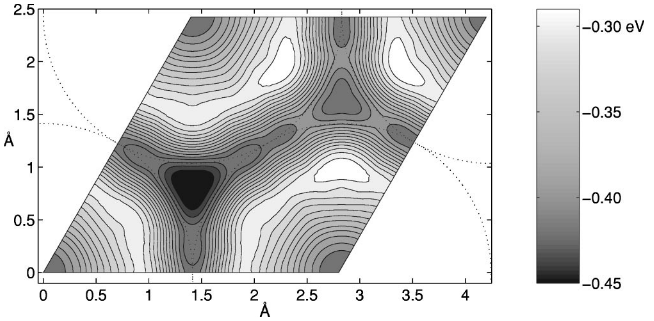

FIG. 1. Minimum energy surface for 1/4 monolayer of H on Pt(111), i.e., the minimum energy in the z-direction for all points in the xy-plane. The dotted lines indicate the positions of the Pt atoms. The distance between the isoenergy lines is 10 meV. The triangular minimum down to the left is the fcc site, the triangular minimum up to the right is the hcp site, and the minimum at the corners is the top site. The potential is highly anharmonic. The barrier for H to go from fcc to hcp (60 meV) is much smaller than to go from fcc to top (150 meV). For low energies H is thus confined to the fcc-hcp-fcc valleys.

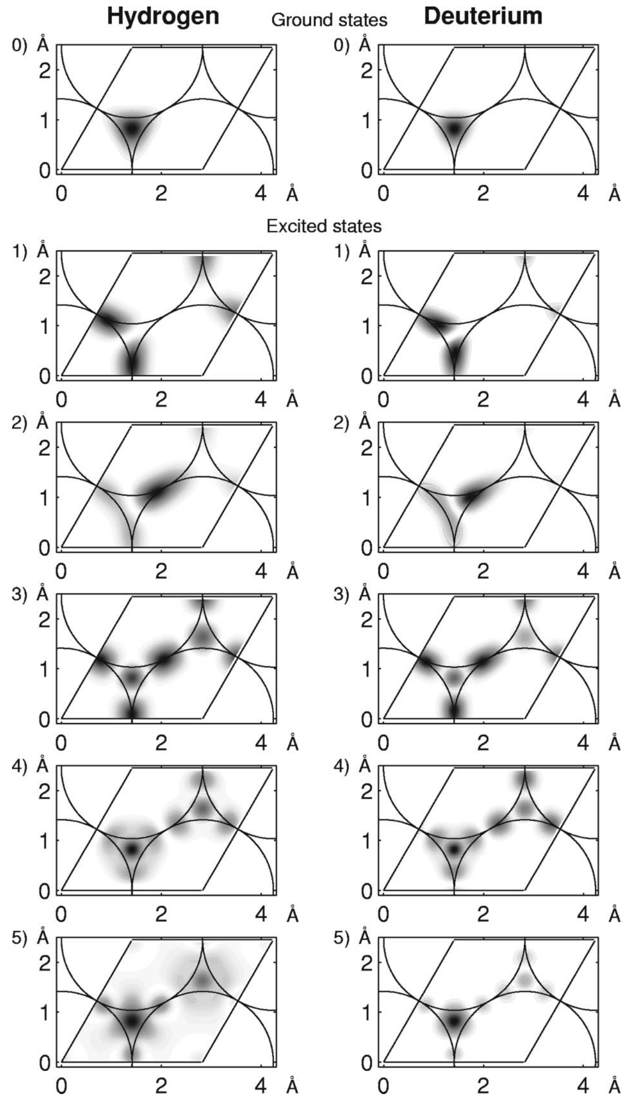

FIG. 2. Probability distributions as projected on the plane of the surface for H and D at the fcc site for the ground state (0), and the excited states (1)–(5), evaluated at the center of the Brillouin zone. The excitation energy for the vibrational states for H(D) is: (1),(2) 44 meV (39 meV), (3) 65 meV (49 meV), (4) 111 meV (74 meV), (5) 141 meV (96 meV). The potential energy surface is calculated for 1/4 of a monolayer of H and the symmetry is C_{3v} . The excited states (1)–(2) have E symmetry while the ground state and the excited states (3)–(5) have A_1 symmetry.

In Fig. 1 we show the minimum energy surface for hydrogen on Pt(111). The energy surface is complex and highly anharmonic. There are minima at the fcc, hcp, and top sites. Similar result has also been obtained by Badescu *et al.*[21] When solving the Schrödinger equation for H we find well defined localized states at all these three sites with zero-point energies 139 meV, 130 meV, and 190 meV, respectively. The corresponding numbers for D are 96 meV, 90 meV, and 125 meV. The resulting adsorption energies for H become −0.45 eV, −0.42 eV, and −0.36 eV for the fcc, hcp, and top positions, respectively, where also the zero-point energy for the hydrogen molecule is included.[22] This result is consistent with the experimental findings that the fcc site is the most stable site.[23–25] For a monolayer hydrogen coverage we find that the difference in adsorption energy between the fcc and hcp sites is 49 meV compared to 37 meV for 1/4 of a monolayer. Both the magnitude of the adsorption energy and the calculated binding distance of 1.87 Å for the Pt–H distance agree well with experimental data.[25]

In order to compare the present calculations with electron energy-loss spectroscopy (EELS)[6,7] and reflection-adsorption infrared spectroscopy (RAIRS)[8] measurements, the excited states with large amplitude at the fcc site are of interest. The probability distributions for the ground state and five selected excited states are shown in Fig. 2. For H(D) the first excited state is found at 44 meV (39 meV). It is parallel in nature, of E symmetry and hence double degenerated. The next state with E symmetry (not shown in Fig. 2) has the energy 113 meV (75 meV). The lowest states with A_1 symmetry are found at 65 meV (49 meV), 111 meV (74 meV), and 141 meV (96 meV), all shown in Fig. 2, and the first with A_2 symmetry at 149 meV (118 meV). The perpendicular nature of the states with A_1 symmetry is investigated by calculating the overlap $I(q_z)=|\langle\psi_0|e^{-iq_z z}|\psi_i\rangle|^2$, between the hydrogen ground state, ψ_0, and the different excited states, ψ_i. For hydrogen the calculated maximum intensities are $I_{\max}=1.5\times10^{-4}$, $I_{\max}=3.3\times10^{-4}$, and $I_{\max}=3.8\times10^{-4}$ for the states with energies 65 meV, 111 meV, and 141 meV, respectively.

Three peaks have been identified experimentally in EELS,[6,7] but the interpretation in terms of parallel and perpendicular vibrations differ in Refs. 6 and 7. In the RAIRS measurements[8] just one peak was found, the one with the highest frequency, around 155 meV. In Ref. 7 the first peak was found at 67 meV with a 16±3 meV full width at half maximum (FWHM) for a monolayer hydrogen coverage. It was interpreted as parallel vibration and the width was large compared to the experimental resolution (8 meV). The second peak around 112 meV with 4±4 meV FWHM was interpreted as perpendicular vibration and the last peak around 153 meV with 24±4 meV FWHM as a mix of parallel and perpendicular vibration. The corresponding values for deuterium were 51 meV, 84 meV, and 108 meV, respectively. When the hydrogen coverage was decreased to 20% of a monolayer, the first peak shifted down with about 10 meV and broadened.

We suggest that the measured peak at 67 meV[7] actually corresponds to two unresolved excitations at 44 meV and 65 meV. This would give a broad peak around $(44+65)/2$ = 55 meV in very good agreement with the measured result for this coverage.[7] According to the calculations this combined peak should have a small dipole moment, which was not observed by Richter and Ho,[7] but indicated in the measurements by Baró *et al.*[6] We also propose that the second peak at 112 meV[7] is due to two unresolved peaks, computed at 111 meV and 113 meV. This was interpreted as a perpendicular mode in Ref. 7 and for low coverages also detected by Baró *et al.*[6] The third measured peak at 153 meV (Ref. 7) agrees well with the computed value 141 meV. Based on the calculated matrix elements, $I(q_z)$, this is the most intense dipole active excitation, in agreement with the conclusions by Reutt *et al.*[8] It should be noticed that we find several excited states in this energy range. The corresponding calculated values for deuterium $(39+49)/2=44$ meV, $(74+75)/2=74$ meV, and 96 meV are in equally good agreement with the measured results.[7]

Finally, we would like to compare our results with the quasielastic helium atom scattering (QHAS) measurements of the diffusive motion.[9] In the temperature range 140–250 K clear evidence was found for a predominantly single-jump mechanism between threefold hollow sites with diffusion coefficients between 5×10^{-6} cm^2 s^{-1} and 5×10^{-5} cm^2 s^{-1}. For both H and D the diffusion coefficient followed an Arrhenius temperature dependence with activation energy and prefactor equal to 68±5 meV (76±7 meV) and $1.1\pm0.5\times10^{-3}$ cm^2 s^{-1} ($1.4\pm0.6\times10^{-3}$ cm^2 s^{-1}), respectively, for H(D). Due to finite resolution of the quasielastic peak the QHAS technique is restricted to high diffusivities ($D>10^{-6}$ cm^2 s^{-1}).

The classical barrier for the hydrogen atom to move along the surface is very low. The saddle point is located between the fcc and hcp sites (see Fig. 1) with an energy only 60 meV above the fcc site. At sufficiently low temperatures we expect H to tunnel between the ground states located at the fcc sites. To estimate the diffusion rate for that process, we have determined the corresponding bare tunneling matrix element J_0 from the width of the energy band of the ground state. For H(D) we obtained the value $J_0=1.5\times10^{-6}$ eV ($J_0=1.1\times10^{-8}$ eV). This results in a diffusion constant $D=5.8\times10^{-10}$ cm^2 s^{-1} ($D=3.5\times10^{-14}$ cm^2 s^{-1}) using the golden rule expression, $D=d^2/4\times n\times2\pi/\hbar\times J_0^2\times1/\hbar\omega$,[26,27] where $n=6$ is the number of jump-equivalent directions, ω is a typical angular frequency (here $\hbar\omega_{\mathrm{H}}=44$ meV and $\hbar\omega_{\mathrm{D}}=39$ meV) and $d=2.82$ Å is the distance between the fcc sites. These diffusion rates are considerably lower than what could be experimentally observed ($D>10^{-6}$ cm^2 s^{-1}) and, furthermore, we expect the true diffusion rate to be even smaller due to coupling to excitations in the substrate.

At higher temperatures transitions between thermally excited states will dominate the diffusion rate. The excited states are close in energy to the classical barrier height and the transition state theory[28] should give a reasonable description. According to that theory the diffusion constant can be expressed as $D_{\mathrm{TST}}=d^2/4\times n\times k_BT/h\times(Q^{\#}/Q)$, where $d=2.82$ Å, $n=3$ is the number of jump-equivalent directions, and Q ($Q^{\#}$) is the partition function for the system when the adatom is located at the stable site (the transition state). We evaluate both these partition functions quantum-mechanically for H and D and the resulting diffusion constants are very well approximated by the Arrhenius expression $D=D_0\times\exp(-E/k_BT)$ in the temperature range 140–250 K. We obtain the activation energy $E=55$ meV ($E=60$ meV) and a prefactor $D_0=4.0\times10^{-3}$ cm^2 s^{-1} ($D_0=3.7\times10^{-3}$ cm^2 s^{-1}) for H (D).

The magnitude of the activation energies is quite similar to the experimental numbers. The somewhat lower value for H compared with D is consistent with the experiments and is caused by the discreteness of the energy levels. The prefactors are similar for H and D, also consistent with experiments, but about a factor of 3 too large. This is, however, not unreasonable. We have neglected recrossing effects as well as corrections for tunneling and nonclassical reflection.

In conclusion, a potential energy surface for a 1/4 of a monolayer of adsorbed hydrogen atoms on a Pt(111) surface has been mapped out by first-principles density-functional-theory calculations. We find agreement with experiment for the stable site, binding distance, and adsorption energy. The hydrogen vibrational motion is found to be strongly anharmonic with several modes close in energy. We reinterpret the measured vibrational modes and give a consistent account for both the electron energy-loss spectroscopy (EELS)[6,7] and the reflection-adsorption infrared spectroscopy (RAIRS)[8] data. The measured prefactors and activation energies for diffusion of H and D[9] are well described by the transition state theory with the vibrational degrees of freedom treated as quantum oscillators. In summary, by combining first-principles electronic-structure calculations with a quantum treatment of the hydrogen motion a consistent and detailed understanding of the H/Pt(111) has been acquired.

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