

ATR SPECTROSCOPY IN THE UNDERGRADUATE CHEMISTRY LABORATORY



Figure 1. The AccessATR™.

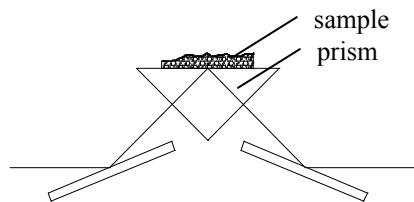


Figure 2. Optical Drawing of the AccessATR™.

Table 1. Critical Angle for 3-Iodoaniline with a Refractive Index of 1.68.

Material	Refractive Index (n)	Critical Angle
ZnSe	2.4	43.9°
Ge	4.0	24.8°

INTRODUCTION

ATR spectroscopy has become one of the leading infrared spectroscopic methods used in industry today. However, it is not yet routinely included in many undergraduate educational programs. The reason for this is two-fold. It is more difficult to present a simplified version of the theory. Many of the texts only discuss transmission and the 'response' in ATR does differ from transmission spectroscopy. In addition, the equipment tends to be expensive. This makes it difficult for colleges and universities to acquire, particularly when compared to traditional KBr pellets and mulls. ATR spectroscopy is used currently in some undergraduate programs, but mostly in those programs where particular professors have the expertise and the appropriate equipment is borrowed from their research laboratories.

This note introduces a relatively inexpensive ATR accessory and demonstrates its use in an undergraduate organic chemistry experiment.

THEORETICAL DISCUSSION

The theoretical foundations of ATR were developed by Harrick and duPre^{1,2} and have been described in detail elsewhere^{3,4}. In brief, radiation

is directed through a prism, the ATR crystal, at an incident angle higher than the critical angle for internal reflection. The critical angle, θ_c , is defined as:

$$\theta_c = \sin^{-1}\left(\frac{n_2}{n_1}\right)$$

where n_1 is the refractive index of the ATR crystal and n_2 is the refractive index of the sample. Above the critical angle, an evanescent wave is created at the reflecting surface. When a sample comes in contact with the surface, this evanescent wave interacts with the sample and a spectrum can be recorded to measure this interaction. This interaction is described by the Fresnel equations, as is the interaction that occurs for transmission measurements. However, the spectral response is slightly different.

For thin films, the ATR spectra are the same as transmission spectra. For thick films, the absorption bands are more intense at longer wavelengths. As the angle of incidence approaches the critical angle, the bands tend to broaden on the long wavelength side and the minima are displaced to longer wavelengths (lower wavenumbers). Dispersion type spectra are observed very close to and below critical angle.

EXPERIMENTAL

One of the common organic microscale experiments used in

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undergraduate teaching labs is the synthesis of 4-bromo-2-chloro-6-iodoaniline. The experimental details have been published elsewhere.⁵

Spectra were obtained using an FTIR spectrometer equipped with a DTGS detector and the AccessATR™ single reflection ATR accessory. All spectra were collected from 4000 to 550cm⁻¹ using 32 scans at a resolution of 8 cm⁻¹.

The AccessATR™ was chosen due to its low cost and simple optical design (see Figure 2). The beam from the infrared spectrometer is directed by a planar mirror into a 45° triangular prism. The light internally reflects from the top surface of the prism and is redirected to the detector of the spectrometer using a second planar mirror.

To select an appropriate ATR crystal, the refractive index of the products formed was investigated in the literature. No published data could be readily located. The closest material found was a less-highly substituted 3-iodoaniline with a refractive index of 1.68⁶.

Table 1 shows the critical angle for two common ATR crystal materials. Since the incident angle of the AccessATR™ prism (45°) is above the critical angle for both ZnSe and Ge, either material would technically be suitable as

an ATR crystal. Ge is probably a better choice. The infrared beam is focused rather than collimated, typically with a +/- 10° beam spread, so there will be contributions from rays slightly below and above 45°. In addition, as the aniline under investigation is more highly substituted than 3-iodoaniline, it would be expected to have a higher refractive index. These two factors may make ZnSe unsuitable as an ATR crystal.

Experiments were performed with both materials. The bulk of the measurements were done with Ge. The data presented using a ZnSe ATR crystal has been included to demonstrate the spectral features observed near or below critical angle.

Each sample was measured as follows. The accessory was installed in the spectrometer and its height was adjusted to optimize performance. Both the ATR crystal and pressure applicator were thoroughly cleaned using methyl ethyl ketone, a low residue solvent. A single beam background spectrum was recorded. The powdered sample was placed in the center of the ATR crystal and the thumbscrew on the top of the accessory was tightened finger-tight to compress the powder against the ATR crystal. Then the sample spectrum was recorded. The spectra are presented with no corrections

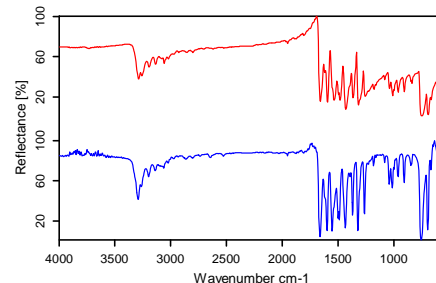


Figure 3. Normalized ATR Spectra of the Acetanilide Recorded with ZnSe (red) and Ge (blue) ATR crystals.

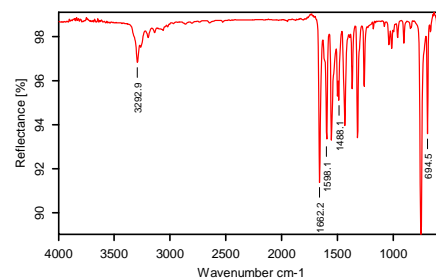


Figure 4. ATR Spectrum of Acetanilide.

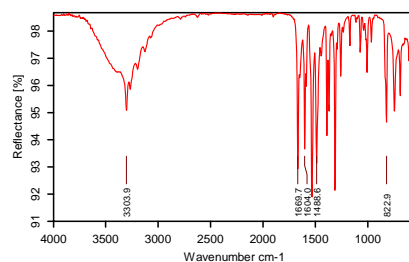


Figure 5. ATR Spectrum of 4-Bromoacetanilide.

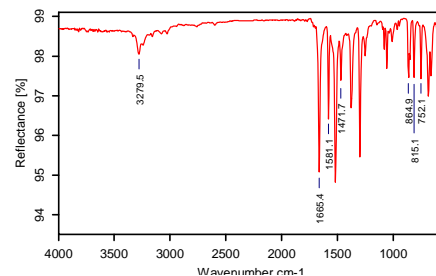


Figure 6. ATR Spectrum of 4-Bromo-2-Chloroacetanilide.



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applied to the raw data.

Both the synthesis and the spectroscopic measurements presented herein were performed by an undergraduate student.⁷

RESULTS AND DISCUSSION

To confirm that Ge is the better choice of ATR crystal for this experiment, the spectrum of the first product of the synthesis, acetanilide, was measured using both a Ge and ZnSe ATR crystal. The results are shown in Figure 3. Note that the high wavenumber edge of the C-H stretching band at 3340cm^{-1} is much sharper in the spectrum recorded with the ZnSe crystal. Also, around 1700cm^{-1} , there is an inverted band in the spectrum recorded with ZnSe. This inversion is significantly less pronounced in the Ge-ATR spectrum. Thus Ge is a better choice for the ATR crystal for this sample, since fewer dispersion effects are evident.

Figures 3 through 6 show the measured ATR spectra of the intermediates and Figure 7 shows the spectrum of the final product. For all the products, the bands were assigned to functional groups using the standard transmission functional groups. The results are summarized in Table 2.

In addition to the peaks listed, the spectra show bands around 3000cm^{-1} , characteristic

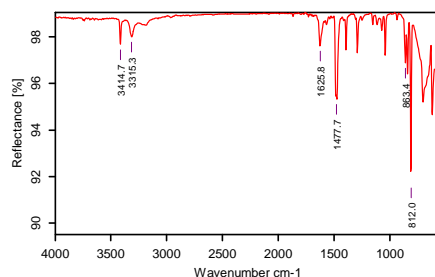


Figure 7. ATR Spectrum of 4-Bromo-2-Chloroanilide.

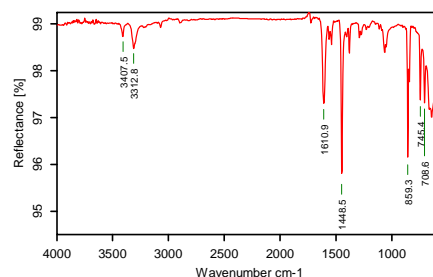


Figure 8. ATR Spectrum of 4-Bromo-2-Chloro-Iodoanilide.

Table 2. Functional Group Assignments for the Synthesized Products.

Compound	Peak (cm^{-1})	Functional Group
Acetanilide (Figure 3)	3292.9	N-H stretch
	1662.2	C=O stretch
	1598.1	Aromatic ring C=C
	1488.1	
	752.0	Mono-substituted aromatic ring out-of-plane bend
	694.5	
4-Bromoacetanilide (Figure 4)	3303.9	N-H stretch
	1669.7	C=O stretch
	1604.0	Aromatic ring C=C
	1488.7	
822.9	Para-substituted aromatic ring =C-H bend	
4-Bromo-2-Chloroacetanilide (Figure 5)	3279.5	N-H stretch
	1665.4	C=O stretch
	1581.1	Aromatic ring C=C
	1471.7	
	864.5	Tri(1,2,4)-substituted aromatic ring =C-H bends
	815.1	
752.1	C-Cl stretch	
4-Bromo-2-Chloroanilide (Figure 6)	3414.7	N-H stretch
	3315.3	
	1625.8	C=C from the aromatic ring
	1477.7	
	863.4	Tri(1,2,4)-substituted aromatic ring =C-H bends
	813.2	
4-Bromo-2-Chloro-Iodoanilide (Figure 7)	3407.5	N-H stretch
	3312.8	
	1610.9	Aromatic ring C=C
	1449.5	
	859.3	=C-H out-of-plane bends
	745.4	
708.6		



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of the C-H stretches. All of the bands assigned are consistent with the chemical structures of the compounds.

Note that the spectrum of 4-bromoacetanilide shows a broad band around 3300 cm^{-1} . This is characteristic of the -O-H stretch and is probably due to contamination of this particular intermediate with either water or acetic acid. Significant contamination by the reactants or solvents used in the synthesis is not seen in any of the other products.

CONCLUSION

This study demonstrates that the AccessATR™ can be used effectively for the spectroscopic identification of the intermediates and products from the synthesis of 4-bromo-2-chloro-6-iodoaniline. In addition to the functional group analysis carried out here, additional identification could be carried by comparing the peak locations to that of the transmission spectra of the products. Note that due to the differences in the response of ATR and transmission, only the peak positions could be compared. Alternatively, a set of standards could be examined using ATR for a direct comparison.

Single reflection ATR offers a number of advantages over the KBr pellets and nujol mulls for

spectroscopic analysis in undergraduate chemistry labs. It requires less same preparation and is simple to use for all types of liquids and powders. With a low-cost accessory like the AccessATR™, it is also an affordable alternative to the traditional methods. Furthermore, it gives the students the opportunity to utilize the state-of-the-art sampling methods that are more frequently used in industrial quality control and research laboratories.

REFERENCES

- ¹N. J. Harrick and F. K. DuPre, *Appl. Opt.* **5**, 1739 (1966).
- ²N.J. Harrick, Internal Reflection Spectroscopy (Interscience Publishers, New York, 1985).
- ³F.M. Mirabella, Jr and N.J. Harrick, Internal Reflection Spectroscopy: Review and Supplement (Harrick Scientific Corp., Ossining, NY, 1985).
- ⁴M. Milosevic, N.J. Harrick, S.L. Berets, *Appl. Spectrosc.* **45**, 126-131 (1991).
- ⁵Allen Schoffstall, Barbara Gaddis, and Melvin Druelinger, Microscale and Miniscale Organic Chemistry Lab Experiments, 2nd edition (McGraw Hill Higher Education, 2004), p. 579-599.
- ⁶<http://www.chemblink.com/products/626-01-7.htm>
- ⁷Special appreciation to Prof. Ali Kocak and his students at the John Jay College of Criminal Justice for their contributions.



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