RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 60, NUMBER 20 15 NOVEMBER 1999-II

# Dissociative chemisorption of hydrogen on Ir(111): Evidence for terminal site adsorption

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(Received 9 June 1999)

Dissociative chemisorption of $H_2$ and $D_2$ on the Ir(111) surface at liquid nitrogen temperature has been studied with high-resolution electron energy loss spectroscopy and thermal desorption mass spectrometry. Quantum delocalized motion of the H adatoms parallel to the surface is responsible for the absence of a significant isotopic frequency shift in the vibrational spectra collected for low surface coverages of H and D. Vibrational coupling between this delocalized motion and iridium phonon modes is suggested by the broad linewidth of these low frequency loss features. As the surface coverage is increased, hydrogen adatoms shift into the terminal adsorption site from the delocalized overlayer that is present at low coverage. The high vibrational frequency of 2030 $\mathrm{cm}^{-1}$ (1460 $\mathrm{cm}^{-1}$) observed for high surface coverages of H (D) adatoms enables unambiguous assignment of this mode to the perpendicular motion of the adatoms adsorbed at the terminal site. This is evidence of terminal site hydrogen adsorption on unmodified single-crystalline transition metal surfaces under ultrahigh vacuum conditions. [S0163-1829(99)51544-0]

Hydrogen adsorption on solid surfaces, particularly those of transition metals, has been one of the most extensively studied areas in surface physical chemistry during the past 25 years. Determination of the local adsorption site of chemisorbed hydrogen adatoms on these surfaces has been of specific interest in these investigations. In particular, an early study by Christmann *et al.*[1] demonstrated that the local adsorption geometry of hydrogen adatoms on Ni(111) could be successfully determined using low-energy electron diffraction (LEED). High-resolution electron energy loss spectroscopy (HREELS), another powerful technique used to probe the local adsorption geometry of hydrogen adatoms due to a strong correlation between coordination and vibrational frequency,[2] is utilized in the present study to ascertain the adsorption geometry of hydrogen adatoms on Ir(111).

In most HREELS studies involving hydrogen adsorption on single-crystalline transition metal surfaces under ultrahigh vacuum (UHV), it has been concluded that hydrogen adatoms generally prefer sites of high coordination.[2] Adsorption at twofold (bridge) sites has been reported, however, on a few surfaces, including W(100),[3–6] Mo(100),[6] and Fe(110).[7] In all cases, the fundamental vibrational modes have loss energies below 1300 $\mathrm{cm}^{-1}$. The data presented here which describe $H_2$ ($D_2$) dissociative chemisorption on Ir(111) will reveal the existence of a strong vibrational mode at 2030 $\mathrm{cm}^{-1}$ (1460 $\mathrm{cm}^{-1}$) which is unambiguously assigned to H (D) adatom terminal site adsorption on the clean Ir(111) surface.

In this paper, HREELS, thermal desorption mass spectrometry (TDMS), Auger electron spectroscopy (AES), and LEED have been utilized in a UHV chamber to study the dissociative chemisorption of $H_2$ and $D_2$ on the hexagonally close-packed Ir(111) surface. A detailed description of the experimental apparatus can be found elsewhere.[8–10] The Ir(111) surface was cleaned by annealing the sample to 1700 K in the presence of $1\times10^{-7}$ Torr of $O_2$, followed by annealing to 1700 K in UHV in order to desorb any trace amounts of chemisorbed oxygen. Argon ion sputtering was performed periodically to ensure surface cleanliness. Following these cleaning procedures, hydrogen TDMS spectra[11] and AES verified surface cleanliness. The clean Ir(111) surface was exposed to $H_2$ and $D_2$ at background pressures ranging between $1\times10^{-8}$ and $1\times10^{-6}$ Torr for times ranging from 100 to 1000 s. These exposures, which varied between 1 and 1000 L (1 L$=1\times10^{-6}$ Torr s), were performed while maintaining the sample temperature at 90 K.

Figure 1 shows TDMS spectra of $D_2$ desorption ($m/e$

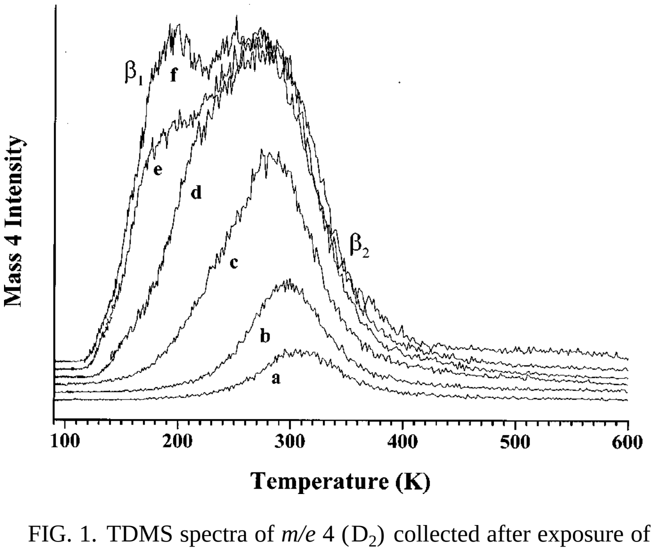

FIG. 1. TDMS spectra of $m/e$ 4 ($D_2$) collected after exposure of the clean Ir(111) surface at 90 K to $D_2$ exposures of [in Langmuir (L)] *a*: 1.0 ($\theta$=0.09); *b*: 2.0 ($\theta$=0.18); *c*: 5.0 ($\theta$=0.44); *d*: 20.0 ($\theta$=0.77); *e*: 100.0 ($\theta$=0.90); and *f*: 1000.0 ($\theta$=1.00). The heating rate for all spectra was 20 K/s.

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=4) after exposure of $D_2$ to the surface at 90 K; thermal desorption spectra for comparable $H_2$ exposures are nearly identical to those displayed here for $D_2$. At low $D_2$ exposures, a single $\beta_2$ desorption peak is observed. The peak temperature of $\beta_2$ in the low coverage limit is 310 K and shifts lower in temperature to approximately 270 K at saturation coverage. This downshift in temperature of $\beta_2$ with increasing D adatom coverage, combined with the symmetrical shape of the peak, are characteristic of second-order recombinative desorption of $D_2$. As the $D_2$ exposure increases above 5 L, a second $\beta_1$ desorption peak appears at approximately 190 K. This $\beta_1$ peak continues to grow in intensity with increasing exposure until the surface saturates at a coverage of $\theta \cong 1$ (one D adatom per surface Ir atom)[12] at an exposure of 1000 L.

In order to determine the local adsorption geometry, HREELS spectra (cf. Fig. 2) were collected as a function of $H_2$ and $D_2$ exposure to the Ir(111) surface at 90 K. It is evident that there are two regions of interest in the vibrational spectra: the intense loss features present at 2030 and 1460 $\mathrm{cm}^{-1}$ for $H_2$ and $D_2$, respectively, and the broad loss features present below 700 $\mathrm{cm}^{-1}$. The broad loss features centered at 525 and 540 $\mathrm{cm}^{-1}$ for 1-L exposures of $D_2$ and $H_2$, respectively, exhibit only a slight isotopic frequency shift.[13] On the Rh(111) surface, H and D adatom coverages of $\theta = 0.4$ produced loss features at 450 and 430 $\mathrm{cm}^{-1}$, respectively, which were assigned to transitions from the ground state energy band to the first excited state band for the motion of H and D adatoms parallel to the surface.[14] The lack of a significant isotopic shift in this previous work was explained as adatom quantum delocalization parallel to the surface. This delocalization, which is attributed to an anharmonic surface potential in the direction perpendicular to the surface, occurs due to H adatom wave functions which extend further above the surface than the D adatom wave functions. Thus, the expected isotopic frequency shift tends to cancel because motions parallel to the surface have a smaller barrier for H adatoms than for D adatoms.[14] Therefore, the broad vibrational features at 525 and 540 $\mathrm{cm}^{-1}$, respectively, are assigned to delocalized D and H adatom motions. While the vibrational spectra of H and D on Rh(111) are most similar to those collected here, there have been many other studies dealing with quantum delocalization,[15–20] including a seminal paper concerning H adatom adsorption on Ni(111),[1] which first made mention of the possibility of atomic, as opposed to electronic, band structure. The broad linewidth of this low frequency band is attributed to both dispersion and to vibrational coupling between delocalized adatom motions and substrate phonons.[21,22] The iridium Debye temperature of 430 K (Debye cut-off frequency of 299 $\mathrm{cm}^{-1}$) is in excellent agreement with the low-intensity vibrational mode located at 295 $\mathrm{cm}^{-1}$ in Fig. 2).

As the exposure is increased to 5 L ($\theta = 0.44$), the vibrational mode located below 700 $\mathrm{cm}^{-1}$, displayed in curves *f* and *b* of Fig. 2 for H and D, respectively, has a narrower linewidth than the same loss feature observed for a 1-L ($\theta = 0.09$) exposure. Comparing the spectra for 1- and 5-L exposures, the linewidth of this loss feature located below 700 $\mathrm{cm}^{-1}$ narrows with increasing coverage of delocalized H and D adatoms. Since this low energy mode broadens as the exposure is increased from 5 to 20 L ($\theta = 0.77$), the coverage of delocalized hydrogen adatoms evidently decreases with increasing coverage above an exposure of 5 L. This leads to the conclusion that above an exposure of 5 L, delocalized adatoms are shifting into the terminal site with increasing exposure. The sharp (1×1) LEED pattern observed for all adatom coverages is consistent with hydrogen adatom delocalization at low coverage and (1×1) terminal-site adsorption of hydrogen adatoms at high coverage.

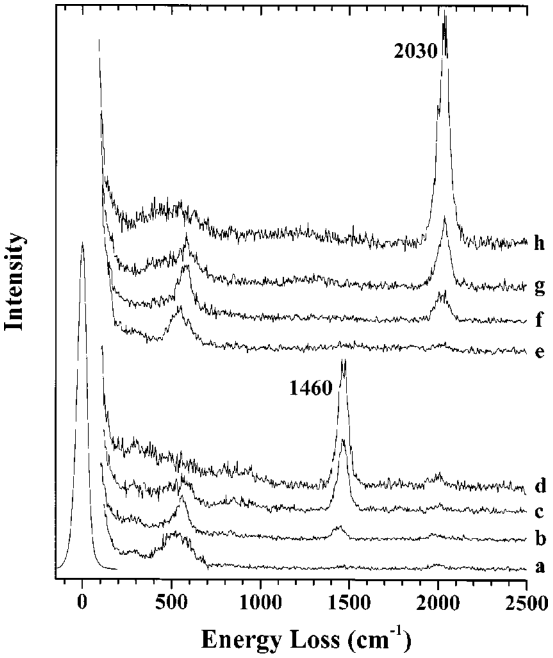

FIG. 2. HREELS spectra collected after exposure of the clean Ir(111) surface at 90 K to exposures of *a*: 1.0 L $D_2$; *b*: 5.0 L $D_2$; *c*: 20.0 L $D_2$; *d*: 100.0 L $D_2$; *e*: 1.0 L $H_2$; *f*: 5.0 L $H_2$; *g*: 20.0 L $H_2$, and *h*: 100.0 L $H_2$. All spectra have been normalized to have the same elastic peak intensity and have been multiplied by a factor of 33 relative to the elastic peak displayed in the figure. The electron beam angle of incidence was 52.5° from the surface normal and a scattering angle of 15° was used in these experiments. The electron impact energy was 5 eV for all spectra shown here. The resolution of full width at half maximum (FWHM) of all spectra was approximately 60 $\mathrm{cm}^{-1}$.

The intense vibrational modes present at 2030 and 1460 $\mathrm{cm}^{-1}$ in curves *h* and *d* of Fig. 2 for saturation exposures of $H_2$ and $D_2$, respectively, are unambiguously assigned to terminal site adsorption of hydrogen adatoms based upon the high frequency of this peak, and the observed isotopic shift of this mode of $\nu_H/\nu_D = 1.39$, which is in excellent agreement with the expected value of $(2)^{1/2}$. There is negligible coupling of this mode to the iridium phonon modes, as expected at this high frequency, since the linewidth of this mode is narrow. The extremely broad loss features centered near 500 and 450 $\mathrm{cm}^{-1}$, respectively, for $H_2$ and $D_2$ saturation exposures are assigned to a small coverage of delocalized hydrogen adatoms on the saturated surface. The broad linewidth of these modes is again a result of vibrational coupling of delocalized adatom motions to substrate phonons. Since the $\beta_1$ thermal desorption peak intensity and the intensity of the terminal site modes at 2030 and 1460 $\mathrm{cm}^{-1}$ increase simultaneously with increasing coverage, the $\beta_1$ thermal desorption peak can be assigned to terminal site hydrogen adatoms. Assignment of the $\beta_2$ thermal desorption peak to delocalized hydrogen is possible at low coverages. However, this assignment is not valid for higher coverages where delocalized hydrogen adatoms are believed to shift to terminal sites with increasing coverage.

Although terminal site adsorption of hydrogen adatoms on unmodified single-crystalline transition metal surfaces under UHV conditions is heretofore unprecedented, there are a number of results that are consistent with our observation of terminal site hydrogen adsorption on Ir(111). Recent work involving hydrogen adsorption on Pt electrode surfaces in an aqueous $H_2SO_4$ solution, studied by infrared absorption spectroscopy, revealed loss features between 1990 and 2080 $cm^{-1}$ which were assigned to terminally adsorbed hydrogen adatoms.[23] Experiments involving x-ray structure determination of $[H_2Ir_4(CO)_{10}]^{2-}$ revealed indirect evidence for the presence of two terminal hydrides in this Ir cluster compound.[24] This result is significant due to the close analogy between molecular metal clusters and metal surfaces that contain chemisorbed species.[25] Another infrared spectroscopic study concerning $H_2$ ($D_2$) adsorption on $Al_2O_3$-supported Ir clusters at pressures ranging from $1\times10^{-4}$ to 400 Torr revealed a loss feature at 2050 $cm^{-1}$ (1490 $cm^{-1}$) which was assigned to terminal site hydrogen adsorption on these Ir clusters.[5,26] Finally, theoretical work involving hydrogen adsorption on Ir(111) by Goddard *et al.* has resulted in a determination of the terminal site as the lowest energy adsorption site on this surface.[27]

In conclusion, the data unambiguously support the experimental observation that hydrogen adatoms occupy the terminal site on Ir(111) at cryogenic temperatures under UHV conditions. At low surface coverages of H and D, quantum delocalized motion of H adatoms is responsible for the absence of a significant isotopic frequency shift in the vibrational spectra. The broad linewidth of the vibrational modes observed below 700 $cm^{-1}$ for delocalized motion of H adatoms is attributed to coupling of this motion to Ir phonon modes. As the exposure increases, the terminal site vibrational mode appears and eventually dominates the vibrational spectra at saturation coverage.

The authors thank Michael Sushchikh, Horia Metiu, Jeremy Kua, and William A. Goddard for useful discussions. Support of this research was provided by the National Science Foundation (Grant No. CHE-9626338).

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