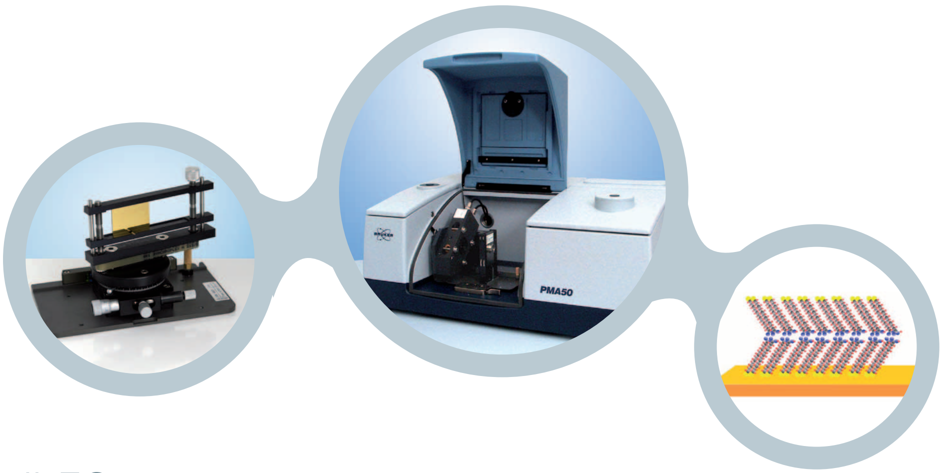


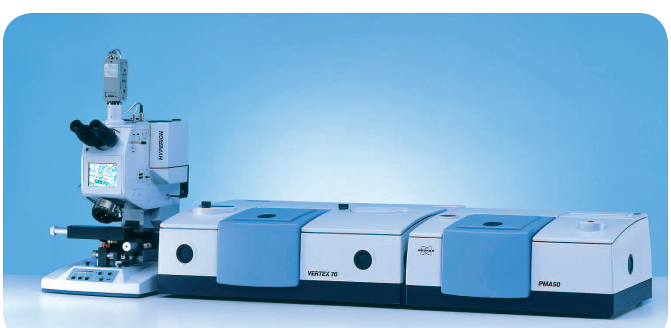
Application Note AN # 53

Modulation overcomes frustration: Investigation of ultrathin layers with PM-IRRAS

The investigation of ultrathin layers and monolayers of organic compounds on substrates is becoming more important for many R&D applications. These chemically activated surfaces provide promising future applications, such as chemical sensor devices, biofunctional implantates or biochips.

IRRAS (InfraRed Reflection Absorption Spectroscopy) technique is a commonly used, but a difficult method to investigate such ultrathin layers using FT-IR spectroscopy. In order to increase the sensitivity to the layer, the measurement is carried out with grazing incidence (~80°) in reflection geometry. However, this method has two distinct disadvantages: first, due to the extremely weak absorbance of the layer, residual atmospheric noise tends to cover the desired spectral information even in purged spectrometers. And secondly, the classical IRRAS technique requires an absolutely clean substrate for the reference measurement, which is a nontrivial demand.

These two disadvantages can be overcomed by using the much more powerful PM-IRRAS (Polarization Modulation) technique. While the principle geometry of the conventional IRRAS method is maintained, the polarization of the IR-beam is additionally modulated with high frequency (~100kHz) between s- and p-polarization with respect to the sample surface, utilizing a photoelastic modulator (PEM). On metallic or at least metal like (e.g. highly doped semiconductors) substrates, only the p-polarized light interacts with the ultrathin layer of interest. The PM-IRRAS spectrum is directly correlated to the absorption of the investigated layer. Furthermore, the atmospheric absorptions (mainly H_2O and CO_2) are polarization independent and therefore completely suppressed. Using PM-IRRAS, the complete required data can be collected from the sample itself and thus a measurement of an absolutely clean reference substrate becomes obsolete.



VERTEX70 coupled to PMA50 and Hyperion infrared microscope

Although the underlying technique is sophisticated, Bruker Optics PM-IRRAS solution is easy to operate and the user does not have to be aware of the details described above. The measurement is performed within the PMA50 module which can be adapted to any of Bruker Optics FT-IR spectrometer, including the routine TENSOR27 spectrometer, which does not require the step-scan technique.
Bruker Optics routine and research grade spectrometers, such as the VERTEX70, are equipped with dual channel 24 bit ADC which can acquire the two required spectra (polarization sum and difference) simultaneously in the usual continuous scan mode. Compared to solutions based on Step Scan techniques, this approach also drastically decreases the measurement time. For sample sizes in the order of 1cm, spectra as depicted in figure 1 and 2 can be typically obtained within 1 to 5 minutes. The whole measurement can be conducted with the OPUS standard software package.

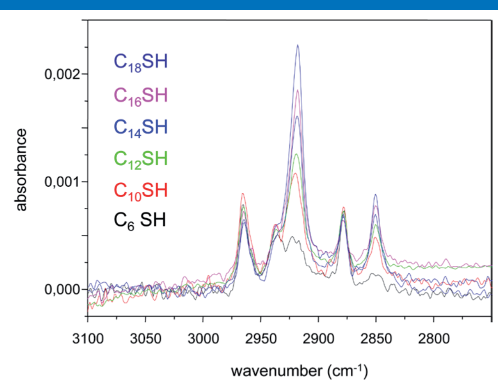


Figure 1: Absorption spectra of different alkanethiole monolayers on a gold coated substrate. Note how the CH_2 stretching modes (~2850cm^{-1} and ~2920cm^{-1}) scale with increasing CH_2 chain length.

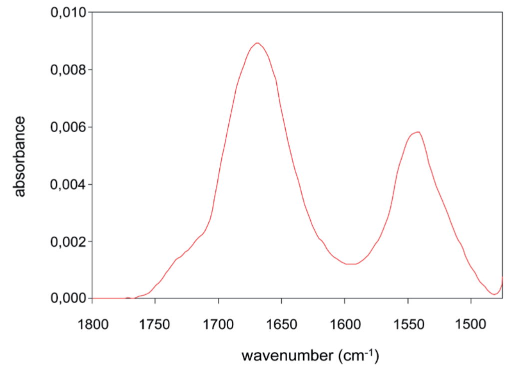


Figure 2: Absorption spectrum of an ultrathin protein layer on a gold coated substrate. The shape of the amide bands at ~1540cm^{-1} and 1670cm^{-1} can give valuable information about the conformation of the protein molecules.

The PMA 50 PM-IRRAS module is the ideal tool for the reliable detection, identification and investigation of ultrathin layers. Ongoing trend in the R&D field, based on the PM-IRRAS technique is the in-situ investigation of the growth of ultrathin layers in vacuum chambers or in liquid.
Furthermore the PMA50 module is also capable of performing other polarization modulation experiments, such as VCD (Vibrational Circular Dichroism) for the investigation of chiral molecules.

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