

## Delocalized quantum nature of hydrogen adsorbed on the Rh(111) crystal surface

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We observe, by electron-energy-loss spectroscopy (EELS), excitations between the ground-state band and all low-lying energy bands for the motion of hydrogen and deuterium atoms on the Rh(111) surface. The absence of a deuterium isotope shift for the lowest-energy excitation, the observation of broad energy bands, and good agreement with theoretical calculations for hydrogen on Ni(111) provide strong experimental evidence for delocalized quantum behavior of hydrogen atoms on the Rh(111) surface. We also observe a remarkable energy dependence of the intensity and linewidths of the EELS excitations.

Vibrational spectra for hydrogen adsorption on metal surfaces have usually been interpreted as resulting from the harmonic motion of the hydrogen atoms at well-localized adsorption sites.<sup>1</sup> In this Rapid Communication we present evidence, obtained by high-resolution electron-energy-loss spectroscopy (HREELS), indicating that hydrogen atoms, adsorbed on the Rh(111) crystal surface, exhibit delocalized quantum behavior in their motion. This behavior can be described as the existence of a two-dimensional band structure for motion parallel to the surface. Evidence for this quantum motion of adsorbed hydrogen atoms includes (1) the absence of a deuterium isotope shift for the lowest-energy-loss excitation [this excitation is associated with quantum motion of hydrogen atoms parallel to the Rh(111) surface], (2) broadened energy-loss peaks as a result of the delocalized nature of hydrogen adsorption, and (3) good agreement with theoretical predictions for hydrogen adsorption on the Ni(111) surface by Puska *et al.*,<sup>2</sup> whose calculations indicate that quantum behavior needs to be taken into consideration in the appropriate description for the motion of hydrogen atoms on metal surfaces.

The possibility of quantum motion of atoms on surfaces was originally proposed by Christmann *et al.*<sup>3</sup> in connection with hydrogen chemisorption. They pointed out that, if diffusion barriers are ignored, the de Broglie wavelength resulting from the thermal energy of hydrogen atoms moving parallel to a surface is on the order of 1 Å. Consequently, these authors proposed that the motion of hydrogen atoms parallel to a surface should be described in terms of a band structure with band gaps arising from the diffraction of hydrogen atoms from the two-dimensional periodic potential. In the limit of small diffusion barriers, the band gaps would be approximately equal to twice the appropriate Fourier component of the periodic potential.

More recently, Puska *et al.*<sup>2</sup> have reported the results of detailed calculations for the quantum motion of hydrogen adsorbed on nickel surfaces. As well as supporting the delocalized quantum nature of adsorbed hydrogen, these calculations also indicate that the motion of hydrogen perpendicular to the surface couples strongly to the motion parallel to the surface because of the anharmonicity of the combined perpendicular and parallel potentials and the

delocalized nature of hydrogen adsorption. The coupling between the perpendicular and parallel motions results in both these motions having bandlike properties.

The delocalized quantum model of hydrogen adsorption is in many ways analogous to the nearly-free-electron-gas model, which is commonly used to describe the formation of electronic bands in simple metals. Since hydrogen is bound in a deep potential well perpendicular to the surface, it might form a "hydrogen fog" along the surface, a term we use to describe the delocalized quantum behavior of hydrogen adsorption on a metal surface in the same way as an "electron gas" is used to describe conduction electrons in a metal.

Our experiments with hydrogen and deuterium adsorption on Rh(111) were conducted in a ultrahigh-vacuum chamber with a background pressure of  $5 \times 10^{-11}$  Torr. The electron-energy-loss spectra for hydrogen and deuterium adsorbed on Rh(111) were obtained using a high-resolution electron-energy-loss spectrometer similar to other designs in use.<sup>4</sup> The spectrometer was operated at an overall system resolution between 55 and 65  $\text{cm}^{-1}$ , and at beam energies between 0.5 and 10.0 eV. The rhodium surface was cleaned by cycles of  $\text{Ar}^+$  sputtering,  $\text{O}_2$  treatments, and annealing in vacuum at 1200 K. Surface cleanliness was monitored by Auger electron spectroscopy and HREELS. The most troublesome impurities were  $\text{H}_2$  and CO, which adsorbed from the residual background gases, and boron oxide [with characteristic vibrational frequencies at  $\sim 700$  and  $\sim 1400$   $\text{cm}^{-1}$  (Ref. 5)], which occasionally formed during the  $\text{O}_2$  treatments. At chamber pressures  $\sim 5 \times 10^{-11}$  Torr, CO adsorption was negligible, and background hydrogen adsorption could be kept to less than 10% of a monolayer. The boron oxide could be removed by flashing to 1400 K. An HREEL spectrum of the clean Rh(111) surface was taken before each experiment to ensure that no detectable impurities were present.

Figure 1(a) shows the electron-energy-loss spectra obtained in the specular direction for several coverages of hydrogen and deuterium on the Rh(111) surface at 80 K, as well as for the clean Rh(111) surface. Coverages were determined by comparing the hydrogen thermal desorption yield with that of a  $(2 \times 2)$  ethylidyne overlayer.<sup>6</sup> A coverage of  $\Theta_{\text{H}} = 1.0$  corresponds to one adsorbed hydrogen

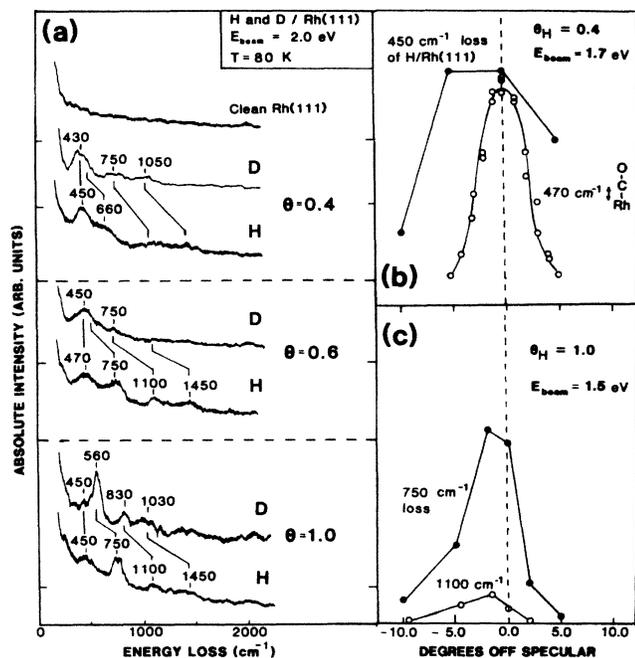


FIG. 1. (a) Electron-energy-loss spectra for hydrogen and deuterium adsorbed on Rh(111). The instrumental resolution is  $65\text{ cm}^{-1}$ . (b) Angular dependence of the  $450\text{-cm}^{-1}$  loss intensity for  $\Theta_H = 0.4$ . For comparison, the angular dependence of the dipole-active Rh-C mode for CO adsorbed on Rh(111) is also shown. (c) Angular dependence of the  $750\text{-}$  and  $1100\text{-cm}^{-1}$  loss intensities for  $\Theta_H = 1.0$ .

atom per surface rhodium atom. For these spectra, the incident electron beam energy was  $2.0\text{ eV}$ . At this beam energy, the Rh(111) surface has an exceptionally high electron reflectivity making it impossible to measure accurately the intensity of the elastic electrons due to saturation of our counting electronics. However, only at beam energies near  $2.0\text{ eV}$  was the lowest-energy excitation at  $450\text{ cm}^{-1}$  clearly visible. No vibrational modes were observed above  $1450\text{ cm}^{-1}$  that could be attributed to the H-H vibration of molecularly adsorbed hydrogen, indicating that the hydrogen adsorbs dissociatively at  $80\text{ K}$  on Rh(111).

First, we discuss the  $\Theta = 0.4$  hydrogen spectrum, which is characteristic of the spectra for low hydrogen coverages. The most prominent feature of this spectrum is the loss peak at  $450\text{ cm}^{-1}$ . Great care was taken to ensure that this excitation was not due to an impurity on the surface. We assign the  $450\text{-cm}^{-1}$  loss to transitions from the ground-state band to the first excited-state band for the motion of hydrogen on the Rh(111) surface. For hydrogen on Ni(111), a surface with the same structure as Rh(111), the calculations of Puska *et al.*<sup>2</sup> indicate that the first excited-state band has *E* symmetry, corresponds mainly to quantum motion parallel to the surface, and is centered  $320\text{ cm}^{-1}$  above the ground-state band, close to the frequency of  $450\text{ cm}^{-1}$  we observe on Rh(111).

If the  $450\text{-cm}^{-1}$  excitation does indeed correspond to transitions to an *E*-symmetry band, then this excitation should have little or no contribution from dipole scattering.<sup>7</sup> This was checked by monitoring the angular depen-

dence of the  $450\text{-cm}^{-1}$  loss intensity, as shown in Fig. 1(b). The intensity decreases at angles away from the specular scattering directions, but in a manner uncharacteristic of dipole scattering [exemplified by a Rh-CO stretch in Fig. 1(b)], indicating that impact scattering dominates for this loss.

A surprising characteristic of the  $450\text{-cm}^{-1}$  loss peak is that no corresponding loss peak exists in the deuterium spectrum at a frequency reduced by a factor  $\sqrt{2}$ , which would be expected if hydrogen and deuterium were bound in a totally harmonic potential; instead, the  $450\text{-cm}^{-1}$  loss appears to shift only slightly in the corresponding deuterium spectrum [Fig. 1(a)]. The calculations by Puska *et al.*<sup>2</sup> predict that all bands, for hydrogen adsorbed on Ni(111), should shift in energy by about a factor of  $\sqrt{2}$ . However, a suitably anharmonic potential for hydrogen adsorption on Rh(111) could provide a possible explanation for the lack of an observed shift in the  $450\text{-cm}^{-1}$  loss. If the potential is suitably anharmonic in the direction perpendicular to the surface, the hydrogen position wave functions can extend further above the surface than the deuterium wave functions due to the larger zero-point motion of hydrogen. Consequently, hydrogen atoms can see a substantially smaller barrier to delocalized motion parallel to the surface than deuterium atoms; this effect tends to cancel the expected isotopic shift. A similar effect has been reported for the motion of the different isotopes of helium on graphite surfaces.<sup>8</sup> Recent calculations by Tomanek, Louie, and Chan<sup>9</sup> for hydrogen adsorbed on Pd(100) indicate that the large interatomic spacing between palladium atoms contributes to the anharmonicity of the hydrogen potential on Pd(100). Therefore, the larger lattice spacing of rhodium compared to nickel should result in a more anharmonic potential for hydrogen adsorption on Rh(111) compared to Ni(111). However, more detailed calculations for both the potential and the motion of hydrogen and deuterium adsorbed on Rh(111) are needed to confirm this interpretation.

Next, we discuss the higher energy-loss peaks that appear in the spectra for adsorbed hydrogen and deuterium. In the  $\Theta = 0.4$  spectra, these excitations are broad and weak. For coverages greater than  $0.4$ , these become narrower and more intense, as well as shifting slightly to higher energies. The reduction in bandwidth at higher coverages can be explained within the delocalized model of hydrogen adsorption as resulting from a reduction in hydrogen mobility due to blocking by neighboring hydrogen atoms.<sup>2</sup> The shifts in energies of the excitations may be due to hydrogen-hydrogen interactions, which become apparent at higher coverages. No ordered overlayers were observed by low-energy electron diffraction (LEED) for hydrogen and deuterium on Rh(111) down to  $T = 80\text{ K}$ .

Within the "hydrogen fog" model, we interpret these higher energy excitations centered at  $750$ ,  $1100$ , and  $1450\text{ cm}^{-1}$  as corresponding to transitions from the ground-state band to excited-state bands, which result from the combination of motion both perpendicular and parallel to the surface. Evidence that the  $750\text{-}$  and  $1100\text{-cm}^{-1}$  excitations correspond to a significant amount of motion perpendicular to the surface comes from off-specular measurements of the loss intensities shown in Fig. 1(c). These

two losses decreased in intensity at angles away from the specular scattering direction in a manner characteristic of dipole scattering. Dipole scattering is expected if these excitations are associated with motion perpendicular to the surface and with transitions between the ground-state band and  $A_1$  symmetry states.<sup>7</sup> Consequently, we assign the 750- and 1100-cm<sup>-1</sup> losses to transitions from the ground-state band to the  $A_1^1$  and  $A_1^2$  bands, respectively, which are predicted to occur at 590 and 1100 cm<sup>-1</sup> for hydrogen adsorption on Ni(111).<sup>2</sup> Because of the low intensity of the 1450-cm<sup>-1</sup> loss, it was not possible to determine the scattering mechanism of this loss. We assign this loss to transitions to the  $E^2$  band, even though there may be overlapping contributions from transitions to the  $A_1^2$  band. The  $E^2$  and  $A_1^2$  bands are predicted to occur at 1090 and 1040 cm<sup>-1</sup>, respectively, for hydrogen adsorbed on Ni(111).<sup>2</sup> If these excitations do indeed correspond to a large degree of motion perpendicular to the surface, then their observed deuterium shift of about  $\sqrt{2}$  is not surprising, since the potential perpendicular to the surface, even though anharmonic, approximates that of a harmonic oscillator.

The higher excited-state bands, as well as the 450-cm<sup>-1</sup> band, involve a significant amount of quantum motion parallel to the surface, as indicated by the broadness of the loss peaks in the HREEL spectra. The excited-state bands are expected to be fairly broad within the "hydrogen fog" model, since the delocalized quantum nature of hydrogen adsorption results in extensive overlap of hydrogen position wave functions for excited states centered over neighboring adsorption sites.<sup>2</sup> Further, the calculations by Puska *et al.* indicate that, for hydrogen on a close-packed surface [like Ni(111) or Rh(111)], the ground-state energy band is fairly narrow,  $\sim 4$  meV. Consequently, at the temperature for which the spectra in Fig. 1(a) were taken (80 K), all the states of the ground-state band should be thermally populated, and vertical transitions ( $\Delta k_{\parallel} = 0$ ) between the ground-state band and the excited-state bands should be observable at any point in the Brillouin zone. Therefore, the observed excitations in the HREELS spectra should have a width dominated by that of the excited-state band. For the  $\Theta_H = 1.0$  spectra in Fig. 1, the full width at half maximum (FWHM) widths of the 450-, 750-, 1100-, and 1450-cm<sup>-1</sup> excitations are, respectively, 110, 110, 95, and 160 cm<sup>-1</sup> after deconvolution of the instrumental resolution of 65 cm<sup>-1</sup>. These experimental values give approximate values of 220, 220, 190, and 320 cm<sup>-1</sup> for the energy bandwidths of hydrogen on Rh(111), which agree reasonably well with the values of 350, 320, 210, and 470 cm<sup>-1</sup> predicted for similar energy bands for hydrogen on Ni(111).<sup>2</sup> The discrepancies may be due to the difference in metals, to finite-coverage effects, or to the dependence of the measured widths on the incident beam energy, as is discussed below.

Other mechanisms, besides delocalization, that can broaden vibrational lines of adsorbates have been considered quite generally by Gadzuk and Luntz<sup>10</sup> and are often found to have a characteristic temperature and/or isotope dependence. Where it was possible to measure the bandwidths for hydrogen and deuterium on Rh(111) under similar conditions, the 750-cm<sup>-1</sup> (560-cm<sup>-1</sup>) and

1100-cm<sup>-1</sup> (830-cm<sup>-1</sup>) bandwidths showed, within experimental error, no isotope or temperature dependence over the 80–200-K temperature range. This isotope and temperature dependence points away from mechanisms such as inhomogeneous broadening from defects or exchange-coupling dephasing, which are expected to have a strong isotope or temperature dependence;<sup>10</sup> other broadening mechanisms, however, cannot be completely ruled out. The observed isotope dependence is consistent though, with the irregular changes in band shapes predicted by Froyen, Holloway, Norskov, and Chakraborty,<sup>11</sup> for the quantum motion of hydrogen and deuterium on Ni(100).

Finally, for hydrogen adsorbed on Rh(111), we have also observed a remarkable dependence of the intensity and widths of the HREELS losses on the beam energy at which the HREEL spectra are taken. First, the 450-cm<sup>-1</sup> loss is only clearly visible at beam energies near 2 eV. Second, the dipole-active 750- and 1100-cm<sup>-1</sup> losses go through a strong resonance near a beam energy of 4.7 eV as is shown in Fig. 2. This figure shows the loss intensities as a function of beam energy, along with the elastically re-

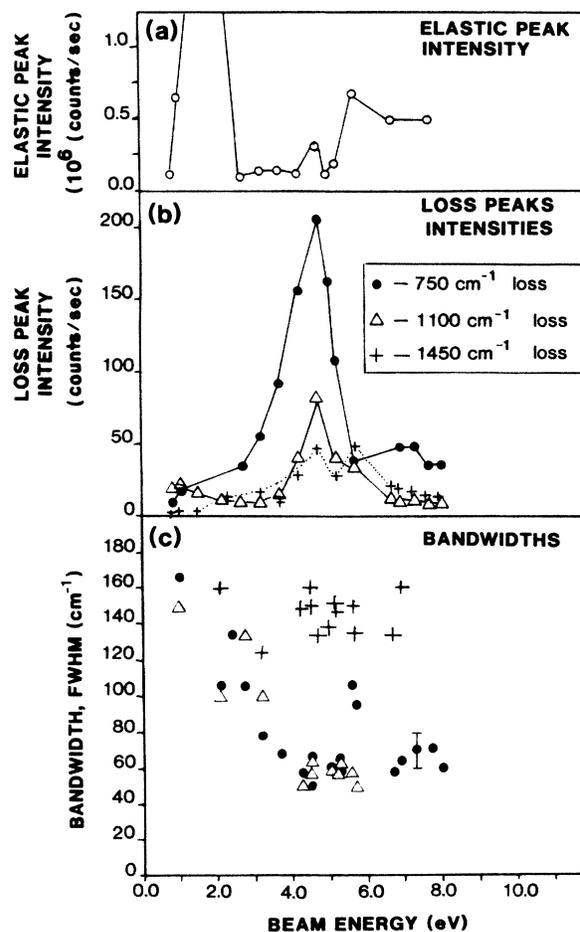


FIG. 2. (a) Elastic peak intensity, (b) loss peak intensities, and (c) bandwidths observed in the  $\Theta_H = 1.0$  HREEL spectra. Bandwidths are given after deconvoluting out the instrumental resolution of 55 cm<sup>-1</sup>.

flected electron intensity and the measured widths of the transitions. Off-specular measurements indicate that the impact scattering is the predominant scattering mechanism for beam energies greater than 3 eV. Similar resonances in inelastic scattering intensities have been observed for adsorbed molecules<sup>12</sup> on other metal surfaces, where the resonances are thought to be due to the incident electrons, at particular beam energies, being trapped for a short period of time in surface or molecular electron states. Further, a dramatic decrease in bandwidths of the dipole-active 750- and 1100-cm<sup>-1</sup> excitations is observed as the beam energy goes from energies (less than 3 eV), where the principal scattering mechanism is dipole scattering, to energies (greater than 3 eV), where the principal scattering mechanism is impact scattering. As far as we can ascertain, this is the first report of any energy dependent linewidth for an excitation in an electron-energy-loss spectrum and as yet is not understood.

To summarize, we have made HREELS observations that strongly favor a delocalized, quantum description of adsorbed hydrogen ("hydrogen fog") over the classical harmonic-oscillator model. Specifically, we have been able to observe excitations between the ground-state band and the broad low-energy bands expected for quantum

motion of hydrogen on a close-packed surface. We also observe that the lowest-energy excitation in the hydrogen spectra appears not to shift in energy in the corresponding deuterium spectra; this excitation is interpreted to result from quantum motion parallel to the surface.

The question remains, however, as to what extent hydrogen is delocalized on other metal surfaces. Vibrational spectra have also been reported for hydrogen adsorption on other close-packed surfaces: Ni(111),<sup>13</sup> Pt(111),<sup>14</sup> and Ru(001).<sup>15</sup> While the data for these systems are incomplete in terms of coverage, beam energy, and angle dependence, the observed excitations can be assigned in a consistent manner to transitions predicted for delocalized quantum hydrogen adsorption.<sup>16</sup> However, we feel that hydrogen adsorption on these metal surfaces should be re-examined more carefully by vibrational spectroscopy for features characteristic of delocalized hydrogen.

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