Polarization Modulation FT-IR Spectroscopy

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KEYWORDS

FT-IR, polarization modulation (PM), dual channel, IRRAS, monolayers, grazing angle analysis

INTRODUCTION

Several infrared absorption measurements such as molecular orientation, thin films on reflective surfaces and crystal structure studies are enhanced with the use of polarized light. Sequentially collected sample and reference spectra are measured using infrared polarizer accessories. Infrared Reflection Absorption Spectroscopy (IRRAS) uses p-polarized light at a grazing angle of incidence to measure thin films on metallic substrates.

The reflectance measurement is done at a grazing angle to increase the polarized absorption from the thin film. Often the absorptions from these samples are relatively weak, as with molecular monolayers, or possibly masked by interstitial absorptions from the sample. Subtraction techniques may be used for some experiments to eliminate sample matrix absorptions, but often the weaker polarization effect is lost in the result.

When the sample is a monolayer, the surface sensitivity of the IRRAS technique may not be sufficient even if spectral information is signal averaged over a long period of time. The greater the time separating sample and background data collections, the larger are the effects of the minute instabilities of the spectrometer atmosphere and detection system, resulting in relatively large spectral contributions from carbon dioxide and water. These atmospheric absorptions make the measurement of the sample impossible.

With simultaneous collection of differentially polarized signals in the PM-IRRAS (Polarization Modulation – Infrared Reflection Absorption Spectroscopy) technique, this problem is eliminated. This note reviews the essentials of this simultaneous, dual-channel technique and then introduces an application of the technology.

EXPERIMENTAL

The PM-FTIR experiment requires a high speed, high performance FT-IR spectrometer capable of receiving a dual channel input. The system was equipped with a photoelastic modulator (PEM) to provide a polarized modulation of infrared light, grazing angle sampling optics, a lock-in amplifier to demodulate the spectral information and specialized FT-IR software to process the resulting spectral data.

The FT-IR spectrometer used for these experiments was a Nicolet Magna-IR® 850 equipped with an SST™ (Simultaneous Synchronous Techniques) module. The SST module provides a secondary independent digitizer channel that is electronically balanced and synchronized to the data collection events that occur in the main digitizer of the Magna-IR System 850. The digital signal processor (DSP) controlling the Magna-IR spectrometer provides a wide range of interferometer sampling velocities, independent channel high and low pass filter parameters and independent channel gain settings for dual-channel measurements.

Infrared photoelastic modulators (PEM) consist of two components: the modulator head and the control unit. The modulator head is made up of a cubic infrared-transparent crystal (ZnSe or CaF_2) and is placed in the beam path. The control unit generates a high frequency oscillation that is used to drive stress transducers that are attached to the polarization modulator crystal. The stress applied to the PEM crystal induces a high frequency polarization modulation on the infrared beam alternating between polarization states. The fundamental frequency of the polarization oscillation is dependent upon the individual crystal and is either 37 or 50 KHz for ZnSe. Depending upon the experiment, the modulation of interest can be either the linear (parallel and perpendicular) or circular (left and right) polarization states. The polarization state is determined from the specific point in the stress cycle.

Figure 1 illustrates the polarization states induced upon incident plane polarized

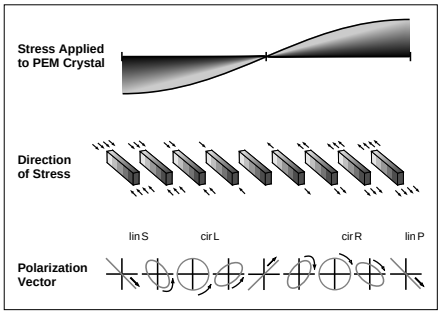

Figure 1: Polarization states produced by the PEM accessory

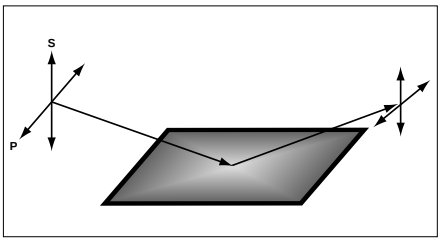

Figure 2: Linear polarization states incident upon a sample

light by the PEM linear *p* (parallel) and *s* (perpendicular) polarization states. These states are achieved at the maxima and minima of the stress/strain cycle. Figure 2 illustrates the orientation of linear *p* and *s* polarization states incident to a sample surface. A phase reference output frequency from the control unit is used as a synch signal for the lock-in amplifier. In PM-IRRAS experiments, the synch signal is set at twice the modulator head operating frequency. The photoelastic modulator is an achromatic polarizer. Adjustments can be made on the modulator control box that effect the location of the peak modulation wavelength. In PM-IRRAS experiments the researcher should adjust the maximum modulation wavelength so that it coincides with the spectral features of interest. The peak modulation wavelength of the PEM was set at 6.5 microns for these PM-IRRAS experiments.

Figure 3 illustrates the optical layout for a PM-IRRAS experiment on the Magna-IR spectrometer. The collimated external beam from the FT-IR is reflected and focused through a wire grid polarizer, the PEM and onto the sample. The angle of incidence of the focused beam is positioned at a grazing angle. This angle is typically 86 degrees normal for gold substrates. The reflected beam from the sample is

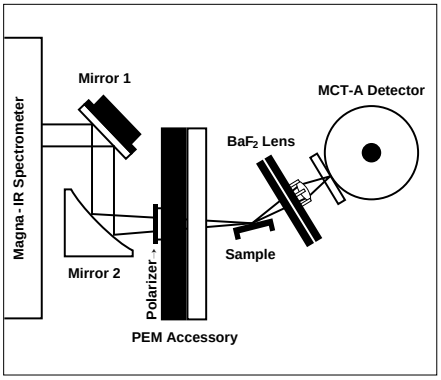

Figure 3: Example optical layout for a PM-IRRAS experiment

refocused onto the narrow-band mercury cadmium telluride (MCT-A) detector using a barium fluoride lens. Using a lens-based configuration after the sample, instead of a focusing mirror, minimizes polarization artifacts that may dominate the measured spectrum.

The infrared signal at the detector has a double modulation in experiments that involve a photoelastic modulator: an intensity modulation and a polarization modulation. Intensity modulation is related to the velocity of the interferometer moving mirror and has frequencies that are described by the Fourier relationship (the product of the optical mirror velocity and wavenumber of the spectral feature of interest). Polarization modulation occurs at a fixed frequency that is due to the photoelastic modulator operation. The spectra illustrated were collected using a 37 KHz ZnSe photoelastic modulator. The polarization modulation of interest (perpendicular and planar linear polarizations) for PM-IRRAS is at twice the operating frequency of the photoelastic modulator.

The PM-IRRAS experiment measure the following digitized signals to produce the differential reflectivity spectrum:

$$\frac{\Delta R}{R} = \frac{(R_p - R_s)}{(R_p + R_s)}$$

Where ΔR is the differential reflected R_s and R_p linearly polarized signals and is obtained from the demodulation of the polarization modulation interferogram through the use of a lock-in amplifier. R is the sum of these two signals and is the low pass filtered intensity modulated signal from the MCT-A detector. These two interferograms (ΔR and R) are collected simultaneously into the synchronized independent digitizers on the Magna-IR 850 and subsequently Fourier transformed using Research OMNIC® software. The ratio of these two spectra is the PM-IRRAS spectrum of the sample of interest.

RESULTS

Figure 4 illustrates the 32 scan, 4 cm^{-1} resolution, single beam spectra from the PM-IRRAS measurement of a single monolayer of cadmium arachidate on a gold substrate. The top spectrum represents the differential information which is the result of the demodulation of the polarization modulation and intensity modulation information. The bottom spectrum in the illustration is the result of the low-pass filter

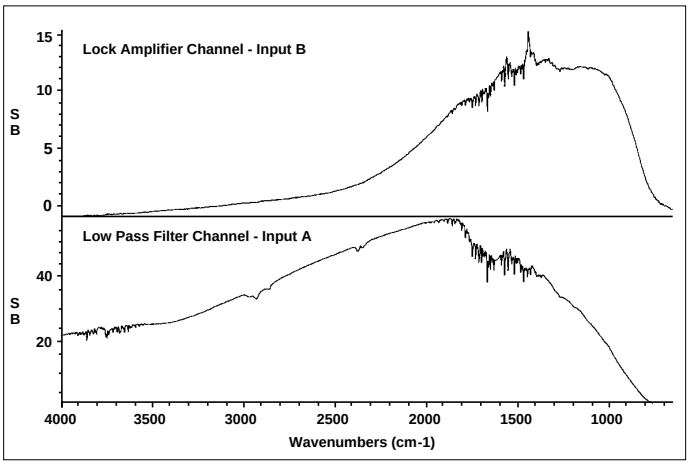

Figure 4: Simultaneously measured differential (top) and reference (bottom) single beam spectra from a PM-IRRAS experiment of a monolayer on gold

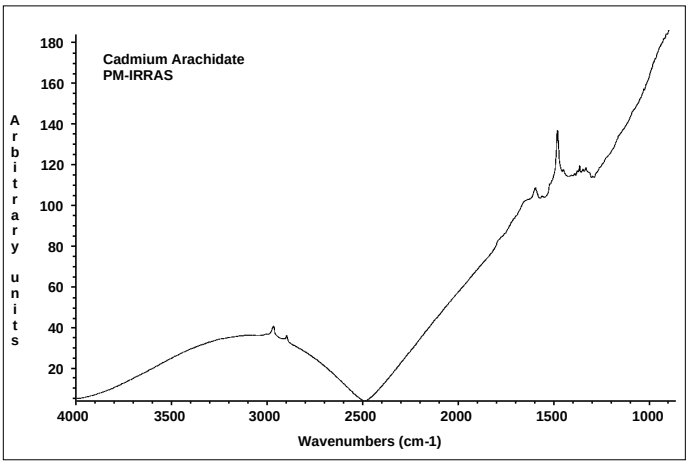

Figure 5: Ratioed differential and reference spectra producing a PM-IRRAS spectrum of a monolayer of cadmium arachidate on gold

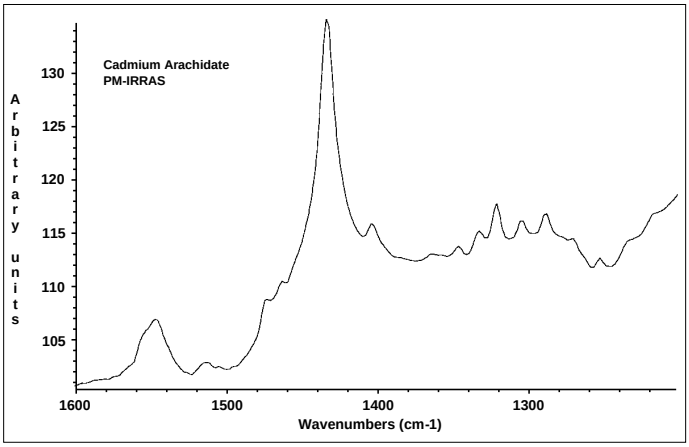

Figure 6: Baseline correction of a PM-IRRAS spectrum of a monolayer of *cadmium arachidate* on gold illustrating the CH_2 wagging and twisting region

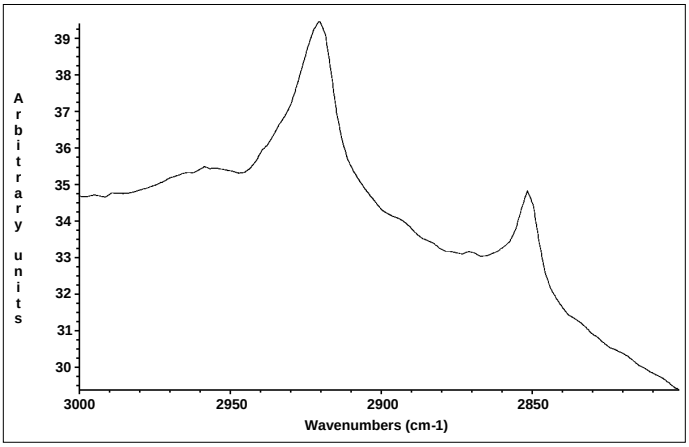

Figure 7: Baseline correction of a PM-IRRAS spectrum of a monolayer of *cadmium arachidate* on gold illustrating the CH_2 and CH_3 Stretching Region

output intensity modulation information. Data collection time for the simultaneous measurement was 90 seconds. The spectrometer atmosphere was not completely purged for these experiments and carbon dioxide and water vapor absorption bands are evident in each single beam.

Figure 5 illustrates the ratioed differential and reference spectra producing a PM-IRRAS spectrum of a monolayer of cadmium arachidate [$(CH_3(CH_2)_{18}COO\text{-})_2$, Cd^{++}] on gold. Note that in the ratio spectrum the absorptions of the carbon dioxide and water are eliminated.

Figure 6 illustrates the result of a cubic spline baseline correction in the CH_2 wagging and twisting region of the PM-IRRAS spectrum of a monolayer of cadmium arachidate on gold. Since polarization modulation is not achromatic, this baseline correction eliminates its dependence upon the spectrum. Figure 7 illustrates the baseline correction in the CH_2 and CH_3 stretching region of the PM-IRRAS spectrum of a monolayer of cadmium arachidate on gold. These spectra illustrate the sensitivity of this technique to surface monolayers and the tolerance to the atmosphere surrounding the sample.

Some clean metallic surfaces placed at the sample position result in a reflectance spectrum of the surface with no bands that indicate absorption by the substrate. When a clean gold mirror is placed at the sample position in the PM-IRRAS optics, the resulting spectrum can be used to eliminate the polarization versus wavenumber dependence of the PEM with a point-by-point divide of the sample on gold spectrum to the clean gold mirror spectrum.

The spectrum that results when an aluminum foil is placed at the sample position is illustrated in Figure 8. The spectrum shows no characteristic absorption bands except for one occurring at 960 cm^{-1}. This band is related to the native oxide that forms upon the surface of the metallic aluminum and is typically on the order of tens of nanometers in thickness.

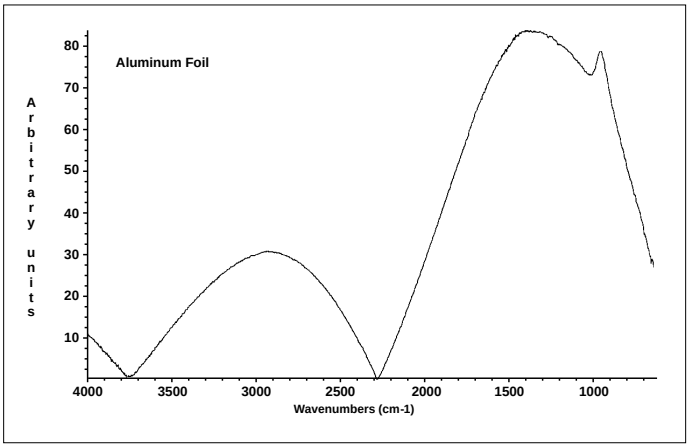

Figure 8: PM-IRRAS spectrum of an aluminum foil

CONCLUSIONS

It is important to note that polarization modulation experiments simultaneously measure a differential and a reference spectrum of the sample. Compared to a sequential collection these differential measurements of the polarization states eliminate the amorphous sample matrix of the sample.

Compared to sequential polarized measurements of monolayer layers, PM-IRRAS provides superior signal-to-noise ratio because the system electronics is optimized for the relatively small differentially polarized signal. PM-IRRAS provides significantly reduced sampling time due to the simultaneous collection of the differential polarization and reference signals. And finally, PM-IRRAS eliminates atmospheric absorptions; a critical step when measuring monolayered samples because these samples have very weak infrared absorptions.

ACKNOWLEDGMENTS

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