



## APPLICATION NOTE 2

# Polarization modulated infrared spectroscopy of thin films at the nanometer scale

This application note illustrates how the KSV NIMA PM-IRRAS can be used to characterize ultra thin films in order to obtain information such as molecular orientation and chemical composition.

### Introduction

Precise methods for thin film surface preparation and characterization are key factors in modern nanotechnology. Polarization modulation infrared reflection adsorption spectroscopy (PM-IRRAS) is a powerful method for measuring FT-IR from molecules on substrates. From the surface specific IR-spectrum obtained with this method it is possible to deduce chemical composition of films, orientation of molecules and relative amount of material on the surface. This is important in many industrial areas utilizing or planning to utilize nanofabrication and self assembly, molecular electronics, coatings, corrosives, sensors and catalysis.

The Langmuir-Blodgett (LB) deposition technique is a way to create one molecule thick films. It offers control over the molecular orientation and film thickness in the molecular scale. Stearic acid (SA) was used as a model compound to present how the KSV NIMA PM-IRRAS can be used to characterize nanofabricated thin films. A self-assembled film of a well known anticorrosive compound for copper containing metals, methylbenzo triazole (MBT), was created on brass and the layer was studied with the KSV NIMA PM-IRRAS.

The KSV NIMA PM-IRRAS is a FT-IR spectrometer mounted on a goniometer and equipped with a photoelastic modulator. The IR-light is modulated at high frequency (different from the FT-IR source frequency) and at the signal processing the two are separated electronically. The result is that two IR-spectra are obtained simultaneously, a so-called sum spectrum and difference spectrum. Because p- and s-polarized light reflect differently from surfaces, any differences between the two spectra come from surface specific absorptions. Furthermore on conductive surfaces so called mirror effect will enhance p-polarized components and diminish s-polarized of dipoles, which makes it possible to deduce conformational information of molecules from the spectrums [1].

Also the use of sum and difference spectra diminishes environmental effects on the spectra, such as CO<sub>2</sub> and water vapor, and removes the need for protective gasses in reflection measurements. This property allows the KSV NIMA PM-IRRAS to have a very open architecture, enabling measurements from liquid surfaces and solid samples of almost any size. The open design also allows combined use of external UV light source, heater or other complementary equipment.

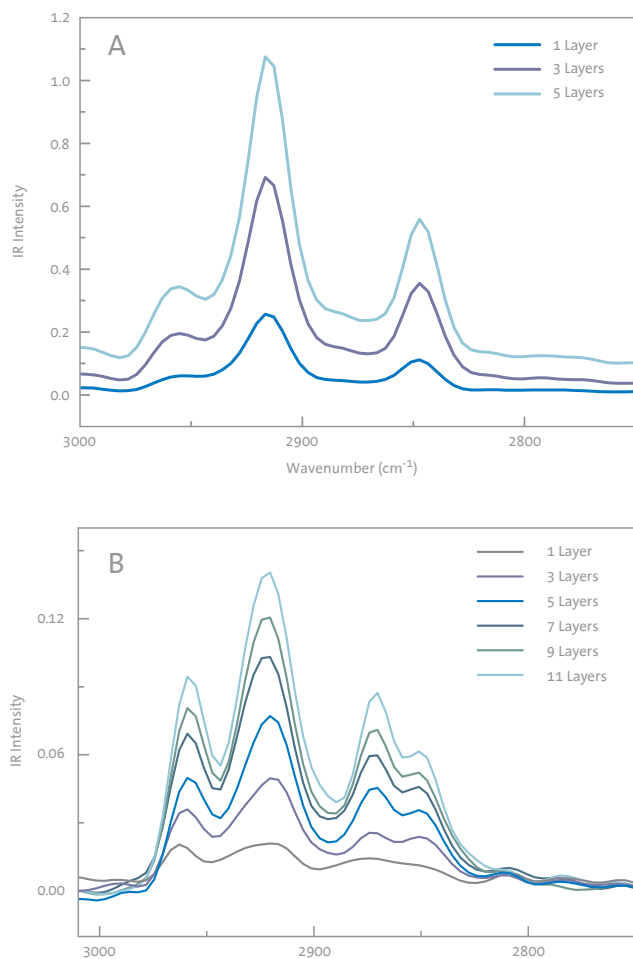
### Materials and methods

SA films were created by LB-method from 0.1 mM CdCl<sub>2</sub> subphase onto a glass substrate that had a 300 nm gold coating. Two different sets of LB films were prepared, one with subphase pH 2 and other with pH 6. PM-IRRAS measurements were performed on the films after each LB-cycle.

MBT was self assembled by dipping a brass substrate into a 60 mg/L solution dissolved in ethanol for one hour.

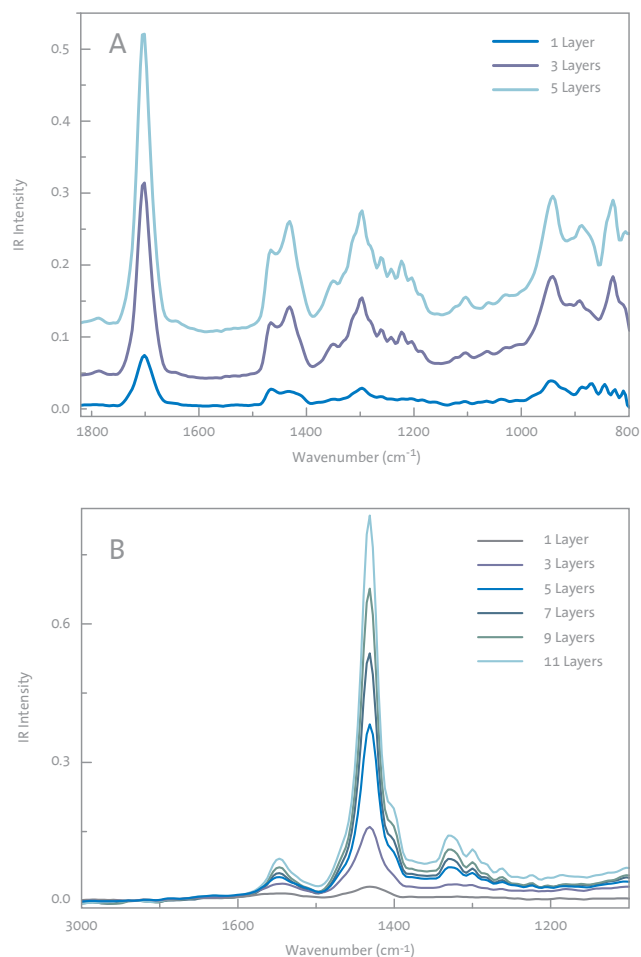
## Results and discussions

From the FT-IR spectra of deposited SA LB-film, it is possible to distinguish  $\text{CH}_3$  symmetric stretch ( $2960\text{ cm}^{-1}$ ),  $\text{CH}_2$  symmetric ( $2850\text{ cm}^{-1}$ ) and asymmetric ( $2918\text{ cm}^{-1}$ ) stretches (Figure1).



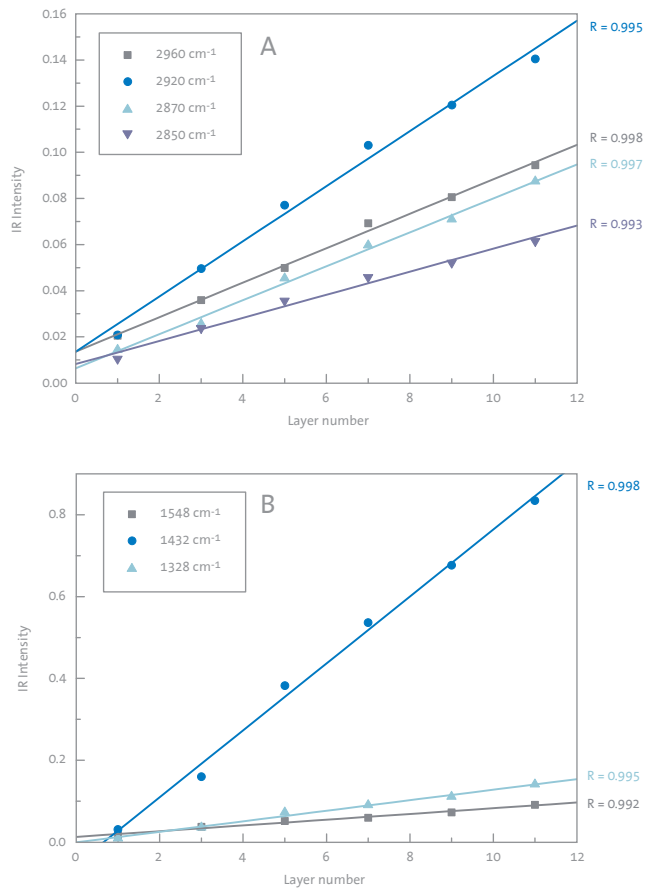
**Figure1.** PM-IRRAS spectra of SA Langmuir-Blodgett films of increasing thickness on gold at (A) pH 2 and (B) pH 6 in the C-H stretch region

For the LB films made from pH 2, the  $\text{C}=\text{O}$  stretch ( $1710\text{ cm}^{-1}$ ),  $\text{COO}^-$  symmetric stretch ( $1430\text{ cm}^{-1}$ ) and  $\text{CH}_2$  wagging and twisting ( $1200\text{-}1350\text{ cm}^{-1}$ ) were identified (Figure2A). For pH 6 films there was no  $\text{C}=\text{O}$  stretch, but the  $\text{COO}^-$  symmetric stretch was much more pronounced and also  $\text{COO}^-$  asymmetric stretch ( $1540\text{ cm}^{-1}$ ) was identified (Figure2B).



**Figure2.** PM-IRRAS spectra of SA Langmuir-Blodgett films of increasing thickness on gold at (A) pH 2 and (B) pH 6 between  $1800$  and  $800\text{ cm}^{-1}$

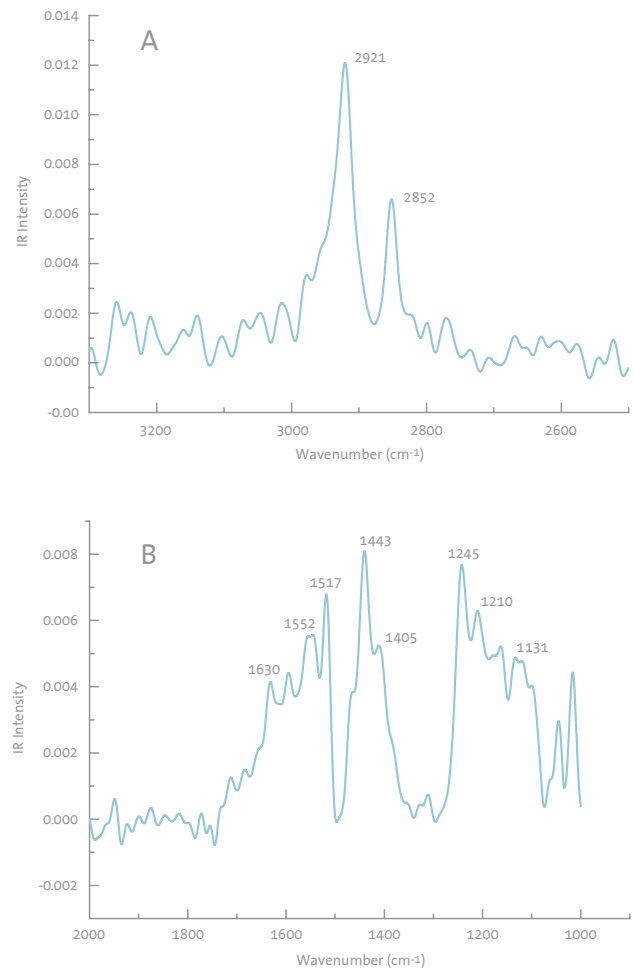
Peak intensity increased with layer number with excellent linearity, as shown in Figure 3.



**Figure 3.** Linear fits of peak intensity versus layer number of SA deposited at pH6. (A) C-H region and (B) between 1800 and 1200  $\text{cm}^{-1}$

MBT PM-IRRAS spectrum shows peaks at 2920  $\text{cm}^{-1}$  and 2850  $\text{cm}^{-1}$  (Figure 4). Even though these are usually assigned to  $\text{CH}_2$  stretches, bulk spectra of MBT from KBr disk shows  $\text{CH}_3$  peaks at 2914 and 2829  $\text{cm}^{-1}$ , and toluene bulk spectra shows 2920 and 2973  $\text{cm}^{-1}$ . [2]

Based on this, the peaks can be assigned to the  $\text{CH}_3$  group of MTB. Other peaks in the MTB spectrum were assigned to the aromatic part of the molecule (1517-1600, 1443, 1405 and 1245-1100  $\text{cm}^{-1}$ ) based on the bulk spectrum of MTB and IR-tables from literature [3]. The fact that C-H stretch form benzene ring is missing from the spectrum (at 3030  $\text{cm}^{-1}$ ) indicates that the aromatic ring has planar orientation in relation to the metal surface. This is due to the Surface Dipole Selection Rule effect that enhances the p-component and cancels out s-component of electric dipole on conducting surfaces. [1] No PM-IRRAS or IRRAS studies of MTB were found from literature, and to our best knowledge this is the first time such experiments are reported.



**Figure 4.** PM-IRRAS spectra of self assembled MBT film on brass (A) C-H region and (B) between 2000 and 1000  $\text{cm}^{-1}$

## Conclusions

The PM-IRRAS method was found to be excellent for FT-IR experiments of nanometer scale thin films. It was possible to acquire FT-IR spectrums of films of around 2 nm thick, and also deduce molecular orientation from the experiments. Linear correlation between LB layer number and peak intensities was found. This demonstrates that the KSV NIMA PM-IRRAS is a powerful tool for thin film characterization and analysis. The measurements are fast and simple to perform thanks to KSV NIMA PM-IRRAS unique design.

[1] Griffiths, P and Haseth, J., *Chemical Analysis 83: Fourier Transformation Infrared Spectrometry*, Wiley, 1983, Chapters 8 and 17

[2] SDBS, Available at: [http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre\\_index.cgi?lang=eng](http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng) [Accessed on 30 March 2010]

[3] Hase, T., *Tables for Organic Spectrometry*, Otatioto, 1992



## ***KSV NIMA – at the creative interface of people and technology***

We create value for our customers by providing advanced, innovative instruments for thin film fabrication and characterisation, by constantly exchanging knowledge with our customers and through building open, trusting relationships with customers and partners.

### **Availability**

KSV NIMA products and services are provided to customers all over the world through Biolin Scientific in co-operation with a highly competent network of Distribution Partners. For a list of relevant contact details, visit [www.ksvnima.com](http://www.ksvnima.com)

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