

# CO Oxidation on Electrified Platinum Surfaces in Acetonitrile/Water Solutions Studied by Sum Frequency Generation and Cyclic Voltammetry

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Sum frequency generation (SFG) vibrational spectroscopy in combination with cyclic voltammetry (CV) was used to investigate the oxidation of carbon monoxide (CO) in acetonitrile (CH<sub>3</sub>CN)/water (H<sub>2</sub>O) solutions at the platinum (Pt) electrode surface. CO oxidation on Pt was studied as a function of water concentration and electrode potential. In electrolyte solutions containing small concentrations of water, a preoxidation wave was observed at +900 mV vs SCE whereby a small amount of the adsorbed CO was oxidized. This preoxidation wave was followed by the main oxidation of CO on Pt at approximately +1700 mV vs SCE. Spectroscopy and voltammetry data in these essentially nonaqueous electrolytes indicate an oxidation intermediate of CO to CO<sub>2</sub> that was nearly parallel to the Pt electrode surface.

## Introduction

The useful lifetime of an electrochemical cell is dominated by chemical reactions that occur at the electrode/electrolyte interface.<sup>1</sup> One specific example of such a reaction is the adsorption and oxidation of CO, a well-known poison in electrochemical cells. CO adsorption on platinum has been extensively studied in aqueous and nonaqueous solutions using several in-situ spectroscopy techniques.<sup>2–10</sup> However, previous studies of CO electrooxidation on platinum have been performed solely in aqueous solutions.<sup>11–14</sup>

In this laboratory, adsorbed CO and its oxidation have been previously monitored by sum frequency generation (SFG)–surface vibrational spectroscopy in aqueous electrolytes.<sup>13</sup> An intermediate CO species, which was invisible to SFG, was reported 200 mV before the main oxidation peak of the CO layer. The use of SFG in these studies has the advantage that SFG is sensitive to only the electrode/electrolyte interface and therefore no reference spectrum is necessary to achieve surface sensitivity.

In this study, SFG has been used successfully to monitor the oxidation of adsorbed CO at the Pt/acetonitrile interface as a function of external potential and water concentration. By using acetonitrile as an electrolyte, the oxidation potential of CO can be increased, making a larger potential range where an SFG invisible species is observed before oxidation occurs.

In acetonitrile/water electrolytes the vibrational band of adsorbed CO is not observed at potentials above +900 mV, while CV data suggest that the CO remains on the surface and is oxidized at +1700 mV. We attribute the CO peak disappearance in SFG spectra to a reversible reorientation of the CO molecules at the electrode interface and not to an artifact of the thin film arrangement used in this experimental setup.<sup>14</sup>

Studies described herein confirm that the intermediate oxidation steps of CO in acetonitrile were similar to those intermediates observed in previous studies using aqueous electrolytes.<sup>13</sup>

SFG vibrational spectroscopy is a unique surface probe with which molecular level studies of an electrified surface can be performed.<sup>13,15</sup> In contrast to many other surface techniques, SFG vibrational spectroscopy can be performed at any interface accessible by light, including buried interfaces such as the electrode/electrolyte interface.<sup>13,15–18</sup> SFG provides vibrational spectra of adsorbed surface species, while cyclic voltammetry (CV) studies provide information about oxidation/reduction reactions occurring at the electrode surface. Combined SFG and CV studies provide valuable insight into the effects of applied electric fields on interfacial chemistry.

In this paper we describe the potential dependent CO behavior on Pt electrodes in neat acetonitrile and acetonitrile solutions containing 0.05 and 0.10 mole fractions of water. All experiments were carried out with preadsorbed CO monolayers with and without CO also present in the bulk electrolyte.

## Experimental Details

A clean polycrystalline Pt electrode was prepared by flame annealing to 1300 °C in a H<sub>2</sub>/air flame and cooling to room temperature in a flow of argon. The electrode cleaning preparation procedure was confirmed by cyclic voltammetry of Pt in 0.05 M H<sub>2</sub>SO<sub>4</sub> and observing the characteristic hydrogen adsorption/desorption features.<sup>19</sup>

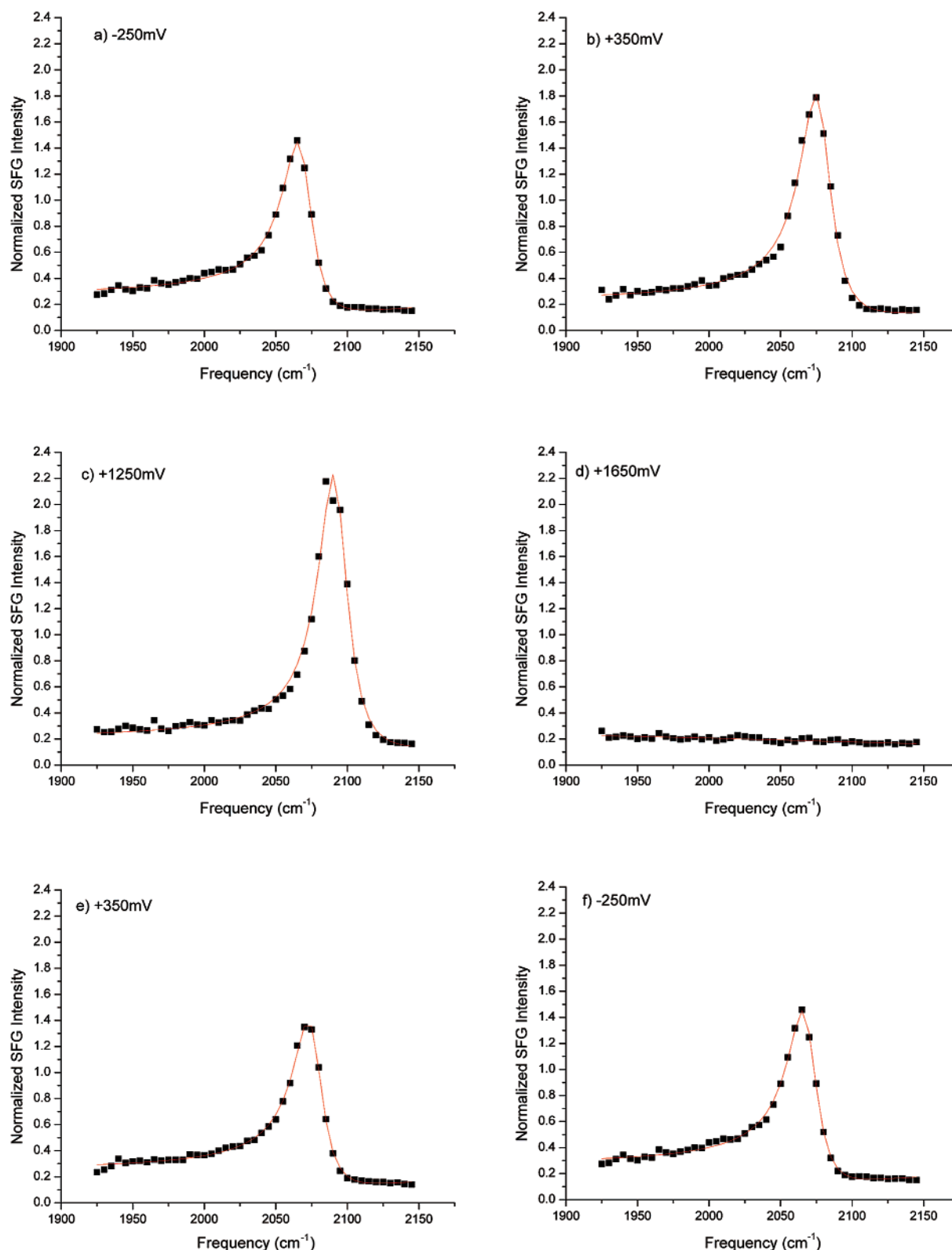
Upon removal from the argon stream, the electrode was immediately covered with a drop of pure acetonitrile and transferred into the spectroscopy cell. The cell was then filled with Ar purged and CO saturated neat acetonitrile or acetonitrile/water solutions. Because acetonitrile is an aprotic solvent, 0.1 M LiCF<sub>3</sub>SO<sub>3</sub> was added as a supporting electrolyte. CO was adsorbed onto the surface at a slightly negative potential, –250 mV (SCE), for approximately 30 min to ensure monolayer coverage.<sup>5,9,13,20</sup>

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**Figure 1.** SFG spectra, ppp polarization combination, of CO on Pt in neat acetonitrile with applied potential (a)  $-250$  mV, (b)  $+350$  mV, (c)  $+1250$  mV, (d)  $+1650$  mV, and returning to (e)  $+350$  mV and (f)  $-250$  mV (■, data points; lines, fitted data using eq 1).

Because of the significantly higher solubility of CO in nonaqueous electrolytes, i.e., approximately 10 times higher than that in aqueous solutions,<sup>5</sup> particular care was taken to remove excess CO from the bulk electrolyte. While maintaining a slightly negative potential, fresh Ar-purged electrolyte was flowed through the cell to ensure no CO was present in the bulk electrolyte. In several instances, CO-saturated electrolytes were also used to serve as control experiments.

Spectroscopy was performed in a thin layer electrochemical cell, described elsewhere,<sup>13</sup> with  $\sim 10$   $\mu\text{m}$  layer of electrolyte trapped between the CaF<sub>2</sub> window and the polycrystalline Pt electrode. The infrared is attenuated  $<10\%$  in this geometry in the CO stretching region. The thin layer cell is equipped with the polycrystalline Pt working electrode and a Pt wire counter electrode. Several experiments were performed using Ag/AgCl, KCl saturated ( $0.197\text{V}$  vs NHE<sup>21</sup>) as a reference electrode while

other described experiments were performed using a standard calomel electrode (SCE) (0.241V vs NHE<sup>21</sup>); however, all potentials are reported relative to the SCE.

Acetonitrile/water electrolytes were made volumetrically using standard dilution procedures. The acetonitrile, ACS or HPLC grade ( $<0.001 \times$  mole fraction water), and the  $\text{LiCF}_3\text{SO}_3$  electrolyte were both obtained from the Sigma-Aldrich Chemical Co. Deionized water, triply distilled with resistivity greater than  $18.2 \text{ Mohm cm}^{-1}$ , was used for these experiments. Ultrahigh purity Ar, 99.9995%, used for electrolyte purging, was obtained from Bay Airgas. CO, 99.5% purity, was obtained from Scott Specialty Gases and used in conjunction with a cold trap to minimize metal carbonyl contamination.

The spectroscopic cell was transferred under potential control to the SFG optics setup where spectroscopy was performed. The potential range investigated in this study is  $-400$  to  $+2000$  mV vs SCE. Voltammetry studies indicate the oxidation of acetonitrile at potentials above  $+1800$  mV. With the addition of water, the positive potential is limited to  $+1600$  mV due to the formation of a Pt oxide.<sup>22</sup>

Details of the optical setup for the SFG experiment have been described previously.<sup>13,22</sup> Tunable mid-infrared light ( $1300\text{--}4000 \text{ cm}^{-1}$ ) was generated by difference frequency mixing tunable near-infrared light with the fundamental beam of the Nd:YAG pump laser in a  $\text{LiNbO}_3$  or  $\text{AgGaS}_2$  crystal. The near-infrared light was produced through optical parametric generation and amplification of  $532 \text{ nm}$  light in angle tuned barium borate crystals. The infrared and visible beams were incident on the liquid/solid interface at  $40^\circ$  and  $35^\circ$  and have energy densities of  $4 \text{ mJ/cm}^2$  and  $15 \text{ mJ/cm}^2$ , respectively. All experiments were done with the ppp polarization combination (p-polarized SF, p-polarized visible, and p-polarized infrared). SFG spectra presented herein are an average of three to five scans. SFG signal was collected for 1 to 5 s, i.e., 20 to 100 shots, at every  $5 \text{ cm}^{-1}$  interval.

## Results and Discussion

**Data Analysis.** To obtain proper resonance peak position, the normalized sum frequency signal,  $I_{\text{SFG}}$ , was fitted to eq 1:<sup>18</sup>

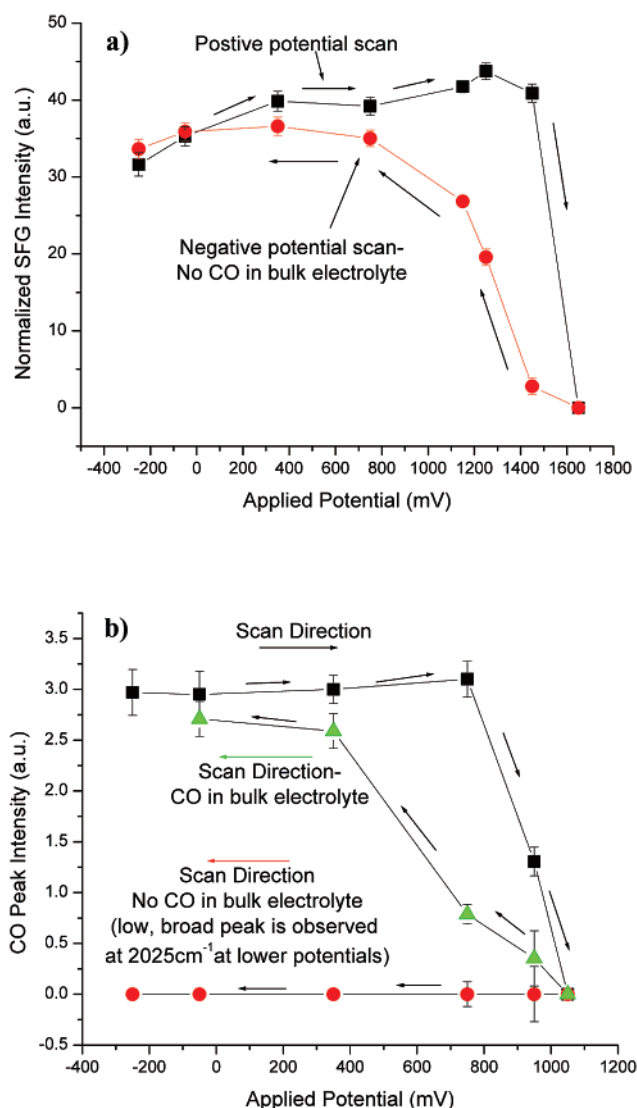
$$I_{\text{SFG}} = \left| A_{\text{NR}} + \sum_n \frac{A_{\text{R}}}{(\omega - \omega_n - i\gamma)} \right|^2 \quad (1)$$

where  $A_{\text{NR}}$  is the nonresonant contribution,  $\omega_n$  is the  $n$ th resonant vibrational frequency,  $\gamma$  is the line width, and  $A_{\text{R}}$  is the resonant strength. The resonant strength is proportional to the number and orientation average of the molecules at the interface of interest as well as their infrared and Raman transition moments.

Collected SFG signal was normalized with respect to the reflected IR beam from the electrode to ensure that no false SFG peaks were observed due to IR absorption by the thin film of electrolyte above the electrode surface.

**Sum Frequency Generation Studies of CO on Pt in Neat Acetonitrile.** Figure 1 presents SFG spectra obtained from a CO monolayer adsorbed at  $-250$  mV on Pt in neat acetonitrile electrolyte. The peak at  $2065 \text{ cm}^{-1}$  is assigned to the vibration of CO adsorbed to one Pt atom, an atop site.<sup>7,23</sup>

On the positive potential sweep the CO peak is no longer detected by SFG above  $+1600$  mV, Figure 1d. However, by immediately scanning to a potential below  $+1600$  mV, the CO vibrational peak is observed again, and once the potential is returned to  $-250$  mV (Figure 1f), the initial intensity of the CO peak is reobtained. As seen in Figure 2a, data indicate a

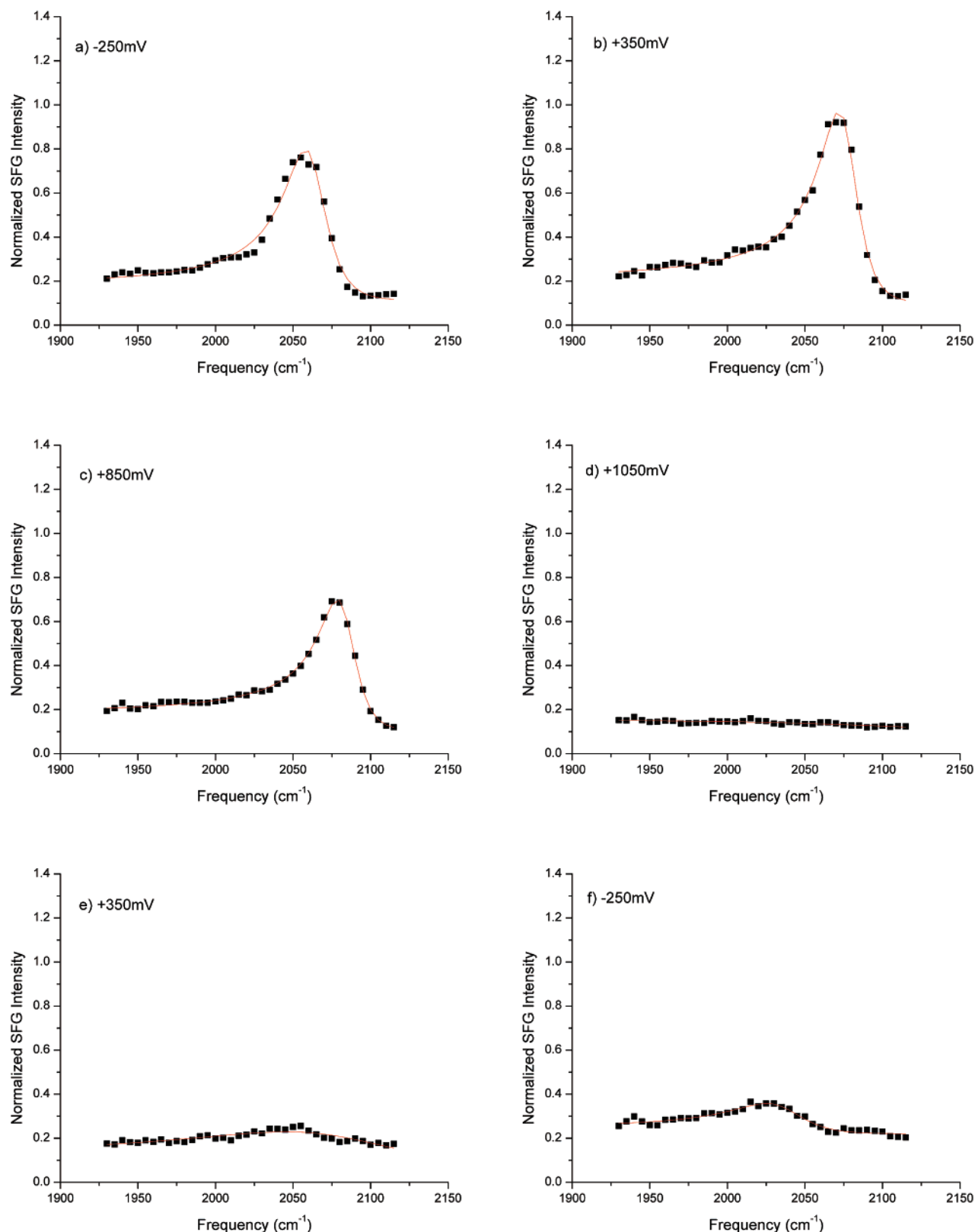


**Figure 2.** CO peak intensity as a function of potential for CO on Pt in  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solutions. (a) Neat  $\text{CH}_3\text{CN}$ : ■, positive potential sweep; ●, negative potential sweep (no CO in bulk electrolyte). (b)  $\text{CH}_3\text{CN}$  with  $0.05 \times \text{H}_2\text{O}$ : ■, positive potential sweep; ●, negative potential sweep (no CO in bulk electrolyte); ▲, negative potential sweep (CO in bulk electrolyte).

complete recovery of the initial CO vibrational band in neat acetonitrile electrolyte when no CO is present in the bulk electrolyte.

It is suggested that the disappearance of the CO peak in SFG at the electrode at high positive applied potentials is the reorientation of the C–O bond to a nearly parallel position relative to the electrode surface—an SFG invisible species. If the electrooxidized CO was simply desorbed from the electrode surface, it is expected that a feature would appear in the voltammogram corresponding to desorption of a chemisorbed CO species. No corresponding voltammetry peak was observed. These data indicate CO oxidation does not occur in the absence of water and that the disappearance of the CO peak is due to a reorientation of the CO molecule at the electrode interface.

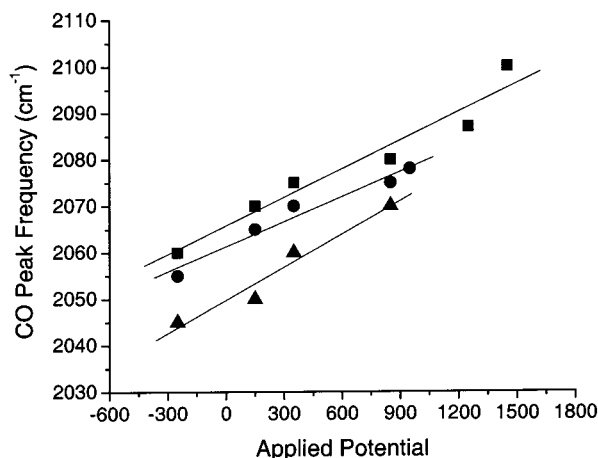
**Sum Frequency Generation Studies of CO on Pt in Acetonitrile/Water Solutions.** With the addition of 0.05 mole fraction of water to the acetonitrile electrolyte solution, a different CO peak behavior is observed. Figure 2b shows that, unlike the pure acetonitrile system, when water is present in small concentrations the original CO peak that was detected by



**Figure 3.** SFG spectra, ppp polarization combination, of CO on Pt in 0.05 mole percent water in acetonitrile with applied potential (a)  $-250$  mV, (b)  $+350$  mV, (c)  $+850$  mV, (d)  $+1050$  mV, and returning to (e)  $+350$  mV and (f)  $-250$  mV (■, data points; lines, fitted data using eq 1).

SFG does not return upon cycling back to lower potentials. After oxidation, a low-intensity, very broad peak is observed at  $2025\text{ cm}^{-1}$ , see Figure 3f. This vibrational feature is likely due to small amounts of CO present in solution during the positive potential sweep and subsequently adsorbing on the surface upon a negative potential sweep (forming a submonolayer CO layer).

The CO vibrational band is observed until the applied potential is raised to  $+1000$  mV, Figure 3d. When no CO is present in the bulk electrolyte, the initial CO vibrational intensity (Figure 3a) is not regained upon returning to negative potentials (Figure 3f). Experiments performed with CO in the bulk electrolyte show that full monolayer coverage is obtained after



**Figure 4.** CO peak shift and intensity change with scanned potential: ■, neat  $\text{CH}_3\text{CN}$ ; ●,  $0.05 \times \text{H}_2\text{O}$  in  $\text{CH}_3\text{CN}$ ; and ▲,  $0.10 \times \text{H}_2\text{O}$  in  $\text{CH}_3\text{CN}$ .

oxidizing the initial CO monolayer and then returning to negative potentials (Figure 2b, triangles).

By increasing the concentration of water in the electrolyte to 0.10 mole fraction, the CO vibrational band shows similar behavior to SFG studies with less water. When CO is not present in the bulk, the CO vibrational feature disappears above +1000 mV and is not regained by returning to lower potentials.

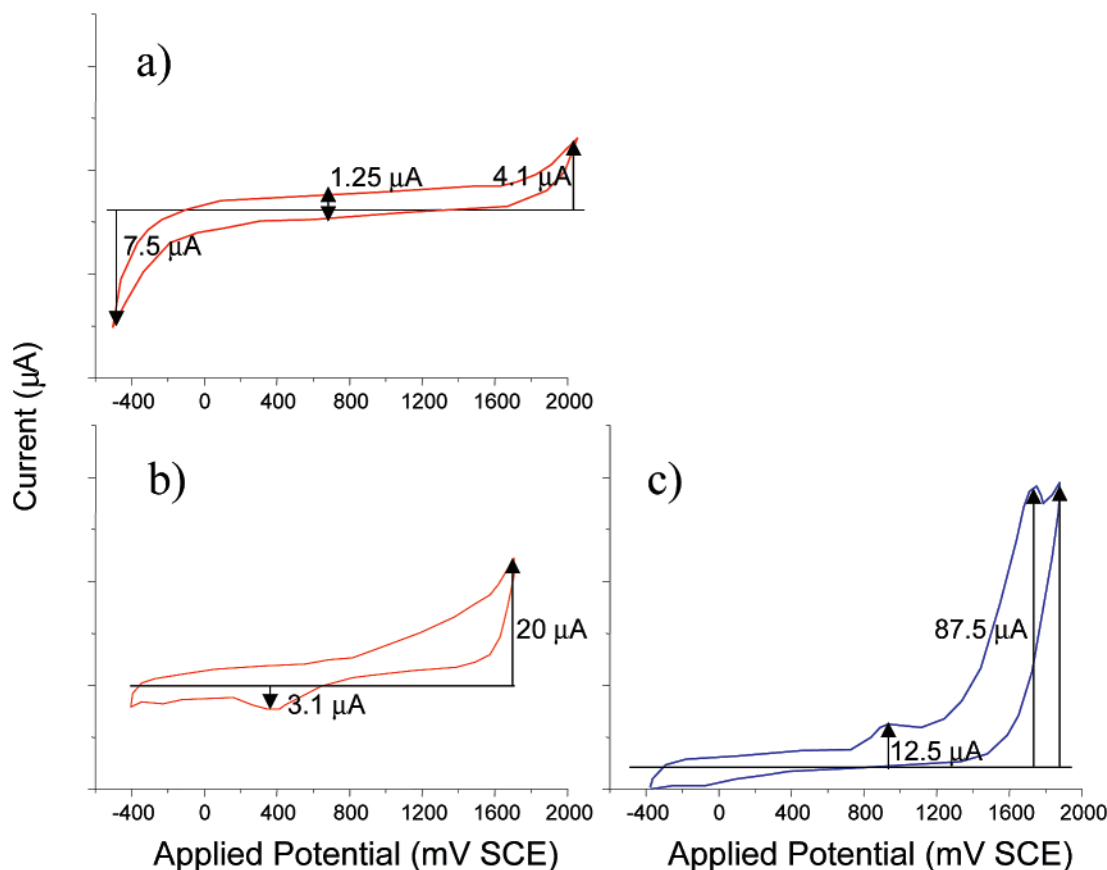
The SFG peak associated with CO does not reappear in the acetonitrile/water solutions (Figure 2b, circles), indicating oxidation of CO to  $\text{CO}_2$ , not simply desorption of CO. These data also indicate that the adsorbed CO layer is not visible by

SFG on the electrode surface above +1000 mV in acetonitrile/water solutions and confirm the necessity of surface oxygen containing species,<sup>24</sup> most likely a hydroxyl species, for the oxidation of CO on the electrified Pt surface.

Previous studies of the Pt–acetonitrile/water electrified interface indicated that at slightly negative potentials, i.e., less than 0 mV vs NHE,  $\text{H}_2\text{O}$  molecules were adsorbed at the surface, while at low and high positive potentials water molecules were displaced by acetonitrile molecules.<sup>22</sup> In these studies, SFG spectra indicate that with the addition of CO the Pt surface is covered with a chemisorbed CO species at all potentials below the CO oxidation potential.

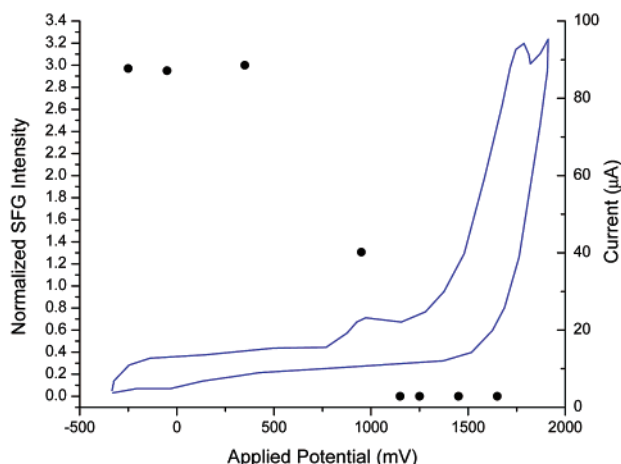
**CO Vibrational Band Behavior versus Applied Potential and Water Concentration.** As indicated in Figures 1 and 3, a  $20 \text{ cm}^{-1}$  blue shift of the CO vibrational peak is observed ( $2085 \text{ cm}^{-1}$  vs  $2065 \text{ cm}^{-1}$ , Figure 1) with applied potential. This typical blue shift is primarily caused by the Stark effect, whereby the applied potential increases the electric field felt by the adsorbed CO molecules and essentially further separates the vibrational energy levels.<sup>4,25,26</sup>

Figure 4 displays the CO vibrational band shift as a function of scanned potential and water concentration. By increasing the water concentration in electrolyte solutions, a red shift was observed in the CO vibrational band frequency. The observed vibrational frequency of adsorbed CO at  $-250 \text{ mV}$  is slightly lower ( $2055 \text{ cm}^{-1}$  vs  $2085 \text{ cm}^{-1}$ ) when the bulk electrolyte contains 0.05 mole fraction of water as compared to neat acetonitrile. The red shift in the CO vibrational peak with increased water concentration is attributed to a change in the dielectric screening of the incident infrared radiation caused by additional water molecules in the double layer region.<sup>7</sup>



**Figure 5.** Voltammetry data obtained from CO monolayers adsorbed on Pt with no CO in solution (a) Pt in  $\text{CH}_3\text{CH}$ ; (b) Pt in  $\text{CH}_3\text{CN}/0.10 \times \text{H}_2\text{O}$ ; (c) Pt in  $\text{CH}_3\text{CN}/0.10 \times \text{H}_2\text{O}$  with CO.





**Figure 6.** CO peak intensity from SFG experiments compared to CV from CO on Pt in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solutions.

By increasing the concentration of water in the electrolyte to 0.10 mole fraction, the vibrational band of the adsorbed CO layer exhibits a larger red shift to  $2030\text{ cm}^{-1}$ . In addition, as the electrode potential is increased, the CO vibrational band blue shifts similar to that observed in the 0.05 mole fraction water in acetonitrile and neat acetonitrile electrolyte studies.

**Cyclic Voltammetry Studies: Confirmation of Spectroscopy Results.** Voltammetry data for Pt in water/acetonitrile solutions are shown in Figure 5. CV studies indicate that, in the potential range of interest, acetonitrile undergoes no chemical reaction with the Pt electrode surface (Figure 5a). With the addition of water to the electrolyte solution a feature attributed to the oxidation of Pt is observed to begin around  $+900\text{ mV}$ , and the reduction of this oxide is seen on the negative potential sweep at  $+400\text{ mV}$  (Figure 5b). Figure 5c shows that with an adsorbed CO monolayer, the observed CV features are significantly altered due to the adsorbed CO layer. A preoxidation wave of CO is observed at the onset of the Pt oxide formation peak,  $+900\text{ mV}$ , as seen in Figure 5b. The second feature at  $+1600\text{ mV}$  in Figure 5c is the main oxidation peak of CO. Last, the third peak at approximately  $+2000\text{ mV}$  is the oxidation of the acetonitrile in the electrolyte. These results have been confirmed by earlier studies performed by this laboratory.<sup>22</sup> These CV data confirm that by using acetonitrile as an electrolyte the oxidation of CO can be delayed, enlarging the potential region where CO is invisible to SFG.

Finally, Figure 6 shows that the disappearance of the SFG CO vibrational feature in water/acetonitrile solutions coincides with the observed preoxidation wave in voltammetry around  $+900\text{ mV}$ . As suggested by Lucas et al.,<sup>12</sup> the preoxidation wave removes a small number of weakly bonded CO from the surface, thereby allowing the rest of the CO layer to relax. The disappearance of a CO SFG signal before the main oxidation wave and the subsequent regaining of the signal by decreasing the potential, as shown in Figure 2, suggest the reorientation of the CO molecules at the surface before oxidation. Desorption and readsorption of CO prior to oxidation would be indicated by additional CV peaks not observed in this study. Voltammetry and spectroscopy studies combined suggest an intermediate CO species, parallel or nearly parallel to the Pt surface, and therefore SFG invisible, is formed after the preoxidation wave before the main oxidation of CO to  $\text{CO}_2$ .

## Conclusions

Combined CV and SFG studies on Pt electrodes confirm that an SFG invisible species is the intermediate in the electrooxi-

dation of CO to  $\text{CO}_2$  in acetonitrile/water electrolytes. Data obtained in both CV and SFG experiments indicate that even small amounts of water, i.e., 0.05 mole fraction, are capable of oxidizing a monolayer of CO on the platinum electrode surface. CV data also indicate the preoxidation wave coincides with the decrease in the intensity of the SFG CO vibrational band associated with the intermediate CO surface species. The preoxidation wave removal of a small number of weakly bonded CO from the surface<sup>12</sup> allows the remaining, more strongly adsorbed CO molecules, to reorient with the CO bond parallel to the surface.

Observed spectroscopic and voltammetry data suggest that the oxidation pathway of CO on Pt in acetonitrile/water solutions is very similar to the oxidation of these monolayers in completely aqueous environments.<sup>13</sup> Previous SFG studies using acetonitrile as an electrolyte have shown this to be an ideal electrolyte system for monitoring surface OH species at the Pt/electrolyte interface.<sup>22</sup> By using acetonitrile as an electrolyte, IR absorption by the bulk solution can be minimized in the vibrational ranges of interest, and therefore the formation and consequent reduction of surface OH species can be more easily monitored in future studies.

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