

Hydrogen Embedded in Ni: Production by Incident Atomic Hydrogen and Detection by High-Resolution Electron Energy Loss

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The vibrational modes of hydrogen embedded in a Ni crystal are shown to be detectable by high-resolution electron-energy-loss spectroscopy and to be unambiguously distinguishable from the vibrational modes of adsorbed hydrogen on the basis of the dependence of the inelastic electron intensity on electron impact energy. The embedded hydrogen has a vibrational frequency of $800\text{--}850\text{ cm}^{-1}$ and is observed to recombine and desorb as H_2 between 180 and 220 K. The absorption of hydrogen into Ni(111) is achieved under UHV conditions by exposure to atomic hydrogen. As much as an equivalent of 8 monolayers has been absorbed.

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While the dissolution of gases into the bulk of metals is pervasive and has long been studied using classical techniques [1], it is only recently that evidence for this process has been provided by ultrahigh-vacuum surface science [2–6] and that the important role of the surface in absorption kinetics has been recognized [7]. However, the use of UHV surface science techniques is frequently stymied by two difficulties. First, dissolution sometimes does not occur under low pressures ($< 10^{-5}$ torr) of gas above the solid because the dissociative absorption is both endothermic and activated, such as in the interaction of H_2 with Ni(111) [8]. Ion implantation of the adsorbate has been used to circumvent this difficulty [9–11] but the structural defects produced in the solid as a result of the high impact energy of the ions cast doubt on the relevance of these systems to the defect-free metal. Second, surface science techniques are largely insensitive to bulk species and much of the existing evidence for bulk adsorbates as obtained from thermal desorption experiments and surface reconstructions is indirect. In this report, we demonstrate that both problems can be overcome. Hydrogen absorption into bulk Ni under low-pressure conditions is shown to be possible without the destruction of the crystalline lattice by exposure of Ni(111) to atomic hydrogen. In addition, we report the spectroscopic identification of bulk species with a technique usually perceived as only sensitive to surface adsorbates, high-resolution electron-energy-loss spectroscopy (HREELS). As Ibach and Mills predicted ten years ago [12], vibrational modes of species buried beneath the surface should be detectable by HREELS because the mean free path of an electron at the low energies ($< 10\text{ eV}$) typically used is long. This study is the first unambiguous demonstration that vibrational modes of species dissolved in the bulk can be detected by HREELS and can be distinguished unequivocally from vibrations of species adsorbed on the surface through the impact-energy dependence of the inelastically scattered electron intensity.

The experiments are carried out in a UHV chamber which is equipped for surface analysis and is precisely coupled to a molecular-beam source. The experimental procedures are similar to our previous studies [13]. Ex-

posure of Ni(111) to $< 10^{-5}$ torr of H_2 does not produce bulk H as confirmed by the thermal desorption trace and HREEL spectrum in Fig. 1, curve *a*, and Fig. 2(a), respectively, which exhibit features typical of a monolayer of chemisorbed H. The desorption maxima at 380 and 340 K correspond to the recombinative desorption of chemisorbed H and saturate at coverages of 0.5 and 1.0 ML (monolayer), respectively [14–16]. In previous work, we assigned the two loss features in the HREEL spectrum at 1170 and 955 cm^{-1} to the symmetric and antisymmetric stretch of H occupying a threefold hollow site in a (1×1) H ordered overlayer [17].

However, we reasoned that it should be possible for incident H atoms to penetrate below the surface because their initial energy level is 39 kcal/mol above the barrier to absorption into Ni and their absorption is exothermic by 48 kcal/mol [1]. To demonstrate this, we generated atomic H by thermal dissociation of H_2 over a 1800-K tungsten filament positioned ~ 0.25 in. from the front face of the crystal [18,19]. The H_2 is introduced as a molecular beam passing through the filament before impinging on the crystal. This procedure results in a flux of both atomic and molecular hydrogen and of unaccelerated ions and electrons on the crystal. The charged particles are determined to have no effect [19]. The flux of atomic H is determined to be $1 \times 10^{14}\text{ cm}^{-2}\text{ s}^{-1}$ [19].

Figure 1, curves *b–d*, show thermal desorption spectra measured after exposure of the crystal held at 130 K to atomic H. At the lowest exposures, not shown here, only the high-temperature desorption features are observed. These surface sites are populated both by chemisorption of atomic H and by the dissociative chemisorption of H_2 . Once the surface sites have been saturated, two other desorption features at 185 and 215 K appear. Unlike the high-temperature features, the low-temperature features can only be populated by atomic H incident on the crystal. The initial sticking coefficient of atomic H into these features is determined to be 0.05 ± 0.01 [19]. A statistical distribution of isotopes is observed after exposure to a mixture of atomic D and H. Long exposures to atomic H have resulted in an equivalent of over 8 ML of hydrogen desorbing at low temperature. This significant increase in

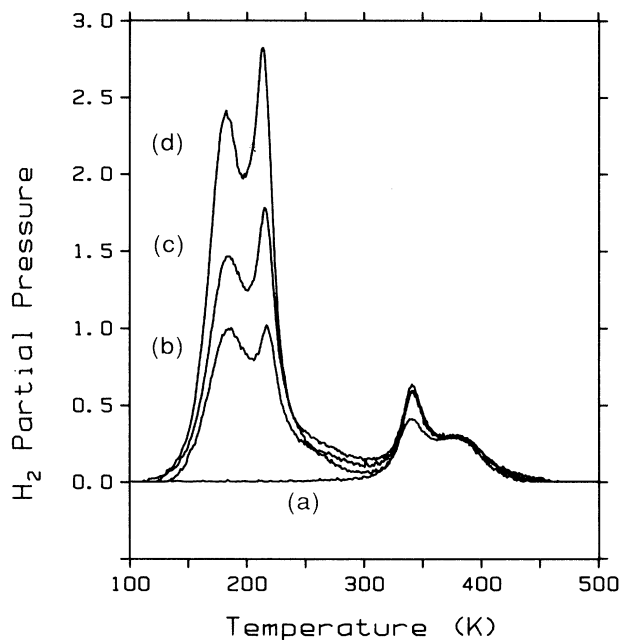


FIG. 1. H_2 partial pressure as a function of crystal temperature for a heating rate of 2 K/s. For curve *a*, the crystal is held at 80 K during exposure to 36000 L of H_2 . For curves *b-d*, the crystal is held at 130 K during exposure to atomic H. Bulk absorbances are given in equivalent ML: curve *a*, 0 ML; curve *b*, 1.7 ML; curve *c*, 2.6 ML; and curve *d*, 3.5 ML.

hydrogen uptake suggests bulk absorption [9-11].

The HREEL spectrum also exhibits an additional feature following exposure to atomic H. This spectrum, Fig. 2(b), is collected from a crystal whose total H uptake is 2.0 ML, with 1.0 ML of the hydrogen desorbing at low temperature. The new loss feature appears at 800 cm^{-1} and the corresponding mode for D appears at 555 cm^{-1} . On the basis of this isotope frequency shift ($\nu_H/\nu_D=1.4$), the feature is assigned to a H vibrational mode. The invariance of the surface H vibrational frequencies, which are a sensitive probe of surface coverage [17], indicate that the H monolayer remains intact in the presence of the H that gives rise to the feature at 800 cm^{-1} . No surface reconstruction or disordering is evident in LEED [19]. These observations suggest that the additional H uptake results from bulk absorption. Raising the crystal temperature to 273 K results in the disappearance of the feature at 800 cm^{-1} concurrent with the low-temperature desorption of H_2 . The resulting HREEL spectrum is identical to that from a H monolayer [Fig. 2(a)].

To demonstrate that the 800-cm^{-1} loss feature is a result of electrons scattered inelastically from H embedded in the Ni, we have measured their intensity as a function of the incident electron energy and their angular distribution. The angular distribution measurement shown in Fig. 3 exhibits a minimum in the scattered electron inten-

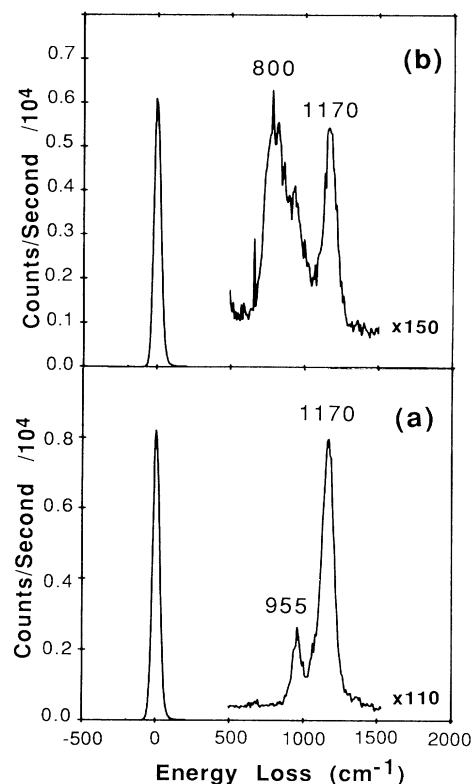


FIG. 2. HREEL spectra collected at 80 K and at 12° off the specular angle with an impact energy of 9.7 eV with respect to the Fermi level. (a) 4800-L H_2 exposure resulting in a coverage of 1 ML. (b) Atomic H exposure of the crystal at 130 K such that the total hydrogen uptake is 2 ML with 1 ML on the surface and 1 ML in the bulk.

sity at the specular angle rather than a maximum indicative of the common dipole excitation mechanism [12]. This observation indicates that dipole excitation is inoperative, which is an expected result for a vibration of an embedded species because its dipole moment is effectively screened by the metal conduction electrons, thereby precluding dipole excitation. Instead, the angular distribution is characteristic of an impact scattering mechanism [12]. The short range of this interaction ($\sim 1\text{ \AA}$) obviates that the mean free path of the incident electron be sufficiently long to reach the buried H and to scatter out of the metal without experiencing any other inelastic collisions. The importance of a long mean free path becomes clear from Eq. (1) which shows that the intensity of an inelastic transition from a bulk species is exponentially dependent on the mean free path [20]:

$$I = I_0 C \sigma A \frac{\Omega}{4\pi} \sum_{l=1}^n e^{-2l/(\lambda \cos\theta)}, \quad (1)$$

where I_0 is the intensity of the electron beam incident at angle θ from the normal, C is the bulk H concentration, σ is the excitation cross section, l is the distance between

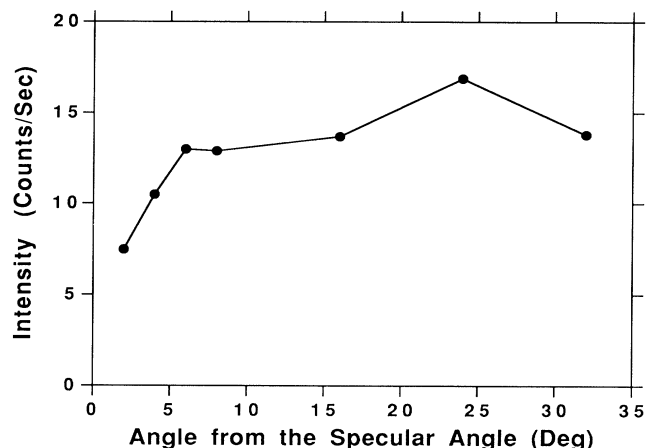


FIG. 3. Absolute intensity at 800 cm^{-1} as a function of the angle from the specular angle. The total hydrogen uptake is 2.2 ML. The electron impact energy is 8.7 eV with respect to the Fermi level of 4.7 eV.

the H layers given by the index i , and λ is the mean free path. According to the universal curve [21], the mean free path of a 8-eV electron (with respect to Fermi level) is long, 24 Å, and decays with approximately an inverse quadratic dependence to 0.5 Å at 25 eV [22,23]. Therefore, if the 800-cm^{-1} loss feature is a bulk vibrational mode, its intensity should exhibit an exponential dependence on electron energy. Figure 4(a) shows this to be the case. The intensity at 800 cm^{-1} decays to zero monotonically as the energy is increased from 8 to 25 eV. The solid line is the intensity calculated from Eq. (1) with the mean-free-path dependence on electron energy taken from the universal curve. It can be seen to describe well the experimentally observed decrease in the intensity. At $\sim 22\text{ eV}$, which is the bulk plasmon frequency expected for Ni [24], the intensity falls to zero because the mean free path is limited by plasmon excitation. In contrast, the intensities of the two modes assigned to surface chemisorbed H are the same at 8 eV as at 25 eV, Fig. 4(b), and oscillate with impact energy as a result of resonances whose origins were not investigated. The cross section for excitation of the bulk mode may also exhibit oscillations with impact energy but it is clear from this result that any such structure is dampened by the steep decay of the electron penetration depth. Therefore, the loss feature at 800 cm^{-1} is assigned to the vibration of H occupying a site beneath the Ni surface.

The H is believed to occupy octahedral interstices, as in Ni hydride [25], because the disappearance of this mode at the specular angle is consistent with the selection rules for impact scattering from a site of octahedral symmetry [12]. The frequency of the bulk H mode is 850 cm^{-1} at the lowest detectable absorbance of an equivalent of 0.4 ML and decreases to 800 cm^{-1} at 1 ML and remains at 800 cm^{-1} for higher absorbances. This change in vibra-

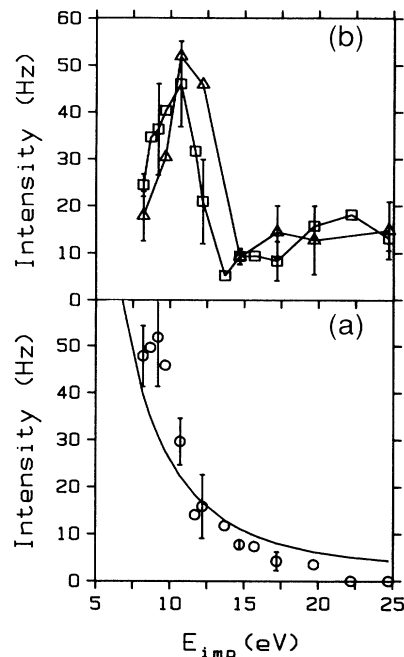


FIG. 4. Absolute intensity of loss features as a function of electron impact energy plotted with respect to the Fermi level. An equivalent of 2 ML of hydrogen is absorbed in the bulk. Crystal temperature is 80 K. Error bars are 70%-confidence limits of a series of 3 to 6 measurements. (a) Bulk H mode at 800 cm^{-1} . Solid line is the intensity calculated from Eq. (1) for $l=2.05\text{ Å}$. (b) Surface H modes at 1170 cm^{-1} (\square) and 950 cm^{-1} (\triangle).

tional frequency is consistent with a 5% expansion of the Ni lattice [19] as in Ni hydride. At the lowest impact energies, it is possible to observe the H embedded about 20 Å into the lattice [19]. A vibrational frequency in the range of 800 cm^{-1} is in reasonable agreement with theory [26] and with inelastic-neutron-scattering results from Ni hydride [27].

A previous study [28] attributed a HREEL feature to H in "near-surface" sites in Nb. The assignment was made on the bases of the broad width and very low intensity of the feature and of the observation that no H_2 was detected to desorb when the loss feature disappeared as the surface temperature was increased. The authors suggest that the feature disappeared because H moved from the near-surface sites into the bulk where it was not detectable. This previous assignment of an HREEL feature to a near-surface mode is in stark contrast to the present study which employs the dependence of the intensity of the inelastically scattered electrons on the electron impact energy to demonstrate unambiguously that species buried deeply in the metal are detectable by HREELS. Our experimental procedure clearly distinguishes adsorbate from adsorbate vibrational modes and is suggested as a general method to identify modes of bulk species.

Vibrations of adsorbates may well have been unknowingly observed in previous spectra but because HREELS has not been generally recognized as a tool for detection of bulk species, they have not been assigned as such. The results presented here, which prove that vibrational modes of embedded species are observable by HREELS, will have impact both on the reinterpretation of previous HREEL spectra and on future assignments. This study also demonstrates how, by exposure to the neutral atomic species, bulk adsorbates can be produced in metals which normally would not exhibit bulk absorption under low-pressure conditions.

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