

## Adsorbate Structure Determination Using Surface Vibrational Spectroscopy

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We show that lattice-dynamical slab calculations and surface vibrational spectroscopy can be used to obtain adsorbate structural parameters directly.

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Surface vibrational spectroscopy has recently reached a state similar to that of bulk vibrational spectroscopy (inelastic neutron scattering) during the 1950's. The energy and wave-vector dependence of surface vibrations can now be accurately measured throughout the two-dimensional Brillouin zone by means of inelastic scattering of electrons<sup>1,2</sup> or helium atoms<sup>3</sup> on the basis of simple kinematical scattering conditions involving conservation of energy and conservation of wave vector parallel to the surface. Various techniques for the calculation of the dynamical properties of crystal surfaces have also been developed.<sup>4,5</sup> The combination of these new experimental and theoretical techniques for the study of surface lattice vibrations now appears to offer a number of novel opportunities for the study of surface phenomena.

Several possibilities for the exploitation of vibrational spectroscopy as a structural tool have been explored recently. Electron-energy-loss spectroscopy (EELS) and lattice-dynamical calculations applied to the O on Al(111) system<sup>6</sup> were able to account for the inability of low-energy electron-diffraction (LEED) investigations<sup>7</sup> to arrive at the overlayer structure for this system. Similar studies<sup>2,8,9</sup> of  $p(2 \times 2)$  and  $c(2 \times 2)$  O on Ni(100) have now established the correct bond height (0.92 Å) for the  $c(2 \times 2)$  O on Ni(100) configuration which was at one time believed to be approximately 0.2 Å based on generalized valence bond calculations<sup>10</sup> and the early LEED<sup>11</sup> investigations.

The idea of using surface phonons to determine surface structure might be viewed with skepticism, for good reason. Forces between atoms in a solid and between solid surfaces and adsorbed atoms are not well understood or accurately predictable on the basis of *ab initio* calculations. One might therefore question a fitting procedure for obtaining structure based on *ad hoc* force-constant models. The primary result of the present paper is to demonstrate that starting from a general parametrized slab model of a crystal surface with an ordered adlayer, one can deduce a unique set of parameters including force constants and adsorbate bond distances by requiring that the slab model correctly yield the experimentally determined surface vibrational properties.

Our experiments were performed with an EELS spectrometer described previously<sup>12</sup> and modified to

operate up to 300-eV electron kinetic energy.<sup>2</sup> High electron energies are necessary to produce large momentum transfer parallel to the surface, and are generally accompanied by higher counting rates for impact scattering peaks observed in off-specular geometry. Figure 1 displays a typical EELS spectrum for  $c(2 \times 2)$  O on Ni(100), and the inset illustrates the experimentally determined dispersion of surface vibrational modes determined by ourselves<sup>2,13</sup> and by Szeftel *et al.*<sup>1</sup> The solid lines in the inset represent our "best calculated fit" to the vibrational data deter-

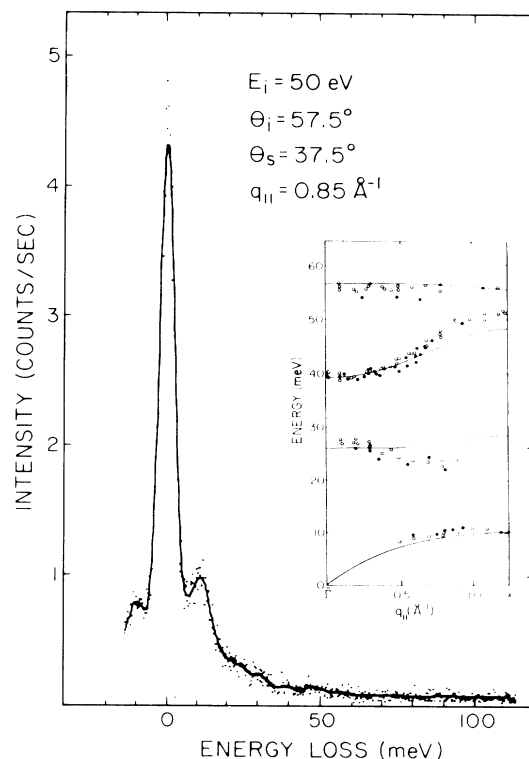


FIG. 1. EELS spectrum for  $c(2 \times 2)$  O on Ni(100), taken in off-specular geometry, displaying the  $S_4$  surface-phonon peak.  $E_i$  is the incident electron kinetic energy;  $\theta_i$  and  $\theta_s$  are the incident and scattering angles measured from the surface normal. Calculated dispersion of the surface modes along  $\bar{\Delta}$  is shown in the inset by solid lines, with filled circles representing our data and open circles representing data from Ref. 1.

mined by lattice-dynamical calculations based on a finite slab model. In the following discussion we will show that a "best fit" of the calculated dispersion curves to the measured dispersion curves is sufficient to uniquely determine the height as well as the interaction parameters. The value we obtained (0.922 Å) is in excellent agreement with the results of other structural studies.

Our finite slab calculations were performed with a computer code supplied to us by Allen, Alldredge, and de Wette<sup>4</sup> which we modified to include angle-bending interactions and for convenient parameter changes required by our iterative approach. Details of the calculation are described elsewhere.<sup>13</sup> For  $c(2 \times 2)$  O on Ni(100), we assume only that the oxygen atoms reside in the fourfold hollow site as we perform a seven-parameter fit to the data. The parameters are the oxygen height above the surface, the nickel-oxygen-nickel angle-bending force constant, the second-nearest-neighbor nickel-oxygen central force constant, and the following first-nearest-neighbor central force constants: nickel-oxygen, oxygen-oxygen, (surface nickel)-(surface nickel), and (surface nickel)-(second-layer nickel). In addition to our obtaining the set of parameters yielding the best fit, the effect on the surface modes of changing each parameter was examined in detail to verify that a best fit had been obtained.

The best fit occurred with no angle-bending forces and no second-nearest-neighbor forces, so that there were effectively five parameters. The outer nickel layer was relaxed outward 5.2%, based on Rutherford backscattering data.<sup>14</sup> However, variation of the relax-

ation between +40% and -40% of the bulk interlayer spacing had no significant effect on the adsorbate modes. The calculations were fitted to two different values of the oxygen parallel mode frequency at two points along  $\bar{\Delta}$  and one frequency on the dispersion curves of each of the other three modes. The best fit was obtained for an oxygen height of 0.92(2) Å, determined primarily by the oxygen perpendicular and parallel mode frequencies near  $\bar{\Gamma}$ . In fact, a two-parameter fit to our data varying only the oxygen height and nickel-oxygen force constant gave a height of 0.93 Å, assuming no reconstruction. This value has now been confirmed by other experiments.<sup>15</sup>

Once the calculation was fitted to the five data points, each parameter was varied over a large range to determine that parameter's effect on the surface mode frequencies at  $\bar{\Gamma}$  and  $\bar{X}$  and to see if, in fact, a best fit had been obtained.<sup>13</sup> Figure 2(a) displays the effect on the surface modes of varying the oxygen height with all other parameters held fixed. The oxygen vibrational modes at  $\bar{\Gamma}$  show the greatest variation with height. More importantly, the energy of the oxygen mode polarized perpendicular to the surface increases monotonically as  $R_{\perp}$  increases, while the energy of the mode polarized parallel to the surface decreases monotonically with increasing  $R_{\perp}$ . Figure 2(b) shows that both of the oxygen-mode energies increase as a function of the nickel-oxygen nearest-neighbor central force constant, so that there can be only one pair of height and force-constant values which fit both oxygen modes at  $\bar{\Gamma}$  simultaneously if only nearest-neighbor central forces are required to obtain a "best fit." Figure 3(a) shows that the nickel-oxygen second-nearest-neighbor central force constant affects only the oxygen mode polarized perpendicular to the surface

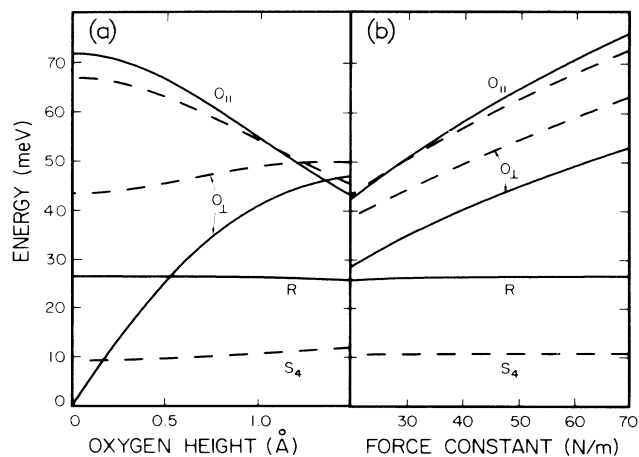


FIG. 2. Variation of surface mode energies at  $\bar{\Gamma}$  (solid lines) and  $\bar{X}$  (dashed lines) with (a) oxygen height and (b) nickel-oxygen nearest-neighbor central force constant.  $O_{||}$  and  $O_{\perp}$  are the oxygen vibrational modes parallel and perpendicular to the surface,  $R$  is the surface-resonance mode, and  $S_4$  is the surface-phonon mode.

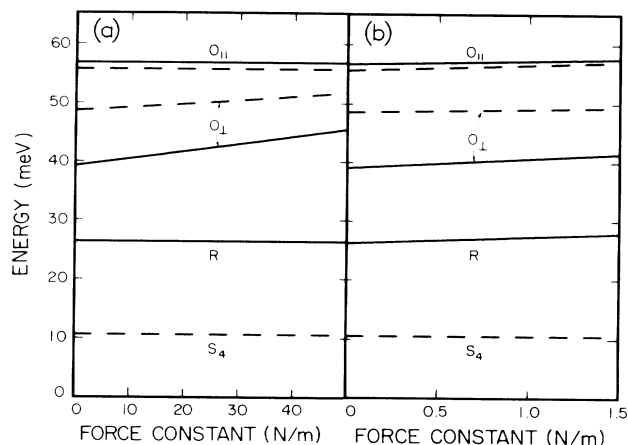


FIG. 3. Variation of surface-mode energies at  $\bar{\Gamma}$  (solid lines) and  $\bar{X}$  (dashed lines) with (a) nickel-oxygen second-nearest-neighbor central force constant and (b) nickel-oxygen-nickel angle-bending force constant.

and that the dispersion of this mode is greatest when this force constant is zero; the experimentally observed dispersion of this mode is thus best fitted when there is no second-nearest-neighbor nickel-oxygen interaction. The same conclusion holds for the nickel-oxygen-nickel angle-bending force constant [see Fig. 3(b)] so that we do indeed have only nearest-neighbor central forces in the model with the best fit.

The dispersion of the oxygen mode polarized parallel to the surface is adjusted with the oxygen-oxygen nearest-neighbor central force constant, which has a very small effect on the  $S_4$  surface phonon and absolutely no effect on the surface modes at  $\bar{\Gamma}$ . The dispersion of the  $S_4$  surface phonon is primarily determined by the (surface nickel)-(second-layer nickel) nearest-neighbor central force constant, which affects all of the surface modes to a small degree. The nickel surface resonance mode frequency can be adjusted up or down by changing the (surface nickel)-(surface nickel) nearest-neighbor central force constant. While this parameter also affects the dispersion of the oxygen mode polarized perpendicular to the surface, the force constant required to fit the perpendicular mode dispersion would be much greater than the bulk nickel-nickel nearest-neighbor central force constant, and this does not seem physically reasonable in addition to producing the wrong frequency of the surface resonance mode. Each mode is therefore associated with one or two parameters, so that it is possible to fit all modes simultaneously in a fairly straightforward manner.

In summary, we have shown that starting with a general slab model for a surface-adsorbate complex and assuming only that the adsorbate site location was known, precise determination of the adsorbate height is achieved by requiring that the model correctly reproduce experimentally determined surface-phonon band structure. We hasten to add that the present study represents the first direct structural determination

based on lattice-dynamical modeling, and the implications for the broader field of surface-phonon spectroscopy await corresponding studies of other systems.

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