

# High-Pressure Ammonia Adsorption and Dissociation on Clean Fe(111) and Oxygen-Precovered Fe(111) Studied by Sum Frequency Generation Vibrational Spectroscopy

Staffan Westerberg,<sup>†,‡</sup> Chen Wang,<sup>†,§</sup> Keng Chou,<sup>†</sup> and Gabor A. Somorjai<sup>\*†</sup>

Department of Chemistry, University of Berkeley, and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, Laboratory of Materials and Semiconductor Physics, Royal Institute of Technology, Electrum 229, SE-164 40, Sweden, and Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, China

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The adsorption of gases N<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, and NH<sub>3</sub> that play a role in ammonia synthesis have been studied on the Fe(111) crystal surface by Sum Frequency Generation (SFG) vibrational spectroscopy using an integrated ultrahigh vacuum/high-pressure system. SFG spectra are presented for the dissociation intermediates, NH<sub>2</sub> ( $\sim 3325\text{ cm}^{-1}$ ) and NH ( $\sim 3235\text{ cm}^{-1}$ ) under high pressure of ammonia (200 Torr) on the clean Fe(111) surface. Addition of 0.5 Torr of oxygen to 200 Torr of ammonia does not significantly change the bonding of dissociation intermediates to the surface. However, it leads to a phase change of nearly 180° between the resonant and nonresonant second-order nonlinear susceptibility of the surface, demonstrated as a reversal of the SFG spectral features. Heating the surface in the presence of 200 Torr of ammonia and 0.5 Torr of oxygen reduces the oxygen coverage, which can be seen from the SFG spectra as another relative phase change of 180°. The reduction of the oxide is also supported by Auger electron spectroscopy. The result suggests that the phase change of the spectral features could serve as a sensitive indicator of the chemical environment of the adsorbates. Clean Fe(111) is found to have a large SFG nonresonant signal. The magnitude of the nonresonant signal was dependent on the adsorption species; O<sub>2</sub> and N<sub>2</sub> decrease, while H<sub>2</sub> and NH<sub>3</sub> increase the SFG nonresonant signal. The change in nonresonant signal is correlated to the change in work function for Fe(111) upon adsorption. Adsorption-induced changes in the SFG nonresonant signal was used as an indicator of surface conditions and to monitor surface reactions.

## 1. Introduction

Iron has been used as the key catalyst for producing ammonia from nitrogen and hydrogen. Consequently, the reaction of ammonia synthesis on iron catalysts has been extensively studied since its discovery in the early 20th century, and it has developed into one of the classical heterogeneous catalytic processes.<sup>1</sup> The industrial reaction typically requires high temperatures (300 to 500 °C) and high pressures (tens of atmospheres or higher). Even though this reaction has been industrialized for nearly a century, the intriguing role of iron surfaces has been the focus of decades of studies to help uncover some of the basic principles of heterogeneous catalysis. Most of the reported fundamental surface science studies are under experimental conditions (high vacuum and low temperatures) far away from industrial conditions, and thus the importance of the information obtained to catalytic ammonia synthesis could be questioned. One of the difficulties of in situ studies is that there has been a lack of instrumentation that could enable characterization of catalyst surfaces under the reaction conditions. The application of SFG vibrational spectroscopy to surface chemistry studies has been explored as one of the possible approaches to tackle

the obstacles for in situ studies of catalyst surfaces under various conditions.<sup>2,3</sup> It should be noted that no SFG studies have been reported on clean iron or iron oxide surfaces so far. Given the active role of iron and iron oxides in heterogeneous catalysis, such effort would be of genuine interest.

Ammonia synthesis, as well as its dissociation process, on iron and other metal surfaces has been pursued for several decades by various surface analysis techniques. Most studies have been performed on high-surface-area iron catalysts or on single crystals as model catalysts where, for example, elementary reaction steps, surface structure, the role of promoters, and adsorption behaviors have been investigated.<sup>4</sup> The iron surface with the highest turnover rate was found to be the Fe(111) crystal face.<sup>5</sup> The focus of this study has been on the ammonia adsorption and dissociation on Fe(111) at high pressure (200 Torr). A newly designed integrated UHV–high-pressure system with capabilities for in situ SFG has been built for the purpose of studying high-pressure catalytic processes and in particular ammonia synthesis. The system has a reaction cell that can be pressurized to several atmospheres to more closely mimic the industrial process. The reaction cell is connected to an ultrahigh vacuum chamber, which allows preparation and characterization of the surface with standard surface science techniques, including ion bombardment, Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and mass spectrometry.

In the present work, adsorption of ammonia has been performed on two surfaces, clean Fe(111) and Fe(111) pretreated

\* Author to whom correspondence should be addressed at Department of Chemistry, University of California, Berkeley, D58 Hildebrand Hall, Berkeley, CA 94720-1460. E-mail: somorjai@cchem.berkeley.edu.

<sup>†</sup> Department of Chemistry, University of Berkeley, and Materials Science Division, Lawrence Berkeley National Laboratory.

<sup>‡</sup> Royal Institute of Technology.

<sup>§</sup> The Chinese Academy of Sciences.

with oxygen. Ammonia dissociation intermediates, NH and NH<sub>2</sub>, were detected on both surfaces under high pressure of ammonia. Coadsorption of oxygen and ammonia is discussed and, in particular, its influence on the SFG spectral features related to the interference between the resonant and nonresonant second-order nonlinear susceptibility. In addition, a large SFG nonresonant signal of the clean Fe(111) surface was observed. It was found that the magnitude of the SFG nonresonant signal was significantly changed by the adsorption of N<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, and NH<sub>3</sub>, species that are most relevant in ammonia synthesis. The change in nonresonant signal was correlated to the change in work function of Fe(111) upon adsorption. A weak resonant signal from the NH stretch, in addition to the large nonresonant signal from iron, made extensive averaging necessary to obtain a good signal-to-noise ratio in the SFG spectra.

## 2. Experimental Section

### 2.1. Sum Frequency Generation Vibrational Spectroscopy.

SFG technique and theory have been described in detail previously.<sup>6–10</sup> Briefly, SFG is a second-order nonlinear optical process, where a visible ( $\omega_{\text{vis}}$ ) and an IR ( $\omega_{\text{IR}}$ ) beam are spatially and temporarily overlapped at an interface, to generate the sum frequency ( $\omega_{\text{sum}}$ ) of two incoming beams. In this study, only the IR beam has been tuned. When the IR energy matches the vibrational frequency of an interfacial molecule, the SFG signal is resonantly enhanced. In general, the sum frequency signal is proportional to the square of the effective second-order nonlinear susceptibility,  $\chi^{(2)}$ , as given by eq 1:

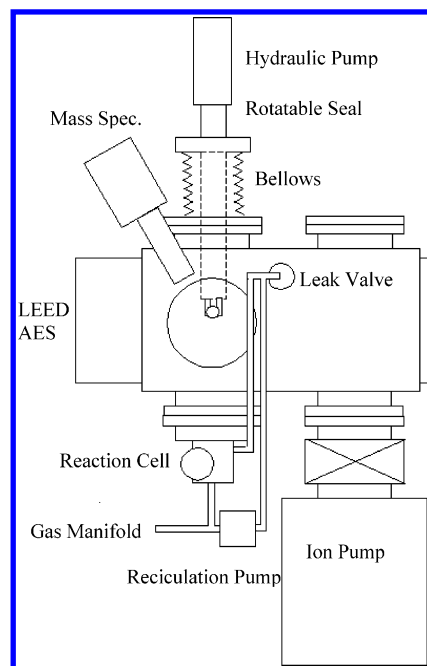
$$I(\omega_{\text{sum}}) \propto |\chi_{\text{eff}}^{(2)}|^2 \quad (1)$$

For vibrationally resonant SFG,  $\chi^{(2)}$  can further be described by eq 2:

$$I(\omega_{\text{sum}}) \propto |\chi_{\text{NR}} + \sum_q \frac{A_q e^{i\theta_q}}{\omega_{\text{IR}} - \omega_q + i\Gamma_q}|^2 \quad (2)$$

where  $\chi_{\text{NR}}$  contains the nonresonant contributions to the measured intensity. The vibrational mode strength,  $A_q$ , is proportional to the surface density and orientational average of adsorbed molecules and the IR and Raman transition moments. The second term in eq 2 is maximized when the IR beam,  $\omega_{\text{IR}}$ , is tuned near a vibrational mode,  $\omega_q$ , of one of the surface species.  $\Gamma_q$  is the damping term, and  $\theta_q$  is the relative phase between the  $q$ th vibrational mode and the nonresonant signal. SFG is a second-order nonlinear optical process and it is therefore forbidden in a centro-symmetric media, while at an interface where the symmetry is broken SFG is allowed. Consequently, SFG is surface-specific and the technique could be used to probe any interface as long as the laser beams have access to the interface.

A Nd:YAG laser (generating ~20 ps long pulses at 20 Hz and 30 mJ/pulse) was used as the laser source. The 1064 nm fundamental output was used to pump two optical parametric generation/amplification (OPG/OPA) systems, one for the IR and one for the visible. Two-thirds of the pump energy was used to generate the tunable IR. Part of the fundamental beam was frequency doubled to 532 nm in a KTA crystal, which subsequently pumped two counter-rotating KTP crystals in an OPG/OPA stage. The near-IR (710–880 nm) output from this stage was difference frequency mixed with the 1064 nm beam in two KTA crystals to generate a tunable IR between 2000 and 4500 cm<sup>-1</sup>. As the visible input, 532 nm light was used in this study. Both IR and visible beams were p-polarized, and



**Figure 1.** Schematics of the integrated ultrahigh vacuum/high-pressure reaction chamber.

they were overlapped spatially and temporarily on an Fe(111) crystal. The incident angles of the visible and IR beams were 53° and 62° with respect to the surface normal. The energies of the incident beams were limited to 200  $\mu$ J per pulse. To control if the adsorption and dissociation of ammonia is influenced by laser power, both IR and visible beam energies were lowered independently to 50  $\mu$ J. No changes in the spectral features could be seen, which indicates that the laser beam does not interfere with the adsorbates. The sum frequency generated light was sent through a monochromator, and the signal intensity was detected by a photomultiplier tube and integrated by a gated integrator. Due to the weak resonant signal of ammonia dissociation products, each spectrum is presented with an average of 2000 to 5000 data points per frequency. The experimental data are fitted to eq 2, using a least-squares method, to extract the values of parameters, such as peak position, peak width, amplitude, phase, and nonresonant background.

### 2.2. Integrated Ultrahigh Vacuum/High-Pressure Reaction Chamber.

The experiments were carried out in a newly designed two-level system, consisting of an UHV, surface analysis chamber, and a high-pressure reaction cell compatible with UHV and SFG; see Figure 1. The base pressure in the UHV chamber was  $1 \times 10^{-9}$  Torr, which could be maintained while the reaction cell was pressurized to 1 atm. The reaction cell was attached below the main UHV chamber; by lowering the sample holder into the cell a knife-edge was pushed against a gasket. By applying pressure from a hydraulic pump onto the sample holder and gasket, a seal was made between the reaction cell and the UHV chamber. The system allowed studies of adsorbates from a fraction of a monolayer obtained at UHV to high coverages obtained at atmospheric pressure. For UHV studies, the pressure was regulated precisely by a leak valve and measured by an ion gauge in the UHV chamber. High-pressure gases were introduced directly from a manifold to the reaction cell where the pressure was monitored by a Baratron gauge. Through a recirculation loop, which was attached to the reaction cell and to a leak valve on the main UHV chamber, the gas composition under high-pressure catalytic conditions could be monitored by a residual gas analyzer. The system was

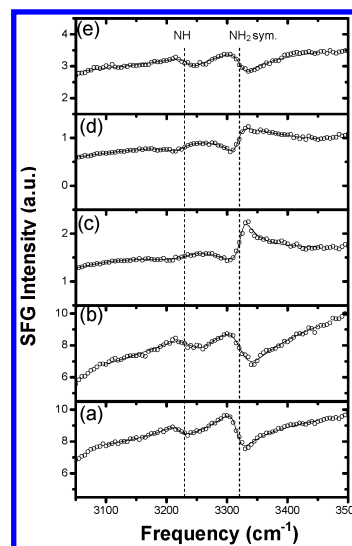
further equipped with a retarding field analyzer, RFA, for Auger electron spectroscopy and LEED analysis. The sample was mounted on the sample holder where it could be resistively heated to 1000 K or cooled by a flow of liquid nitrogen down to 170 K.

For the SFG experiments the reaction cell was equipped with two  $\text{CaF}_2$  windows to allow the IR light to reach the sample. The path length from the window to the sample was approximately 4 cm. To normalize for the gas-phase adsorption in the reaction cell the IR power was monitored before and after the reaction cell. The IR power at the sample surface could thereafter be calculated, and the SFG intensity was calibrated by the IR power.

The Fe(111) single crystal was cut, oriented, and polished by normal procedures. Prior to mounting, the Fe(111) crystal was heated to 800 °C for several days in a flow of hydrogen to remove sulfur impurities. At this temperature the diffusion rate of sulfur is high enough to allow significant amounts of sulfur to segregate to the surface where it is removed by reaction with hydrogen. Thereafter, the Fe(111) crystal was put into the UHV chamber where it was further cleaned by repeated cycles of Ar sputtering at 500 °C to remove additional sulfur. Beside sulfur, carbon was the main impurity. It was found that the most efficient way to remove carbon impurities was to introduce  $1 \times 10^{-7}$  Torr of  $\text{O}_2$  while sputtering at  $3 \times 10^{-5}$  Torr of Ar at 500 °C, followed by sputtering in pure Ar at room temperature. Between sputtering cycles the sample was briefly annealed to 600 °C. This process finally resulted in a clean iron surface with concentrations of impurities below the detection level of AES. Once a clean iron surface had been obtained, only a few sputtering cycles were needed to remove contaminants between each experiment.

### 3. Results and Discussion

**3A.1. High-Pressure (200 Torr) Ammonia Adsorption on Clean Fe(111).** A set of spectra where 200 Torr of ammonia have been adsorbed under various conditions is shown in Figure 2. In the first spectrum, Figure 2(a), 200 Torr of ammonia have been adsorbed on the Fe(111) surface and it resulted in a SFG spectrum with two prominent peaks. After fitting of the experimental data to eq 2, the peak positions were determined to 3232 and 3320  $\text{cm}^{-1}$ . The peaks are shifted from their apparent peak positions due to the interference between the resonant and nonresonant parts of the second-order nonlinear susceptibility. The observed peaks are assigned to NH stretch and  $\text{NH}_2$  symmetric stretch, respectively. Ammonia adsorption has previously been studied by IR adsorption spectroscopy on powdered iron samples.<sup>11</sup> Peak positions observed in this study correspond well with reported values in the literature. The  $\text{NH}_2$  asymmetric stretch is expected to be around 3400  $\text{cm}^{-1}$ , but no such feature could be seen when adsorbing 200 Torr of ammonia on clean Fe(111). There is no evidence of molecular ammonia on the surface, which could be explained by the rapid ammonia dissociation on a clean Fe(111) surface at room temperature.<sup>12</sup> Calculations show that the surface is mostly covered by atomic nitrogen and hydrogen under ammonia synthesis conditions.<sup>13</sup> Only about one to two percent of the sites are covered by intermediates such as NH and  $\text{NH}_2$ . Although we have performed our experiment under different conditions, we believe that the surface is mostly covered by atomic nitrogen and hydrogen. Atomic nitrogen and hydrogen bonded to the surface have vibrational frequencies, 1100–500  $\text{cm}^{-1}$  for atomic nitrogen depending on bonding geometry, and 1950  $\text{cm}^{-1}$  for atomic hydrogen,<sup>14</sup> which are beyond the available frequency



**Figure 2.** SFG spectra of ammonia on Fe(111) and on preoxidized Fe(111). Intensities are shown using the same scale for easy comparison. Experimental data are plotted with circles, and fitted curves are shown with solid lines. (a) 200 Torr of  $\text{NH}_3$  on Fe(111), (b) 200 Torr of  $\text{NH}_3$  on Fe(111) pretreated with  $10^{-5}$  Torr of oxygen, (c) 200 Torr of  $\text{NH}_3$  coadsorbed with 0.5 Torr of oxygen on Fe(111), (d) 200 Torr of  $\text{NH}_3$  coadsorbed with 0.5 Torr of oxygen on Fe(111) pretreated with  $10^{-5}$  Torr of oxygen, (e) 200 Torr of  $\text{NH}_3$  coadsorbed with 0.5 Torr of oxygen on Fe(111) after heating the surface to 150 °C for 20 min and then cooled to room temperature.

range with our SFG setup. Only a small amount of NH and  $\text{NH}_2$  intermediates are present on the surface, which make them hard to detect with SFG since minimum coverage for detection is generally around a few percent of a monolayer, depending on the adsorbed species. Another factor that could make the intermediates difficult to detect with SFG is if there is poor, or lack of proper orientation on the surface. Ammonia is adsorbed with the nitrogen toward the iron surface,<sup>15</sup> but the molecule could be tilted from the surface normal. To the best of our knowledge there are no reports on the tilt angle of ammonia or its dissociation products on iron. However, a tilt angle up to 40° has been reported for ammonia on the  $\text{ZnO}(1010)$  surface.<sup>16</sup> Such a tilt angle would reduce the signal intensity in SFG, since it is most sensitive to dipoles perpendicular to the metal substrate.

**3A.2. High-Pressure (200 Torr) Ammonia Adsorption on Preoxidized Fe(111).** A SFG spectrum nearly identical to the one where 200 Torr of ammonia was adsorbed on clean Fe(111) has been recorded on a preoxidized Fe(111) surface as shown in Figure 2b. In this case, the Fe(111) surface was exposed to  $1 \times 10^{-5}$  Torr of oxygen at room temperature for 20 min. Before the introduction of 200 Torr of ammonia, the oxygen was pumped out and the surface composition was checked with Auger electron spectroscopy. The SFG spectrum was fitted to eq 2, and it shows two peaks at 3241  $\text{cm}^{-1}$  and 3326  $\text{cm}^{-1}$ , which are attributed to NH and  $\text{NH}_2$  symmetric stretches. The peaks are blue-shifted by less than 10  $\text{cm}^{-1}$  compared to Figure 2a. Again, no peaks due to ammonia were detected. The detection of dissociation intermediates shows that the ammonia at 200 Torr was adsorbed and underwent dissociation on the oxidized Fe(111).

**3A.3. High-Pressure Ammonia/Oxygen Coadsorption on Fe(111).** When introducing 200 Torr of ammonia together with 0.5 Torr of oxygen on the clean Fe(111) surface, the spectrum is different from the previous two cases; see curve (c) in Figure 2. There are two major differences; the overall magnitude of the nonresonant signal is lowered by introduction of additional



**TABLE 1: Fitting Parameters for the Experimental Data Shown in Figure 2<sup>a</sup>**

parameters	Fe NH <sub>3</sub>	FeO <sub>x</sub> NH <sub>3</sub>	Fe NH <sub>3</sub> /O <sub>2</sub>	FeO <sub>x</sub> NH <sub>3</sub> /O <sub>2</sub>	Fe NH <sub>3</sub> /O <sub>2</sub> after heating
peak 1 (cm <sup>-1</sup> )	3232	3241	3236	3229	3237
phase 1 (deg.)	168	209	35	52	219
peak 2 (cm <sup>-1</sup> )	3320	3326	3324	3318	3323
phase 2 (deg.)	188	195	10	-27	205

<sup>a</sup> Presented here are the peak positions and the corresponding phases. Uncertainties for peak positions are  $\pm 2$  cm<sup>-1</sup> and for the relative phase  $\pm 20^\circ$ . The substrates are either clean Fe(111) or Fe(111) preoxidized with  $10^{-5}$  Torr of O<sub>2</sub>. Adsorbed gases are 200 Torr of NH<sub>3</sub> or 200 Torr of NH<sub>3</sub> coadsorbed with 0.5 Torr of O<sub>2</sub>.

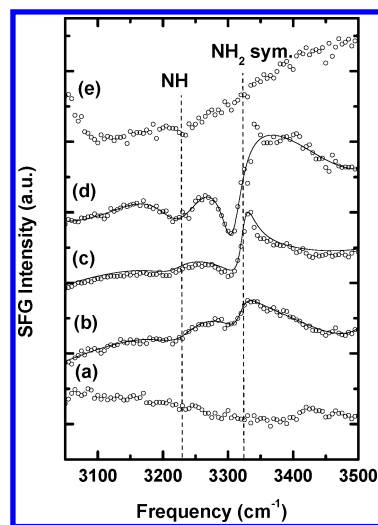
oxygen and the spectral features are changed. If curves (a) and (c) are overlapped, it can be seen that the peaks in curve (a) are changed into minima in curve (c). At the same time, the minima in curve (a) are changed into peaks for curve (c). Fitting the data shows that the peak positions (3236 and 3324 cm<sup>-1</sup>) remained close to the previous values, but the phases were changed by approximately 180° when the surface was exposed to the additional oxygen. See Table 1 for a list of the fitting parameters. The peak positions at 3236 and 3324 cm<sup>-1</sup> were assigned to NH stretch and NH<sub>2</sub> symmetric stretch, respectively. There is no indication of the presence of molecular ammonia.

When oxygen is introduced together with ammonia there will be a competitive adsorption. The fact that oxygen has about 1 order of magnitude higher adsorption energy than ammonia,<sup>1</sup> which has an adsorption energy of 10–12 kcal/mol,<sup>15</sup> means that oxygen adsorption will dominate until the iron surface is fully covered by an oxide layer. The ammonia will then be adsorbed on an essentially oxidized Fe(111) surface. This should be similar to the case of ammonia adsorption on the preoxidized Fe(111) in Figure 2b. Yet, we see a clear difference between spectra (b) and (c), which tells us that the presence of gas-phase molecular oxygen pressure plays an important role. Figure 2d shows the case where 200 Torr of ammonia were coadsorbed with 0.5 Torr of oxygen on an Fe(111) surface preoxidized with  $10^{-5}$  Torr of oxygen. No differences to the coadsorption on clean Fe(111) were found, which confirms that during coadsorption on clean Fe(111) the surface was initially oxidized.

To further explore the coadsorption of oxygen, the Fe(111) was heated to 150 °C for 20 min in the presence of 200 Torr of ammonia and 0.5 Torr of oxygen. The sample was then cooled to room temperature before a new SFG spectrum was recorded; see Figure 2e. After heating, the spectral features were again reversed and the peaks were determined to be 3237 and 3323 cm<sup>-1</sup>, corresponding to NH and NH<sub>2</sub> symmetric stretch, respectively. The relative phase was switched by nearly 180° as seen in Table 1.

### 3A.4. Pressure Effect on Ammonia/Oxygen Coadsorption.

To evaluate the effect of pressure on ammonia coadsorption with oxygen, a series of spectra has been recorded at pressures ranging from  $10^{-5}$  Torr to 600 Torr of ammonia. In all cases, ammonia has been coadsorbed with oxygen. At  $10^{-5}$  Torr of ammonia,  $10^{-5}$  Torr of oxygen was introduced together with the ammonia. For higher pressures, ammonia was coadsorbed with 0.5 Torr of oxygen. At  $10^{-5}$  Torr, no vibrational features could be detected (see Figure 3). By increasing the pressure to 20 Torr, vibrational features due to ammonia adsorption were visible. Fitting the curve to eq 2 gives us two peaks centered at 3235 cm<sup>-1</sup> and 3325 cm<sup>-1</sup>. They are attributed to NH stretch and NH<sub>2</sub> symmetric stretches, respectively. By increasing the pressure to 200 Torr, the peaks become more pronounced.



**Figure 3.** SFG spectra of ammonia coadsorbed with oxygen on preoxidized Fe(111). Experimental data are plotted with circles, and fitted curves are shown with solid lines. (a)  $10^{-5}$  Torr of ammonia and  $10^{-5}$  Torr of oxygen, (b) 20 Torr of ammonia and 0.5 Torr of oxygen, (c) 200 Torr of ammonia and 0.5 Torr of oxygen, (d) 600 Torr of ammonia and 0.5 Torr of oxygen, (e) SFG spectrum after pumping out the ammonia and oxygen.

Further increase in pressure to 600 Torr does not significantly alter the spectrum. After pumping out the ammonia, there are no observable peaks in the spectrum.

**3A.5. Discussion.** When ammonia is adsorbed on clean or preoxidized Fe(111) surfaces, NH<sub>2</sub> and NH species were detectable in a broad range of experimental conditions. In contrast, we were not able to detect molecular ammonia at room temperature in our studied pressure range ( $10^{-5}$ –600 Torr). In this study we have been concentrating on high ammonia pressure and high-temperature experiments (room temperature or above).

When pure ammonia is adsorbed on clean Fe(111), two peaks with asymmetric profiles can be seen at 3232 and 3320 cm<sup>-1</sup>. Preoxidizing the Fe(111) in  $1 \times 10^{-5}$  Torr of oxygen for 20 min does not greatly change the peak positions of the NH and NH<sub>2</sub> surface species. Several conclusions can be drawn from this. First, ammonia can decompose on the preoxidized as well as on the clean Fe(111) surface. There is a possibility that the oxide is reduced by the high-pressure ammonia and exposed iron sites are responsible for the dissociation. However, the oxygen coverage before and after ammonia adsorption was measured by Auger electron spectroscopy, and no reduction of the oxygen peak could be seen. The second conclusion is that the dissociation products are loosely bound to the surface and that the bond strength to the surface does not change appreciably whether adsorbing on the clean or preoxidized Fe(111). Last, the relative phase between the resonant and nonresonant part does not change by preoxidizing the surface.

The largest changes in the spectral features were seen when 0.5 Torr of oxygen was coadsorbed with ammonia and after heating of the surface. Analysis of the data shows a phase shift of close to 180° between the resonant and nonresonant part of the SFG signal when 0.5 Torr of oxygen was present. Upon heating the surface to 150 °C, the spectral features are reversed, and the relative phase was again changed by 180°. The changes in spectral features are caused by an interference between the resonant and nonresonant second-order nonlinear susceptibility, which can cause the SFG spectral profile to be different from those observed in IR spectroscopy. Well-defined symmetric peaks can be expected in the SFG spectrum when  $\chi_{NR}$  is negligibly small and resonances are far apart. However, when

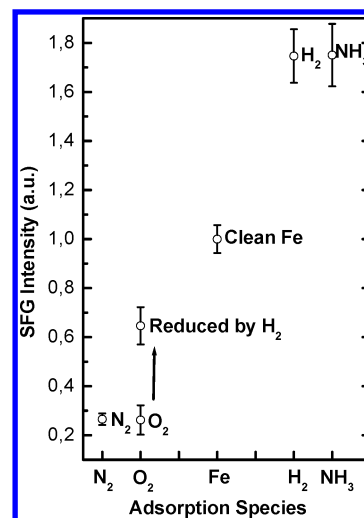
$|\chi_{\text{NR}}|$  is comparable to, or larger than  $|A_q/T_q|$ , spectral profiles can include asymmetric peaks and dips. This is the case when using Fe(111) as a substrate. To deduce the parameters characterizing the resonances, eq 2 is used to fit the observed spectrum.

The relative phase shift could be caused by a shift in phase for either the adsorbates or the substrate, or a combination of both. The phase shift was not observed after preoxidizing at  $1 \times 10^{-5}$  Torr of oxygen, indicating that a higher oxygen pressure is needed to induce the phase shift, either by increasing the oxidation of the iron or by being present as molecular adsorbates on the surface of iron. After heating the surface in the presence of oxygen and ammonia, the oxygen coverage of the surface was reduced as seen by AES, and the spectral features were again reversed. Oxygen readsorption and oxidation of the surface was prevented by higher nitrogen coverage on the surface after the increased dissociation of ammonia at high temperature.

In contrast to the large phase shifts due to oxygen coadsorption, there were no significant shifts in peak positions, which indicates that the bonding to the surface is similar in all cases. In a related study of coadsorption between CO and  $\text{NH}_3$  on Ru(0001), it was concluded that the adsorption of CO, which is an electron acceptor like oxygen, did not modify the electronic interaction between the ammonia and the metal.<sup>17</sup> The electron-donating character of ammonia was the same whether ammonia bonded directly to the metal alone or in the presence of adsorbed CO.

We have also observed that the pressure is important for the detection of ammonia adsorption by SFG. The SFG signal intensity depends on the number density of adsorbed molecules as well as on their molecular orientation. Vibrational features from NH stretches are visible only at higher pressures (above  $10^{-5}$  Torr), as seen in Figure 3. The reason for the pressure dependence could be that the surface coverage is higher at higher pressures. Increasing coverage may induce ordering on the surface where NH and  $\text{NH}_2$  intermediates are aligned with their dipoles perpendicular to the surface. To analyze the orientation of the molecules on the surface, we need at least one more input and output beam polarization combination. The data presented here are from ppp polarization. Therefore, we cannot deduce any orientation of the adsorbates from our experiments. Instead we can only speculate that the higher ammonia pressure increases the surface coverage and causes the molecules to align perpendicular to the surface.

**3B.1. SFG Nonresonant Signal Intensity of Fe(111) and Its Variation with Adsorbed Gases,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$ .** With the visible beam fixed at 532 nm and the IR beam tuned between 3000 and 4300  $\text{cm}^{-1}$ , a large SFG signal has been detected from the clean Fe(111) surface. Within the mentioned frequency range, the nonresonant signal is nearly constant up to 3900  $\text{cm}^{-1}$  after which it is enhanced by more than three times. When adsorbing various molecules on the clean iron surface, we found that the nonresonant signal intensity changed dramatically. The observed changes depend on the adsorption species, as seen in Figure 4. The nonresonant signal of Fe(111) was measured at 3300  $\text{cm}^{-1}$  where the intensity of the clean Fe(111) surface was normalized to 1. Oxygen and nitrogen are found to decrease the nonresonant signal, while hydrogen increases the signal intensity. Adsorption of ammonia initially increases the SFG signal, followed by a gradual decrease as explained later. Changes in second-order nonlinear susceptibility upon adsorption have previously been observed with second harmonic generation (SHG).<sup>18</sup> However, SFG probes the



**Figure 4.** SFG background of various adsorbates on Fe(111) measured at 3300  $\text{cm}^{-1}$ . The SFG background intensity of clean Fe(111) is normalized to 1. The intensities are changed upon adsorption of  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$ . An example of surface reaction monitored by the SFG background is the oxidation of Fe(111) in  $10^{-5}$  Torr of  $\text{O}_2$ , followed by reduction in  $10^{-5}$  Torr of  $\text{H}_2$  at 400 °C.

vibrational features of the adsorbates as well, which could be advantageous over SHG in many experiments.

The gas that was found to have the largest effect on the nonresonant signal was oxygen. The intensity was instantly lowered to 4 times compared to clean Fe(111) when introducing  $1 \times 10^{-5}$  Torr of oxygen. By introducing a lower pressure of oxygen,  $1 \times 10^{-7}$  Torr, the SFG intensity decreased to the same level as for  $10^{-5}$  Torr, but the decline could be followed on a time scale of several tens of seconds. The fact that the iron surface would be covered by a monolayer within 10 s at  $10^{-7}$  Torr indicates that the decline in SFG signal intensity is governed by some other factors besides adsorption of oxygen. A plausible cause could be the formation of iron oxide that could be slower than adsorption, and it would also be dependent on such factors as temperature and partial pressure of oxygen.

No change in intensity has been found when introducing  $1 \times 10^{-5}$  Torr of nitrogen at room temperature. This is not surprising since the sticking coefficient of nitrogen is extremely small at room temperature, as low as  $10^{-7}$  on iron.<sup>19</sup> To increase the nitrogen coverage the temperature was raised to 500 °C while maintaining the nitrogen pressure at  $1 \times 10^{-5}$  Torr for a prolonged time. Subsequently, the nitrogen coverage on the surface was detectable by AES. After cooling to room temperature, the SFG signal had decreased 4 times relative to clean Fe(111). Both oxygen and nitrogen were found to decrease the SFG signal intensity.

In contrast, when  $1 \times 10^{-7}$  Torr of hydrogen was introduced, the signal increased to 1.7 times that of clean Fe(111). Another case where the intensity was increased is the adsorption of ammonia. The signal was increased by 1.7 times that of clean Fe(111) when the reaction cell was pressurized to  $1 \times 10^{-7}$  Torr of ammonia. However, ammonia molecules decompose on Fe(111) at room temperature, and eventually a nitrogen coverage is built up on the surface. As mentioned before, formation of nitride on the surface has an effect of lowering the SFG signal. Over time, as more ammonia decomposed, the surface coverage of nitrogen was increased and the signal intensity dropped below that of clean Fe(111). This is an example of how changes in the nonresonant signal of iron can be used as an indicator of the surface conditions during reaction. As reported above, the formation of oxide on Fe(111) was

followed by measuring the SFG nonresonant signal. Under favorable conditions, the kinetics of the oxide formation is slow enough to be monitored by SFG. Another surface reaction that was monitored was the reduction of iron oxide by heating in hydrogen; see Figure 4. Introduction of  $1 \times 10^{-5}$  Torr of oxygen lowered the SFG signal to 0.25 of that of clean iron. After pumping out the oxygen, the cell was pressurized to  $1 \times 10^{-5}$  Torr of hydrogen and heated to 400 °C. As a result, the signal intensity was restored to close to that of clean Fe(111), indicating that the oxide is reduced by hydrogen. A decrease of the oxygen coverage was also confirmed by AES immediately following the reduction.

**3B.2. Discussion.** The SFG nonresonant signal for metals can in general be related to the surface electronic structure of the substrate, and more specifically the surface density of states of electrons (DOS) and the excitations of those electrons.<sup>20</sup> The large nonresonant signal from clean Fe(111) and its 3-fold enhancement around  $4000\text{ cm}^{-1}$  could be associated with the detailed structure of the surface DOS for Fe(111). By scanning the frequency of the visible light, a more complete picture of the surface electronic structure would be obtained. However, the focus of this study is not to investigate the surface electronic structure of Fe(111). Instead the dependence of the SFG nonresonant signal is used as a sensitive tool to the changes in the surface electronic density due to chemical interaction with adsorbates.

From the adsorption experiments on Fe(111) it is clear that the information gained by SFG is not limited to the vibrationally resonant signal; changes in the nonresonant signal can also provide useful insight into the surface chemistry. Similar ideas have been reported previously in the literature where the nonresonant signal of MgO(001) was monitored during adsorption of formic acid.<sup>21</sup> It was noted that the nonresonant signal intensity decreased upon adsorption of formic acid. Subsequent heating of the surface and desorption of formic acid restored part of the intensity. It was concluded that the nonresonant signal originated from the defect sites, and therefore the concentration of these defect sites could be monitored during adsorption and desorption. In our study, the nonresonant signal intensity can both increase and decrease depending on different adsorption species, suggesting there must be some other effects influencing the SFG nonresonant signal intensity.

A possible explanation was given by Guyot-Sionnest et al. in a study where the adsorption and desorption of CO on W(110) were investigated.<sup>22</sup> It was shown that there was a correlation between the intensity of the SFG nonresonant signal and the change in work function upon adsorption. The idea of a correlation of the nonresonant signal with work function changes has long been reported in SHG studies. One of the earlier ones discussed the adsorption of O<sub>2</sub>, CO, H<sub>2</sub>, and NH<sub>3</sub> on Re(0001).<sup>18</sup> It was shown that the SH signal decreased when the surface was covered by electron-withdrawing adsorbates such as O<sub>2</sub> or CO which increase the work function of the metal. At saturation coverage of oxygen, the work function was increased by 0.45 eV, and the SH signal showed a 5-fold reduction. Upon adsorption of NH<sub>3</sub>, the SH signal was increased by 55 times for NH<sub>3</sub> which correlated with a decrease in work function by 2.1 eV.

This study is one of the first SFG studies where changes, both increase and decrease, of the nonresonant signal could be correlated to work function changes of the metal substrate. Oxygen decreases the nonresonant signal by 4 times when adsorbed on the Fe(111) surface. The work function change for this system has previously been shown to be increased by 1.1

eV for 2 L of oxygen, adsorbed at 77 K, on the Fe(111) surface.<sup>23</sup> Nitrogen adsorption also shows a decrease in nonresonant signal, which correlates with a 0.25 eV increase of the work function for Fe(111) upon adsorption of nitrogen.<sup>24</sup> The change depends on coverage for both O<sub>2</sub> and N<sub>2</sub>, as well as the heat treatment of the surface in order to obtain nitrogen coverage. In contrast to oxygen and nitrogen, ammonia is an electron donor that gives rise to a reduction of the work function, by 2.05 eV, for Fe(111),<sup>15</sup> which agrees with the observed increase of the nonresonant background. Interestingly, the initial reduction was followed by a rise of the work function due to ammonia dissociation and the buildup of nitrogen coverage on the surface. The final work function was increased by about 0.1 eV compared to that of the clean Fe(111). This correlates remarkably well with the changes in the nonresonant background, where we see an initial increase in signal followed by a gradual decrease until the signal stabilizes below the signal intensity of clean Fe(111). In the case of hydrogen adsorption, the picture is not as clear. The work function has been measured to be between -0.1 eV and 0.3 eV, depending on the surface structure of iron.<sup>25</sup> Hydrogen adsorption on Fe(111) is reported to give an increase of 0.3 eV. This should lead to a lowering of the nonresonant signal; however, we have observed an increase. Since the work function change is relatively small and has a different sign, depending on the surface, a small amount of surface defects could alter the total work function change or the nonresonant signal intensity.

#### 4. Conclusions

Sum frequency generation vibrational spectroscopy has been used to study ammonia adsorption and dissociation on Fe(111) and preoxidized Fe(111) under high pressure (200 Torr). Vibrational frequencies for NH and NH<sub>2</sub> have been identified on the clean and preoxidized Fe(111). Ammonia molecules have been found to dissociate at room temperature on both clean and preoxidized Fe(111) under high pressure (20–600 Torr). Introduction of 0.5 Torr of oxygen changes the interference of the resonant and the nonresonant second-order nonlinear susceptibility by changing the relative phase. This can be seen as a reversal of the spectral features in the SFG spectra. Heating the surface in the presence of high-pressure ammonia reduces the oxygen coverage, and there is another relative phase change of 180° to restore the initial spectral features.

Adsorption on Fe(111) causes a distinct change in signal, and a correlation between the work function change and magnitude of the nonresonant SFG signal is proposed. Knowing the effect on work function upon adsorption, the change of nonresonant SFG signal can be predicted. The change in SFG nonresonant signal can be used to follow surface reactions, including iron oxidation, ammonia dissociation, and nitride formation on iron surfaces as well as reduction of iron oxides.

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