# Photoacoustic Spectroscopy (PAS) Technology Overview

Introduction:

The unique aspect of PAS technology, direct detection of light absorption by the sample, allows quick and nondestructive measurement of absorbance spectra without sample preparation or contact, and also advanced measurements such as depth probing to reveal layered or gradient composition.

The basics of how PAS works and some of its applications are discussed in this overview.

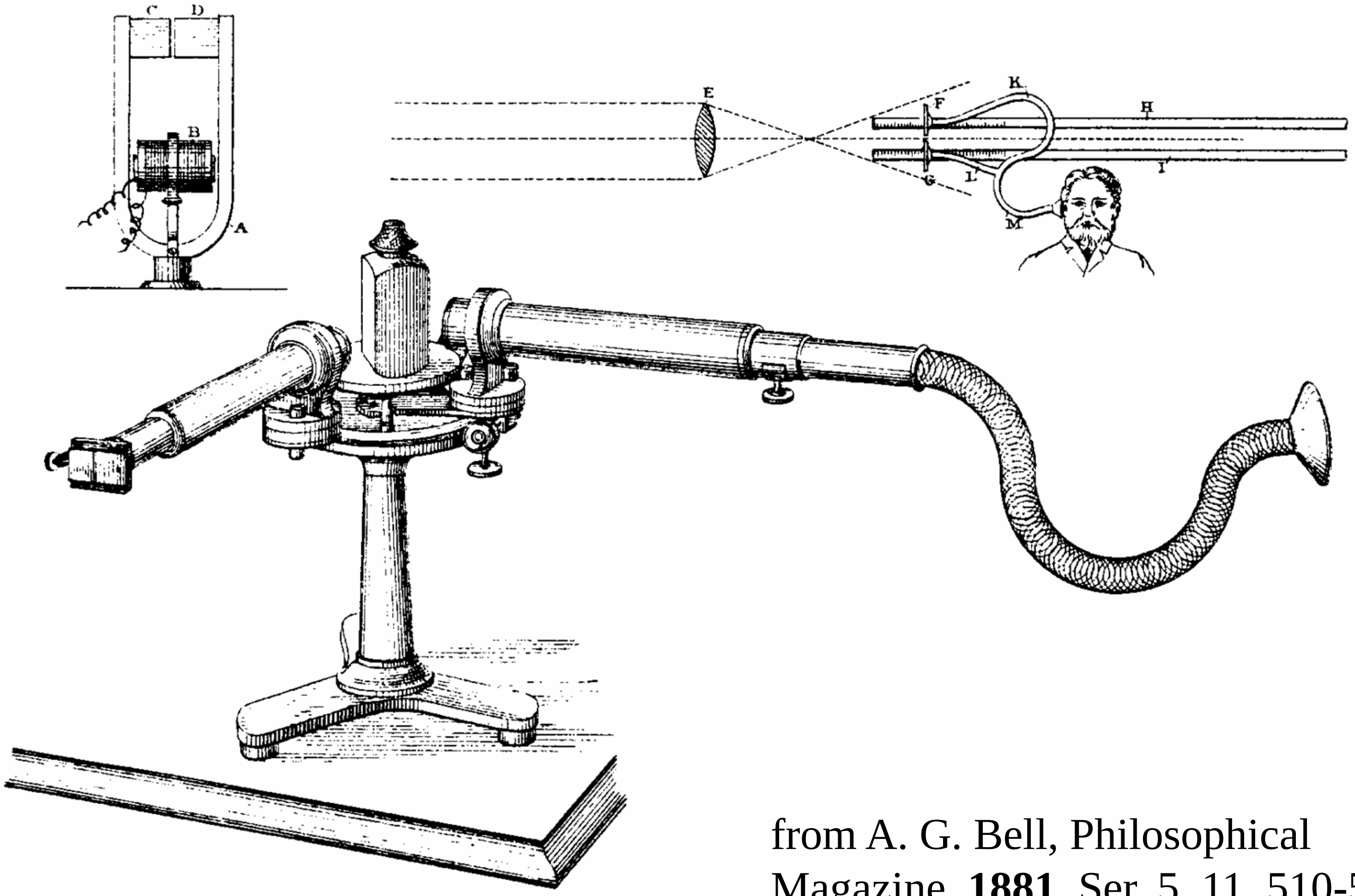
# Topics

- Chemometric Analysis of Photoacoustic Spectra

- Process Study Applications

# AG Bell’s Spectrophone

## from 1881 marks the beginning of photoacoustic spectroscopy



from A. G. Bell, Philosophical Magazine, **1881**, Ser. 5, 11, 510-528.

# Bell also sponsored Michelson's development of the interferometer that lead to FTIR spectrometers which have played a crucial role in PAS.

Heidelberg, Baden, Germany
April 17th, 1881

My dear Mr. Bell,

The experiments concerning the relative motion of the earth with respect to the ether have just been brought to a successful termination. The result was however negative. . . .

At this season of the year the supposed motion of the solar system coincides approximately with the motion of the earth around the sun, so that the effect to be observed was at its maximum, and accordingly if the ether were at rest, the motion of the earth through it should produce a displacement of the interference fringes, of at least one tenth the distance between the fringes; a quantity easily measurable. The actual displacement was about one one hundredth, and this, assignable to the errors of experiment.

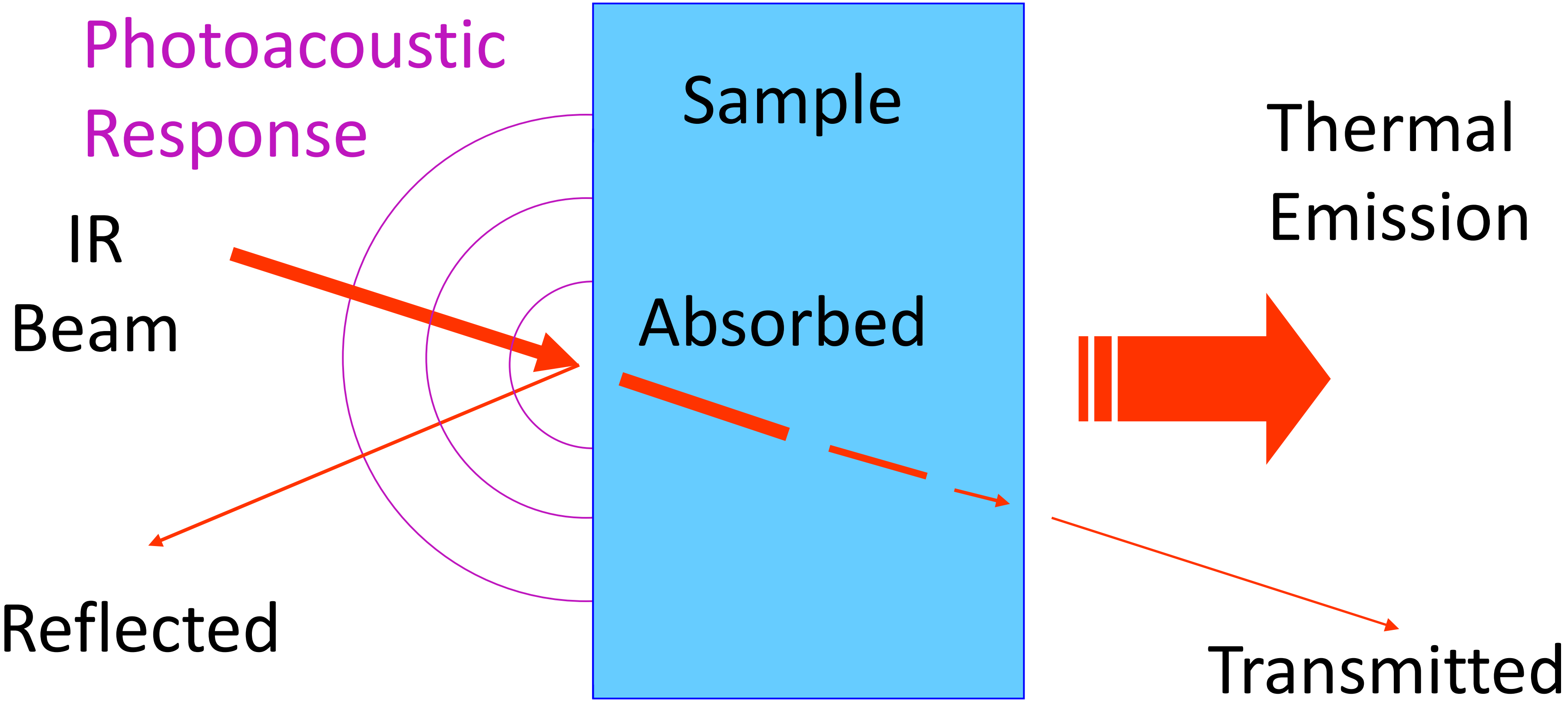
Thus the question is solved in the negative, showing that the ether in the vicinity of the earth is moving with the earth; a result in direct variance with the generally received theory of aberration. . . .

N.B. Thanks for your pamphlet on the photophone,

Very truly yours,

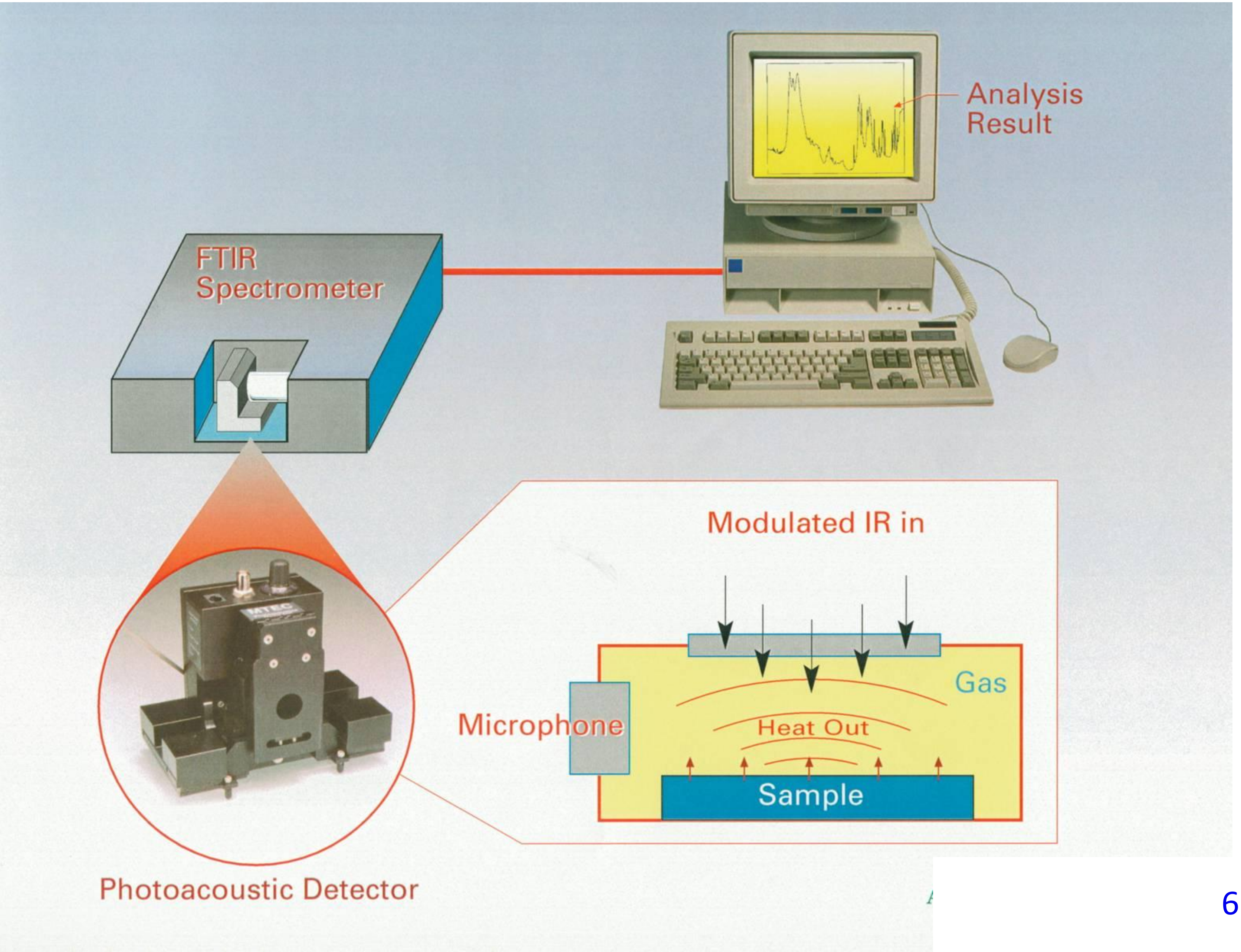
Albert A. Michelson
Master, U.S. Navy

# How does PAS relate to other sampling techniques?

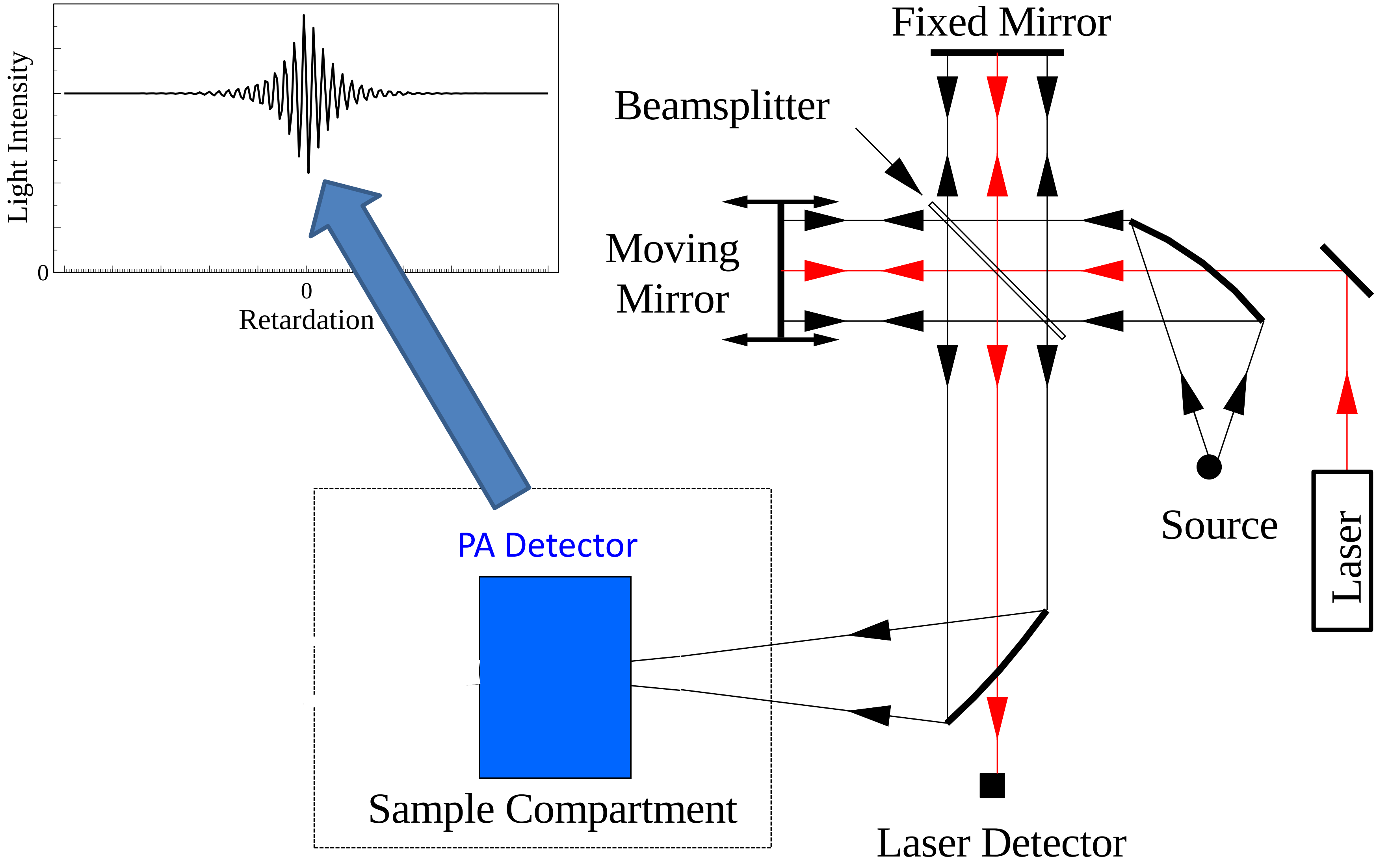


Only PAS measures the actual absorption of light in a sample by sensing the absorption driven heating and thermal expansion that results in a photoacoustic pressure signal.

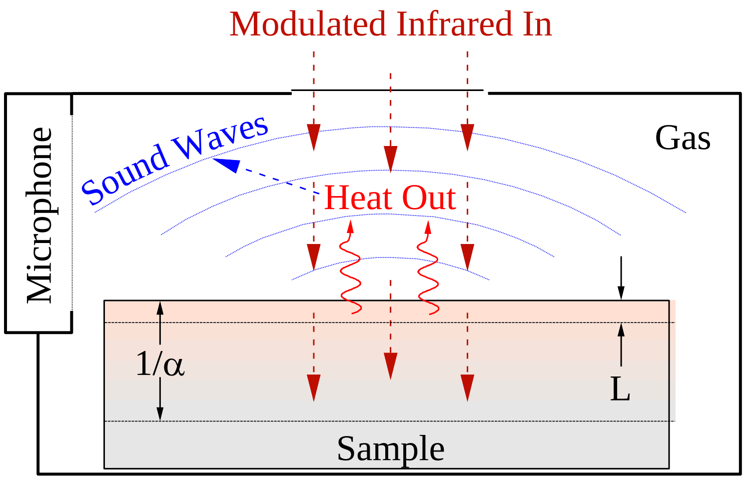
# FT-IR PAS Instrumentation



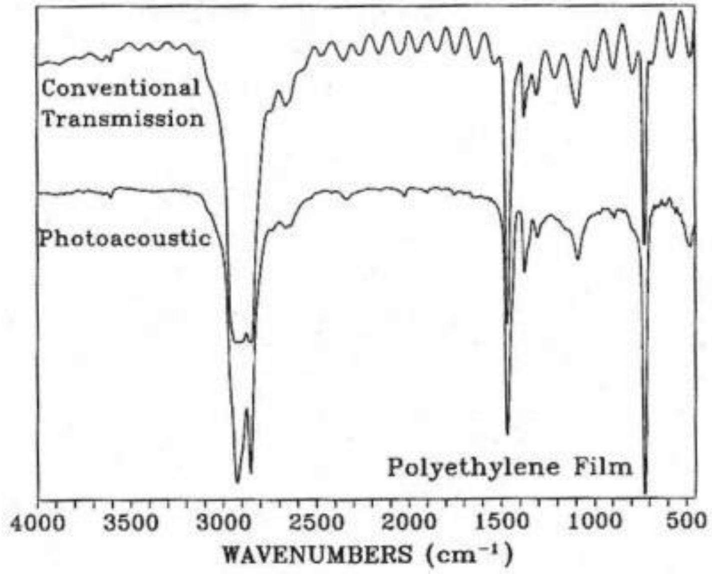
# FTIR-PAS Spectrometer Schematic



# PAS Signal Generation



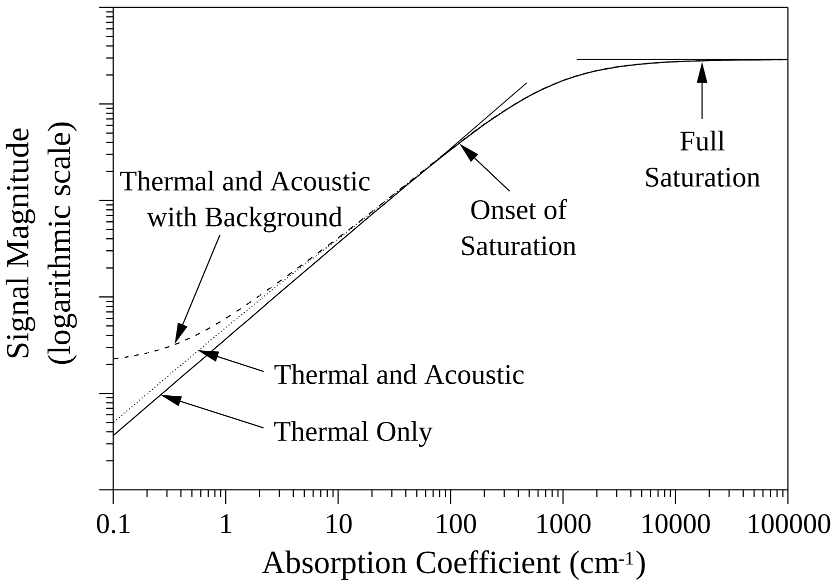
α = absorption coefficient     L = thermal diffusion length

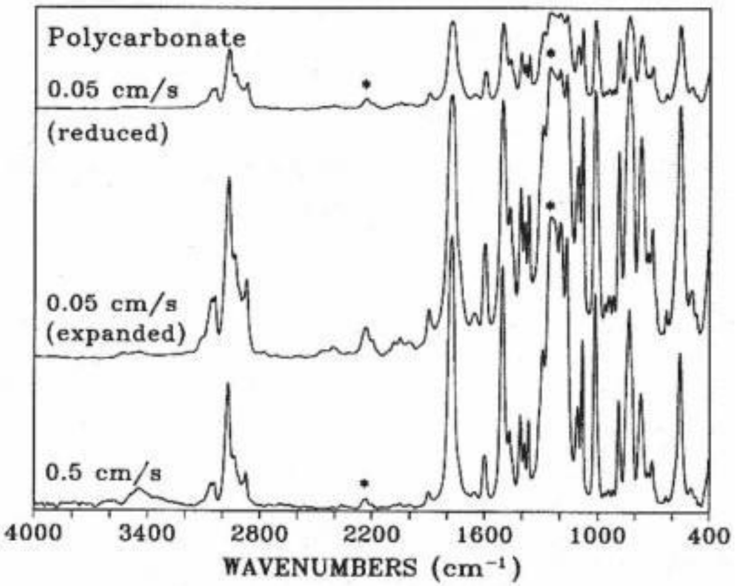


Absorption of intensity-modulated light within the sample results in temperature oscillations and generation of thermal waves resulting in thermal expansion driven pressure oscillations in the gas above the sample. A microphone senses these oscillations as the PAS signal. L and 1/α are the decay lengths for thermal and light waves propagating within the sample.

The direct detection of light absorption in the sample by the heat produced and subsequent acoustic signal results in the absence of interference effects often seen in transmission and reflection spectra of thin films. The spectra plotted above demonstrate this where the photoacoustic spectrum has been converted to a transmission spectrum for comparison.

# PAS Signal Generation

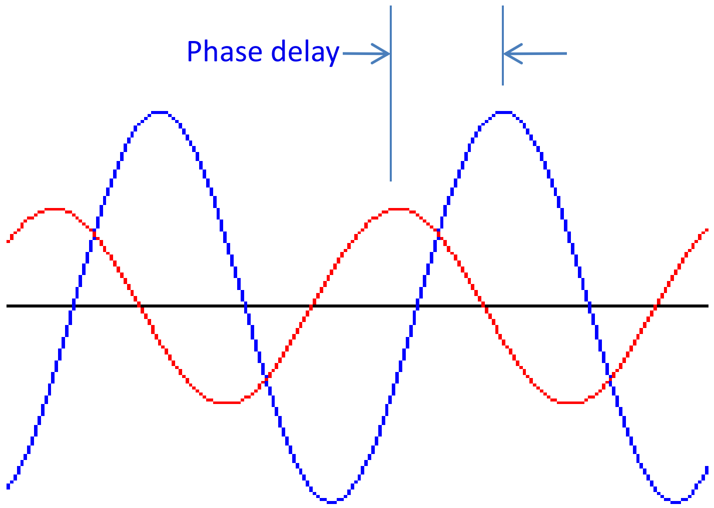


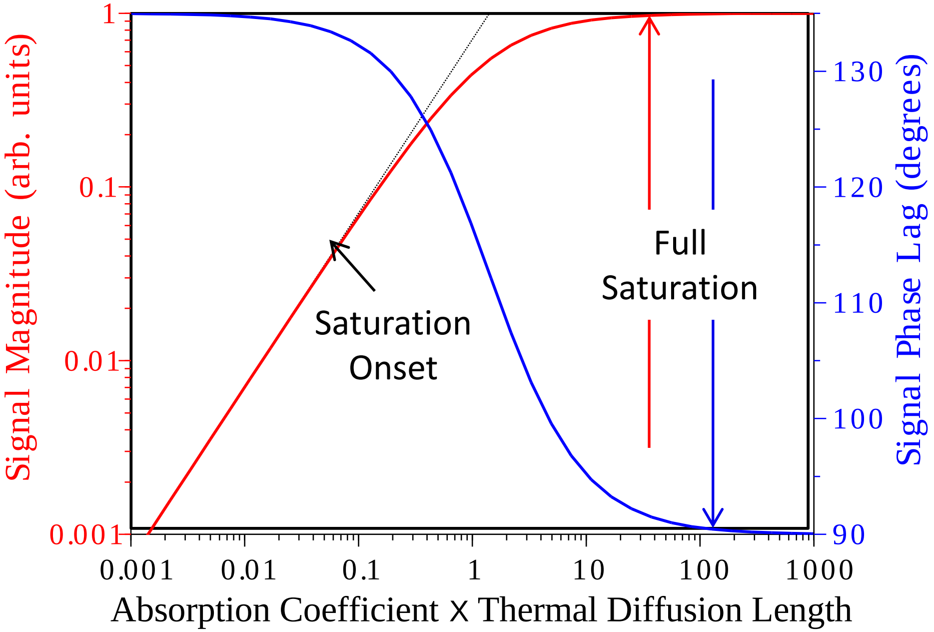


As the absorption coefficient increases, the amount of heat deposited within the layer defined by L increases causing the photoacoustic signal to increase with α thus allowing absorption spectra to be measured. At high values of α, all of the heat is deposited just below the surface of the sample resulting in signal saturation and truncation of strong absorption peaks.

These spectra illustrate the truncation of strong absorbance bands and how it is reduced when the modulation frequencies are increased. The top low frequency spectrum and the bottom high frequency spectrum have been scaled so that the weak unsaturated peak heights near 2200 $cm^{-1}$ are equal. The stronger bands of the top spectrum are all truncated and even when the top spectrum is rescaled for the middle spectrum truncation is present.

# The PAS Signal Has Magnitude and Phase Components



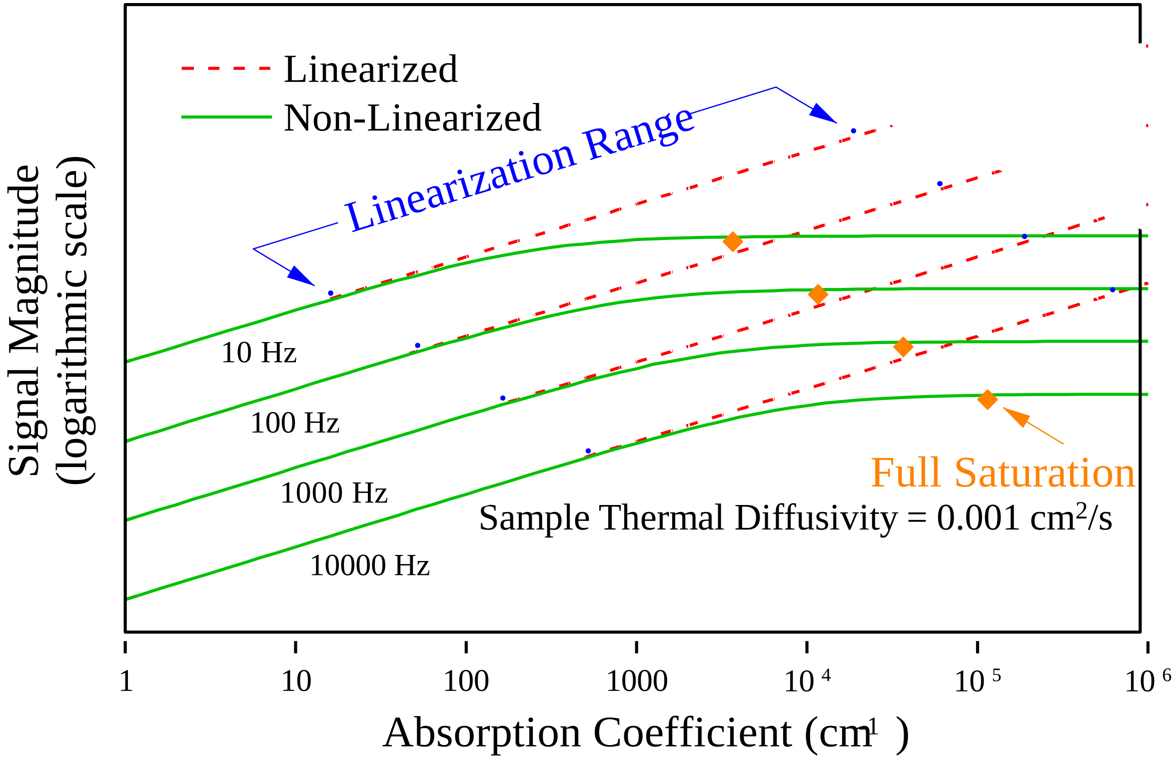


At very high values of α, the PAS response is delayed in phase by 90° relative to the IR beam waveform whereas at very low α the waveform is delayed by a total of 135° due to the longer propagation time required for thermal waves generated deeper within the sample.

This plot shows how the PAS signal magnitude and phase vary with a sample’s absorption coefficient, α. Note that the phase reaches full saturation at higher absorption values than the magnitude. Both of these components can be combined using a theoretical PAS signal generation model to produce “linearized” spectra that move the onset of saturation to higher values of α (see http://tiny.cc/pqgt9).

# Photoacoustic Signal Linearization

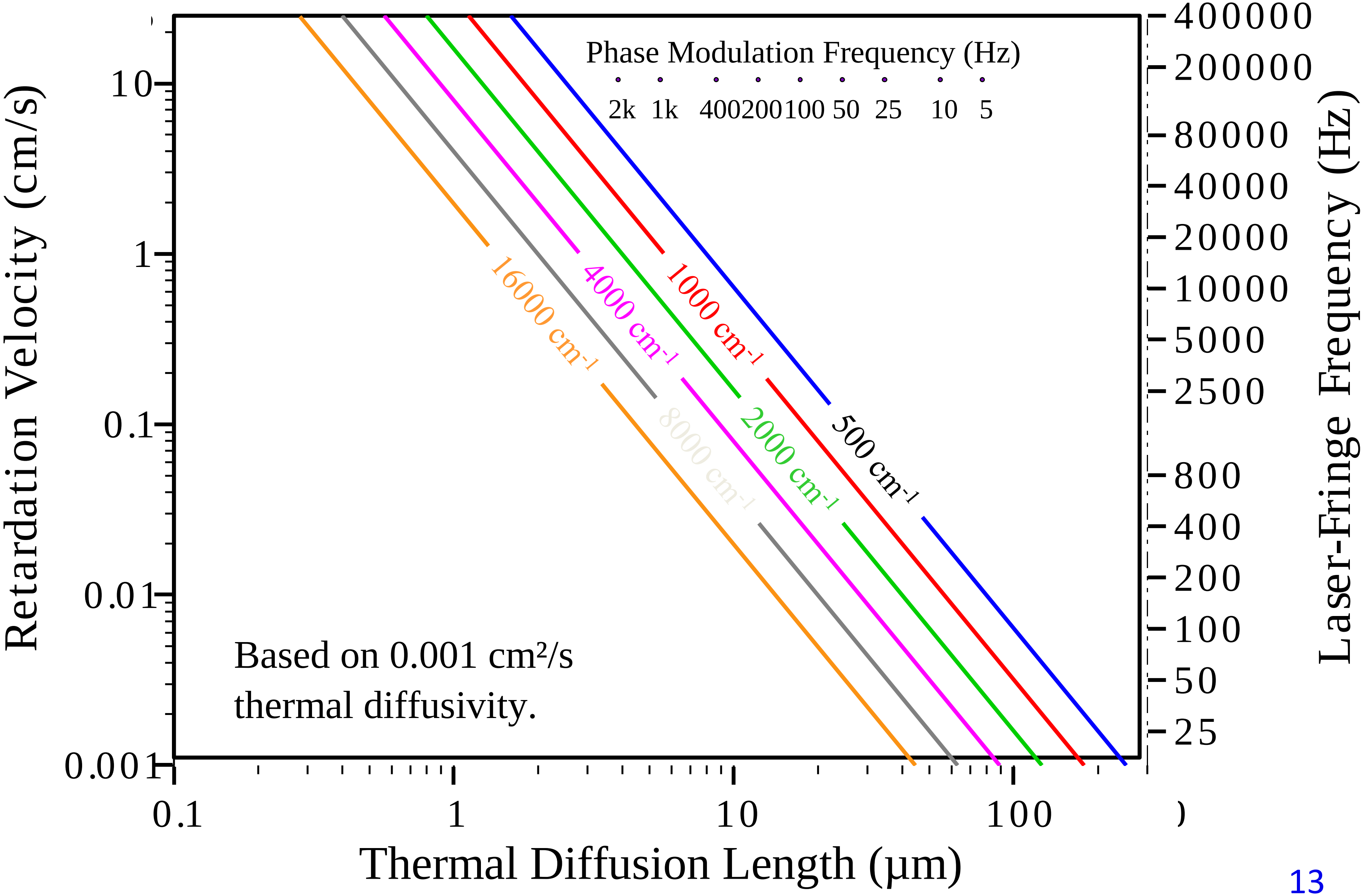
The phase of the photoacoustic signal saturates at higher values of the absorption coefficient as shown in the last figure and this allows calculation of a "linearized" spectrum that has a linear dependence extending to higher values of the absorption coefficient. This reduces the truncation of strong absorbance peaks which are troubling to classical spectroscopists but turn out to actually have little influence when modern chemometrics are use in both quantitative and qualitative analyses. Linearization, however, is very useful in reducing sampling depth and increasing surface specificity as illustrated later in the case of a siloxane treated fabric.



# PAS Sampling Depth

- With rapid scan FTIRs sampling depth, L, depends on the interferometer's OPD mirror velocity, v, the sample's thermal diffusivity, D, and the wavenumber, $\nu$, at a particular point in a spectrum.
- L is defined as the reciprocal of the thermal wave decay coefficient, $a_s = (\pi f/D)^{1/2}$ because thermal oscillations in the gas, where the PA signal is generated, are not efficiently driven, due to thermal wave decay, from deeper than $L = (D/\pi v \nu)^{1/2}$, where the IR beam modulation frequency, $f = v\nu$.
- With step-scan FTIRs sampling depth is constant across the spectrum and controlled by the phase modulation frequency, $f_m$, and given by $L = (D/\pi f_m)^{1/2}$.
- L only defines the sampling depth if the sample's absorption coefficient, $\alpha$, in the spectral region of interest, is low enough to allow light to penetrate deeper than L. If this is not the case, the sampling depth is determined by the decay of light waves rather than of thermal waves and is given by $1/\alpha$ .

# PAS Sampling Depth



Based on 0.001 cm²/s thermal diffusivity.

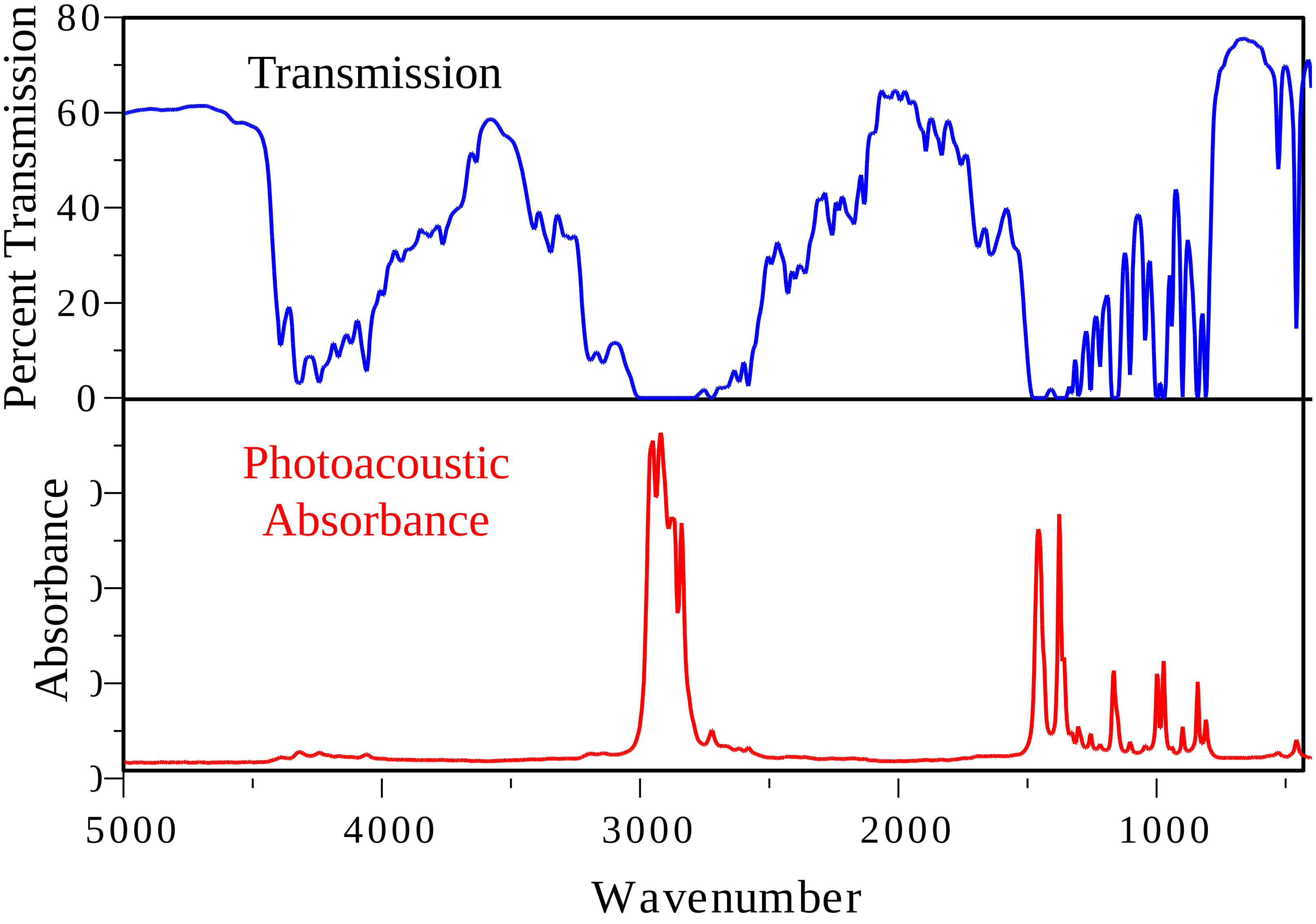
# An example of the importance PAS sampling depth in the case of a 0.57 mm thick polypropylene sample

- A 0.57 mm sample is too thick for a transmission measurement.

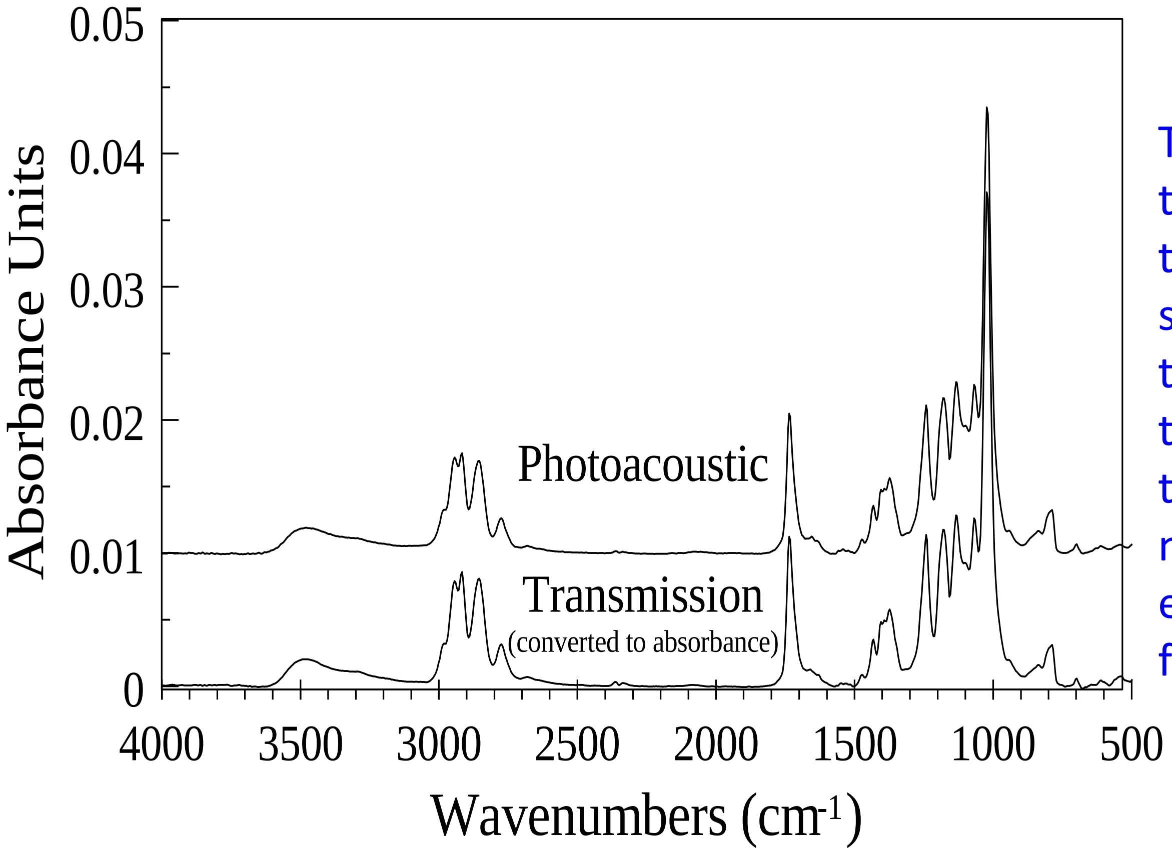
- PAS samples a thickness less than the sample’s physical thickness and produces excellent spectra without sample preparation.

- This is the a key advantage of PAS over transmission spectroscopy.

# Polypropylene Sample 0.57 mm Thick



# How Do PAS and Transmission Spectra Compare When Sampling Depths Are Equal?



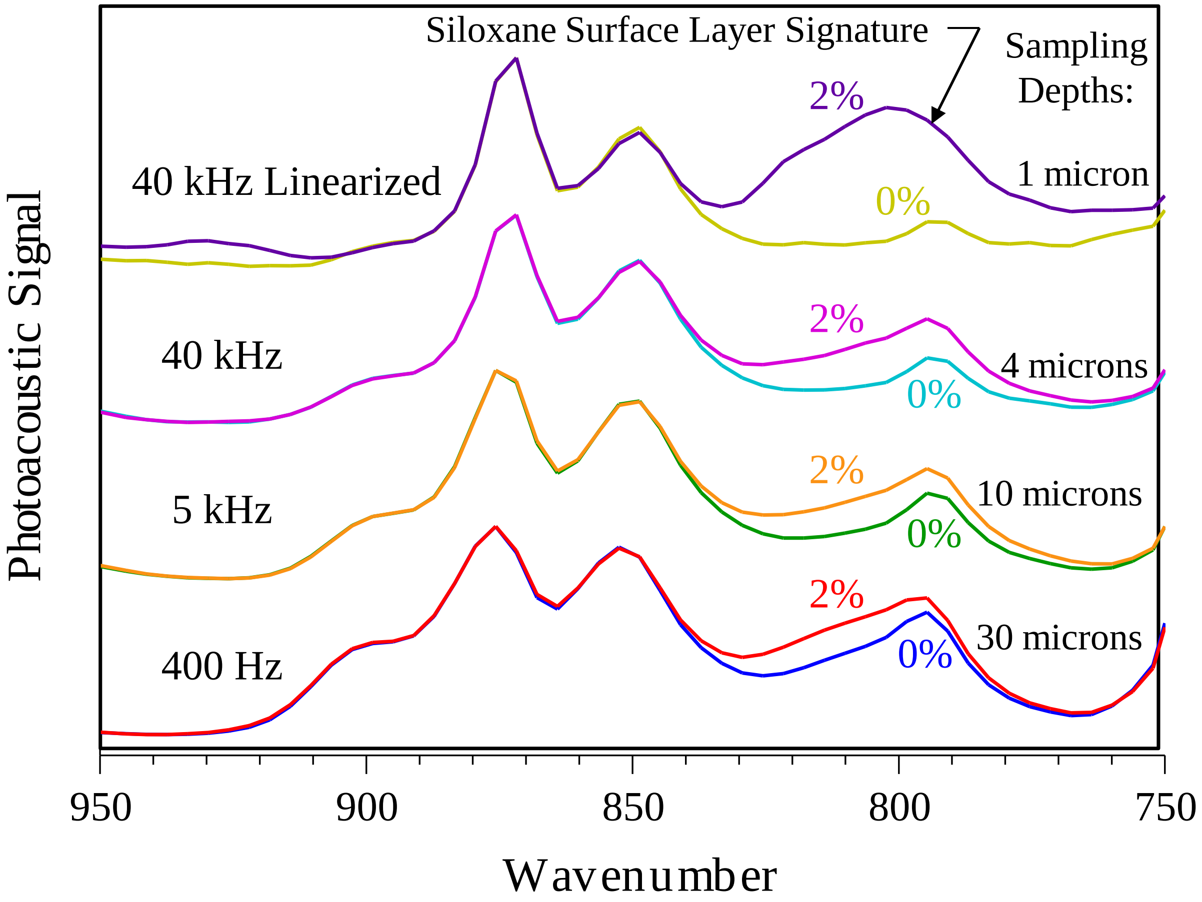
Thse Formvar polymer thin film spectra measured by transmission and photoacoustic spectroscopies show that the two spectra are identical when the sample is very thin, which in this case was approximately 30 nm. Sampling depths are essentially equal with very thin films.

# Varying Sampling Depth to Observe Surface Layers

- Example of surface treatment of a fabric with Siloxane.
- At what concentration does a layer form on the fabric surface?
- Varying the sampling depth of the PAS spectra allows the layer and its depth variation to be observed.
- Note how linearization enhances surface specificity.

# Surface Layer Present at 2% Concentration

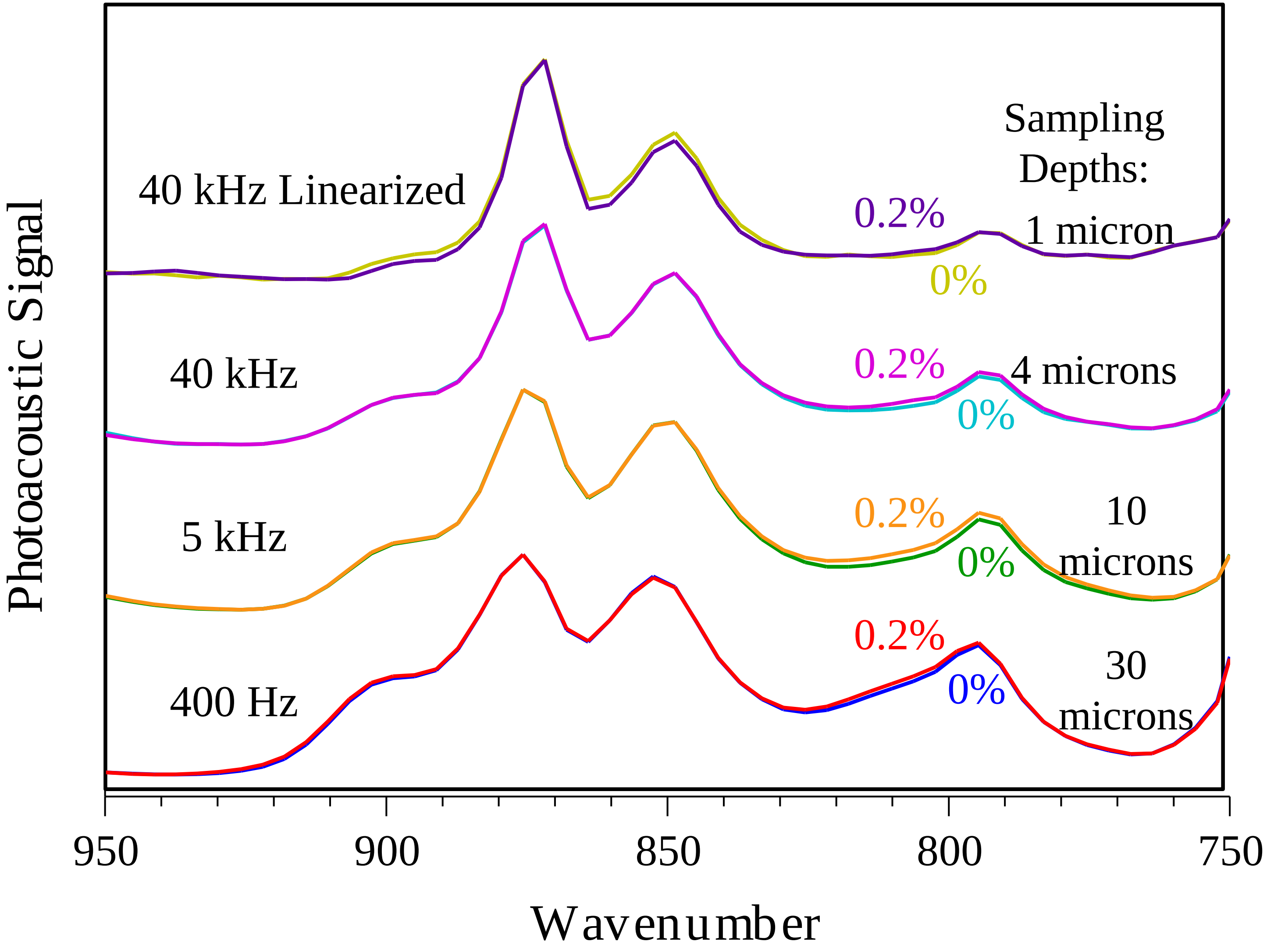
## PA Spectra Untreated and 2% Siloxane-Treated Fabric



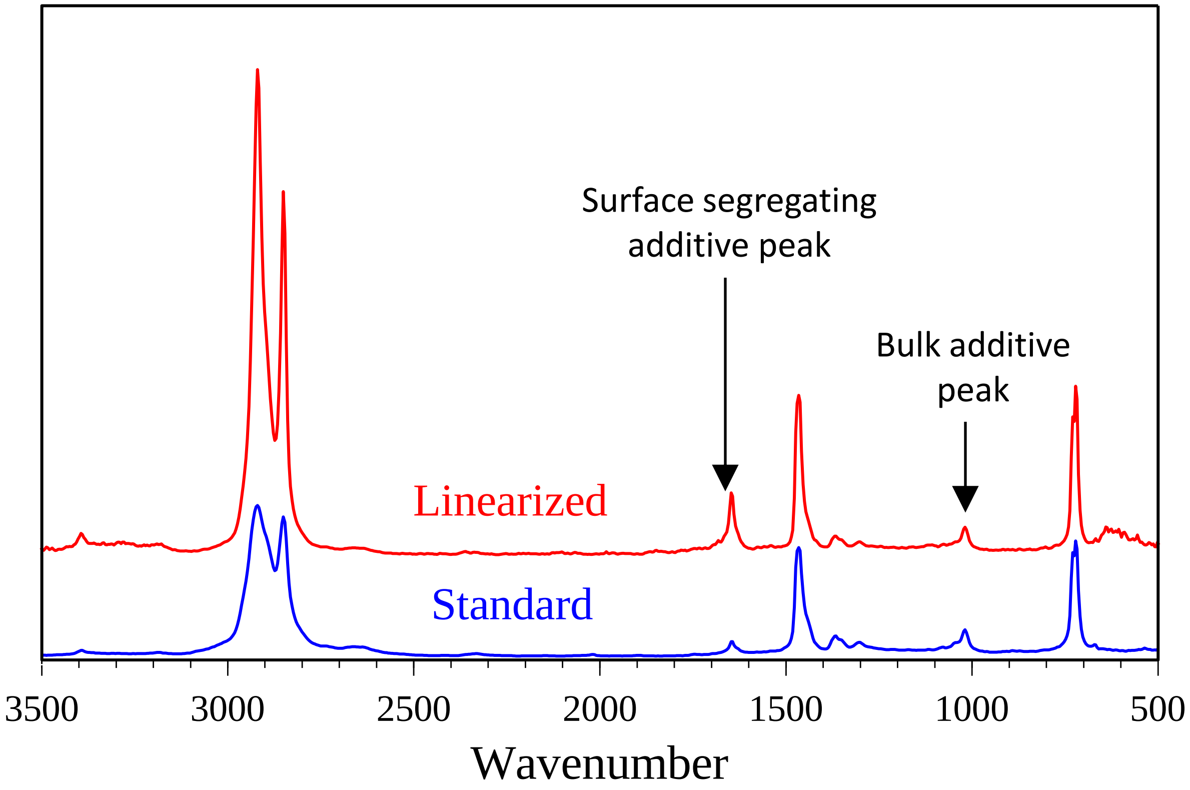
Linearization of the PAS signal allows the siloxane surface layer to be observed and one to see that it is primarily concentrated in a layer approximately one micrometer in thickness.

# Surface Layer Not Present at 0.2% Concentration

PA Spectra Untreated and 0.2% Siloxane-Treated Fabric



# Polyethylene Pellets with a Surface Additive

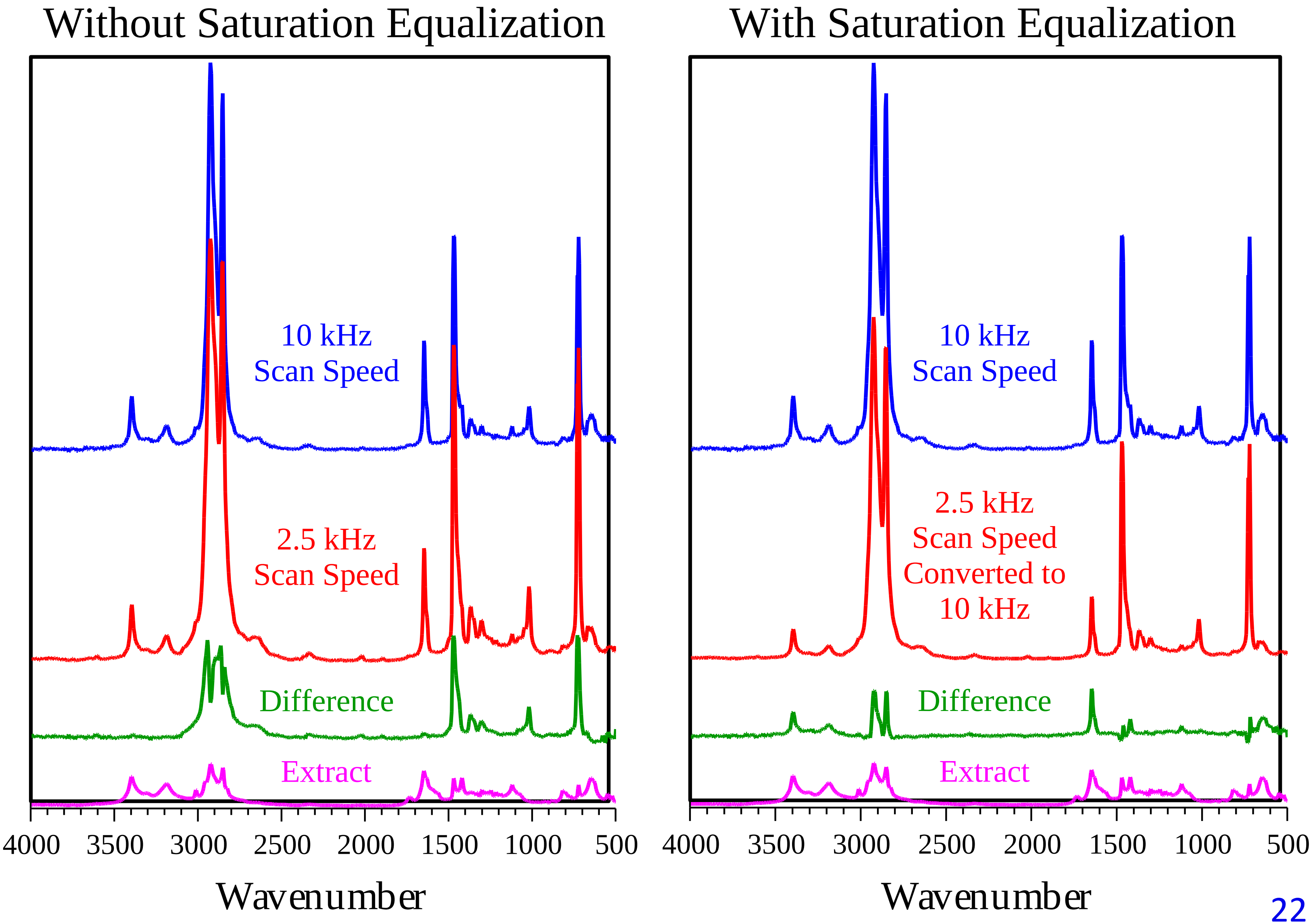


Linerarization can also be used to distinguish between surface segregating and bulk additive peaks. The deeper sampling blue spectrum's surface segregating peak is smaller than the bulk additive peak but the reverse is true for the shallower sampling red linearized spectrum. Its greater surface specificity increases the height of the surface segregating peak.

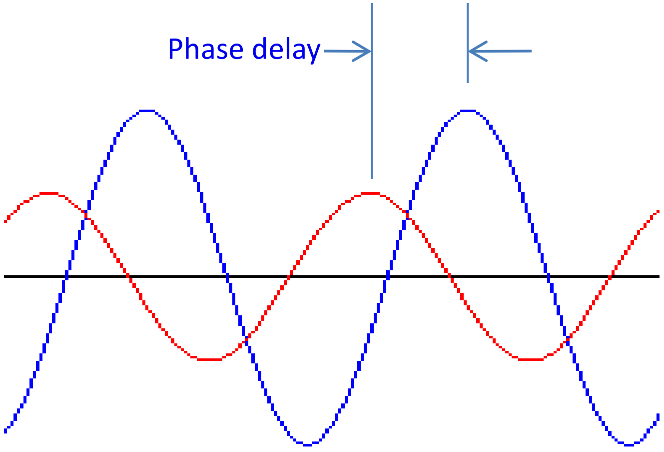
# Spectral Subtraction of Depth Varying Spectra

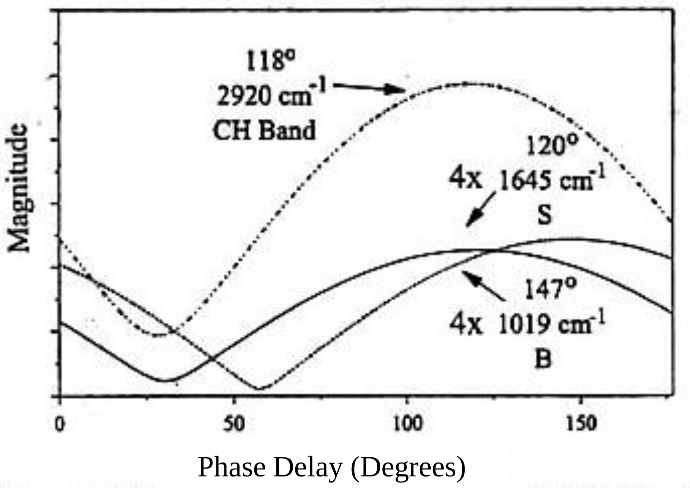
- Spectra of thin surface layers of samples can be obtained by spectral subtraction of a deeper (lower mirror velocity) from a shallower (higher mirror velocity) spectrum.
- Before subtracting, however, it is necessary to mathematically reduce the degree of saturation in the low frequency spectrum so that is equal to that in the higher frequency spectrum (see: http://tinyurl.com/3vm7plo).
- The next figure illustrates how the spectrum of a surface segregating polymer additive on polyethylene pellets can be isolated by this method. Note that the saturation equalization difference spectrum agrees well with the extracted surface additive spectrum while the bulk additive peak near 1000 $cm^{-1}$ appears in neither the extract nor the difference spectrum plotted above.

# Isolating the Spectrum of an Additive



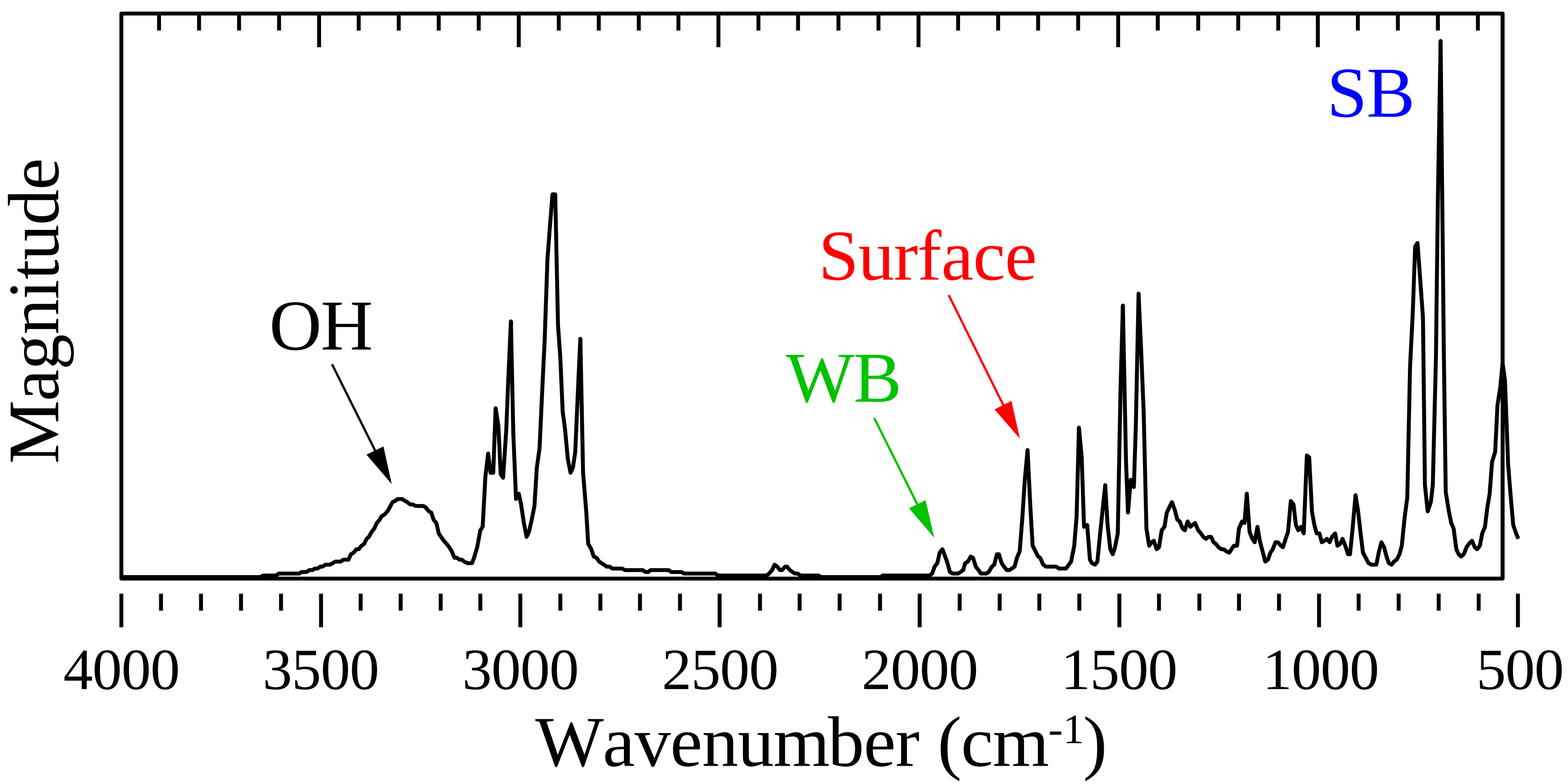
# Phase Analysis



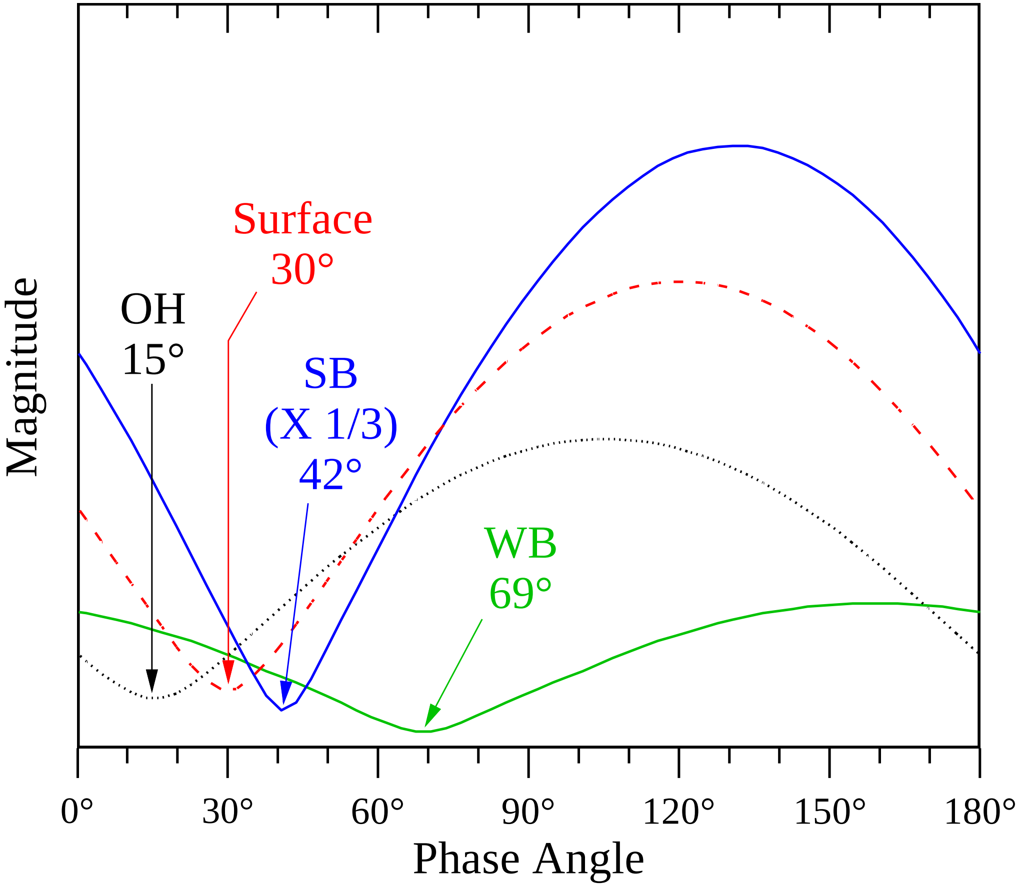


As mentioned in the signal generation discussion, the photoacoustic signal has both a magnitude and a phase. At low absorption values, heat is developed deep within the sample and its transit time to the gas is longer than for high absorption which heats near the surface. This results in a phase delay in the signal. Phase delays in the photoacoustic signal of homogeneous samples are due solely to the sample’s absorption coefficient variations whereas gradient or layered samples can also have phase differences due to absorption depth differences related to their geometry. The plot on the right shows the signal magnitude vs. phase behavior for three points in the spectrum of polyethylene pellets which has surface segregating and bulk additives. The minimum of the bulk additive band (B) lags the minima of the very strong C-H and the surface segregating (S) bands as expected.

# Chemically Modified Polymer Surface

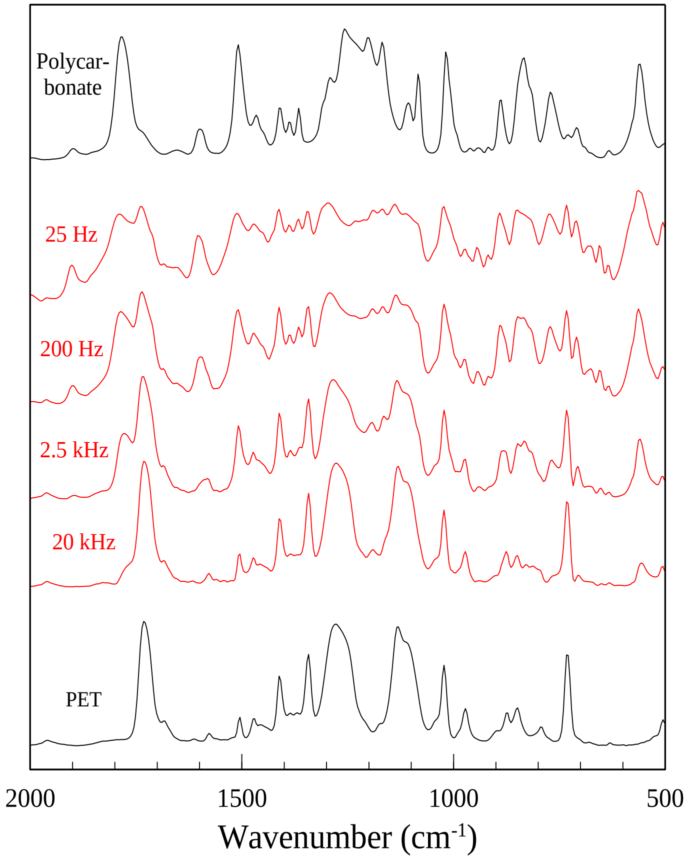


# Phase Analysis for a Surface Treated Polymer

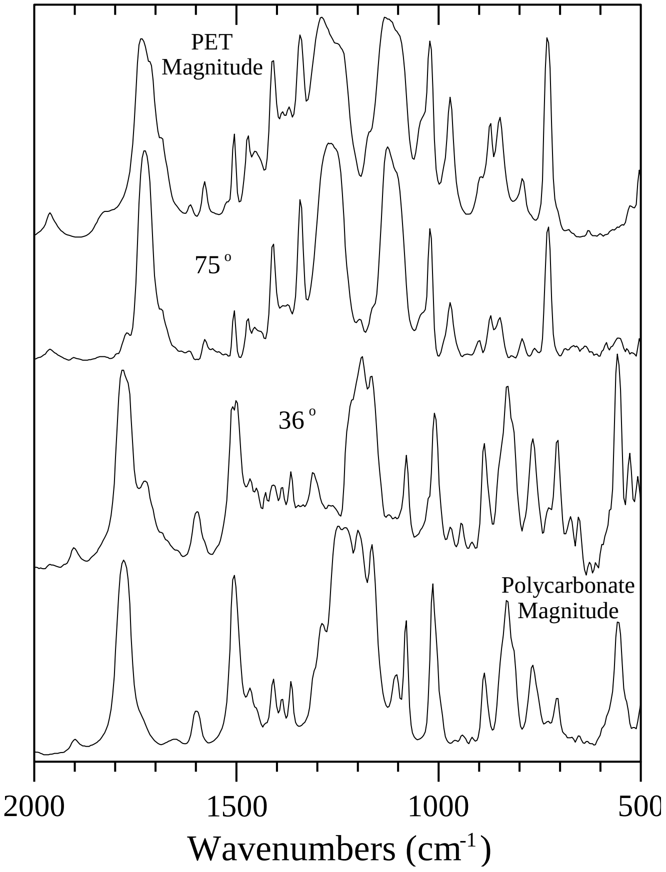


The photoacoustic signal vs. phase plot reveals that the OH species have formed a layer on top of the surface treatment layer.

# Comparison of Varying Sampling Depth by Modulation Frequency and Phase Angle Selection

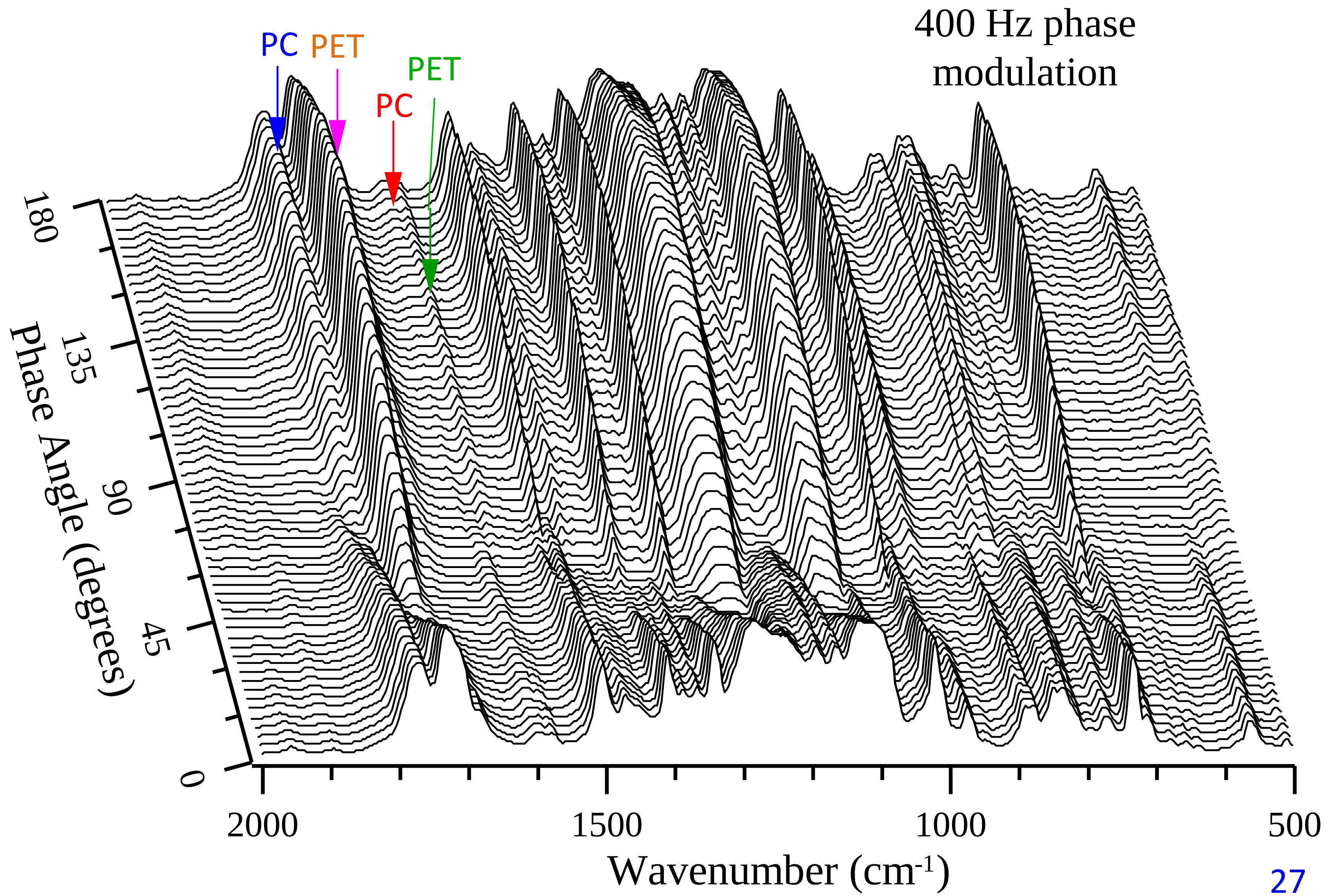


Magnitude spectra of a PET/PC assembly with sampling depth varied by modulation frequency.

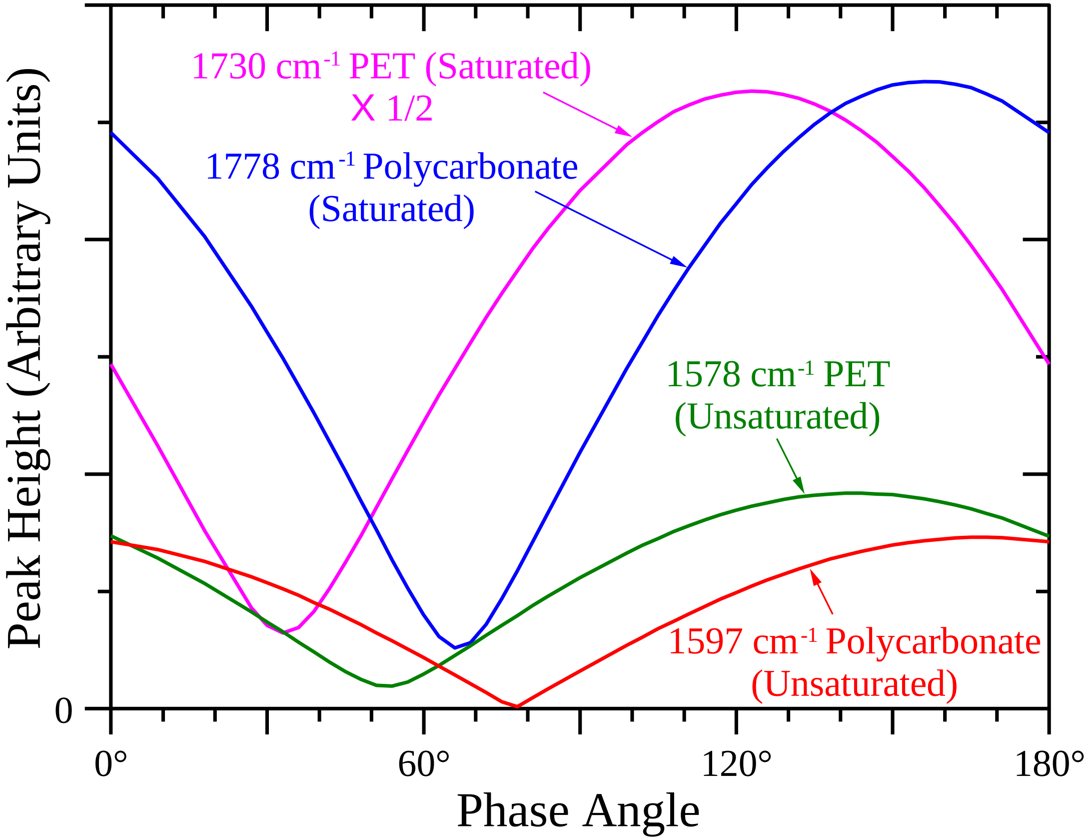


Phase angle selected magnitude spectra of PET/PC assembly show features of the two components more clearly.

# Phase Modulation Spectra of PET/PC Layer Assembly

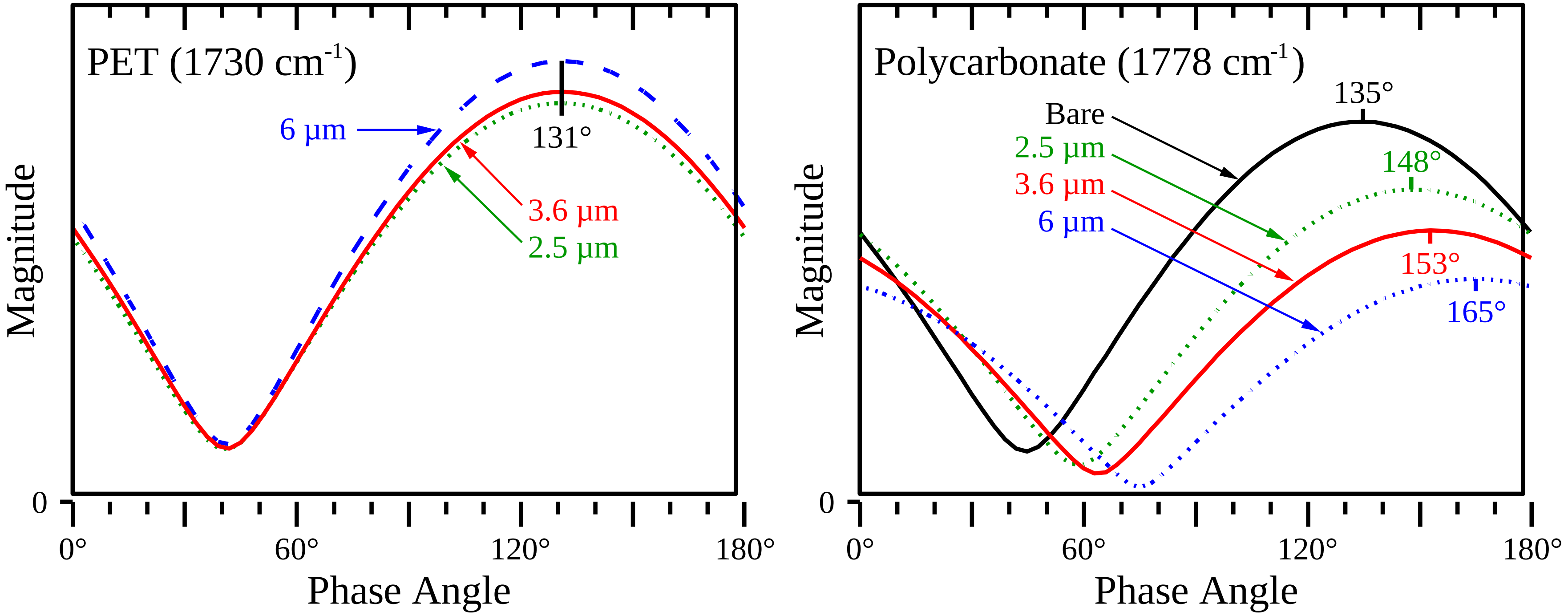


# Magnitude vs. Phase Plot for PET/PC Assembly



The minima of both the saturated and unsaturated PET peak magnitudes lead those of the PC peaks which indicates that PET is the top layer of the assembly.

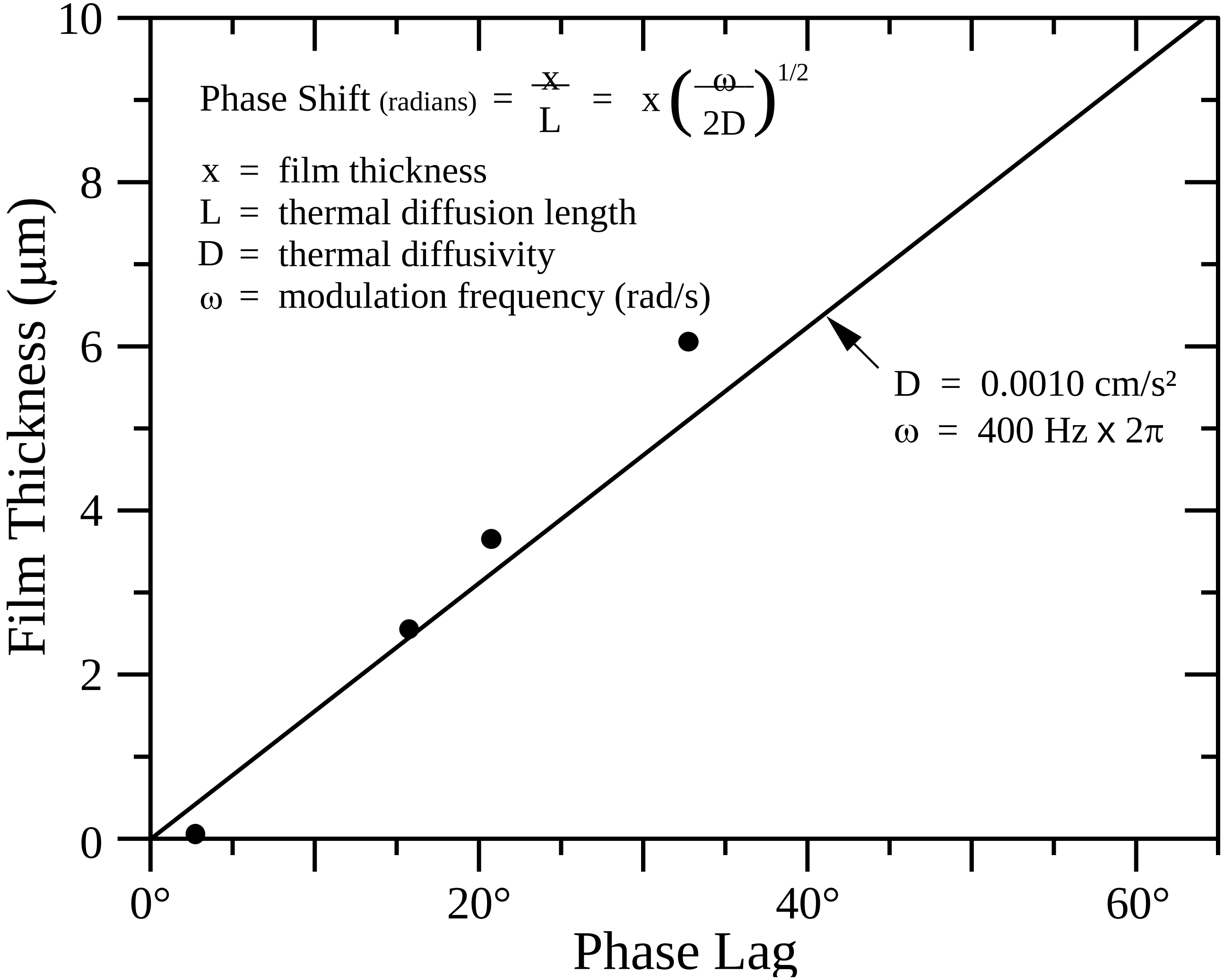
# Phase Dependence on Depth for Varying Thicknesses of PET on a PC Substrate



Increasing thicknesses of PET on PC progressively delays the phase of the signal from the 1778 cm$^{-1}$ PC peak relative to the phase of the 1730 cm$^{-1}$ PET peak which remains constant when the PET thickness is changed. 400 Hz Phase Modulation

# PET Layer Thickness from Photoacoustic Phase

1778 cm$^{-1}$ Polycarbonate Peak



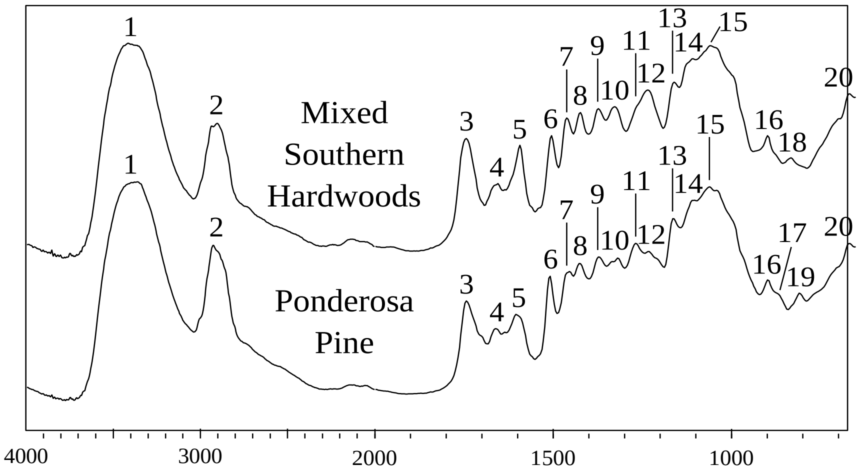
$$\text{Phase Shift}_{\text{(radians)}} = \frac{x}{L} = x\left(\frac{\omega}{2D}\right)^{1/2}$$

$x$ = film thickness
$L$ = thermal diffusion length
$D$ = thermal diffusivity
$\omega$ = modulation frequency (rad/s)

$D$ = 0.0010 cm/s$^2$
$\omega$ = 400 Hz x 2$\pi$

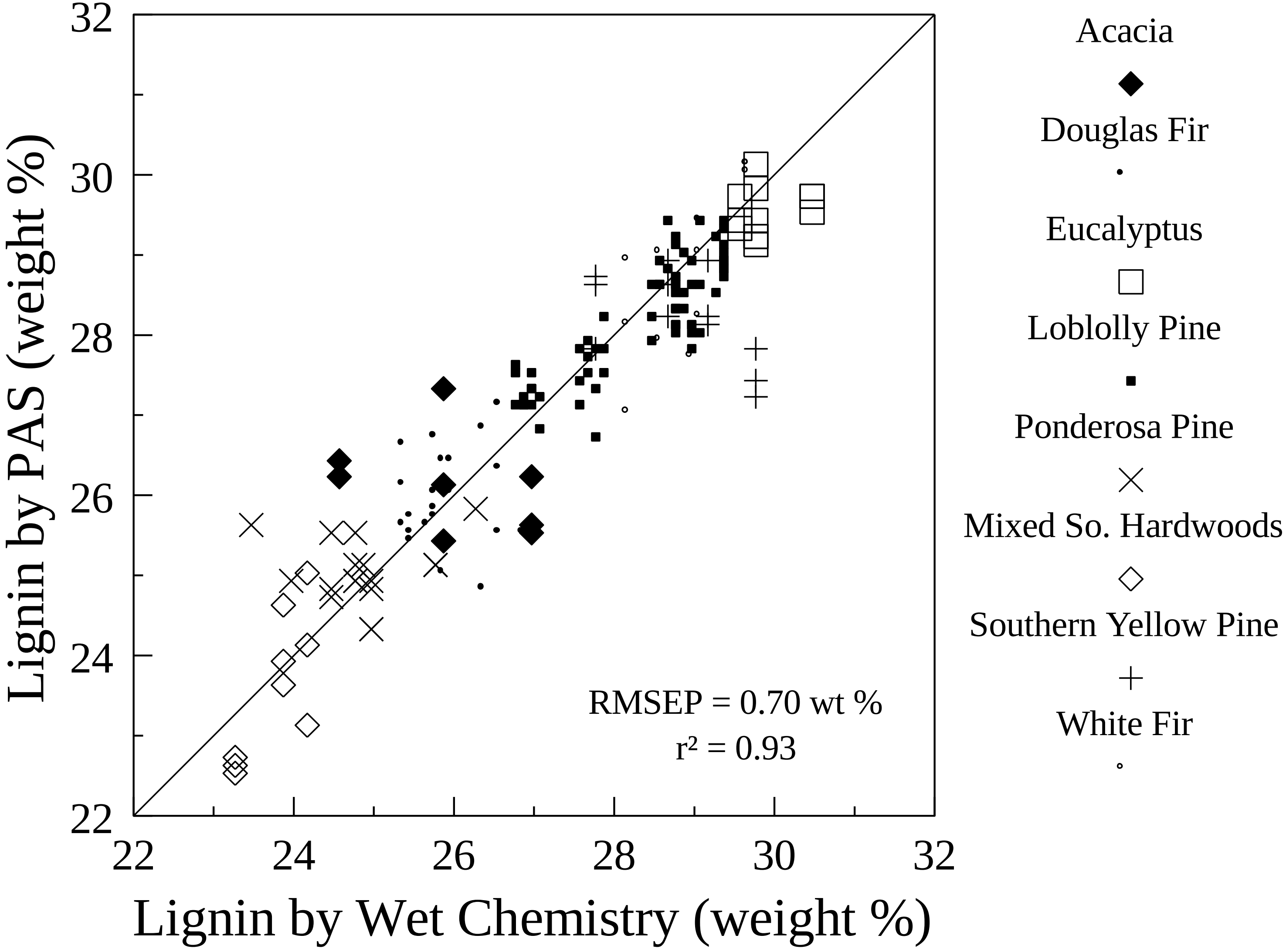
# Chemometric Analysis of FTIR Photoacoustic Spectra of Wood

## Peak Assignments for Woods



| | | |
|---|---|---|
| 1 | 3400 | Bonded O–H stretching |
| 2 | 2900 | C–H stretching |
| 3 | 1730 | C=O stretching in xylan |
| 4 | 1660 | Keto-carbonyl conjugated with benzene ring |
| 5 | 1600 | Benzene ring stretching in lignin |
| 6 | 1505 | Benzene ring stretching in lignin |
| 7 | 1460 | $CH_3$ deformation in lignin and $CH_2$ bending in xylan |
| 8 | 1425 | $CH_2$ scissor vibration in cellulose |
| 9 | 1370 | $CH_2$ bending in cellulose and hemicellulose |
| 10 | 1325 | $CH_2$ wagging vibration in cellulose |
| 11 | 1275 | Guaiacyl nuclei in lignin |
| 12 | 1230 | Syringyl nuclei in lignin and C=O in xylan |
| 13 | 1160 | C–O–C asymmetric band in cellulose & hemicellulose |
| 14 | 1110 | O–H association band in cellulose and hemicellulose |
| 15 | 1050 | C–O stretching band in cellulose and hemicellulose |
| 16 | 895 | C1 group frequency in cellulose and hemicellulose |
| 17 | 870 | 1,3,4-substituted benzene ring in softwood lignin |
| 18 | 830 | 1,3,4,5-substituted benzene ring in hardwood lignin |
| 19 | 810 | 1,3,4-substituted benzene ring in softwood lignin |
| 20 | 680 | COH out-of-plane bending in cellulose |

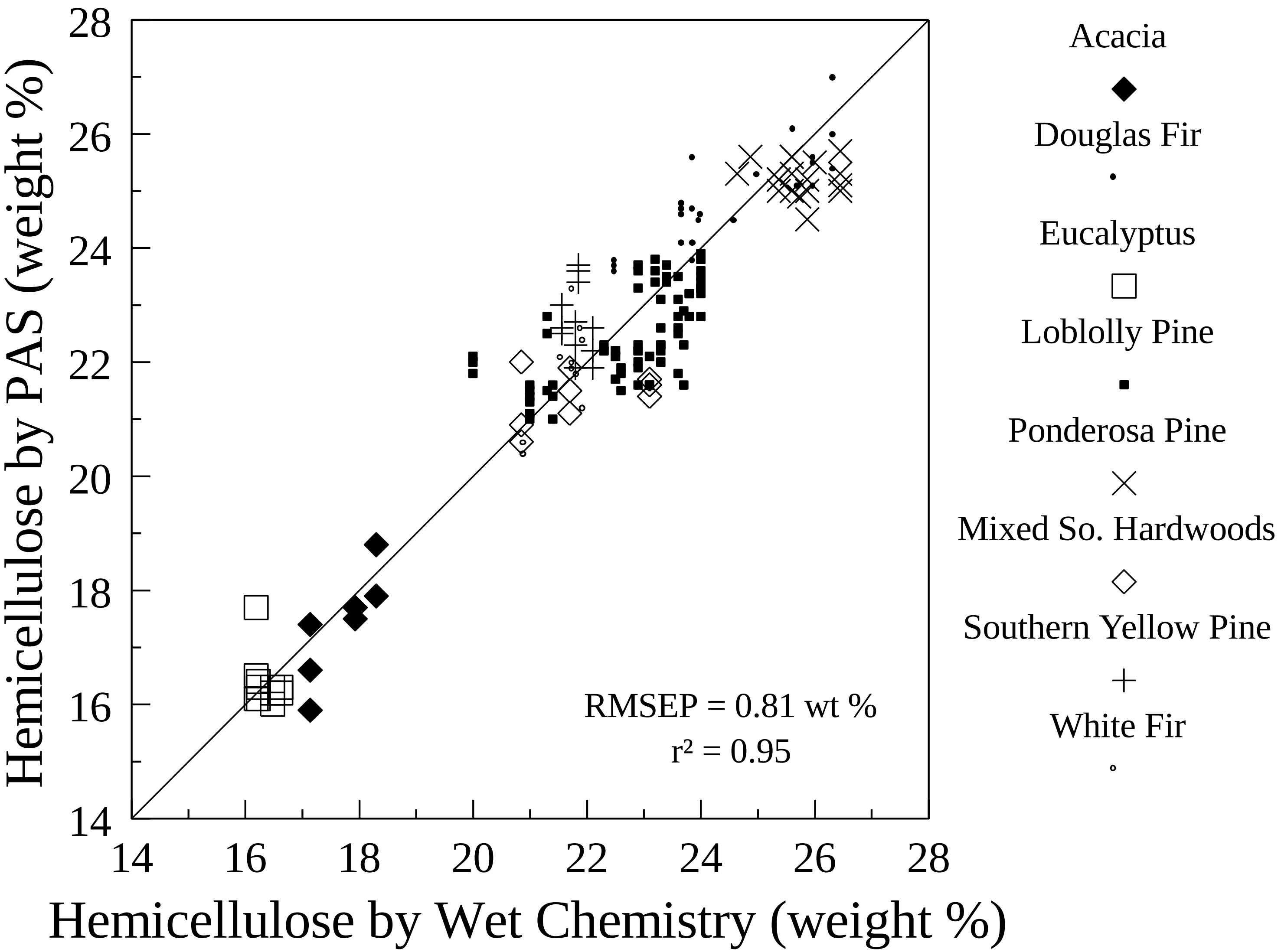
# FTIR Spectra + Chemometrics ➡ Lignin Composition



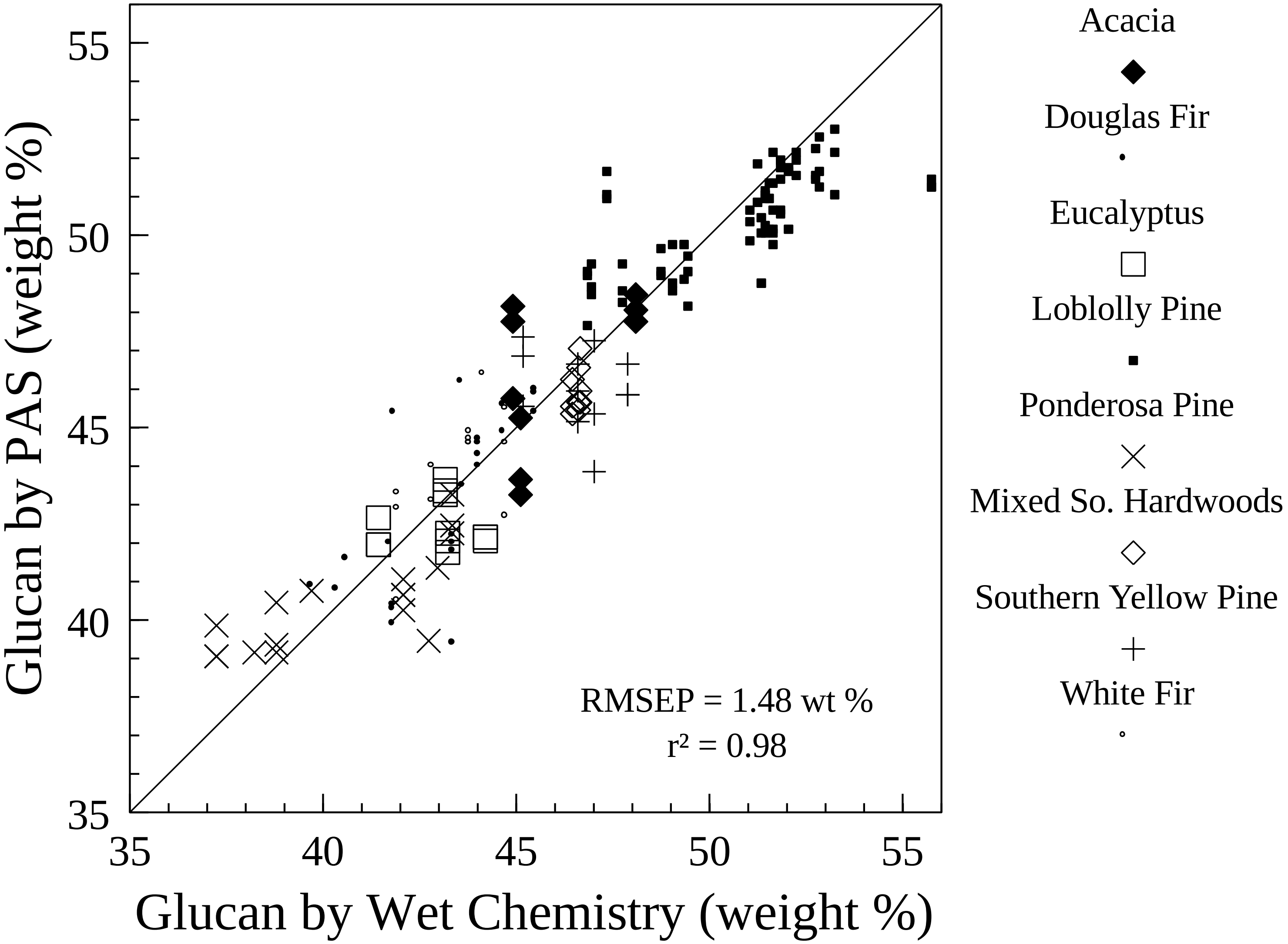
RMSEP = 0.70 wt %

$r^2 = 0.93$

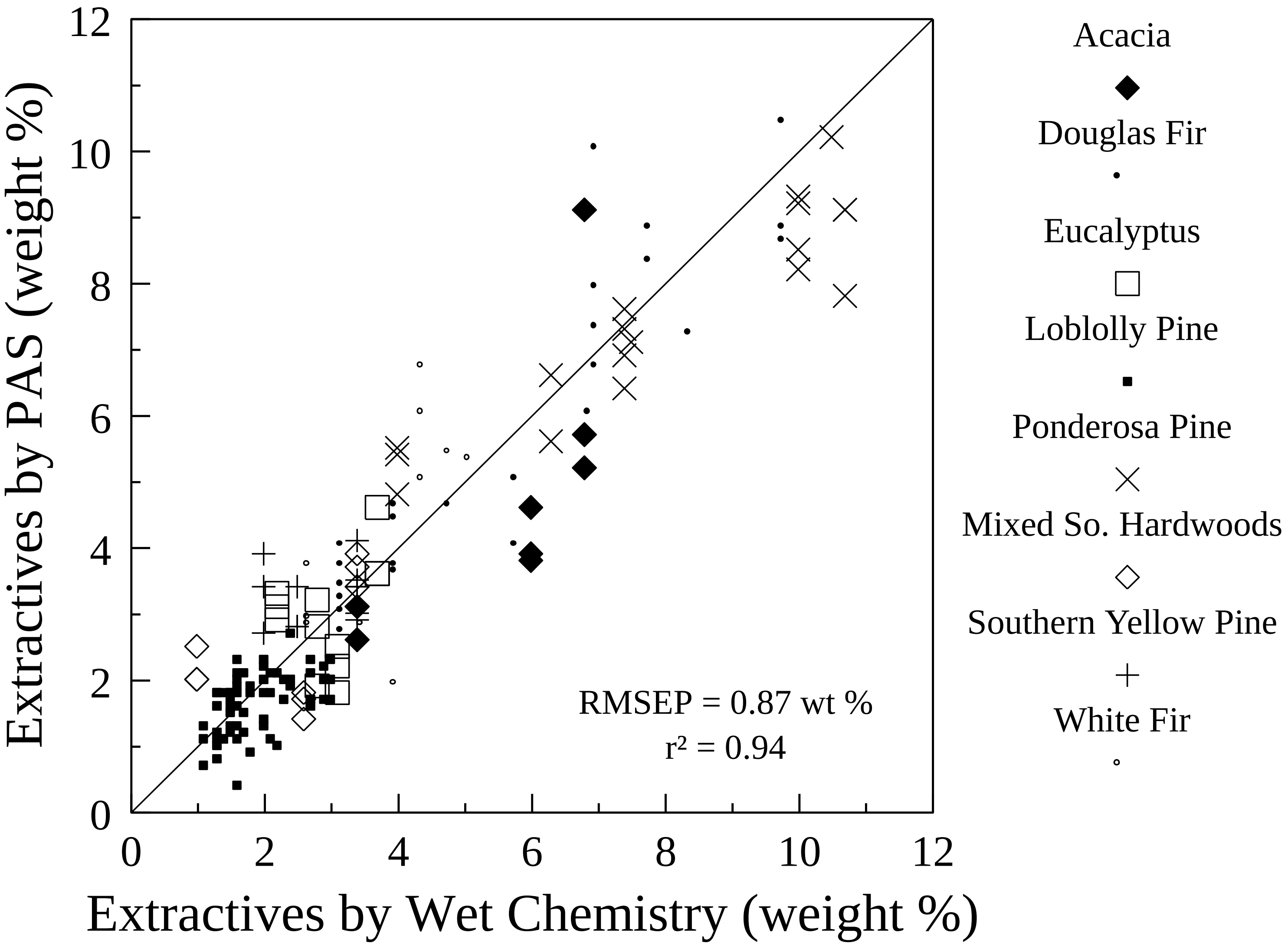
# FTIR Spectra + Chemometrics ➡ Hemicellulose



# FTIR Spectra + Chemometrics ➡ Glucan

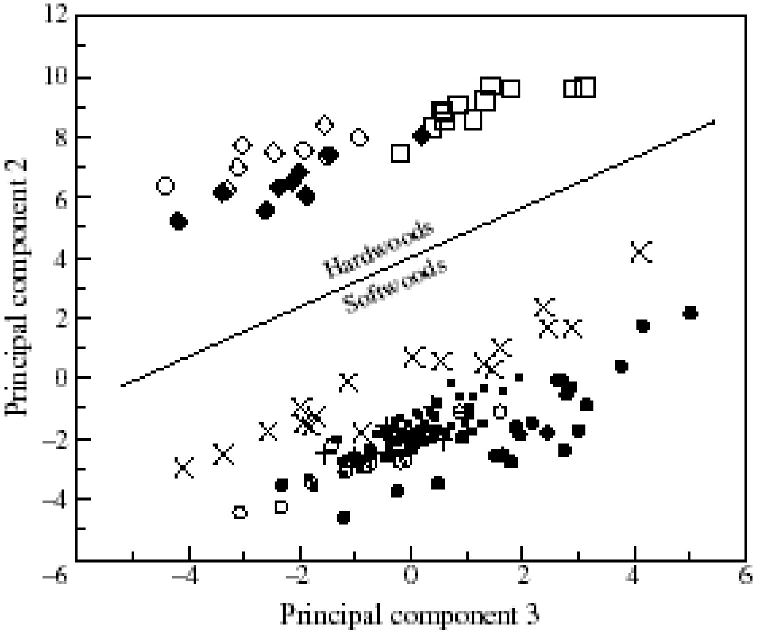


# FTIR Spectra + Chemometrics ➡ Extractives

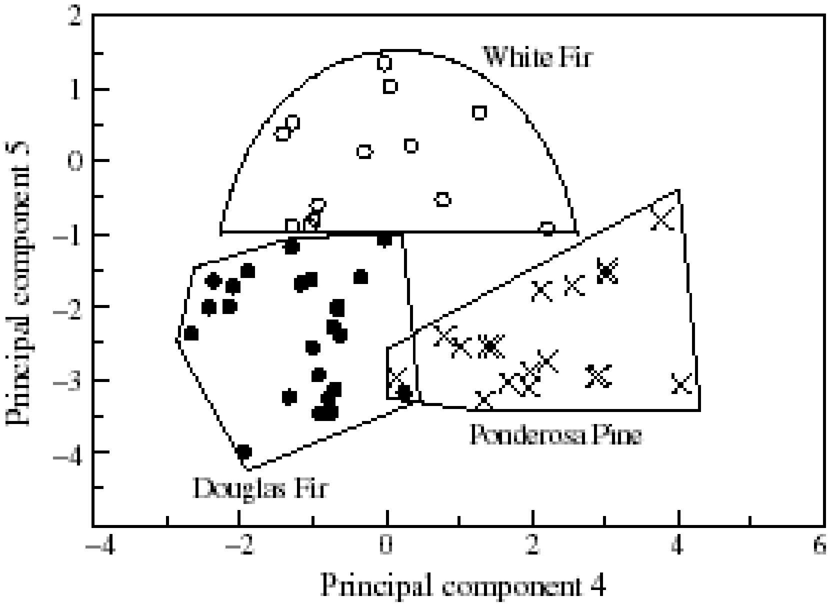


RMSEP = 0.87 wt %
$r^2 = 0.94$

# Qualitative Wood Analyses



Classifying Hardwoods from Softwoods



Classifying Species of Softwoods

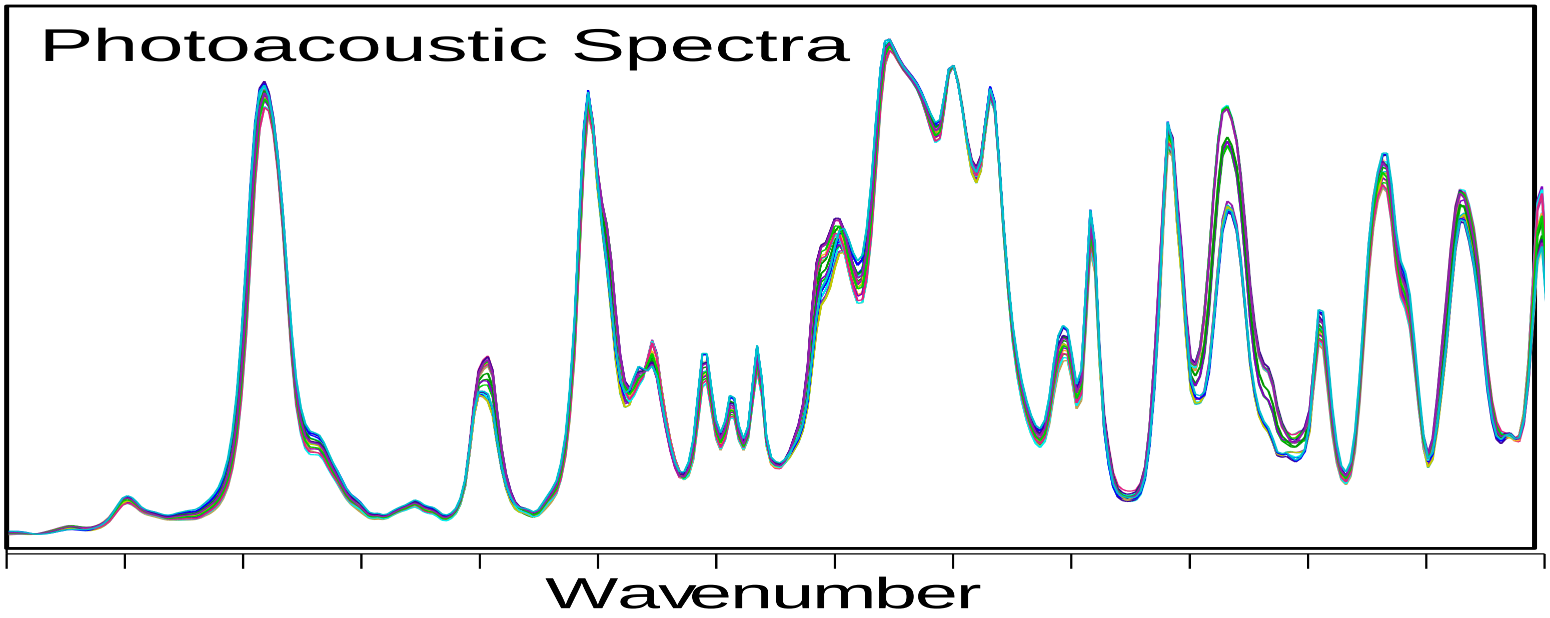
# Comparision of PAS and ATR for Quantitative Analysis of Polymer Blends in Pellet Form

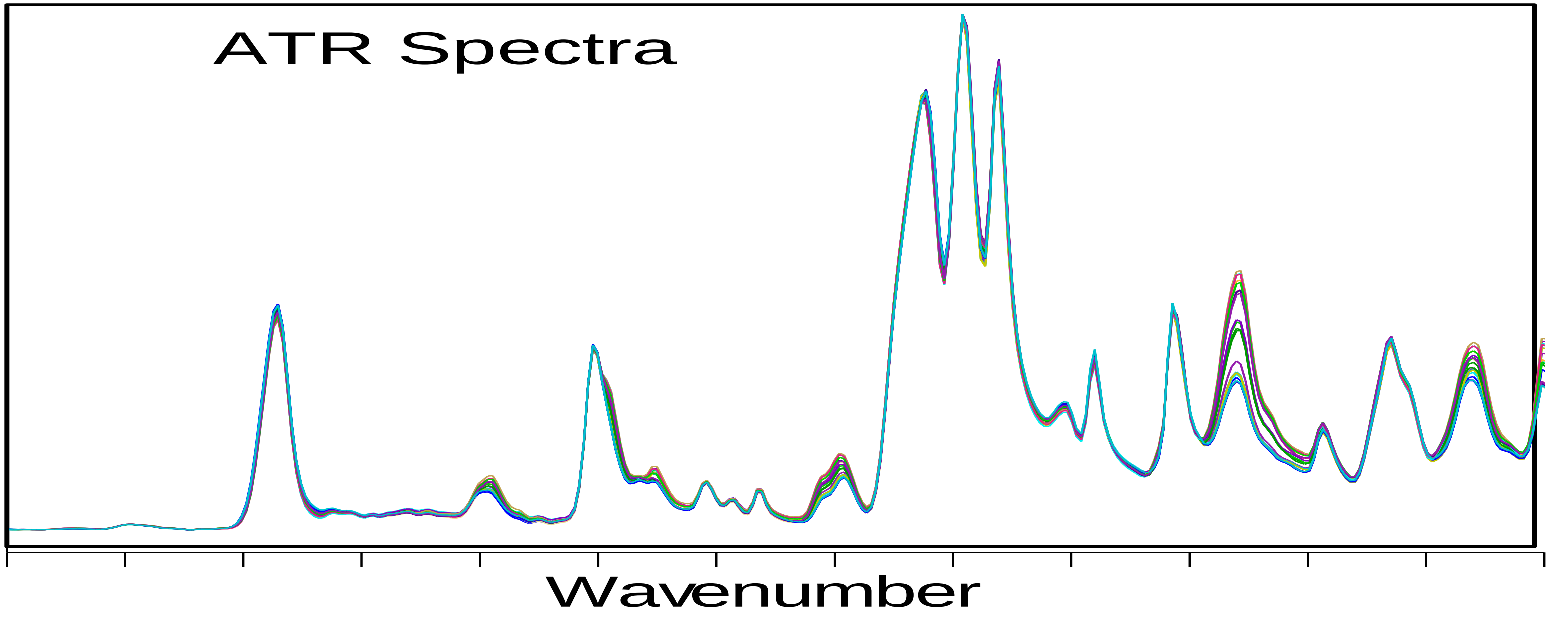
## Standard Error of Prediction (SEP) (wt %) Results

| Blend/Component | PAS/SEP | ATR/SEP |
|---|---|---|
| 2/A | 0.56 | 0.70 |
| 2/B | 0.20 | 0.30 |
| 2/C | 0.55 | 0.61 |
| 3/A | 0.31 | 1.24 |
| 3/B | 0.31 | 1.24 |
| Average SEP | 0.39 | 0.82 |

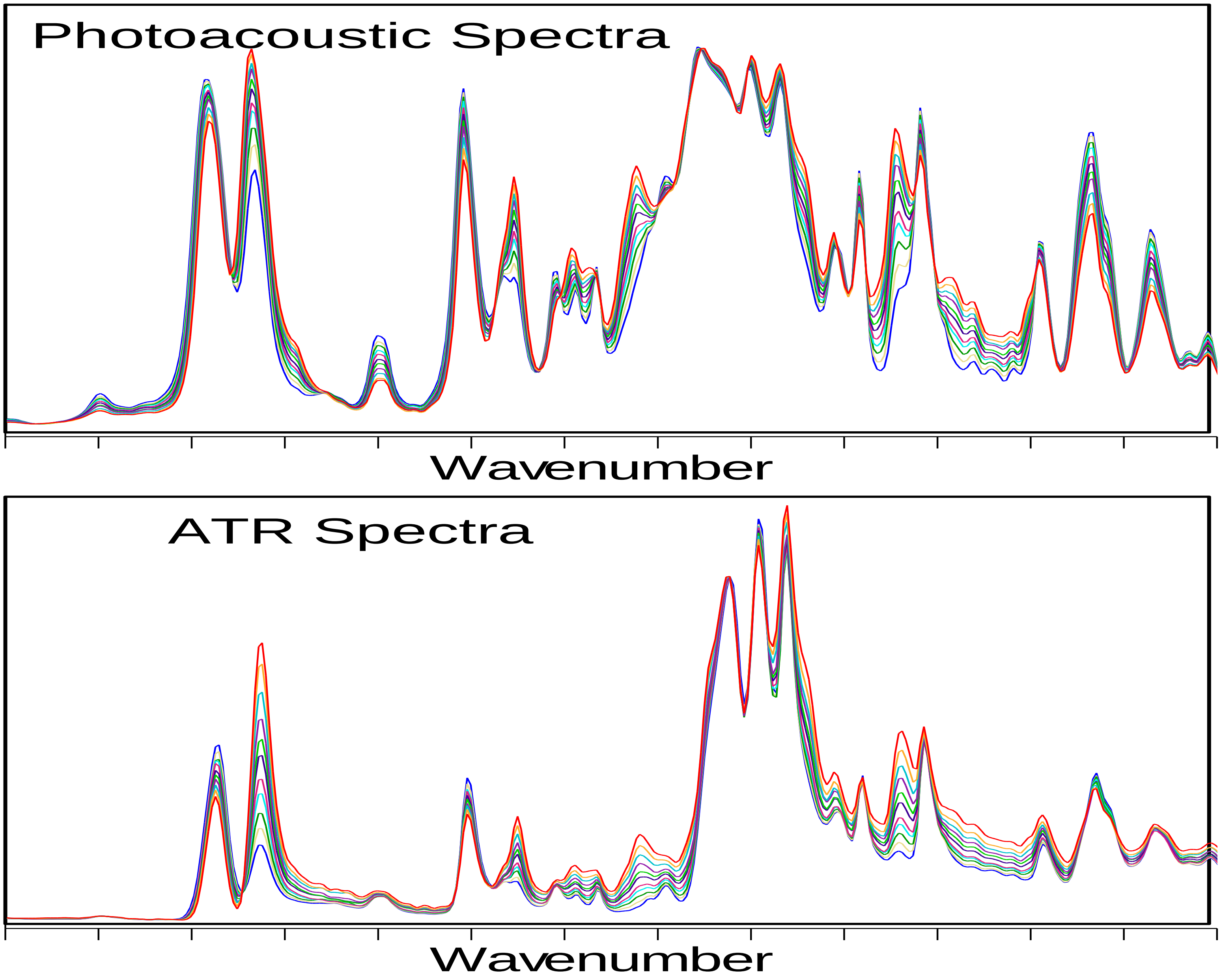
The SEP for the PAS measurements is a factor of two better than for ATR because PAS does not have the ATR crystal contact reproducibility issue and PAS spectra enhance the weak spectral features as demonstrated in the next two figures.

# Polymer Blend No. 2





# Polymer Blend No. 3



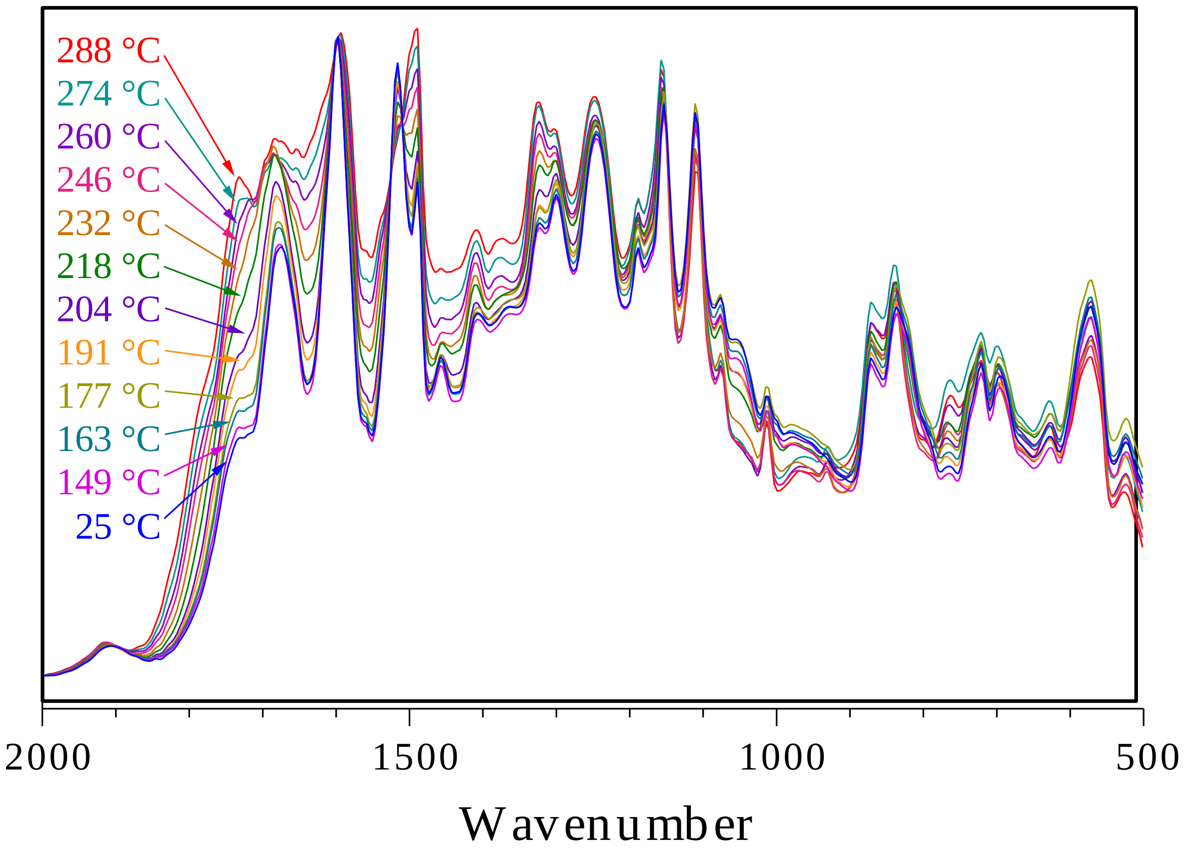
# FTIR-PAS Analysis of Aging Processes in Carbon Fiber/Epoxy Composites

- Increasing use of composites in aircraft make characterizing the aging of prepregs and finished parts important.
- Aging changes in epoxy chemistry causes degradation of mechanical properties.
- FTIR-PAS detected changes in chemistry *near the surface* can predict degradation of *bulk* mechanical properties.

# Artificial Aging of IM7/977-3 Carbon Fiber/Epoxy Composite

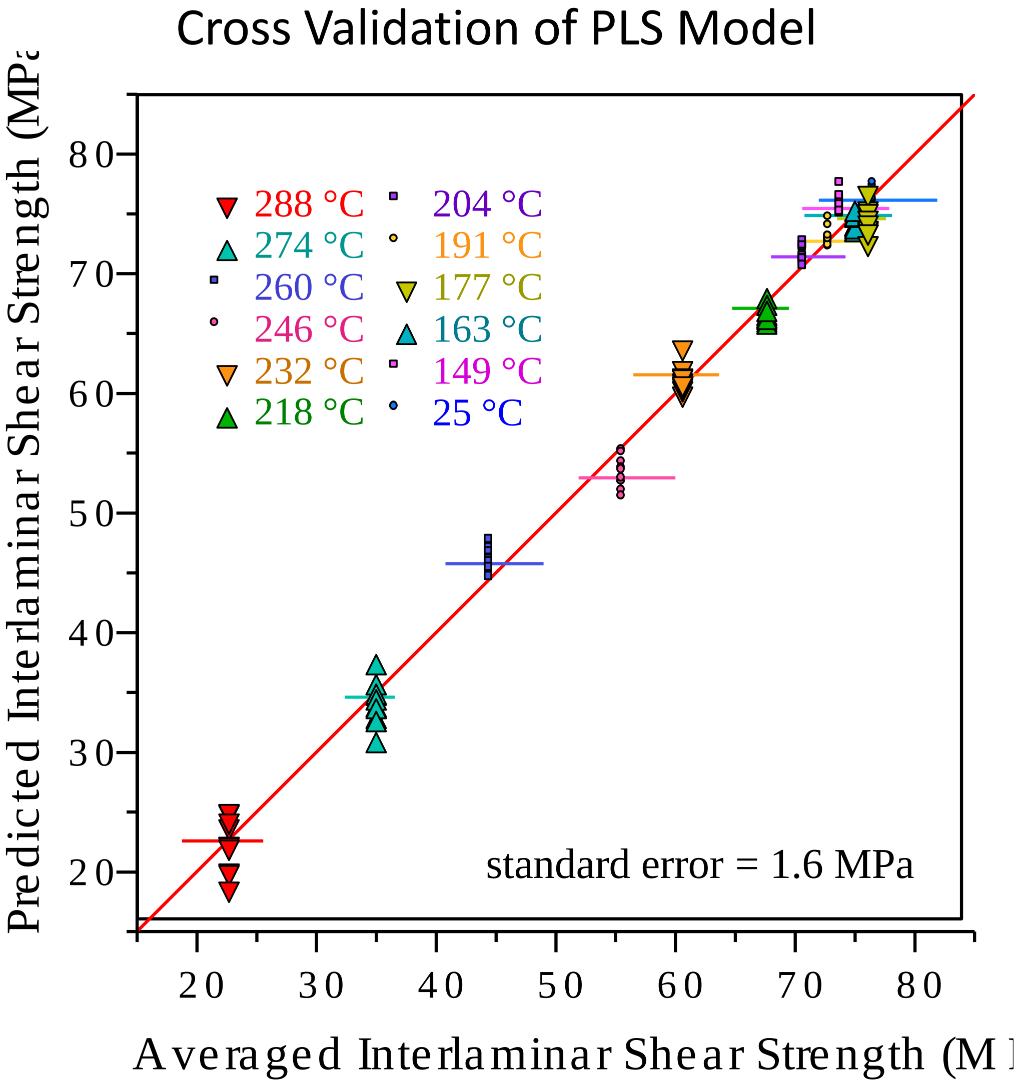
- 25-ply composite panel
- Aging: Baked in air for 4 hours at 11 equally spaced temperatures from 149 to 288 °C (300 to 550 °F). Ten samples at each temperature.
- Interlaminar Shear Strength (ILSS) Test of Mechanical Property Degradation
- Chemometrics relate spectra to ILSS

# PAS Spectra of Thermally Degraded Composites



- PAS spectra of the heat-stressed panels show clear differences at every temperature step.
- The composite has a service limit of 177 °C, so PAS sees changes after four hours of heating even at temperatures <u>well below the service limit</u>.

# PAS/PLS Model Predicting Laminate Degradation

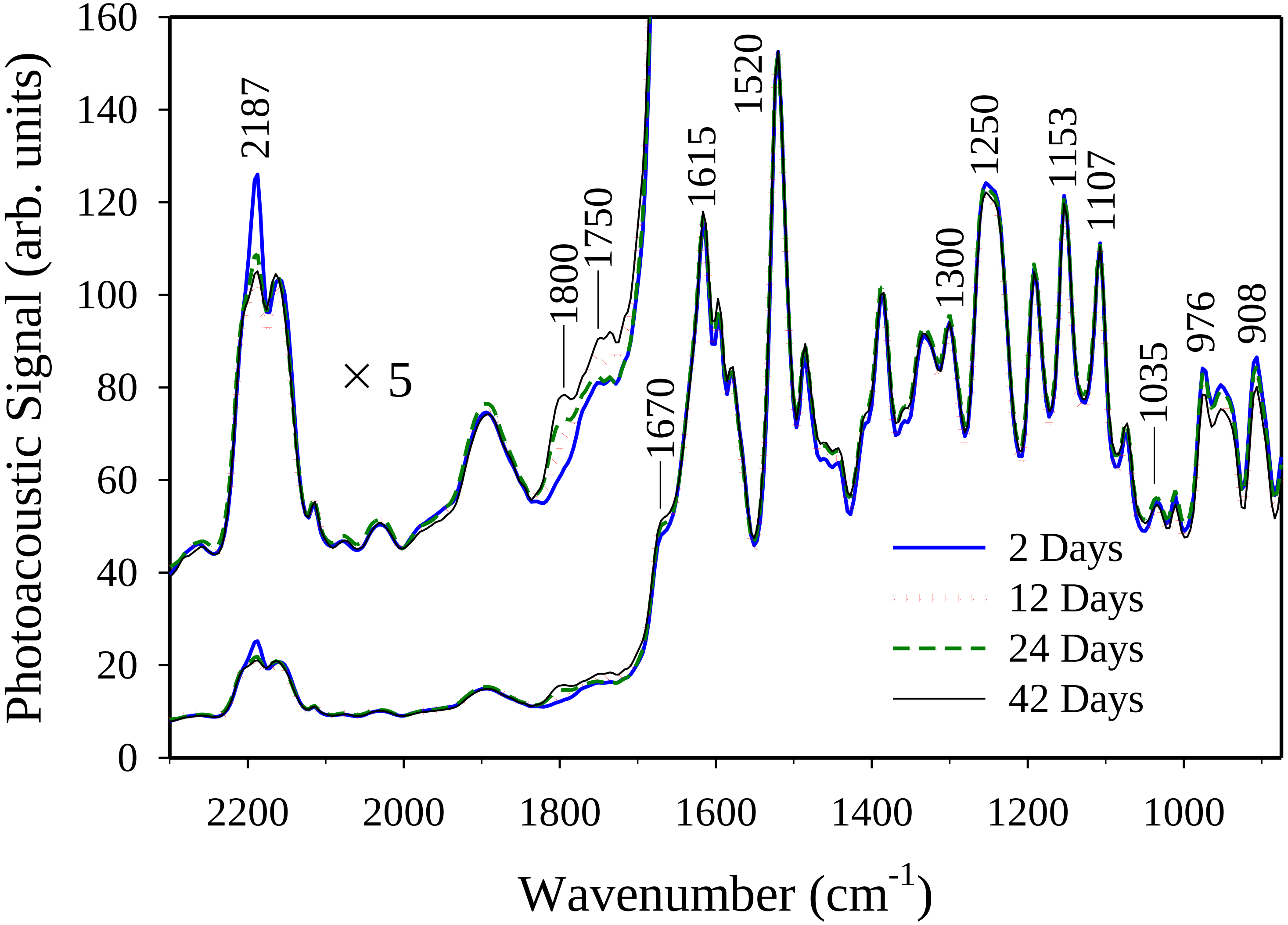


- The PAS spectra and interlaminar shear strengths were measured for ten samples at each temperature, and the ILSS measurements were averaged (horizontal bars indicated standard deviations).
- A partial least squares model was built to predict ILSS from the spectra.

# Analysis of Ambient Temperature Aging of Prepreg Sheets to Determine if Out Lifetime Has Expired

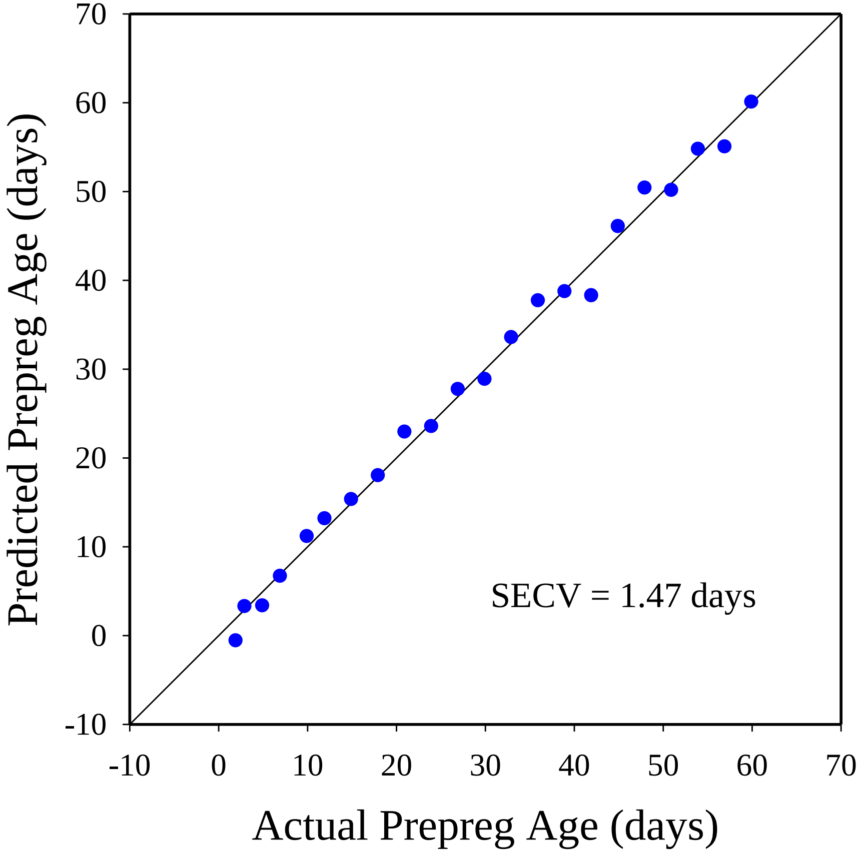
- Carbon fiber/epoxy prepreg sheets are kept in a freezer prior to laying up of sheets to form a part.
- Lay up process can take days, meanwhile cure advances at room temperature.
- In this experiment, prepregs kept at room temperature in dry air up to 60 days.
- PA spectra and other properties measured every few days. On each occasion; 1 sample spectrum acquired for PLS training set and 2 samples as unknowns.
- Laminates made and tested for ILSS on half of the testing occasions.

# PA Spectra of Aging Prepreg

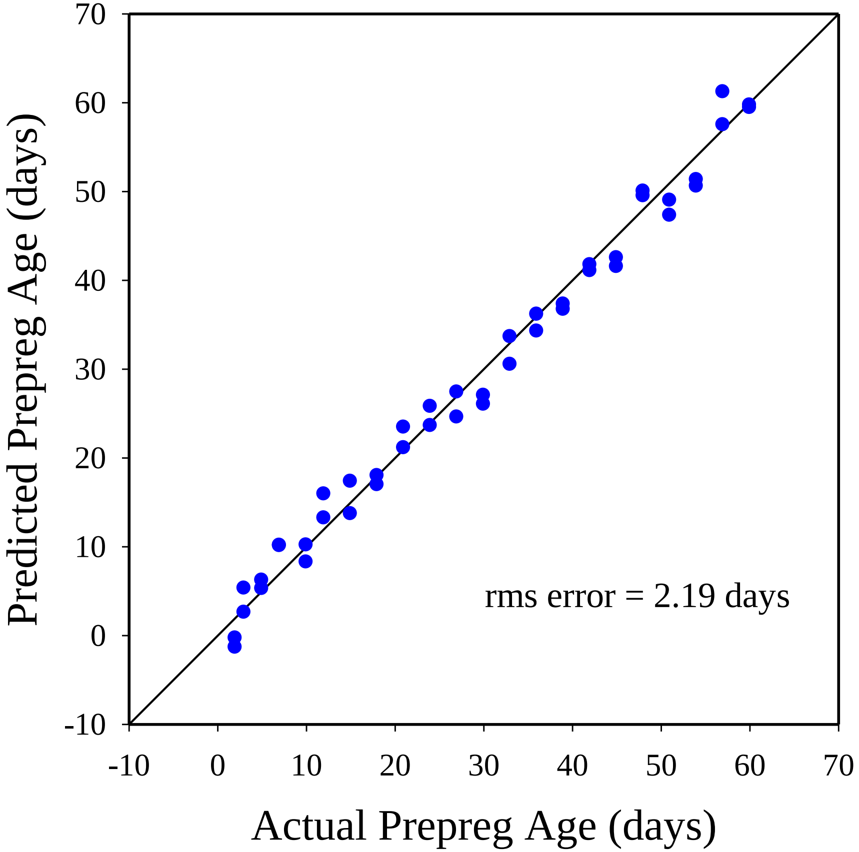


# PLS Model for Prepreg Age from PA Spectra

Cross Validation of Training Set

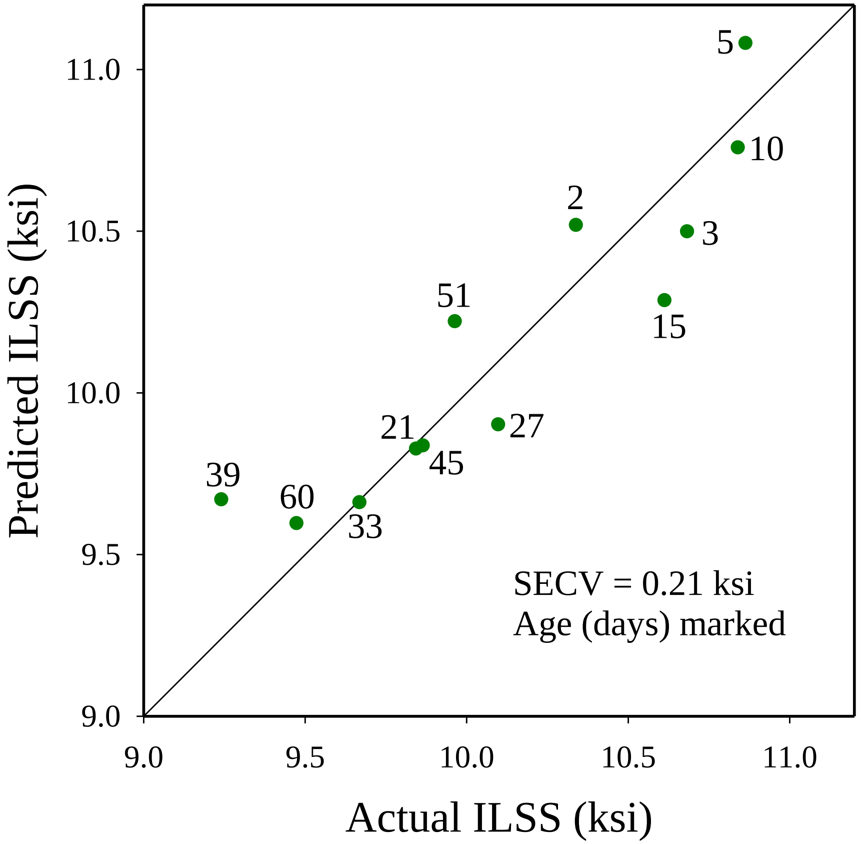


Analysis of Unknowns



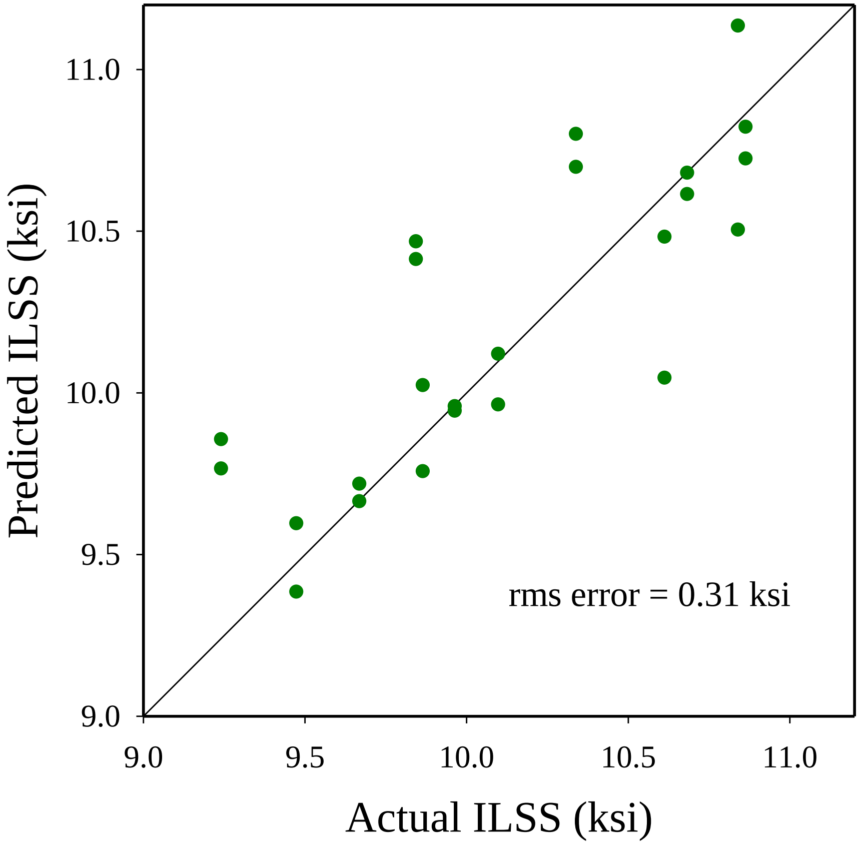
# PLS for ILSS of Aged-Prepreg Laminates

## Cross Validation of Training Set



SECV = 0.21 ksi
Age (days) marked

## Analysis of Unknowns



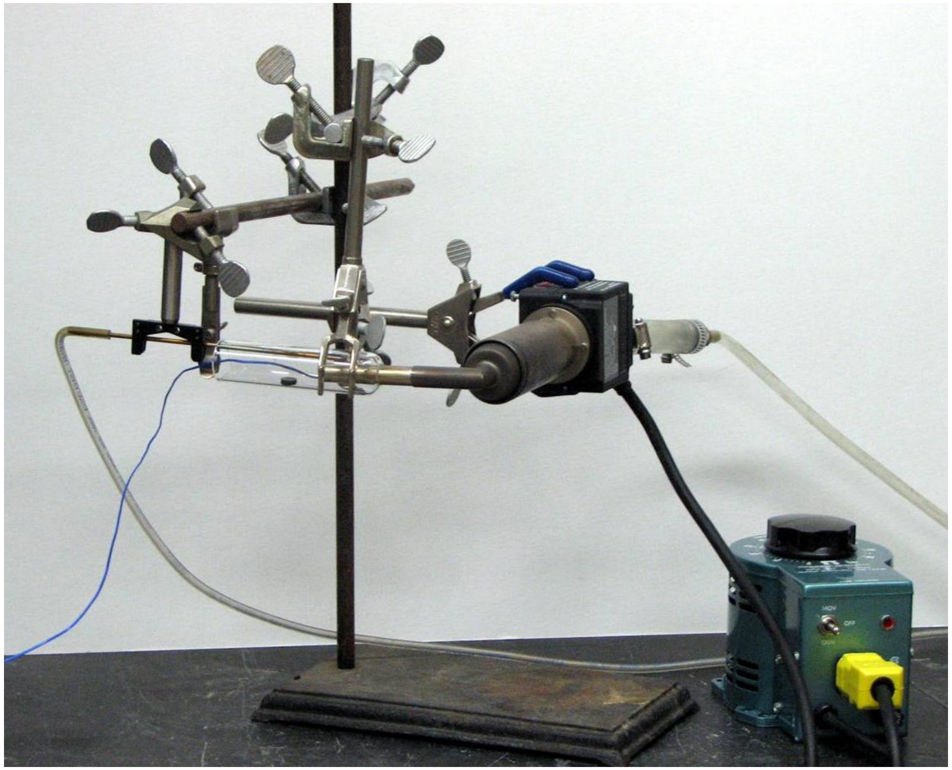
rms error = 0.31 ksi

# Processing Wood into Biochar

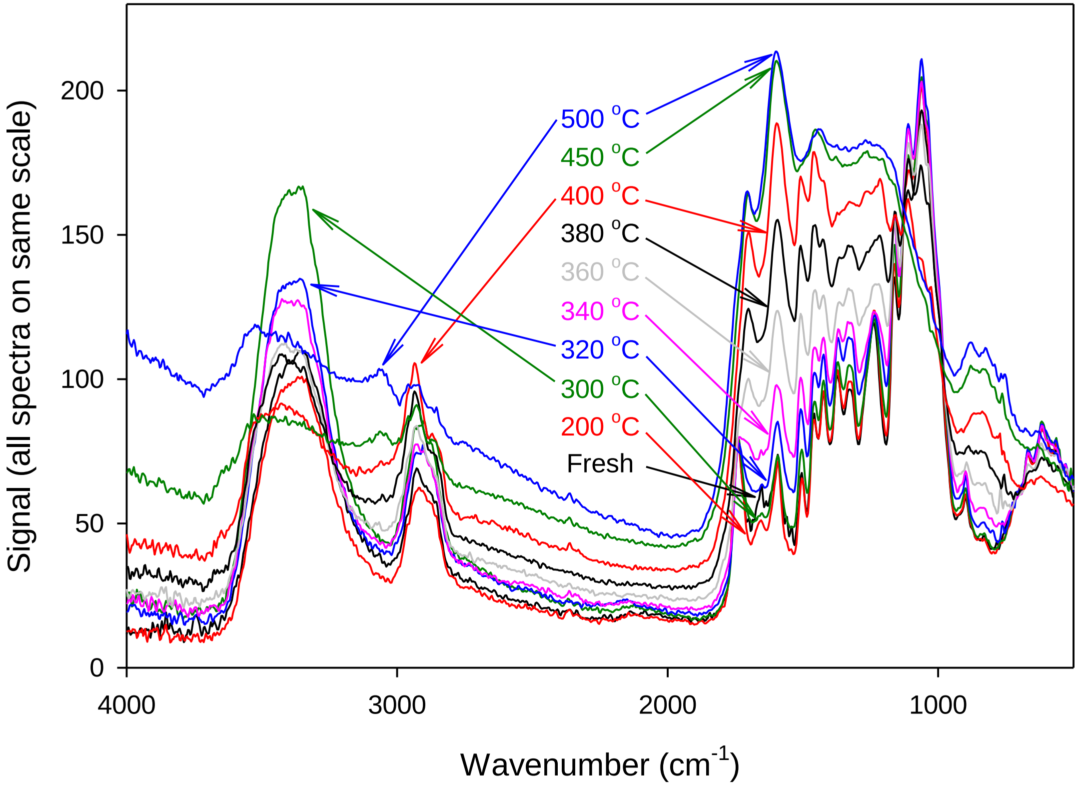
- FTIR Photoacoustic Spectroscopy allows the depletion and generation of chemical compounds to be observed during the pyrolysis and charring of biomass.
- This capability can be used to characterize the role of biochar chemistry, due to different charring conditions and biomass feedstock types, in soil fertility, water quality, and carbon sequestration studies.

# Charring Apparatus

Wood biomass was exposed to a series of 90s long temperature steps starting at a 200°C nitrogen gas temperature and proceeding in 25°C steps to 300°C and on to 500°C in 10°C steps.

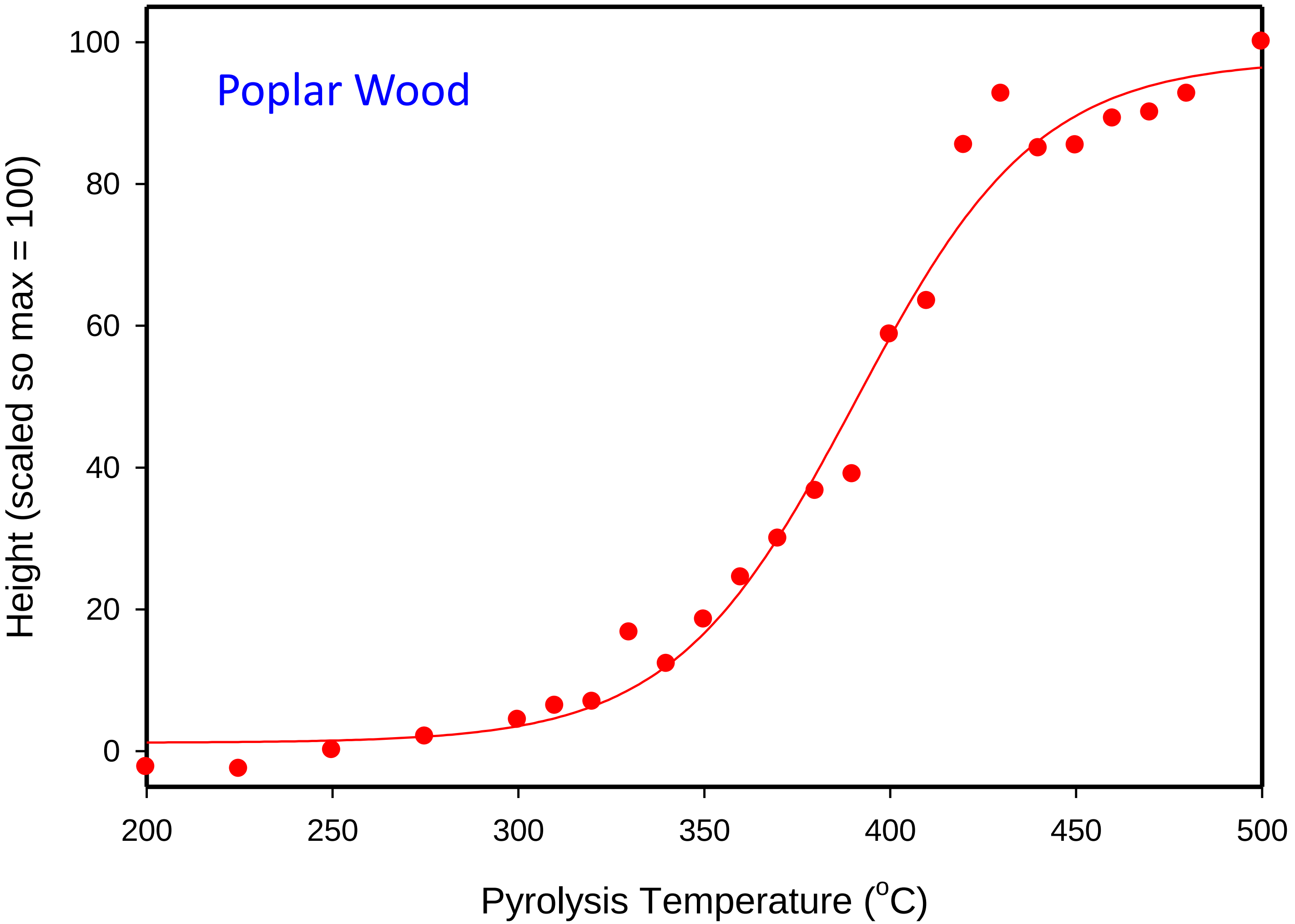


# Infrared Spectra of Poplar: 25°C to 500°C

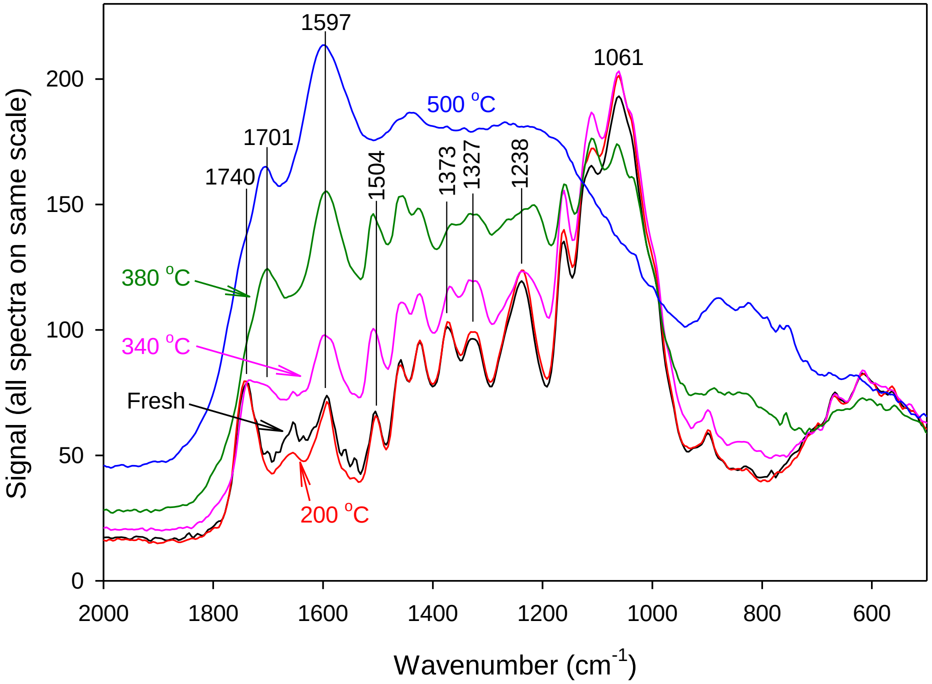


Every absorption feature in the spectrum is altered by pyrolysis. Most of the many absorption peaks of the fresh wood disappear and are replaced by a few broader absorptions from the char. In addition a background absorption begins to push the baseline of the spectra upward starting at roughly 340°C. This rising baseline indicates the formation of biochar, which absorbs all wavelengths of infrared light.

# Char Formation vs. Temperature

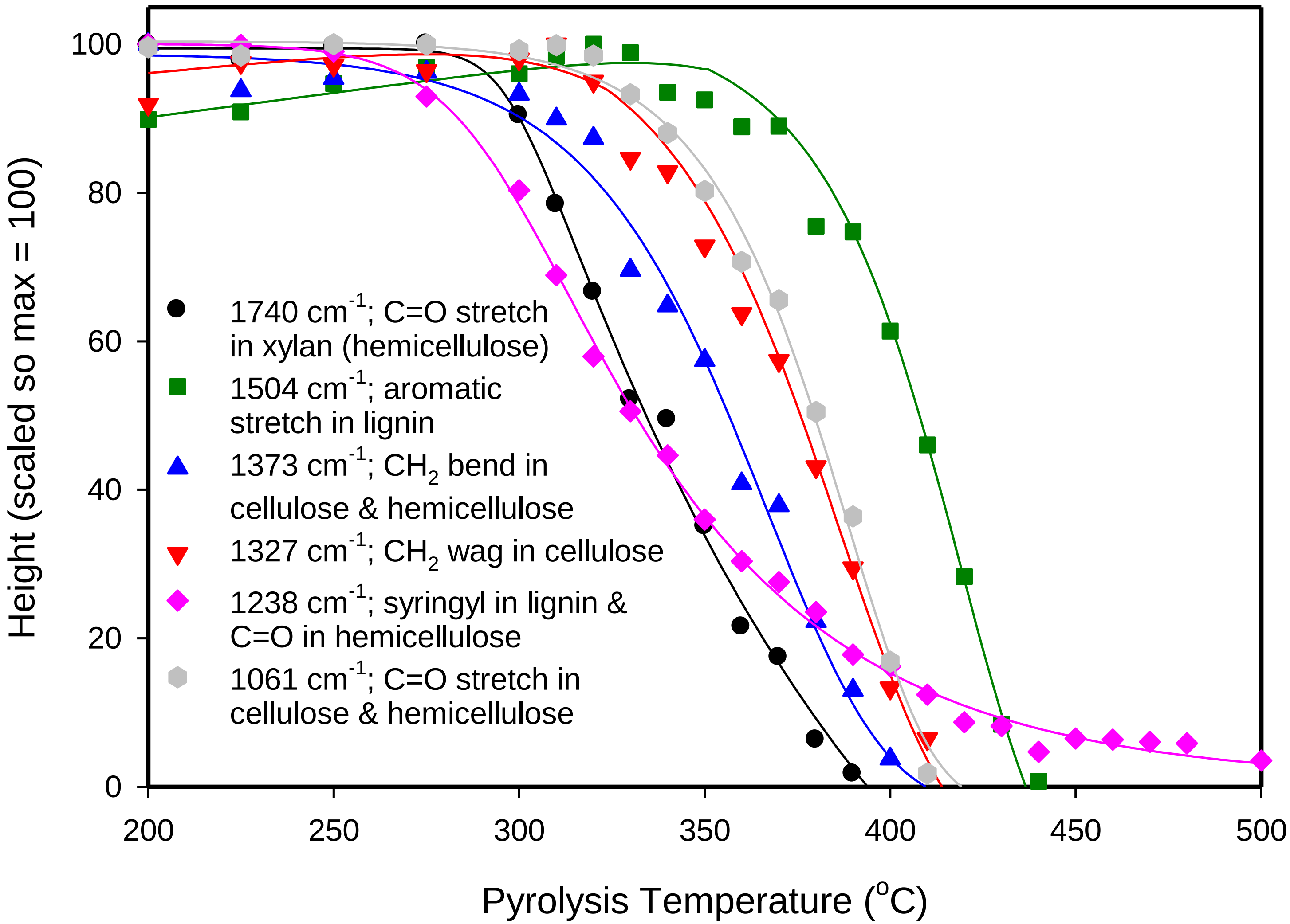


# Sources of the absorption bands whose peak heights were monitored as a function of pyrolysis temperature

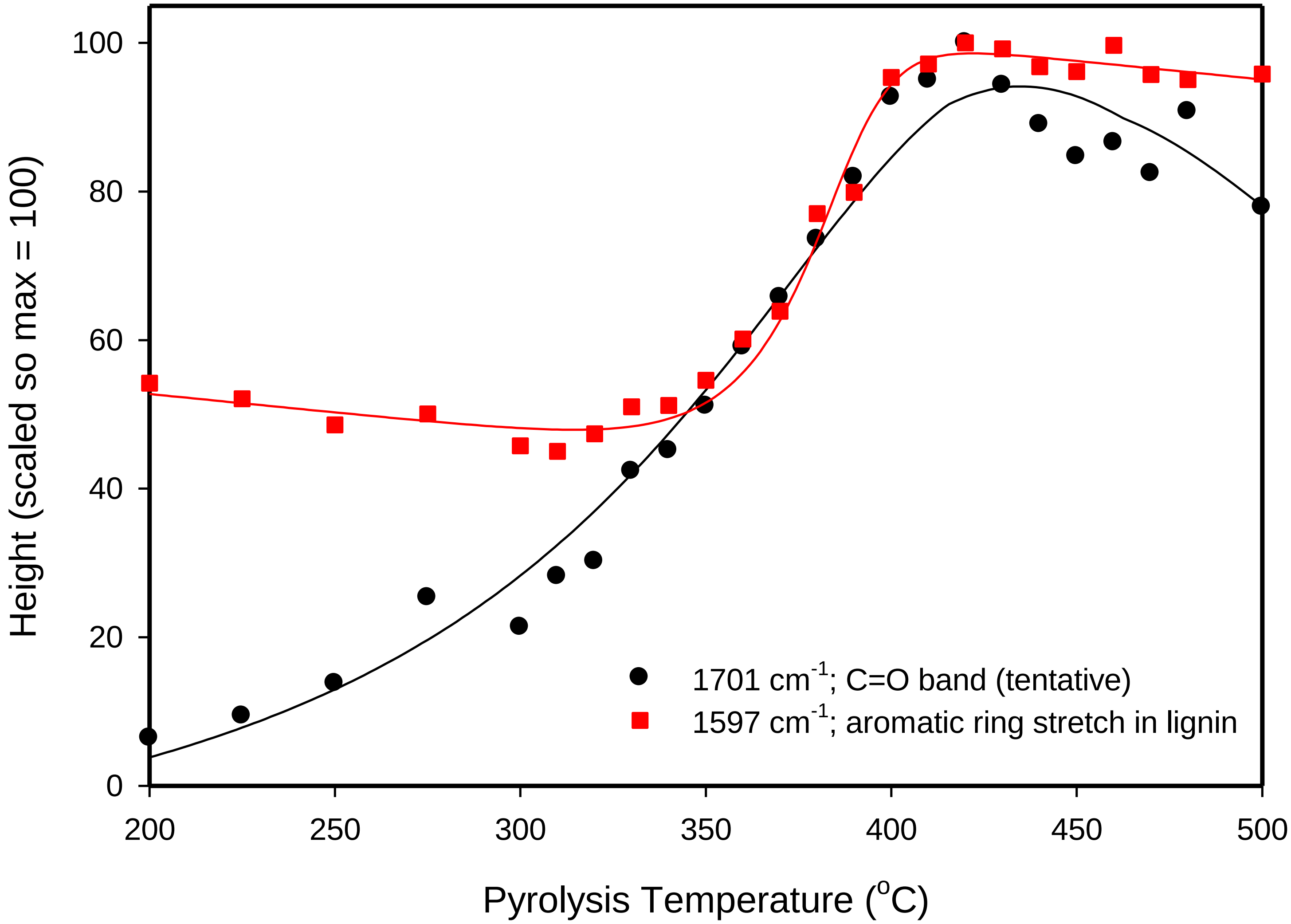


| Wave-number (cm$^{-1}$) | Source |
|---|---|
| 3522 | Bond stretch of O-H hydrogen-bonded to aromatic network |
| 3356 | O-H bond stretch in cellulose, hemicellulose, and lignin |
| 3055 | C-H bond stretch in aromatic hydrocarbons |
| 2932 | C-H bond stretch in aliphatic (non-aromatic) hydrocarbons |
| 1740 | C=O bond stretch in xylan (part of hemicellulose) |
| 1701 | Carbonyl band (tentative assignment) |
| 1597 | Aromatic (benzene) ring stretch (only from lignin in fresh wood) |
| 1504 | Aromatic (benzene) ring stretch in lignin |
| 1373 | $CH_2$ bending in both cellulose and hemicellulose |
| 1327 | $CH_2$ wagging vibration in cellulose |
| 1238 | Mixed source; both syringyl nuclei in lignin and C=O in hemicellulose |
| 1061 | C=O bond stretch in both cellulose and hemicellulose |

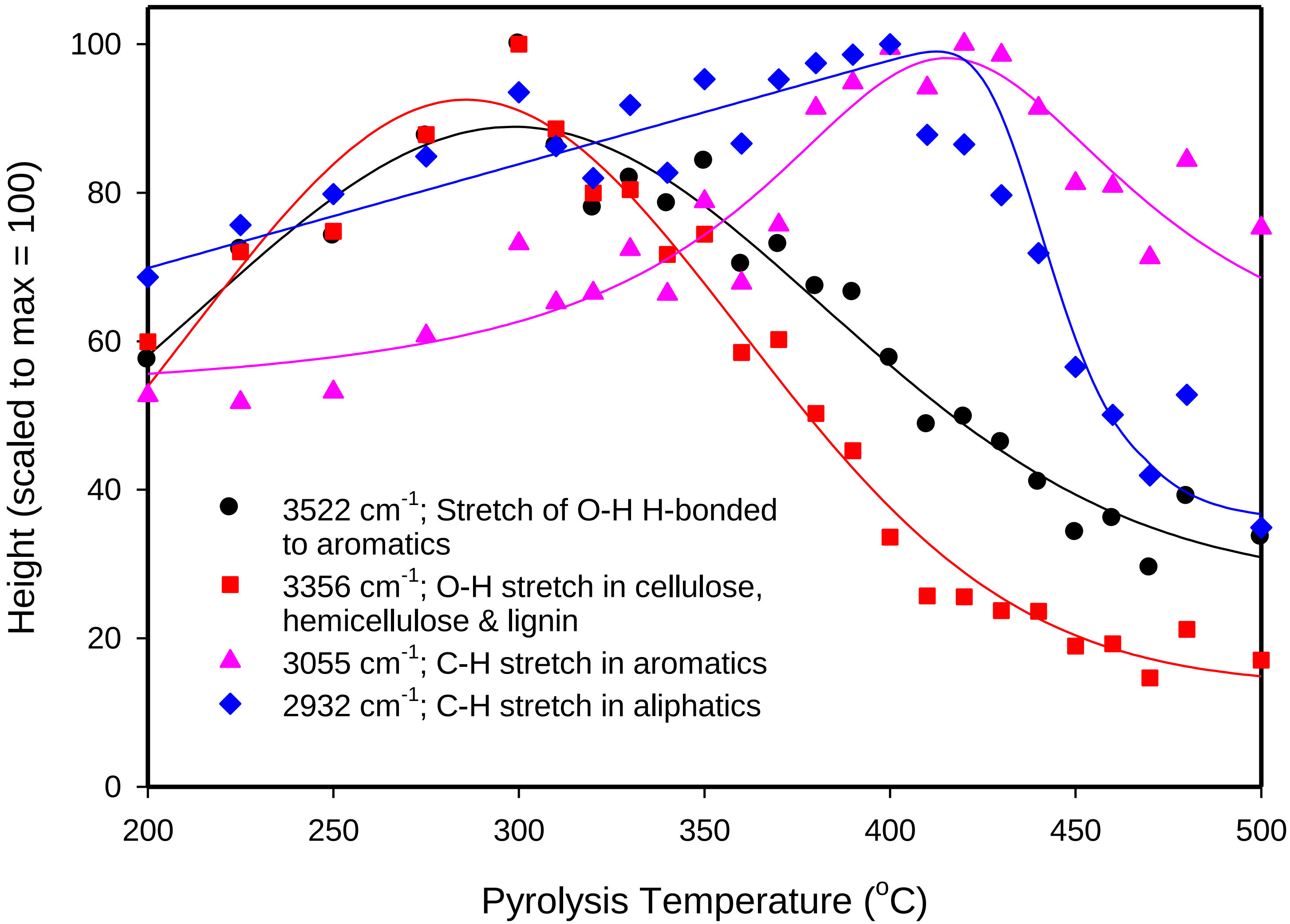
# Species Being Depleted During Charring



# Species Being Formed During Charring



# Formation- Depletion of Species During Charring



# PAS Reference Samples

PAS magnitude spectra of samples must be divided by a spectrum of a black absorber to remove spectral features due to the light source and the spectrometer's optics. PAS phase spectra must be referenced to a specific phase angle in order to be used in linearizing spectra and in other data processing calculations . MTEC has developed special reference samples for these purposes.

Magnitude Reference

Phase Reference