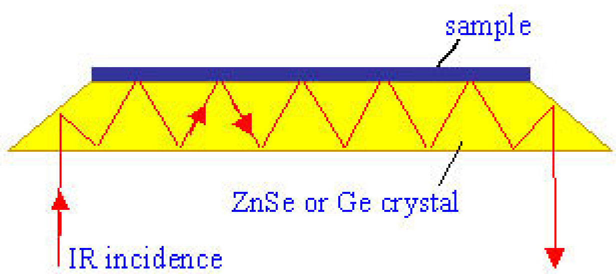
What is ATR?

Attenuated total reflection infrared (ATR-IR) spectroscopy is used for analysis of the surface of materials. It is also suitable for characterization of materials which are either too thick or too strong absorbing to be analyzed by transmission spectroscopy. For the bulk material or thick film, no sample preparation is required for ATR analysis.

For the attenuated total reflection infrared (ATR-IR) spectroscopy, the infrared radiation is passed through an infrared transmitting crystal with a high refractive index, allowing the radiation to reflect within the ATR element several times.



ATR experiment

The sampling surface is pressed into intimate optical contact with the top surface of the crystal such as ZnSe or Ge. The IR radiation from the spectrometer enters the crystal. It then reflects through the crystal and penetrating "into" the sample a finite amount with each reflection along the top surface via the so-called "evanescent" wave. At the output end of the crystal, the beam is directed out of the crystal and back into the normal beam path of the spectrometer.

To obtain internal reflectance, the angle of incidence must exceed the so-called 'critical' angle. This angle is a function of the real parts of the refractive indices of both the sample and the ATR crystal:

$$\theta_c = \sin^{-1}(n_2/n_1)$$

Where n_2 is the refractive index of the sample and n_1 is the refractive index of the crystal. The evanescent wave decays into the sample exponentially with distance from the surface of the crystal over a distance on the order of microns. The depth of penetration of the evanescent wave *d* is defined as the distance form the crystal-sample interface where the intensity of the evanescent decays to *1/e*(37%) of its original value. It can be given by:

$$d = \lambda / \{2\pi n_1 [\sin^2\theta - (n_2/n_1)^2]^{1/2}\}$$

Where l is the wavelength of the IR radiation. For instance, if the ZnSe crystal (n_1=2.4) is used, the penetration depth for a sample with the refractive index of 1.5 at 1000cm^{-1} is estimated to be 2.0µm when the angle of incidence is 45°. If the Ge crystal (n_1=4.0) is used under the same condition, the penetration depth is about 0.664µm. The depth of penetration and the total number of reflections along the crystal can be controlled either by varying the angle of incidence or by selection of crystals. Different crystals have different refractive index of the crystal material. By the way, it is worthy noting that different crystals are applied to different transmission range (*ca.* ZnSe for 20,000~650cm^{-1}, Ge for 5,500~800cm^{-1}).