PHYSICAL REVIEW B VOLUME 38, NUMBER 12 15 OCTOBER 1988-II

Brief Reports

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Azimuthally resolved optical second-harmonic generation from hydrogen on nickel (111)

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(Received 24 May 1988)

We report the first azimuthally resolved measurements of the effect of an adsorbed gas on optical second-harmonic generation (SHG) from a clean, well-ordered metal surface. The second-harmonic intensity from Ni(111) decreases rapidly upon hydrogen adsorption; however, the threefold symmetry with sample rotation about the surface normal is retained. The β_1 and β_2 adsorption states are clearly resolved and their contributions to the second-order susceptibility are determined. For this system, SHG is highly sensitive to local site symmetry and little affected by long-range ordering of adsorbates.

Recent experiments have established the sensitivity of optical second-harmonic generation (SHG) to surface geometry as well as to adsorbate coverage.[1-6] Here we present measurements of the effect of adsorbed hydrogen on the rotational symmetry of second-harmonic (SH) intensity, demonstrating that this technique probes the local site symmetry of the adsorbate-substrate system and that both isotropic and anisotropic contributions are surface specific.

Hydrogen on Ni(111) is a relatively simple system showing two distinct thermal desorption peaks corresponding to β_1 and β_2 adsorption states of hydrogen.[7-9] A half monolayer of hydrogen in the β_2 state is observed to undergo an order-disorder transformation at about 270 K.[7] Multiple-scattering calculations show that hydrogen is adsorbed in the threefold hollow sites and that below 270 K a graphitelike array of hydrogen exists on the surface.[7]

We have measured the SH intensity as a function of both azimuthal orientation (rotation about the surface normal) and surface hydrogen coverage, from which we have inferred the changes in the isotropic and anisotropic components of the second-order susceptibility associated with both the β_1 and β_2 states of hydrogen. Although previous experiments[1] have shown a difference in susceptibilities for the top site and bridge site of CO on Rh(111), this is the first case where susceptibilities for different adsorption *states* associated with the same adsorption site have been measured. We find that the $3m$ symmetry of the Ni(111) surface is manifest by a threefold symmetry in the SH intensity, which persists at coverages and temperatures at which the low-energy electron diffraction (LEED) pattern shows both ordered and disordered hydrogen overlayers, demonstrating that SHG probes local symmetry, not long-range ordering. We find that second-harmonic generation is dramatically reduced by hydrogen adsorption, almost disappearing at saturation coverage. This indicates that the major contribution to the second-order susceptibility comes from the surface, suggesting that resonances with electronic transitions between surface states are responsible for the large SH intensity from clean Ni(111).

The sample was mounted in a UHV chamber (2×10^{-10} torr base pressure) on a manipulator with liquid-nitrogen cooling, resistive heating, and azimuthal rotation over ≈180°. Cleanliness, surface ordering, and azimuthal orientation were confirmed with Auger spectroscopy and LEED. The 700-nm p-polarized beam (20 mJ/cm^2 in a 7-ns pulse at 10 Hz) from a Nd:YAG-pumped dye laser (YAG denotes yttrium aluminum garnet) was incident on the crystal surface at a 60° angle to the surface normal. p-polarized second harmonic radiation was measured with a filter, phototube, and gated integrator and divided on a shot-by-shot basis by a reference SH signal generated in bulk quartz.

For p-polarized excitation and detection, the intensity of the second harmonic generated from a surface of $3m$ symmetry can be written[5]

$$I(2\omega)\propto|\chi^{(2)}|^2I^2(\omega)=|A+B\cos(3\psi)|^2I^2(\omega)\ . \qquad (1)$$

Here $\chi^{(2)}$ is the second-order susceptibility, and A and B are linear combinations of the susceptibility components. A and B depend on the angle of incidence and in general involve both bulk and surface contributions. ψ is the orientation of the plane of incidence measured relative to the surface vector $\langle 2\bar{1}\bar{1}\rangle$. Included in Fig. 1 is the square root of the measured SH intensity for the clean Ni(111) surface over the range of azimuthal angles available to us; this data is fit well by Eq. (1), using $A/B=3.26$. It is generally not possible to separate surface and bulk contributions to the susceptibility for a clean surface.[10,11] However, it is possible to study relative contributions from surface and bulk by chemical means since the bulk contribution will not be affected by adsorption of gases or other surface chemical changes. At azimuthal angles $\psi=0°$, 30°, 60°, and 90° we have measured SH intensity from Ni(111) during adsorption and thermal desorption of hydrogen. Hydrogen adsorption took place at sample temperatures ranging from 225 to 200 K. After 4.35×10^{17} molecules/cm^2 exposure, corresponding to essentially saturation coverage,[8] hydrogen was removed from the chamber, and thermal desorption was initiated using a heating rate of 0.26 K/s.

Figures 2 and 3 show the data from the adsorption and desorption experiments, respectively. The data are all plotted on a common intensity scale allowing direct comparison of adsorption and desorption data. Adsorption of a full monolayer of hydrogen almost completely quenched the second-harmonic intensity at all orientations, indicating that the dominant contribution comes from the surface susceptibility. For identical, optically noninteracting oscillators, a linear relationship between the components of $\chi^{(2)}$ and coverage will exist.[1] Thus for two nonequivalent states we generalize Eq. (1),

$$\chi^{(2)}\propto A(1-C_{1A}\Theta_1/\Theta_{1s}-C_{2A}\Theta_2/\Theta_{2s}) \\ +B\cos(3\psi)(1-C_{1B}\Theta_1/\Theta_{1s}-C_{2B}\Theta_2/\Theta_{2s})\ , \qquad (2)$$

where Θ_1 and Θ_2 are the absolute coverages in the β_1 and β_2 states, and Θ_{1s} and Θ_{2s} are the saturation coverages for the β_1 and β_2 states. The C_{iJ} are constants giving the linear decrease in the components of the second-order susceptibility caused by hydrogen adsorbed in the β_i state. We assume that the hydrogen overlayer does not alter the $3m$ symmetry of the Ni(111) surface. This is consistent with hydrogen adsorption at the threefold hollow site as determined by LEED,[7] as well as the data of Figs. 2 and 3.

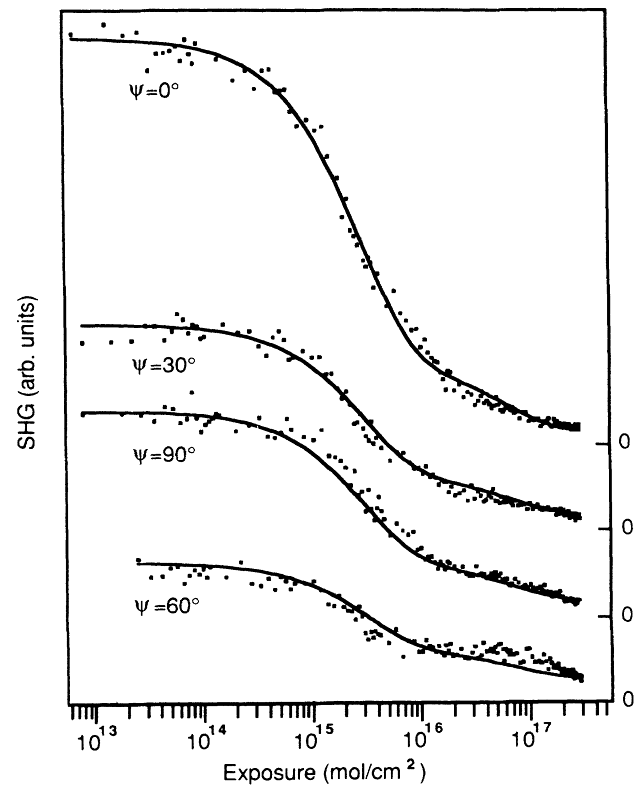

FIG. 2. Optical second-harmonic intensity at four different azimuthal angles as a function of hydrogen exposure on Ni(111). The fits to data are based on Eqs. (2) and (3) using values from Table I.

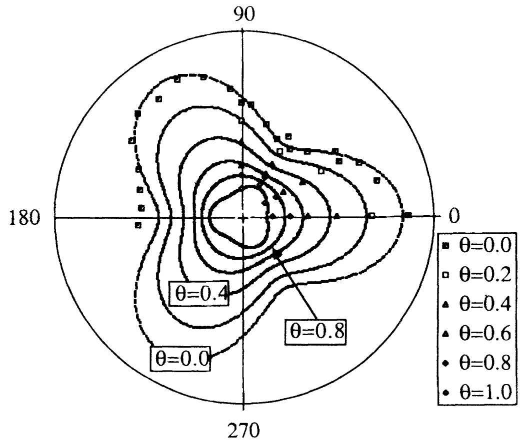

FIG. 1. Continuous curves show the calculated square root of the SH intensity (proportional to $\chi^{(2)}$) as a function of azimuthal angle ψ for hydrogen coverages $\Theta=0.0$, 0.2, 0.4, 0.6, 0.8, and 1.0, using Eq. (2) and the susceptibility coefficients from Table I. Discrete data points are shown for the clean surface (outer curve) and at inferred coverages from the adsorption and desorption data.

The fractional coverage of hydrogen in each state during adsorption was calculated using one-site Langmuirian kinetics.[9] To explain the observed data we found it necessary to assume independent one-site Langmuirian kinetics for both states, an approximation ultimately justified by the large ratio of the sticking coefficients. In this adsorption model

$$\begin{aligned} d\Theta_1/d\varepsilon&=2S_1^0(1-\Theta_1/\Theta_{1s})\ , \\ d\Theta_2/d\varepsilon&=2S_2^0(1-\Theta_2/\Theta_{2s})\ , \end{aligned} \qquad (3)$$

where S_i^0 is the sticking coefficient for a hydrogen molecule in an empty β_i site, Θ_{is} is the saturation coverage of hydrogen for the β_i state, and ε is the hydrogen exposure. We have used $\Theta_{1s}=\Theta_{2s}=0.93\times10^{15}$ sites/cm^2.[7-9] The evolution of second-harmonic intensity during thermal

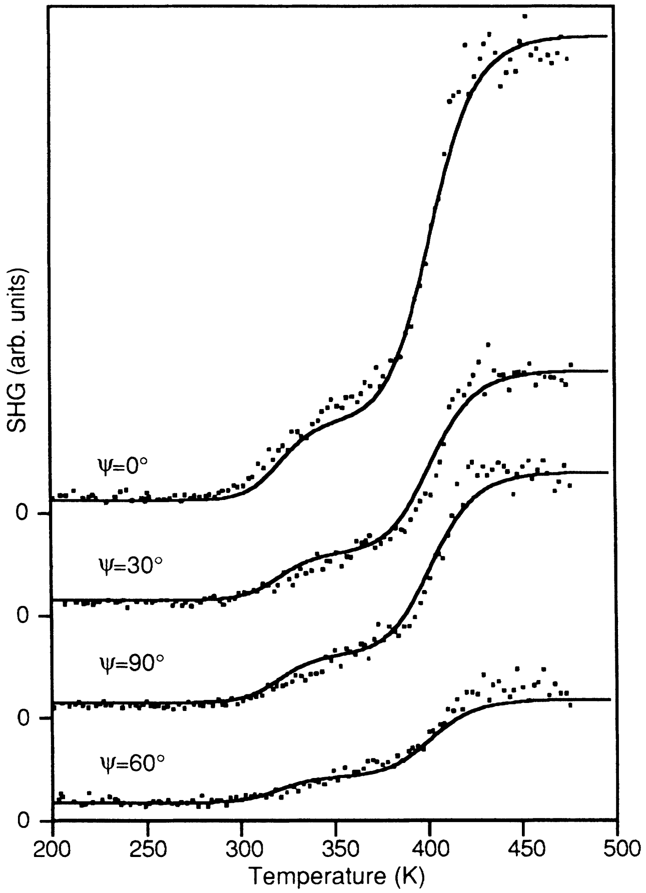

FIG. 3. Optical second-harmonic intensity at four different azimuthal angles during thermal desorption of hydrogen from on Ni(111). The fits to data are based on Eqs. (2) and (4) using values from Table I.

desorption was modeled using the Polanyi-Wigner differential equation.[12] For a state i on the surface, the rate of desorption is

$$d\Theta_i/dt = \nu_i \Theta_i^{n_i} \exp(-E_i/RT) \ , \qquad (4)$$

where ν_i is a frequency factor, n_i is the reaction order for desorption from the ith state, and E_i is the desorption activation energy. For hydrogen on nickel, second-order desorption kinetics for both states has been demonstrated previously.[7,8] The adsorption and desorption data at all four azimuths were fitted collectively by varying A/B, S_1^0, S_2^0, E_1, E_2, C_{1A}, C_{2A}, C_{1B}, and C_{2B} of Eqs. (2)–(4) using a least-squares fitting routine. The fits to the data are shown in Figs. 2 and 3 and the values of the parameters are listed in Table I. While A/B and the susceptibility coefficients, C_{iJ}, are generally complex, varying phases of these parameters in no way improved the fit to the data. To minimize the number of adjustable parameters we used $\nu_1 = 2\times 10^{-4}$ cm^2/s and $\nu_2 = 1\times 10^{-3}$ cm^2/s in agreement with literature values.[7]

The good agreement between these results obtained with SHG and results using traditional techniques demonstrates the validity of this model and of the inferred dependences of $\chi^{(2)}$ on the hydrogen coverage. We calculate an initial sticking probability $S_1^0 + S_2^0 = 0.084$, in good agreement with literature measurements ranging from 0.02 to 0.15.[7–9] To our knowledge, we are the first to apply an adsorption model for hydrogen on Ni(111) that utilizes independent sticking coefficients for β_1 and β_2. Attempts to fit the data of Fig. 2 using a one-site Langmuirian model with a single sticking coefficient (as in Russell *et al.*[9]) did not reproduce the slow decrease in the SHG signal seen in Fig. 2 at exposures over about 10 langmuirs (L) (1 L$=10^{-6}$ torr s). Actually, of course, hydrogen will occupy the β_1 state only after the β_2 state is partially filled, thus the sticking probability for the β_1 state should be coupled to the fractional coverage in the β_2 state. In our calculations the initial sticking coefficient for β_2 is 24 times larger than for β_1, so the error introduced by ignoring this coupling is insignificant. The calculated coverages of β_1 and β_2 reproduce the observation that β_1 is populated only after β_2 is largely filled. The activation energy for thermal desorption from the β_1 state, $E_1 = 18.9$ kcal/mol, is essentially identical to that of Christmann *et al.*,[7] while the energy for β_2, $E_2 = 25.0$ kcal/mol, is in reasonable agreement.

The azimuthal dependence of $\chi^{(2)}$ was calculated as a function of total fractional coverage, $\Theta = (\Theta_1 + \Theta_2)/(\Theta_{1s} + \Theta_{2s})$, and is shown in Fig. 1. Data points representing $[I(2\omega)]^{1/2}$ at appropriate coverages from averaged adsorption and desorption data of Figs. 2 and 3 are also plotted along with additional measurements taken for the clean surface at 10° azimuthal increments. The isotropic component of the susceptibility is considerably greater than the anisotropic component at all hydrogen coverages. The change in the susceptibility associated with adsorption of a half monolayer into the β_2 state is about twice the change in susceptibility associated with subsequent adsorption of a half monolayer into the β_1 state. Furthermore, the anisotropic portion of the sus-

TABLE I. Susceptibility coefficients (60° incidence), initial sticking probabilities, and desorption activation energies used in Eqs. (2)–(4) to calculate second-order susceptibility, obtained from least-squares fit to data shown in Figs. 2 and 3. Values in parentheses are standard deviations in the least significant figure.

Isotropic susceptibility coefficients	Anisotropic susceptibility coefficients	Initial sticking probability	Desorption activation energy (kcal/mol)	Zero-coverage susceptibility components
$C_{2A} = 0.499(7)$	$C_{2B} = 0.78(2)$	$S_2^0 = 0.081(5)$	$E_2 = 25.0(1)$	$A/B = 3.26(2)$
$C_{1A} = 0.260(7)$	$C_{1B} = 0.33(3)$	$S_1^0 = 0.0034(3)$	$E_1 = 18.9(1)$	

ceptibility decreases more rapidly than the isotropic portion as hydrogen is adsorbed, passing through zero at total fractional coverage 0.84 and reversing the sign of the contribution at full coverage. The calculated angular patterns and discrete data points combine to show graphically the progressive reduction of the total susceptibility and the sign reversal of the anisotropic component. Based on the quality of the fits shown in Figs. 2 and 3, we believe that this model gives a reasonable representation of the effects of hydrogen adsorption on the isotropic and anisotropic components of the second-order susceptibility.

Given the excellent fit to data obtained with Eq. (2), it appears that the $3m$ symmetry persists for all hydrogen coverages. This is somewhat surprising since hydrogen occupies disordered sites at coverages significantly below or above $\Theta=0.5$.[7] Since a disordered hydrogen layer would not have $3m$ symmetry on a scale of several unit cells, we conclude that the nonlinear susceptibility reflects primarily the local symmetry of bonding sites on the surface. This conclusion was confirmed by an experiment in which we attempted to see a change in the SH intensity associated with the order-disorder transformation of hydrogen, which occurs for the β_2 state at about 270 K. We adsorbed hydrogen at low temperature until a well-ordered (2×2) LEED pattern was obtained. The sample was then warmed and cooled to verify that the order-disorder transformation could be seen using LEED. Next the same heating and cooling cycle was performed while monitoring the SH intensity. Finally we verified that the order-disorder transformation was still observable using LEED. At no time did we see any significant change in the second-harmonic generation at the surface. We conclude that for this adsorbate-surface system, the *local* point-group symmetry of surface and adsorbate plays the major role in determining the form of the second-order susceptibility and thus the azimuthal symmetry of optical second-harmonic generation.

Recent work on Cu(111) attributes the existence of azimuthal anisotropy to bulk interband transitions at the energy of the second harmonic (2.33 eV).[5] For nickel, interband transitions occur in the vicinity of 1.4 eV, between d-band levels in the vicinity of the L symmetry point in the Brillouin zone.[13] However, in view of the fact that adsorbed surface hydrogen so markedly affects the magnitude of both isotropic and anisotropic components of the susceptibility, we find it difficult to attribute the presence of anisotropy to bulk interband transitions. Rather it is more likely that $\chi^{(2)}$ derives strength from a resonance between our incident light at 1.77 eV energy and a transition involving surface states. Studies of Ni(111) using angle-resolved photoemission show an occupied sp-derived surface state of symmetry Λ_1 about 0.25 eV below the Fermi energy (E_F) at $\overline{\Gamma}$ that disperses to about -1.0 eV at the $\overline{K}$ point of the surface Brillouin zone (SBZ) and is dramatically shifted and quenched by the adsorption of hydrogen.[14] Observed bulk bands are much less strongly affected by hydrogen adsorption. Furthermore, momentum-resolved inverse photoemission experiments on clean Ni(111) show a crystal-induced surface state or resonance about 0.5 eV above E_F at $\overline{\Gamma}$ that disperses rapidly upward along $\overline{\Gamma}\,\overline{M}$.[15] Since χ^2 gains oscillator strength from any dipole-allowed (vertical, or k-conserving) transition, we suggest that the 1.77-eV exciting light is resonant with a direct transition between these surface states at some point in the SBZ. Also, at the resonance energy these surface levels carry the projection of the bulk symmetry onto the (111) surface, which is point group $3m$, accounting qualitatively for the threefold rotational symmetry of SH intensity. Transitions involving bulk d bands may be responsible for the residual signal from the hydrogen-saturated surface. An adequate quantitative description of the anisotropy for clean and partially covered surfaces must await calculations that include the size of the transition dipole connecting these surface states as a function of the E-field component parallel to the surface. We hope that the experimental results reported here will encourage such calculations.

It is a pleasure to acknowledge R. H. Stulen, G. D. Kubiak, T. E. Felter, and B. M. Palmer for stimulating and illuminating discussions. This work is supported by the U.S. Department of Energy (Division of Material Sciences, Office of Basic Energy Sciences) under Contract No. DE-AC04-76DP00789.

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