Observation of Molecular H_2 Chemisorption on a Nickel Surface

A.-S. Mårtensson, C. Nyberg, and S. Andersson

Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden

(Received 30 May 1986)

We report the observation of molecular H_2 chemisorption at the edge sites of a stepped Ni (100) surface that is covered with a dense layer of atomic hydrogen. No such state is observed on the flat Ni (100) surface. We suggest that this H_2 chemisorption state can form stably as a result of residual unfilled *d* states at these step sites, while the dissociative channel is blocked by the saturated atomic adsorbate layer.

PACS numbers: 68.35.Bs, 68.35.Ja

Model calculations for jellium surfaces have proposed an adsorption process for H_2 on simple metals which can be summarized as follows[1-3]: The molecule approaches the surface and passes through a physisorption potential well.[4] It crosses an activation barrier and enters a molecular chemisorption state. In this "precursor" state it may move along the surface and hit a site where the activation energy for dissociation is low. Finally, the molecule ends up as two chemisorbed hydrogen atoms. A similar picture is thought to be valid also for real metals, though the activation barrier heights differ substantially from simple and noble to transition metals.[5,6] Physisorbed H_2 molecules have been experimentally observed on Cu and Ag surfaces,[7,8] which are understood to have a large barrier for dissociation.[6,9] In contrast to the dissociative adsorption state, experimental information of chemisorbed hydrogen molecules is scarce. The chemisorption energy for two H atoms is evidently larger than for the H_2 molecule at most examined surfaces and a molecular adsorption state will only be observed provided that the well is deep enough or alternatively, the dissociative channel is blocked in some way, e.g., by a dense monolayer of H atoms.[10]

In this Letter we use vibrational spectroscopy [high-resolution electron-energy-loss spectroscopy (EELS)] to examine molecular chemisorption of hydrogen at a stepped Ni (100) surface, Ni[5(100)×(110)], or simply Ni(510). We will show that dissociative adsorption is followed by molecular chemisorption at the step sites. We find that this molecular state structurally resembles recently observed molecular-hydrogen complexes formed by certain transition metals.[11]

The experiments reported here were performed in an ultrahigh vacuum chamber with a base pressure of $\sim 1\times10^{-11}$ Torr. The vibrational spectra were recorded with use of a high-resolution electron-energy-loss spectrometer operated at an energy resolution of ~ 5 meV and an analyzer acceptance half-angle of 1.3°. All spectra, shown here, were obtained in the specular direction with an electron impact angle of 60° towards the specimen surface normal. The scattering plane is defined by the surface normal and the [001] crystal direction (i.e., parallel to the surface steps). The structure and cleanliness of the specimen were checked by use of low-energy electron diffraction (LEED) and EELS in conjunction. Details about the experimental setup, the crystal preperation, and the hydrogen adsorption studies will be given elsewhere.[12]

The hydrogen (H_2, D_2, and HD) adsorptions and the EELS measurements were carried out at a nickel substrate temperature of about 100 K. Vibrational and thermal-desorption data for Ni(510) exposed to doses between 0.1 and 0.6 L [1 L (langmuir) $=1\times10^{-6}$ Torr-sec] H_2 reveal that the stepped surface has a considerably larger sticking coefficient than the flat Ni (100) surface.[13,14] At 0.8-L H_2 exposure the vibrational loss peaks related to the H-atom adsorbate have decreased in intensity. Increasing the H_2 dose further results in the appearance of new vibrational loss peaks, among them a broad high-energy loss at 398 meV. The isotope shift of this loss was examined by use of D_2 and HD gases. The observed spectra are summarized in Fig. 1. D_2 and HD adsorbates show broad high-energy losses at 286 and 345 meV, respectively. The isotope ratios $\nu_{H_2}/\nu_{D_2}=1.39$ and $\nu_{H_2}/\nu_{HD}=1.15$ agree well with the values for the intramolecular stretch modes of the gas-phase molecules, 1.39 and 1.15, respectively.[15] This proves that a molecular adsorbate is present on the surface. The energy shifts compared to the free-molecular values (e.g., 516 meV for H_2) are considerable, however, and the molecules must accordingly be chemisorbed, since physisorbed molecules show minute energy shifts.[7,8]

The EEL spectra in Fig. 1 also show three pronounced loss peaks in the low-energy region, ν', ν'', and ν'''. It should be noted that the losses associated with the atomic adsorbates, e.g., at ~ 78 meV for deuterium in the D_2 and HD spectra, are weak compared to these new loss peaks. Off-specular measurements have revealed that all the molecular losses are dipole excited. The intensity of the ν', ν'', and ν''' losses have a similar exposure dependence and it seems reasonable to assume that the three loss peaks are related to one single adsorption site. Trace impurities of

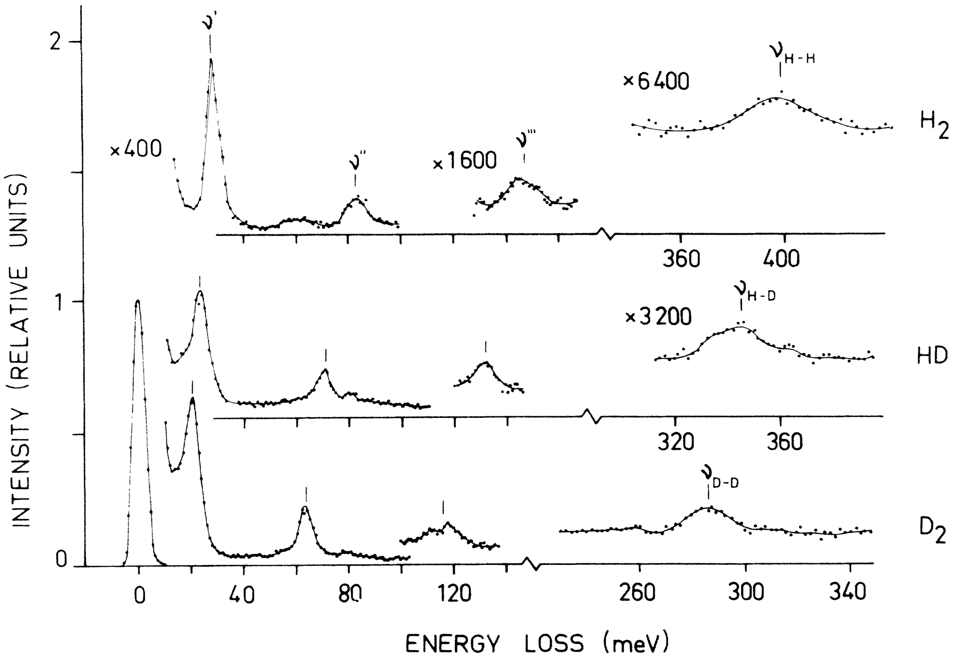

FIG. 1. EEL spectra of H_2, HD, and D_2 adsorbed on Ni(510) at about 100 K. The surface was saturated with the corresponding hydrogen isotope. In the case of H_2 the spectrum was recorded in an ambient hydrogen pressure of about 4×10^{-9} Torr. The impact energy was 1.9 eV.

presumably CO cause the growth of a weak loss at ~60 meV without inducing any observable change in the molecular-hydrogen losses.

An estimate of the amount of adsorbed molecules was achieved by thermal-desorption measurements. The mass spectrometer was tuned to record the D_2 pressure when the specimen temperature was raised after a saturation dose of 21 L D_2. Two different desorption regimes were clearly separated, one centered at ~125 K and a much broader region ranging from ~210 to ~450 K. The last desorption peak was also present after exposures lower than 1.1 L, i.e., when only dissociative adsorption was observed by EELS. The EEL spectra revealed that the molecular adsorption state left the surface in the 125-K desorption peak. After this desorption, the spectrum was similar to the 1.1-L D_2 spectrum. The number of adsorbed D_2 molecules was found to be ~10% of the number of adsorbed atoms by comparison of the amount of deuterium in the two desorption peaks. From a previous EELS study of hydrogen adsorption on the flat Ni (100) surface[13] we know that there is no molecular adsorption state populated at 80 K substrate temperature. The molecules must evidently adsorb at the step sites of the Ni (510) surface. This assumption is well supported by the relatively low concentration of molecules derived from the thermal-desorption measurements. Our LEED observations show that the Ni (510) surface remains unreconstructed during hydrogen adsorption. We accordingly suggest molecular adsorption at the step sites of an unreconstructed Ni (510) surface where all adsorption sites for dissociative adsorption are occupied. From the observed concentration of molecules we judge that every second step site is populated.

Figure 2 pictures schematically some possible adsorption configurations of the kind mentioned above. We will discuss these models with respect to our vibrational spectroscopic observations and make correlations with vibrational data for molecular-hydrogen complexes[11] and H_2 adsorbed on jellium. The vibrational spectra for H_2, D_2, and HD shown in Fig. 1 all reveal four distinct vibrational losses. The energies are listed in Table I. The ν''' lines for H_2 and D_2 are broad and appear to have two components at about 145,152 and 112,120 meV, respectively. A plausible explanation of this observation is that the true ν''' lines are the 152- and 112-meV EELS peaks, which yield an isotope ratio of 1.36, i.e., fairly close to the harmonic value 1.41. The 145- and 120-meV lines would then be due to the overtone $2\nu''$. The isotope ratio $\nu''_{H_2}/\nu''_{D_2}=1.30$ is low and we would predict from a simple anharmonicity analysis $2\nu''_{H_2}/2\nu''_{D_2}=1.22$, i.e., close to the observed value 1.21. The appreciable intensity of $2\nu''$ must be related to this substantial mechanical anharmonicity but also to electrical anharmonicity. For HD, we find that ν''' and $2\nu''$ will prac-

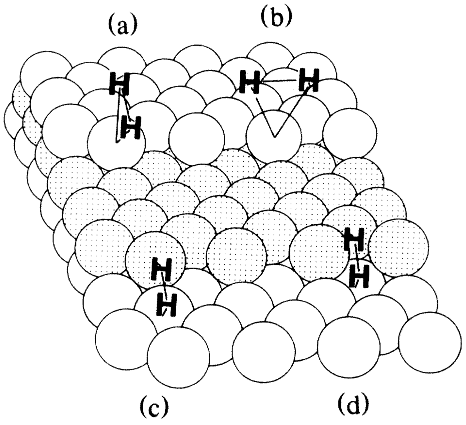

FIG. 2. Model of the Ni (510) surface, showing some different adsorption sites (a)-(d). Case (a) is consistent with the EEL spectra.

tically coincide if we use the isotope and anharmonicity arguments above. This is also confirmed by the EELS peak at 132 meV which is not split but simply rather broad.

We observe no splitting of the HD modes which implies that the molecule must be side-on bonded. Furthermore, we observe for all isotopes four dipole-active fundamental vibrational excitations associated with the molecular hydrogen species adsorbed at the Ni (510) step sites. If we stick to this observation the molecular axis must lie in the (001) plane, i.e., obey the symmetry of the Ni (510) surface which is C_{1h}, and four of the possible six modes can be dipole excited for both H_2 (D_2) and HD adsorbates. If, on the contrary, the molecular axis was perpendicular to the (001) plane only three modes would be dipole active for H_2 (D_2) while HD would break the symmetry and allow all six modes to be dipole excited. The molecular loss peak intensities are large compared to the atomic-adsorbate peaks, which indicates that the molecule is poorly screened by the metal electrons, i.e., it occupies a site where it "sticks" out well above the "electronic" metal surface. The most likely adsorption site that fulfills all these criteria is a single Ni-atom site at the step edge pictured as case (a) in Fig. 2.

Such an adsorption configuration is indeed very similar to the side-on bonded H_2 in the $W(CO)_3(PCy_3)_2H_2$ (Cy is cyclohexyl) complex found by Kubas *et al.*[11] For this complex all six of the expected fundamental vibrations have been located and the relevant mode energies are listed in Table I. Using this complex as a gauge we can give a tentative assignment of the losses observed for the molecular-hydrogen adsorbates on Ni(510): ν' is a bending mode, δ, in the (001) plane; ν'' and ν''' are the symmetric, ν_s, and antisymmetric, ν_a, stretch modes, respectively. From the potential-energy curves for H_2 on jellium ($r_s = 2.65$)[3] we derive the vibrational energies $\nu_s \sim 95$ meV and $\nu_a \sim 115$ meV. This indicates that the smoothening of the electron density at a metal surface will result in lower vibrational energies of these modes.

The intramolecular stretch vibrational energy, $\nu_{\text{H-H}}$, for H_2 in the complex and H_2 adsorbed at the step sites of the Ni (510) surface is much lower than for the free molecule. This energy critically depends on the electronic state of the molecule; e.g., a missing electron in the bonding $1\sigma_g$ orbital[15] as well as partial filling of the antibonding $2\sigma_u$ orbital of the adsorbed molecule[16] lowers $\nu_{\text{H-H}}$. Nørskov and co-workers have calculated $\nu_{\text{H-H}}$ for an H_2 molecule standing upright on a jellium surface.[16,17] When, e.g., the center of the molecule is 1 a.u. out from the jellium edge, $\nu_{\text{H-H}}$ is shifted down by ~ 30 meV compared to the gas-phase value. The decrease in energy of $\nu_{\text{H-H}}$ seems to be proportional to the filling of $2\sigma_u$, and since this antibonding level is lower in energy when the molecule lies down on the surface, we can expect even lower values for $\nu_{\text{H-H}}$ in a parallel configuration.

In the previous discussion we have argued that the molecular-H_2 adsorption state that we observe on the H-saturated Ni (510) surface is bonded to the surface

TABLE I. Vibrational energies (millielectronvolts) for molecular hydrogen on Ni(510) and $W(CO)_3(PCy_3)_2$.

	X_2 on Ni(510)				$W(CO)_3(PCy_3)_2X_2$[a]		
	H_2	$X_2=$ HD	D_2		H_2	$X_2=$ HD	D_2
ν_{X-X}	398	345	286	ν_{X-X}	334	293	~ 236
				$\delta(MX_2)$	~ 41		
ν'	28	23	21	$\delta(MX_2)$	~ 56		40
				$\delta(MX_2)$	~ 77		~ 55
ν''	83	71	64	$\nu_s(MX_2)$	118	98	87
ν'''	~ 147	132	~ 116	$\nu_a(MX_2)$	195	~ 167	~ 140

[a] From G. J. Kubas, to be published.

step sites. The step atoms represent a low-coordination configuration and most likely have a larger d-hole concentration than the average Ni (100) surface atoms. A dense H-atom adsorbate layer is known to reduce drastically the amount of d holes on a flat Ni (100) surface.[18] It is quite likely, however, that step sites still have a substantial number of d holes and remain electronically active in a sense that has been thoroughly discussed with respect to H_2 dissociation at a nickel surface[6,19]: When the H_2 molecule comes close to the step sites, the interaction with the H_2 $1\sigma_g$ electrons causes the itinerant metal s-p electrons to revert to the unoccupied d states, a switch which costs little energy in a metal like Ni, because the s-p electrons and the d electrons share a common Fermi level. This gradual local transfer of s-p electrons to the d shell weakens the Pauli repulsion and allows the molecule to enter the chemisorption regime. Normally dissociative chemisorption would occur along this route, but if that step is blocked somehow, e.g., by a saturated atomic-hydrogen overlayer, a molecular chemisorption state may result.

Calculations for simple[1-3] and noble metals[5,6] show a different behavior. A substantial activation barrier, caused by the Pauli repulsion between H_2 $1\sigma_g$ electrons and the metal band electrons, effectively hinders thermal molecules from entering the true "chemical" region where dissociative[5,6] and possibly associative[1-3] chemisorption occur.

We summarize our observations and conclusions as follows: We have observed a molecular-H_2 chemisorption state on a Ni (510) surface covered with a dense atomic-hydrogen layer. The H_2 molecules adsorb at the step sites of this crystal face. The adsorption occurs essentially nonactivated. We propose that unfilled d states at the step atoms act to reduce the Pauli repulsion barrier between the physisorption and chemisorption regions and allow the molecule to enter the chemisorption regime. The observed H_2 chemisorption state can form stably if the dissociative channel is blocked by a saturated adsorbate layer of atomic hydrogen. Otherwise, the molecule will move, as a "precursor," to adsorbate vacancies in this layer and dissociate.

We thank our collegues John Harris, Bengt Lundqvist, Mats Persson, and Jens Nørskov for numerous valuable discussions, and G. Ertl and G. J. Kubas for supplying us with valuable information and a number of preprints concerning H_2 complexes. Financial support from the Swedish Board for Technical Development and The Natural Science Research Council is gratefully recognized.

---

[1] B. I. Lundqvist, J. K. Nørskov, and H. Hjelmberg, Surf. Sci. **80**, 441 (1979).

[2] J. K. Nørskov, A. Houmøller, P. K. Johansson, and B. I. Lundqvist, Phys. Rev. Lett. **46**, 257 (1981).

[3] P. K. Johansson, Surf. Sci. **104**, 510 (1981).

[4] A physisorbed state is expected on all simple and noble metals [see Ref. 3, and M. Weinert and J. W. Davenport, Phys. Rev. Lett. **54**, 1547 (1985)].

[5] P. E. M. Siegbahn, M. R. A. Blomberg, and C. W. Bauschlicher, J. Chem. Phys. **81**, 1373, 2103 (1984).

[6] J. Harris and S. Andersson, Phys. Rev. Lett. **55**, 1583 (1985).

[7] S. Andersson and J. Harris, Phys. Rev. Lett. **48**, 545 (1982).

[8] Ph. Avouris, D. Schmeisser, and J. E. Demuth, Phys. Rev. Lett. **48**, 199 (1982).

[9] M. Balooch, M. J. Cardillo, D. R. Miller, and R. E. Stickney, Surf. Sci. **46**, 358 (1974).

[10] Thermal-desorption and field-emission spectroscopy have indicated molecular adsorption of hydrogen on W surfaces. See P. W. Tamm and L. D. Schmidt, J. Chem. Phys. **54**, 4775 (1971); E. W. Plummer and A. E. Bell, J. Vac. Sci. Technol. **9**, 583 (1972).

[11] G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini, and H. J. Wassermann, J. Am. Chem. Soc. **106**, 451 (1984); G. J. Kubas, to be published.

[12] A.-S. Mårtensson, to be published.

[13] P.-A. Karlsson, A.-S. Mårtensson, S. Andersson, and P. Nordlander, to be published.

[14] K. Christmann, Z. Naturforsch **34A**, 22 (1979).

[15] G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand, New York, 1945), Vol. 2.

[16] H. Hjelmberg, B. I. Lundqvist, and J. K. Nørskov, Phys. Scr. **20**, 192 (1979).

[17] J. K. Nørskov, H. Hjelmberg, and B. I. Lundqvist, Solid State Commun. **28**, 899 (1978).

[18] Weinert and Davenport, Ref. 4.

[19] J. Harris, S. Andersson, C. Holmberg, and P. Nordlander, to be published.