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# A New Approach to Quantitative Spectral Conversion of PM-IRRAS: Theory, Experiments, and Performance Comparisons with Conventional IRRAS

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**Key Words**

- PM-IRRAS
- IRRAS
- Polarization Modulation
- PEM Module
- Dual Channel
- Monolayer Film

## Abstract

This paper presents a new extension to the classic PM-IRRAS theory for spectral data processing. A new easy-to-use formula that directly converts PM-IRRAS spectral intensities to absorbance units is proposed and experimentally confirmed. This work not only clears up the confusions in PM-IRRAS spectral data processing but also demonstrates the significant advantages of dual-channel PM-IRRAS over conventional IRRAS for studying monolayer samples in detection sensitivity, data collection time and final spectral quality.

## Introduction

Infrared reflection absorption spectroscopy (IRRAS) is a useful technique for studying thin films on reflective substrates. Molecular orientations of a thin film on a metallic substrate can be determined based on the selective absorption of s- and p-polarized light by the adsorbed molecules when the incident angle is in the grazing angle range. Polarization modulation (PM) is highly recommended for IRRAS measurement in order to increase the sensitivity of the measurement. In a typical PM-IRRAS experiment, two modulations are applied simultaneously: the Fourier modulation produced by the FT-IR interferometer and the polarization modulation by the photoelastic modulator. Thus, the raw detector signal contains contributions from both modulations when proper electronic flittering is used.

In order to obtain direct quantitative information of monolayer absorptivities, conversion of PM-IRRAS spectral intensity to absorbance units is necessary. In this paper, a new theoretical formula that directly links experimental PM-IRRAS spectral intensities to absorbance units is derived from the classic PM-IRRAS theory and experimentally confirmed with spectral data of a monolayer film on a gold substrate. In addition, the data generated for confirming the proposed theoretical formula also demonstrate the significant sensitivity enhancement of dual channel PM-IRRAS over conventional IRRAS for monolayer studies.

## Theory

In the classic PM-IRRAS theory,[1] normalized PM-IRRAS spectral intensity is expressed as

$$\left(\frac{\Delta I(d)}{\Sigma I(d)}\right)_{norm} = \frac{\left(\frac{\Delta I(d)}{\Sigma I(d)}\right)_{exp}}{\left(\frac{\Delta I(0)}{\Sigma I(0)}\right)_{exp}} = \frac{\frac{J_2(\varphi_0)g[\gamma I_p(d)-I_s(d)]}{\gamma I_p(d)+I_s(d)}}{\frac{J_2(\varphi_0)g[\gamma I_p(0)-I_s(0)]}{\gamma I_p(0)+I_s(0)}} = 1+\frac{2\gamma\rho}{1-\gamma^2\rho^2}A(d)_{pseu} \quad (1)$$

where $I_p$, $I_s$ = intensities of reflected p- and s-polarized light;
$J_2(\varphi_0)$ = second-order Bessel function;
$g = G_+/G_-$ = ratio of overall gain for the two channels;
$\gamma = C_p/C_s$ = ratio of overall optoelectronic responses for p and s polarizations;
$\rho = I_p(0)/I_s(0)$;
$A(d)_{pseu} = 1-I_p(d)/I_p(0)$ = pseudo absorption spectrum.

In Equation (1) the numerator $[\Delta I(d)/\Sigma I(d)]_{exp}$, represents the PM-IRRAS demodulated signal (difference) ratioed over the non-demodulated detector raw signal (sum) for a sample with monolayer thickness of d, and the denominator, $[\Delta I(0)/\Sigma I(0)]_{exp}$, represents the same quantity for a reflective bare substrate reference (i.e. zero thickness of film), such as a gold-coated glass slide.

An expression for spectral intensity in absorbance is obtained through derivation:[2]

$$A(d) = \log(1/R) \approx 0.434A(d)_{pseu} = 0.217\left(\frac{1-\gamma^2\rho^2}{\gamma\rho}\right)\left[\left(\frac{\Delta I(d)}{\Sigma I(d)}\right)_{norm}-1\right] \quad (2)$$

A(d) in general should be positive according to Equation (2), since when $\gamma\rho < 1$, the surface bands on a raw experimental PM-IRRAS spectrum (ratio of demodulated signals over detector raw signals) are oriented upwards above the $J_2(\varphi_0)$ curve, and subsequently the normalized PM-IRRAS signal is greater than 1, and when $\gamma\rho > 1$, the surface bands are oriented downwards below the $J_2(\varphi_0)$ curve and subsequently the normalized signal is less than 1. For a typical monolayer sample, such as an organic thin film on a gold-coated substrate, $\rho \approx 0.95$ (at 1000 $cm^{-1}$, e varies very little across the entire mid-IR spectrum) and $\gamma \approx 1$. Equation (2) then reduces to

$$A(d) \approx 0.0223\left[\left(\frac{\Delta I(d)}{\Sigma I(d)}\right)_{norm}-1\right] \quad (3)$$

Equation (3) is readily applied to PM-IRRAS spectral data processing for monolayer films on gold (or gold-coated) substrates. It is a more straightforward and mathematically strict approach than other procedures reported in the literature.[3]

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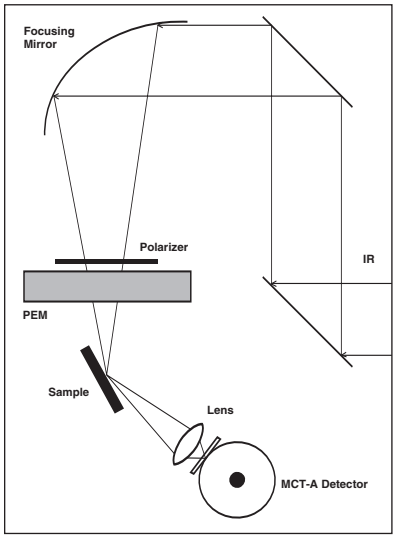
## Experimental

A dual-channel Nicolet® Nexus® 870 research spectrometer with a PEM module for PM-IRRAS and a SAGA™ grazing angle accessory for conventional IRRAS was used in the experiment. The optical diagram of the PEM module is shown in Figure 1. A liquid nitrogen cooled MCT detector was used for both experiments. In the PM-IRRAS experiment, the sum and difference PM-IRRAS spectra were collected simultaneously. The PM-IRRAS spectrum was collected with 100 scans at 8 $cm^{-1}$ resolution and 83° reflection angle. In the conventional IRRAS experiment, 100 and 400 scans were respectively used to collect background and sample spectra at 8 $cm^{-1}$ resolution. The sample consists of (poly)-l-lysine monolayer on a gold-coated glass slide, and the reference is a clean gold-coated glass slide.



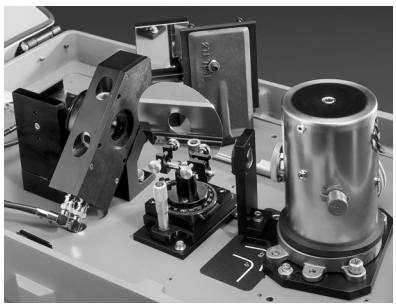



Figure 1: Optical layout of the PEM module for PM-IRRAS

## Results and Discussion

Figure 2 shows a directly measured absorbance spectrum of a poly-l-lysine film on a gold-coated glass substrate by using a Smart SAGA grazing angle accessory (top) and a converted absorbance spectrum of the same sample, collected by using dual-channel PM-IRRAS and processed by Equation (3) (bottom). The grazing angle difference between the regular IRRAS (80°) and PM-IRRAS (83°) was also factored into the calculation of the converted absorbance spectrum.

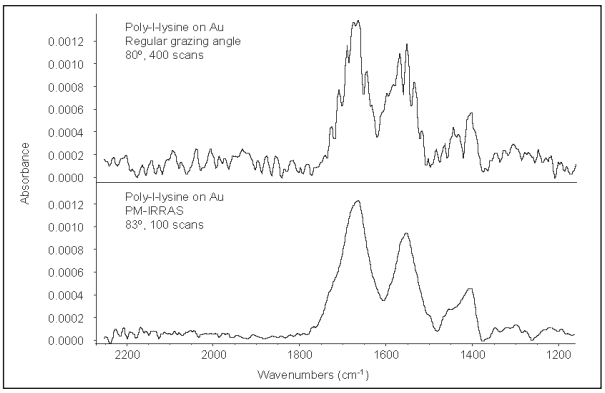



Figure 2: Comparison of IRRAS spectra of a poly-l-lysine thin film on a gold-coated glass substrate collected by using a conventional (top) and dual channel polarization modulation (bottom) methods.

It can be seen by comparing IRRAS spectra in Figure 2 that: 1) The dual channel PM-IRRAS has tremendous advantages over conventional IRRAS in terms of signal-to-noise ratio, clean removal of spectral interferences from water vapor and other randomly oriented environmental species, and data collection time, even though the large PEM chamber was opened repeatedly for placing the samples; and 2) The converted PM-IRRAS spectrum in absorbance units using Equation (3) corresponds well with the values measured by regular IRRAS as indicated by the band intensity at 1664 $cm^{-1}$ (0.00123 abs. vs. 0.00138 abs, respectively). An attempt has also been made to digitally correct water vapor interferences on the conventional IRRAS spectrum with the post-processing option in OMNIC® software. There is some improvement with digital suppression of water vapor, but the monolayer peaks are still noisy.

## Conclusions

A new theoretical formula for converting PM-IRRAS spectral intensities to absorbance units has been derived from the classic PM-IRRAS theory and confirmed experimentally. Comparison of spectral data of PM-IRRAS and conventional IRRAS shows that the dual channel PM-IRRAS is an effective and easy-to-use vibrational spectroscopic technique for studying monolayer films on reflective substrates. Its tremendous advantages over conventional IRRAS in sensitivity, speed and SNR performance have been demonstrated.

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