the insertion of a \( \text{C}_6\text{F}_6 \) molecule into \( \text{RP}^2 \). In other solvents the polarized formaldehyde is detected. The analysis of the CIDNP of formaldehyde in \( \text{CD}_3\text{CN} \) with the help of the expressions similar to (1) shows that the formaldehyde is an "in-cage" product of \( \text{RP}^2 \). It is reasonable to assume that the insertion of a solvent molecule into \( \text{RP}^2 \) in the case of the substitution of \( \text{C}_6\text{F}_6 \) with \( \text{CD}_3\text{CN} \) will hamper the formaldehyde formation.

Strong emission of the acetone is observed in all the investigated solvents in low fields with the isopropanol alcohol as a donor. The field dependence for acetone has a broad maximum within the range \( 50-80 \, \text{G} \) (Figure 4). The field dependence shows good agreement with that calculated with the use of the semiclassical approximation for an \( \text{F}^+ \text{F}^- \) pair of two alcohol radicals. Let us note that this interpretation is not consistent with the conclusions of ref. 18. Analogously to the results in high fields the authors of ref. 18 have suggested that in low fields acetone is polarized as the escape product of the primary RP of an alcohol and semiquinone free radicals with a positive exchange interaction. Note that the field dependences of the recombination products of various RPs, which we have studied previously (see, e.g., ref. 11), were in agreement with those calculated without the exchange interaction.

The field dependences of the CIDNP of DQ in similar reactions in low fields show only the presence of semiquinone free radicals, according with known tendency of the substance to self-quenching reactions.20 Thus, the joint analysis of the CIDNP effects in high and low magnetic fields allows one to make the following conclusions about the elementary stages of quinone photoreduction by aliphatic alcohols. First, the main contribution to the polarizations brings the RP with an oxygen-centered alcohol radical. The appearance of CIDNP in RP with the alkoxyl radical was already described in the literature.4 It is possible due to the great \( \text{hf} \) constant \( (A = 52 \, \text{Oe}^2) \). In this case the noticeable CIDNP proportional to \( A^2 \text{I}_{\text{Is}} \) will form even at \( T_{\text{Is}} = 10^{-9} \, \text{s} \). Second, when the reaction proceeds in hexafluorobenzene, the insertion of a \( \text{C}_6\text{F}_6 \) molecule into a primary RP occurs with the subsequent cyclohexadienyl radical formation. If the reaction proceeds in pure alcohols or acetonitrile, the main channel of the decay of semiquinone radicals is their disproportionation in solution followed by the formation of the initial quinone and hydroquinone. Disproportionation is also the main reaction of the alcohol radicals escaped into the bulk.

In situ spectroscopic measurements are required to verify that the surface order of these Pt(111) single crystals is preserved upon immersion into the electrochemical environment. Optical second harmonic generation (SHG) is an in situ spectroscopic measurement that can be used for this purpose. The rotational anisotropic response of the SHG from the surface for various combinations of input and output polarizations reflects the symmetry of the first few atomic layers of the metal surface. SHG rotational anisotropy has been applied both in UHV46 and in electrochemical environments.8,10 In addition to the symmetry information that...
can be obtained from the sensitivity of the SHG signal to the electronic structure of the surface, changes in the SHG signal can be used to indirectly monitor chemisorption. We have previously used changes in the SHG signal from polycrystalline Pt surfaces to monitor the chemisorption of hydrogen, halides, and bisulfite.\(^{11}\) In particular, the large response of the surface SHG to the underpotential deposition of atomic hydrogen at polycrystalline surfaces suggests that SHG measurements can help identify the potential range over which a hydrogen species is present at a well-ordered Pt(111) surface.\(^{2}\) In this paper we utilize in situ SHG anisotropy and potential dependence to measure the average surface symmetry of a Pt(111) surface during the adsorption of iodine, carbon monoxide, and hydrogen on a well-ordered Pt(111) electrode.\(^{2}\)

**Experimental Considerations**

The SHG signal measured in these experiments was created on the electrode surface from the 2-ps pulses of light at 605 nm generated by a 4-MHz laser system described previously.\(^{12}\) The electrode in the experiments was a 6-mm polished Pt(111) crystal obtained from Aremco. Prior to the immersion of the electrode the Pt crystal was heated to 800 °C in a hydrogen flame and then cooled in an argon/iodine vapor stream. The electrode was then mounted on a glass rod, sealed around the edge with Teflon tape, and immersed into a two-window spectroelectrochemical cell.\(^{11}\) The SHG experiments were performed at an incident angle of 60° with respect to the surface normal; the anisotropic SHG response of the electrode was obtained by rotating the azimuthal angle of the crystal with respect to the plane of incidence for the fundamental beam. This angle was defined to be zero at a maximum in the s,p anisotropy of the iodine-coated Pt(111) surface, and was controlled to better than a degree with a stepper motor. The SHG signal was obtained with a photon-counting system normalized by a separate reference channel and is expressed in counts s\(^{-1}\).\(^{12}\)\(^{12}\) Each point of the anisotropic SHG response corresponds to 4 s of integration time (or 16 million laser pulses). The spectroelectrochemical cell contained approximately 100 mL of 0.1 M HClO\(_4\) (doubly distilled from Vycor GFS Chemicals) solution prepared from water that was Millipore-filtered and then doubly distilled. The electrode potential was controlled by a Princeton Applied Research 173/175 potentiostat; all potentials are referenced versus a Ag/AgCl(4 M NaCl) reference that was isolated from the main solution. The SHG anisotropy experiments were all performed at an electrode potential of +0.200 V. Cyclic voltammograms (CVs) were obtained by cycling the electrode potential at 100 mV/s and were captured digitally and stored on a computer.

**Results and Discussion**

The SHG measurements employed in this paper are obtained with either s-polarized input light and p-polarized second harmonic light, or p-polarized input light and s-polarized second harmonic light. We found these polarization combinations to be the most useful for probing the surface electronic structure. A phenomenological theory for the rotational anisotropy of optical second harmonic generation has been presented by Sipe.\(^{13}\) The second harmonic intensity \(I_{\text{p,p}}(2\omega)\) from a (111) surface with crossed input and output polarizations can be described by

\[
I_{\text{p,p}}(2\omega) \propto |a_{\text{p}} + c_{\text{p}} \cos(3\phi)|^2
\]

\[
I_{\text{p,s}}(2\omega) \propto |b_{\text{p}} \sin(3\phi)|^2
\]

where the subscripts [s,p] refer to the polarizations of the fundamental and second harmonic beams with respect to the surface, \(\phi\) is the azimuthal angle between the crystallographic axes and the component of the incident light wavevector parallel to the surface, and the complex coefficients \(a, b, c\) contain Fresnel factors, bulk susceptibility terms, and the various surface nonlinear susceptibility elements.\(^{13}\) For a (111) crystal surface, the first three monolayers have \(C_{3v}\) symmetry, and the only four nonzero tensor elements are \(x_{zzz}, x_{zxx} = x_{zzy} = x_{zyz}, x_{zzz} = x_{zxx} = x_{zyz}\), and \(x_{zxx} = x_{zyz} = x_{xzy}\).\(^{14}\) For an isotropic surface, \(x_{zzz}\) is zero. For the crossed polarization measurements \(I_{\text{p,s}}(2\omega)\) and \(I_{\text{p,p}}(2\omega)\) the constant \(a_{\text{p}}\) only contains \(x_{zzz}\) and the constants \(c_{\text{p}}\) and \(b_{\text{p}}\) only contain \(x_{zxx}\).

The SHG signals \(I_{\text{p,s}}(2\omega)\) and \(I_{\text{p,p}}(2\omega)\) from a Pt(111) electrode biased at a potential of +0.200 V in 0.1 M HClO\(_4\) with a monolayer of atomic iodine that has been chemisorbed from an argon atmosphere immediately after annealing in a hydrogen flame are plotted as a function of azimuthal angle in Figure 1, a and b, respectively. The angular dependence of \(I_{\text{p,s}}(2\omega)\) can be fit by eq 1 with the ratio \(|a_{\text{p}}/b_{\text{p}}| = 1.14\) and a phase difference between \(a_{\text{p}}\) and \(b_{\text{p}}\) \(\Delta \gamma = 22°\) [since the coefficients \(a, b, c\) are complex we must define both a relative magnitude and phase]. In contrast, the angular dependence observed for \(I_{\text{p,p}}(2\omega)\) in Figure 1b is an alternating 6-fold pattern which cannot be fit by the present theory of SHG from a \(C_{3v}\) surface\(^{15}\) (eq 2, which predicts a uniform 6-fold pattern). Instead, the anisotropic response observed from the surface implies that there must be a constant term \(a_{\text{ps}}\) contributing to \(I_{\text{p,p}}(2\omega)\):

\[
I_{\text{p,p}}(2\omega) \propto |a_{\text{p}} + b_{\text{ps}} \sin(3\phi)|^2
\]

The experimental data in Figure 1b can be fit by eq 3 with a ratio \(|a_{\text{p}}/b_{\text{ps}}| = 0.25\) and a phase difference between \(a_{\text{p}}\) and \(b_{\text{ps}}\) \(\Delta \gamma = 240°\). We attribute the presence of a large nonzero \(a_{\text{ps}}\) to the adsorbed iodine monolayer. After the removal of iodine and CO, \(a_{\text{ps}}\) becomes very small, producing an almost symmetric 6-fold pattern in the \(I_{\text{p,p}}(2\omega)\) anisotropy (see below).

There are two possible explanations for the observation of a nonzero \(a_{\text{ps}}\) constant in eq 3. The first is that the presence of the adsorbate creates an additional nonlocal contribution to the surface.
nonlinear susceptibility. This additional contribution must be anisotropic, because any isotropic contributions (such as those due to the dc electric field effects) are zero by symmetry for the polarization combination \( \epsilon_{xxz} \) and \( \epsilon_{yxy} \). The second possibility is that the adsorbate has reduced the average surface symmetry. Such symmetry reductions have been observed previously on a reconstructed Au(111) electrode.\(^\text{(10)}\)

The chemisorbed iodine on Pt(111) flame annealed surfaces is known from UHV\(^\text{14}\) and STM\(^\text{15}\) measurements to form a \((\sqrt{7} \times \sqrt{7})R19.1^\circ\) ordered monolayer on the Pt(111) surface. With the chemisorbed iodine monolayer the local electrode surface symmetry is reduced from \( C_{6v} \) to \( C_3 \). For surfaces with \( C_3 \) symmetry the additional surface nonlinear susceptibility tensor elements \( \chi_{XZY} = \chi_{YXZ} = -\chi_{YZX} \) and \( \chi_{YXZ} = -\chi_{YXY} = -\chi_{XYX} \) can be nonzero.\(^\text{14}\) The presence of the tensor element \( \chi_{XZY} \) will lead to a constant term \( a_{YY} \) in the expression for \( I_{x,y}(2\omega) \) and the tensor element \( \chi_{YXX} \) will lead to an additional \( \epsilon_{xxz} \cos(3\phi) \) in eq 3. Experimentally, we find no evidence for a nonzero \( \chi_{YXX} \) or the experimentally observed \( a_{YY} \) can be attributed to a nonzero \( \chi_{XZY} \). We also note that the nonlinear susceptibility tensor element \( \chi_{XZY} \) does not appear in the \( I_{x,y}(2\omega) \) measurements, so that eq 1 is still valid.

The reduction of the average surface symmetry from \( C_{6v} \) to \( C_3 \) by the iodine monolayer is somewhat surprising and varied slightly in magnitude from day to day. There are two possible domains for the iodine \((\sqrt{7} \times \sqrt{7})R19.1^\circ\) structure on the Pt(111) surface, and if there were equal amounts of these two domains the average surface symmetry probed by the SHG signal should be \( C_{3v} \). A reduction of the average surface symmetry to \( C_3 \) indicates the presence an unequal distribution of the two domains of adsorbed iodine. In a recent SHG study of gold single-crystal electrodes, Friedrich et al.\(^\text{16}\) also observed the presence of unequal domain distributions on the surface with the anisotropic SHG response.

Figure 2, a and b, plots (with the circles) the anisotropic response of \( I_{x,y}(2\omega) \) and \( I_{x,y}(2\omega) \) from the Pt(111) electrode at a potential of \(+0.200\) V after the iodine monolayer is replaced with carbon monoxide from a saturated CO solution at an electrode potential of \(+0.150\) V. The replacement reaction in saturated CO solution at this electrode potential leads to a highly packed CO monolayer with a surface density of 0.62-0.68 CO molecules per Pt surface atom.\(^\text{15}\)A striking change in the angular dependence of \( I_{x,y}(2\omega) \) is observed. This change can be described by the \( C_{3v}/C_{3v} \) symmetry of eq 1 if we let \( \rho_{xx} = 0.74 \) and \( \Delta \gamma = 55^\circ \). The change in the SHG signal of the surface indicates that the adsorption of CO has modified the surface electronic structure but has not changed the average surface symmetry. Ex situ LEED measurements indicate that the structure of the highly packed CO monolayer is \((\sqrt{3} \times 3) \) rect.\(^\text{5} \) If the three possible domains for this structure on the Pt(111) surface were equally populated, then the average surface symmetry would still be \( C_{3v} \). Increases in \( I_{x,y}(2\omega) \) from Pt(111) surfaces upon adsorption of a CO monolayer have been observed previously in UHV.\(^\text{17}\) The \( I_{x,y}(2\omega) \) SHG signal plotted in Figure 2b is larger after the replacement of the adsorbed iodine with CO but maintains the same functional form (eq 3 with \( \rho_{xx} = 0.19 \) and \( \Delta \gamma = 210^\circ \)). Again, the observation of a nonzero \( a_{YY} \) is attributed to the presence of the adsorbate, which has either created an additional anisotropic nonlocal contribution to the surface nonlinear susceptibility or reduced the average surface symmetry.

The highly packed CO monolayer can be oxidized electrochemically to CO\(_2\) at \(+0.540\) V (at a scan rate of 100 mV s\(^{-1}\)); integration of the current peak observed in the CV obtained during CO oxidation led to a surface charge density for the monolayer of 305 \( \mu \)C cm\(^{-2}\) in good agreement with the results of other authors.\(^\text{15,16}\) Continued cycling between \(-0.220\) and 0.840 V results in the steady-state CV shown in Figure 3. This CV is indicative of the highly ordered Pt(111) surface obtained originally by Clavilier,\(^\text{1} \) with the reversible "butterfly" peaks at 0.510 V. The presence of these peaks can be used as a verification of the preparation of a well-ordered Pt(111) surface.\(^\text{19}\)

The angular dependence of \( I_{x,y}(2\omega) \) from the well-ordered Pt(111) electrode at a potential of \(+0.200\) V is plotted in Figure 2a (diamonds). This \( I_{x,y}(2\omega) \) signal is greatly reduced in magnitude compared with the Pt(111) surfaces with an iodine or CO monolayer. After oxidation of the CO, the level of the \( I_{x,y}(2\omega) \) signal from the Pt(111) surface at a fixed potential was found to change over the course of an anisotropy measurement (ca. 20 min) due to the readsorption of CO from any small amount of residual CO in solution. Figure 4a plots a partial angular scan for \( I_{x,y}(2\omega) \) (diamonds) that was attempted under such conditions. A 3-fold pattern grows in during the scan due to the adsorption of a partial CO monolayer; this 3-fold pattern is similar to that obtained from

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The angular dependence of $I_{p2}(2\omega)$ from the well-ordered Pt(111) electrode at a potential of +0.200 V is plotted in Figure 2b (diamonds). The $I_{p2}(2\omega)$ signal has been reduced and modified to an almost uniform 6-fold pattern predicted by C6v symmetry (eq 2). The SHG anisotropic response of the Pt(111) crystal has contributions to the nonlinear susceptibility from the surface and from the bulk (via magnetic dipole and electric quadrupole contributions). In general, there is no a priori way of separating the bulk and surface nonlinear optical response; however, any changes in the SHG signal that occur during electrochemical cycling can be attributed to changes in the surface contribution to the nonlinear susceptibility. The quantity $|\alpha_{\phi}|^2$ can be obtained as a function of potential by measuring $I_{p2}(2\omega)$ at an azimuthal angle $\phi$ of 0° (see eq 3); Figure 3 plots the value of $|\alpha_{\phi}|^2$ obtained during a cyclic voltammogram of the well-ordered Pt(111) surface. At all potentials $|\alpha_{\phi}|^2$ is greatly reduced as compared to the surface with an adsorbed monolayer of CO and is virtually zero at potentials positive of the butterfly peaks (>+0.480 V).

Below an electrode potential of +0.480 V, $|\alpha_{\phi}|^2$ remains small but rises as the potential is scanned negatively. We attribute this rise to the presence of an adsorbed hydrogen species on the electrode surface. The broad current wave at 0.0 to -0.200 V is associated with hydrogen adsorption, and some authors attribute the current shoulder at +0.450 V to hydrogen adsorption (there is a long-standing controversy over the assignment of this peak in the electrochemical literature). A complete description of the potential dependence of the various SHG signal polarizations and a comparison to polycrystalline and Pt(100) electrodes will be presented in another paper. Briefly, the $I_{p2}(2\omega)$ and $I_{p2}(2\omega)$ SHG signals from polycrystalline and Pt(100) surfaces in perchloric acid are found to be independent of potential in the double-layer region and to rise sharply upon the adsorption of hydrogen. For Pt(111) electrodes, both $I_{p2}(2\omega)$ and $I_{p2}(2\omega)$ increase steadily at potentials below +0.480 V, suggesting that hydrogen is adsorbed onto the surface in that entire potential range.

Conclusions
In summary, in this paper we have demonstrated that the surface structure of a well-ordered Pt(111) electrode is maintained throughout the series of electrochemical chemisorption and oxidation steps required during its formation. The formation of an iodine monolayer and a highly packed CO monolayer is easily observed with the SHG anisotropy measurements. Additional contributions to the surface SHG signal are observed with these monolayers and can be attributed either to additional anisotropic nonlocal contributions to the nonlinear susceptibility or to a reduction of the average surface symmetry. The formation of a partial monolayer of CO results in changes in the SHG and electrochemical response from the surface; the changes in the SHG signal demonstrate that the electronic structure of the surface is different with a partial CO monolayer than with the highly packed CO structure. In the absence of iodine or CO adsorption, the order of the Pt(111) surface is preserved and the presence of adsorbed hydrogen is detected at potentials negative of +0.450 V. The use of SHG in this paper demonstrates its utility not only for elucidation of average surface symmetry but also for the identification of various chemisorption processes that can modify electrode surfaces.

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