HARRICK Scientific Products
Solutions in Optical Spectroscopy

Background measurement methods for the RefractorReactor

For routine grazing angle specular measurements, the background spectrum is generally recorded using a mirror or an uncoated substrate. However, this approach can be problematic for *in-situ* spectroscopy where absorbing gases may make it difficult to discern the changes on the surface of the sample. The practical approach to eliminate this problem is to collect the single beam background spectrum with s-polarization and the sample spectrum with p-polarization. This is the method used for IRRAS spectroscopy, where the polarization is automatically flipped during data collection and the data is automatically processed. Here, we review the theory behind that method and discuss the methodology than can be used in lieu of IRRAS equipment.

THEORETICAL DISCUSSION

Let us begin by defining some terms:

$R_p^M(k)$: reflectance of the reference mirror for p-polarization
$R_s^M(k)$: reflectance of the reference mirror for s-polarization
$R_p^S(k)$: reflectance of the sample for p-polarization
$R_s^S(k)$: reflectance of the sample for s- polarization

$I(k)$: intensity of the single beam of the spectrometer plus the accessory
$T_{p,s}(k)$: transmittance of the polarizer for p- and s- polarization

Then the single beam spectra acquired for the above four cases can be written as:

$$S_p^M(k) = R_p^M(k)T_p(k)I(k)$$
$$S_s^M(k) = R_s^M(k)T_s(k)I(k)$$
$$S_p^S(k) = R_p^S(k)T_p(k)I(k)$$
$$S_s^S(k) = R_s^S(k)T_s(k)I(k)$$

We normally measure the ratio of the single beam sample spectrum to the single beam background spectrum, which can then be expressed as:

$$\frac{S_p^S(k)}{S_p^M(k)} = \frac{R_p^S(k)}{R_p^M(k)} \quad (1)$$

For the grazing angle specular reflection measurement in a reaction chamber, the proposed alternative is to measure the single beam p-polarization spectrum relative to the single beam s-polarization spectrum. That is:

$$\frac{S_p^S(k)}{S_s^S(k)} = \frac{R_p^S(k)T_p(k)}{R_s^S(k)T_s(k)} \quad (2)$$

To get $\frac{T_p(k)}{T_s(k)}$ we measure

$$\frac{S_p^M(k)}{S_s^M(k)} = \frac{R_p^M(k)T_p(k)}{R_s^M(k)T_s(k)}$$

Taking the ratio gives:

$$\frac{\frac{S_p^S(k)}{S_s^S(k)}}{\frac{S_p^M(k)}{S_s^M(k)}} = \frac{\frac{R_p^S(k)}{R_s^S(k)}}{\frac{R_p^M(k)}{R_s^M(k)}}$$

This doesn't quite give (1). If we assume that:

$$R_s^M(k) = R_s^S(k) \quad (3)$$

Then we would get (1).

Next, the reflectance was calculated to see if assumption (3) was reasonable.

Figure 1 shows the reflectance of a metal for s-polarization at a 75° angle of incidence and the reflectance of a non-absorbing thin film with a refractive index, n, of 1.35 for thicknesses of 100, 150, 200 and 250 nm on the metal. So assumption (3) is better fulfilled for very thin films.

As the film becomes thicker, the problem becomes more than just a sloping baseline. Figure 2 shows the same film with a 750 nm thickness, where a noticeable peak has appeared due to the film. So using this method for films that are too thick, where assumption (3) no longer holds, could lead to spectral anomalies unrelated to the characteristics of interest.

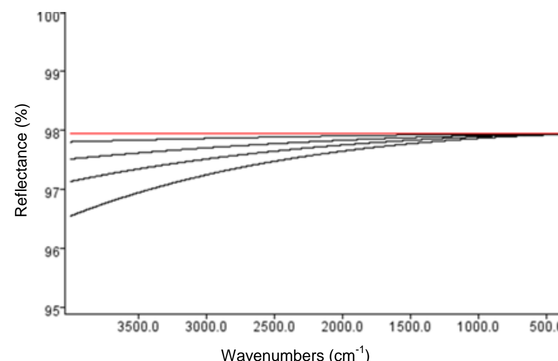

Figure 1. Reflectance of a metal (red) and a non-absorbing thin film with a refractive index, n, of 1.35 for thicknesses of 100, 150, 200 and 250 nm atop the metal.

EXPERIMENTAL DISCUSSION

To illustrate this method, measurements were taken using the non-reaction chamber model of the RefractorReactor, the Refractor2. The built-in polarizer was removed and replaced with a wire grid polarizer, as is typically used with the reaction chamber. Data was collected with the Refractor2 installed in a commercial FTIR set to collect 32 scans at 8 cm^{-1} resolution. Two materials were measured: a front-surface Al mirror and a 500 Å SiO coating on Al. Both were on glass substrates.

The reflection spectrum of the coated sample was measured relative to the uncoated mirror for comparison purposes. Then for both materials, the background single beam spectrum was recorded with p-polarized radiation and the sample spectrum was collected s-polarization. The ratio of these two spectra was then calculated. The resulting spectra are shown in Figure 3.

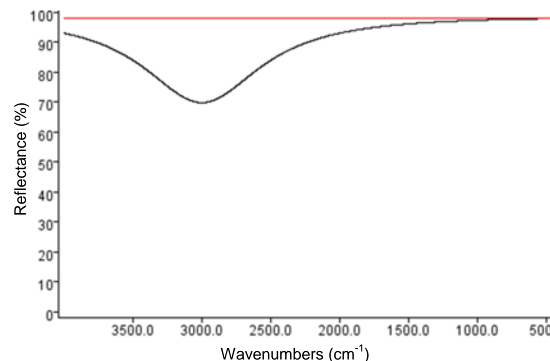

Figure 2. Reflectance of the film with a 750 nm thickness.

The two spectra are very similar. The slight differences in baseline and band intensity could be due to deviation from assumption (3) for the ratio-ed spectrum or from variations in the thicknesses of the aluminum coating on the coated mirror and the uncoated mirror. But these spectra show that the overall features are preserved using this method for referencing.

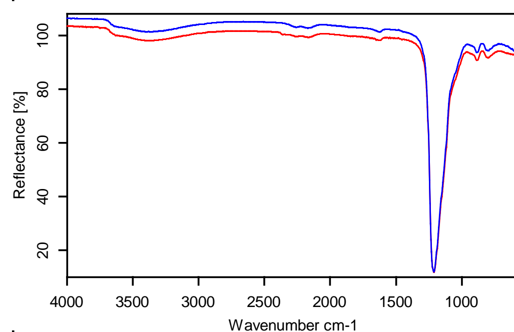

Figure 3. Reflectance of a 500 Å SiO coating on Al measured relative to a mirror (red) and using the polarization ratio method (blue).

SUMMARY

This is a convenient and effective method for collecting spectra with the RefractorReactor in lieu of an IRRAS module. Since the background and sample spectrum can be measured very close to each other in time, this method reduces errors related to thermal effects. Further, since the spectrum of a gas is polarization independent, it should minimize interference from gaseous species inside the chamber during *in-situ* measurements, making it easier to distinguish the species on the surface of the sample.