PHASETECH
spectroscopy shaping science

APPLICATION NOTE

Voltage-modulated transmission FT IR spectroscopy measuring the Stark shift of a molecular monolayer

Abstract

A Stark shift of a molecular monolayer of 4-mercaptobenzonitrile was measured by transmission FT IR spectroscopy using the using the Volt IR Spectroelectrochemistry Cell. A three-electrode electrochemical configuration was used to apply voltages and measure the resulting changes in vibrational frequency of the nitrile functional group.

LEARN MORE

Introduction

Electrochemistry is common in a wide range of applications and industries. Batteries, chemical electrolysis, electroplating, and biological systems are among the many applications of this technique. Since electrochemical reactions occur at an electrode surface, studying the electrode-electrolyte interface during reactions is an important aspect for understanding and optimizing electrochemistry. Surface-enhanced infrared absorption (SEIRA) spectroscopy is a powerful technique for studying interfacial systems with vibrational spectroscopy.

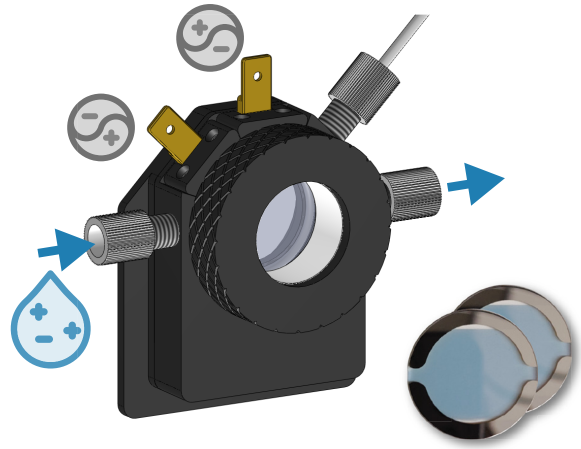

Figure 1. PhaseTech Spectroscopy and PIKE Technologies Volt IR Spectroelectrochemistry Cell with Volt IR SEIRA working electrode window inset.

Here, we use transmission FT IR with the Volt IR Spectroelectrochemistry Cell (Figure 1) to apply voltage and measure SEIRA spectra of a monolayer of 4-mercaptobenzonitrile (4-MBN) at the working electrode surface[1] (Figure 2). We show a Stark frequency shift of the nitrile functional group frequency.

Experimental Conditions

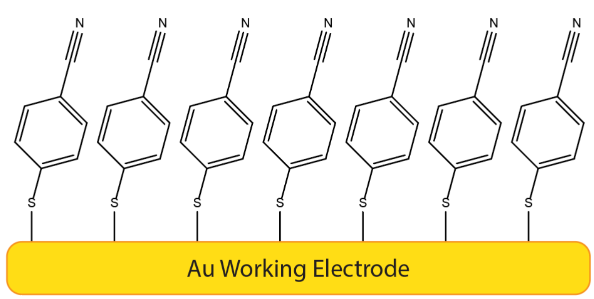

Figure 2. Structure of the 4-MBN monolayer on the working electrode surface.

The 4-MBN monolayer was formed by soaking a Volt IR SEIRA working electrode window in a 30 mM solution of 4-MBN in ethanol for eight hours. The Volt IR spectroelectrochemistry cell was used in a three-electrode configuration with a platinum counter electrode and Ag/AgCl reference electrode. The electrolyte used was phosphate-buffered saline. The spectra were collected using a commercial FT IR spectrometer in transmission geometry. All voltages reported are referenced to Ag/AgCl.

4916 East Broadway, Suite 125, Madison, WI USA
+1 608 712-1857
contact@phasetechspectroscopy.com

Voltage-modulated transmission FT IR spectroscopy measuring the Stark shift of a molecular monolayer

Results

Molecules are known to vibrate at different frequencies under the influence of external electric fields, known as the vibrational Stark effect.[2] Figure 3 shows transmission FT IR spectra of the same 4-MBN monolayer sample with two applied voltages. The nitrile stretching mode gives rise to this peak at ~2227-2230 cm^{-1}, depending on the voltage. Upon the application of different voltages, the center frequency of the peak shifts and the peak intensity changes. From +300 mV to -200 mV, the nitrile center frequency redshifts by 4 cm^{-1}. The peak intensity increases from +300 mV to -200 mV due to a voltage-dependence of the transition dipole strength of the nitrile mode. From the Stark shift of 4 cm^{-1}, we can estimate an 11.1 MV/cm change in the electric field at the electrode surface when applying +300 mV or -200 mV.[3]

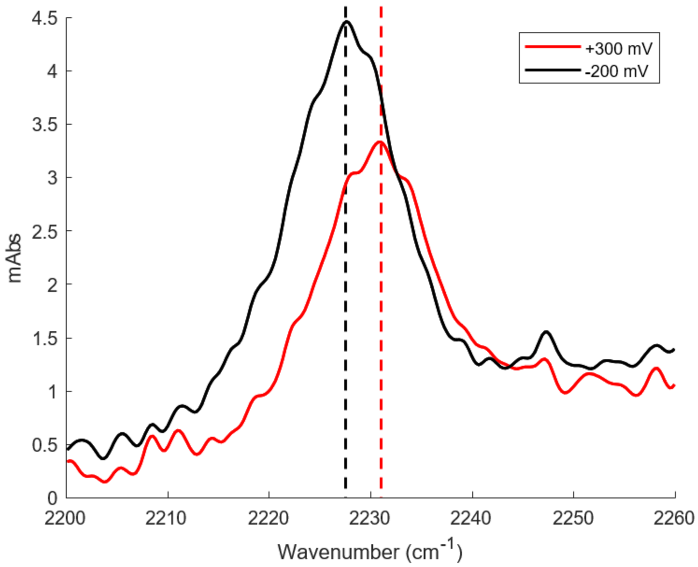

Figure 3. Voltage-dependent spectra of 4-MBN nitrile stretching mode. Vertical lines at the peak centers demonstrate the Stark shift.

Conclusions

The voltage-dependent spectra of a monolayer of 4-MBN shown here demonstrate the high sensitivity and precise voltage control of the Volt IR Spectroelectrochemistry Cell. The Volt IR system enables the collection of surface-sensitive infrared spectra while performing electrochemical experiments and can be used to analyze any number of complicated electrochemical systems.

References

1. Yang N., Ryan M.J., Son M., Mavric A., and Zanni M.T., J. Phys. Chem. B (2023) 127, 2083.
2. Fried, S.D. and Boxer, S.G., Acc. Chem. Res. (2015), 48, 4, 998-1006.
3. Shi, H. et al., ACS Appl. Mater. Interfaces. (2018), 10, 39, 33678-33683

For More Information, Contact:

PHASETECH spectroscopy shaping science
contact@phasetechspectroscopy.com

PIKE TECHNOLOGIES
info@piketech.com