

Measurement of Monomolecular Layers Using Specialized FTIR Grazing Angle Accessories

The analysis of monomolecular layers has traditionally been a challenging spectroscopic measurement due to the relatively low signal obtained from the sample. Specular reflectance at high “grazing” angles (around 80 degrees from normal to the surface) has been recognized as one of the best spectroscopic techniques to monitor monomolecular layers on reflective surfaces due to the enhancement of the infrared signal^(1, 2). The versatility of this sampling technique is further optimized using different specialized grazing angle accessories.

Experimental

An FTIR spectrometer was equipped with an MCT detector and with three different grazing angle accessories; an 80Spec™ - fixed grazing angle, an AGA™ - variable illumination area and with a VeeMAX™ II - variable angle reflectance accessory. The fixed angle 80Spec is a dedicated single reflection accessory with simple input and output optics channeling the infrared light with two gold flat mirrors. While this is a powerful tool, its use is limited to larger area samples. When the light from an FTIR instrument is directed to the sample at a high angle, the illuminated area is not as well controlled, its shape is elongated and the IR image size becomes relatively large. When the sample is smaller than the illuminated spot, apertures could be used to limit the size of the infrared beam. In this case, however, the contrast and repeatability of the measurement usually suffers considering the sensitivity required to detect monomolecular quantities of materials. The controlled projected image size therefore is a very important advantage of the AGA accessory, which has a special imaging system with a set of variable diameter mirrors. In this unique optical design, the illuminated spot on the sample is the same as the size and shape of the gold mirror at the base of

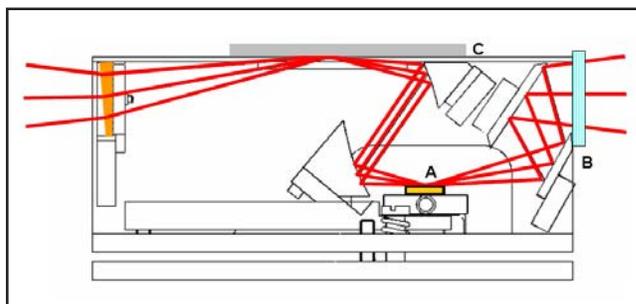


Figure 1. Advanced grazing angle accessory (AGA) with optimized spot size defined precisely by selectable circular reflecting optics.

the optical layout (Fig. 1). The selector mirrors in this design are round and are variable in five steps from 3 mm to 12.5 mm diameter.

The variable angle VeeMAX accessory (Fig. 2) on the other hand allows other reflectance and reflectance-absorbance measurements in addition to grazing angle measurements³. This analysis capability is provided through its continuously variable angle of incidence selection from 30 to 80 degrees.

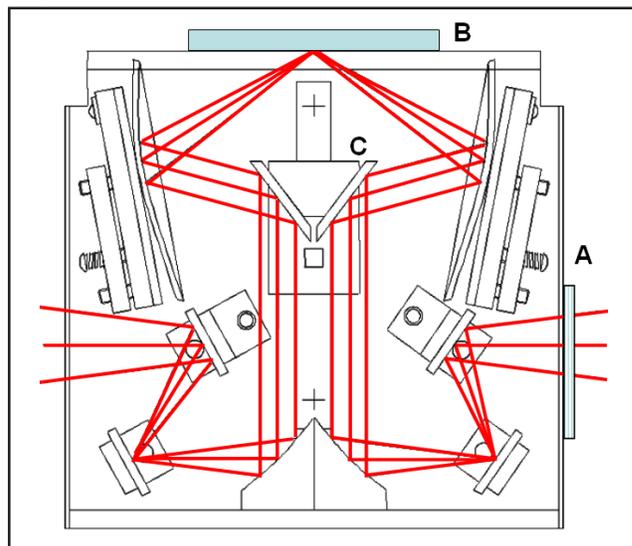


Figure 2. The variable angle VeeMAX II accessory for monolayers to thick films.

All three optical arrangements can be used with an optional IR polarizer to enhance the monomolecular surface species. In this work, a ZnSe wire grid polarizer was used for all samples. All measurements were done using the MCT detector as the IR throughput is relatively low at grazing angle of incidence in combination with an IR polarizer. All spectra were collected at 8 cm⁻¹ resolution with a 1 minute data collection time.

Results and Discussion

For the comparison of the performance of different optical geometries, monolayer systems used in various biotechnologies were selected. Monolayers are considered initial surface coverages with reactive groups to be modified further for various bio-specific and ligand interactions, fabrication of protein, DNA and carbohydrate chips and biosensors. Gold is known to have high affinity to sulfur containing groups, such as thiols, and generate more or less well-ordered monolayers (4). One of the systems is a self assembled hydroxyl-terminated alkanethiolate monolayer that was formed on a freshly evaporated gold surface using the method and materials from Platypus Technologies, Inc (Madison, WI, www.platypustech.com). The monomolecular layer is formed over a timeframe of several hours in a dilute solution of HS(CH₂)_n(OCH₂CH₂)_nX, where X can represent different functional groups. The ω-functionalized alkanethiolate layer (5) was stable throughout the experiment and was easily measured on all of the accessories.

Figure 3A shows the NH-terminated monolayer measured on the 80Spec with a ZnSe polarizer. The example shown using the AGA is an OH-terminated thiol (Fig.3B). The accessory was adjusted to project a 12.5 mm diameter spot on the gold

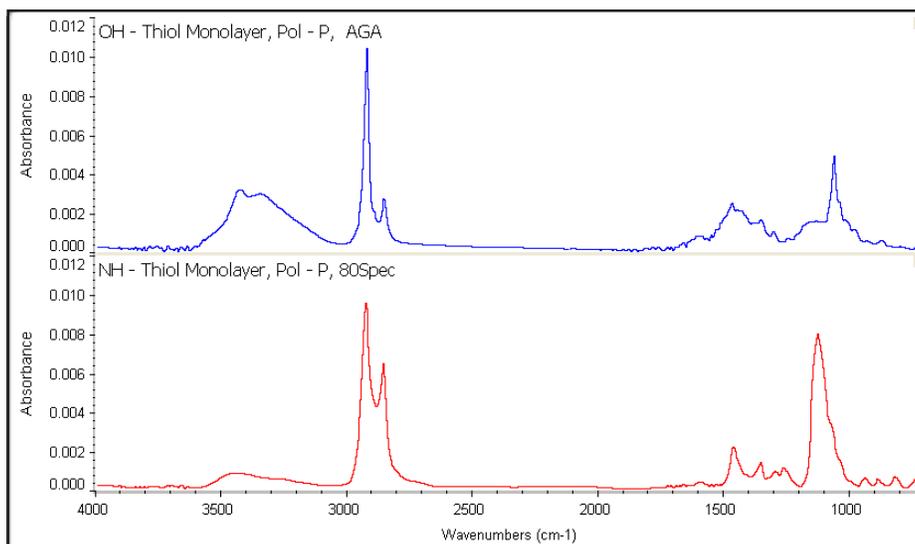


Figure 3: 3A shows the NH-terminated monolayer run on the 80Spec; 3B shows an OH-terminated thiol measured with the AGA.

coated slide. Due to the better definition of the illuminated area, smaller samples can be measured easily without apertures which in some cases can introduce artifacts. Grazing angle measurements with the VeeMAX is shown with a third kind of monolayer, a CH-terminated alkanethiol. CH terminated alkanes are generally more difficult to identify, due to the lack of characteristic differentiating molecular groups in comparison to organic contamination from ambient air, solvents on the sample or the background slides. For the experiment the VeeMAX was set to 78 degrees and produced the characteristic pattern seen in Figure 4. This carbon-hydrogen stretch region of the IR spectrum shows excellent signal-to-noise ratio in spite of the relativ-

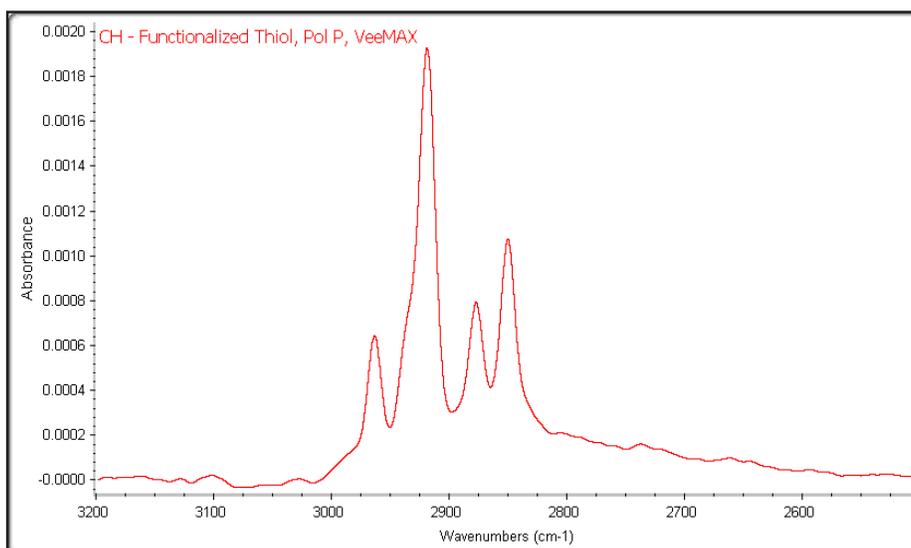


Figure 4: For this spectrum the VeeMAX II was set to 78 degrees and was configured with an IR polarizer.

ely low absorbance intensity from the monolayer sample.

Conclusions

Infrared spectroscopic measurements of monomolecular layers can be performed using all of the different grazing angle reflectance accessories discussed in this work and are capable of producing excellent quality spectra. The intensity of the monomolecular signal is significantly enhanced with polarized light, and the quality of the resulting spectra is greatly enhanced by using an MCT detector. By controlling the illuminated area with a special optical design of the AGA, one can measure small samples or examine small areas of larger samples. When, in addition to monomolecular layers analysis, measurement of thicker films is needed; the variable angle VeeMAX is an excellent choice for these specular reflectance experiments.

References:

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