

## Infrared Spectrometry

Orientation Effects  
in ATR Spectra

Spectrum™ Two

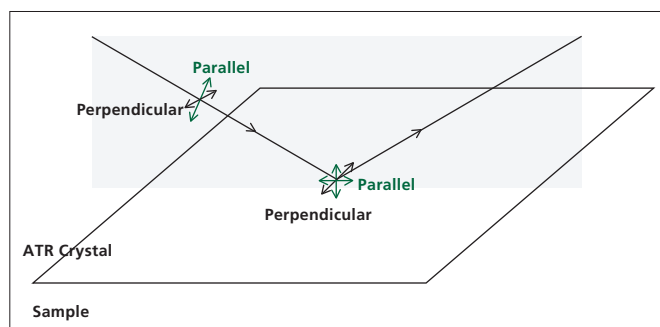


Figure 1. Polarization in the ATR experiment.

**Orientation effects in ATR spectra**

In an ATR measurement IR radiation that is totally reflected produces an evanescent electric field beyond the surface of the crystal. The evanescent field has components in all directions but it is not uniform, with the result that ATR spectra are sensitive to any anisotropy in the sample. Because of this relative band intensities may vary, depending on how the sample is presented. This has been exploited to measure the degree of orientation in surface films and polymers. However it may also lead to unexpected changes when the possibility of anisotropy has not been considered.

The incident radiation has components of its electric field both parallel to the plane of incidence and perpendicular to it (Figure 1). For a zinc selenide or diamond crystal the effective pathlength in ATR is higher for the component polarized parallel to the plane of incidence. This enhances the absorbance of vibrations with a dipole change in the plane of incidence relative to those with a dipole change perpendicular to the plane.<sup>1</sup>

## Orientation in manufactured products

Manufacturing processes such as molding and extrusion often generate products where polymer chains have a preferred orientation with the result that the ATR spectra may vary significantly. The two spectra in Figure 2 are from a cup made of polylactic acid, the difference being only that the sample was rotated through ninety degrees between the two measurements. There are large differences in relative intensities, for example between the C=O band at  $1750\text{ cm}^{-1}$  and the bands around  $1200\text{ cm}^{-1}$ . Where bands overlap there are also apparent shifts in peak frequencies. These differences are quite large enough to cause problems in identifying materials. Using a correlation algorithm that is commonly employed to check identity the correlation between these two spectra gives a value of 0.903 while a typical threshold for identity checking would be 0.985. This is a molded product where the manufacturing process results in preferential orientation of the polymer chains. ATR measurements can be used to measure quantitatively the degree of orientation, which may be an important parameter in determining mechanical properties such as the resistance to hoop stress in bottles used for carbonated drinks.

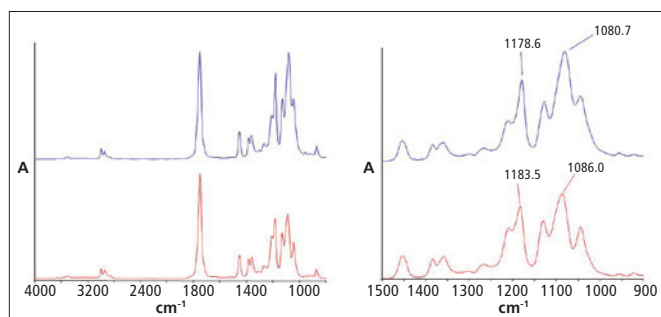
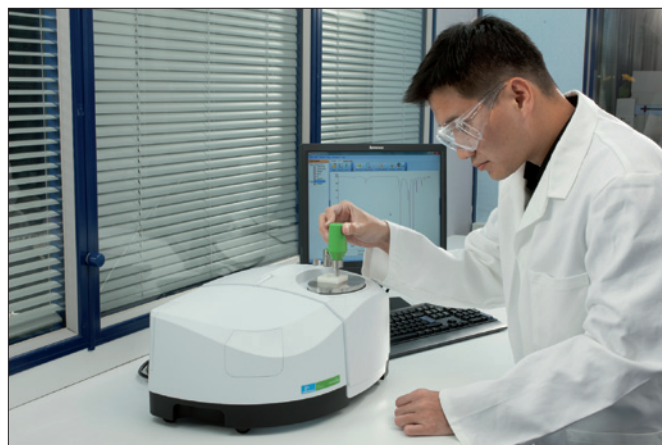


Figure 2. Spectra of a polylactic acid cup, rotated  $90^\circ$  between measurement.

A second example is seen Figure 3. This shows spectra of a glossy paper coated with polypropylene when the sample is rotated through 90 degrees. The relative intensity changes seen in bands between 1200 and  $900\text{ cm}^{-1}$  are similar to those seen in transmission spectra of drawn polypropylene films using polarized radiation.



Spectrum Two spectrometer with UATR accessory.

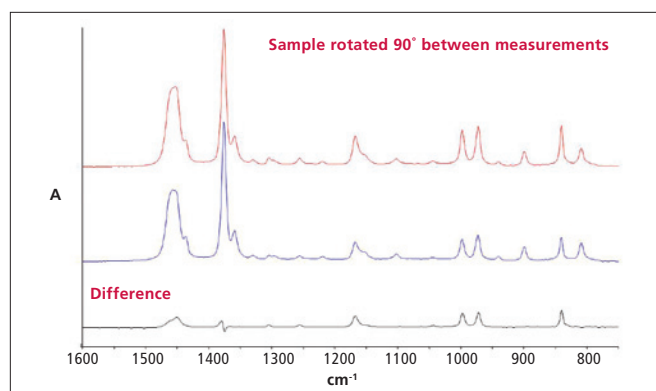


Figure 3. Spectra of polypropylene-coated paper, rotated  $90^\circ$  between measurements (normalized at  $1370\text{ cm}^{-1}$ ).

## Using polarized radiation

More dramatic effects are observed when using a polarizer. The evanescent electric field has components both parallel and normal to the interface. With a polarizer set perpendicular to the plane of incidence the evanescent field is parallel to the surface and has no component normal to the surface. If a sample has some degree of orientation relative to the surface then intensity changes will be seen when the polarization is changed. This has been used to study orientation effects in surface films and membranes.<sup>2</sup> An example is seen in the spectrum of paper that contains kaolinite (china clay) to provide a smooth surface. This has plate-like crystals which tend to orient themselves parallel to the surface. Some vibrations have dipole moment changes aligned largely in the plane of the crystals with others perpendicular. In unpolarized radiation the ATR spectrum of the OH absorptions has similar relative band intensities to those seen in transmission of a KBr pellet. Setting the polarizer perpendicular to the plane of incidence greatly reduces the intensities of OH bands at  $3694$  and  $3653\text{ cm}^{-1}$ , indicating that the dipole moment changes are largely normal to the surface, while bands at  $3670$  and  $3620\text{ cm}^{-1}$  are little changed (Figure 4). Large effects are also seen in the Si-O region around  $1100\text{ cm}^{-1}$ .

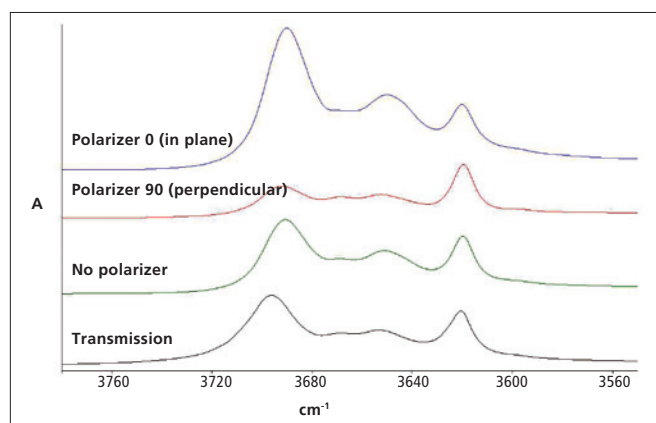


Figure 4. OH absorption bands of kaolinite-coated paper.

## Polarized spectra of crystalline powders

The ATR spectra of many crystalline powders show similar effects even though the bulk materials are not anisotropic. This happens when there is a degree of preferential orientation of the crystallites on the surface of the ATR crystal. A very striking example is seen in the spectra of the anti-convulsant drug carbamazepine (Figure 5). Although the spectra obtained with different polarizations appear largely similar there are clear differences revealed by spectral subtraction. The region above 3000  $\text{cm}^{-1}$  includes stretching vibrations from an  $\text{NH}_2$  group at 3465 and 3160  $\text{cm}^{-1}$ , and from C-H bonds. Changing the polarization angle from 0 to 90 degrees reduces the intensities of the symmetric NH band at 3160  $\text{cm}^{-1}$  and of the CH stretching bands considerably more than those of the asymmetric NH stretch and amide I bands. Spectral subtraction to cancel the C-H stretch absorptions shows that the polarization behavior of the band at 3465  $\text{cm}^{-1}$  is different from that of the other absorption bands in this region, but similar to that of the amide I band at 1675  $\text{cm}^{-1}$ . This clearly contains information about the relative orientations of the dipole moment changes associated with these vibrations. This can be used to help assign observed bands to vibrational modes and to investigate molecular geometry.

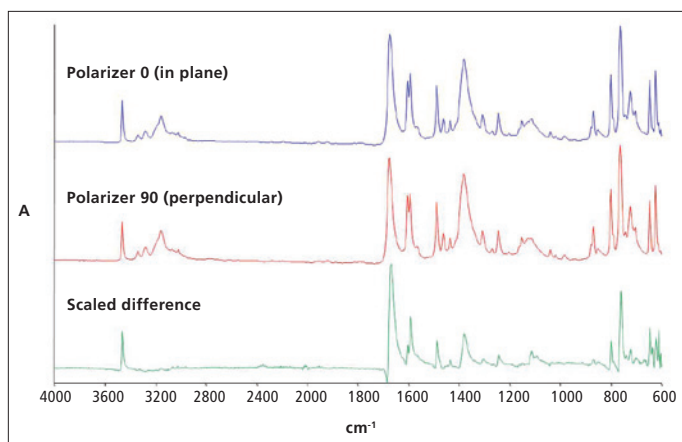


Figure 5. Polarized ATR spectra of carbamazepine.

## Summary

Care must be taken in measuring the spectra of materials that may be anisotropic. In particular the spectra of products formed by processes such as molding or extrusion may vary significantly depending on how the sample is presented. The intensity changes can be large enough to affect identification. The spectra of powders may show marked orientation effects when measured with polarized radiation. However orientation effects in powders are generally negligible with unpolarized radiation.

## References

1. Harrick, N.J. *Internal Reflection Spectroscopy*. John Wiley & Sons Inc. (1967).
2. F. Friedrich and P.G. Weidler, *App. Spectry.*, 64(5) 500-506 (2010).