In recent years ATR has become the preferred method for many routine IR measurements. The introduction of sampling accessories with small crystals greatly reduced the contact problem that had previously restricted the technique to liquids and soft solids while the hardness and chemical resistance of diamond has made ATR an almost universal sampling method. However solid samples require pressure to bring them into good contact with the ATR crystal. Increasing this pressure changes the relative intensities of bands at different wavelengths and may also induce structural changes. This note explains and illustrates the effects that occur.

**The ATR measurement**

When radiation is totally internally reflected at an interface with a material of lower refractive index the electric field penetrates a short distance beyond the interface. This field, called an evanescent wave, can be absorbed by a sample on the surface (Figure 1). The electric field decreases away from the surface and the penetration depth $d_p$ is defined as the distance at which it falls to $1/e$ of its value at the surface. $d_p$ is proportional to the wavelength and also depends on the angle of incidence $\theta$ and the refractive indices of crystal and sample.\(^1\) For a diamond ATR element the penetration depth at 1000 cm\(^{-1}\) is typically 1-2 $\mu$m. Because of the wavelength dependence the penetration depth increases by a factor of ten between 4000 and 400 cm\(^{-1}\). In ATR measurements the sample has to be brought sufficiently close to the surface to interact with this evanescent field. When the sample contact is perfect the absorbance values at 1000 cm\(^{-1}\) are similar to those that would be observed in transmission with a pathlength of around 2-4 $\mu$m. This is considerably larger than $d_p$ since the evanescent field extends significantly beyond the penetration depth.

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**Figure 1.** The evanescent electric field in ATR.
The effects of changing the applied force
Most solid samples have to be pressed into contact with the ATR crystal to obtain adequate band intensities. The observed absorbance depends not simply on the area of material in contact with the crystal surface but also on the distribution of the sample within the evanescent field. The intensities increase as air gaps between the sample and the crystal are reduced, bringing more of the sample into the evanescent field. Generally the band intensities at shorter wavelengths increase more rapidly than those at longer wavelengths. This is because material that is already contributing to the spectrum at longer wavelengths starts to contribute at shorter wavelengths as it is forced closer to the crystal. An example is seen in the spectra of low density polyethylene in Figure 2. The ratio of the intensities between the C-H stretching bands at 2900 cm\(^{-1}\) and the CH\(_2\) rocking bands at 720 cm\(^{-1}\) increases to a maximum and then remains fairly constant as the applied force is increased further (Figure 3).

The ability to achieve consistent band intensity ratios is essential for quantitative analyses but may also impact material identification applications. Because of the difficulty of ensuring perfect contact, analyses typically require some sort of spectral normalization or are based on band intensity ratios. Quantitative analyses should be restricted to as narrow a wavenumber range as is practicable to minimize the difference in penetration depth for the absorption bands involved.

A common practice is to adjust the applied force so that the strongest band intensities reach a specified level. The PerkinElmer UATR accessories display both the applied force and the spectrum as the pressure is adjusted. It is advisable to check the force as well as the intensities, especially with powders where the sample may not be spread evenly. Although some ATR accessories provide a ‘pressure’ readout this assumes that the force is distributed uniformly across the crystal.

Increasing the applied force may introduce other changes than those resulting from increased penetration. In polyethylene, the increased pressure deforms the polymer and changes the crystallinity. This is evident from the CH\(_2\) rocking bands at 730/720 cm\(^{-1}\). Crystalline regions have two bands at 730 and 720 cm\(^{-1}\) while amorphous regions have a single broader band. In the example shown in Figure 4 a highly crystalline sample of polyethylene is converted to largely amorphous material by the applied force. This is unexpected as applied pressure is expected to increase crystallinity because the crystalline material has higher density. However it is not simply a surface effect since transmission spectra of the material after compression show the same changes. While the pressures involved in achieving good contact are insufficient to induce polymorphic changes in crystalline materials they can result in large changes in band positions. This is seen in Figure 5 where a Si-O band in the spectrum of the mineral kaolin has a shift of over 10 cm\(^{-1}\) that is attributed to deformation of the crystal lattice.\(^2\)

**Figure 2.** LDPE film at low and high applied force. (Intensities normalized at 1470 cm\(^{-1}\)).

**Figure 3.** Ratio of intensities at different applied force.

**Figure 4.** CH\(_2\) rocking bands of HDPE at low (red) and high (blue) applied force. (Normalized at 730 cm\(^{-1}\)).

**Figure 5.** Band shift in kaolinite with increased force.
The effect of penetration depth

Because of the limited depth of penetration ATR spectra may be unrepresentative of the bulk material. This can be an advantage when surface species are of interest. However it is a problem if it is not realized that the surface and bulk are different. A typical example is seen in the spectra of chocolate in Figure 6. The ATR spectrum has much stronger bands from the fat content, for example the C=O bands at 1740 cm\(^{-1}\), relative to those from the sugar such as the OH bands above 3000 cm\(^{-1}\), than the transmission spectrum. This is because the surface of the chocolate in contact with the crystal has a much higher fat content than the bulk of the material. Such behavior is very common in the spectra of suspensions and emulsions, making quantitative measurements problematic.

Residues on ATR crystals

The pressure applied to achieve good contact may result in residual material on the surface of the crystal after the sample has been removed. Well known examples include plasticisers and release agents such as those seen in Figures 7 and 8. In the case of the PVC insulation the phthalate plasticizer contributes strongly to the original spectrum. However, the presence of the silicone slip agent would not be apparent in the spectrum of the polyester food packaging. The importance of cleaning the crystal carefully after each sample is well known. However it can also be very instructive to look at the residual spectrum before cleaning the crystal.

References
