INFRA RED SPECTRA BY ATTENUATED TOTAL REFLECTANCE (ATR)

In traditional absorption spectrophotometry, a source of radiation in the wavelength (or frequency) range shines light on the sample of interest. The intensity of the light reaching the detector is collected as the wavelength impinging on the sample is varied. This is accomplished by introducing an element that selects specific frequencies of the incident light (a monochromator). The intensity of the transmitted radiation is measured by a detector and recorded as a function of incident wavelength.

The FTIR spectrometers that we use to obtain infrared spectra in CHE 133-134 use a different technique. Instead of varying the frequency of the incident light, the sample is exposed to a continuously varying, but known, mixture of intensities of radiation over the entire frequency range of the IR instrument. The total intensity for each mixture of radiation is collected and from the collection of these intensities, the frequencies at which the sample absorbs is computed. The mixture of intensities at different wavelengths is accomplished by moving mirrors that change the interference patterns of different wavelengths of the IR radiation (an interferometer). The positions of the mirrors are determined by using a visible light laser. The light of the visible laser is not directed to the sample – only the light from the separate source of broad IR radiation is directed to the sample.

The mathematical process by which the absorptions are extracted from the signal collected by the detector is called a Fourier Transform. (Hence, the FT in the designation of the spectrometer.) Fourier Transforms permit the conversion of data that depends on time to a representation in which the data depend on frequencies. (The interested student will find the Wikipedia article enlightening.) This technique is used widely in spectroscopy, especially notably in Nuclear Magnetic Resonance (NMR) – a technique widely used in Chemistry and which is the basis of the medical imaging technique called MRI.

A second feature of the spectrometers that we use is their ability to obtain absorption spectra without actually passing the incident light through the sample. ATR (Attenuated Total Reflectance) makes use of the fact that an incident beam of radiation permitted to enter a sample at a sufficiently sharp glancing angle will

be reflected internally in a very shallow (0.5 – 2.0 μm) surface layer of the sample. For short wavelengths, the number of such reflections will be very large so that the effective path length of the radiation becomes large even though the sample may be quite small. Each reflection enhances the absorption of radiation by the sample at the frequencies where it absorbs. The result is equivalent to passing the radiation through a thick sample.

For ATR to work, the substance whose spectrum is desired must be in intimate contact with the window through which the infrared radiation is incident. The windows must have appropriate optical properties such as high index of refraction (in the IR region). In the laboratory spectrophotometers, the window is made of zinc selenide (ZnSe).