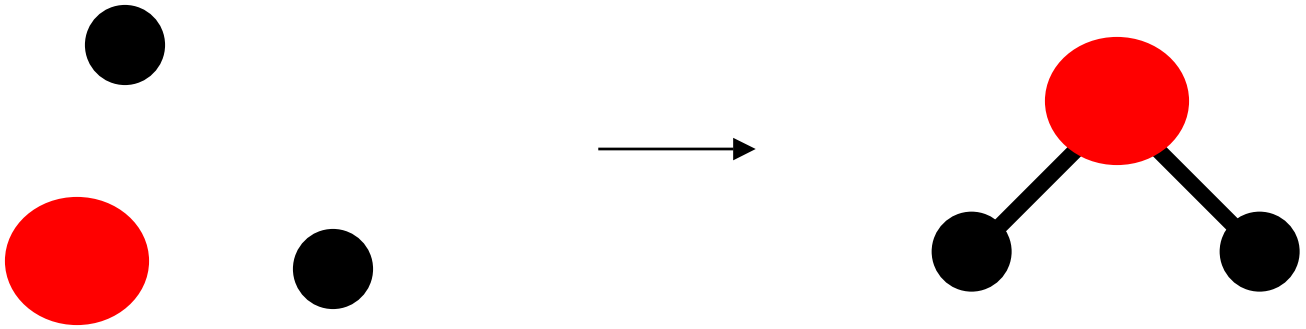
Henry Buijs

# IR Spectroscopy and FTIR

# Molecular Vibrations

- Material is made up of atoms
- A group of atoms linked together by chemical bonds is called a  molecule



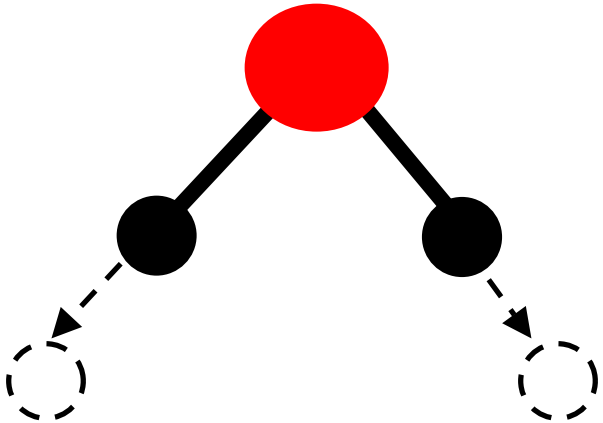
**Atoms of hydrogen and oxygen**

**Molecule of water**

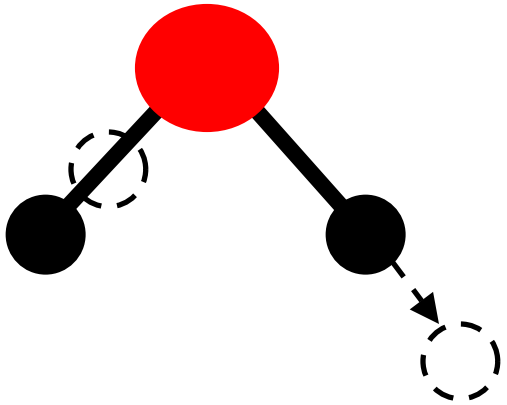
 

# Molecular Vibrations

- The atoms of a molecule are always in motion
- These motions are called vibrations



**symmetrical vibration**
**H-O-H**



**asymmetrical vibration**
**H-O-H**

# Properties of Molecular Vibrations

- The rate of vibration is millions of cycles per second (it never stops)
- Each vibration has a unique frequency
- The frequency of a vibration depends on:
  - The strength of the chemical bond between atoms
  - The mass of each atom

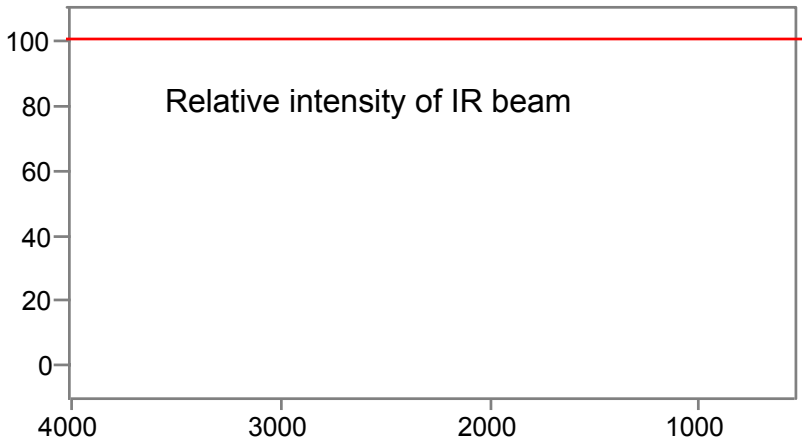
So we can learn a lot about a molecule when we study its vibrations!

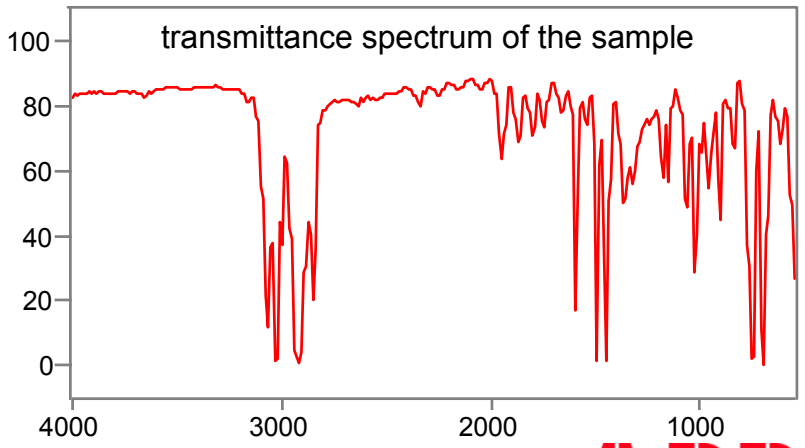
Infrared spectroscopy is a method for the analysis of molecular vibrations

# IR Spectroscopy

- Analysis based on the absorption at different wavelengths of an infrared beam by a sample

# Principles of Infrared Spectroscopy

- When a frequency of light corresponds to a molecular vibration it is absorbed by the sample

- The fraction of light transmitted by the sample compared with the light incident as a function of frequency gives the infrared spectrum of the sample

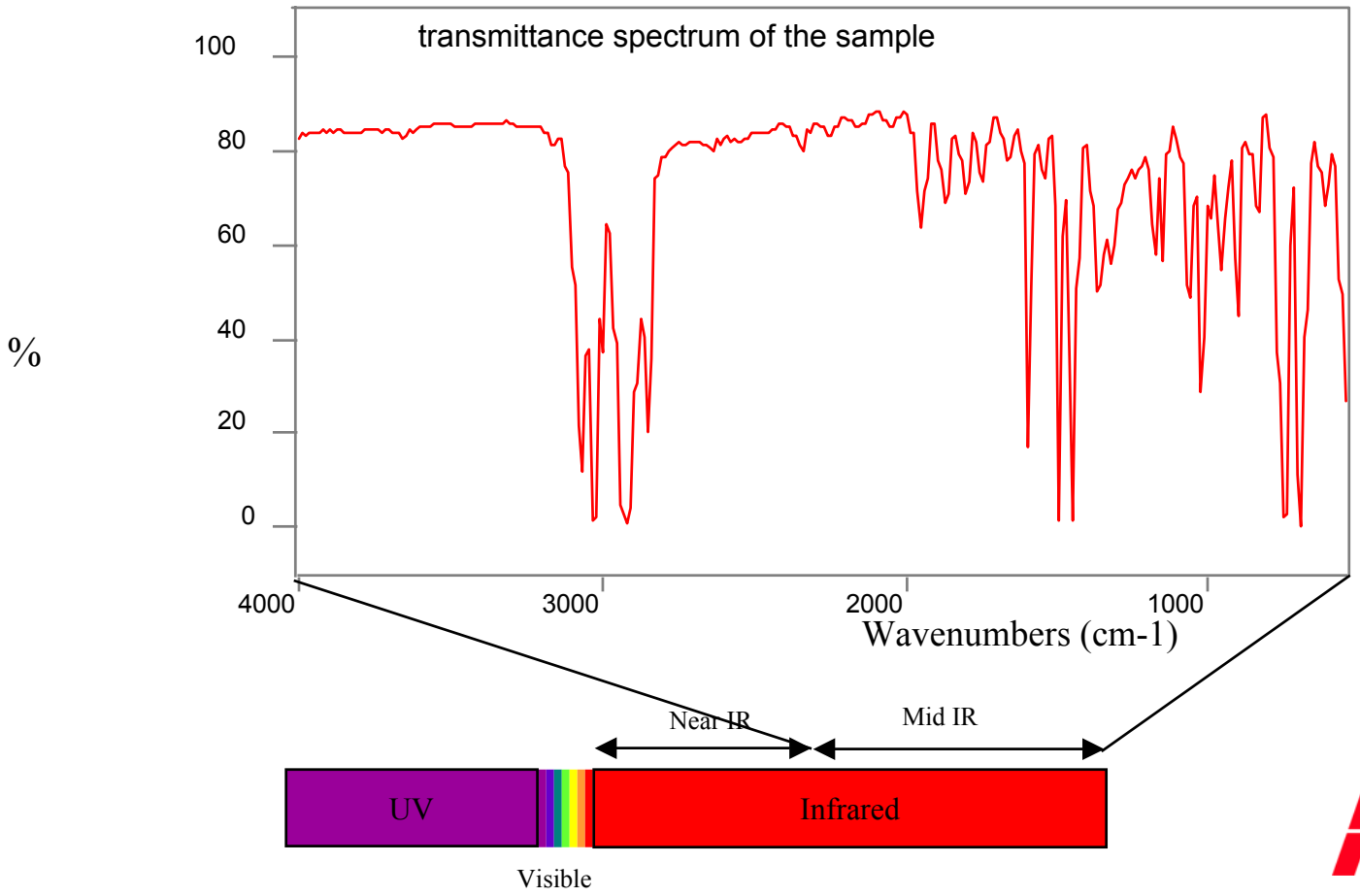
 

# Infrared Spectrum of a Polystyrene Film

- Wavelength is expressed in number of waves per cm.

  (e.g. 1000 /cm  is the same as wavelength λ=1/1000th cm)

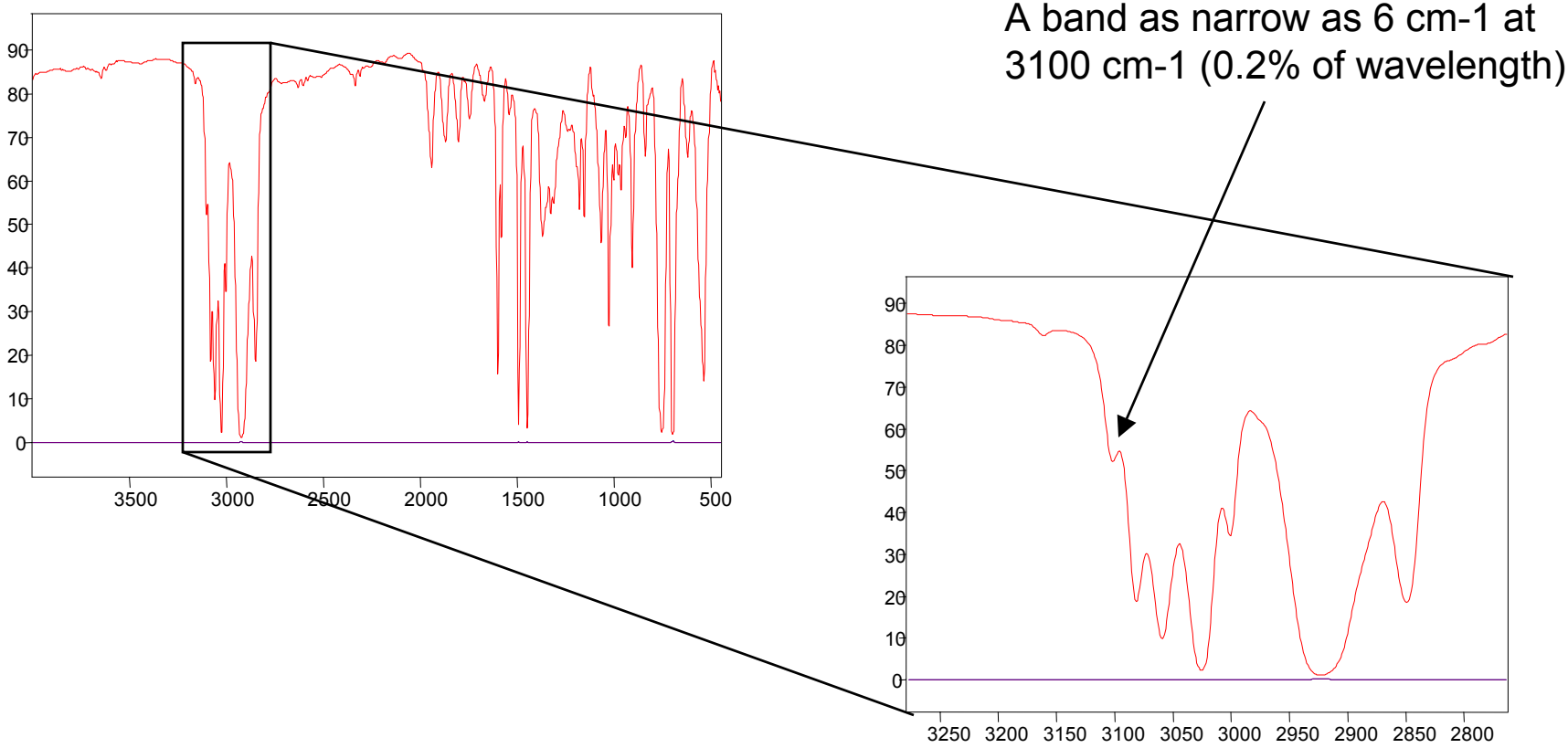
- Vertical scale is percent remaining intensity



# Properties of an IR Spectrum

- There is much detail in a spectrum.
- Much of it is unique to a sample



# But What Is Really Happening Here?

In fact recording a spectrum is a little like tuning in to radio stations...

- We turn the button (change the frequency)
- Sometimes we catch a signal, and we hear music (we “absorb” the signal at this frequency)
- We know which stations to find, because we know the frequency where they are (we know which vibrations to pickup)
- Sometimes the signal is strong, sometimes weaker (the peak is higher or lower)
- Sometimes we hear nothing at all!

# Absorbing and Non-Absorbing Species

Absorbing:

- Any molecular vibration which displaces an electric charge will absorb infrared radiation.
- Diatomic molecules with dissimilar atoms HCl, CO
- Asymmetric vibrations in polyatomic molecules
- Functional groups

Non-absorbing:

- Atomic Species: He, Ne, Ar, Kr
- All Atomic Species
- Molecular Species: H2, N2, O2, F2, Cl2, Br2
- <u>These cannot be analyzed by infrared</u>

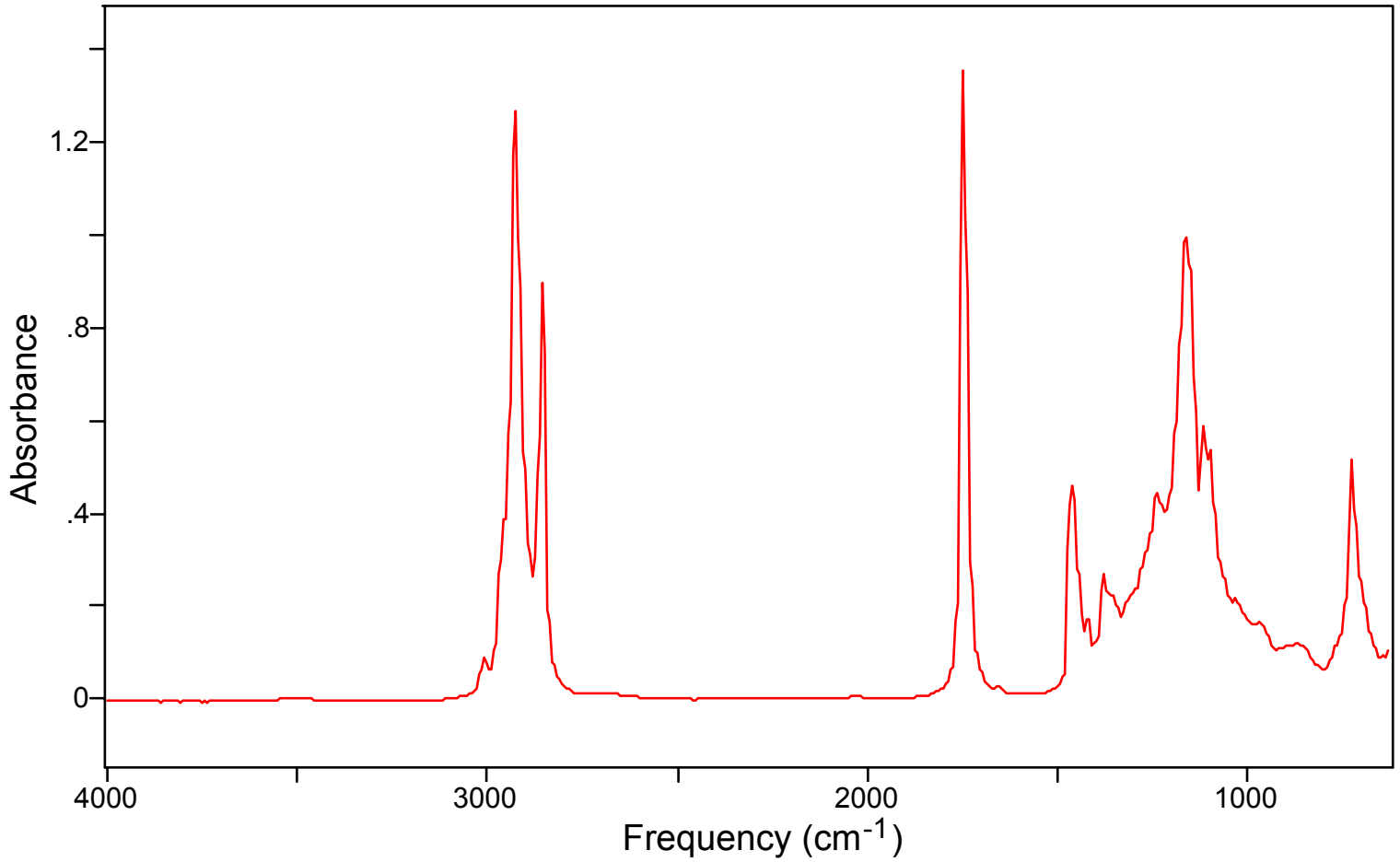
 

# Mid IR Spectroscopy

- Wavelength range 2500 nm to 25000 nm
- Frequency range 4000 to 400 cm-1
- Mid IR spectra provide distinctive patterns for many compounds
- Permits distinction of several hundred thousand different compounds
- Most compounds have high absorptivity in mid IR
  - Condensed phase compounds
    - >50% transmittance for sample thickness in 10 to 100 micrometer range
    - Need sample accessories that assure short light path through sample
      - Capillary liquid transmission cell, ATR and diffuse reflectance
  - Gas phase compounds
    - >50% transmittance for sample thickness in 10 to 100 cm range
    - Mid IR is suitable for quantitative gas phase analysis

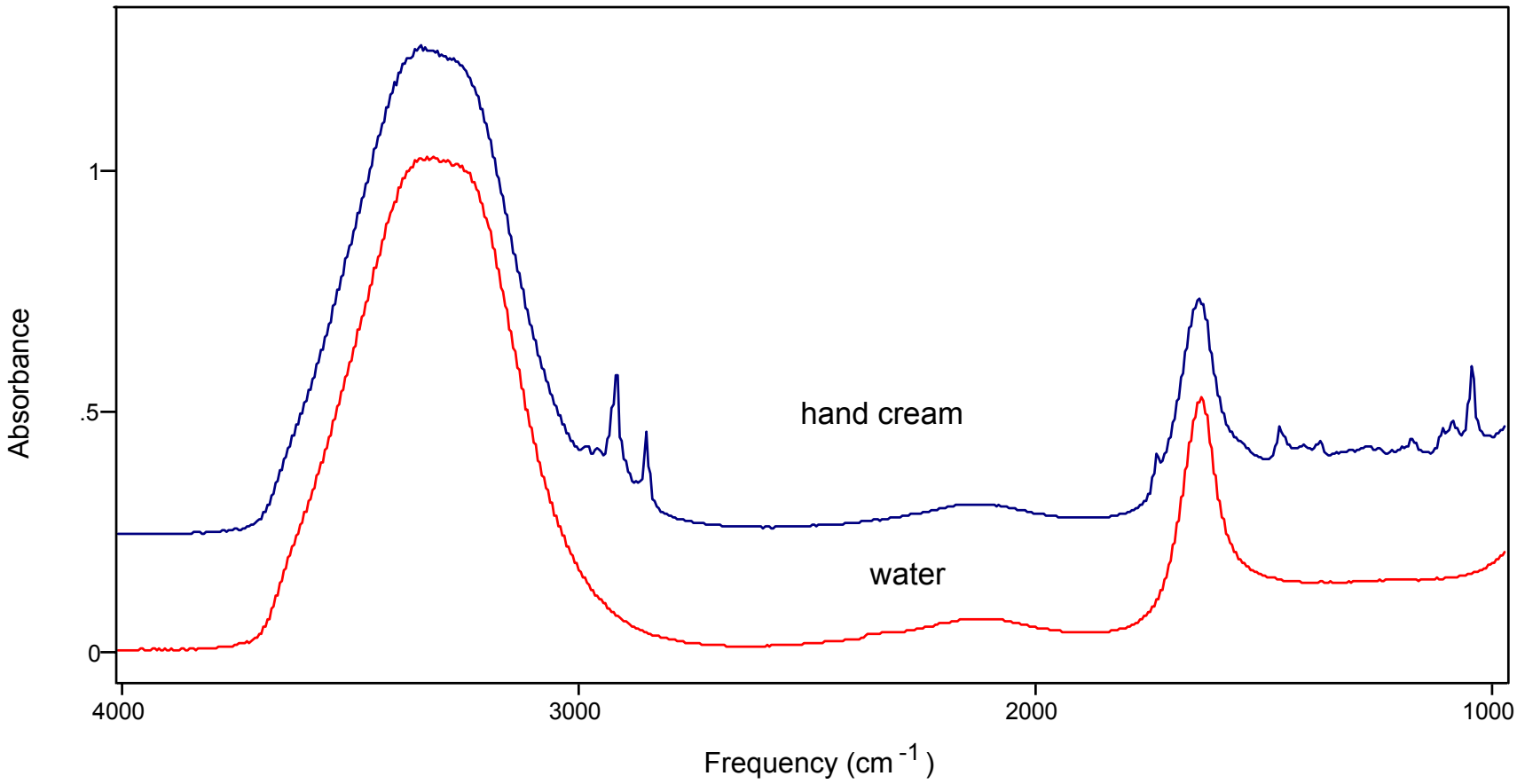
 

# IR Spectrum of a Liquid Vegetable Oil (path: 12 microns)



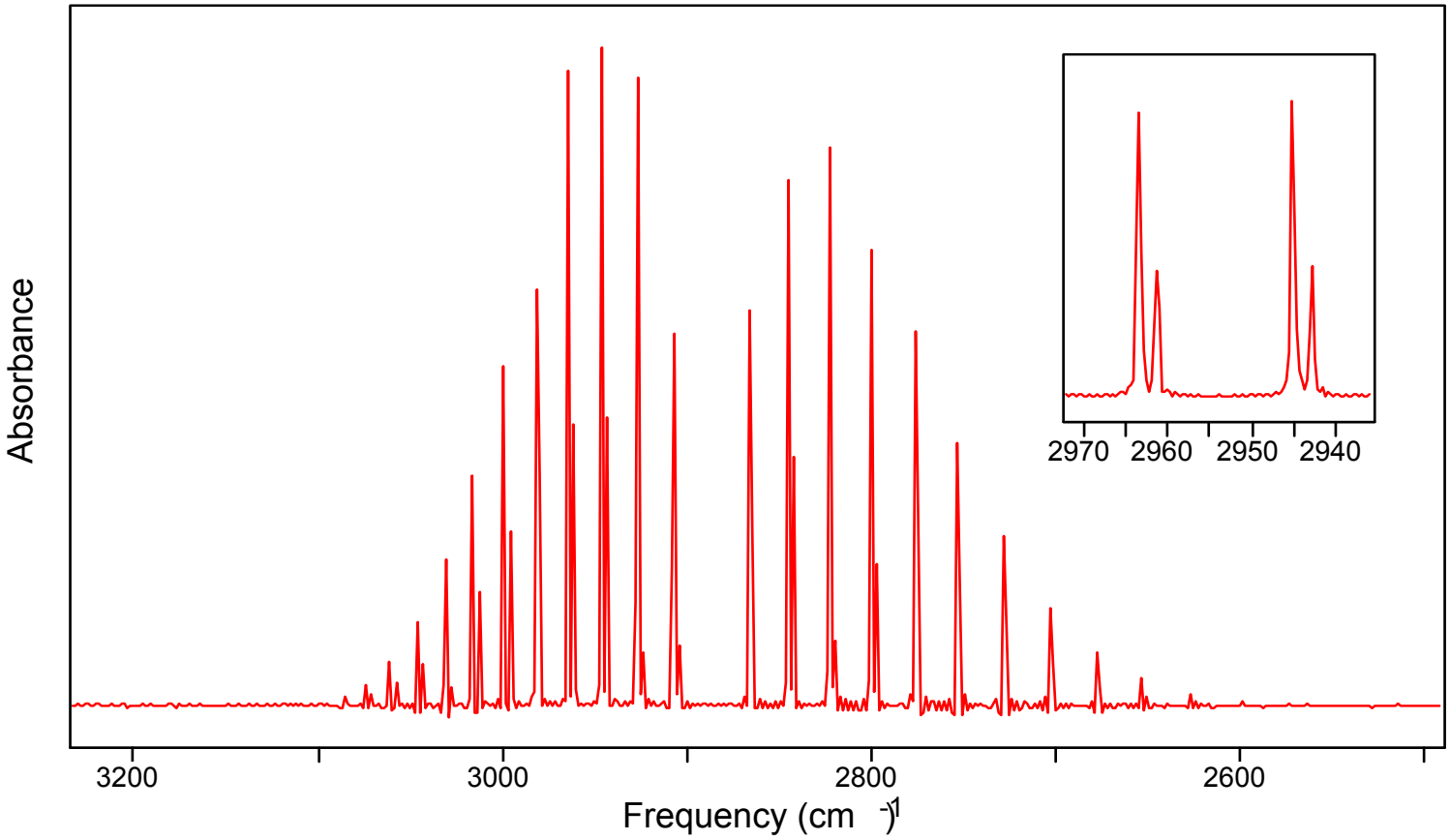

 

# IR Spectra of Hand Cream and Water (path: 12 microns)



# Infrared Spectrum of Gaseous HCl (10-cm path cell, resolution 1 $cm^{-1}$)



# Near IR Spectroscopy

- Wavelength range 700 nm to 2500 nm
- Frequency range 14000 to 4000 cm-1
- Near IR spectra have less distinctive patterns than Mid IR spectra
  - Harmonics and combination frequencies of mid IR bands
    - Principally harmonics of H-C, H-N, H-O vibrations
- Absorptivity is lower than in mid IR
- Low absorptivity is offset with longer path sampling
  - Sampling with pathlength of several millimeters is much easier and permits greater reproducibility
    - Disposable glass vial sampling
    - Sampling of flowing sample in process pipe
- Quantitative analysis using chemometrics

# Overtones (Harmonics) and Combinations

- Infrared spectrum of $H_2O$:
  - OH stretching: 3400 $cm^{-1}$
  - OH bending: 1630 $cm^{-1}$

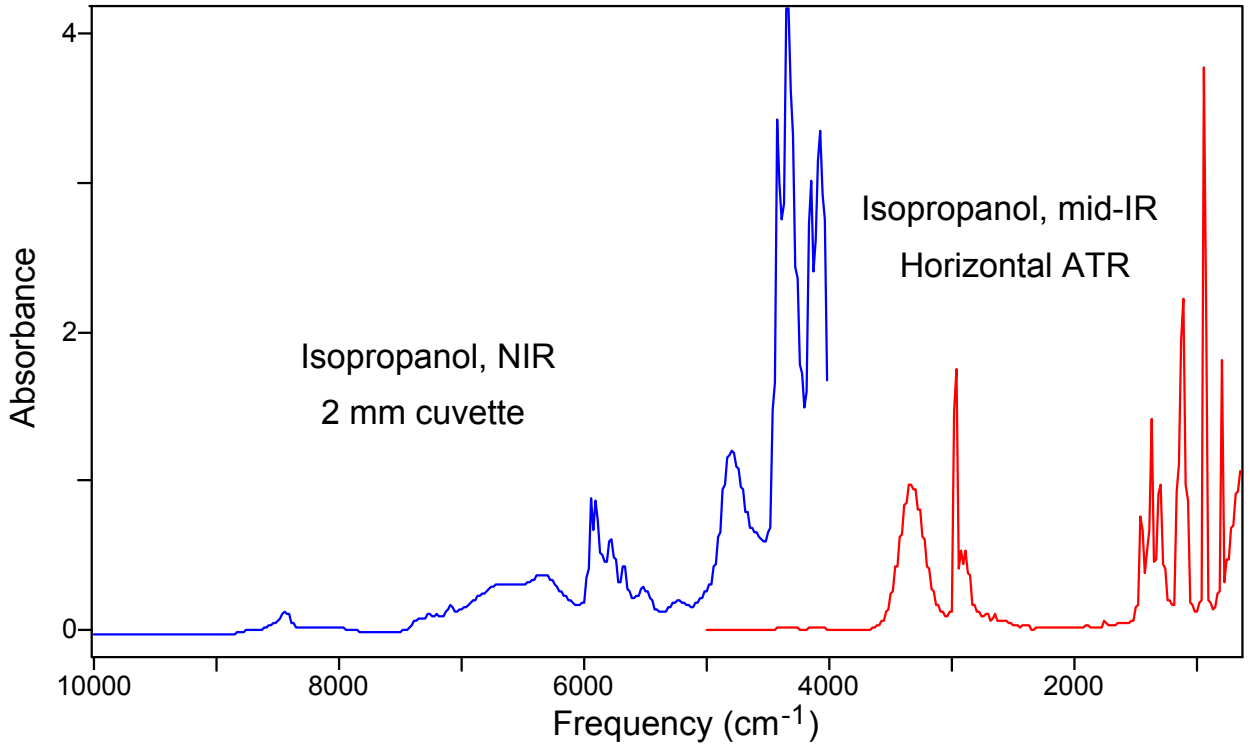
- First overtone: 2 x 3400 = 6800 $cm^{-1}$
- Second overtone: 3 x 3400 = 10200 $cm^{-1}$

- Combination: 3400 + 1630 = 5030 $cm^{-1}$

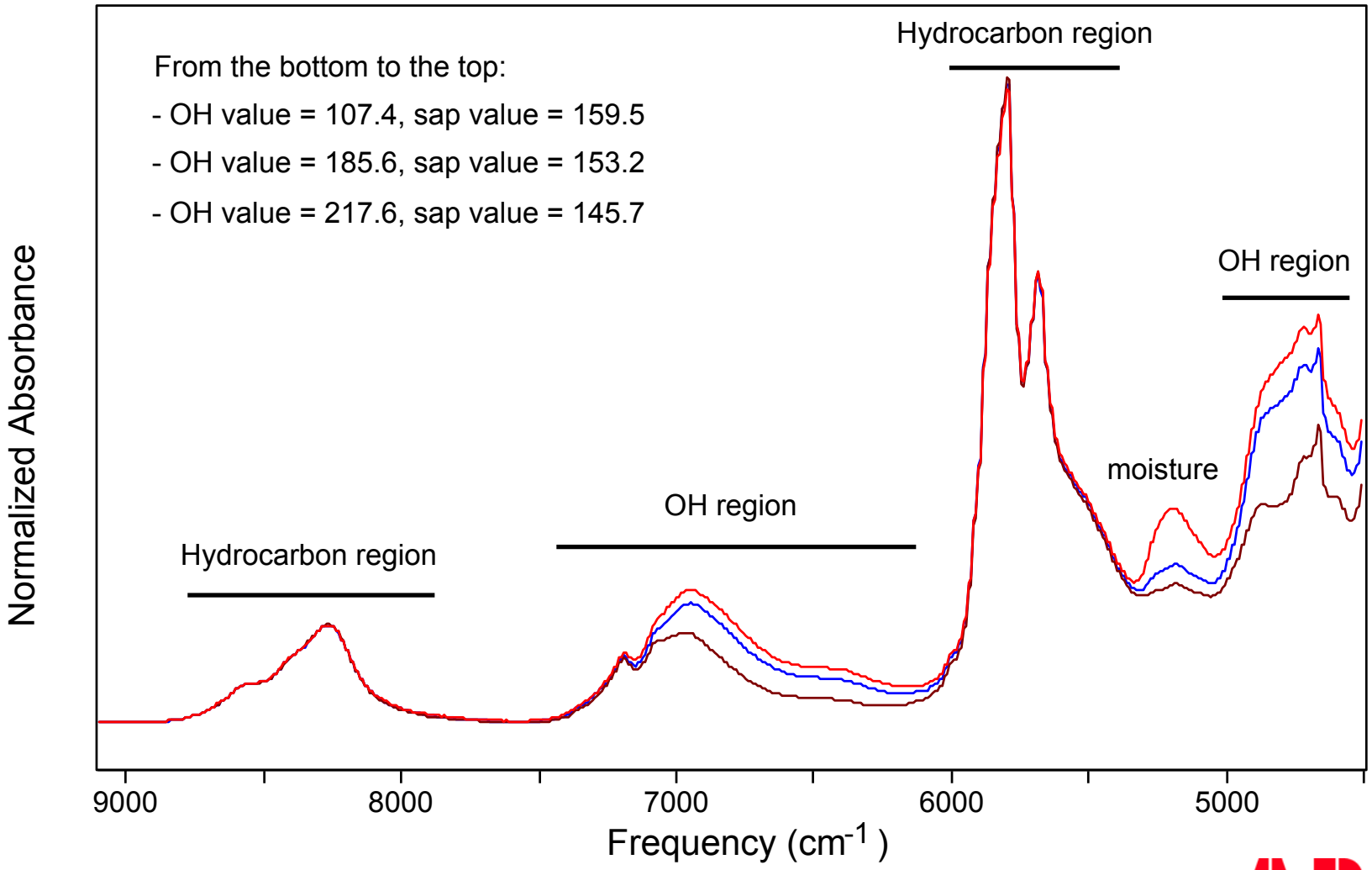
# Mid and Near Infrared Spectra of Isopropanol

- The pathlength is increased by a factor of 150 in the NIR to get intensity similar to the mid-IR



# NIR Spectra of Surfactants



# Fundamentals and Overtones

## The C-H Stretching Vibration for $CHCl_3$ Liquid

| Transition $\upsilon = 0$ to $\upsilon =$ | Observed wavenumber ($cm^{-1}$) | Anharmonic oscillator calculation ($cm^{-1}$) | Absorbance for a 1 cm cell | Pathlength for measurement |
|---|---|---|---|---|
| 1 | 3019 | 3019 | 170 | 5 μm |
| 2 | 5912 | 5912 | 17 | 0.5 mm |
| 3 | 8677 | 8679 | 0.55 | 1.0 cm |
| 4 | 11318 | 11320 | 0.02 | 5.0 cm |
| 5 | 13850 | 13835 | 0.001 | N/A |
| 6 | 16270 | 16224 | 0.0001 | N/A |

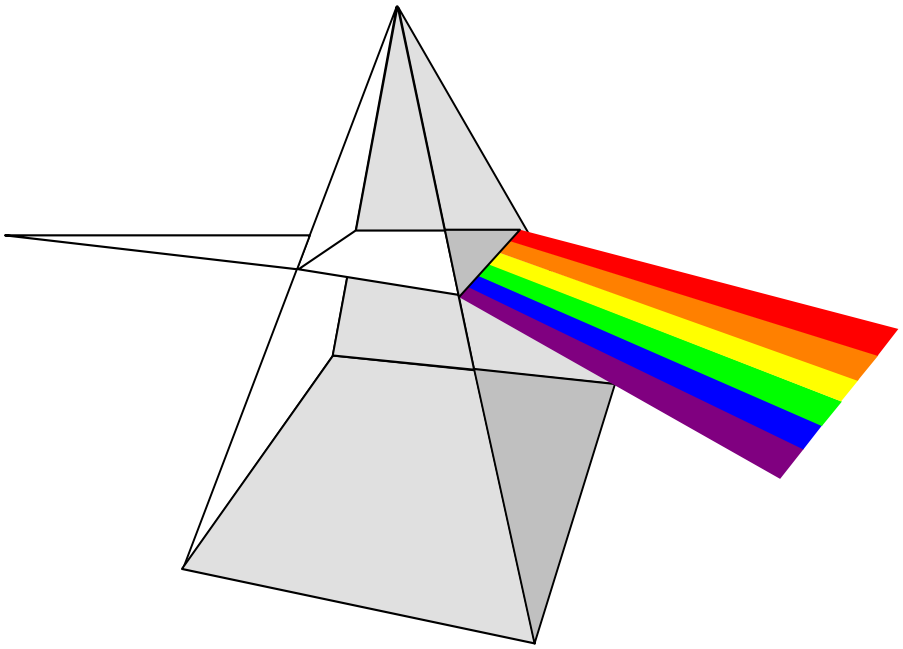
Note the reduction in absorbance. This requires very short path at 3019$cm^{-1}$, convenient 0.5 mm and 10 mm path at 5912 and 8677 respectively.

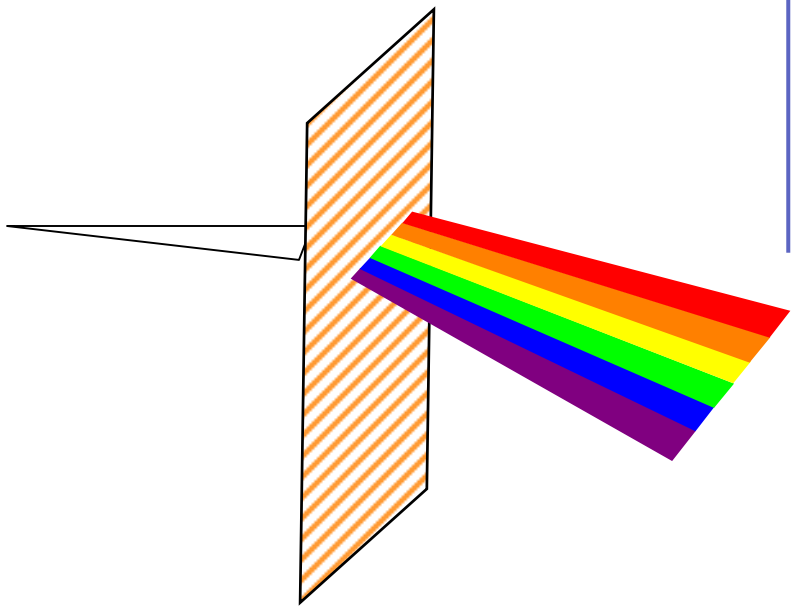
Henry Buijs

# FTIR principles

# Dispersive Infrared Spectroscopy



Prism dispersion



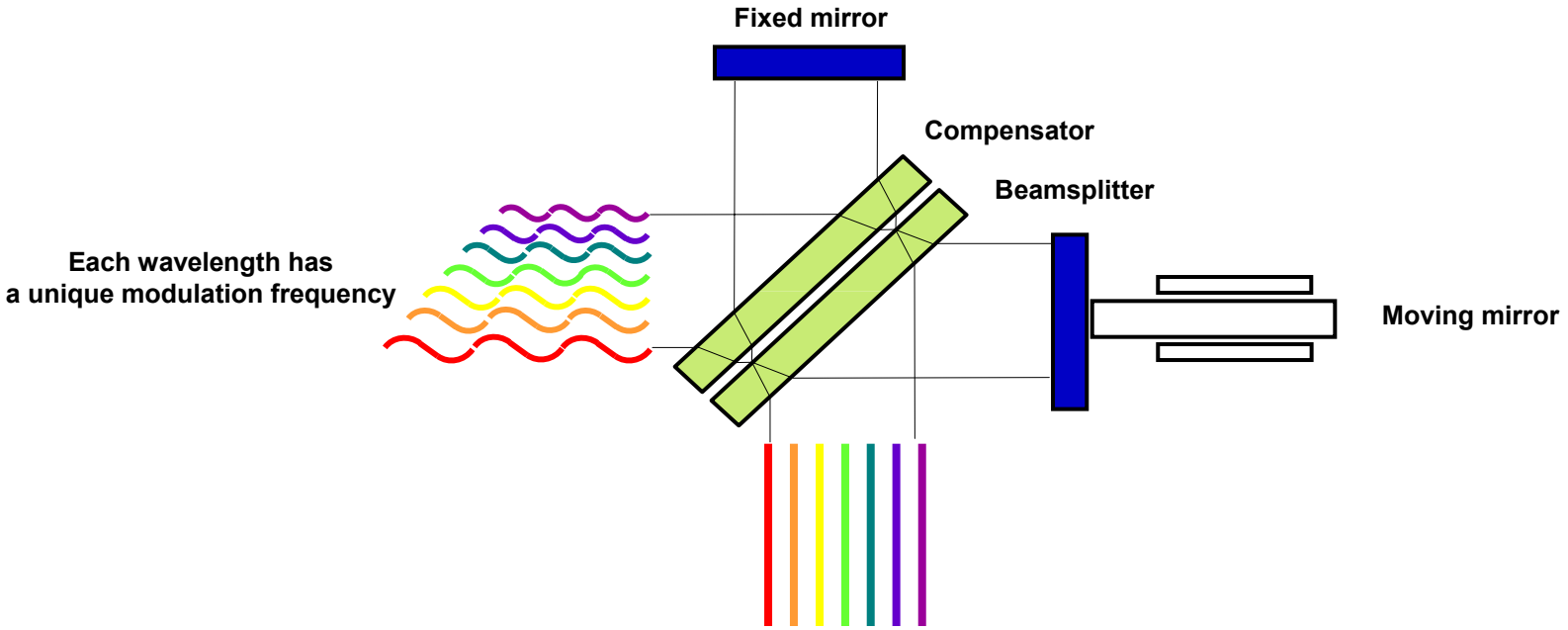
Diffraction grating

## Geometric wavelength separation

# The Michelson Interferometer

- Optical part of FT-IR
- 2 flat mirrors and a beamsplitter
  - One mirror moves
    - Changes optical path of split light beams
    - Recombine light and get variable interference

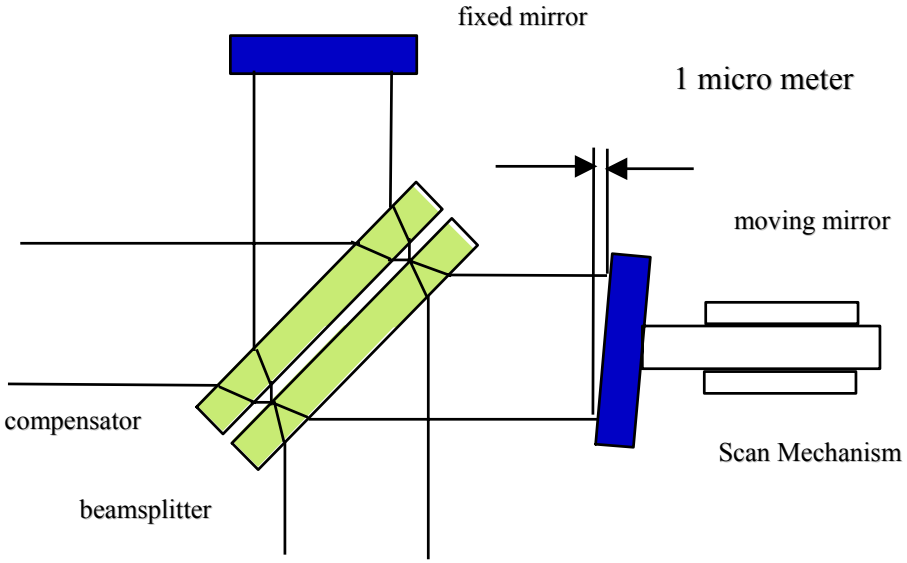



**Wavelength separation by modulation**

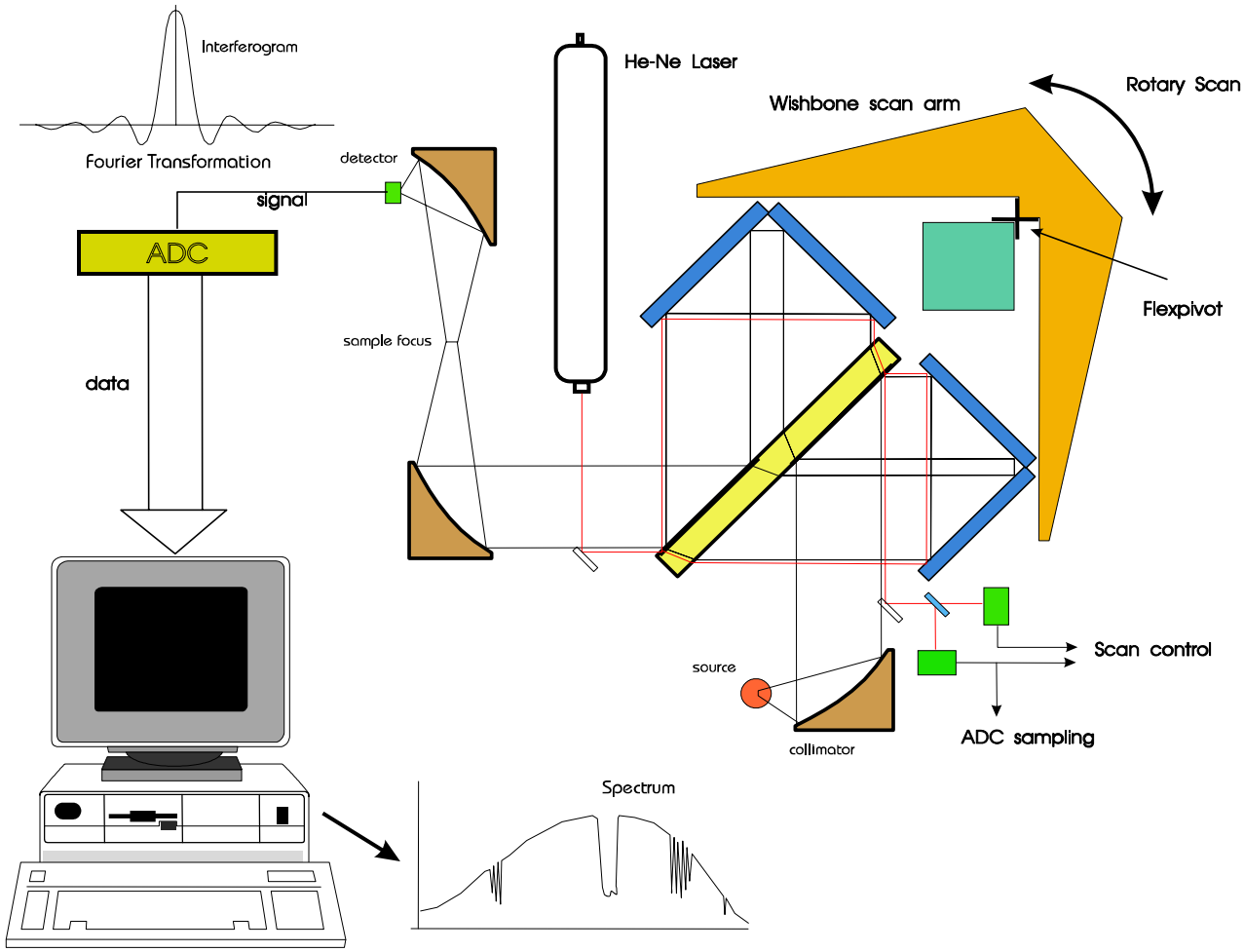
# FTIR technology

- Many Interferometer types are used by different FT-IR manufacturers. Why?
  - **To achieve more <u>stable</u> and <u>reproducible</u> operation**
    - **The original Michelson interferometer is sensitive to misalignment**
    - **Tilt of 1 micrometer across the IR beam (25 micro radians) will change interferogram by >10%**
    - **The scan mechanism can wear out or become irratic**



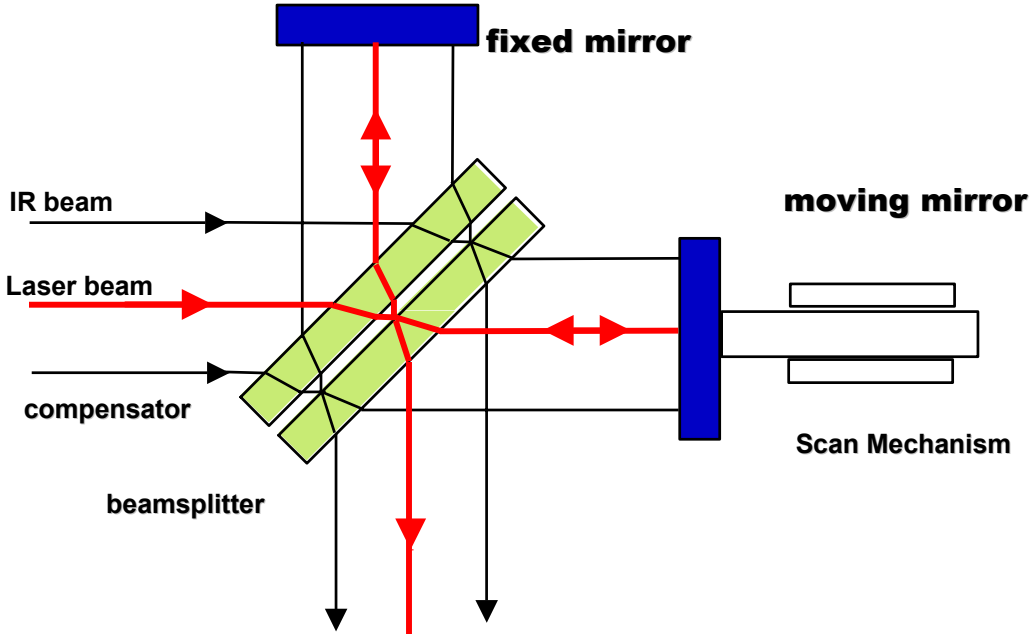
# The ABB Michelson FT-IR



# FT-IR with Laser Controlled Measurement

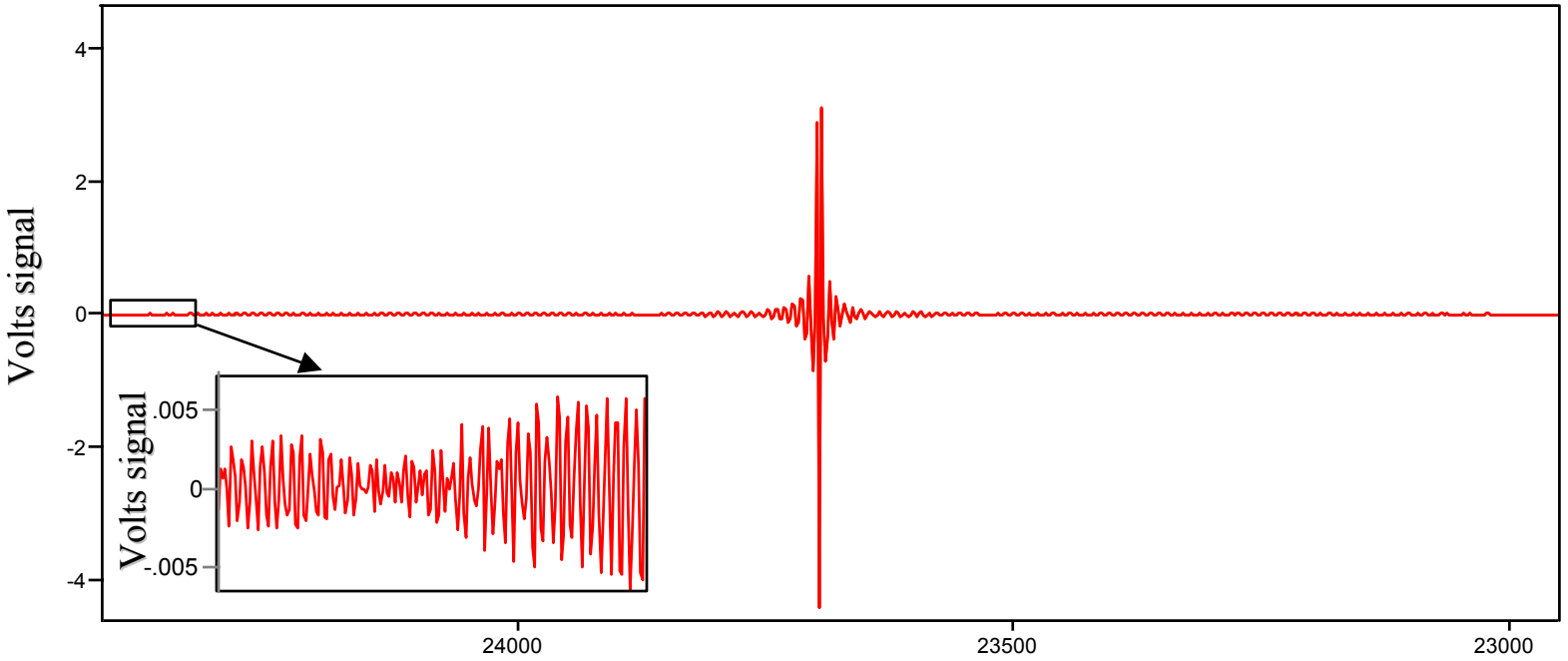
- Modulation frequencies of all wavelengths are locked to modulation frequency of an internal He-Ne laser
  - Provides ultra precise measurement of spectral frequencies
  - Provides reproducible measurement of spectral frequencies



# Measurement with FT-IR

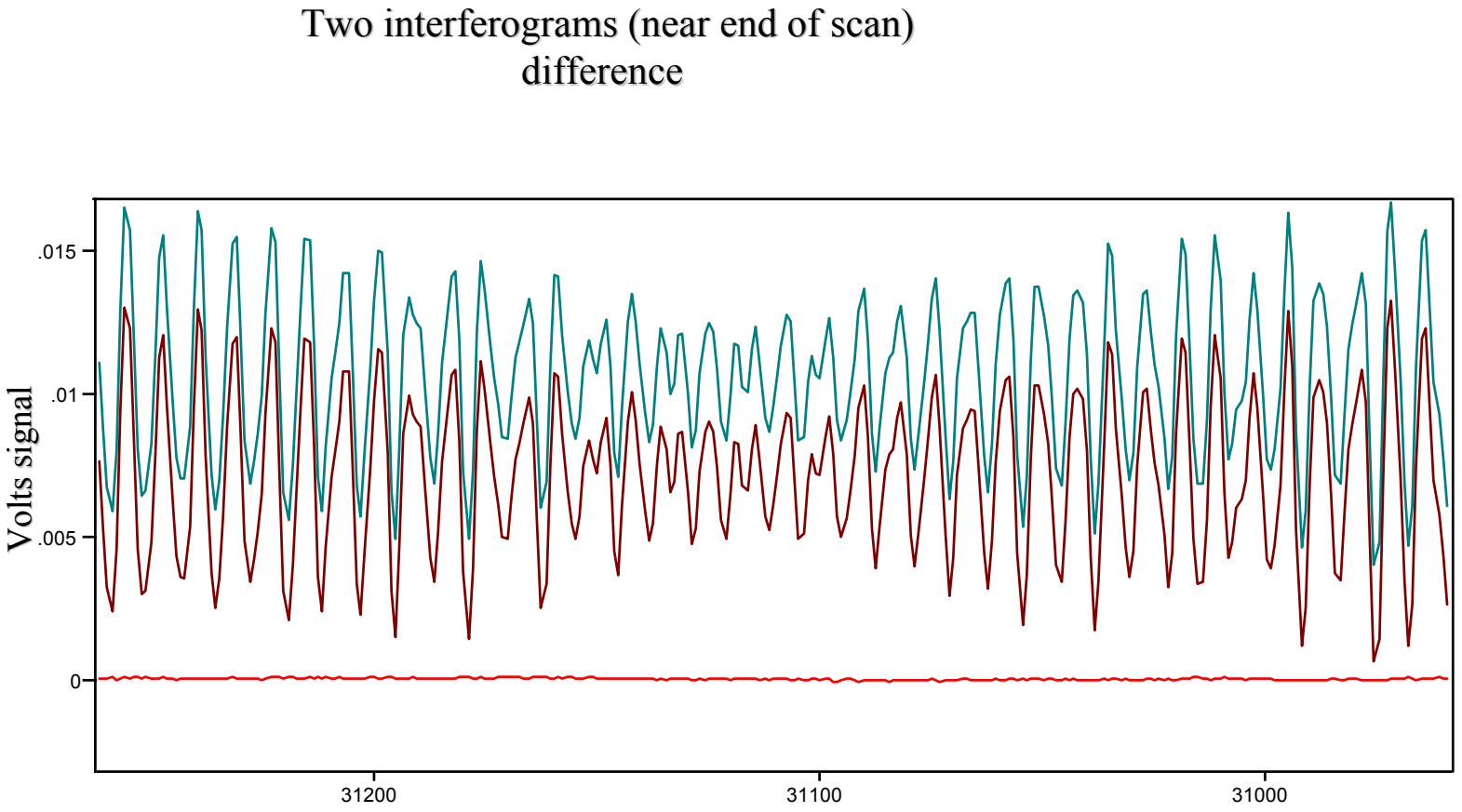
Typical interferogram
4 volts at centerburst
0.004 volts at end of scan




Interferogram / Arbitrary X

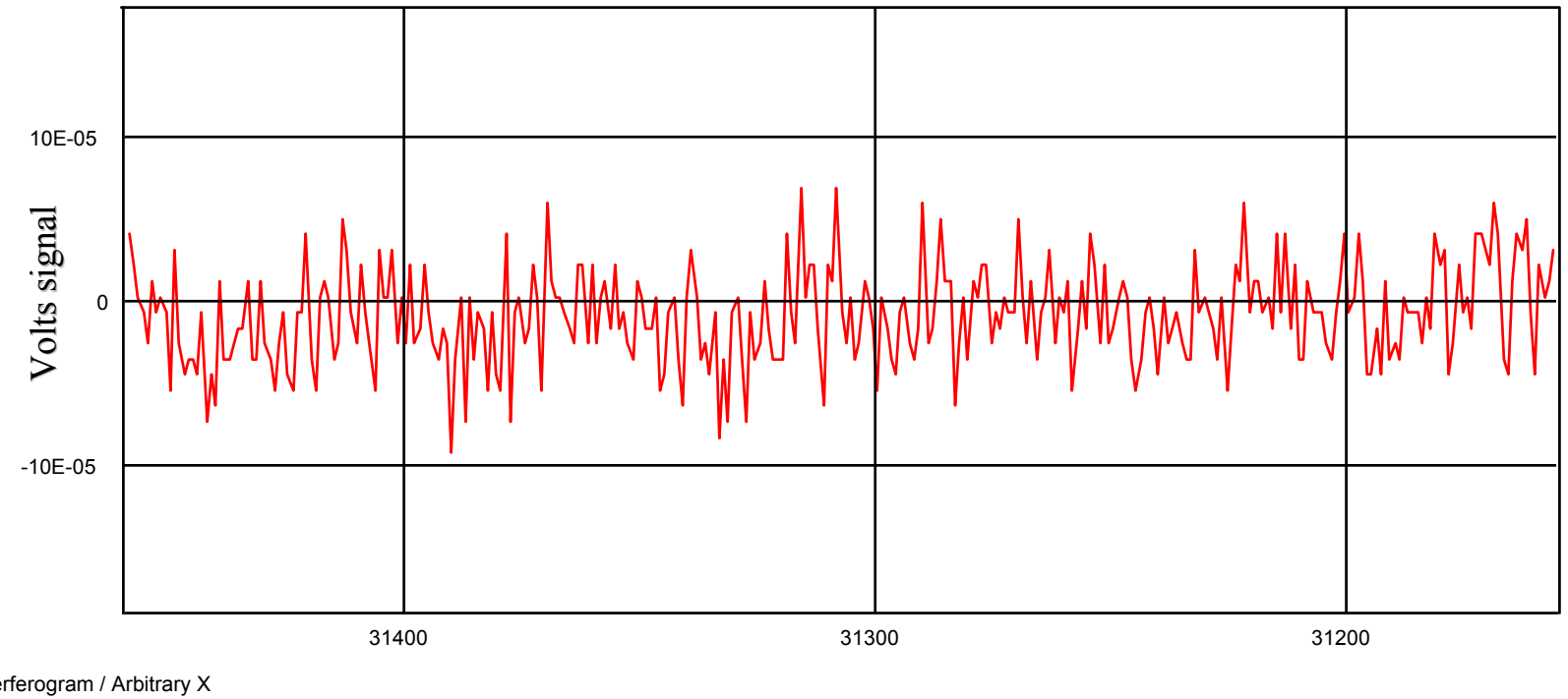
# Measurement with FT-IR



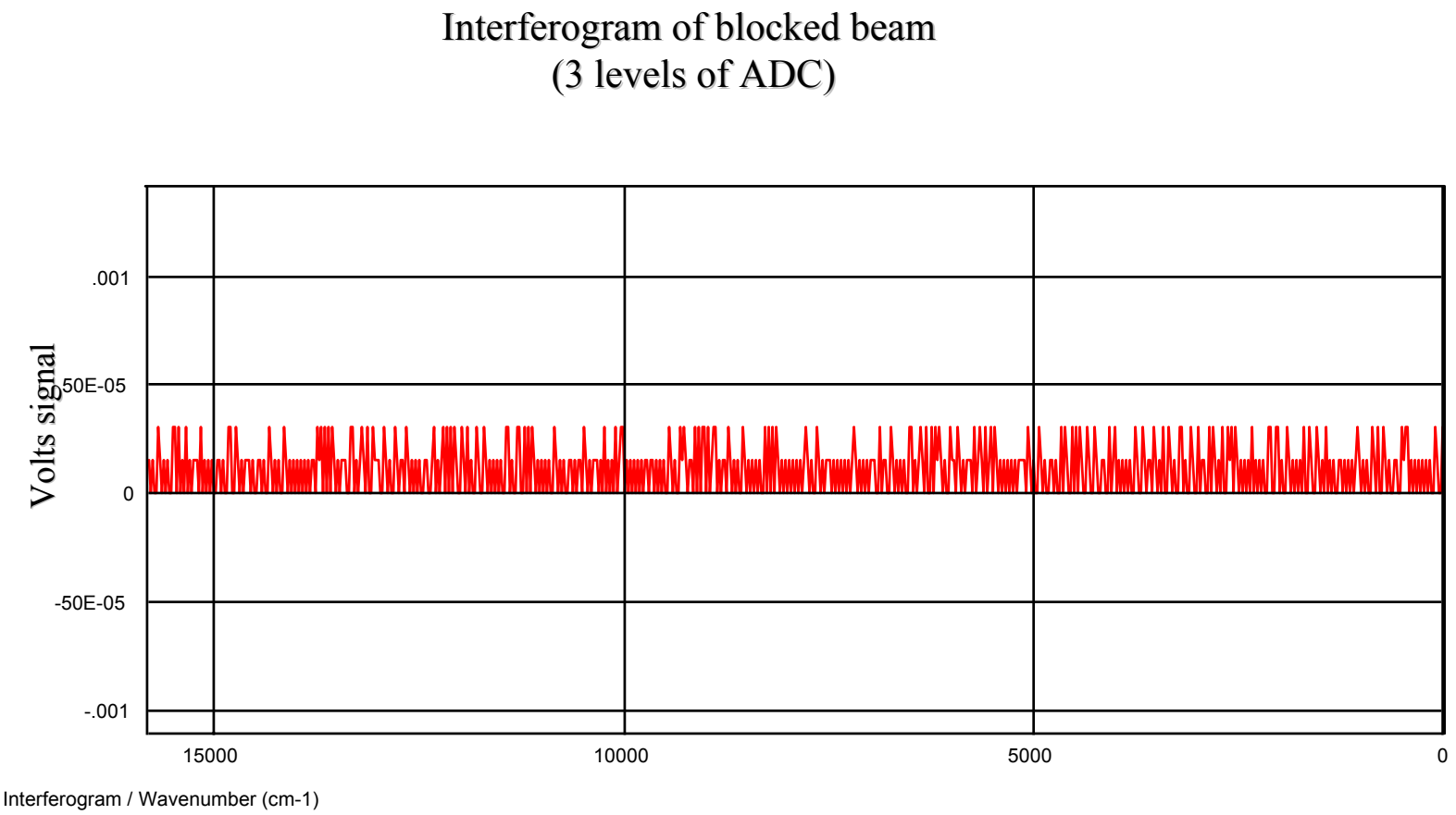
# Measurement with FT-IR

Difference between 2 interferograms (16 coadded scans )
(peak signal (4volts)/p. to p. noise =40000:1)



# Measurement with FT-IR

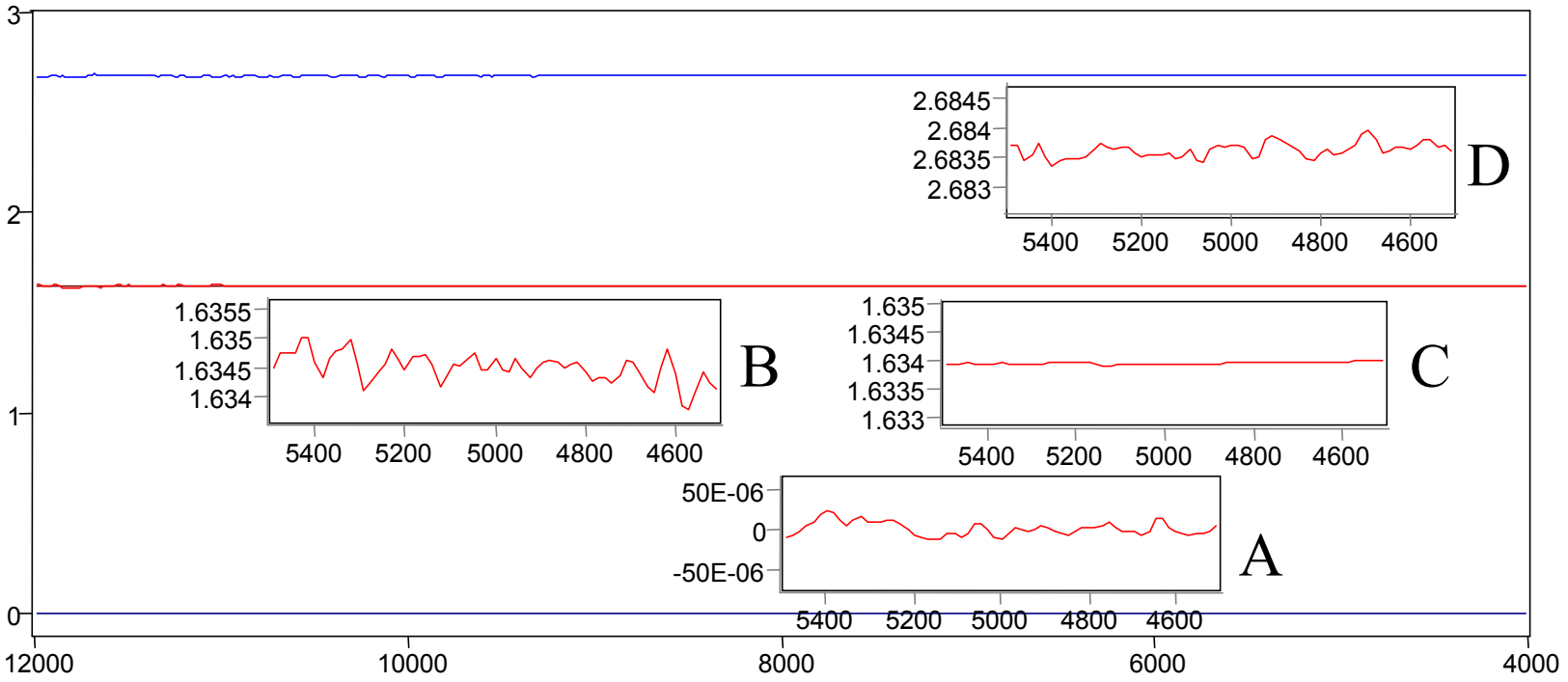


# S/N achievable

Table 1

| figure | RMS noise in Micro A | At 4000 cm-1 2500nm | At 5000 cm-1 2000nm | At 5800 cm-1 1725nm | At 6600cm-1 1515nm |
|---|---|---|---|---|---|
| A | 0A | 4.3 | 2.6 | 3.25 | 4.6 |
| B | 1.634A | 168 | 160 | 148 | 177 |
| C | 1.634A +gain | 11 | 6 | 8.5 | 14 |
| D | 2.683A +gain | 125 | 83 | 105 | 145 |

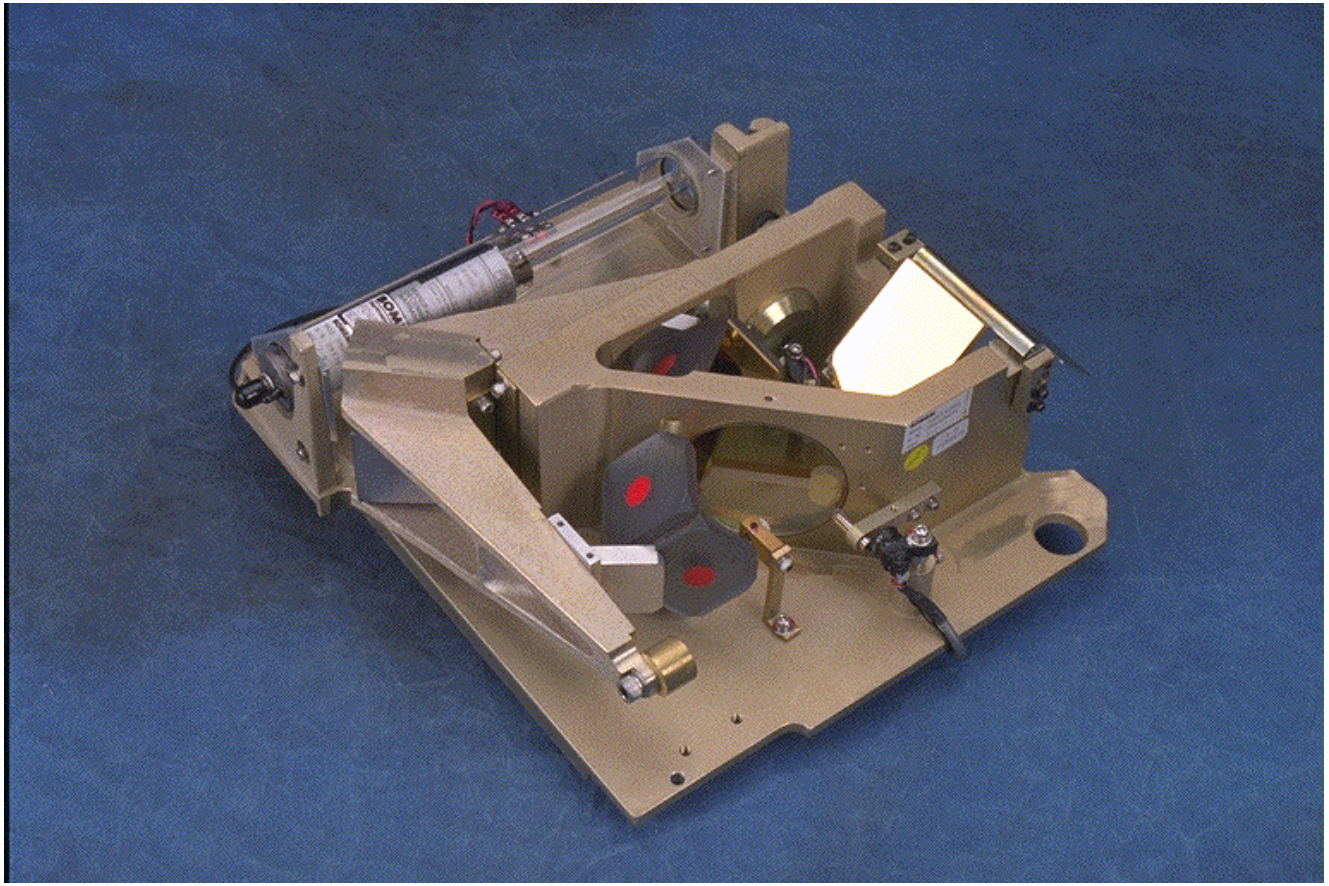


# Interferometer Features

- Patented Michelson type interferometer
  - Cube corner retroreflectors mounted on a "wishbone" swing arm.
- Factory prealigned interferometer
  - and input/output optics. Does not require any adjustment by user.
- Scanning by rotating the swing arm on a flex pivot, driven by an induction motor
  - This provides smooth, constant-velocity, perturbation-free scanning without wear.

# The ABB Michelson FT-IR



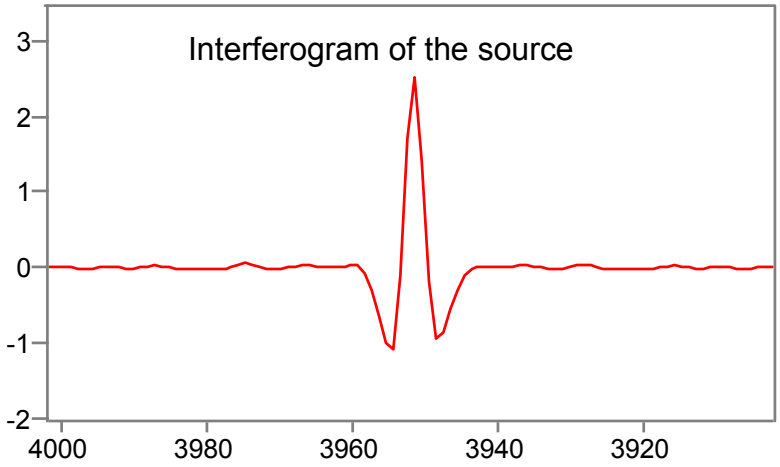
 

# Acquisition of an Infrared Spectrum

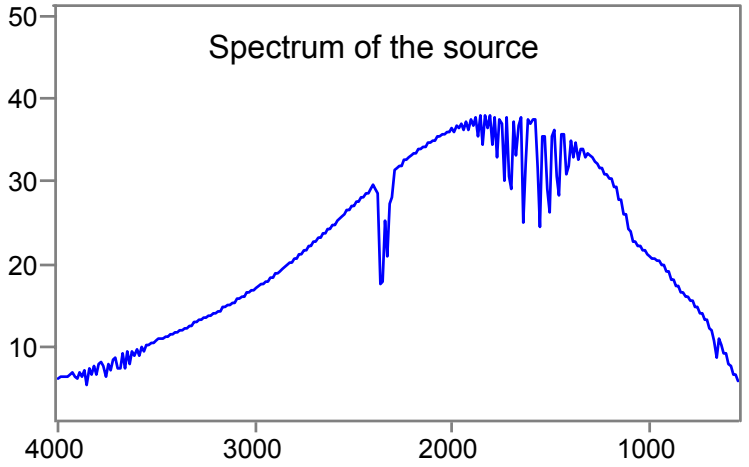
- The light coming from the source goes through the interferometer; the movement of the mirrors causes an interference pattern which is called the interferogram
- Next the light passes through the sample; the interferogram of the source is modified as the light is absorbed by the sample
- The interferogram is measured by the detector
- The interferogram is transformed into a spectrum by a mathematical operation called the Fourier Transform algorithm

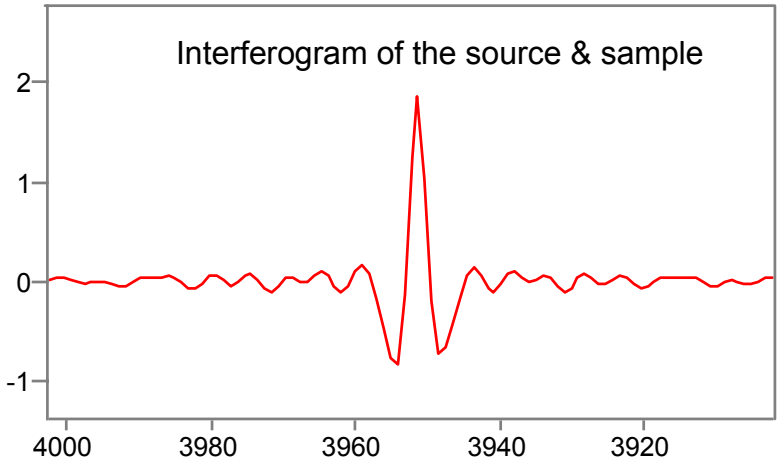
 

# Acquisition of an Infrared Spectrum

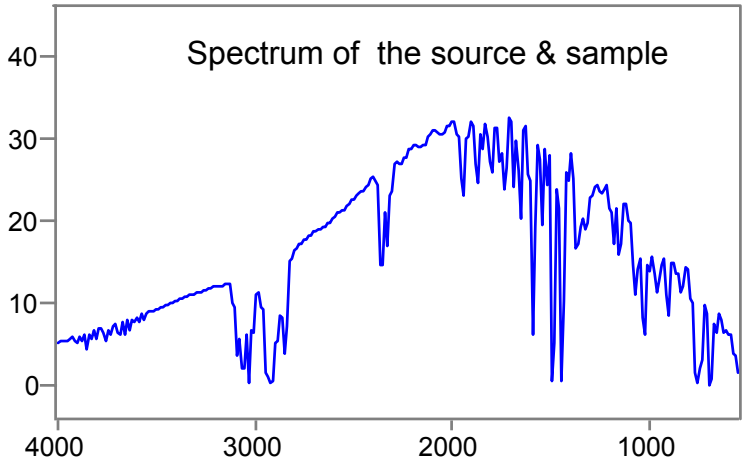



FT



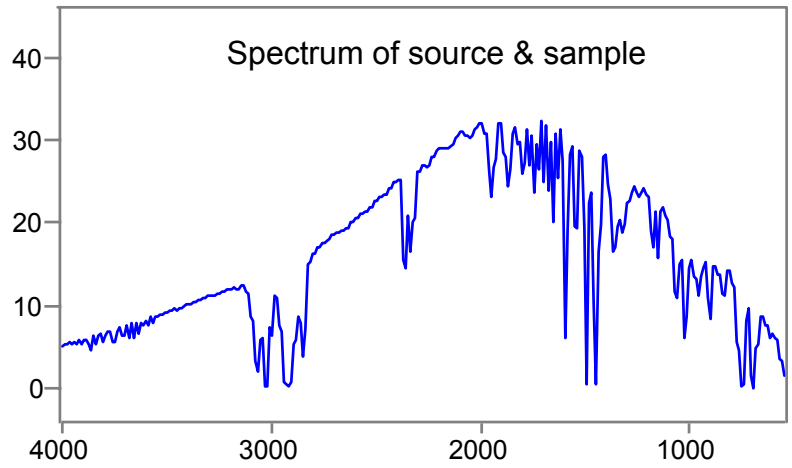




FT

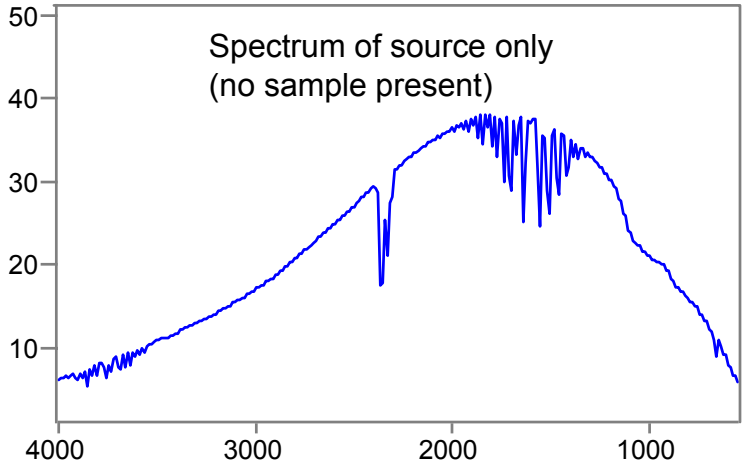


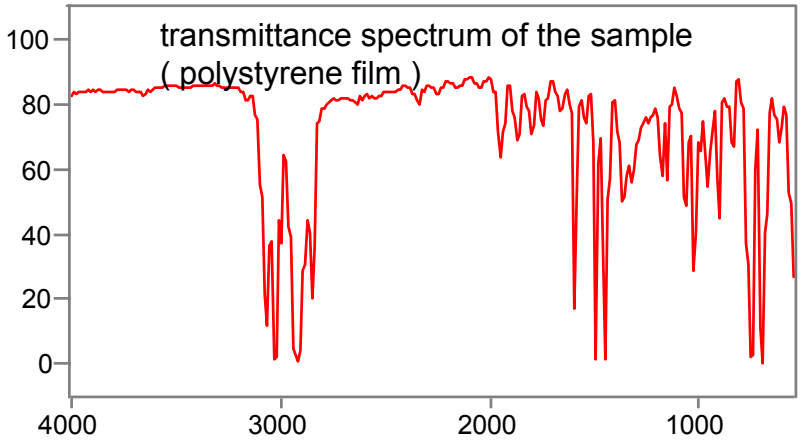
# Acquisition of an Infrared Spectrum




divided by




gives



# Advantages of FT-IR Over Dispersive

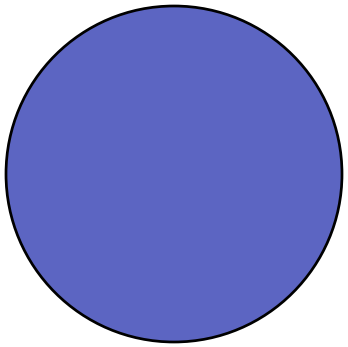
- Optical efficiency
- Measurement efficiency
- Precision of measurement

# Optical Efficiency of FT-IR

- A dispersive spectrometer has much greater light restriction than FT-IR for the same size and resolution spectrometer
  - A Dispersive spectrometer has a slit width of 0.25mm by 5mm high
  - FT-IR has a round aperture of 7.5mm diameter
    - Ratio of areas for FT-IR/dispersive is 35

Dispersive spectrometer
Slit 0.25x 5mm
1.25mm2



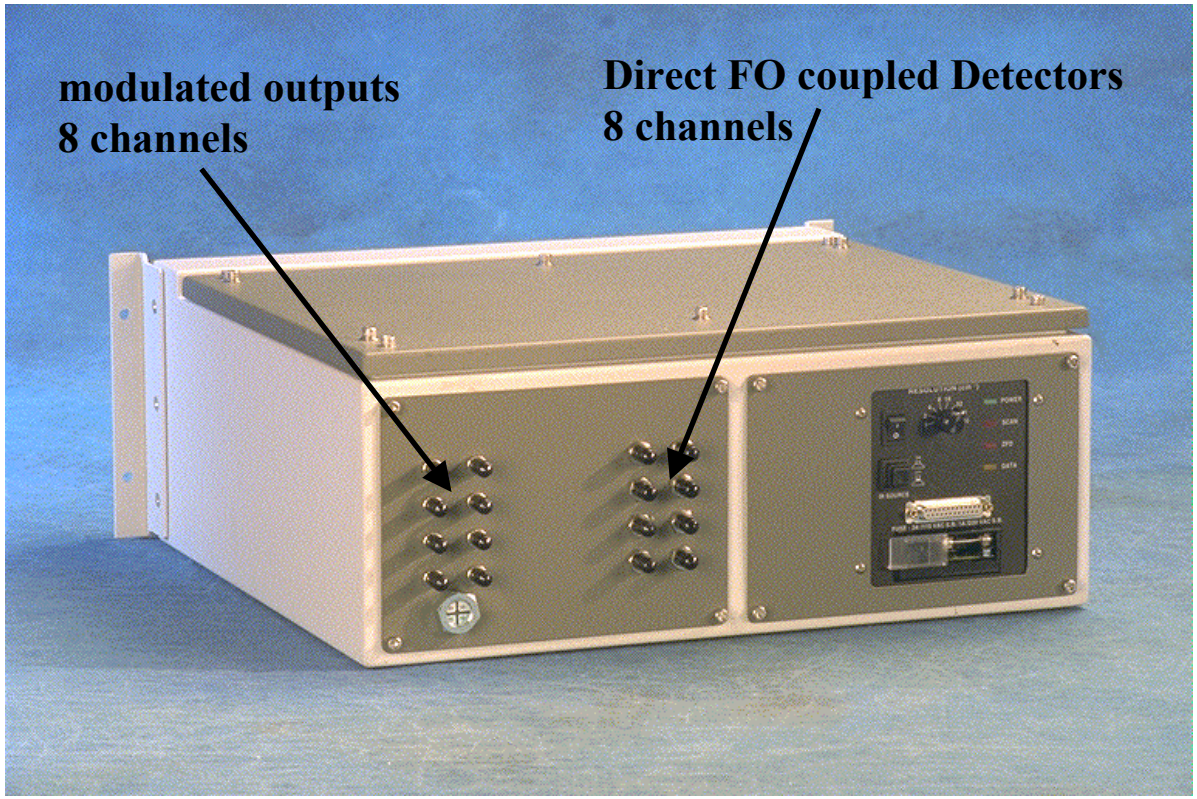
FT-IR
Jacquinot stop 7.5 mm diam
44 mm2

## Optical efficiency of FT-IR

- FT-IR has sufficient throughput to simultaneously illuminate 8 sampling accessories via fiber optic cables

The ABB FTPA2000-200 (Network*ir)*



# Measurement Efficiency of FT-IR

- Multiplexing
  - Grating observes 1 spectral element at a time
    - 1000 to 2500 nm with 4 nm resolution = 375 elements
  - FTIR observes all spectral elements at the same time
    - 4000 to 10000 cm-1 at 16 cm-1 =375 elements
    - Typical advantage 20x
- All wavelengths are modulated simultaneously
  - A single detector measures all wavelengths continuously

# Precision Requirements in IR Spectroscopy

- For quantitative analysis via IR spectroscopy, the spectra of a sample should be reproducible

- For a reproducibility of 1%,
  - The absorbance scale must be reproducible to <1%
    - Requires <1% error in transmittance when transmittance is >50%
    - Requires <0.1% error in transmittance when transmittance is near 10%
  - Frequency scale must be reproducible to <1% of resolution
    - At 4 cm-1 resolution error must be <0.04 cm-1

# Precision: Dispersive Spectrometry vs. FT-IR

- Dispersive Spectrometers
  - Wavelength is established by mechanical tolerance on slit position
    - Best mechanical tolerance is
      - 1 micrometer
      - 1 part in 25000
        - for 2.5 cm structure
    - +/-0.3 cm-1 at 7500 cm-1
  - Any detected light not passing through spectrometer adds offset to transmittance of sample
    - Absorbance scale reproducibility limited by stray light
- Reproducibility limited to low resolution and low absorbance applications only

- FT-IR
  - Wavelength is established by internal He-Ne Laser
    - 1 part in 1 000 000
    - repeatability <+/-0.008 cm-1 at 7500 cm-1
  - For ABB FT-IRs
  - Guaranteed Absolute Accuracy of frequency scale
    - +/-0.04 cm-1 at 7300 cm-1
  - Any detected light not modulated by FT-IR does not cause offset to transmittance of sample
    - There is no stray light in FT-IR
- Better Reproducibility over a wider range of resolution and absorbance

# Repeatability and Stability of ABB's FT-IRs

- Internal laser controlled mirror scan
- Laser coaxial with IR beam provides frequency scale repeatability of +/-0.001 cm-1 (2 $\sigma$ )
- Permanent factory alignment of interferometer provides
  - 100% line repeatability  < 0.1% short term
  - 100% line repeatability < 2% over 16 hour interval
  - Long-term 100% line repeatability of spectral structure <0.1%
    - Linear baseline shift and tilt < 2%
  - It is common to use the same spectral response reference for as long as a year.

# Identical Spectral Response

- All units have identical spectral response
  - Reproducibility of spectral response approaches repeatability
  - Calibration transfer without chemometric correction
    - From analyzer to analyzer
    - After repair of an analyzer

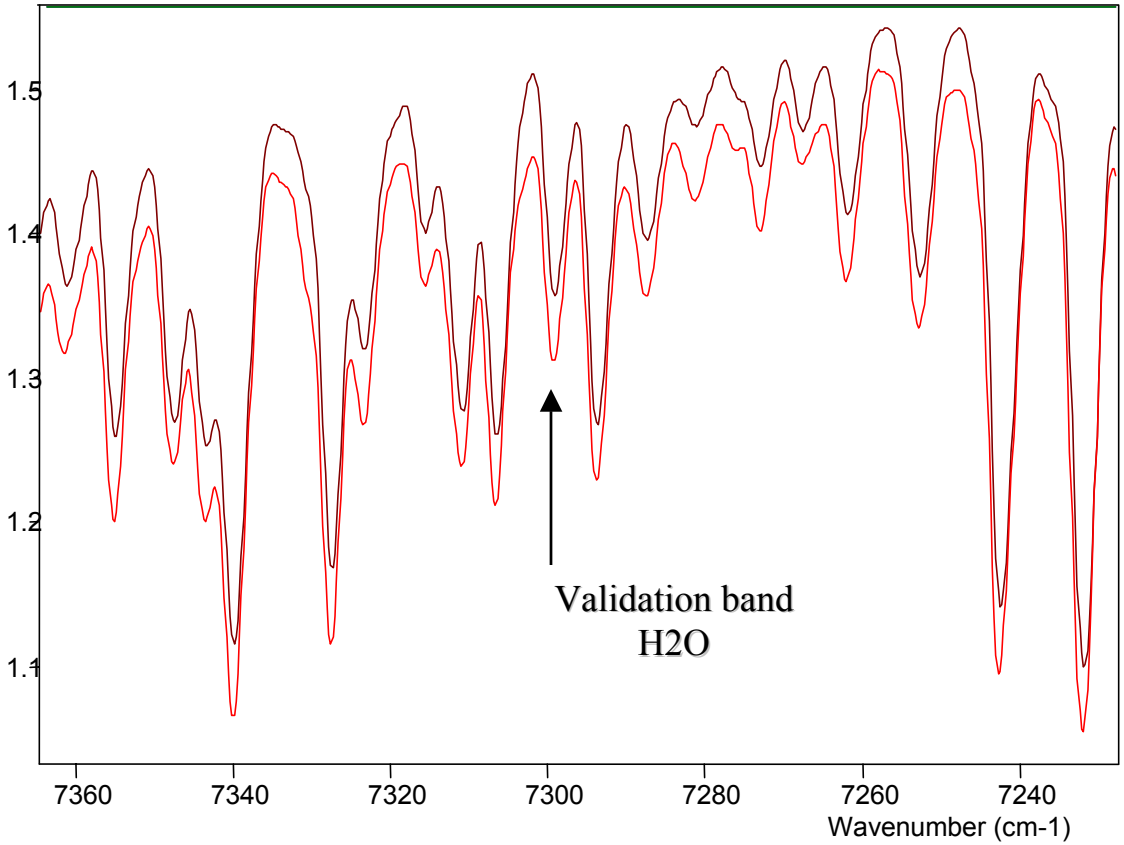
 

# Reproducibility of ABB's FT-IRs

- Spectrometer validation using standard samples provides
  - Frequency scale reproducibility within +/- 0.04 cm-1 ($2\sigma$ )
    - For FT-NIR, narrow water vapor line at 7299.85 cm-1
    - For FT-IR, narrow water vapor line at 1917.65 cm-1
  - Absorbance reproducibility within +/-0.002A ($2\sigma$ )
    - High purity Toluene in temperature controlled liquid cell or sealed vial, 0.5 mm path at 28ºC

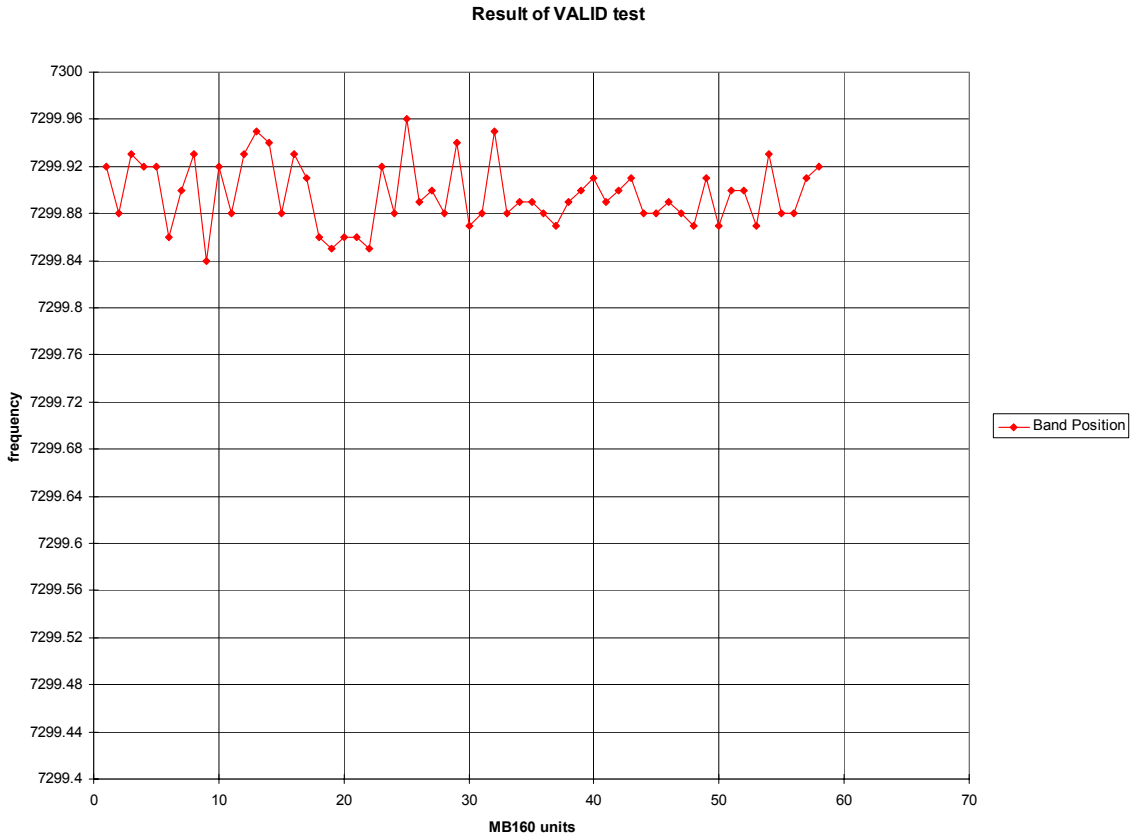
 

# Frequency Validation Water Spectrum



# Frequency Reproducibility



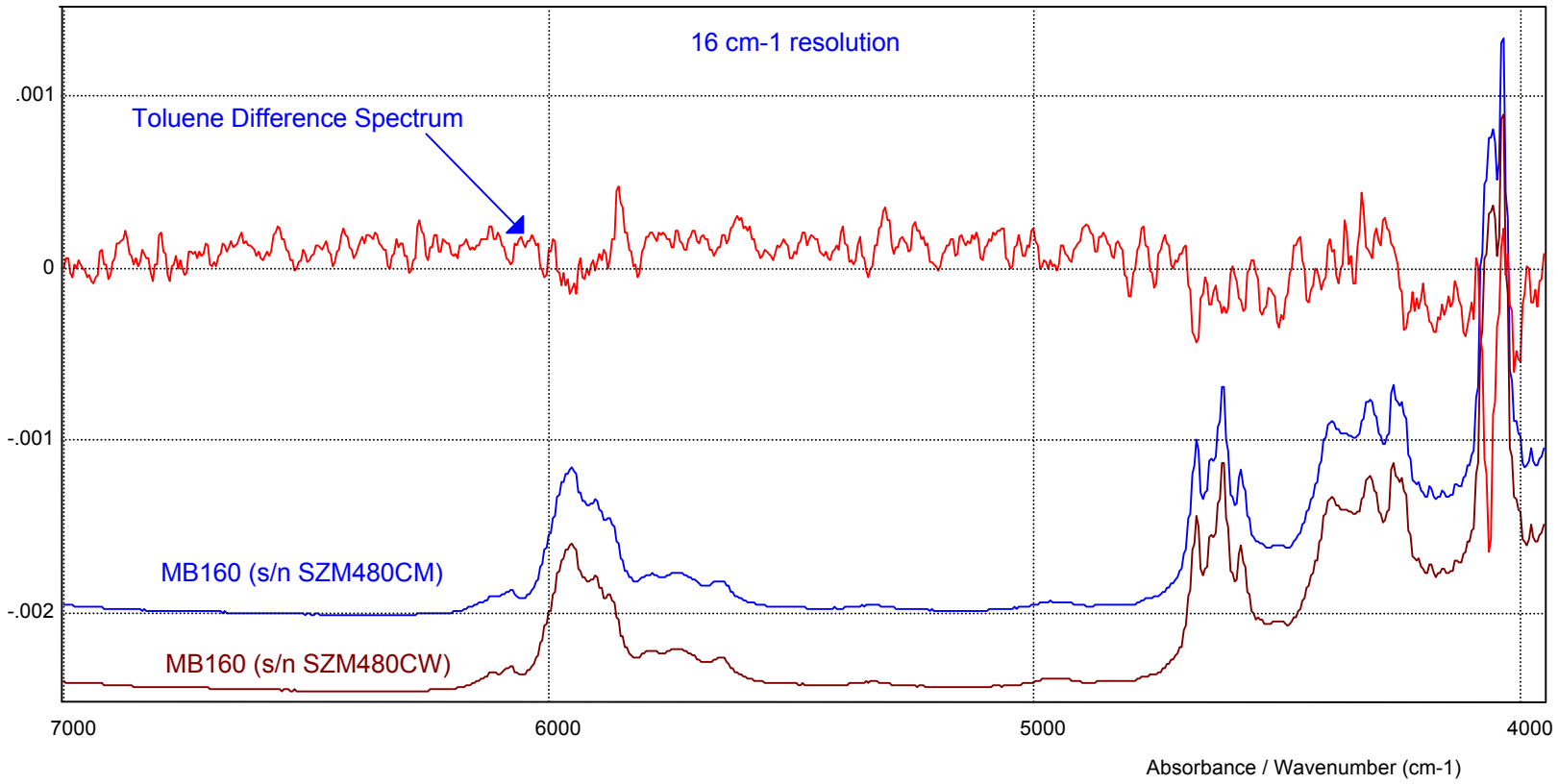

 

# Absorbance Reproducibility: Toluene

- Toluene Spectrum
  - Peak absorbance = 1.2 at 4050 cm-1
  - Average peak heights = 0.5 at 4200 to 4700 and near 6000 cm-1
  - Maximum absorbance deviation <0.002 A from 4200 to 7500 cm-1 ( 2 cm-1 resolution, 50 scans)

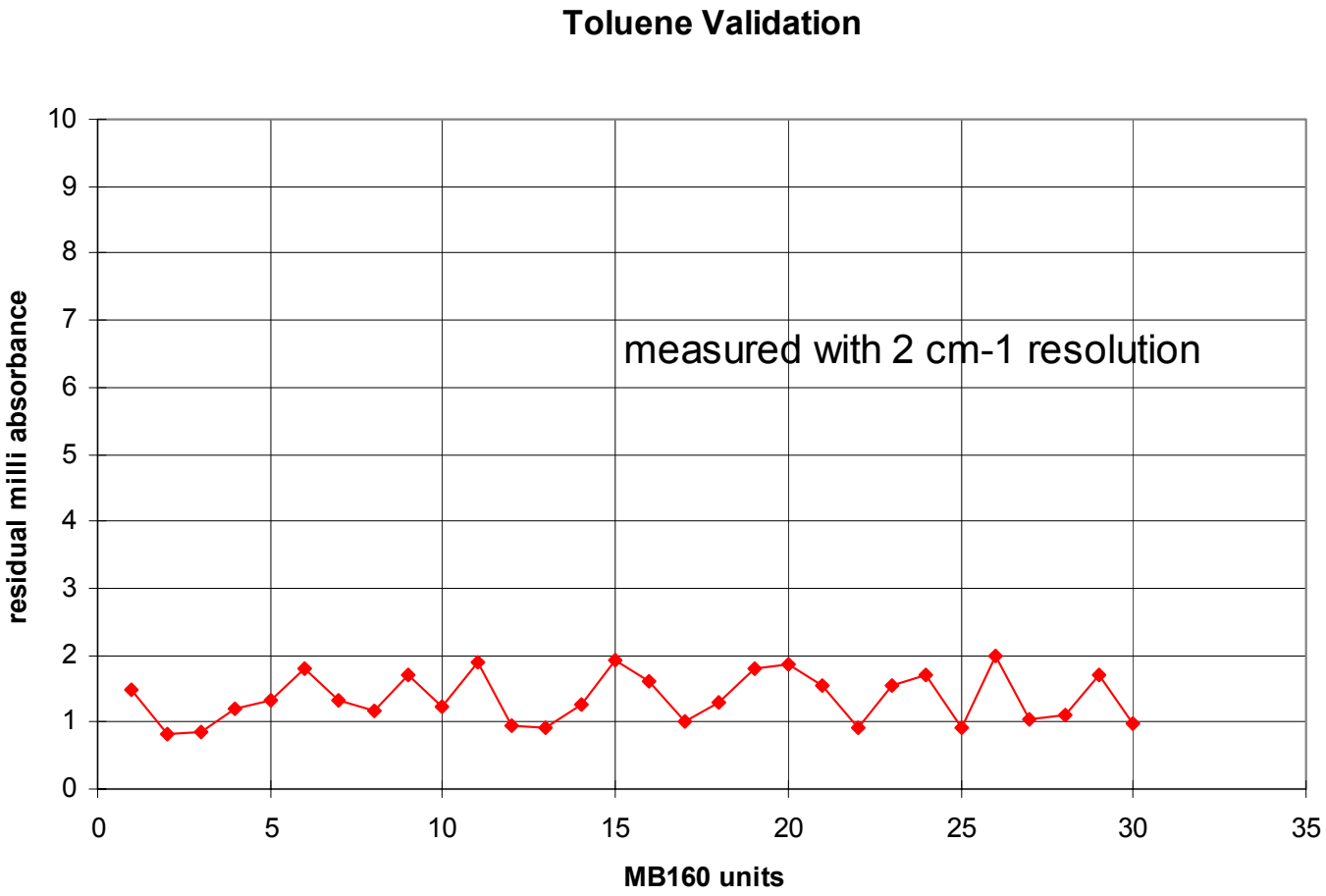
 

# Typical Toluene Reproducibility



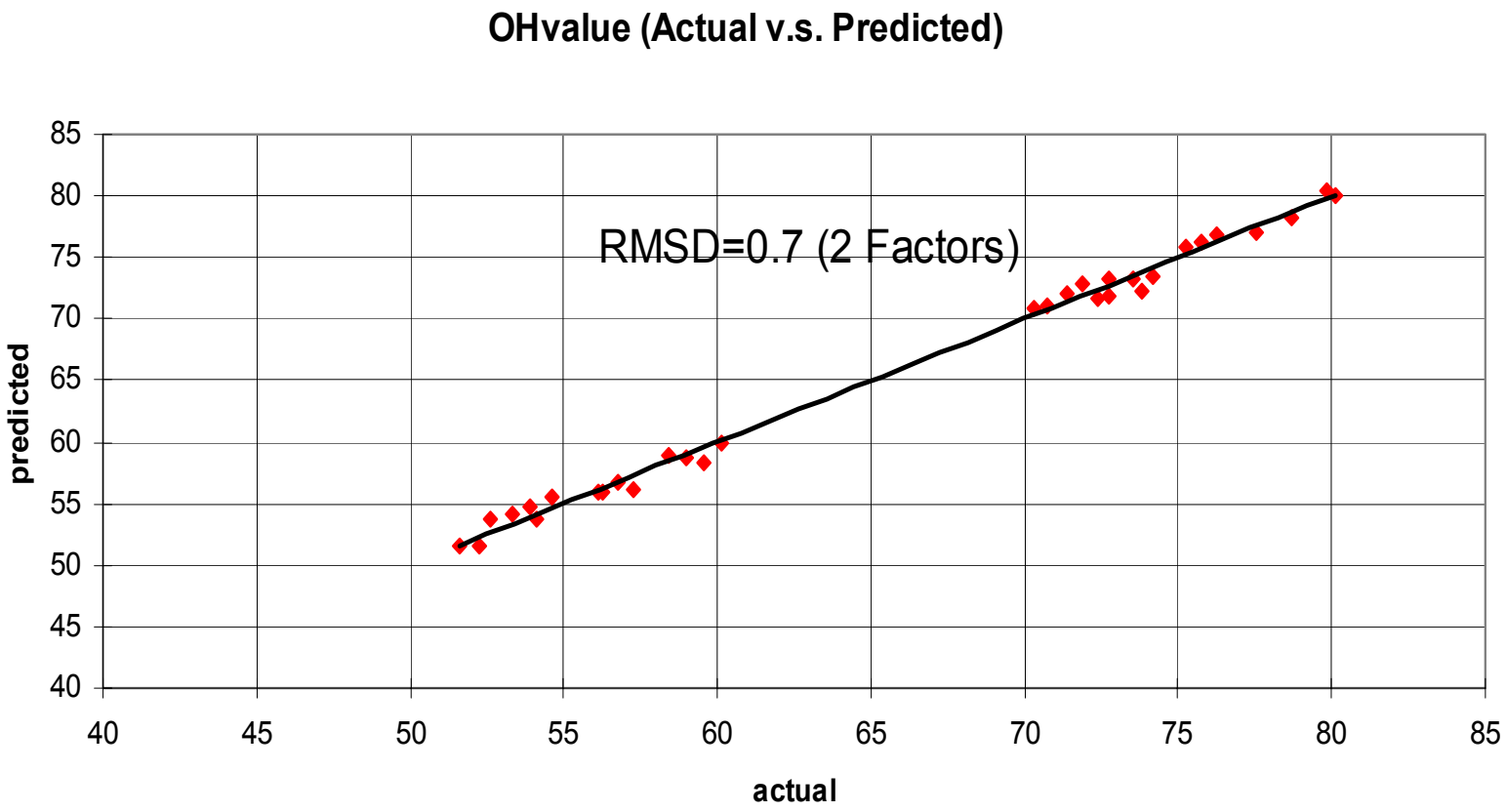

 

# Toluene Reproducibility Statistic



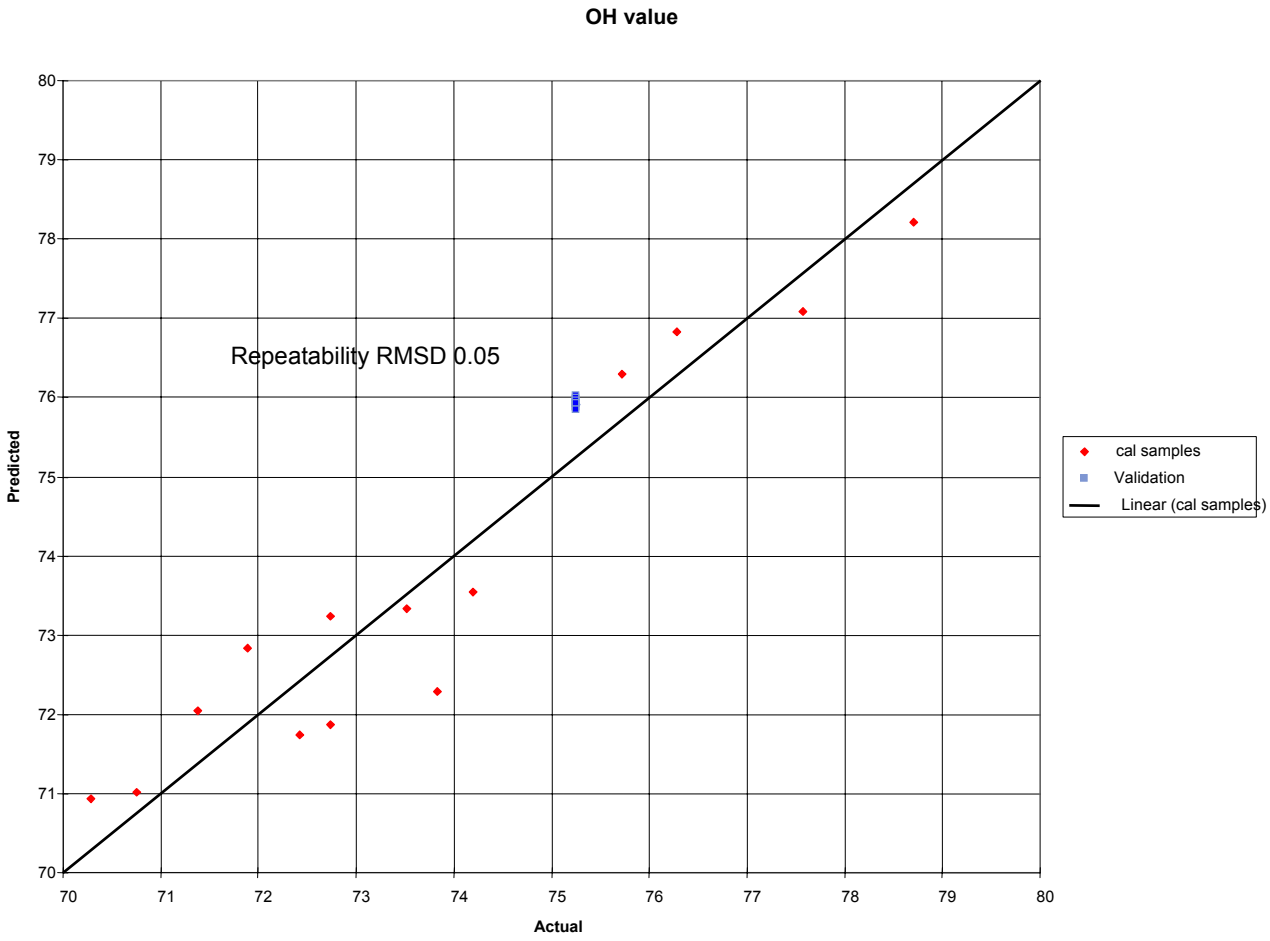

 

# An Example: OH Value Calibration



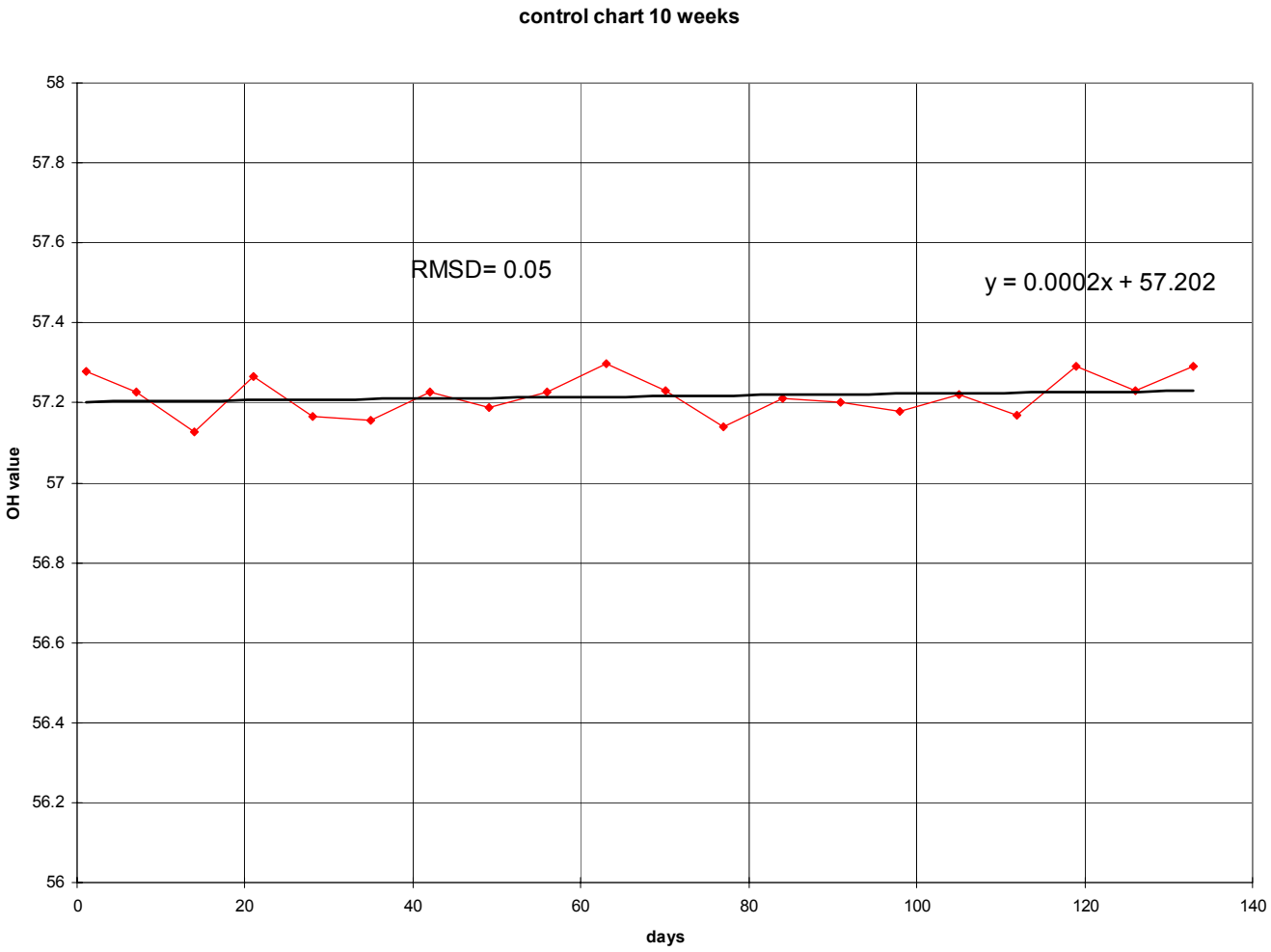

 

# OH Value Repeatability



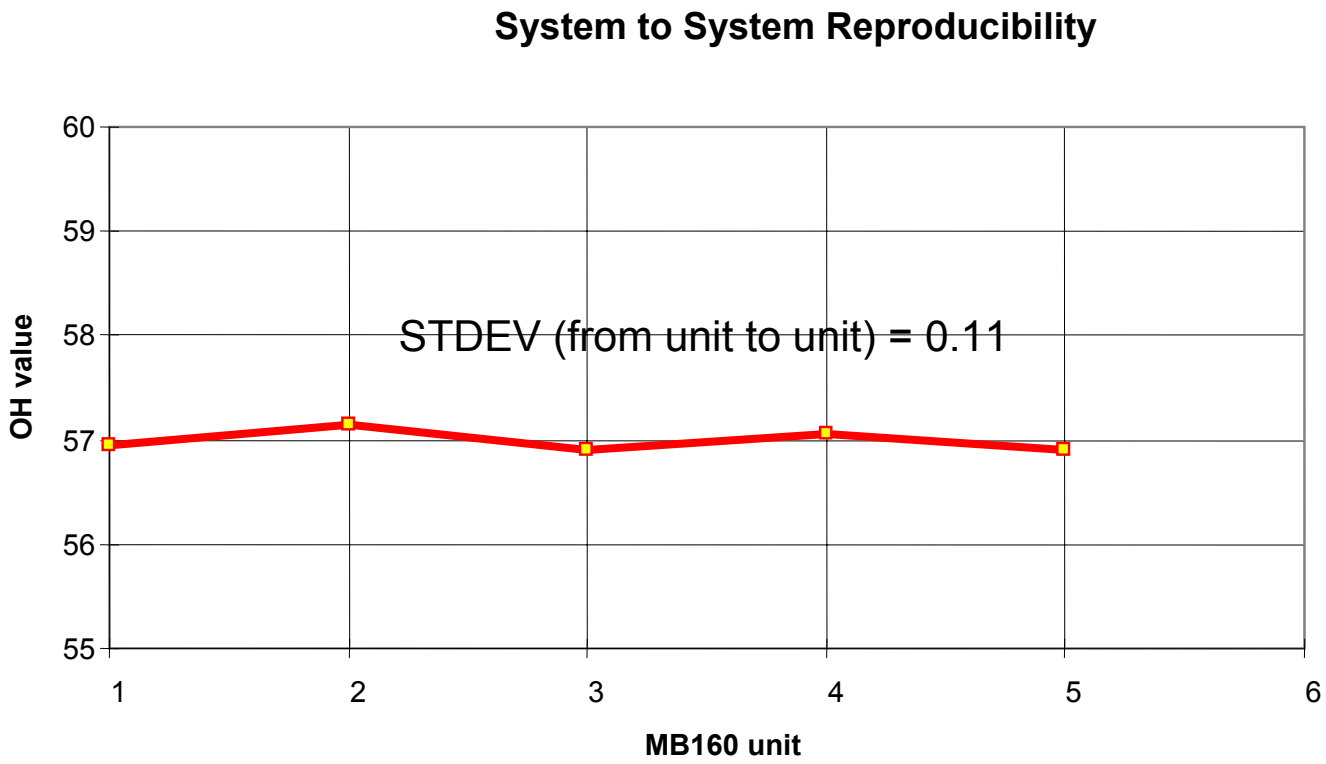

 

# OH Value Repeatability



# OH Value Reproducibility



# Advantages of No Drift and Identical Spectral Response

- Less effort is required to develop a calibration
  - There are no analyzer variations to model
    - A robust calibration for OH value for a polyol requires 10 to 15 reference samples.
- Less calibration maintenance
  - Once a calibration is developed it can be used indefinitely as long as the product does not change
    - Some customers are working more than 5 years with the same calibration without any need for adjustment
- Can do applications that are difficult or costly to calibrate
  - Costly reference methods
  - Processes that are difficult to vary.

# The ABB Spectrometer Line

The infrared band can be divided into three regions: The Far infrared, the Mid infrared and the Near infrared.

- In the Far Infrared (< 400 $cm^{-1}$), we particularly study the structure of complex solids. This region is covered by the FTLA2000-102
- In the Mid Infrared (4000 - 400 $cm^{-1}$), we study the structure of many natural products and gas phase samples. This region is covered by the FTLA2000-100, FTLA2000-104, FTLA2000-154
- The Near Infrared (12000 - 4000 $cm^{-1}$) region is used particularly for quantitative analysis. It is covered by the FTLA2000-154, and FTLA2000-160

# The ABB Spectrometer Line

On-line analyzers:

- FTPA2000-300 (Work*ir)*
  - Single-point analyzer existing in Mid IR and Near IR versions.

- FTPA2000-200 (Network*ir)*
  - Near IR fiber-optic coupled multipoint analyzer. Can monitor up to eight sampling points.

# Summary

- With FT-NIRs from ABB expect
  - Analyzers that do not drift over time
  - Analyzers that have identical spectral response
    - Calibrations give the same results on any analyzer
    - Calibrations require no correction after repair of analyzer