

ATR-FTIR Spectroscopy in the Undergraduate Chemistry Laboratory

Part I: Fundamentals and Examples

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Attenuated total reflectance–Fourier transform infrared (ATR-FTIR) spectroscopy is a versatile tool for measuring infrared spectra of solids and liquids. Spectra are easily obtained without the need to dilute the sample in a matrix such as Nujol or dichloromethane. As shown in this article, the quality of the spectra is quite high and the time it takes to make the measurement is less because no special preparation is needed.

There are two potential drawbacks to using the technique in the chemistry curriculum. First, the cost of the optics and ATR element is approximately two thousand dollars (1). Second, the ATR element is relatively fragile and should be handled with care. Despite these drawbacks, once the initial investment is made, ATR-FTIR spectroscopy can be used in both lower- and upper-level chemistry laboratory courses as well as in undergraduate research. After a brief discussion of the fundamentals and basics of ATR-FTIR spectroscopy, specific examples of the technique in different undergraduate chemistry laboratories and in undergraduate research are given.

Fundamentals

ATR-FTIR spectroscopy of solids and liquids requires that the sample of interest be placed onto an internal reflection element (IRE). The IR beam from the spectrometer is directed onto the element at an angle, θ , greater than the critical angle, θ_c , so that the infrared light undergoes internal reflection. At each point of internal reflection an evanescent wave is produced, from which, the radiation can be absorbed by a sample that is placed in direct contact with the IRE. The evanescent wave of the infrared radiation has a limited penetration depth on the order of $1\ \mu\text{m}$ (2, 3). A pictorial representation is shown in Figure 1. The absorption of the infrared light by the solid or liquid

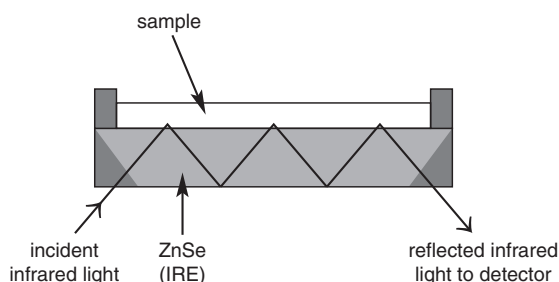


Figure 1. A pictorial representation of internal reflections through a high refractive index medium, for example, ZnSe, used as the internal reflection element (IRE). At each reflection, an evanescent wave is produced that decays exponentially into the medium above.

sample in direct contact with the IRE can be measured in this way. The absorbance is proportional to the path length, which is similar to transmission infrared spectroscopy. However, in the case of ATR-FTIR spectroscopy, the effective path length, b' , is equal to the number of reflections of the IR beam times the penetration depth,

$$b' = Nd_p \quad (1)$$

where N is the number of reflections and d_p is the penetration depth per reflection. The penetration depth, d_p , is

$$d_p = \frac{\lambda_1}{2\pi n_1 [\sin^2 \theta - n_{21}^2]^{1/2}} \quad (2)$$

where n_1 is the index of refraction of the IRE, n_2 is the index of refraction of the sample medium in contact with the crystal, n_{21} is equal to n_2/n_1 and $\lambda_1 = \lambda_{\text{vacuum}}/n_1$ (4–6). The small penetration depth and short path length allow for infrared absorption measurements of a strongly adsorbing medium such as those for infrared measurements of aqueous solutions or polymers (2).

A slightly modified Beer–Lambert law can be used to describe the linear relationship between the concentration, c , and absorbance. The modified Beer–Lambert law is

$$A = \epsilon cb' \quad (3)$$

where A is the absorbance, ϵ is the molar absorptivity, and b' is the effective path length as defined in eq 1 (2).

The type of IRE used is an important consideration. The compatibility of the materials being used on the IRE should be taken into account as well as the refractive index, transmission range, and pH range of the IRE. Different IREs are available for different experimental conditions (3). In the experiment presented in this article, a horizontal ATR or HATR internal reflection element, ZnSe (Pike Technologies, Trough Plate, part #022-2010-45), was chosen for the compatibility, refractive index, and transmission range as well as durability and lower cost that still produced quality spectra. In addition, since d_p is wavelength dependent, the relative intensities of the absorption bands measured with different internal reflection elements can differ and these may also differ from a transmission FTIR spectrum of the sample. For other applications, IREs such as germanium or diamond can be purchased to facilitate the implementation of this technique into undergraduate laboratories depending on the conditions (i.e., pH, transmission range, reactivity, single or multi-reflection, etc.) of the experiment of interest.

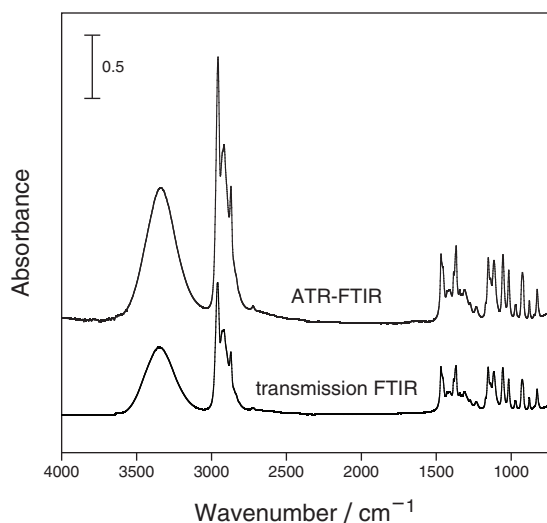


Figure 2. A comparison of the infrared spectrum of liquid 4-methyl-2-pentanol using ATR-FTIR spectroscopy and transmission FTIR spectroscopy.

ATR-FTIR Spectroscopy in the Undergraduate Laboratory

In the Organic Chemistry Laboratory

Organic unknowns are a way for students to use the skills they have developed over the course of the semester. At this university, students are given an unknown and then are allowed to use a variety of spectroscopic techniques, such as FTIR spectroscopy, in an attempt to identify their unknown. ATR-FTIR spectroscopy can assist in the characterization of an organic unknown using only a drop of the liquid or by dispersing a solid sample onto the IRE. The spectrum produced by a small drop of an organic liquid is more intense than a spectrum taken using a salt plate, as shown in Figure 2. Here the spectrum of a typical organic unknown, 4-methyl-2-pentanol (Aldrich, 99 %), is shown. The top spectrum was taken using ATR-FTIR spectroscopy compared to the bottom spectrum that was taken using transmission FTIR spectroscopy. For this comparison, infrared spectra were obtained using a Nicolet spectrometer (Nexus model 670) equipped with a DTGS KBr detector, where 250 scans were acquired at an instrument resolution of 4 cm^{-1} over the spectral range between 750 and 4000 cm^{-1} . For the ATR-FTIR experiments a ZnSe IRE was used and for the conventional method salt plates were used to collect spectra. For both experiments a comparable sample quantity was used: one drop of the unknown organic liquid was used on the ATR crystal and one drop was used on the salt plate. As can be seen from Figure 2, the spectra are similar.

The infrared spectrum of a typical solid organic unknown, 2-chlorobenzoic acid (Aldrich, 98%), is shown in Figure 3. To obtain this spectrum, the sample was sprinkled onto the surface of the IRE and the spectrum was recorded. This provides an advantage to using the ATR-FTIR technique for solid samples over conventional methods; the sample can be re-used after the infrared spectrum has been taken because the sample was not modified (e.g., combined in matrices with Nujol or KBr or dissolved in dichloromethane). The powder samples used in organic laboratories were found to work well with the exception

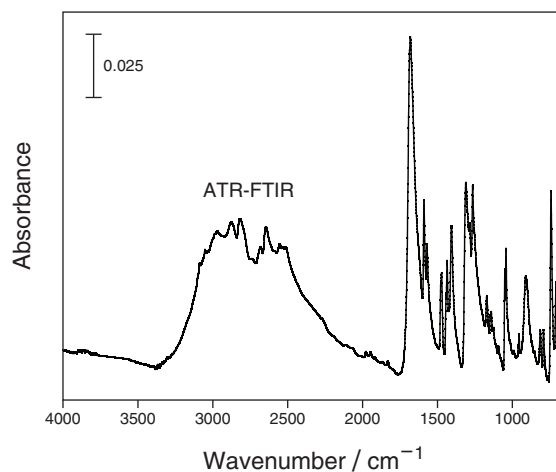


Figure 3. An infrared spectrum of solid 2-chlorobenzoic acid using ATR-FTIR spectroscopy.

of analyzing some polymers as these materials did not easily make good contact with the IRE. The implementation of ATR-FTIR spectroscopy in the undergraduate organic laboratory presents the opportunity to expose students to the ATR-FTIR technique and to obtain quality spectra.

In the Inorganic Chemistry Laboratory

For an inorganic chemistry laboratory, ATR-FTIR spectroscopy can be used in a manner similar to the organic chemistry laboratory discussed above. At this university, students are asked to synthesize compounds and analyze their products. For solids, as shown above, ATR-FTIR spectroscopy can be a non-invasive method of characterization. Thus the implementation of ATR-FTIR into the inorganic chemistry laboratory setting is possible as well.

In the Analytical Chemistry Laboratory

ATR-FTIR spectroscopy can also be implemented into analytical laboratories. It has been shown in the literature (7–11) that ATR-FTIR spectroscopy is commonly used in industry for the analysis of substances such as milk and butter to quantify fat and proteins as well as in the analysis of biodiesel and other automotive fluids, which could be demonstrated in an analytical laboratory setting. It has also been implemented into undergraduate analytical laboratories as well. Gebel et al. (4) discussed the use of this technique to determine the ethanol content in an aqueous solution of vodka, illustrating that ATR-FTIR can also be used as a quantitative technique. Both single and multiple reflection techniques were used to demonstrate the increased sensitivity with the multiple reflection IRE. This allowed the students to see the significance of path length as the single reflection IRE is equivalent to a shorter path length.

In Undergraduate Research

ATR-FTIR experiments have also been implemented in undergraduate research. At this university, ATR-FTIR spectroscopy was used as an undergraduate project to acquire spectra of concentrated aqueous nitrate solutions to better understand

aqueous nitrate aerosols that form in the atmosphere from reactions of sea salt and mineral dust particles with nitrogen oxides (12). Undergraduates have also used ATR–FTIR to investigate processes such as salt deliquescence as a function of relative humidity (13). In particular, ATR–FTIR spectroscopy was used to determine deliquescence relative humidity values for the following salts: NaCl, NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, NaNO_3 , and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. The undergraduate student was included as a co-author on an article and was able to write an honor's thesis on this project. ATR–FTIR spectroscopy has been used in other undergraduate projects to determine the uptake of water as a function of relative humidity on mineral dust particulates, to investigate the adsorption of aqueous phosphate and phenol, as well as the co-adsorption of these solutions onto thin films of TiO_2 particles as a function of concentration and pH. Thus, a variety of projects involving undergraduate students using ATR–FTIR spectroscopy have been successfully implemented and has allowed undergraduates to obtain high-quality, publishable data as well as gain experience in the analysis and write-up of data for honors theses.

Hazards

These experiments should be carried out using the proper protective eyewear. Students are instructed to collect waste in specific waste bottles that will be collected by the Health Protection Office at the University of Iowa. The organic reagents used for unknowns can be hazardous as some are flammable, volatile, and can be irritants.

Conclusions

We have illustrated that ATR–FTIR spectroscopy can be incorporated into different levels of the undergraduate curriculum, including undergraduate research, providing a multi-use investment for chemistry departments. In addition, a new physical chemistry experiment has been developed as described in Part II (14).

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Supplement

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