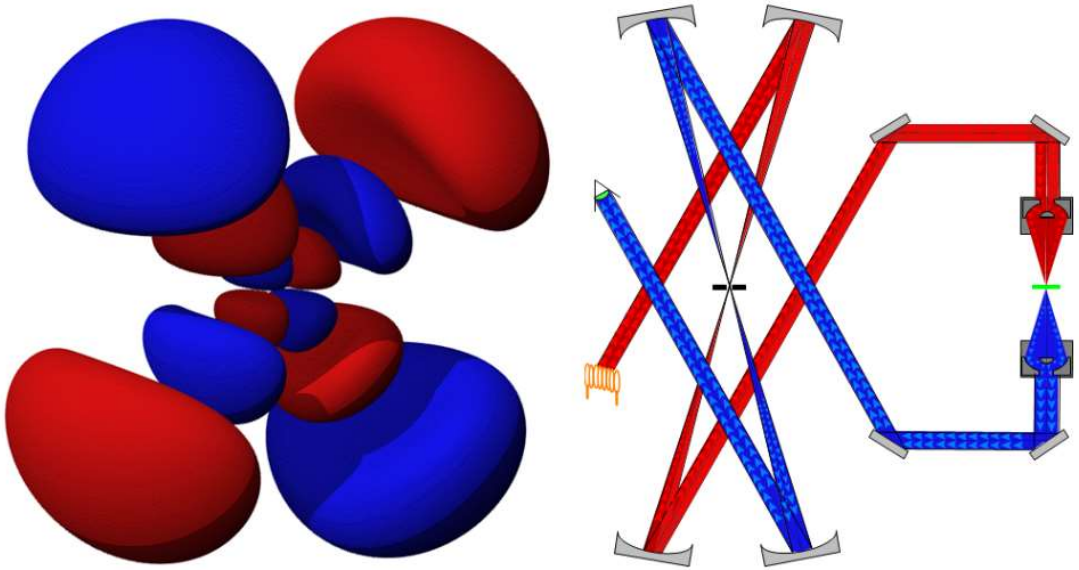
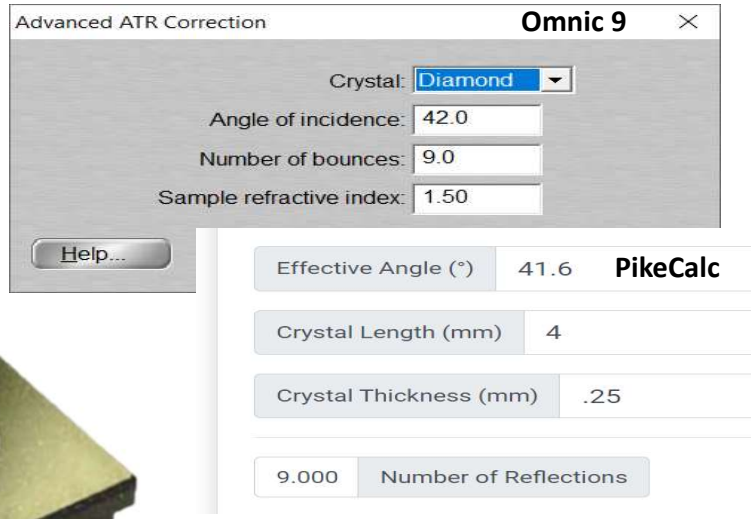
FTIRPros



- DurasamplIR II ATR calculations: Diamond/ZnSe optics and a sample with n=1.5
- Critical angle and penetration depths of evanescent waves…s, p and (s+p)/2
- Spectral characteristics of long path diamond ATR and library matching
- Difficultly of multicomponent mixtures with variable n and N

DurasamplIR II - 9 bounce ATR



$\text{Sin}(\theta_{crit}) = n_1/n_2$

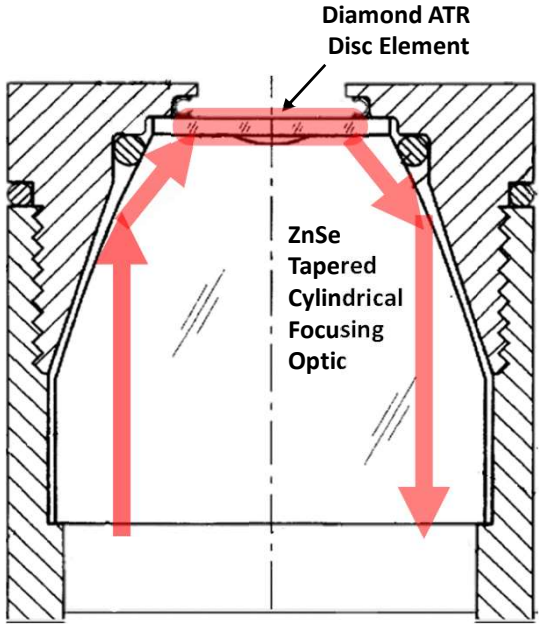
$\theta_{atr} > \theta_{crit} = 24.6$

$n_{Diamond} \sim n_{ZnSe} \sim 2.4$

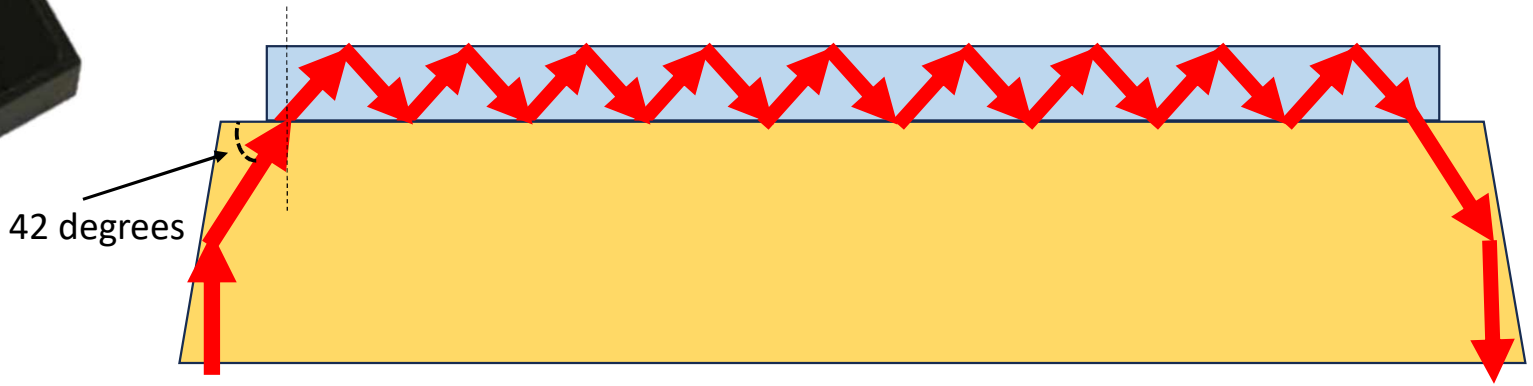
$n_{Air} = 1$

$n_{sample} = 1.5$

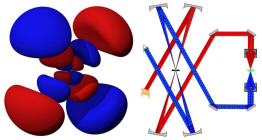
$\theta_{sample} > \theta_{crit} = \underline{38.7}$



The 4 mm diameter x .25 mm thick disc gives 9 reflections at ~42 degrees.



FTIRPros LLC

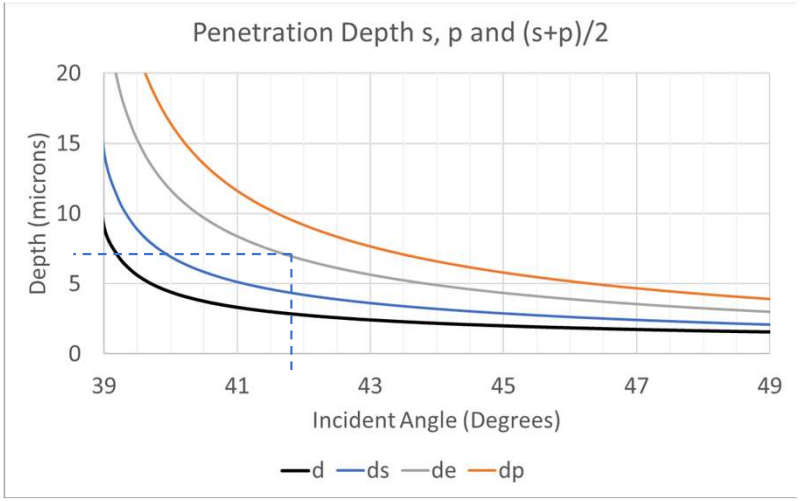


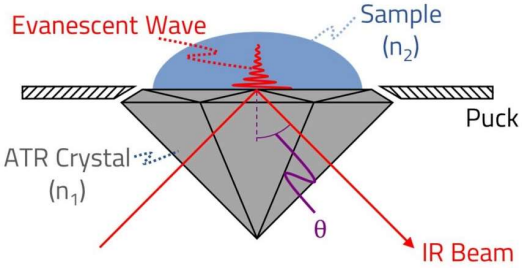
The **wavelength of light at 1000 cm^{-1} is <u>10 microns</u>**

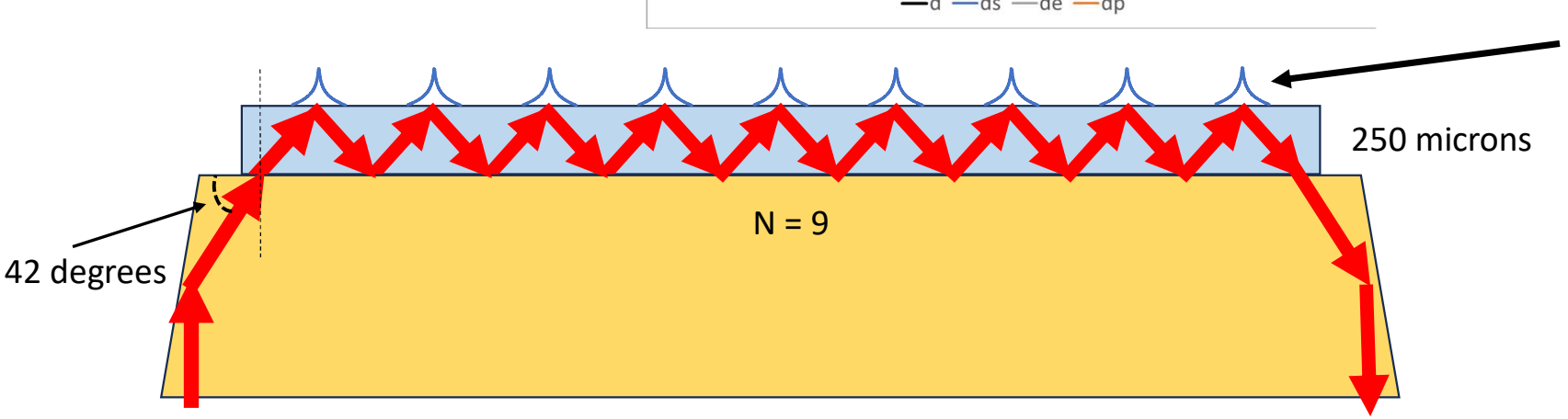
Pathlength = N x d_e= 9 x 7.3 microns
= 66 microns. A perfect thickness for FTIR

d_p is on the order of the wavelength of light, ~10 microns, but more like half. Accounting for polarization gives the effective depth d_e= 7.3 microns.

$$\mathbf{E(x) = E_0 e^{\left(-\frac{x}{d_p}\right)}}$$





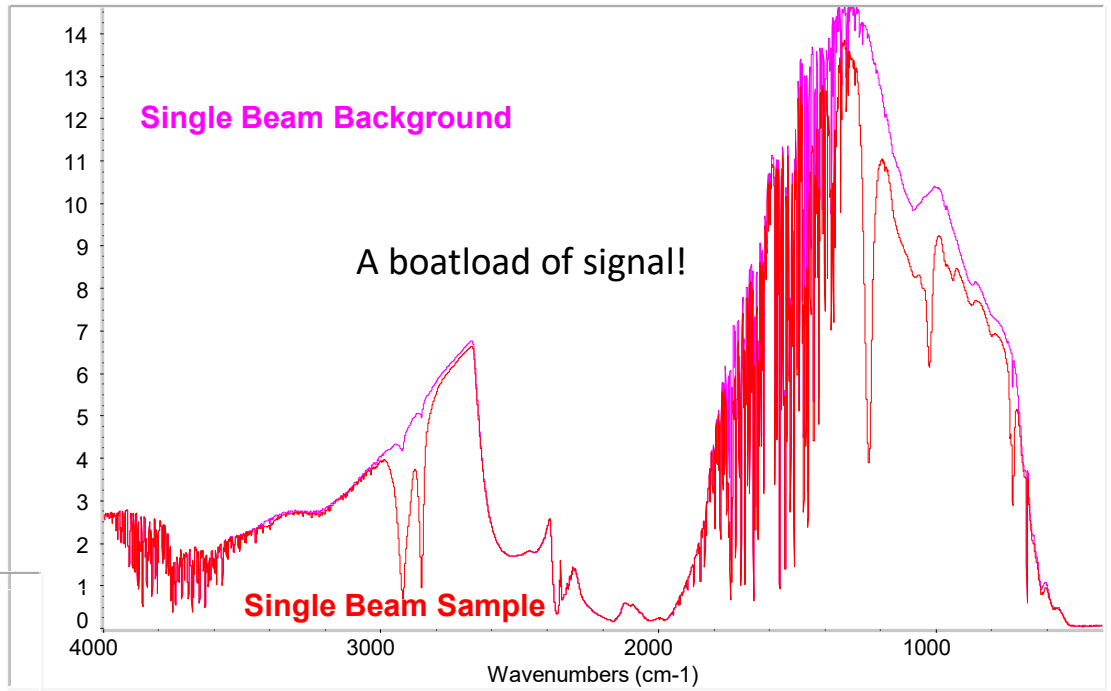


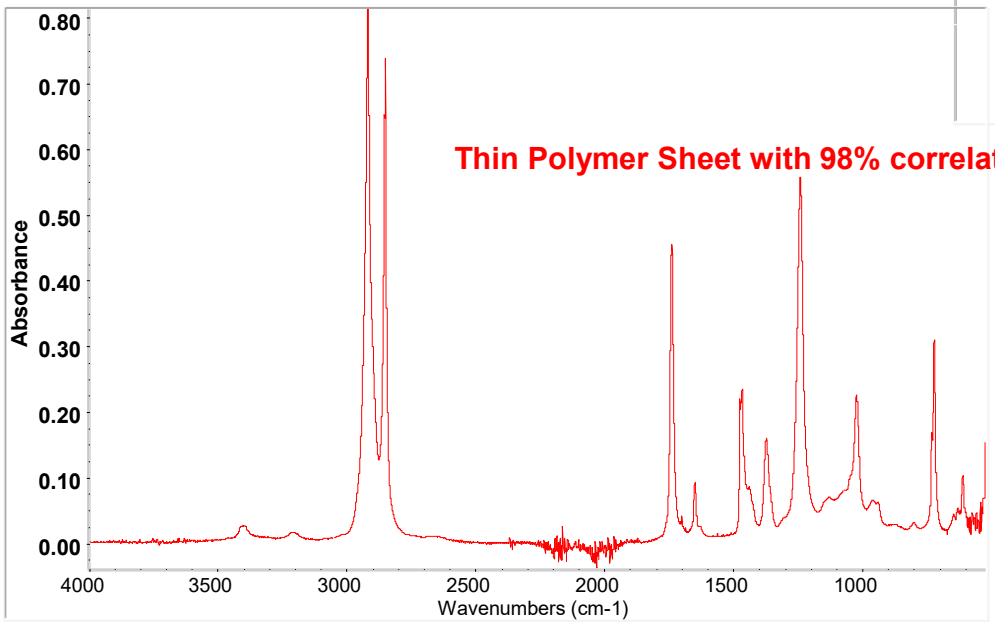
DurasamplIR II - 9 bounce ATR Spectra

SPECTROMETER DESCRIPTION
- Spectrometer: Nexus 870
- Source: IR
- Detector: DTGS TEC
- Smart Accessory ID: Unknown
- Beamsplitter: KBr
- Sample spacing: 2.0000
- Digitizer bits: 20
- Optical velocity: 0.6329
- Aperture: 69.00
- Sample gain: 8.0
- High pass filter: 20.0000
- Low pass filter: 11000.0000

DATA COLLECTION INFORMATION
- Number of sample scans: 32
- Collection length: 38.0 sec
- Resolution: 2.000
- Number of scan points: 8338
- Laser frequency: 15798.3 cm-1
- Interferogram peak position: 128

DATA DESCRIPTION
- Number of points: 8320
- X-axis: Data points
- Y-axis: Volts
- First X value: 0.0000
- Last X value: 8319.0000
- Data spacing: 1.000000





<u>9 bounces is ideal</u> with the sample absorbing ~ 85% of the light.

The crystal absorbs too much in the 1900-2400 cm^{-1} region after 9 bounces and cannot be used. Similarly, < 650 cm^{-1} is not useful.

https://www.piketech.com/pikecalc/

Depth of penetration

$$d_p = \frac{\lambda_1}{2\pi\sqrt{sin^2\theta - n_{21}^2}}$$ where $\lambda_1 = \lambda/n_1$ and $n_{21} = n_2/n_1$

$$\mathbf{E(x) = E_0 e^{\left(-\frac{x}{d_p}\right)}}$$

$$\lambda_2 = \lambda_0 / n_2$$

Effective penetration, parallel polarization

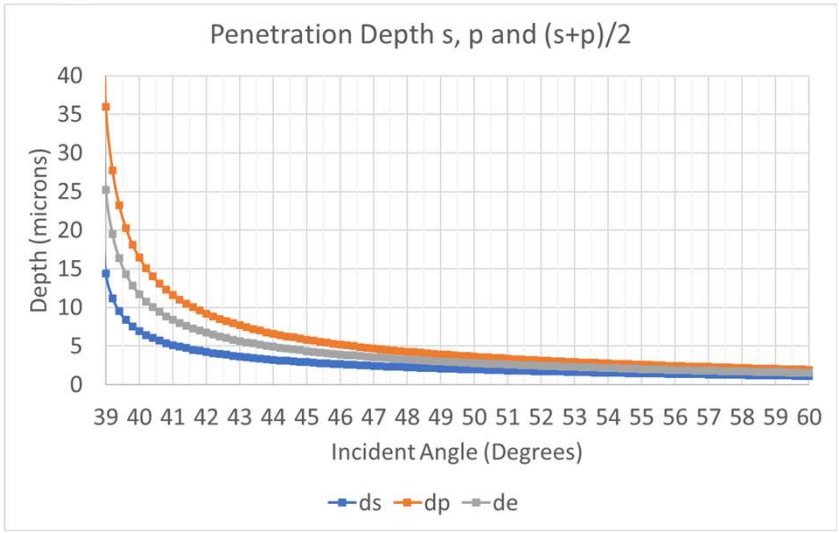
$$d_p = \frac{\lambda}{n_1} \cdot \frac{n_{21}\cos(\theta)\left[2\sin^2(\theta) - n_{21}^2\right]}{\pi\left(1 - n_{21}^2\right)\left[\left(1 + n_{21}^2\right)\sin^2(\theta) - n_{21}^2\right]\sqrt{\sin^2(\theta) - n_{21}^2}}$$

Effective penetration, perpendicular polarization

$$d_s = \frac{\lambda}{n_1} \cdot \frac{n_{21}\cos(\theta)}{\pi\left(1 - n_{21}^2\right)\sqrt{\sin^2(\theta) - n_{21}^2}}$$

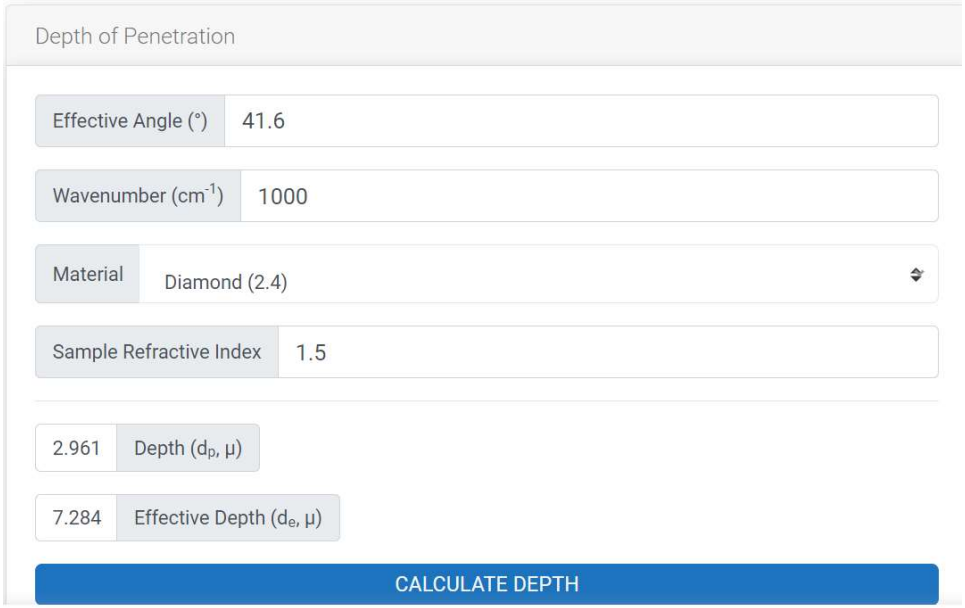
Effective penetration

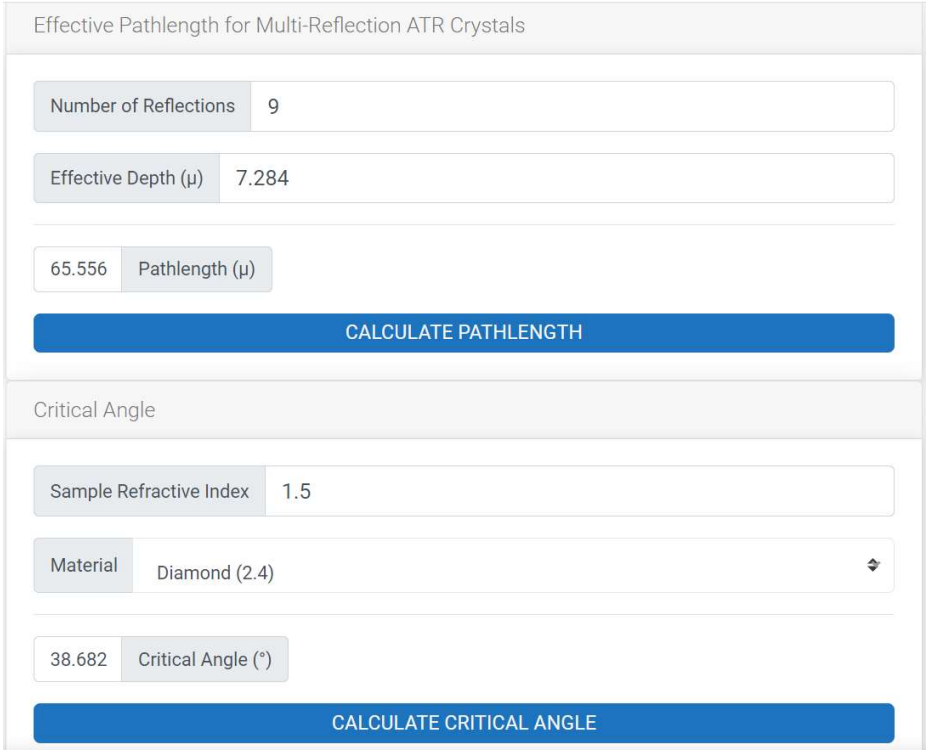
$$d_e = \frac{(d_{e\perp} + d_{e\parallel})}{2}$$



DurasamplIR II - 9 bounce ATR pathlength estimate

https://www.piketech.com/pikecalc/



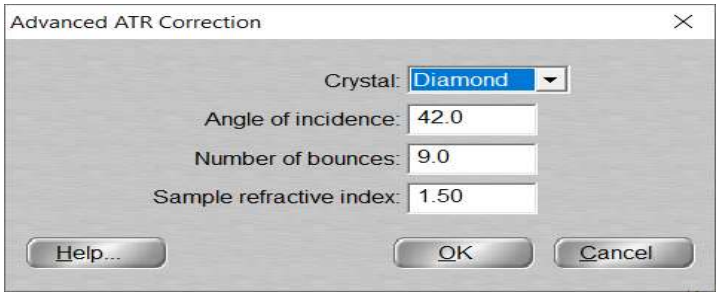


The number of bounces depends on the sample's refractive index and crystal angle.

The pathlength is convolved with the refractive index and poses an underdetermined system of equations requiring successive approximation.

With compositional changes the refractive index and pathlength change and the application of Beer's Law is problematic.
Factor based methods, PCA, PLS, etc. chemometric methods are needed for real multicomponent quantitation and or low concentrations.

Thermo's Advanced ATR algorithm…what we know



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

$$A = -\log\left(\frac{I}{I_0}\right) = \alpha l C$$

$$\mathbf{E(x) = E_0 e^{\left(-\frac{x}{d_p}\right)}}$$

Putting it all together you can numerically correct the spectra by back calculating alpha and E_0 as a function of wavelength with the calculated d_p.

$$\frac{I}{I_0} = e^{-\alpha\, d_e} \qquad d_e = \frac{n_{21} E_0^2 d_p}{2\cos\theta} \qquad A = -\log\left(\frac{I}{I_0}\right) = \frac{(\log_{10} e)}{2} \frac{n_2}{n_1} \frac{E_0^2}{\cos\theta} d_p \alpha$$

Interdependent terms
Makes multicomponent mixtures analytically intractable requiring factor analysis or successive approximation with known mixtures…not simple, see references.

$$A = -\log\frac{I}{I_0} = \frac{(\log_{10} e)}{2} \frac{n_2}{n_1} \frac{E_0^2}{\cos\theta} d_p \alpha = .0.217 \frac{n_2}{n_1} \frac{E_0^2}{\cos\theta} d_p \alpha = \underbrace{\frac{.0.217 E_0^2}{n_1}}_{\text{Constant}} \times \frac{n_2 \alpha\, d_p}{\cos\theta}$$

$$A = \frac{n_2}{n_1} \frac{\alpha}{\cos\theta} \int_0^t E^2\, dz$$

$\alpha = absorption\ coefficient\ per\ unit\ thickness\ and\ varies\ with\ composition.$

$E_0 = electric\ field\ strength\ of\ evanescent\ wave\ at\ interface\ and\ is\ awavlength\ independant\ constant$

$\frac{n_2}{n_1}$ = *the ratio of fast to slow indices of refraction*

$$R = \frac{I_{\text{Reflected}}}{I_0} \equiv T = \frac{I_{\text{Transmitted}}}{I_0}$$

R ≡ T, since all we are talking about the fraction of light hitting the detector, so $I_{\text{Reflected}} = I_{\text{Transmitted}}$, a definition of a light fraction not a statement of conservation of energy.

Applied Spectroscopy Volume 76, Issue 1 2022 Pages 1-152

Applied Spectroscopy Volume 40, Number 7, 1986 Pages 1019-1022

Trends in Analytical Chemistry, Vol. 29, No. 6, 2010 Pages 544-552