Specular Reflectance – Theory and Applications

Specular reflectance sampling in FTIR represents a very important technique useful for the measurement of thin films on reflective substrates, the analysis of bulk materials and the measurement of mono-molecular layers on a substrate material. Often this technique provides a means of sample analysis with no sample preparation – keeping the sample intact for subsequent measurements.

The basics of the sampling technique involve measurement of the reflected energy from a sample surface at a given angle of incidence. The electromagnetic and physical phenomena which occur at and near the surface are dependent upon the angle of incidence of the illuminating beam, refractive index and thickness of the sample and other sample and experimental conditions. A discussion of all of the physical parameters and considerations surrounding the specular reflectance sampling technique is beyond the scope of this overview. We will present this technique from an applications-oriented perspective.

Types of Specular Reflectance Experiments

- Reflection-absorption of relatively thin films on reflective substrates measured at near-normal angle of incidence
- Specular reflectance measurements of relatively thick samples measured at near-normal angle of incidence
- Grazing angle reflection-absorption of ultra-thin films or mono-layers deposited on surfaces measured at a high angle of incidence

In the case of a relatively thin film on a reflective substrate, the specular reflectance experiment may be thought of as similar to a "double-pass transmission" measurement and can be represented as shown in the following illustration.

At the reflective substrate, the beam reflects back to the surface of the thin film. When the beam exits the thin film it has geometrically passed through the film twice and is now represented as $I_A$. Infrared energy is absorbed at characteristic wavelengths as this beam passes through the thin film and its spectrum is recorded. The specular reflectance spectra produced from relatively thin films on reflective substrates measured at near-normal angle of incidence are typically of high quality and very similar to spectra obtained from a transmission measurement. This result is expected as the intensity of $I_A$ is high relative to the specular component ($I_R$).

For relatively thick samples, the specular reflectance experiment produces results which require additional considerations as the specular component of the total reflected radiation is relatively high.

Again, the incident FTIR beam represented by $I_0$ illuminates the sample of a given refractive index ($n_1$) and at an angle of incidence ($\theta_1$). Some of the incident beam is reflected from the sample surface, represented by $I_R$ at the incident angle ($\theta_1$). Some of the incident beam is transmitted into the sample represented by $I_T$ at an angle of $\theta_2$. As predicted by Fresnel equations, the percent of reflected versus transmitted light increases with higher angles of incidence of the illuminating beam. Furthermore, the refractive index of the sample, surface roughness, and sample absorption coefficient at a given wavelength all contribute to the intensity of the reflected beam.

The incident FTIR beam represented by $I_0$ illuminates the thin film of a given refractive index ($n_2$) and at an angle of incidence ($\theta_1$). Some of the incident beam is reflected from the sample surface, represented by $I_R$ at the incident angle ($\theta_1$) and is also known as the specular component. Some of the incident beam is transmitted into the sample represented by $I_T$ at an angle of $\theta_2$ – calculated from Snell’s Law.

$$n_1 \sin \theta_1 = n_2 \sin \theta_2$$
At wavelengths where the sample exhibits a strong IR absorption, the reflectivity of the sample increases. The superposition of the extinction coefficient spectrum with the refractive index dispersion results in a spectrum with derivative-shaped bands. This specular reflection spectrum can be transformed using the Kramers-Kronig conversion to a transmission-like spectrum as shown in the example below.

Our third application of specular reflectance is the measurement of relatively thin films and mono-molecular layers at grazing angle of incidence. At high angles of incidence, between 60 and 85 degrees, the electromagnetic field in the plane of the incident and reflected radiation is greatly increased relative to a near-normal angle of incidence. The perpendicular component of the electromagnetic field of the reflecting radiation is not enhanced.

Because of the orientation of the electromagnetic field at the surface for grazing angle measurements, the use of an IR polarizer greatly improves the sampling result. By collecting the spectrum at grazing angle of incidence with p-polarization, we only examine the enhanced portion of the electromagnetic field at the sample surface, thereby producing a stronger absorbance spectrum.

Specular reflectance is a valuable FTIR sampling technique for the analysis of thin films on reflective substrates, for relatively thick films on reflective materials and for bulk materials where no sample preparation is preferred. PIKE Technologies offers a complete line of specular reflectance accessories to perform these analyses.