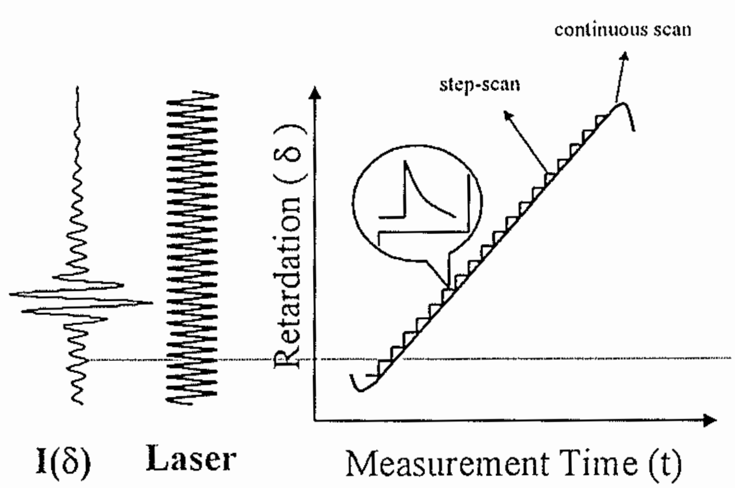
Outline

- FT-IR Interferometery
  - Continous-scan vs. step-scan
  - Nexus 870 vectra-piezo interferometer
  - Applications overview
- Dual-Channel Experiments
  - Polarization Modulation (IRRAS, VCD)
- Step-Scan Experiments
  - Amplitude Modulation
  - Phase Modulation
  - Time Resolved Spectroscopy
  - Sample Modulation

Continuous Scan vs. Step-Scan

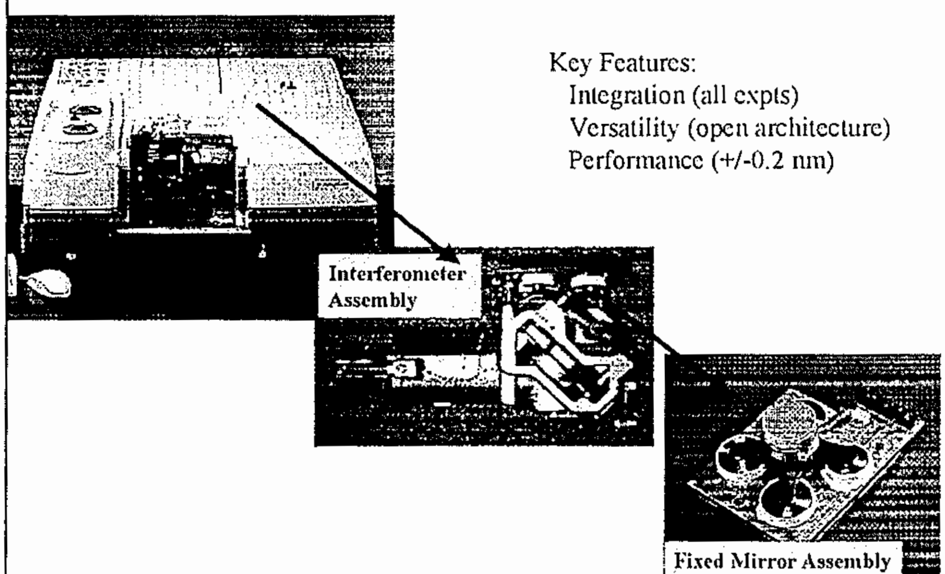


Features of Step-Scan

- **Independent of Fourier frequency**
- **Constant phase modulation (uniform probing depth in PAS)**
- **Convenient to extract dynamic signal phase (modulation experiments)**
- **High time resolution fast kinetic process (μs to ns TRS)**

Thermo Nicolet Nexus 870 Research FT-IR

Key Features:
- Integration (all expts)
- Versatility (open architecture)
- Performance (+/-0.2 nm)



Nexus 870 Vectra-Piezo Interferometer

- **Moving Mirror Control:**

  positions and holds *moving mirror* at desired laser crossing (+/- 0.2 nm accuracy).

- **Fixed Mirror Control:**

  generates *phase modulation* at desired frequency and amplitude using closed loop control of 3 piezoelectric transducers (5 - 1000 Hz, 0.5- 3.5 $\lambda_{He\text{-}Ne}$)

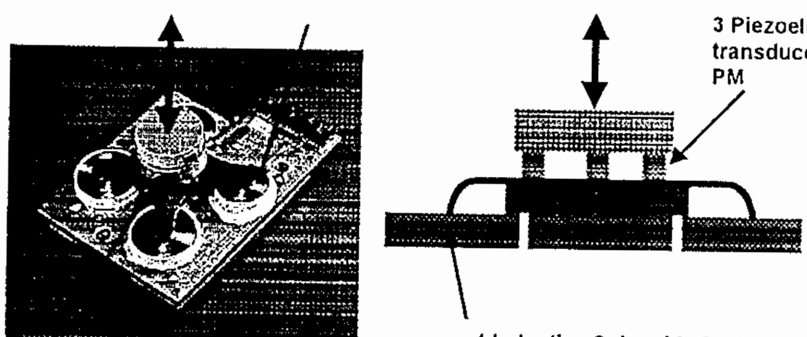
- **Dynamic Alignment Control:**

  checks and corrects alignment *only* during stepping using the fixed mirror assembly (smart dynamic alignment)

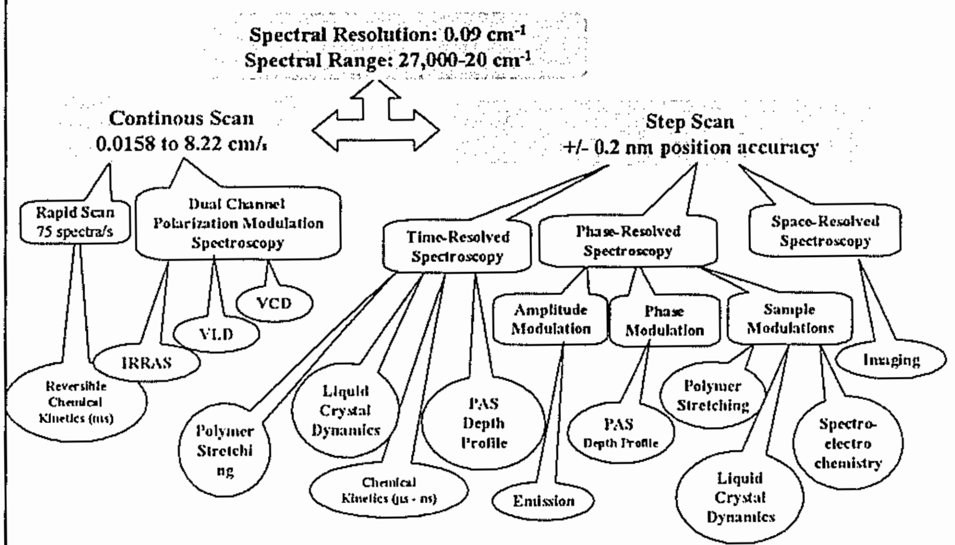
- **Flexibility in Experiment Design:**

  best accommodates TRS, modulation and imaging experiments

Dynamic Alignment (DA) and Phase Modulation (PM)



Overview of Advanced FT-IR Applications



Dual Channel Polarization Modulation

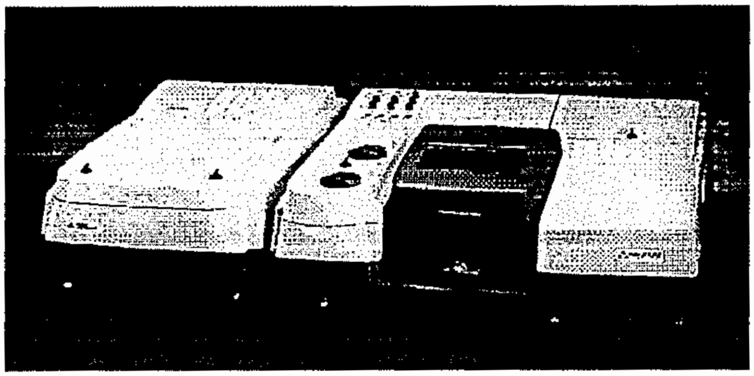
Why dual channel?
- Remove water and CO2 contamination

Why polarization modulation?
- Increase detection sensitivity

Why PEM module not TOM box?
- Pin-in-place optics. Installation time reduced by 95 %

Applications
- IRRAS (film on solid or liquid)
- VCD
- VLD
- Dynamic dichroic polymer stretching.

Nexus PEM Module



Polarization Modulation

Definition

Optical polarization direction is modulated at very high frequency (37 kHz or 50 kHz)

Advantages

Increase measurement sensitivity and detectivity.

Measure very small dichroic difference (dichroism) directly.

($\Delta A = A_0 - A_{90}$)

Cancels out species with randomly oriented dipoles.

Applications

IRRAS: thin films on metal substrate, air/water interface (LB).

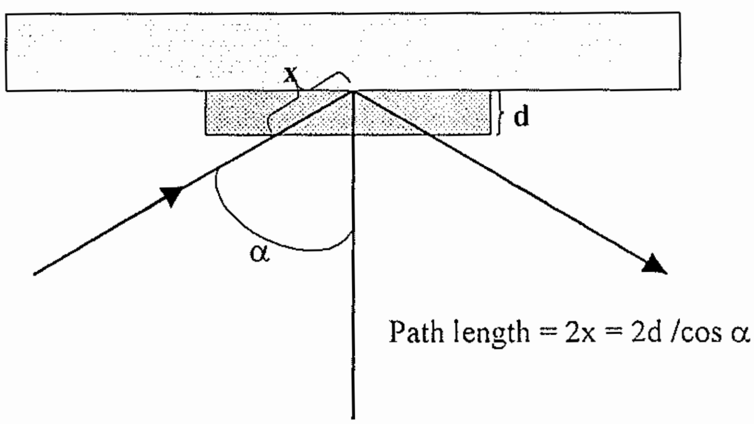
VCD: chirality of molecules.

VLD: vibrational linear dichroism of materials.

PM-IRRAS Experiment

- Dual Channel Spectroscopy
- Collect Sample and Background at the Same Time
- SST (Synchronous Sampling Technique)
- Two Independent, Electronically Matched Digitizers
- Double Modulation Experiment

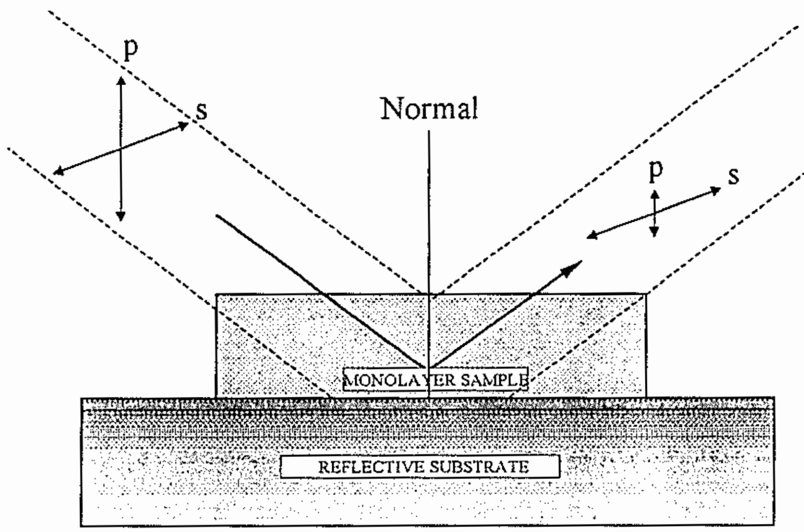
Reflection - Absorption



Transmittance: d = pathlength = 10 μm

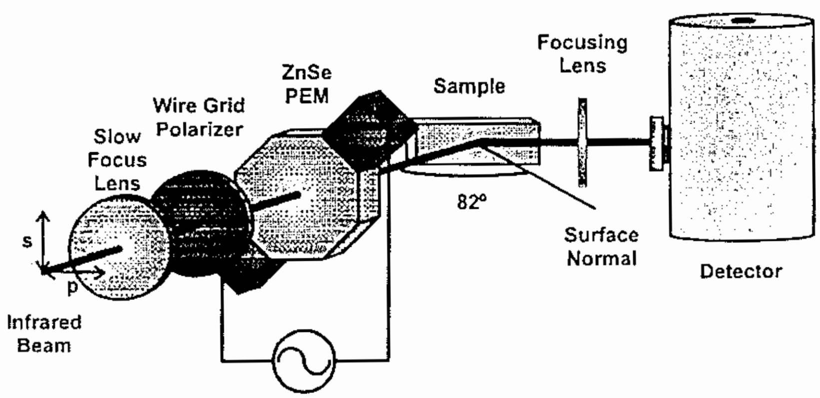
Reflection - Absorption: d (pathlength = 10 μm, $\alpha = 85°$) = 0.44 μm

Differential Spectroscopy
p - Polarized Light vs s - Polarized Light



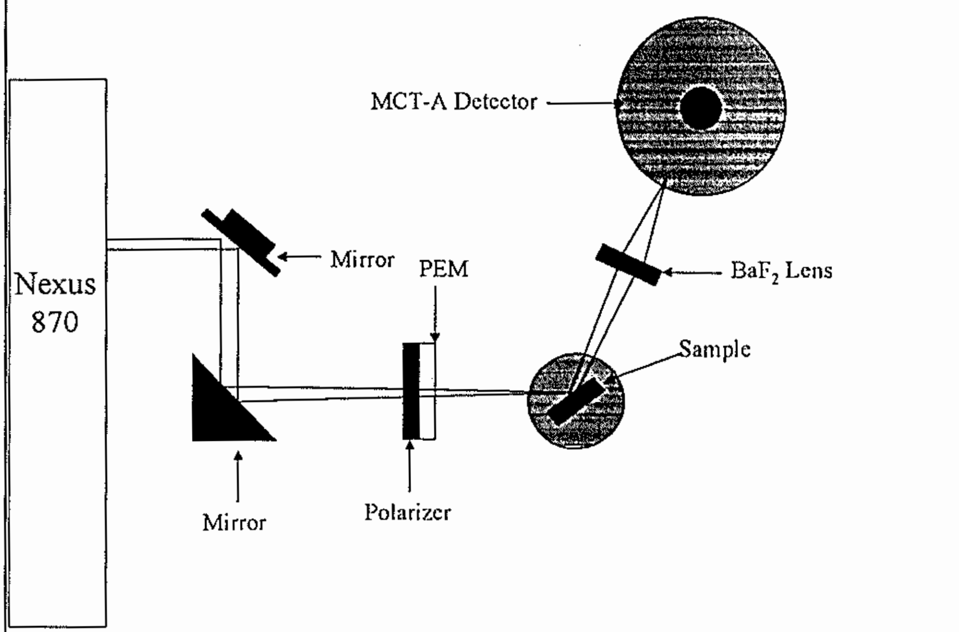
Nexus PEM Module:

Dual Channel PM-IRRAS Optical Setup - 3D View

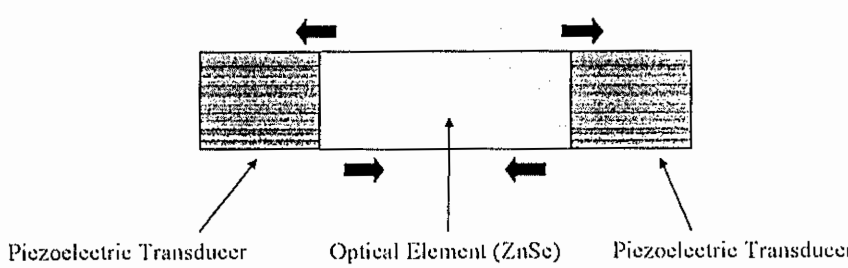


Notes:

1) IR transparent crystal (ZnSe) with piezoelectric actuators;
2) Resonant periodic stress on one axis induces anisotropy of refractive index
3) Anisotropy produces phase retardation and thus rotation of polarization



Photoelastic Modulator (PEM)



Compression and Stretching Causes an Oscillating Birefringence
The Frequency of the Oscillation is Constant for each Optical Head

Photoelastic Effect

Birefrigence - Different Linear Polarizations of Light have Slightly Different Speeds Through the Material

The Difference is Known as Retardation ($A(t) = z[n_x(t)-n_y(t)]$) ($A(t)$ in length)

Retardation can be Expressed in Terms of Distance (nm), Waves ($^1/_2$ or $^1/_4$) or Phase Angle (degrees or radians)

Modulation is Wavenumber Dependent - Bessel Function Describes the Variation with Wavenumber

Double Modulation Experiment

Regular Interferometer Modulation

Fourier Frequency = $2v\nu$
(v = mirror velocity and ν = wavenumber)

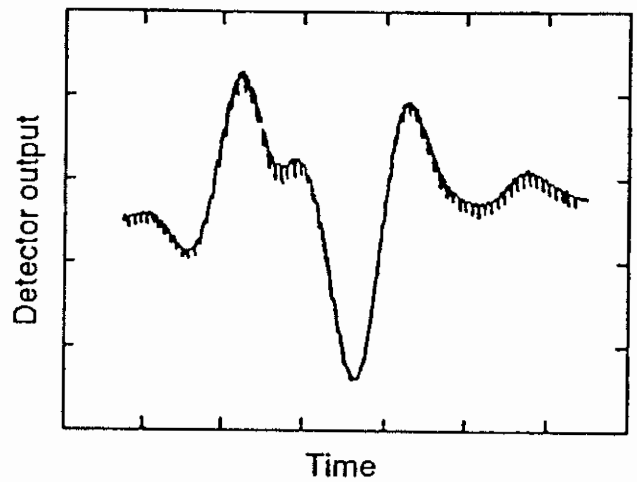
Example: 4000-400 cm^{-1} at $v = 0.6329$ has Fourier frequencies of 5-0.5 kHz

Photoelastic Modulation (PEM)

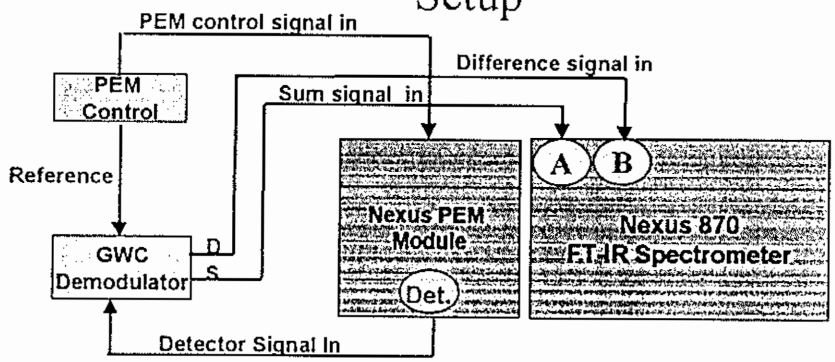
Modulates the Light between Different Polarization States
Must have a Frequency (100 kHz) that is at Least an Order of Magnitude Higher than Fourier Frequencies

Double Modulation

Interferometer Modulation & Polarization Modulation



Nexus PME Module: Dual Channel PM-IRRAS Electronic Setup

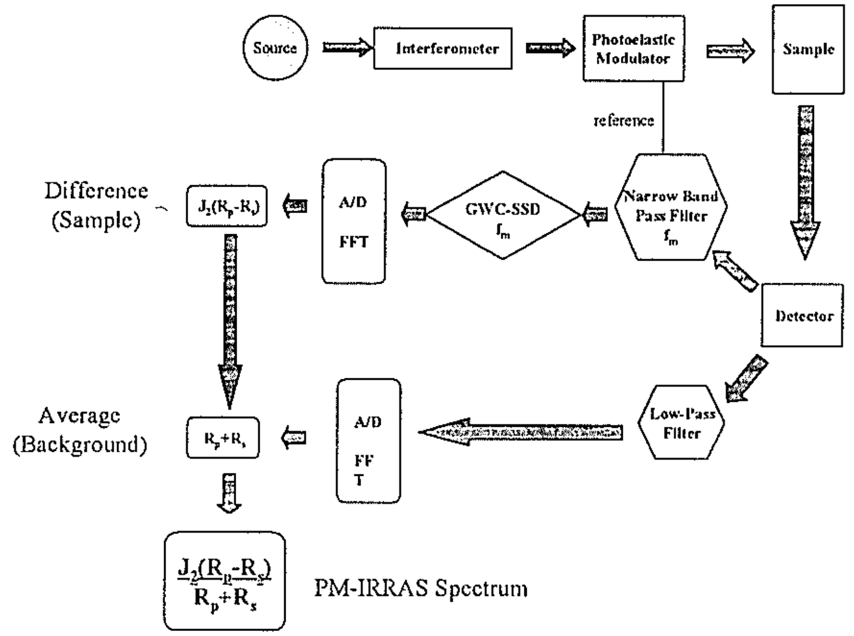


Channel A:

1) Sum out of GWC with built-in Low Pass Filter (11 kHz)
2) Channel A: A/D Converter
3) Output = $I_p + I_s$ "Background"

Channel B.

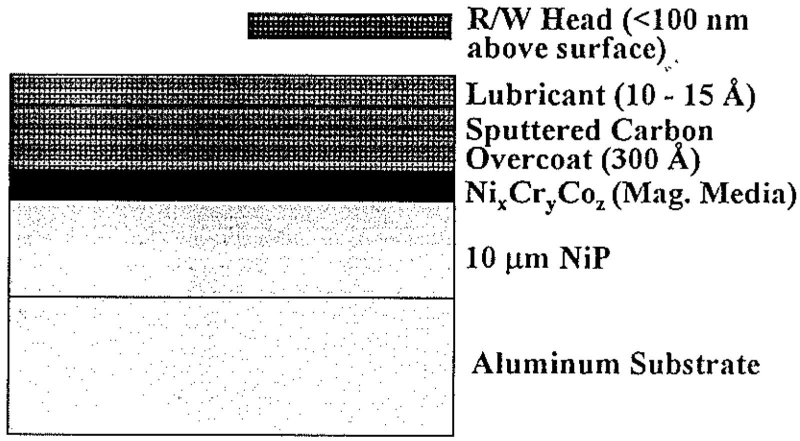
1) Difference out of GWC with built in High Pass Filter (25 kHz)
2) Channel B: A/D Converter
3) Output = $I_p - I_s$ "Sample"



Application Examples of PM-IRRAS

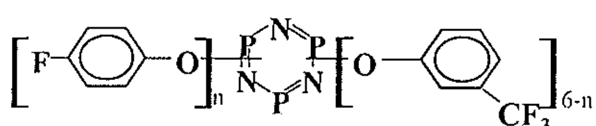
- Metal surfaces - ex situ
  - SAMs (self-assembled monolayers) in C-H stretching and finger print regions
- Metal surfaces - liquid phase in situ
  - structure studies of SAMs
  - electrochemical studies
- Metal surfaces - gas phase in situ
  - corrosion studies on Cu
  - carbon monoxide on Co (0001)
  - organic vapors on SiO_2 film on Au
- Air/water interface (LB film)

Cross-Sectional Composition of Hard Disk Drive



Chemical Structure of Lubricants

Dow X-1P



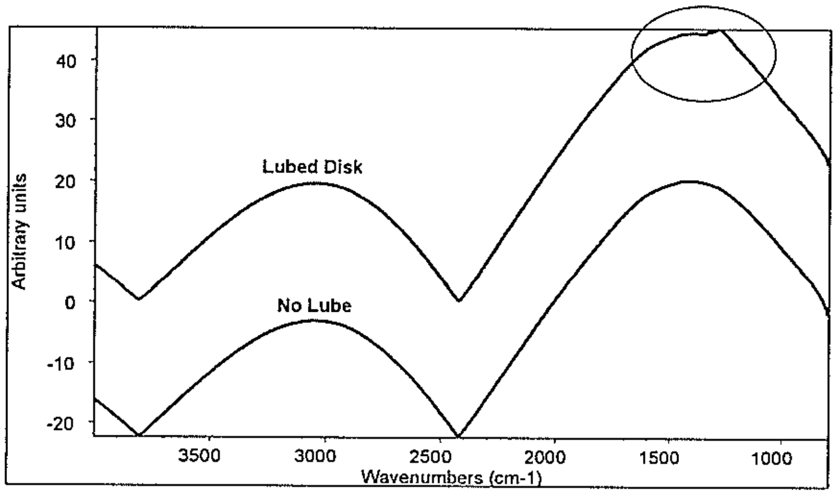
n=0 - 6

Fomblin Z-DOL

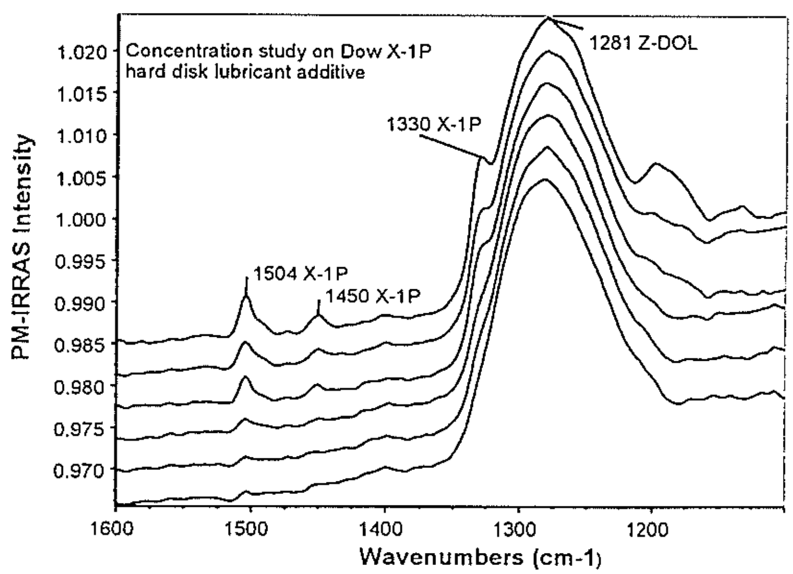
$HOCH_2CF_2O(CF_2CF_2O)_m(CF_2O)_nCF_2CH_2OH$

Average Molecular Weight 2000

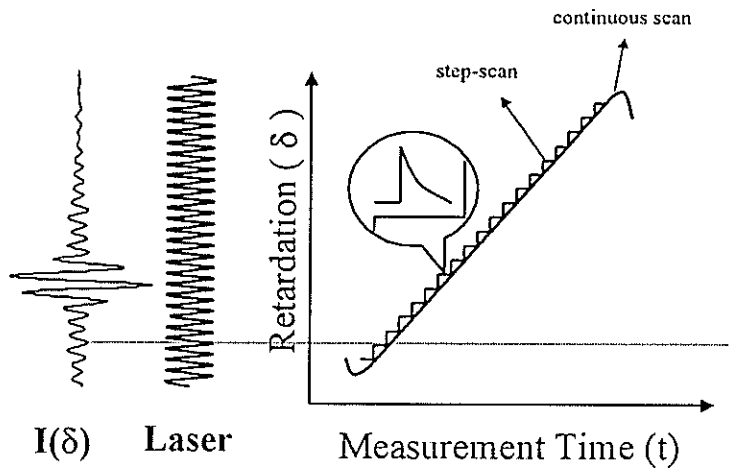
PM-IRRAS of Lubed/Unlubed Disk



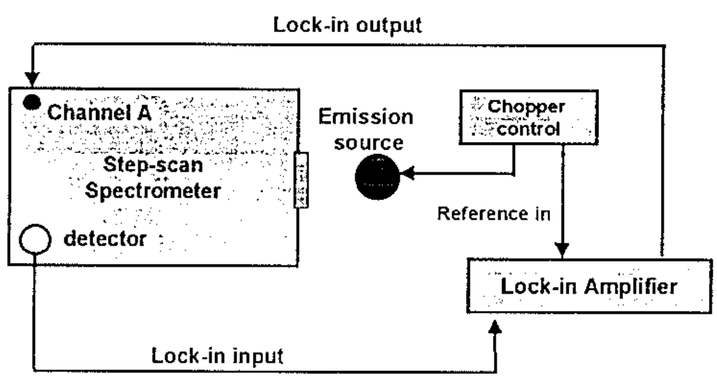
PM-IRRAS of Hard Disk Lubricants



Continuous Scan vs. Step-Scan



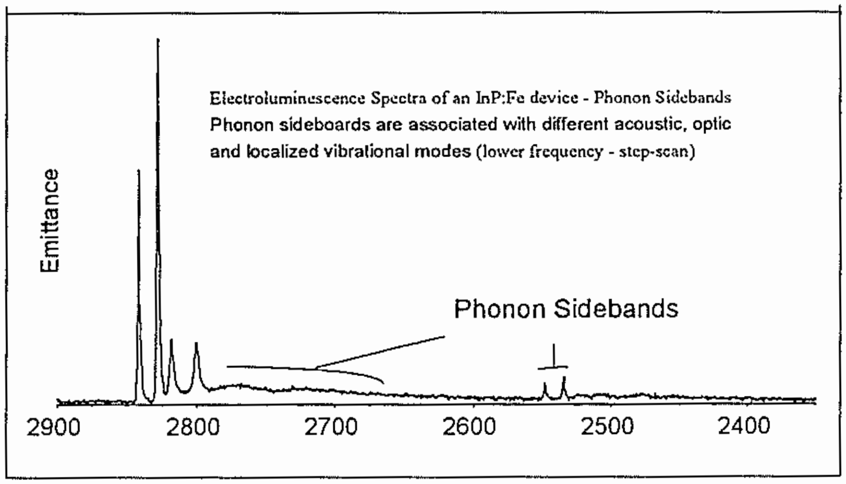
Amplitude Modulation Experiment Setup



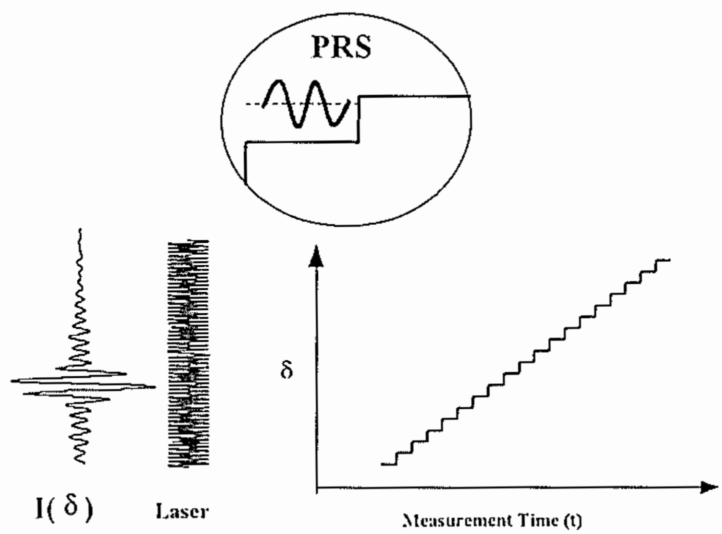
Notes:

1) When high frequency modulation is well above Fourier frequency - ok with continuous scan
2) Step-Scan must be chosen when lower frequency modulation overlaps with Fourier frequency

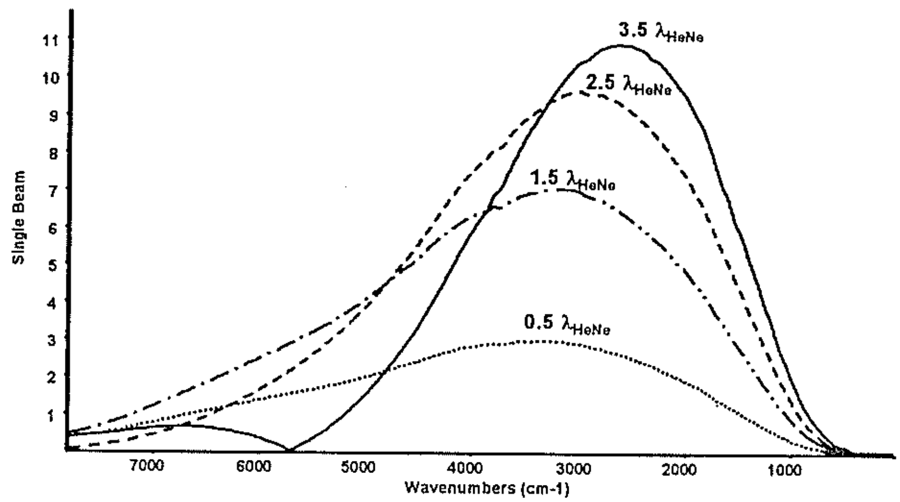
AM Modulation - Electroluminescence



Phase Modulation Step-Scan

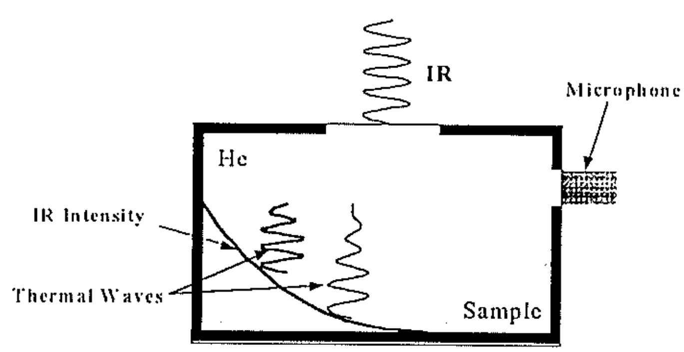


Phase Modulation Single Beams

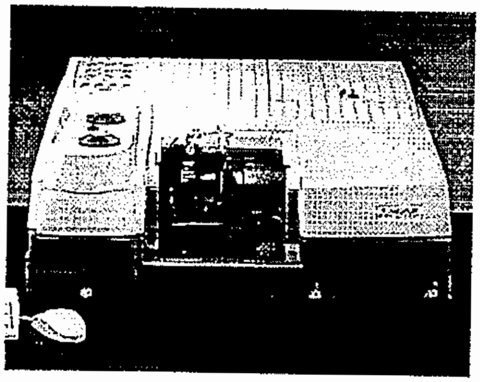


FT-IR Photoacoustic Spectroscopy (PAS)

- Signal generation
  - modulated light ⇒ modulated thermal wave ⇒ pressure modulation = sound = photoacoustic signal



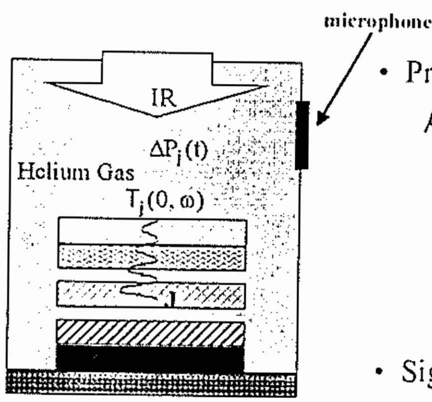
Step-Scan Phase Modulation PAS Experiment Setup



Nicolet Nexus 870 Research FT-IR

MTEC 300 Photoacoustic ESP

Frequency and Phase Dependent PAS Signal



- Probing Depth

  $$\mu_S = (\alpha/\pi f)^{1/2}$$

  μ_S = Thermal diffusion depth
  f = Modulation frequency (hz, $= 2\pi f$)
  α = Thermal diffusivity ($\alpha = K/\rho C_p$)

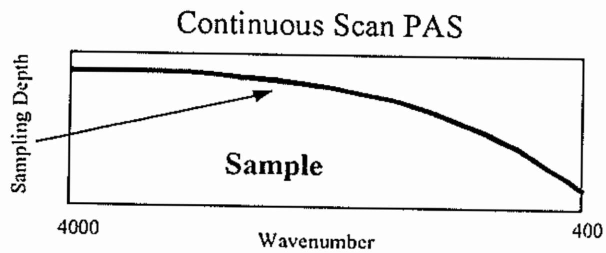
  (K - thermal conductivity; ρ - density; C_p -heat capacity)

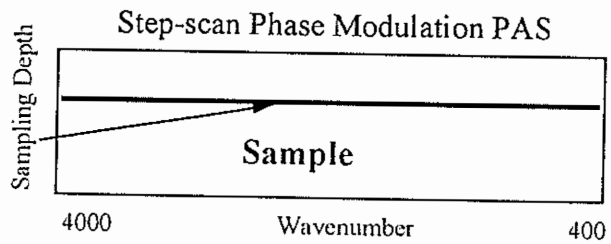
- Signal phase

  $$\Phi = arctan\ (Q\ /\ I)$$

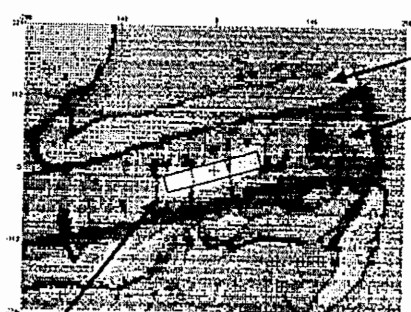
  I - in-phase spectrum
  Q - quadrature spectrum

Continuous-Scan and Step-Scan PAS





Kapton*: Infrared Microscopy

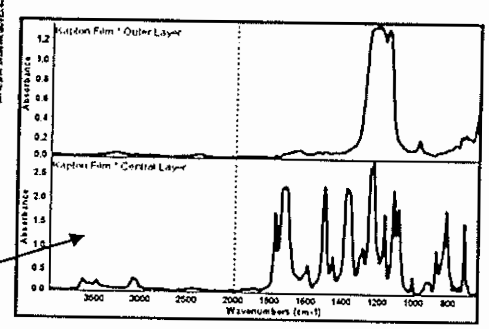


12 μm layer of Teflon*

25 μm layer of polyimide

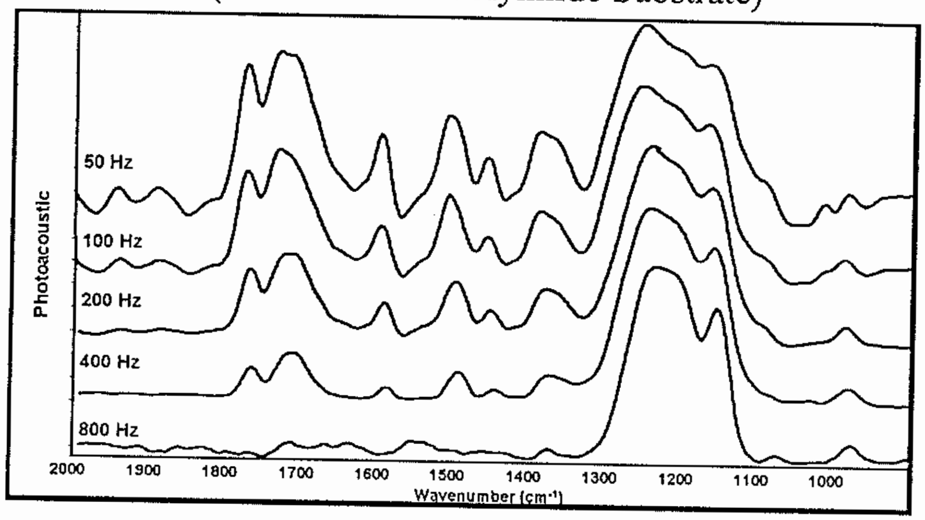
Sample prepared by microtome cross section

1. View the Sample
2. Aperture the Area
3. Measure the Spectrum

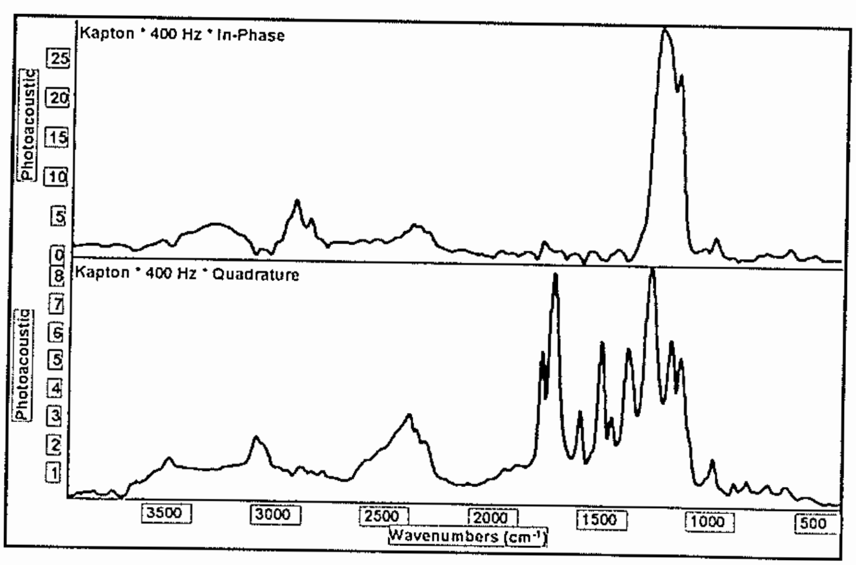


*Kapton and Teflon are Trademarks of Dupont Corporation

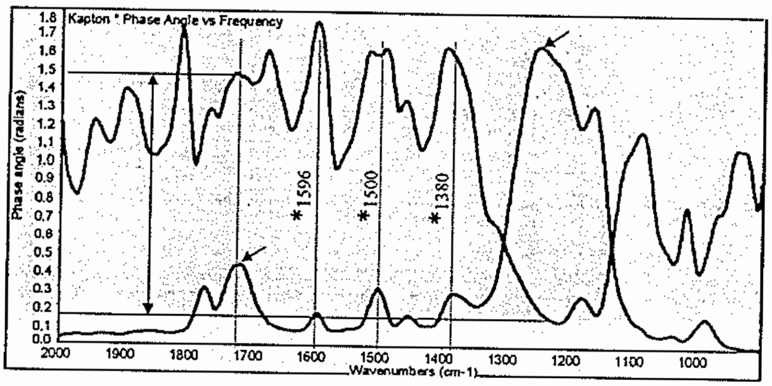
Frequency-Resolved PA Spectra of Kapton Film (12 mm Teflon/Polyimide Substrate)



Kapton Film Depth Profiling



Kapton Film Depth Profiling - Signal Phase



Quantitative Analysis - Thickness Determination:

$d_{Teflon} = \Delta \Phi_{1700\text{-}1225}\ \mu_{400Hz} = (1.475 - 0.150)\ 8.9 = 11.8\ \mu m$

(real thickness = 12 μm)

FTIR Time-Resolved FT-IR Spectroscopy (TRS)

Step-Scan
External Digitizer
(50 ns)

Step-Scan
Internal Digitizer
(10 μs)

TRS

Continuous scan
(Rapid-scan)
kinetics (20 ms)

Rapid Scan

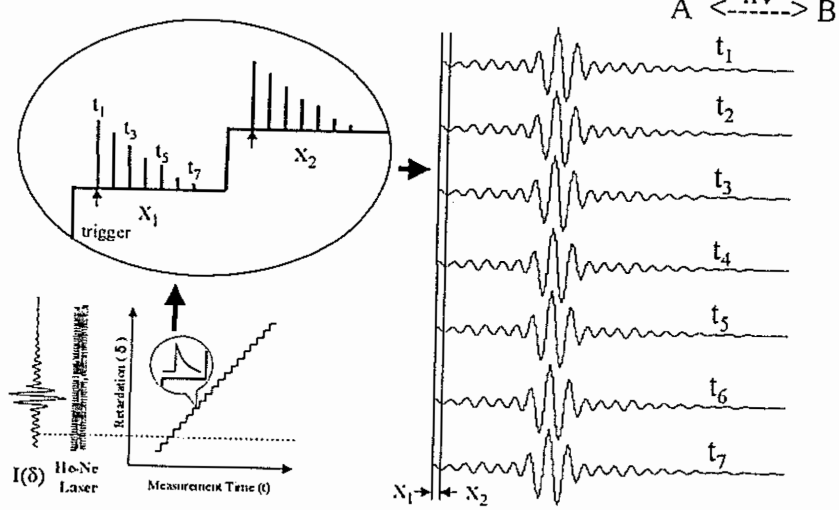
- Continuous Scanning Method
- Upper Limit about 20 ms (50 scans/s)
- Dynamic Process does not have to be repeatable
- Accessed through Series Software

Step-Scan FT-IR Time-Resolved Spectroscopy

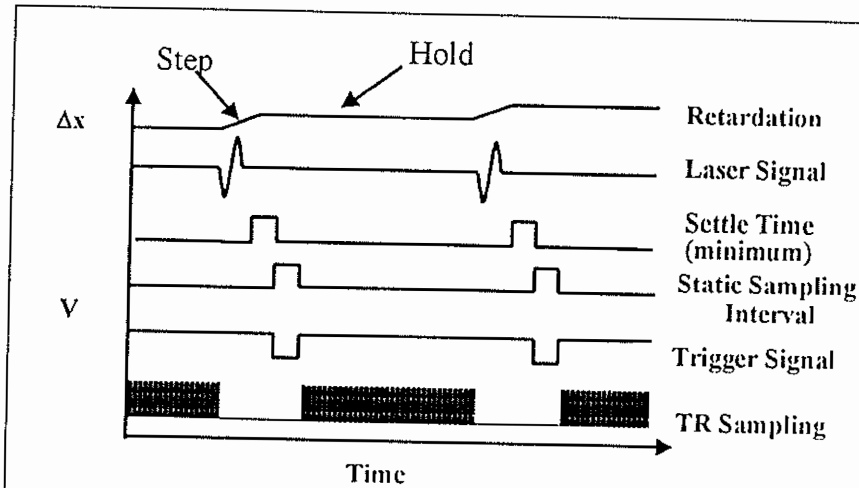
- Simultaneous Acquisition of Spectral and Kinetic Information on Repeatable Processes Initiated by:
  - Electric Pulse
  - Light Pulse
  - Temperature Jump
  - Rapid Mixing
- Data Acquisition from Nanosecond (ns) to Millisecond (ms) Time Scales
- Large Spectral Range and High Resolution

Step-Scan TRS

- **Reversible/Repeatable Reactions and Processes**



Time Resolved Step-Scan Timing Scheme



Applications of Step-Scan TRS Spectroscopy

- Material Science
  - Liquid Crystals and Polymer-Dispersed Liquid Crystals
  - Characterization of LED's or Laser Diodes
  - Polymer Stretching
- Biology and Biophysics
  - Protein Conformational Changes
  - Bacteriorhodopsin
- Photochemistry
  - Excited States of Metal Complexes
  - Photochemical Reactions in Condensed or Gaseous Phase

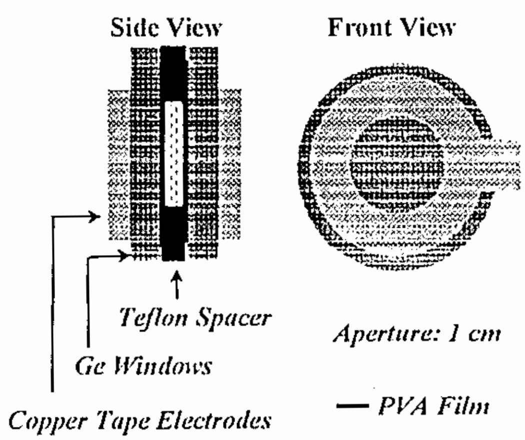
Liquid Crystal Dynamics

__Parts__

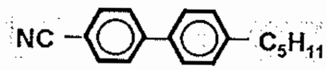
- *Ge Windows - 25mm x 2mm*
- *Teflon Spacer - 10μm*
- *Copper Tape Electrode Ring*

__Cell Preparation__

- *0.1% Aqueous PVA Solution*
- *Apply solution to Ge Windows*
- *Rub Residual PVA in a Uniaxial Direction*
- *Place windows face-to-face, anti-parallel to rubbing direction*



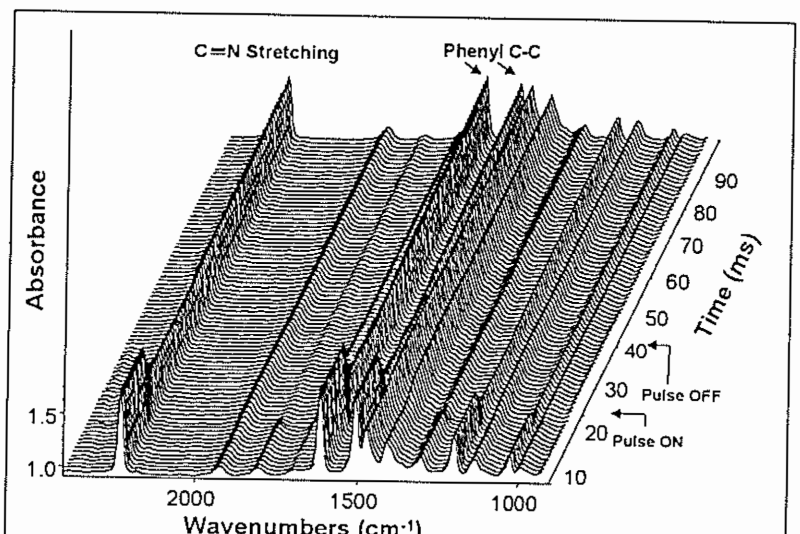
S^2TRS Application (1) - 5CB Liquid Crystal



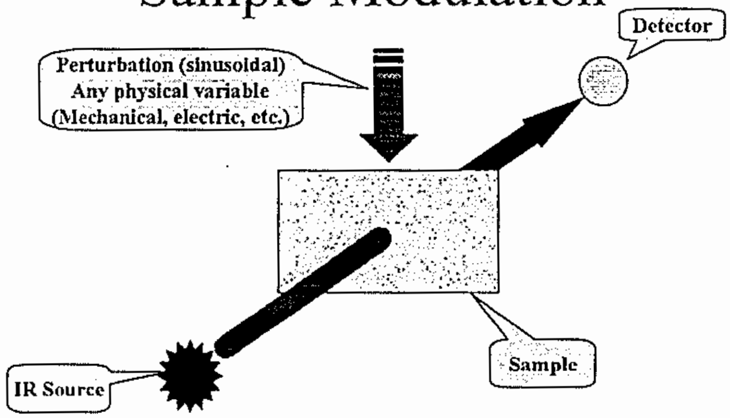
4-pentyl-4'-cyanobiphenyl (5CB)

Wavenumber (cm^{-1})	Band Assignment
2226	CN stretching
1606	phenyl C-C stretching
1496	phenyl C-C stretching
1460	C-H deformation of pentyl chain
1397	C-H deformation of pentyl chain
1378	C-H deformation of pentyl chain
1285	C-C stretching of biphenyl ring
1006	phenyl C-H in-plane deformation

5CB - Liquid Crystal Time-Resolved Spectra



Sample Modulation



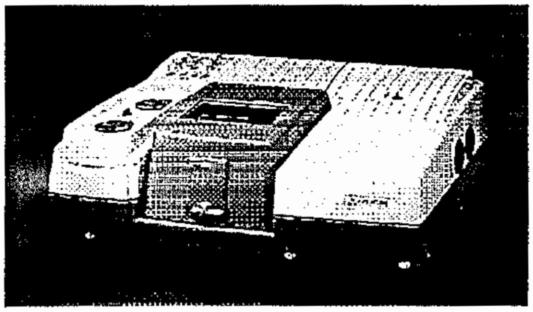
Notes: 1) Perturbation can be any physical parameter such as mechanical strain, electric voltage, pressure, etc.
2) Step-scan multiple modulation (phase and sample) mode is used to collect I and Q dynamic spectra.

Polymer Stretching Experiments

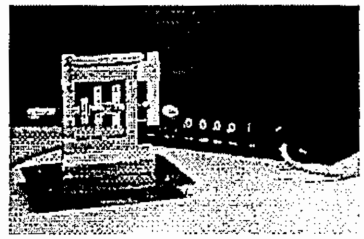
- Rheo-optical studies of polymer films
- Study molecular level responses of samples undergoing flow, deformation and relaxation
- Study dynamic linear dichroism of samples as a function of sinusoidally modulated strain

Dynamic IR Sample Modulation Spectrometer

Nexus 870



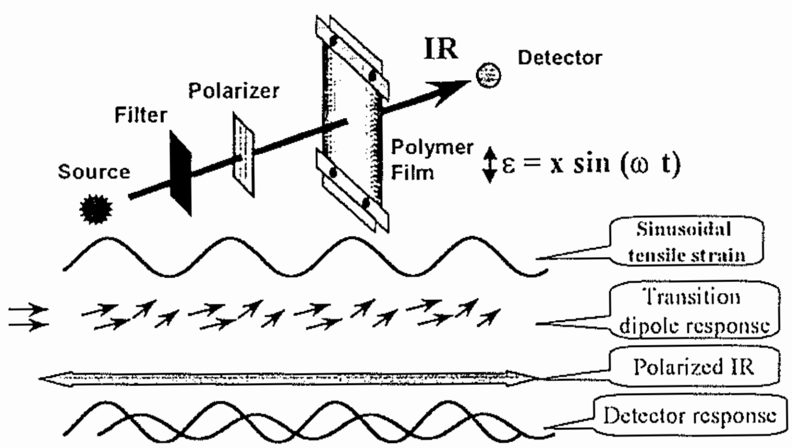
Manning Polymer Modulator™



Mirror Position Accuracy: +/- 0.2 nm: 10 - 80 Hz
Signal demodulation: DSP-based 2 stage demodulation
Typical data collection time: 20 min (modulation mode).

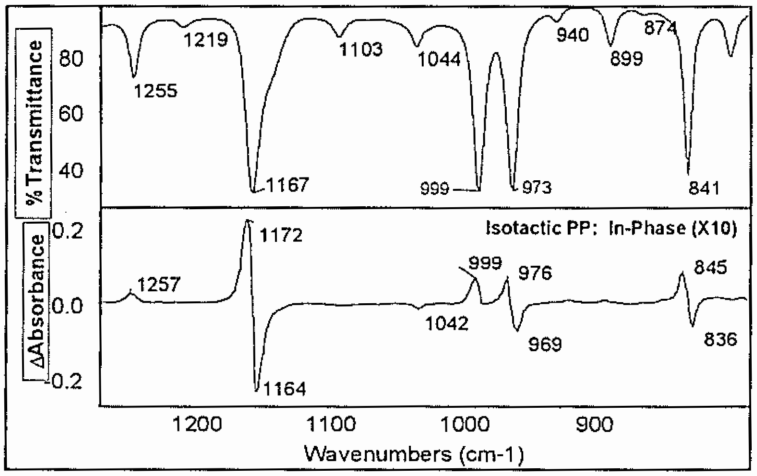
Strain Amplitude: *0 - 75 micronsHz)*
Static Strain: *0 - 1.25 cm*

Rheo-Optical Layout of Polymer Stretching



—— I (Elastic - In-phase) —— Q (Viscous - Quadrature)

SMM - Isotactic polypropylene



As the polymer is stretched, a reorientation of the backbone chain occurs leading to pick shifts and intensity changes across the spectrum

Summary

- **The fully integrated DSP-based Vectra-Piezo Dual Channel Step-Scan FT-IR (Nexus 870) provides solutions to the following advanced applications:**
  - Phase modulation PA depth profiling;
  - Time-Resolved Experiments up to ns, with a choice of an external digitizer;
  - PM-IRRAS, PM-VCD, PM-VLD with dual channel advantages;

    (angstrom-Å thick mono-layers, 10^{-5} absorbance unit in VCD).