Technical Note

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ATR Penetration Depth

In this issue: This note compares the pathlengths of IR light within a sample in transmission or in contact with the internal reflection element (IRE) of an ATR.

The Quest™ is our routine sampling ATR Accessory. It is suitable for a wide range of common sample types including liquids, pastes, powders and solids.

- **Interchangeable pucks** allow easy switching between different crystals and sampling modes.
- **All reflective optics and robust monolithic crystals** give market leading performance.
- **Pressure tower** for consistent pressure application on solid and powder samples. The built in "click" feature indicates a full 40 lb load has been reached.

Introduction

ATR has become the dominant method for obtaining a spectrum of a solid sample. The ATR method exploits a phenomenon whereby an evanescent wave of infinite wavelength is generated at the interface of an IRE and a sample of interest, Figure 1. The intensity of the wave is a function of the wavelength of light and decays exponentially with distance into the sample, falling to fractions of its starting intensity within a few microns.

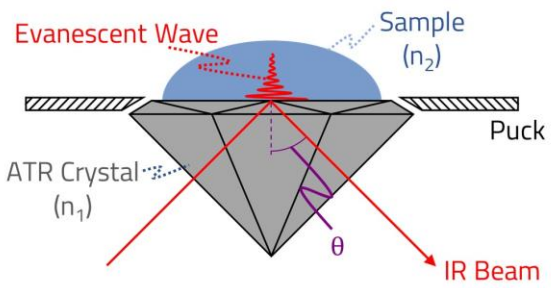

Figure 1: Graphical representation of a single bounce ATR.

Compared to the transmission method, ATR has a shorter effective pathlength which changes across the spectrum as a function of the wavelength of incident light. When a spectrum of a sample collected in ATR and transmission mode are scaled to match at the low wavenumber range (for instance at 1000 cm^{-1}) the peaks to higher wavenumber will show a marked difference; the ATR spectrum will exhibit reduced intensity peaks relative to the transmission spectrum [1]. This is due to the decreasing depth of penetration of the incident light with increasing wavenumber. Several mathematical models are available to account for this effect and this note discusses the most common methods.

Depth of Penetration (d_p)

d_p is a good first approximation correction method for converting an ATR spectrum to a more transmission like spectrum, relating the penetration depth of the IR beam into the sample to the wavelength of the incident light (λ), the angle of incidence (θ), and the refractive indexes of the IRE (n_1) and sample (n_2), which are highlighted in

Figure 1. It is defined as the distance required for the intensity of incidence light to fall to e^{-1} of its starting intensity and is derived from the Maxwell equations. Most of the information contained in the ATR spectrum comes from this region of the sample, with decreasing contributions as the wave propagates further into the sample.

$$d_p = \frac{\lambda}{2\,\pi\,\sqrt{(n_1^2\,sin^2\theta\,-\,n_2^2)}}$$

Effective Penetration Depth (d_e)

In practice the d_p provides a useful method for comparing the differences in peak intensity across a spectrum, however the intensity of a peak with a d_p of 1 micron will not be equivalent to a transmission spectrum peak at a pathlength of 1 micron. d_e is dependent upon the strength of the electric field amplitudes within the denser medium. For light polarized perpendicular to the plane of incidence (⊥, s-polarized) this comprises the y component of the incident electric field amplitude and for light polarized parallel to the plane of incidence (∥, p-polarized) this is comprised of the square root of the sum of the squares of the x and z components of the incident electric field amplitude [2]. Consequently, d_e varies with the degree of polarization of the IR beam as given by the two formulas below†.

$$d_{e\perp} = \frac{2\,d_p}{n_1}\,\frac{n_1^2\,n_2\,cos\theta}{(n_1^2\,-\,n_2^2)}$$

$$d_{e\parallel} = d_{e\perp}\,\frac{2n_1^2\,sin^2\theta\,-\,n_2^2}{(n_1^2\,+\,n_2^2)\,sin^2\theta\,-\,n_2^2}$$

If it is assumed that an unpolarized beam in an FTIR spectrometer is comprised of equal amounts of s- and p-polarized light then the unpolarized $d_{e,av}$ is simply the average of the $d_{e\perp}$ and $d_{e\parallel}$. In reality, this is not the case as the beam splitter efficiency is different for s- and p-polarizations of light, but it provides a good approximation.

†The authors are aware of an error that has occurred in reproducing this formula at some point in history; this error has been replicated in numerous locations. Therefore, we recommend sourcing the formula for de from the original derivation [2]. The formulas given above are obtained directly from this source, although we have taken the liberty of reducing the complexity of the formula by expressing them as functions of the preceding formula.

Effective Pathlength (EPL)

The EPL of an ATR system is simply d_e multiplied by the number of bounces. At 1000 cm^{-1}, and n_2 of 1.5 this gives an EPL of 4.36 µm for a ZnSe (or diamond) Quest, whilst for the ZnSe gateway the EPL is 26.18 µm.

Anomalous Dispersion

As can be seen from d_p and d_e the degree of penetration into a sample is dependent upon the sample refractive index, n_2. For most of the spectrum this is approximately constant (although it can vary by a small amount throughout the spectrum). However, around an adsorption peak the refractive index changes considerably as shown in figure 2. The net result of this is to red shift the peak position relative to a transmission spectrum and to introduce asymmetry into the peak shape. Anomalous dispersion is more pronounced for lower n_1, for more intense peak adsorptions, and at angles close to the critical angle. Specac products are engineered to minimize the anomalous dispersion present in a spectrum; the Quest performs significantly better than other competitor products when comparing the degree of asymmetry present in peaks of the ATR spectrum.

Crystal	λ / cm^{-1}	$d_{e\parallel}$ / µm	$d_{e\perp}$ / µm	$d_{e,av}$ / µm	d_p / µm
Diamond / ZnSe	1000	5.82	2.91	4.36	2.01
	2000	2.91	1.45	2.18	1.00
Si	1000	1.31	0.66	0.98	0.85
	2000	0.66	0.33	0.49	0.42
Ge	1000	0.82	0.41	0.61	0.66
	2000	0.41	0.20	0.31	0.33

Table 1: Summary of various parameters for the penetration of light into a sample, at a fixed angle of incidence of 45° and a sample n_2 of 1.5.

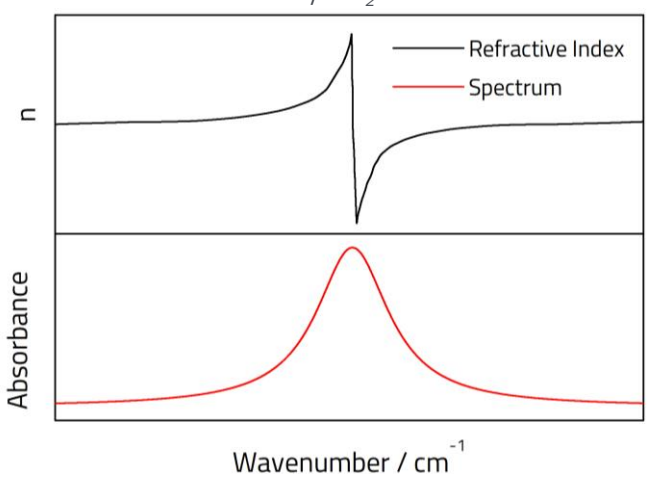

Figure 2: Effect of variation of the refractive index across an adsorption band

Comparison of Theory and Experimental Results

To compare theory and experiment, spectra of n-heptane at known pathlength (calculated from the interference fringes caused by two parallel windows [3]) were recorded in an Omni Cell fitted with CaF_2 windows. Pathlengths were changed using spacers ranging from 6 to 50 microns. Unpolarized and polarized ATR spectra were collected on a Golden Gate ATR system fitted with a diamond or Ge top plate using a Specac CaF_2 Benchmark Wire Grid Polarizer. Spectra were recorded on a commercially available spectrometer. The degree of polarization of the FTIR spectrometer light was investigated and found to be very close to a 1:1 ratio, suggesting that $d_{e,av}$ should provide a good estimate of the equivalent pathlength. Two crossed polarizers were used to confirm that the ATR did not significantly depolarize the IR beam.
The calibration plot using the C-H bending vibration at 1380 cm^{-1}, and ATR spectra of n-heptane are shown in Figure 3. This peak was chosen due to its relatively low intensity to reduce anomalous dispersion to an absolute minimum. Where anomalous dispersion is significant more advanced methods for spectral correction have been reported [4]. This allows the experimentally determined pathlength to be compared to d_e and d_p as given in table 2. Excellent correlation is observed between the experimentally determined value and theoretical d_e calculations. Most commercially available spectrometers have a correction algorithm that can use these formulae to correct an ATR spectrum and produce a transmission-like spectrum.

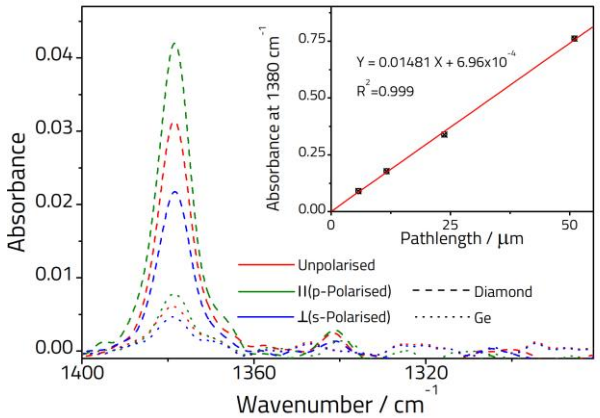

Figure 3: n-heptane spectra measures on a Golden Gate with diamond and Ge IRE's with polarized and unpolarized light.

	Polarisation:	Unpolarised	⊥	∥
Diamond	Experimentally measured / mm	2.15	2.88	1.46
	d_e / mm	2.13	2.83	1.42
	d_p / mm	1.18	-	-
Ge	Experimentally measured / mm	0.38	0.50	0.28
	d_e / mm	0.39	0.52	0.26
	d_p / mm	0.47	-	-

Table 3: Comparison of experimentally determined pathlengths with theoretical d_p and d_e calculated values using n_1= 2.4 or 4.0 (Diamond or Ge, respectively), n_2=1.38 (heptane) [5] and θ=45°.

References

[1] Specac Application Note TN21-01: Basics of ATR Spectroscopy
[2] "Electric Field Strengths at Totally Reflecting Interfaces", Harrick, N.J., *J. Opt. Soc. Am.*, **55**, (1965), 851-857
[3] Specac Application Note AN18-04: Determining Pathlength in Parallel Window Liquid Cells
[4] "Effective Path Length in Attenuated Total Reflection Spectroscopy", Griffiths, P.R. & Averett, L.A., *Anal. Chem.*, **80**, (2008), 3045-3049
[5] "Optical Constants of Liquid Hydrocarbon Fuels", Tuntomo, A., Tien, C.L. & Park, S.H., *Combust. Sci. Technol.*, **845**, (1992), 133-140

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