Vibrational Interaction between Hydrogen Atoms Adsorbed on Pd(100)

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Vibrational energy shifts have been observed for the substitutionally disordered $p(1\times1)(\mathrm{H}+\mathrm{D})$ and $c(2\times2)(\mathrm{H}+\mathrm{D})$ structures on Pd(100). Between 0 and 1 hydrogen concentration the hydrogen vibrational energy shifts by 3.5 and 0.5 meV for the $p(1\times1)$ and $c(2\times2)$ structures, respectively. It is argued that the relatively large energy shift of the $p(1\times1)$ structure is mainly due to adatom-adatom interaction mediated by the metal electrons.

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The lateral interaction between chemisorbed atoms or molecules is of great importance in describing the static and dynamic properties of chemisorbed layers. A number of theoretical models have addressed this problem and four interaction mechanisms have been discussed. Two of them are direct, through space, and two are indirect, through substrate. The mechanisms are dipole-dipole interaction,[1,2] direct overlap between adsorbate electronic levels, indirect interaction mediated by the nonrigid substrate ion cores,[3] and indirect interaction mediated by the metal electrons.[4-10] Vibrational spectroscopy is one experimental method to study adsorbate-adsorbate interactions. With use of isotopic mixtures of varying composition at a constant coverage it is possible to study the effects of dynamical interaction while the static interaction is kept constant. In this way the dynamical effects of one interaction mechanism have been verified. The composition-induced shift of about 5 meV of the CO stretch vibration which has been observed for CO adsorbed on several metals[1,11,12] is satisfactorily described by the dynamical dipole-dipole interaction.[1] In a recent neutron vibrational spectroscopy investigation, dynamical coupling between hydrogen atoms on Raney nickel was observed,[13] but no specific interaction mechanism was proposed. This Letter reports a single-crystal study of energy shifts in the adsorbate-substrate vibration due to dynamical interaction. Electron energy-loss spectroscopy (EELS) and low-energy electron diffraction (LEED) have been used to investigate two structures of H+D on Pd(100). We argue that the observed shift for the more dense structure is caused by indirect interaction mediated by the metal electrons.

The measurements reported here were obtained with use of an EEL spectrometer with an optimum resolution of 4 meV and with an analyzer acceptance half angle of 0.7°. The scattering plane, containing both the incoming and scattered electron beams, is defined by the specimen surface normal and the [001] crystal direction. The experimental chamber and its equipment and the preparation of the Pd(100) specimen have been described elsewhere.[14]

Hydrogen adsorbs dissociatively on the Pd(100) surface[14] and nucleates in $c(2\times2)$ islands at low temperatures.[15] The $(\frac{1}{2},\frac{1}{2})$ LEED beams eventually disappear after increased hydrogen exposure $\{\gtrsim 2\ \mathrm{L}\ [1\ \mathrm{L}\ (\mathrm{langmuir}) = 10^{-6}\ \mathrm{Torr\ sec}]\}$ and the $c(2\times2)$ structure is replaced by a (1×1) structure. Intensity measurements of the $(\frac{1}{2},\frac{1}{2})$ beams, at different substrate temperatures, revealed that (1×1) islands start to form prior to completion of the $c(2\times2)$ structure. By preadsorbing one of the isotopes (i.e., H or D) to the estimated half monolayer coverage (0.5), adsorbing the other isotope to the (1×1) structure, and comparing relative intensities in mass spectra recorded during thermal desorption, the coverage of the (1×1) structure was measured to be 1.0 ± 0.1, indicating a $p(1\times1)$ structure.

In this work vibrational spectra have been measured at a substrate temperature of 80 K for the $c(2\times2)$ and $p(1\times1)$ substitutionally disordered overlayers. The clean Pd(100) surface was exposed to both isotopes simultaneously. The relative concentration was obtained from mass spectra recorded during adsorption with the assumption of equal sticking coefficients for the two isotopes and corrected for the $\sqrt{2}$ lower impingement rate of deuterium. These concentration values were cross checked by measuring the relative intensities in mass spectra recorded during thermal desorption. The agreement was within a few percent.

A typical set of EEL spectra for the $p(1\times1)$ structure is shown in Fig. 1. These spectra were recorded in the specular direction with an impact energy of 1 eV. Each vibrational energy is reproducible to within 0.2 meV. Although the absolute energy calibration of the spectrometer is esti-

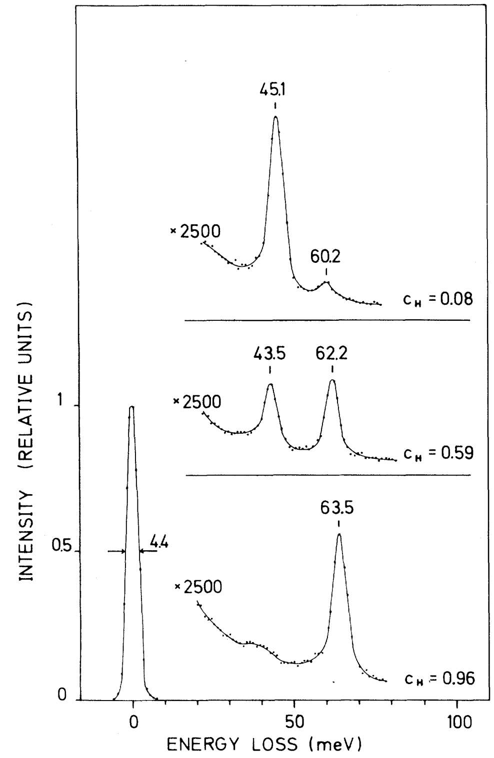

FIG. 1. EEL spectra of Pd(100)/$p(1\times1)$(H + D) at 80 K for various hydrogen concentrations, c_H. Primary electron energy is 1 eV and angles of incidence and detection are 51°.

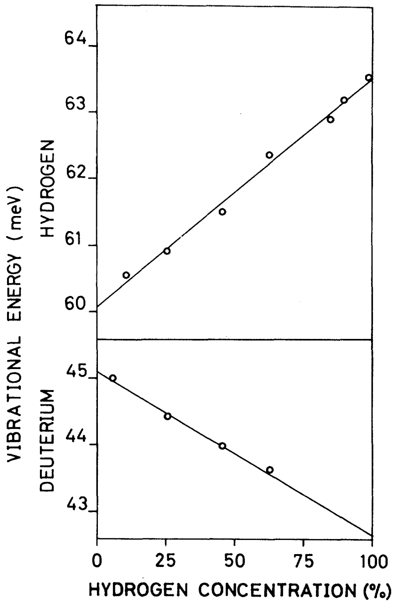

FIG. 2. Vibrational energy of hydrogen and deuterium vs hydrogen concentration; conditions as in Fig. 1. The solid lines are obtained from a least-squares fit of an ATA expression; see text.

mated to be 0.5 meV, the energy values in Fig. 1 are given in tenths of millelectronvolts to emphasize the shift in vibrational energy versus concentration. The 63.5-meV loss ($c_H = 0.96$) has been assigned to the stretch vibration of hydrogen atoms adsorbed in the fourfold hollow site.[14] Angular measurements have shown that this loss is dipole active.[14] The loss at about 44 meV is due to deuterium. The loss intensity is proportional to concentration, the proportionality constant being approximately equal for the two isotopes. The vibrational spectra reveal no extra losses in the 15–300-meV region. This shows that the adsorption does not go beyond one monolayer since otherwise a new adsorption site would be occupied. An upper limit of 0.02 monolayer of additional hydrogen is obtained if hydrogen in a new site has the same cross section as hydrogen in the $c(2\times2)$ structure.

Figures 2 and 3 show the vibrational energies versus hydrogen concentration for the $p(1\times1)$ and $c(2\times2)$ structures, respectively. These data may be analyzed within the average T-matrix approximation (ATA)[1,16] which should be reasonable for small energy shifts and well-separated vibrational energies for the two isotopes. For a substitutionally disordered overlayer ATA gives

$$[\Omega/\omega]^2 \approx 1 + c(K/m\omega^2),$$

where Ω is the concentration-dependent vibrational frequency, ω is the vibrational frequency in the dilution limit, c is the concentration, m is the reduced mass, and K is the sum of force constants felt by an adsorbed atom due to its interac-

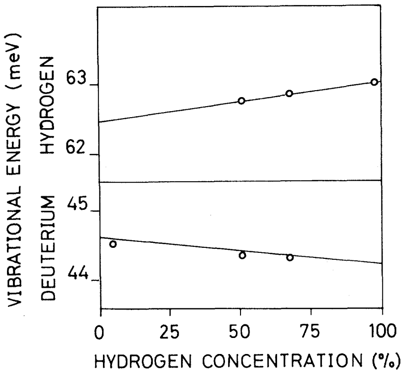

FIG. 3. Vibrational energy of hydrogen and deuterium vs hydrogen concentration for Pd(100)/$c(2\times2)$(H + D); otherwise conditions as in Fig. 1. The solid lines are obtained from a least-squares fit of an ATA expression; see text.

tion (whatever mechanism) with all other adsorbed atoms. The ATA expression agrees well with the experimental data and a least-squares fit gives $K/m\omega^2 = 0.12$ for the $p(1\times1)$ structure and $K/m\omega^2 = 0.017$ for the $c(2\times2)$ structure. The corresponding hydrogen energy shifts (between $c=0$ and $c=1$) are 3.5 ± 0.4 and 0.5 ± 0.4 meV, respectively. Both values are given with 95% confidence level.

As the energy shifts are observed at a constant coverage they must be due to a dynamical interaction between the chemisorbed atoms. Four possible mechanisms have been discussed in the literature: dipole-dipole interaction, direct overlap between adsorbate electronic orbitals, indirect interaction mediated via the nonrigid substrate ion cores, and indirect interaction mediated via the metal electrons. The smallness of the chemisorbed hydrogen atom[17] means that a shift caused by a direct overlap is unlikely. The indirect interaction via the substrate ions[3] should cause a small energy shift because of the small mass ratio of hydrogen to palladium. The maximum positive energy shift has been calculated, with the assumption of nearest-neighbor interaction, to a few tenths of a millielectronvolt.[16]

The dipole-dipole interaction has been investigated in detail in the case of CO adsorbates.[1,11,12,18] For the present experimental conditions it is possible to estimate the energy shift due to this interaction by use of the formula[1,2]

$$[\Omega/\omega]^2 \approx 1 + c\,\alpha_v U/(1+\alpha_e U).$$

α_v and α_e are the vibrational and electronic polarizabilities, respectively. U is the sum of dipole fields in the adsorbate layer. For a dipole-active system the quantity $\alpha_v(1+\alpha_e U)^{-2}$ can be evaluated from the measured loss intensity.[18] The EELS intensities yield values of 0.01 and 0.02 Å^3 for the $p(1\times1)$ and $c(2\times2)$ structures, respectively. U can be calculated in the Thomas-Fermi screening model of Heinrichs.[2,19] For adsorption close to the image plane (which has been found in a calculation using an effective medium theory[20]) U becomes 0.7 Å^{-3} for the $p(1\times1)$ structure and 0.3 Å^{-3} for the $c(2\times2)$ structure.[21] The energy shifts due to the dipole-dipole interaction can now be estimated[22] to be 0.4 and 0.3 meV for the $p(1\times1)$ and $c(2\times2)$ structures, respectively. Thus, dipole-dipole interaction may explain the observed shift for the $c(2\times2)$ structure but cannot account for the energy shift of the $p(1\times1)$ structure.

The indirect interaction mediated by the metal electrons remains to be examined. An adsorbed atom disturbs the metal electronic wave functions. Because of the sharp Fermi surface the screening of this perturbation is not complete and there will be Friedel oscillations in the electron density nearby the adatom. These oscillations will provide a coupling between adsorbed atoms. The nature of the oscillations and the influence on the adatom-adatom static interaction energy has been extensively studied theoretically.[4-9] The interaction energy between two protons on a jellium surface has been calculated, giving[6,8]

$$E_{\text{int}} \propto R^{-5}\cos(2k_F R + \Phi)$$

for large proton-proton distance R. Φ is a phase factor and k_F is the Fermi wave vector. Hence this interaction is oscillatory and of short-range nature. However, it has been shown that application of the free-electron model to the study of hydrogen adsorption on transition metals is inadequate in describing the hydrogen-metal and hydrogen-hydrogen interactions.[7,20] Recent work on the hydrogen–transition-metal interaction has shown that an extended version of the effective-medium theory, which includes hybridization of the hydrogen-induced states with the metal d band, yields good results for the adsorption site, the binding energy, and the vibrational energy.[20,23] If the induced density is calculated in the jellium model, the effective-medium theory can be used to estimate the hydrogen-hydrogen static and dynamic interaction. Such calculations are in progress.[16] The preliminary results are energy shifts of a few millielectronvolts for the $p(1\times1)$ structure and an order of magnitude less for the $c(2\times2)$ structure, which agrees well with the experimental data.

In conclusion, we have shown that only the dynamical indirect electronic interaction can account for the main part of the 3.5-meV vibrational energy shift observed for the $p(1\times1)$ structure of hydrogen on Pd(100). The dynamic as well as the static hydrogen-hydrogen interactions are critically sensitive to the character of the hydrogen-induced electron structure, e.g., the influence of the transition-metal d states. Our work provides novel experimental information of direct relevance for the theory of the hydrogen chemisorption on such metals.

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edged.

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[21] These values have been obtained with $r_s = 4$. They are not changed very much if different values are chosen for r_s.

[22] If we assume that α_v and α_e are the same for the two structures, the values of U and $\alpha_v(1+\alpha_e U)^{-2}$ give $\alpha_v = 0.04$ Å^3 and $\alpha_e = 1.5$ Å^3.

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