Surface Studies by Optical Second-Harmonic Generation: The Adsorption of O_2, CO, and Sodium on the Rh(111) Surface

H. W. K. Tom,[a] C. M. Mate,[a] X. D. Zhu,[a] J. E. Crowell,[b] T. F. Heinz,[a],[c]
G. A. Somorjai,[b] and Y. R. Shen[a]
Materials and Molecular Research Division, Lawrence Berkeley Laboratory,
University of California, Berkeley, California 94720
(Received 26 October 1983)

Optical second-harmonic generation is used to study the adsorption of atomic and diatomic species on a well characterized Rh(111) crystal surface in ultrahigh vacuum. The results correlate well with those obtained by other surface probes.

PACS numbers: 68.45.Da, 42.65.Cq, 73.40.-c, 82.65.Jv

Recently, it has been demonstrated that optical second-harmonic generation (SHG) can be used to study molecular adsorbates at an interface between two media with inversion symmetry.[1] A question arises as to how well the SHG technique correlates with or supplements the existing tools for surface studies. This Letter reports the first application of the SHG technique to well-characterized surface systems that are also of catalytic importance. Working with an atomically clean Rh(111) surface in ultrahigh vacuum (UHV), we found that SHG is sensitive to adsorption and desorption of 5% of a monolayer of atomic or diatomic species on Rh, and can distinguish between adsorption at different sites. The technique also is nondestructive, and has high time-resolving capability. Therefore, it can yield dynamic information difficult to obtain by the more standard UHV surface probes.

We were interested in studying the adsorption and coadsorption of O_2, CO, and alkali-metal atoms on Rh(111). These are systems which have been actively investigated for their importance in catalysis involving hydrocarbon and oxidation reactions.[2] Our experiments were conducted on Rh(111) in a UHV chamber with a background pressure of 2×10^{-10} Torr. The Rh surface was cleaned by cycles of Ar^+ sputtering, O_2 treatment, and annealing in vacuum at 900 °C, and was monitored by Auger-electron spectroscopy. Surface coverages of atoms or molecules were measured by thermal desorption yield and calibrated by low-energy electron diffraction (LEED). For the SHG measurements, Nd-doped yttrium aluminum garnet laser pulses at 532 nm or 1.06 μm with ~10-nsec pulse width and ~6-mJ pulse energy were p polarized and incident on the Rh sample at an angle of 62.5° with a beam diameter of 1 mm. At this intensity, no laser-induced desorption or surface damage could be detected. The p-polarized SH signal from the surface was detected by an appropriate detection system.

Because SHG has an intrinsically fast time resolution (limited here by the pulse repetition rate), it can be used to monitor the surface during adsorption and desorption processes, which are often too fast for most other surface probes. In Fig. 1, we show how the SH signal from the Rh(111) surface at 315 K varied as the surface was continuously exposed to O_2 gas. It dropped from the normalized bare metal value of 1 to a saturation value of 0.12 at about 1.8 langmuirs (L) of O_2 (1 L $=10^{-6}$ Torr sec). The sharp LEED pattern of adsorbed oxygen[3,4] was observed only when the coverage exceeded ~20 L.

The result in Fig. 1 can be explained by a model assuming that oxygen adsorption obeys Langmuir kinetics and that all adsorption sites are equivalent and noninteracting. The former assumption has been confirmed experimentally by Yates, Thiel, and Weinberg.[5] The latter allows us to say that the surface nonlinear susceptibility with oxygen adsorption can be written as

$$\chi^{(2)} = A + B\theta/\theta_s, \tag{1}$$

where θ is the fractional surface coverage of oxygen with respect to Rh surface atoms, θ_s is

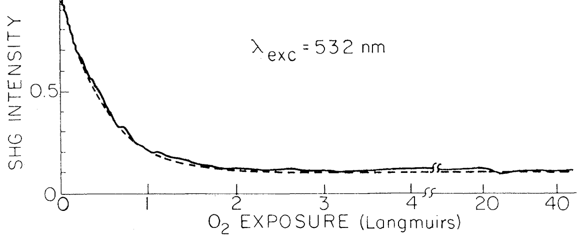

FIG. 1. Second-harmonic signal from the Rh(111) surface during O_2 exposure. Solid curve, experimental result; dashed curve, theoretical fit.

the saturation value of θ, and A and B are constants. When the desorption rate is negligible, as in our case, the Langmuir adsorption kinetics dictates that the variation of θ with time follows

$$d\theta/dt = Kp(1-\theta/\theta_s), \tag{2}$$

where K is a constant accounting for the sticking coefficient and p is the oxygen pressure. Knowing that the SH signal is proportional to $|\chi^{(2)}|^2$, and taking B/A and K/θ_s as adjustable parameters, we can use the solution of Eqs. (1) and (2) to fit the experimental data as shown in Fig. 1. We find $B/A = 1.03\exp(i160°)$ and $K/\theta_s = 0.93$/layer. This value of K/θ_s is in good agreement with the value of 0.78/layer obtained by Yates, Thiel, and Weinberg, when we consider possible differences in pressure calibration.[5] The sticking coefficient for O_2 to Rh(111) surface atoms is then determined to be ~0.5 if O atoms form a 2×2 overlayer ($\theta_s = 0.25$),[3] or ~1.0 if O atoms form three domains of 2×1 overlayers ($\theta_s = 0.5$).[4]

The SHG intensity from Rh(111) also decreased dramatically when it was exposed to CO. This is seen in Fig. 2 in which the SH signal is plotted as a function of CO fractional surface coverage θ. The CO coverage was calibrated by the $\sqrt{3}\times\sqrt{3}$ $R30°$ and 2×2 LEED patterns at $\theta = \frac{1}{3}$ and $\theta = \frac{3}{4}$, respectively. Previous studies have shown that CO can adsorb to two sites on Rh(111) with the carbon end down.[6] For $\theta \le \frac{1}{3}$, CO bonds only to the top sites. For $\frac{1}{3} < \theta < \frac{3}{4}$, CO bonds to both the top sites and the bridge sites. The surface coverage saturates at $\theta = \theta_s = \frac{3}{4}$. The SHG data in Fig. 2 exhibit a rather sudden change in slope at $\theta \sim \frac{1}{3}$. This suggests that CO bonded to a top site has a different nonlinear polarizability than CO bonded to a bridge site. We can indeed fit the data in Fig. 2 by assuming the surface nonlinear susceptibility to have the form

$$\begin{aligned}\chi^{(2)} &= A + B\theta/\theta_s \text{ for } \theta \le \tfrac{1}{3}\\ &= A + B/3\theta_s + C(\theta-\tfrac{1}{3})/\theta_s \text{ for } \tfrac{1}{3} < \theta < \tfrac{3}{4}.\end{aligned} \tag{3}$$

From the measured values of the phase and amplitude of the SH field at $\theta = \frac{1}{3}$ and $\frac{3}{4}$, we found $B/A = 1.36\exp(i157°)$ and $C/A = 0.484\exp(i169°)$. The fit of the data by Eq. (3) is fairly good, as seen in Fig. 2. The result indicates that SHG is site specific for CO on Rh(111).

Both CO and O_2 adsorption decrease the SH signal with respect to that from the clean Rh(111) surface. This is presumably because the delocalized electrons of the metal surface which are largely responsible for the SHG are depleted through localization in the chemisorption bond. That the nonlinear response is dominated by the metal surface electrons, rather than by adsorbates or by localized electrons via charge-transfer resonances, is substantiated by both the similar magnitude of CO- and O-induced changes in SHG and there being almost no difference in the SH response to adsorption with 1.06- or 0.532-μm excitation. One would expect a complementary effect, that is, an increase in the SH signal upon adsorption of alkali-metal atoms which donate electrons to the Rh surface. This is indeed what we found.

Figure 3 shows the experimental data of SHG versus Na surface coverage on Rh(111) at 210 K with 532-nm excitation. The surface coverage of

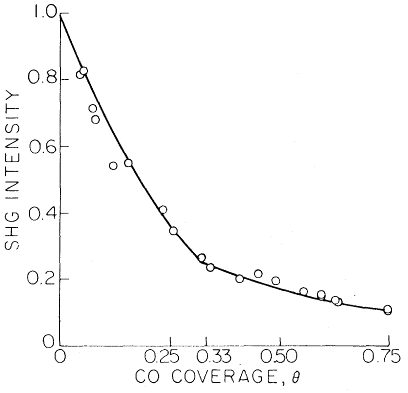

FIG. 2. Second-harmonic output from the Rh(111) surface vs CO fractional coverage, θ. Circles, experimental points; lines, theoretical fit.

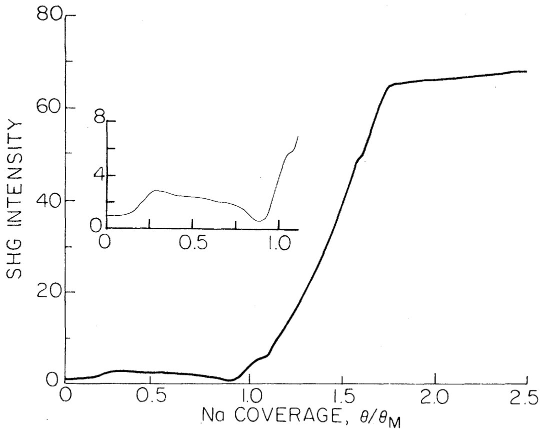

FIG. 3. SH output from the Rh(111) surface vs Na surface coverage, θ, calibrated against the hexagonal close-packed monolayer of Na at $\theta = \theta_m = \frac{1}{2}$. The low-coverage portion is enlarged in the inset.

Na was calibrated by the LEED pattern for a hexagonal close-packed monolayer of Na at $\theta = \theta_m = 0.5$. For $\theta < 0.5\theta_m$, the SH signal increases presumably because Na atoms donate electrons to Rh. This donation is known to saturate around $0.5\theta_m$ from work-function measurements on alkali metals adsorbed on other transition metals.[7,8] Our SHG data also exhibit a saturation behavior at $\theta \sim 0.5\theta_m$. For $\theta > 0.5\theta_m$, surface-plasmon studies indicate that the adsorbed Na atoms begin to interact to form a metallic film.[9] In our SHG data, this is evidenced by the large change in signal for $\theta > 0.6\theta_m$. The dip at $\theta \sim 0.9\theta_m$ is believed to come from the fact that the contributions from the Na film to $\chi^{(2)}$ and from the electron-enhanced Rh surface become comparable and nearly opposite in phase. The dramatic change in SHG for $\theta > 0.5\theta_m$ is quite similar to that observed in an earlier study of Na on Ge.[10] The SH signal in Fig. 3 saturates around $\theta \sim 2\theta_m$ at a value about 70 times larger than that from the bare Rh(111) surface. This clearly illustrates the surface specificity of the SHG. Being more free-electron-like, the Na metal is more nonlinear than Rh. With the Rh surface covered by two atomic layers of Na, the SH signal is completely dominated by the contribution from Na. That additional Na coverage does not appreciably change the SH signal implies that the SH signal results mainly from a Na surface film two atomic layers thick.

We have also studied coadsorption of CO and Na on Rh(111). Figure 4 shows the SHG during CO exposure to and thermal desorption from the Rh surface predeposited with $\theta \sim 0.6\theta_m$ of Na. The dosage curve in Fig. 4(a) has a nearly zero initial slope, in contrast to the cases of adsorption on clean Rh seen in Figs. 1 and 2. This suggests that the presence of Na must have significantly influenced the adsorption of CO. The fast drop in SHG from 1 to 2 L and the slow saturation after 2 L are similar to the SHG behavior observed for CO exposure to clean Rh. CO adsorption during the first langmuir of exposure is different presumably because the Na layer can replenish the Rh surface charge that is withdrawn by low coverages of CO. After the CO coverage on Na/Rh(111) was allowed to saturate, the SHG was again used to monitor the subsequent thermal desorption at a rate ~15 °C/s, as seen in Fig. 4(b). The curve shows a desorption onset temperature of ~300 °C, which is ~200 °C higher than that for CO on clean Rh(111), indicating a stronger bonding of CO to the surface in the presence of Na. A similar increase in desorption onset temperature was observed for CO on K/Rh(111).[11] A distinguishable plateau (see arrow) appears between 450 and 520 °C in the desorption curve followed by another rise in the SH signal to a value consistent with only Na on Rh(111) with $\theta \sim 0.5\theta_m$. This suggests the existence of another CO state on Rh which desorbs starting around 520 °C. Two adsorption states have been distinguished in other work on Rh(111), Pt(111),[11] Fe(110),[12] and Ni(100)[13] surfaces. The dosage curve in Fig. 4(a) seems to have a plateau at roughly the same SH signal level as the one in Fig. 4(b), although further work is required to substantiate the correlation. Finally, the SH signal displayed in Fig. 4(b) shows that the Na atoms desorb quickly once CO leaves the surface, and at ~800 °C, the SHG returns to the level of the clean Rh surface.

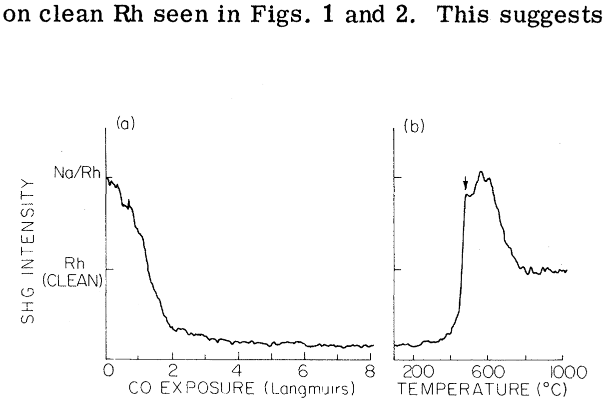

FIG. 4. Second-harmonic signal during (a) the CO adsorption on Rh(111) predeposited with 0.6 monolayer of Na and (b) the thermal desorption process from the Na/Rh(111) sample in (a) after 15 L of CO exposure.

In another experiment, we found that with a Na coverage of $\theta \sim 1.0\theta_m$ on Rh(111), the CO adsorption on Na/Rh(111) was greatly reduced. The SH signal drops only 20% for 1200 L CO exposure. With a Na coverage of $\theta \sim 1.3\theta_m$, no change in SHG was observed for 600 L CO exposure. These results indicate that CO adsorption on Rh is effectively blocked by the Na film, and that the interaction of CO with Na must be very weak. In contrast, O_2 adsorption on Na/Rh always causes the SHG to drop precipitously because oxygen can chemisorb to either Rh or Na.

In conclusion, we have demonstrated in this study that the results of surface SHG correlate very well with those obtained with conventional surface probes. This clears the way for the successful application of SHG to other systems of interest in surface science and catalysis. The very high detection sensitivity, the extremely fast response, and the nondestructive nature of the technique should make it a unique and most useful surface tool.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098. The authors gratefully acknowledge fellowships from Hughes Aircraft (H.W.K.T.), Dupont (X.D.Z.), and IBM (T.F.H.).

(a)Also associated with the Department of Physics, University of California at Berkeley, Berkeley, Cal. 94720.

(b)Also associated with the Department of Chemistry, University of California at Berkeley, Berkeley, Cal. 94720.

(c)Permanent address: IBM Research Laboratory, Yorktown Heights, N.Y. 10598.

[1] C. K. Chen, T. F. Heinz, D. Ricard, and Y. R. Shen, Phys. Rev. Lett. 46, 1010 (1981); H. W. K. Tom, T. F. Heinz, and Y. R. Shen, Phys. Rev. 51, 1983 (1983).

[2] See, for example, G. A. Somorjai, *Chemistry in Two Dimensions: Surfaces* (Cornell Univ. Press, Ithaca, 1981).

[3] D. G. Castner, B. A. Sexton, and G. A. Somorjai, Surf. Sci. 71, 519 (1978).

[4] D. G. Castner and G. A. Somorjai, Appl. Surf. Sci. 6, 29 (1980).

[5] J. T. Yates, P. A. Thiel, and W. H. Weinberg, Surf. Sci. 82, 45 (1979).

[6] M. A. Van Hove, R. J. Koestner, and G. A. Somorjai, Phys. Rev. Lett. 50, 903 (1982), and references therein.

[7] S. A. Andersson and U. Jostell, Surf. Sci. 46, 625 (1974).

[8] G. Broden and H. P. Bonzel, Surf. Sci. 84, 106 (1979).

[9] U. Jostell, Surf. Sci. 82, 333 (1979); S. A. Lindgren and L. Wallden, Phys. Rev. B 22, 5969 (1980).

[10] J. M. Chen, J. R. Bower, C. S. Wang, and C. H. Lee, Opt. Commun. 9, 132 (1973).

[11] J. E. Crowell, E. L. Garfunkel, and G. A. Somorjai, to be published, and (for CO/K/Pt) Surf. Sci. 121, 303 (1982).

[12] G. Brodén, G. Gafner, and H. P. Bonzel, Surf. Sci. 84, 295 (1979).

[13] M. P. Kiskinova, Surf. Sci. 111, 584 (1981).