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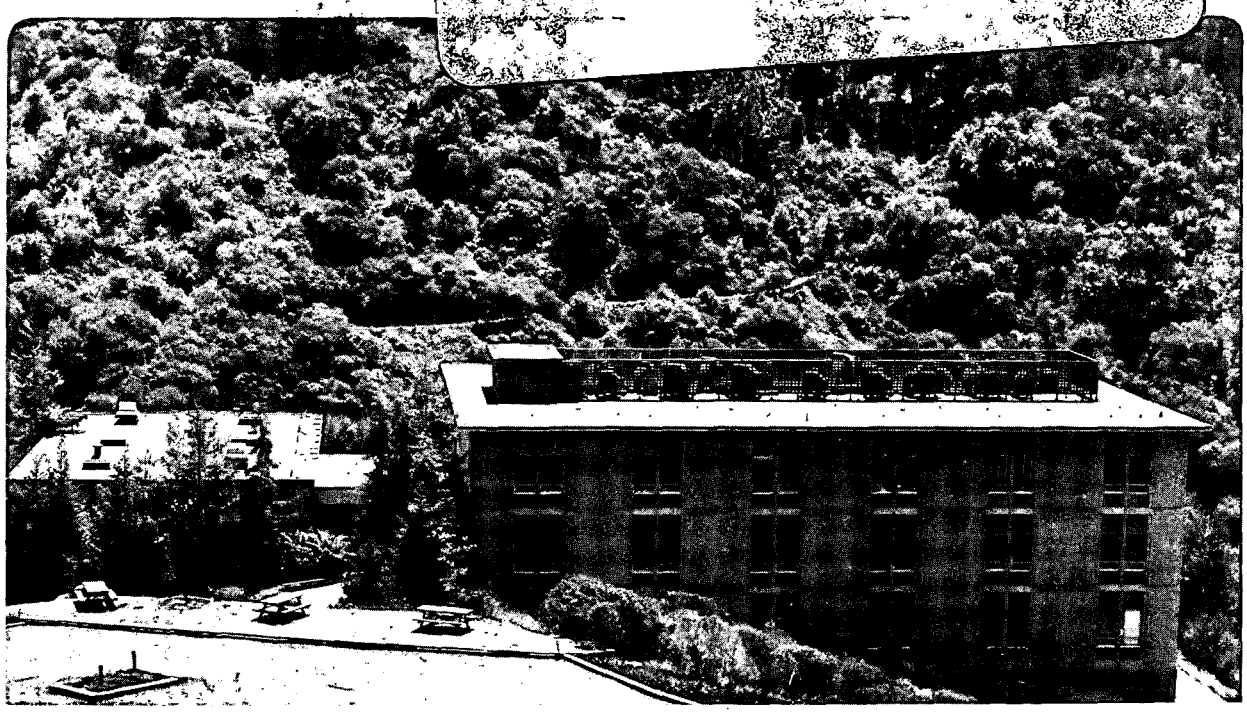

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THE DELOCALIZED, QUANTUM NATURE OF HYDROGEN ADSORBED ON THE RH(111) CRYSTAL SURFACE

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ABSTRACT

We observe, by electron energy loss spectroscopy, excitations between the ground-state band and all low-lying energy bands for the motion of hydrogen and deuterium atoms on the Rh(111) crystal 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) all provide strong experimental evidence for delocalized, quantum behavior of adsorbed hydrogen atoms on the Rh(111) surface.

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Vibrational spectra for hydrogen adsorption on metal surfaces have usually been interpreted to result from the harmonic motion of the hydrogen atoms at well localized adsorption sites [1]. In this letter we present evidence, obtained by high resolution 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. [2], 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 orginally proposed by Christmann et al. [3] 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. In this circumstance the model that describes hydrogen adsorption is 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.

More recently, Puska et al. [2] 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.

Our experiments with hydrogen and deuterium adsorption on Rh(111) were conducted in an ultra high vacuum chamber with a background pressure of 5×10^{-11} torr. The electron energy loss spectra for hydrogen and deuterium adsorbed on Rh(111) were obtained using a high-resolution electron energy loss (HREEL) spectrometer similar to other designs in use [4]. The spectrometer was operated at an overall system resolution between 55 cm^{-1} and 65 cm^{-1} and at beam energies between 0.5 and 10.0 eV. The rhodium surface was cleaned by cycles of Ar^+ sputtering, O_2 treatments, and annealing in vacuum at 1200 K. Surface cleanliness was monitored by Auger electron spectroscopy and HREELS.

Hydrogen and deuterium adsorption on the Rh(111) surface has been previously studied by Yates et al. [5] using thermal desorption spectroscopy and low energy electron diffraction. Based on thermal desorption spectroscopy, these researchers concluded that hydrogen adsorbs dissociatively on the Rh(111) surface; this is supported by our HREEL spectra taken at 80 K, which

show no vibrational modes above 1450 cm^{-1} that could be attributed to the H-H vibration of molecularly adsorbed hydrogen. Also in agreement with Yates et al., we observed no ordered overlayers for adsorbed hydrogen and deuterium on Rh(111).

Fig. 1 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. Coverages were determined by comparing the hydrogen thermal desorption yield with that of a (2x2) ethylidyne overlayer [6]. A coverage of $\Theta_H = 1.0$ corresponds to one adsorbed hydrogen atom per surface rhodium atom. For these spectra, the incident electron beam energy was 2.0 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 eV was the lowest energy excitation at 450 cm^{-1} clearly visible.

First, we discuss the $\Theta = 0.4$ hydrogen spectrum. The most prominent feature of this spectrum is the loss peak at 450 cm^{-1}. Great care was taken to ensure that this excitation was not due to an impurity on the surface. Also, it is unlikely that this excitation is a phonon loss since it is substantially higher in frequency than the maximum bulk phonon frequency of rhodium, 290 cm^{-1} [7]. Therefore, we assign this loss to the excitation of atomic motion of adsorbed hydrogen. However, no corresponding loss peak in the $\Theta = 0.4$ deuterium spectrum exists 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 cm^{-1} loss appears to shift only slightly in the corresponding deuterium spectrum. Consequently, the 450 cm^{-1} excitation cannot be interpreted by using a model based solely on an

harmonic approximation of the hydrogen adsorption potential, since it does not show a deuterium isotope shift.

This excitation can however be interpreted by means of the "hydrogen fog" model of hydrogen adsorption. In the limit of low diffusion barriers, the band gap between the ground-state band and the first excited-state band for parallel motion should correspond to the first Fourier component of the periodic potential parallel to the surface and should therefore not depend strongly on the mass of the adsorbed atom. If the 450 cm^{-1} excitation corresponds to transitions to such a band, this would imply a Fourier component on the order of 0.03 eV, a value in reasonable agreement with one-fourth of the calculated value of 0.1 eV for the potential energy barriers between hydrogen adsorption sites on other closed packed surfaces [8].

If the 450 cm^{-1} excitation does indeed correspond to motion that is mainly parallel to the surface, then this excitation should have little or no contribution from dipole scattering, since the metal effectively screens the dynamic dipole moment of motion parallel to the surface. This was checked by monitoring the angular dependence of the 450 cm^{-1} loss intensity. The intensity decreased at angles away from the specular scattering directions, but in a manner uncharacteristic of dipole scattering, indicating that impact scattering dominates for this loss [9].

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

[2]. The shifts in energies of the excitations may be due to hydrogen-hydrogen interactions, which become apparent at higher coverages.

Within the "hydrogen fog" model, we interpret these higher energy excitations centered at 750, 1100, and 1450 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 and 1100 cm^{-1} excitations correspond to a significant amount of motion perpendicular to the surface comes from off-specular measurements of the loss intensities. These measurements showed that 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 [10]. Because of the low intensity of the 1450 cm^{-1} loss, it was not possible to determine the scattering mechanism of this loss. If these excitations do indeed correspond to a large degree to motion perpendicular to the surface, then their observed deuterium shift of about $\sqrt{2}$ is not surprising, since the potential perpendicular to the surface approximates that of a harmonic oscillator.

The higher excited-state bands, as well as the 450 cm^{-1} 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 wavefunctions for excited states centered over neighboring adsorption sites [2]. However, 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, $\sim$ 4meV. Consequently, at the temperature for which the spectra in Fig. 1 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 FWHM widths of the 450, 750, 1100, and 1450 cm^{-1} excitations are, respectively, 110, 110, 95, and 160 cm^{-1} after deconvolution of the instrumental resolution of 65 cm^{-1}. These experimental values give approximate values of 220, 220, 190, and 320 cm^{-1} for the energy bandwidths of hydrogen on Rh(111), which agree reasonably well with the values predicted for similar energy bands for hydrogen on Ni(111) [see Table 1]. The discrepancies may be due to the difference in metals and to finite coverage effects, as mentioned previously.

Finally, we examine whether results previously reported for hydrogen adsorbed on other close packed surfaces with the same surface structure as Rh(111) can also be interpreted within the delocalized, "hydrogen fog" model. Table 1 lists the experimentally observed excitation energies, which are assigned by us to transitions between the energy bands expected for delocalized hydrogen. Also listed in Table 1 are the calculated transition energies and band widths for hydrogen on Ni(111). In Table 1, the notation A_1^0, E^1, etc. refers to the symmetry of the bands, with the superscript referring to the order of the bands relative to other bands of the same symmetry. The 750 and 1100 cm^{-1} excitations of hydrogen on Rh(111), the 820 and 1140 cm^{-1} of hydrogen on Ru(001), and the 550 cm^{-1} excitation on Pt(111) are assigned to $A_1^0 \rightarrow A_1^n$ transitions since off-specular measurements indicate they are dipole active. The remaining observed excitations listed in Table 1 occur predominantly by

impact scattering. Since there could be a small dipole scattering contribution to these losses, it is not clear whether they should be assigned to non-dipole active $A_1^0 \rightarrow E^n$ transitions or to dipole active $A_1^0 \rightarrow A_1^n$ transitions. Consequently, these frequencies have been assigned by us simply to transitions that are closest to those predicted theoretically for hydrogen on Ni(111). Since many of the excitations observed are very broad, they could also be due to transitions to several overlapping bands rather than to single band as assigned in Table 1.

Table 1 shows that previously reported experimental results for hydrogen adsorbed on closed packed surfaces can be interpreted in a consistent manner within a delocalized, quantum description of hydrogen adsorption. Further, where bandwidths have been reported, they are fairly large, which also supports a delocalized, quantum description for hydrogen adsorption on these surfaces. That not all the predicted transitions have been observed for hydrogen adsorbed on these various surfaces may be due to the very low HREELS excitation probabilities for hydrogen. We have only been able to observe a relatively large number of transitions by HREELS by choosing an appropriate incident beam energy (2.0 eV). Consequently, we feel that hydrogen adsorption on these surfaces, as well as on other metal surfaces, should be re-examined more carefully by vibrational spectroscopy for features characteristic of delocalized, quantum behavior.

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 "hydrogen fog" model is also consistent with previously measured HREELS data for hydrogen on hexagonally closed-packed surfaces of other metals.

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Table 1

Transition energies (and band widths) in cm^{-1} for hydrogen adsorbed on hexagonally closed-packed surfaces.

	$A_1^0 \rightarrow A_1^1$	$A_1^0 \rightarrow A_1^2$	$A_1^0 \rightarrow E^1$	$A_1^0 \rightarrow E^2$
Calculated Ni(111) [2]	590(350)	1100(320)	320(210)	1090(770)
Experimental				
Rh(111)	750(220)	1100(190)	450(220)	1450(320)
Ni(111) [11]	710	1120	--	--
Ru(001) [12]	820	1140	--	1550
Pt(111) [13]	550	1230	--	--

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Figure Captions

Fig. 1. Electron energy loss spectra for hydrogen and deuterium adsorbed on Rh(111). The instrumental resolution is 65 cm^{-1}.

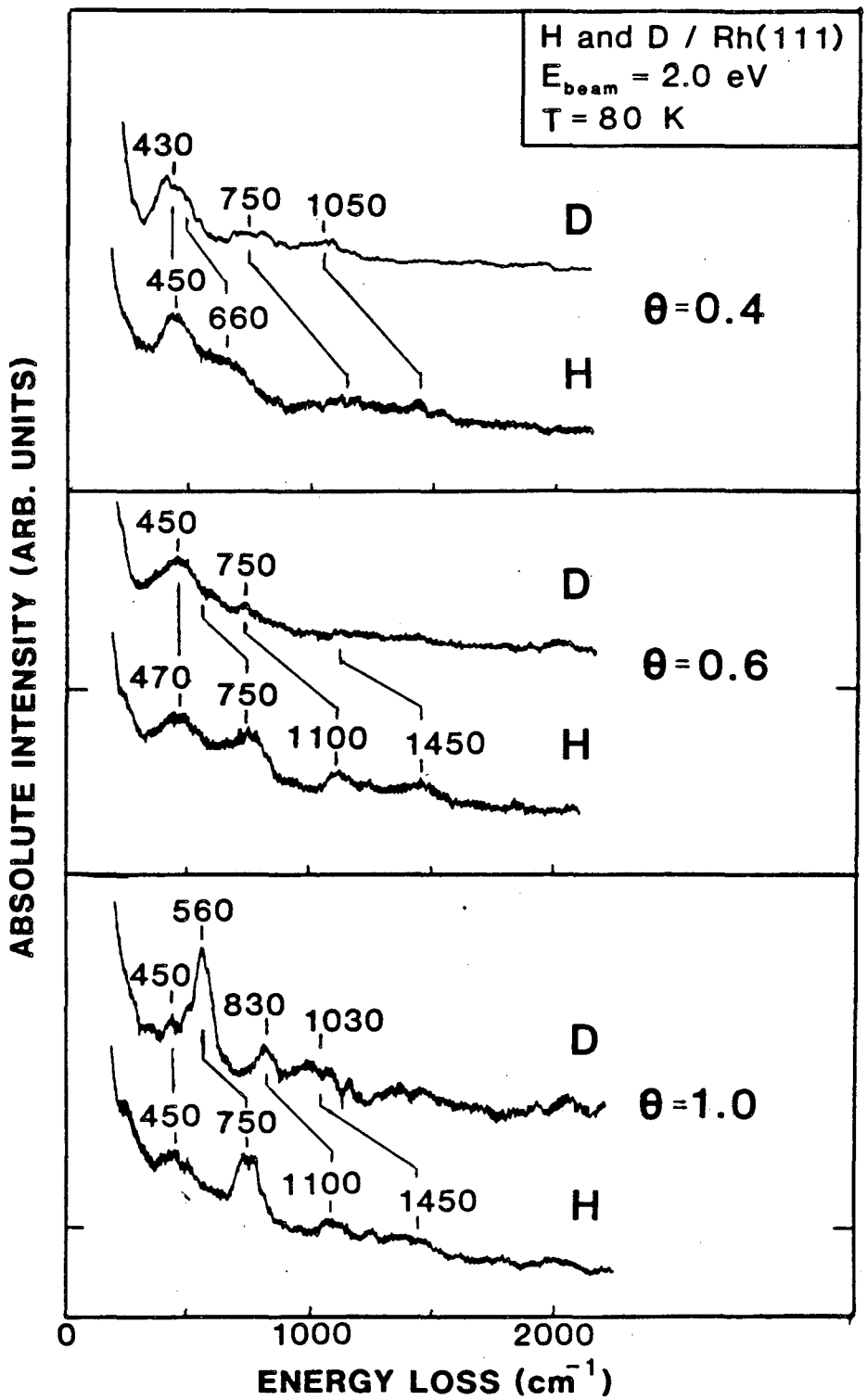

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Fig. 1

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