What is Band Distortion and Band Shift in ATR?

When obtaining an Infra Red spectrum via ATR spectroscopy, the spectrum will be different to that obtained for the same sample when collected as a transmission spectrum. The differences can be accounted for by the fundamental way the sample information is being collected. Principally, transmission spectroscopy is the passage of light through an entire sample, whereas ATR spectroscopy is the interaction of light by passage into the surface of a sample species – the sample being in contact with a suitable ATR crystal material to facilitate the measurement. Note that neither method can be regarded as giving the "correct" spectrum – they are simply different. However, as most spectral libraries are made using transmission measurements it can sometimes be useful to understand the differences and even be able to mathematically modify an ATR spectrum so that it more closely resembles the transmission mode and can be more reliably used in spectral searches.

Any differences in the spectra may be described as wavelength dependence, band distortion and band shift and can be explained thus.

Wavelength Dependence

In a transmission measurement of a sample, all wavelengths traverse the same total physical thickness of the sample material. However, in an ATR measurement the penetration depth of the light is a function of both the wavelength and the refractive index difference between the sample and the ATR crystal. The result of this is that the band intensities at different wavelengths will differ between a transmission measurement and an ATR measurement of the same material. The penetration depth (and therefore the apparent absorption intensity of the material) increases linearly with wavelength – bands at long wavelengths appear relatively stronger than bands at short wavelengths. This effect can be corrected mathematically to give a more "transmission-like" spectrum if desired, and most instrument software packages include some form of "ATR correction" algorithm to do this.

Note that these algorithms cannot allow for any change of sample refractive index with wavelength – but as this is normally fairly small it is usually ignored.

Band Shifts

Band shifts (movement of the peak wavenumber position) will occur for two main reasons.

- Broad bands can be slightly shifted to longer wavelengths due to the wavelength dependent penetration depth change across the band (as described above). This will be corrected with the same ATR correction algorithm that is used to give more "transmission-like" band intensities.
- In many materials the refractive index can change significantly across an absorption band. This causes a variation in the penetration depth across the band and will "skew" it to longer wavelengths compared to the transmission spectrum

band positions. The amount of shift will depend on the refractive index change across the band and this will be different for different bands in the spectrum. In practice, these shifts are not usually sufficient to cause any problem in library searching.

Band Distortion

Sometimes in ATR measurements the absorption bands can become slightly asymmetric compared to the bands seen in transmission measurements. This is illustrated in the attached spectra where a polythene film has been used to show the effect. The changes seen in the band shape arise because of the rapid change of refractive index of the sample across the bands. The refractive index of the sample varies from a low value on the short wavelength side of the band to a high value on the long wavelength side. This causes the effective penetration depth to also rapidly increase toward the long wavelength side and causes the characteristic shape of the bands seen. The effect is more pronounced if the ATR is working near to the critical angle (where the effective penetration depth goes to infinity).

To achieve the best sensitivity from any ATR it is important that it operates reasonably near to the critical angle. However, the critical angle varies depending on the refractive index of the sample and this means that high index materials (such as some polymers) end up working closer to the critical angle than the majority of samples that have a lower index. If the sample also has a significant variation of refractive index across its bands then distortion becomes very obvious.

There are several solutions to minimise the effect.

- The first is to ignore it (it is irrelevant for most quantitative analyses, as it is entirely reproducible between the calibration and sample data).
- The second is to use a higher refractive index ATR material. The order of refractive index (RI) for the most common ATR materials is:

Refractive Index as per ATR material

ATR Material	Refractive Index
ZnSe	RI 2.4
Diamond	RI 2.43
Silicon	RI 3.42
Germanium	RI 4.0

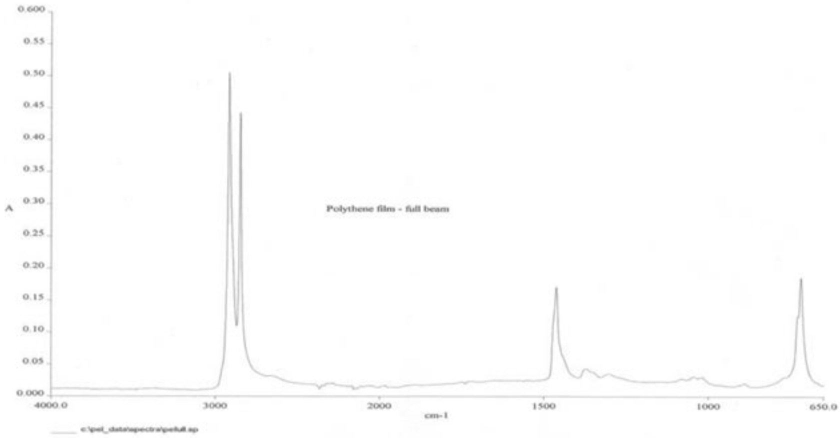
With a Germanium crystal, the critical angle is much smaller so the effect is greatly reduced. However, the disadvantage is that the sensitivity of the ATR is also reduced.

- The third possibility is to mask off some of the rays in the ATR that are close to the critical angle. The Golden Gate ATR accessory has the advantage that this can be done very easily by masking off the lower part of one of the Zinc Selenide lenses. The effect of masking is seen between the two polythene spectra at the end of this document. The energy loss is very small (because the rays close to critical angle were being strongly absorbed anyway) but the improvement in band shape is significant. Specac's view has been to keep the sensitivity of the Golden Gate as high as possible and just add a simple mask on the rare occasions that this is a problem. Specac can supply one that drops over one of the lenses if required.

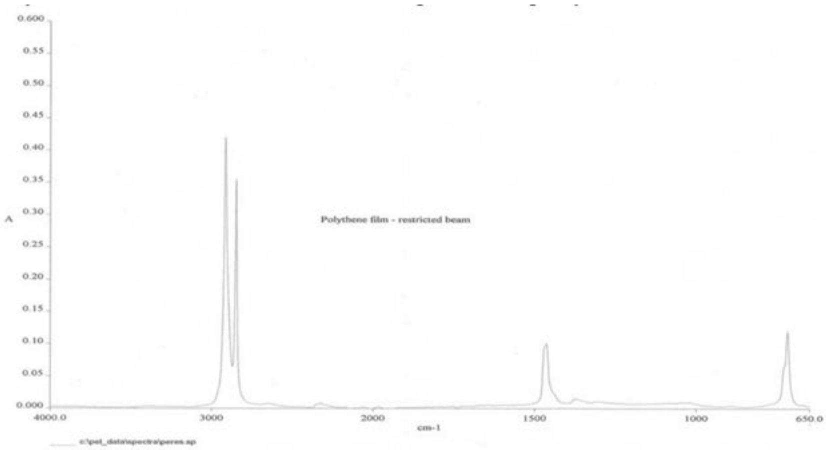
Conclusions

None of these observations are indicative of a "fault" in the technique or the accessory. All ATR measurements will show these effects but the band distortion effect can vary between different accessories. If an ATR system shows less band distortion then it will be operating further from the critical angle or with a higher refractive index crystal and will therefore be less sensitive.

Spectra



Polythene film on Golden Gate ATR with no masking of critical angle rays



Polythene film on Golden Gate ATR with masking of critical angle rays

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