

Coverage and Chemical Dependence of Adsorbate-Induced Bond Weakening in Metal Substrate Surfaces

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Strongly coverage-dependent outward relaxation and enhanced in-plane vibrational amplitudes of metal surface atoms have been observed from S- and Cl-covered Ni(001) and Cu(001) by means of temperature- and polarization-dependent surface extended-x-ray-absorption fine-structure measurements. These results explicitly demonstrate the weakening of *both* interlayer and intralayer metal-metal substrate bonds. A model based on adsorbate-metal charge rearrangement explains these chemisorption-induced changes in the geometric and dynamic properties of the metal surface.

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The chemisorption of atoms on metal surfaces affects both the geometric structure and dynamical properties of the substrate. A growing number of experimental and theoretical studies have been devoted to the measurement of these effects and to the understanding of their mutual dependence.¹ However, interpretations of how the adsorbate-metal (*A-M*) bond modifies the metal surface force constants and how these quantities relate to intralayer reconstruction or interlayer relaxation have invariably been limited by either approximate assumptions about the force constants or unavailable information about the structure. In this Letter we report on temperature- and polarization-dependent surface extended-x-ray-absorption fine-structure (SEXAFS) measurements² from *p*(2×2) and *c*(2×2) overlayers of S and Cl on Ni(001) and Cu(001) surfaces. The data provide direct determination of the chemisorption geometry, the substrate interlayer expansion, and the relative mean square displacements for different directions as a function of adsorbate, substrate, and coverage. We find that the first-neighbor *A-M* bond lengths and relative vibrational motions are both insensitive to coverage but are strongly dependent on the strength of the *A-M* bond. By contrast, the chemisorption process induces a weakening of the substrate metal-metal (*M-M*) surface bonds which in these systems depends much less on *A-M* bond strength and almost exclusively on coverage. We present arguments to explain this behavior and show that not only interlayer *M-M* bond weakening, which is usually considered in dynamical studies, but also *intralayer M-M* weakening, which is usually ignored, are *both* essential for describing the data. Our results support recent theoretical calculations³ of adsorption-induced in-plane surface stress and underscore the importance of considering all the modified surface force constants in understanding the dynamical and geometric properties of chemisorption systems.

The S and Cl *K*-edge SEXAFS data were measured at

the Stanford Synchrotron Radiation Laboratory with fluorescence yield detection.² In-plane and out-of-plane coordination shells were emphasized by the orientation of the sample relative to the x-ray polarization. At saturation coverages, sharp *c*(2×2) low-energy electron diffraction patterns were observed for $\frac{1}{2}$ -monolayer S on Ni(001) and Cl on Ni(001) and Cu(001), while for S on Cu(001) only a $\frac{1}{4}$ -monolayer *p*(2×2) pattern was obtained. Below saturation no *p*(2×2) structure could be prepared with Cl on either substrate. The more reactive Ni(001)*p*(2×2)-S surface was periodically flashed at $\sim 300^\circ\text{C}$ to remove possible residual gas adsorption during our measurements at $< 10^{-10}$ Torr.

The fourfold hollow chemisorption site already identified for Ni(001)*p*(2×2)-S,⁴ Ni(001)*c*(2×2)-S,⁴ Cu(001)*c*(2×2)-Cl,⁵ and Cu(001)*p*(2×2)-S⁶ was also established here for the Ni(001)*c*(2×2)-Cl surface with standard EXAFS analysis procedures.⁷ Measurement of all the coordination shell distances r_i shown in Fig. 1 make these assignments particularly reliable. Within our uncertainties of $\pm 0.015 \text{ \AA}$ for r_1 , $\pm 0.02 \text{ \AA}$ for r_2 , and $\pm 0.03 \text{ \AA}$ for r_4 and r_5 , these values indicate the

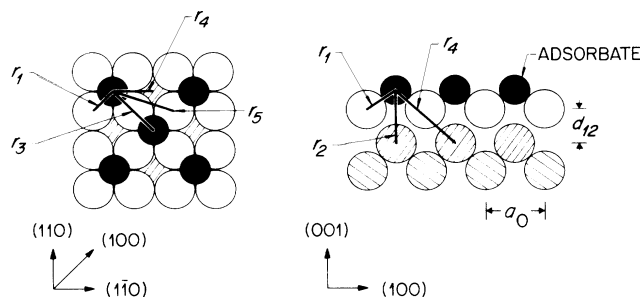


FIG. 1. Top (left) and side (right) views of a *c*(2×2) overlayer structure on a fcc metal (001) surface. Distances r_i and interlayer spacing d_{12} are indicated.

presence of outward interlayer relaxation in the interlayer spacing d_{12} and the absence of metal surface reconstruction or buckling for all five systems. A full account of these geometric structures will be reported elsewhere.⁸

Fourier transforms of the normal incidence SEXAFS data for S on Ni(001) and Cl on Ni(001) and Cu(001) are shown in Fig. 2 at two different temperatures. Peaks labeled 1, 4, and 5 as a result of the corresponding $A-M$ coordination shells r_1 , r_4 , and r_5 are evident for all four systems, whereas the adsorbate-adsorbate ($A-A$) shell at r_3 is observed only for the $c(2 \times 2)$ surfaces, as expected. SEXAFS data taken at grazing incidence (not shown)

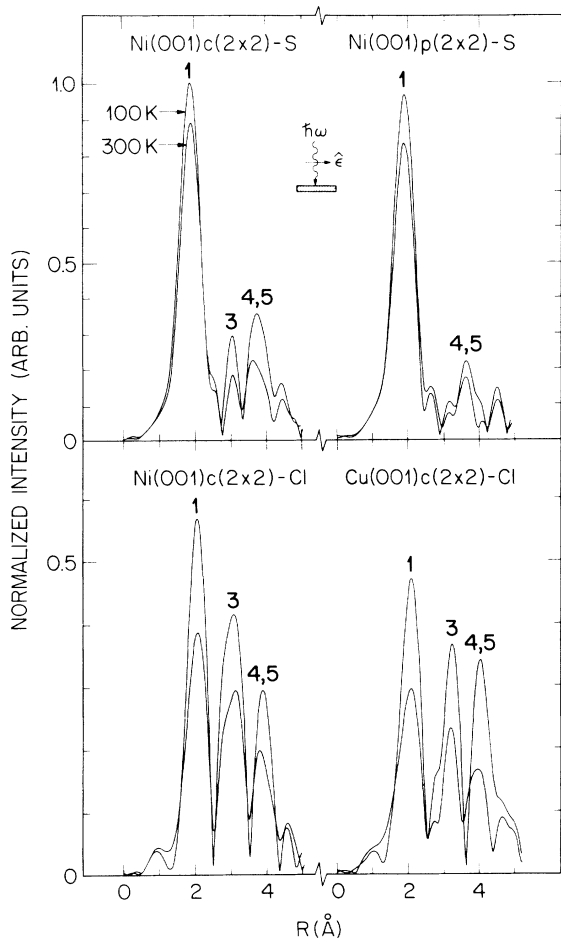


FIG. 2. Fourier transforms of 100- and 300-K S K -edge (top) and Cl K -edge (bottom) SEXAFS data taken at normal photon incidence. The background-subtracted k -multiplied raw data were transformed over identical k ranges of 2.8–10.0 \AA^{-1} . The i th bold-labeled peaks correspond to atoms lying at distances r_i in Fig. 1. Shells at r_4 and r_5 are isolated by appropriately weighted linear combinations of these data with those at grazing incidence (not shown); the ratio of their intensities in the data shown is $I_5/I_4 \sim 5$. The first-neighbor peak intensity in Ni(001) $c(2 \times 2)$ -S, normalized to unity, set the scales for the other three surface systems (note different scales for top and bottom data).

are used to probe the $A-M$ distance at r_2 and, combined with the normal incidence data, to isolate the shells at r_4 and r_5 .^{2,8} The temperature variations of the i th peak intensities are due to thermally induced changes in the EXAFS Debye-Waller factors $\exp[2k^2\sigma_i^2(T)]$,⁷ where $\sigma_i^2(T)$ is the mean square relative displacement between the absorbing and i th-shell atoms. The logarithmic ratio of SEXAFS data taken with a common incidence angle at two different temperatures thus gives $\Delta\sigma_i^2 = \sigma_i^2(T_2) - \sigma_i^2(T_1)$. The adatom geometry is inherently anisotropic, so the Δ_i^2 's for $i=1, 2, 3, \dots$ reflect the relative vibrational motions of different atom pairs lying along different surface directions.^{2,9,10}

Understanding how the dynamic and geometric properties of the metal substrate are affected by the forma-

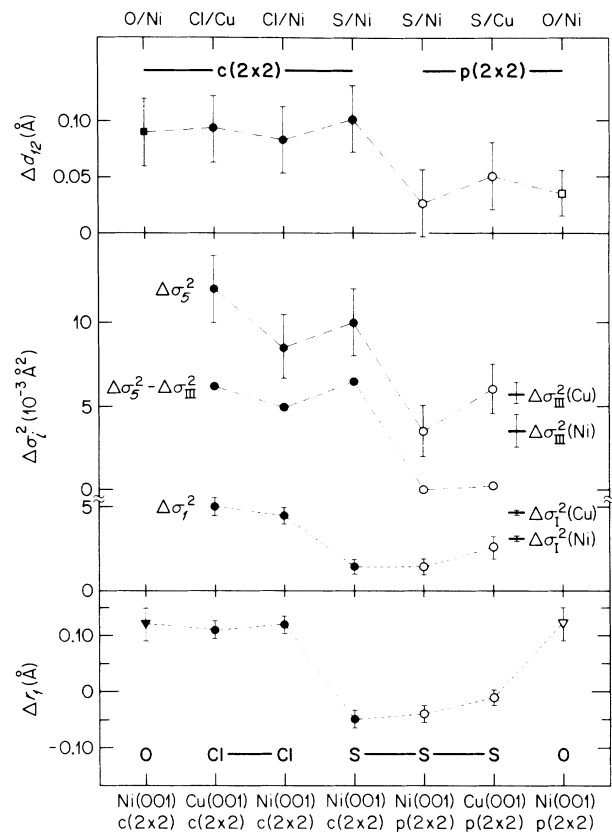


FIG. 3. Correlation of adsorbate-induced interlayer expansion Δd_{12} (geometric property), relative mean square displacements $\Delta\sigma_i^2$ (dynamic property), and ionicity parameter Δr_1 (electronic property) as a function of adsorbate, substrate, and coverage. Filled shapes are for $\frac{1}{2}$ -monolayer $c(2 \times 2)$ over-layers, open shapes are for $\frac{1}{4}$ -monolayer $p(2 \times 2)$. Circles are from this work, triangles are from Ref. 11, and squares are from Ref. 12. Values of $\Delta\sigma_i^2$ and $\Delta\sigma_{ii}^2$ for the first- and third-shells in bulk Cu (Ref. 13) and Ni (Ref. 14) are also shown. Note the strong similarity in trends between $\Delta\sigma_i^2$ and Δr_1 , which depend primarily on adsorbate, and between Δd_{12} and $\Delta\sigma_i^2 - \Delta\sigma_{ii}^2$, which depend primarily on coverage.

tion of different kinds of A - M bonds requires first that the corresponding properties and chemical nature of the A - M bond itself be experimentally well defined. Figure 2 shows that despite identical chemisorption sites for the systems studied here, the absolute intensities of the $i=1$ peaks for S on Ni(001) are about twice as large as those for Cl on Ni(001) and Cu(001). That this is due to dynamic disorder (as opposed to temperature-independent static disorder) is revealed by the measurement of $\Delta\sigma_1^2$, shown in the middle panel of Fig. 3. There is a weak dependence on substrate, but the predominant change in $\Delta\sigma_1^2$ occurs with adsorbate. The smaller relative vibrational motions of the S- M bonds indicate that these bonds are stiffer, and therefore stronger, than the Cl- M bonds. This implies that $\kappa_{S-M} > \kappa_{Cl-M}$, where κ is the force constant, consistent with the S- M stretching frequencies in these systems being larger than those of Cl- M .¹⁵ The strength of the A - M bond is determined by its chemical character, which is related to an ionicity parameter $\Delta r_1 = r_1(\text{expt}) - r_1(\text{calc})$.¹⁶ Here $r_1(\text{expt})$ is the SEXAFS-measured bond length and $r_1(\text{calc})$ is the distance of a hypothetically pure covalent bond made up of adsorbate single-bond covalent and bulk metal radii. Thus, if $\Delta r_1 > 0$ (< 0), the actual A - M bond order is smaller (larger) than unity, i.e., the surface bond has increased ionic (covalent) character. Values of Δr_1 from this work are shown in the bottom panel of Fig. 3, along with values derived from previous r_1 measurements of O-covered Ni(001) surfaces.^{11,16} The striking similarity between the trends in Δr_1 and $\Delta\sigma_1^2$ make apparent the direct relationship between length, strength, and chemical character of the A - M bond.

We now address how the number and strength of the A - M bonds modify the properties of the metal substrate by measuring as a function of coverage and adsorbate two quantities involving M - M surface bonds, Δd_{12} , and $\Delta\sigma_5^2$. We first discuss Δd_{12} , the relaxation between the two outermost (001) metal planes. In this work $\Delta d_{12} = d_{12}(\text{expt}) - d_{12}(\text{bulk})$ is directly obtained from $r_1(\text{expt})$, $r_2(\text{expt})$, and $a_0(\text{Cu, Ni})$. Our results are shown in the upper panel of Fig. 3, along with the Δd_{12} values measured with medium energy ion scattering from O-covered Ni(001) surfaces.¹² We see that the interlayer relaxation is always positive, being uniformly similar in the four $c(2 \times 2)$ surfaces, $(5 \pm 1.5)\%$, and in the three $p(2 \times 2)$ surfaces, $(2 \pm 1.5)\%$. This behavior clearly indicates an out-of-plane M - M surface bond weakening which increases with coverage. The similarity in sign and magnitude of Δd_{12} for the Cl-Cu, Cl-Ni, and O-Ni $c(2 \times 2)$ surfaces could be explained as a consequence of the similar chemical (i.e., ionic) character of their A - M bonds, see Δr_1 in Fig. 3. However, the simple relationship between Δd_{12} and A - M bond character is not obeyed for the Ni(001) $c(2 \times 2)$ -S surface,¹⁷ where Δd_{12} remains unchanged despite the very different Δr_1 value for its S-Ni covalent bond. An analogous breakdown be-

tween trends in Δd_{12} and Δr_1 is also observed for the $p(2 \times 2)$ surfaces, viz. the different O-Ni and S- M bonds induce comparable degrees of substrate relaxation.

To see whether similar adsorbate-induced behavior is also present for the intralayer M - M bonds, we study the coverage dependence of $\Delta\sigma_5^2$. This approach is justified by the following reasoning. $\Delta\sigma_5^2$ represents the nearly parallel relative displacements between adsorbate and fifth-shell metal surface atoms (r_5 is $\sim 70^\circ$ from the normal, see Fig. 1). The relevant nongeometric factors governing the magnitude of $\Delta\sigma_5^2$ are κ_{A-M} , κ_{11} , and κ_{12} , where the latter force constants are for the in-plane and out-of-plane surface M - M bonds. Since κ_{A-M} is itself independent of coverage for these systems (see Δr_1 and $\Delta\sigma_1^2$), any increase of $\Delta\sigma_5^2$ with increasing coverage must reflect a weakening of κ_{11} and κ_{12} .

Our results for $\Delta\sigma_5^2$ are shown in the middle panel of Fig. 3, where an overall enhancement for the $c(2 \times 2)$ over the $p(2 \times 2)$ surfaces and only a small dependence on adsorbate is observed. The effect of comparing different chemisorption surfaces whose bulk substrate atoms have different vibrational and correlated motions can be approximately accounted for by subtracting the corresponding third-neighbor bulk values $\Delta\sigma_{\text{III}}^2(\text{Cu})$ (Ref. 13) and $\Delta\sigma_{\text{III}}^2(\text{Ni})$.¹⁴ These latter values and the difference $\Delta\sigma_5^2 - \Delta\sigma_{\text{III}}^2$ are also shown in Fig. 3 (error bars have been omitted for clarity). The remarkable similarity between the trends of $\Delta\sigma_5^2 - \Delta\sigma_{\text{III}}^2$ and Δd_{12} might suggest that the in-plane weakening of κ_{11} is simply a manifestation of the out-of-plane weakening of κ_{12} , but this cannot be the case. Even if κ_{11} were kept at the bulk metal value, the four softened interlayer surface M - M bonds at 45° would contribute at most 40% to the enhanced vibrational motion along r_5 . In fact, Fig. 3 shows that the nearly parallel vibrational motions of the $c(2 \times 2)$ surface atoms measured by $\Delta\sigma_5^2$ are 2-3 times larger than the corresponding values for either $\Delta\sigma_5^2$ in the $p(2 \times 2)$ surfaces or $\Delta\sigma_{\text{III}}^2$ in the bulk. Our measurements of Δd_{12} and $\Delta\sigma_5^2$ therefore provide direct experimental evidence for adsorbate-induced weakening of interlayer and intralayer surface M - M bonds. Both types of bond weakening, though distinctly different, exhibit a very similar dependence on coverage and insensitivity to adsorbate.

We explain our results using simple physical concepts. The formation of an ionic A - M bond involving metal charge transfer to an electronegative adsorbate creates a dipole layer with positively charged surface metal atoms. Some of this positive charge must also be present in the subsurface layer, but to a lesser extent. The resulting Coulombic repulsion between the first and second metal layers leads to outward relaxation, and the even larger repulsion between the first-layer atoms leads to increased in-plane vibrational motion. The formation of a covalent A - M bond produces similar results even though the bonding charge is now localized between A and M . As

shown by recent cluster calculations,³ there is an analogous repulsion between the incompletely screened interlayer and intralayer metal nuclei, where again the intralayer repulsion is larger. It follows that regardless of whether the A - M bond is ionic or covalent, the magnitude of the surface M - M bond weakening should depend primarily on the total amount of charge removed from the metal, and this is just determined by the *number* of adsorbates, i.e., the coverage, and the *amount* of metal charge removed per adsorbate. Our results, showing interlayer and intralayer M - M bond weakenings which both increase with coverage, are fully consistent with this model. They further imply that in these systems the net amount of metal charge withdrawn (redistributed) to form the covalent S - M and the ionic Cl - M , and O - M bonds must be comparable.

There are other, more general implications of this simple model. Because the chemisorbed atom removes charge predominantly from the first metal layer, the intralayer surface M - M bonds are predicted to be weakened more than the interlayer M - M bonds. Such anisotropic weakening of κ_{11} vs κ_{12} is directly responsible for the surface-atom vibrational anisotropy observed in saturated chemisorption systems.^{2,8} In addition, the dependence of the κ_{11} weakening on not only coverage but also on the amount of charge removed by the adatom provides a framework for understanding the origin of certain adsorbate-induced reconstructions. In the similarly strong chemisorption systems studied here, where no reconstruction is identified within our experimental uncertainties, the amount of charge per atom removed by O, Cl, or S turns out to be comparable. However, as shown by recent calculations for $\frac{1}{2}$ monolayer of C and of O on Ni(001),³ the amount of charge removed by C is substantially larger, explaining why C (and not O) reconstructs that surface.¹⁸ By analogy with C, a very strongly covalent adsorbate, it follows that ionic adsorbates should also induce reconstruction in cases where the amount of metal charge withdrawn per intralayer M - M bond is increased. This can occur on surfaces with comparatively fewer intralayer M - M bonds, e.g., the saturated system of O on Ni(110) reconstructs¹⁹ whereas O on Ni(100) does not.

In summary, we have experimentally shown that both interlayer and intralayer surface metal-metal bonds (force constants) are weakened by the chemisorption process. A simple model was used to explain our results, from which the roles of coverage and adsorbate-metal bond character were elucidated and from which general implications about vibrational anisotropy and adsorbate-induced reconstruction were inferred. The challenge remains for more advanced theoretical approaches to account for these geometric and dynamic phenomena.

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¹For example, see J. Electron. Spectrosc. Relat. Phenom. **44**, 1 (1987), and references therein.

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