

# Carbon Monoxide Detection through Sum Frequency Generation (SFG)

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## Introduction:

Sum frequency generation (SFG) spectroscopy has become a useful technique in surface chemistry due to high surface selectivity and high time resolution. Specifically, time resolved sum frequency generation (TR-SFG) spectroscopy is useful in understanding chemical states of surface adsorbates and studying solid/liquid interfaces. In this study, we investigate the SFG response of adsorbed carbon monoxide (CO) from dissociated  $\text{CH}_3\text{OH}$  on a platinum (Pt) electrode surface in a 0.1M  $\text{HClO}_4$ /0.1M  $\text{CH}_3\text{OH}$  electrolyte solution to irradiation of infrared pulses on the surface.

## Experimental Procedure:

An electrochemical cell is set up with the working electrode (platinum (Pt) disk), the reference electrode (Ag/AgCl), the counter electrode (Pt wire), and an electrolyte solution of 0.1M  $\text{HClO}_4$ /0.1M  $\text{CH}_3\text{OH}$ .

A voltage potential is rapidly cycled repeatedly from -0.2 V to 1.25 V to first clean the surface of the working electrode. It is then cycled again at a slower speed to obtain the cycle voltammogram (CV) of the system. Using the CV, we can obtain the different potential ranges for different oxides and adsorbates within the system and compare it to a CV of 0.1M  $\text{HClO}_4$ .

An SFG spectra is obtained by introducing infrared light and 532 nm green light in order to create SFG light from the sum of the two lights. The wavenumber is then adjusted within a range of 2000-2100  $\text{cm}^{-1}$  in order to obtain the CO spectra. A spectrum is obtained every 50 mV from 100-350 mV.

The probe light for TR-SFG spectroscopy is the SFG light made from infrared light and 532 nm green light, and the pump light is 1064 nm infrared light. Afterwards, pump light was introduced to perform a time resolved measurement using TR-SFG spectroscopy to obtain the delay scan of our system.

## Results and Discussion:

CO adsorption occurs on the Pt surface at a voltage potential range of 100-300 mV according to the CV. Afterwards, CO desorption occurs, and oxides begin to form at the surface. A CO peak was detected at about 2060  $\text{cm}^{-1}$  for the SFG spectra. A peak shift to higher wavenumbers occurs within the range of 100-200 mV. The peak shift is due to the weakening of the bond between Pt and carbon. At voltages of at least 250 mV, red shift occurs as the peak shifted to a lower wavenumber. The red shift is due to loss of CO coverage on the surface from oxidation. This also coincides with the decrease in peak intensity as the voltage increased.

The delay scan reveals a sharp peak intensity increase at about 55 ps. The intensity is shown to decrease with increasing voltage potential. This would suggest that there is more CO coverage on the Pt electrode surface.

## Conclusions and Future Work:

A peak was apparent at about 2060  $\text{cm}^{-1}$ , representing CO adsorption onto a Pt surface through dissociative  $\text{CH}_3\text{OH}$ . As the voltage potential increased, a peak shift occurred within the range of 100-200 mV due to weakening of the Pt-CO bond. The peak shifted back to a lower wavenumber at voltages of 250-350 mV and the peak intensity was shown to decrease with increasing voltage. Both occurred due to decrease in CO coverage. When introducing the pump pulse, a peak intensity increase was shown. This would suggest that there is more CO coverage during this peak intensity increase but further study needs to be conducted.

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