Vibrational spectroscopy of H on Pt(111): Evidence for universally soft parallel modes

Lee J. Richter and W. Ho
Laboratory of Atomic and Solid State Physics and Materials Science Center, Cornell University, Ithaca, New York 14853
(Received 15 July 1987)

The vibrational properties of H adsorbed on Pt(111) have been studied with high-resolution electron energy-loss spectroscopy. A new assignment of the principal features indicates that the parallel modes are softer than predicted by the near-neighbor central force-constant (NNCFC) model. It is proposed that H parallel modes are consistently soft on fcc (111) and hcp (0001) surfaces; the implications of this vibrational mode analysis on both the utility of the NNCFC model and the accuracy of various theoretical models for H–metal bonding are discussed.

The bonding of H to transition metals is important to applications as diverse as catalysis and embrittlement, and by virtue of its simplicity, has been frequently studied as a model for adsorption. Unfortunately, very few surface probes have the sensitivity to reliably determine the properties of adsorbed H; however, high-resolution electron energy-loss spectroscopy (HREELS) is sensitive to H, and comparison of calculated and observed vibrational spectra have provided quantitative tests of our understanding of chemisorption. A near-neighbor central force-constant (NNCFC) model[1,2] is often used in the interpretation of HREEL spectra; when both the symmetric and asymmetric vibrations (ν_{sym} and ν_{asy}) of multiply coordinate species are observed, the model allows absorption geometries to be calculated. The NNCFC model has been experimentally confirmed for a variety of $(\mu_2\text{-H})M_2$ transition-metal hydrides;[3] however, it has not been rigorously tested when applied to the adsorption of H on metals, since few structural studies have been able to provide independent determinations of H adsorption geometries. HREELS studies by Conrad and coworkers[4] and recent surface linearized augmented plane-wave (SLAPW) calculations[5,6] have questioned the utility of the NNCFC model applied to H on hcp (0001) and fcc (111) surfaces. Effective medium theory (EMT) studies on H on the low-index faces of Ni (Ref. 7) have questioned not only the validity of the NNCFC model, but also the usual assumption that H is a localized oscillator. An early HREELS investigation of H/Pt(111) by Baró, Ibach, and Bruchmann[2] (BIB), when interpreted by NNCFC, is in reasonable agreement with low-energy recoil scattering results.[8] Their assignment of $\nu_{\mathrm{sym}} < \nu_{\mathrm{asy}}$, however, is inconsistent with recent SLAPW calculations.[6] In light of these conflicting results and the importance of the NNCFC model to the interpretation of H-metal vibrational spectra we have reinvestigated the H/Pt(111) system. We conclude that $\nu_{\mathrm{asy}} < \nu_{\mathrm{sym}}$ and explore the implications of the generalization that ν_{asy} is consistently softer than NNCFC predicts for H on all closed-packed trigonal surfaces.

The experiments were performed in a two-tier ultrahigh-vacuum (UHV) chamber providing facilities for Auger electron spectroscopy (AES), thermal desorption spectroscopy (TDS), and HREELS.[9] The spectrometer has a fixed scattering angle of 120°; off-specular measurements were performed by rotating the crystal about an axis perpendicular to the scattering plane. The angle ($\Delta\theta$) between the specular direction and the collection axis in the scattering plane is positive towards the surface plane. The reported incident energies (E_i) are computed from the cathode bias voltage corrected for work functions.[10] The Pt(111) crystal was cut and polished to within 0.5°, mounted with the scattering plane nominally along the [001] direction, and cleaned by oxidation-reduction cycles and Ne-ion sputtering. H coverage was determined by the integrated area under TD spectra. Saturation coverage at 85 K is taken to be 1 ML (1 ML$=1.49\times10^{15}$ cm^{-2}) in accord with He diffraction.[11]

HREEL spectra of a H-saturated surface at $E_i=5.7$ eV are shown in Fig. 1. Two loss features (I and III) are observed for collection angles out of the specular direction at 67 and 153 meV, in agreement with BIB; in the specular direction an additional feature (II) is observed at 112 meV which was not previously reported. Both I and III are significantly broader than the instrumental resolution, II is narrow and difficult to study quantitatively; however, deconvoluting the resolution (typically 8–10 meV) we determine the loss full width at half maximum (FWHM) to be as follows: I, 16±3, II, 4±4; III, 26±4 meV. The linewidths are quantitatively unchanged in spectra taken after annealing to 170 K and recooling and in spectra taken at 170 K. All three features are due to H motion as they shift by $\approx 1/\sqrt{2}$ for D-saturated surfaces, as is shown in Fig. 2. From the variation of the integrated loss intensities as a function of $\Delta\theta$ it is clear that the principal scattering mechanism at $E_i=5.7$ eV for II is dipole scattering as the loss intensity mimics the elastic intensity. The dominant scattering mechanism for both I and III is impact scattering, established by their relatively broad angular dependence.

The E_i dependence of the electron reflectivity and the loss intensities was characterized to unambiguously determine the relevant inelastic scattering mechanisms. The reflectivity of the clean and H-saturated Pt(111) surfaces are shown in Fig. 2. The sharp minima D and F are attributed to image potential surface states in analogy with a recent study of H/Pd(111).[12] Loss-feature angular distributions were studied at extrema $C-H$. Loss I is very weak and difficult to resolve from the tail of the elastic beam at $\Delta\theta=0°$. We quantitatively analyzed the spectra by nonlinear least-squares fits to a Gaussian line shape and polynomial background. The loss-I position and width at $\Delta\theta=0°$ were statistically consistent with the position and width at $\Delta\theta\neq0°$ where I is easily resolved; the loss never exhibited statistically significant intensity enhancement in the specular direction. The data taken at reflectivity maxima C, E, and G readily rule out a dipole cross section with S (the ratio of the dipole loss integrated intensity to elastic integrated intensity) greater than 2×10^{-5}. Baró, Ibach, and Bruchmann reported a dipole moment for I based on the observation of $S\approx4\times10^{-4}$; we suggest that their spectra actually reflect trace H_2O contamination. The most intense loss in EEL spectra at low coverages of H_2O/Pt(111) is the dipole active Pt-OH_2 stretch at 68 meV;[13] a H_2O coverage of ≈0.01 ML could account for the specular intensity of I reported by BIB. Loss II was apparent at $\Delta\theta=0°$ at all incident energies, although very weak at specular spectra taken at D, F, and H, as expected for a feature dominated by dipole scattering. The loss was visible in off-specular spectra (see Fig. 2) taken at $E_i\approx6.6$ and 7.5 eV, suggesting resonance enhancement of a diffuse scattering contribution to the excitation mechanism.[12] Enhancement of I and III as reported by BIB was observed at similar E_i.

He diffraction experiments have established that at 160 K H forms a well-ordered (1×1) layer with all the H in identical three-fold hollows,[11] while thermal-energy atom scattering experiments have established that in the absence of H_2O contamination an ordered layer exists at 80 K.[14] The high reflectivity of the H-saturated surface in our study suggests the presence of the well-ordered (1×1) structure and implies only one H site is present and is responsible for all three losses. The coverage dependence of the losses also supports this conclusion. We adjusted the coverage by both varying the exposure at 85 K and by flashing a saturation exposure to different temperatures (see Fig. 2). HREEL spectra prepared by the two procedures were indistinguishable, precluding association of any of the three losses with the irreversibly occupied subsurface state proposed by Eberhardt, Greuter, and Plummer.[15] I and III were observed with a roughly coverage-independent intensity ratio over the coverage range 0.15–1.0 ML; both losses

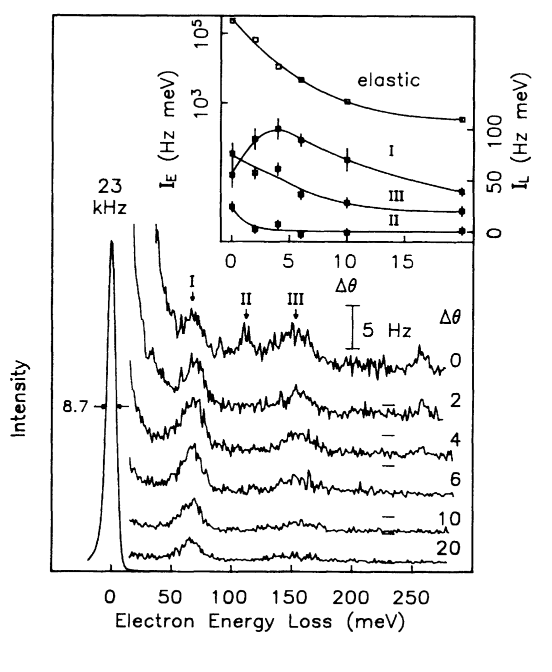

FIG. 1. HREEL spectra of 1 ML H adsorbed on Pt(111) at 85 K as a function of collection angle $\Delta\theta$. The incident energy was 5.7 eV. The hash mark near 230 eV indicates the intensity zero for each spectrum. The inset displays the integrated count rates for the elastic peak (I_E) and the three losses (I_L); note the logarithmic scale for I_E. The lines are drawn to guide the eye; the line through the intensity of loss II is a scaled duplicate of the line through the elastic peak.

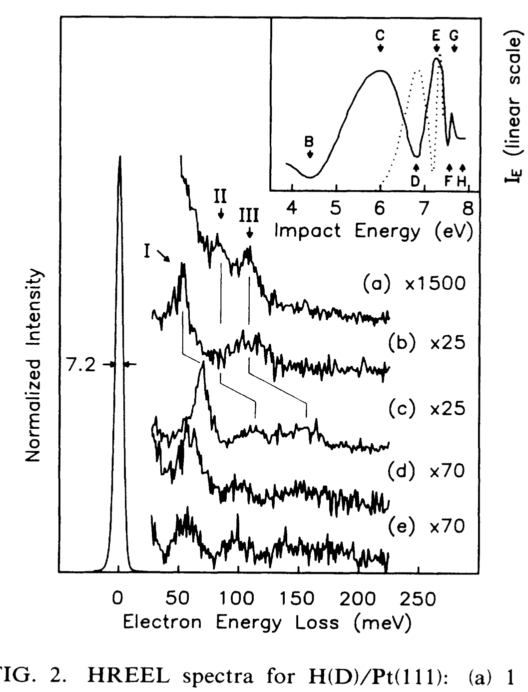

FIG. 2. HREEL spectra for H(D)/Pt(111): (a) 1 ML D, $\Delta\theta=0°$; (b) 1 ML D, $\Delta\theta=4°$; both spectra taken at $E_i=5.7$ eV. (c) 1 ML H, $\Delta\theta=4°$, $E_i=7.4$ eV. (d) 0.2 ML H (0.25 L exposure at 85 K) and (e) 0.2 ML H (1.0 ML flashed to 275 K); both spectra taken at 85 K with $\Delta\theta=4°$, $E_i=7.3$ eV. The inset displays the incident energy dependence of the elastic intensity for a clean (dotted line) and H-saturated (solid line) surface. Extremum A of the H standard surface, not shown, is a broad plateau at 2–4 eV.

TABLE I. HREELS results for saturation H (D) coverages of fcc (111) and hcp (0001) surfaces.

Metal	BE (kcal)	ν_{asy} (meV)	ν_{sym} (meV)	$\nu_{asy}^{0\to 2}$ (meV)	$\nu_{asy}+\nu_{sym}$ (meV)
Ni[a]	63[b]	88(67)	139(89)		
Ru[c]	65[d]	102(74)	141(101)	192(141)	235
Rh[e]	61.5	93(69)	136(103)	180(128)	
Pd[f]	62.5	96(72)	124(89)	175	212
Pt[g]	60	67(51)	112(84)	153(108)[h]	

[a]Reference 20.
[b]Binding energies are taken from references contained in Ref. 16 except where noted.
[c]Reference 4.
[d]Reference 17.
[e]The losses from Ref. 21 are assigned as detailed in the text.
[f]Reference 12 and personal communication.
[g]This work.
[h] $\nu_{asy}^{0\to 2}$ and $\nu_{asy}+\nu_{sym}$ are unresolved.

shifted to lower frequency at low coverages: for I, ≈ 60, and for III, ≈ 140 meV. Loss II was observed at $\Delta\theta = 0°$ with an intensity, normalized to the elastic, that decreased with decreasing coverage. Inadequate intensity in specular scattering prevented its characterization at coverages less than 0.5 ML; however, at these low coverages, as reported earlier by BIB, a loss is observed in off-specular spectra near 100 meV for E_i near 7.4 eV and is attributed to II. The observation of all three losses at all coverages suggests that none of them are due to binding to a defect site or an impurity since these sites are not expected to be in equilibrium with the threefold hollow at 85 K.

The losses are attributed to one species, H in a threefold hollow, and assigned in Table I. Rush, Cavanagh, and Kelly have recently reported inelastic neutron scattering (INS) spectra for H on Pt black[18] with three distinct losses at 65, 116, and 164 meV, with the loss at 65 meV approximately twice as intense as that at 116 meV. For adsorbed H, the normal modes have comparable cross sections;[19] thus the INS is consistent with I being the doubly degenerate ν_{asy}. The assignment of II is consistent with its dipole activity as ν_{sym} is the only fundamental of A_1 symmetry. The assignment of III to unresolved overtone ($\nu_{asy}^{0\to 2}$) and combination losses ($\nu_{asy}+\nu_{sym}$) naturally accounts for the energy of the feature. Since III is unresolved with our instrumental resolution of 8 meV, the width of the two components must be of the order of 15 meV, consistent with the width of the ν_{asy} fundamental.

Table I includes a compilation of available HREELS data for H adsorbed in the threefold hollow of close-packed metal surfaces. The Ru (Ref. 4) and Pd (Ref. 12) mode assignments are taken from the HREELS of Conrad and co-workers. Ho, DiNardo, and Plummer did not definitively assign their H/Ni(111) spectra as both losses were dominated by impact scattering;[20] we have assigned the losses based on the INS assignment of analogous features on Raney Ni.[19] The tabulated losses for H/Rh(111) were originally assigned by Mate and Somorjai[21] to transitions from the ground state to delocalized bands of H excited states in accord with the EMT calculations of Puska and Nieminen.[7] We have reassigned their spectra to the two fundamentals and first overtone of H in a threefold hollow. Our proposed mode assignment for H/Pt(111) is supported by comparison with the Ni, Ru, and Pd data, and the consistency of the five surfaces motivated our reassignment of the H/Rh(111) data.

The ν_{sym} in the table appear correlated with binding energy (BE). As one goes down the group-VIII metals, Ni,Pd,Pt, ν_{sym} decreases as BE decreases; across the second row metals, Ru,Rh,Pd, ν_{sym} exhibits the same trend, however Rh and Pd are inverted with respect to binding energy. The H binding energy on Rh is considered anomalously low.[22]

The ν_{asy} do not exhibit a systematic trend, however the ratio $\nu_{asy}/\nu_{sym} \equiv \mathcal{R}$ is approximately constant at 0.68 ± 0.07 for the five metals. If one assumes the M—H bond length is the sum of the metal atomic radius and a fixed H radius of 0.56 Å (consistent with known structures), the NNCFC model predicts $\mathcal{R}$ to lie in the range 0.93–1.02 in the order following: $\mathcal{R}_{Ni} < \mathcal{R}_{Ru} \approx \mathcal{R}_{Rh} < \mathcal{R}_{Pd} < \mathcal{R}_{Pt}$. The observed ν_{asy} are consistently softer than implied by NNCFC; experimental values of $\mathcal{R}$ are 69 ± 6 % of the NNCFC prediction. Hydrogen on the closest-packed Fe(110) surface provides additional evidence for soft ν_{asy}. LEED (Ref. 23) has determined the adsorption site to be the pseudothreefold hollow. NNCFC and the experimental geometry predict $\mathcal{R} = 1.23$; however, the vibrational spectrum for H/Fe(110) (Ref. 24) consists of a dipole active mode at 131 meV and a nondipole mode at 109 meV which, if assigned to ν_{sym} and ν_{asy}, respectively, determine $\mathcal{R} = 0.83$. The experimental $\mathcal{R}$ is 67% of the predicted value, in agreement with the 69% softening found for threefold coordinated H on fcc and hcp metals. This softness cannot be easily accounted for by considering next-nearneighbor or longer interactions. In particular, a sum of Morse potentials over a 22-metal-atom cluster still gives a $\mathcal{R}$ that agrees with NNCFC to within 6%. Inclusion of a M—H—M bond-angle-bend force constant will result in stiffer ν_{asy}. The failure of the NNCFC and its logical extensions suggests that the vibrational properties of H are not quantitatively described by a localized bonding interaction. As suggested by Feibelman and Hamann,[5] the soft ν_{asy} can be motivated by consideration of the interaction of the H with the electron density which has relaxed at the surface, weakening the corrugation. The fact that all six surfaces exhibit roughly the same deviation of $\mathcal{R}$ from the predicted value from NNCFC implies that the softening of ν_{asy} is dominated by the local structure of the hollow site and not by the chemical details of the M—H interaction.

The softness of ν_{asy} provides insight into the acuity of recent theoretical models of H adsorption. Using the generalized valence bond (GVB) method, Upton and Goddard[25] have calculated the vibrational frequencies for H adsorbed on (111) facets of a 28-atom Ni cluster. Their calculated frequencies ($\nu_{sym}=150$, $\nu_{asy}=140$ meV) result in an $\mathcal{R}$ of 0.91, higher than observed; however, their $\mathcal{R}$ is 66% of the NNCFC prediction for the calculated geometry. The GVB technique, while consistently overestimating the potential corrugation, contains the essential feature of the softening of ν_{asy}. For H/Ni(111) the EMT frequencies generated by Puska *et al.*[7] ($\nu_{sym}\approx 72$, $\nu_{asy}\approx 38$ estimated from the band centers) result in an $\mathcal{R}$ of 0.53, lower than observed, yet 60% of the NNCFC prediction for the calculated geometry. This indicates that EMT is underestimating both the perpendicular and parallel corrugation; however, the preferential softening of ν_{asy} with respect to ν_{sym} is evident in the calculation. SLAPW calculations have predicted $\mathcal{R}=0.71$ and 0.69 for H/Ru(001) (Ref. 5) and H/Pt(111),[6] in excellent agreement with experiment and in 70% and 57% discord with NNCFC, respectively. The calculated frequencies ($\nu_{sym}=140$, $\nu_{asy}=100$ meV) for H/Ru agree quantitatively with experiment; however, the calculated frequencies ($\nu_{sym}=166$, $\nu_{asy}=114$ meV) for H/Pt are significantly larger than observed. The apparent discrepancy in the H/Pt frequencies is notable[6] since the SLAPW technique was quantitatively correct in previous applications. It is interesting that the SLAPW calculations result in a stronger H-Pt BE than H-Ru (2.65 versus 2.40 eV), correlating with the calculated vibrational frequencies but in disagreement with the very low BE of H-Pt.

Support for this research was provided by the National Science Foundation—Solid State Chemistry Grant No. DMR-8413561. We wish to thank P. J. Feibelman and D. R. Hamann for a copy of their work prior to publication and enlightening discussion.

[1] H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic, New York, 1982).

[2] A. M. Baró, H. Ibach, and H. D. Bruchmann, Surf. Sci. **88**, 384 (1979).

[3] M. W. Howard, U. A. Jayasooriya, S. F. A. Kettle, D. B. Powell, and N. Seppard, J. Chem. Soc. Chem. Commun. 18 (1979).

[4] H. Conrad, R. Scala, W. Stenzel, and R. Unwin, J. Chem. Phys. **81**, 6371 (1984).

[5] P. J. Feibelman and D. R. Hamann, Surf. Sci. **179**, 153 (1987).

[6] P. J. Feibelman and D. R. Hamann, Surf. Sci. **182**, 411 (1987).

[7] M. J. Puska and R. M. Nieminen, Surf. Sci. **157**, 413 (1985).

[8] B. J. Koelman, S. T. de Zwart, A. L. Boers, B. Poelsema, and L. K. Verheij, Phys. Rev. Lett. **56**, 1152 (1986).

[9] J. A. Stroscio and W. Ho, Rev. Sci. Instrum. **57**, 1483 (1986); J. A. Stroscio, S. R. Bare, and W. Ho, Surf. Sci. **148**, 499 (1984).

[10] P. R. Norton and J. W. Goodale, Solid State Commun. **31**, 223 (1979).

[11] J. Lee, J. P. Cowin, and L. Wharton, Surf. Sci. **130**, 1 (1983).

[12] H. Conrad, M. E. Kordesch, R. Scala, and W. Stenzel, J. Electron Spectrosc. Relat. Phenom. **38**, 289 (1986).

[13] B. A. Sexton, Surf. Sci. **94**, 435 (1980).

[14] B. Poelsema, L. S. Brown, K. Lenz, L. K. Verheij, and G. Comsa, Surf. Sci. **171**, L395 (1986).

[15] W. Eberhardt, F. Greuter, and E. W. Plummer, Phys. Rev. Lett. **46**, 1085 (1981).

[16] P. Nordlander, S. Holloway, and J. K. Nørskov, Surf. Sci. **136**, 59 (1984).

[17] P. Feulner and D. Menzel, Surf. Sci. **154**, 465 (1985).

[18] J. J. Rush, R. R. Cavanagh, and R. D. Kelley, J. Vac. Sci. Technol. A **1**, 1245 (1983).

[19] H. Jobic and A. Renouprez, J. Chem. Soc. Faraday Trans. 1 **80**, 1991 (1984).

[20] W. Ho, N. J. DiNardo, and E. W. Plummer, J. Vac. Sci. Technol. **17**, 134 (1980).

[21] C. M. Mate and G. A. Somorjai, Phys. Rev. B **34**, 7417 (1986).

[22] V. V. Gorodetskii, B. E. Nieuwenhuys, W. M. H. Sachtler, and G. K. Boreskov, Surf. Sci. **108**, 225 (1981).

[23] W. Moritz, R. Imbihl, R. J. Behm, G. Ertl, and T. Tatsushima, J. Chem. Phys. **83**, 1959 (1985).

[24] A. M. Baró and W. Erley, Surf. Sci. **112**, L759 (1981).

[25] T. H. Upton and W. A. Goddard, CRC Crit. Rev. Solid State Mater. Sci. **10**, 261 (1981).