

Reflection Measurements in IR Spectroscopy

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Reflection spectra

Most materials absorb infrared radiation very strongly. As a result samples have to be prepared as thin films or diluted in non-absorbing matrices in order to measure their spectra in transmission. There is no such limitation on measuring spectra by reflection, so that this is a more versatile way to obtain spectroscopic information. However reflection spectra often look quite different from transmission spectra of the same material. Here we look at the nature of reflection spectra and see when they are likely to provide useful information. This discussion considers only methods for obtaining so-called external reflection spectra not ATR techniques.



The nature of reflection spectra

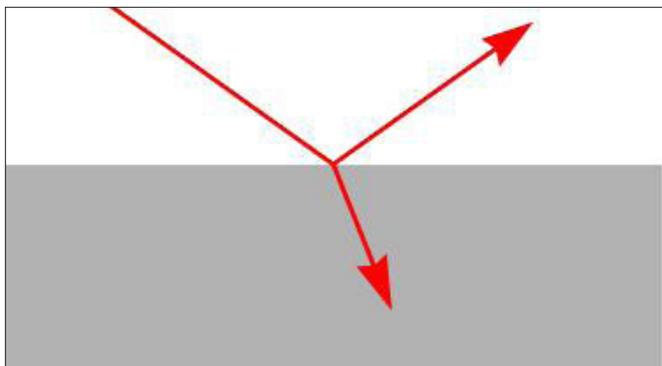


Figure 1. Reflection and transmission at a plane surface

Reflection takes place at surfaces. When radiation strikes a surface it may be reflected, transmitted or absorbed. The relative amounts of reflection and transmission are determined by the refractive indices of the two media and the angle of incidence. In the common case of radiation in air striking the surface of a non-absorbing medium with refractive index n at normal incidence the reflection is given by $(n-1)^2/(n+1)^2$. So for a material with a refractive index of 1.5 the reflection at the surface is 4%. At other angles of incidence the reflection depends on the polarisation of the radiation. The situation becomes more complicated, but also more interesting, when the second medium is absorbing. The refractive index is closely related to the absorption. Because the amount of reflection is determined by the refractive index the reflection changes wherever there is an absorption band. For an isolated absorption band the refractive index has a minimum on the high wavenumber side of the band and a maximum on the low wavenumber side. The reflection spectrum therefore resembles a first derivative, with a minimum to high wavenumber and a maximum to low wavenumber of the band centre. This can be seen in the spectra obtained by reflection from the surface of a block of polymethylmethacrylate and by transmission through a film of the same material in Figure 2. Absorption in the near IR is typically about 100 times weaker than in the mid IR. The very weak absorptions in the near IR are accompanied by correspondingly small changes in refractive index so the component reflected directly from the surface in the near IR has little or no structure.

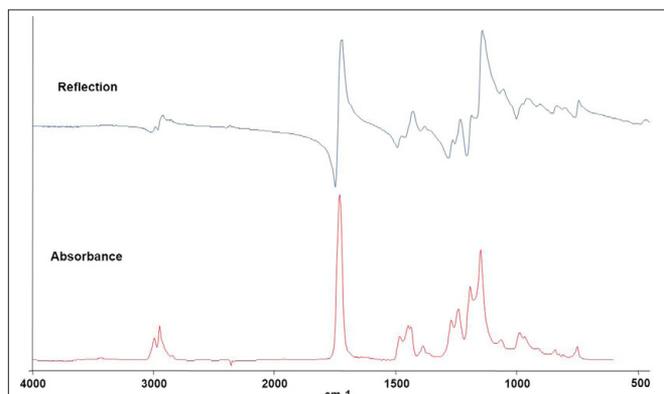


Figure 2. Reflection and transmission spectra of polymethylmethacrylate

The absorption spectrum can be calculated from the measured reflection spectrum by a mathematical operation called the Kramers-Kronig transformation. This is provided in most data manipulation packages used with FTIR spectrometers. Below is a comparison between the absorption spectrum of polymethylmethacrylate obtained by Kramers-Kronig transformation of the reflection spectrum and the transmission spectrum of a thin film.

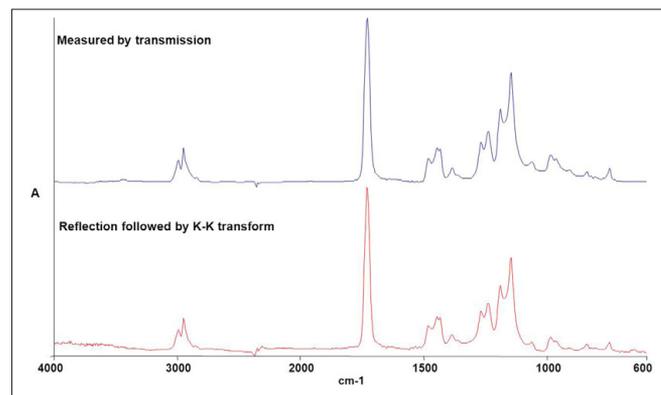


Figure 3. Transmission and Kramers-Kronig transformation of the reflection spectrum of polymethylmethacrylate

This kind of spectrum can be obtained from thick samples of non-scattering materials as above or from carbon-filled polymers but in practice the spectra obtained after Kramers-Kronig transformation often have distorted band shapes and uneven baselines.

The previous examples consist of reflection from the front surface of a sample, sometimes called surface or Fresnel reflection. In many situations, for example reflection from a powder, the reflection spectra do not come from the front surface alone. Radiation that penetrates into the material can reappear after scattering or reflection at a second surface. When this radiation emerges it will have experienced some absorption, depending on the path traversed. This component of the spectrum will have the general character of a transmission spectrum. Spectra of this type are called diffuse reflection spectra but it is important to remember that they always contain some amount of reflection from the surface of the sample.

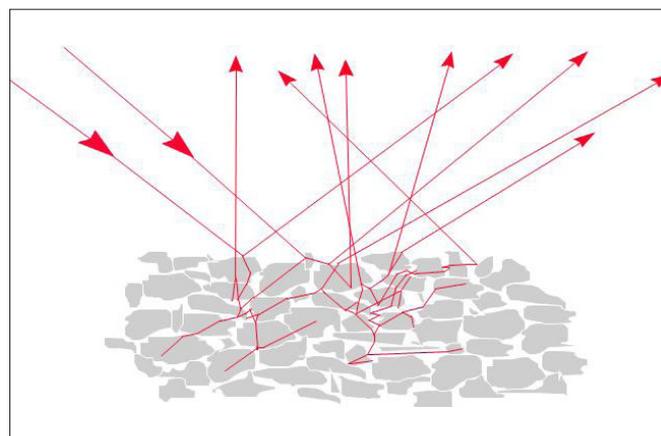


Figure 4. Diffuse reflection by a powder

The appearance of the spectra depends on the relative amounts of surface reflection and of radiation that has penetrated the sample. Particle size and the strength of absorptions are the main factors that influence this. The typical distance light travels inside the sample before it is scattered or reflected back to the surface increases with the particle size so reducing the amount of light reappearing from within the sample. If particles are much larger than a few tens of microns then many mid-IR bands become totally absorbing. In Figure 5 the spectrum of coarse glycine powder is clearly dominated by the derivative-like features of surface reflection while that of finely ground material looks much more like a transmission spectrum.

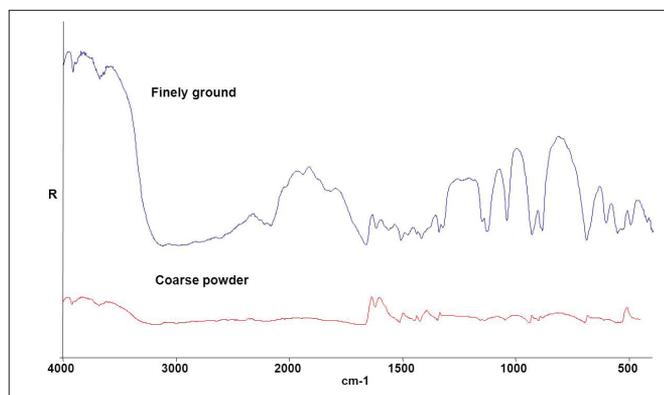


Figure 5. Diffuse reflection spectra of glycine (the upper one is offset for clarity).

Because absorption is much weaker in the near IR reflection spectra of powders have a larger component from radiation that has penetrated the sample than mid IR spectra of the same materials. This is seen in the spectrum of sodium saccharin in Figure 6 where features in the near IR region look like normal absorption bands while the mid IR region has strong derivative-like features.

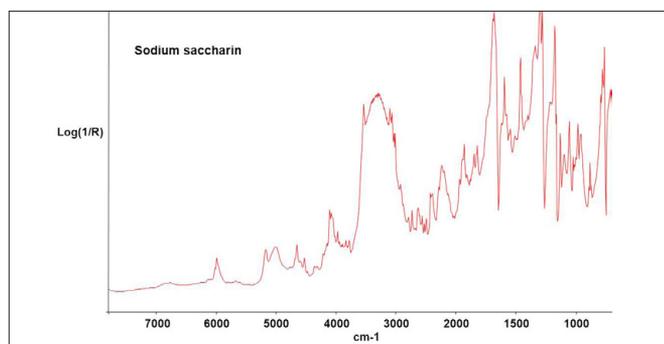


Figure 6. Reflection spectrum of sodium saccharin powder

Mid IR spectra of powders are often rather intractable because the shapes and positions of the absorption bands cannot be identified. For qualitative identification it is necessary to minimise the relative contribution from surface reflections. This can be done in the mid IR by diluting the sample in a non-absorbing matrix such as KBr. Because the refractive index of KBr is similar to that of many organic materials the amount of reflection at interfaces is much less than at interfaces with air. In addition reducing the particle size, ideally to less than 10 µm, increases the amount of radiation that returns to the

surface before it is absorbed internally. The resultant spectrum resembles a transmission spectrum except that there is a range of different pathlengths within the sample which enhances the intensities of weaker bands relative to those of stronger bands. Dilution in KBr reduces this distortion of the band intensities is minimised by ensuring that all the absorptions are weak.

Figure 7 shows diffuse reflection spectra of aspirin as a neat powder and diluted in KBr. In the spectrum of the neat powder the stronger bands in the region 1800-1200 cm⁻¹ all have approximately the same intensities and their shapes are distorted by the contribution of surface reflection. However the weaker bands appear similar in both spectra. The spectrum of the diluted sample is very similar to the transmission spectrum of a KBr pellet.

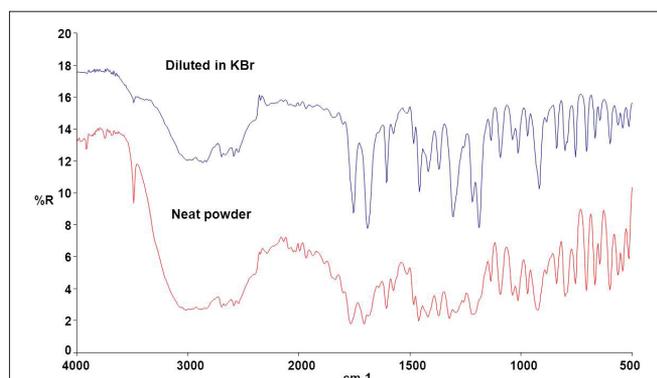


Figure 7. Diffuse reflection spectra of aspirin.

Diffuse reflection spectra are often presented in what is called the Kubelka-Munk format rather than in absorbance or more correctly $\log(1/R)$. The Kubelka-Munk intensity K-M is related to the measured reflectance R by an equation of the form: $K-M = (1-R)^2/2R$. This is said to provide band intensities that are proportional to concentration, as absorbance is for spectra measured by transmission. However the Kubelka-Munk relation was derived for conditions that are not usually met in mid-IR measurements, specifically that absorptions are weak. Its use owes more to convention than to any practical advantage. It is unsuitable for quantitative analyses because relative band intensities depend on the value assumed for reflectance in regions of low absorption. A comparison between Kubelka-Munk and $\log(1/R)$ presentations is shown in Figure 8.

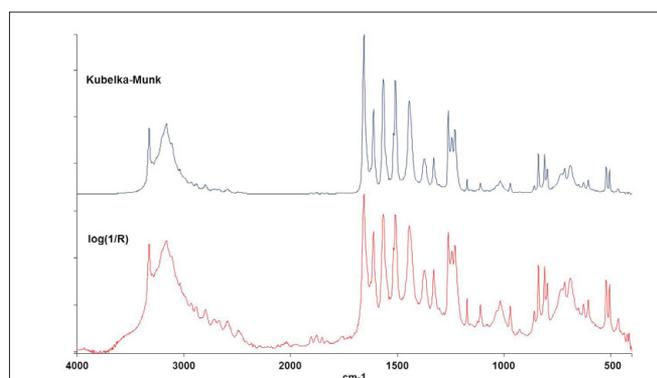


Figure 8. Diffuse reflection spectra of acetaminophen in Kubelka-Munk and $\log(1/R)$ formats

Practical reflection measurements

Reflection accessories are generally described as being designed for measuring either specular or diffuse reflection. However if the sample generates both specular and diffuse components then accessories will measure a combination of the two. The one exception is that for a sample with a mirror-like surface the spatial distribution of the surface reflection is known and can be blocked to leave a pure diffuse reflection spectrum.

Specular reflection

Reflection from a single surface is called specular reflection, as if from a mirror. Accessories for measuring specular reflection can be very simple, for example just involving two flat mirrors (Figure 9). This type of accessory would be suitable for measuring the reflection from a polished surface, such as the block of polymer used for the spectrum of Figure 1. For many samples the reflection spectrum is complicated by additional reflections from the back surface or by scattering within the sample. This kind of measurement is very successful for carbon-filled polymers with a suitably flat surface. The reason is that any light not reflected from the front surface is totally absorbed and so does not contribute to the spectrum.

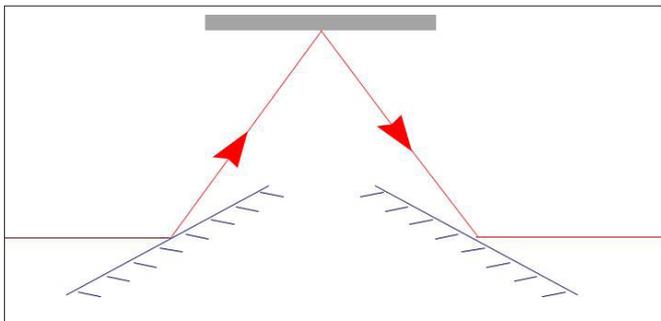


Figure 9. Optical arrangement for measuring specular reflection.

This type of accessory can also be used to measure what is called a transmission-reflection (or transmittance) spectrum from thin coatings on metal surfaces. In this case the spectrum consists largely of radiation that passes through the coating and is reflected back from the metal surface. It resembles the spectrum that would be obtained from transmission through a film of the coating material. The spectrum will contain a contribution that is directly reflected from the front surface of the coating, but reflection from the metal surface is much higher. A typical spectrum from the coated inner surface of a soft drink can is seen in Figure 10. Coatings

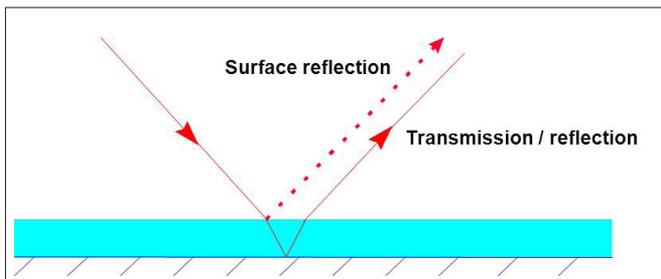


Figure 10. Transmission/reflection through a coating.

on non-metals are generally more difficult to examine. The spectra are not always dominated by the transmission-reflection component and absorption features of the substrate complicate the spectrum. ATR would be the preferred approach for such samples.

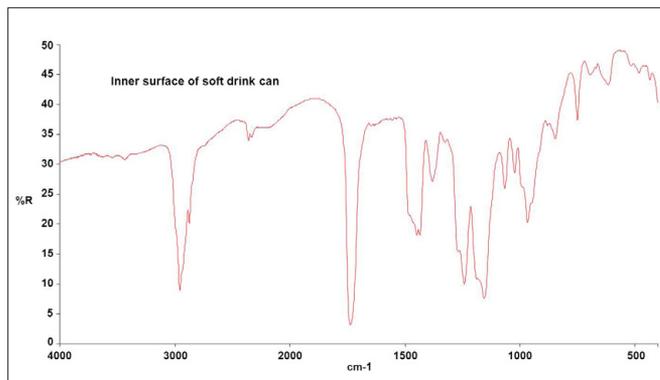


Figure 11. Transmission-reflection spectrum of drink can coating.

Transmission-reflection spectra are most useful for protective coatings and contaminants on metal surfaces. These are typically thicker than the wavelength of the infrared radiation being used. It is worth mentioning the rather different case of very thin layers on metal surfaces. Spectra of monomolecular layers can be measured fairly easily but special measurement conditions are used. These involve grazing incidence where the light path is almost parallel to the metal surface, because this greatly enhances the absorption intensity. The enhancement is caused by interaction between the electric field of the radiation and the conducting metal and extends only for a very short distance from the surface. Special grazing angle accessories are available for these measurements. For monolayers on non-metals such as silicon the appearance of the spectrum is dependent both on the angle of incidence and on polarisation.

Diffuse Reflection

The radiation contributing to a diffuse reflection spectrum is typically spread over a range of angles and so cannot be collected efficiently with accessories designed to measure specular reflection. A typical arrangement for diffuse reflection measurements is shown below.

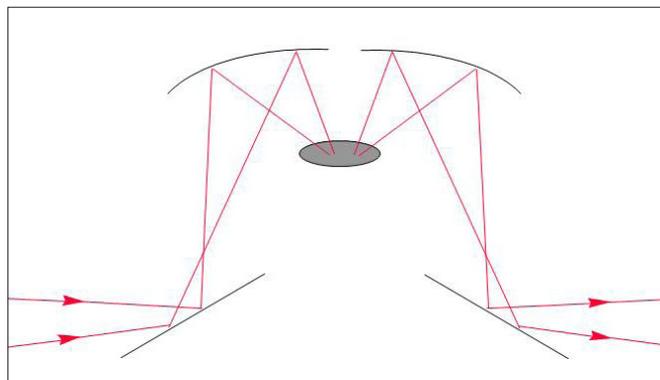


Figure 12. Optical arrangement for diffuse reflection.

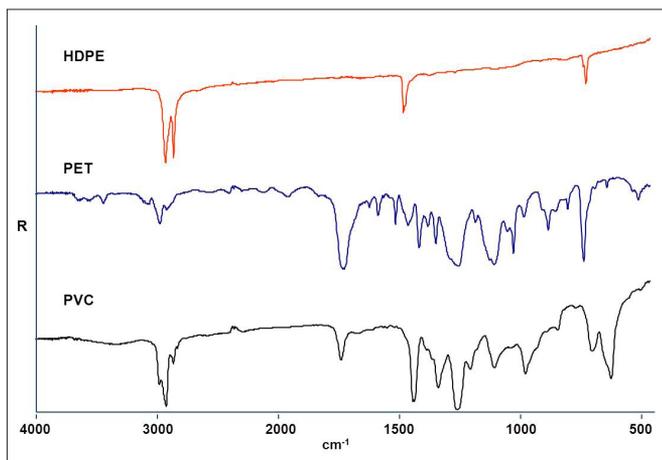


Figure 13. Spectra of soft drink bottles on silicon carbide abrasive.

Diffuse reflection spectra in the mid-IR are generally used for qualitative identification of powders. Because sample preparation need involve no more than mixing with KBr the method is simpler and more rapid than making a KBr pellet. In principle diffuse reflection spectra can be used for quantitative analysis but this has proved much more successful with near IR data than in the mid-IR.

Diffuse reflection can be a very convenient way of obtaining spectra from the surface of hard objects such as polymer mouldings. A small amount of material is removed as a powder by rubbing the surface with abrasive paper. The spectrum can be obtained simply by placing the abrasive paper in a diffuse reflection accessory. Because the sample is a thin layer of fine particles these spectra resemble spectra measured in transmission. Figure 13 shows some typical spectra obtained from soft drink bottles obtained in this way.

Summary

Reflection measurements allow spectra to be obtained from a wide range of sample types. The appearance of the spectra depends on the relative contributions of specular reflection from the front surface and of diffuse reflection from radiation that has penetrated into the sample. In the mid-IR region spectra are hard to interpret unless one or other of these contributions is dominant. When surface reflection dominates the spectrum is determined by refractive index changes associated with absorption bands. The absorbance spectrum can be generated by Kramers-Kronig transformation. In mid-IR diffuse reflection strong bands become totally absorbing unless the particle size is small and the sample is either diluted or is a thin layer. In the near-IR region surface reflection can generally be ignored as it shows little variation with wavelength. Because near-IR absorptions are weak diffuse reflection spectra are readily obtained from scattering materials and can be used for both qualitative and quantitative analyses.