

## ATR ROTATOR FOR STUDIES OF ORIENTED SAMPLES

### INTRODUCTION

Oriented samples are characterized by chemical bonds aligned in a particular direction (axis). Most single crystals are oriented. Liquids are generally not oriented. Polymers and plastics are also generally not oriented, but some production techniques may produce preferential orientation of molecules along certain "machining" directions. Typically, oriented samples will have different mechanical and chemical properties along the axis and perpendicular to it. Analyzing these oriented samples in order to correlate their properties with the degree of orientation is important both in material development and later in the production phase for QC purposes.

This note explores using ATR measurements to probe the orientation. In particular, the Seagull variable angle accessory is used with its ATR Rotator and wire grid polarizer for fixed  $67^\circ$  measurements of a plastic.

### THEORY

The basic principle used to determine molecular orientation by spectroscopic methods relies on the radiation absorbed by a sample for various orientations of the electric field of the polarized incident light with

respect to the sample. The absorbance measured for a particular chemical bond in a particular direction is proportional to the average of the square of the cosine of the angle of the dipoles associated with this bond and the direction. By calculating the ratio of two absorbances measured in two directions, one finds the ratio of the average square cosines for the two directions - purely geometric information on the molecular structure of the sample.

In transmission spectroscopy, for instance, measurements can be taken at normal incidence by rotating the polarization of the incident light and measuring absorbance for different angles of rotation. Alternatively, the polarizer can be kept fixed and the sample rotated. To quantify the degree of orientation, consider a simple model where a certain fraction  $f$  of molecular dipoles is perfectly oriented in a particular direction and the remainder  $(1-f)$  is randomly oriented. The absorbance  $A_1$  can be measured for the field oriented along that direction and the absorbance  $A_2$  can be measured with the field perpendicular to that direction. The absorbance  $A_1$  is due to the fraction  $f$  oriented along this direction plus  $(1-f)/3$  of the randomly oriented bonds (see Figure 1). The absorbance  $A_2$  is

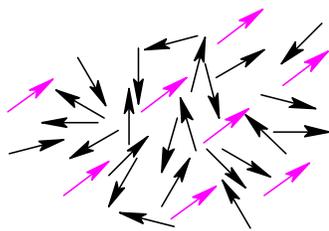


Figure 1. Two dimensional illustration of the oriented fraction  $f$  of dipoles (magenta) imbedded in a background of randomly oriented dipoles (black).

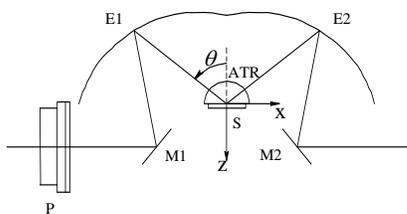


Figure 2. Geometry of the experiment.

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only due to  $(1-f)/3$  of the randomly oriented bonds and thus the ratio comes out to  $(1+2f)/(1-f)$ . This allows the calculation of the fraction  $f$ .

Transmission spectroscopy and the model described above, is limited to optically thin samples. ATR, however, is not restricted by sample thickness. In ATR, the absorption results from the interaction of the sample and the evanescent wave. The electric fields of the evanescent wave at the interface are given by Harrick<sup>1</sup>:

$$E_y = \frac{2n_1 \cos \theta}{\sqrt{n_1^2 - n_2^2}} E_0^s \quad (1)$$

$$E_x = \frac{2n_1 \cos \theta \sqrt{n_1^2 \sin^2 \theta - n_2^2}}{\sqrt{n_1^2 - n_2^2} \sqrt{(n_1^2 + n_2^2) \sin^2 \theta - n_2^2}} E_0^p \quad (2)$$

$$E_z = \frac{2n_1^2 \sin \theta \cos \theta}{\sqrt{n_1^2 - n_2^2} \sqrt{(n_1^2 + n_2^2) \sin^2 \theta - n_2^2}} E_0^p$$

where  $E_0$  is the electric field of the incident light,  $n_1$  and  $n_2$  are refractive indices of the ATR element and the sample respectively and  $\theta$  is the angle of incidence. For s-polarized incident light, only  $E_y$  exists and both  $E_x$  and  $E_z$  are zero. For p-polarized incident light,  $E_y$  is zero, while  $E_x$  and  $E_z$  are non-zero.

Thus, the absorbance depends on the field strength for a particular direction in addition to the average cosine squared for that bond and direction. Thus, in

order to determine geometric information on the molecular structure of the sample, the ratio of the field strengths squared for the two directions must be extracted from the ratio of the measured absorbances to arrive at the ratio of cosines squared for the two directions.

Note that we have assumed that the refractive index of the sample  $n_2$  is the same in all directions. For oriented samples this is generally not true. The refractive index of anisotropic samples generally is direction dependent. However, for weak absorption, this dependence of the refractive index of the sample on the direction is weak and generally ignored.

For s-polarized light, the electric field of the incident light oscillates perpendicular to the plane of incidence, *i.e.* it is along the y-axis (pointing out of paper in Figure 2). Thus the evanescent wave induced in the sample has an electric field that oscillates in the direction of the y-axis. This electric field can only excite those dipoles in the sample that have components along the y-axis, so the dipoles oriented along the x- and z-axes are not excited. However, if the sample can rotate around z-axis, rotating the sample by  $90^\circ$  interchanges x and y directions. The same evanescent wave can now excite dipoles that were originally pointing in the x-direction and now point in the y-

direction. Two different directions, x and y, can thus be analyzed by simply rotating the sample. If the sample can rotate to any angle, the dependence of spectra on sample orientation can be systematically investigated. The orientation of chemical bonds can be deduced from the angular plots of peak height vs. angle, referenced to the outside edges of the sample.

To probe perpendicular to the sample surface, into the sample thickness (z-axis), the electric field needs to oscillate in the z-direction. With p-polarized incident light, the evanescent wave induced in the sample has an electric field oscillating in the xz plane. Only at critical angle does this electric field oscillate purely in the z-direction.

However, experimental measurements at the critical angle produce highly distorted spectra. In practice, the angle of incidence must be several degrees above critical for spectra to become relatively distortion free. Thus z- and x-direction are always probed together. However, as the angle of incidence increases, the relative strength of the field in x-direction grows. By comparing the results obtained at two different angles and therefore differing proportions of the x and z directions, the contributions of the two can be separated.



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Figure 3. The Seagull™ Variable Angle Reflectance Accessory.



Figure 4. The ATR Rotator for the Seagull.

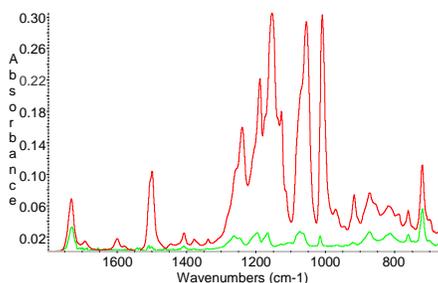


Figure 5. Spectra recorded at a 160° (green) and a 260° (red) rotation of the sample around the z-axis, showing the extremes of the spectral variation

## EXPERIMENTAL

The ATR measurements were carried out using Harrick's Seagull™ (see Figure 3) with its ATR Rotator (Figure 4) and wire grid polarizer (KRS-5 substrate) on a highly oriented plastic. The Seagull was configured for an incident angle of 67° with its ZnSe hemispherical ATR crystal. Such a high angle of incidence was necessary to eliminate spectral distortions that occur when the incident angle is too close to the critical angle. Note that the high angle of incidence prevented variable angle studies of this sample. The Seagull pressure applicator was hand-tightened to compress the sample against the ATR crystal. The ATR Rotator is designed so the ATR hemisphere rotates with the sample and the sample-ATR hemisphere contact remains unchanged as the sample is rotated around the z-axis. Note that the ATR Rotator features a scale in 1° increments to indicate the rotation of the sample and it can be rotated a full 360°.

S-polarized light at a fixed angle of incidence was used for all orientations of the sample, so the electric field direction and strength were identical for all the measurements and could be directly compared. In other words, the ratio of absorbances for the two different angles is

the same as the ratio of the fractions of bonds oriented along these directions. If the angle of incidence changed during the experiment, the electric fields in the sample would change according to (1) and (2) and corrections would need to be applied to the measured absorbances in order to directly compare them.

All spectra were recorded on an FT-IR spectrometer with a DTGS detector. The spectrometer collected 32 scans at an 8 cm<sup>-1</sup> resolution.

## RESULTS AND DISCUSSION

The two spectra, at the extremes of spectral variations, are shown in Figure 5. The most striking feature of these spectra is the overall difference in the strength of absorbance for the two orientations. It appears that all the major bonds in this sample are oriented along the direction defined by the electric field at the sample rotation labeled as 260°. Several peaks appear roughly the same strength (within a factor of two), but most of the peaks show striking dependence on the sample orientation. All the strongly oriented bonds are oriented along the same direction. The variation of peak height with angle is illustrated in Figure 6, which shows the peak at 1500 cm<sup>-1</sup> changing as a function of the angle of



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orientation.

Figure 7 shows all 37 spectra of the sample, taken in  $10^{\circ}$  increments, thus representing a full  $360^{\circ}$  rotation of the sample. This allows one to quickly see which bonds exhibit orientation and which do not. For instance, the bond at  $1000\text{ cm}^{-1}$  exhibits a large degree of orientation while the bond at  $760\text{ cm}^{-1}$  appears largely unaffected by the orientation.

The absorbance is expected to be a function proportional to  $\cos^2(\psi-\beta)$ , where the angle  $\psi$  measures the rotation of the sample from some arbitrary starting orientation, and angle  $\beta$  represents orientation of the projection of the bond into the xy plane with respect to the starting orientation. If another bond had different orientation of its projection into xy plane, then the same plot for that bond would be phase shifted with respect to the  $1500\text{ cm}^{-1}$  bond and the angle of shift would represent the angle between the projections of the two bonds into the xy plane.

Usually, the orientation of a molecular bond is not perfect, *i.e.* not all the dipoles are aligned in the same direction. A majority of dipoles may point in a particular direction while the rest may point in random directions. Or the dipoles may have more or less the same orientation, but each dipole may be just slightly out of the

alignment. In that case, the plot shown in Figure 5 would have minima proportional to the fraction of nonaligned dipole components. The bond, shown in Figure 5, exhibits strength variation from 0.10A in the aligned direction to 0.01A in the perpendicular direction. This particular bond is highly oriented with an orientation fraction  $f = 0.75$  implying that three quarters of the dipoles associated with this bond are perfectly oriented.

## CONCLUSION

In conclusion, it is clear that ATR, using the Harrick Seagull with its ATR Rotator, enables detailed analysis of oriented samples. A study of bond orientations referenced to the external sample dimensions is straightforward.

## REFERENCES

- <sup>1</sup> N. J. Harrick: *Internal Reflection Spectroscopy*, Harrick Scientific Products, Inc., New York 1987.

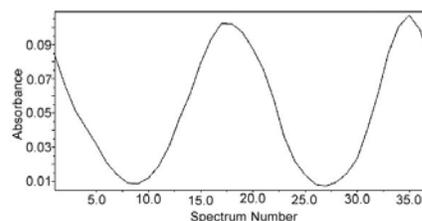


Figure 6. Variation in absorbance of the peak at  $1500\text{ cm}^{-1}$  as a function of sample rotation around the z-axis. The spectra were taken in  $10^{\circ}$  steps so the angular range is  $360^{\circ}$ .

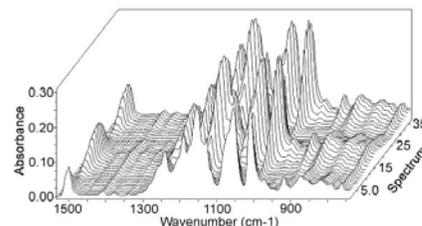


Figure 7. Spectra of oriented sample in  $10^{\circ}$  steps over the  $360^{\circ}$  angle



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