UNESCO/IUPAC Postgraduate Course in Polymer Science

Lecture:

Vibrational Spectroscopy of Polymers: Contemporary Methods

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Vibrational spectroscopy

– ***Infrared*** spectroscopy
– ***Raman*** scattering

interaction of electromagnetic radiation with matter, **10^{-14} – 10^{-11} s**
structure, dynamics

- **theoretical background**
- **experimental techniques**

Vibrational spectroscopy of polymer systems

- ***poly(N-methyllaurolactam), blend with poly(vinylphenol)***
  - crystallinity
  - conformational structure
  - hydrogen bonding

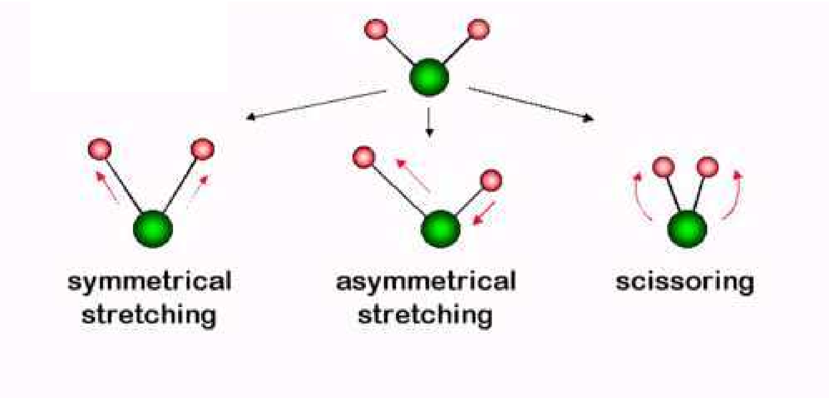
- ***aggregation of PC in solution***
  - time-dependent measurements
  - 2D correlation spectroscopy

- ***PE/PP blends***
  - near infrared spectroscopy
  - Raman microscopy, imaging

- ***aqueous solutions of thermoresponsive polymers***

Vibrational spectroscopy

Vibrational degrees of freedom



normal vibrations (3N – 6):

normal frequency ν_i

normal coordinate q_i

force constants f_{ij}

$$T = 1/2\sum_i q_i^2 \qquad V = 1/2\sum_{i,j} f_{ij} q_i q_j \; ; \qquad f_{ij} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0$$

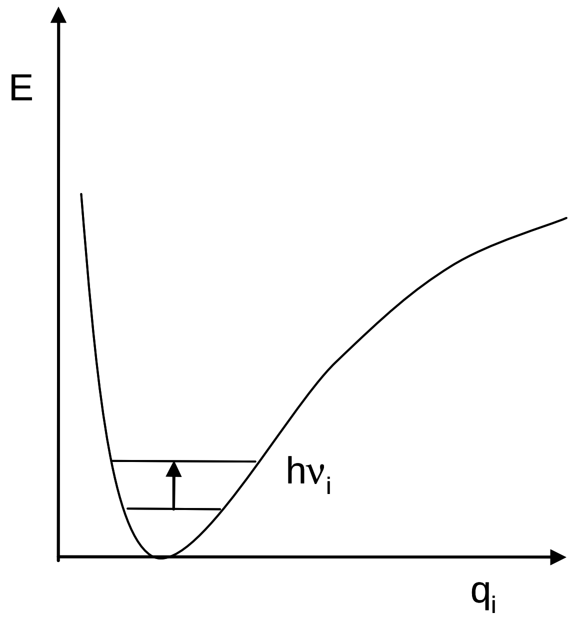
$$E = T + V$$

$$E_{n_i} = h \cdot \nu_i (n_i + 1/2), \; n_i = 0,1,2,\ldots$$

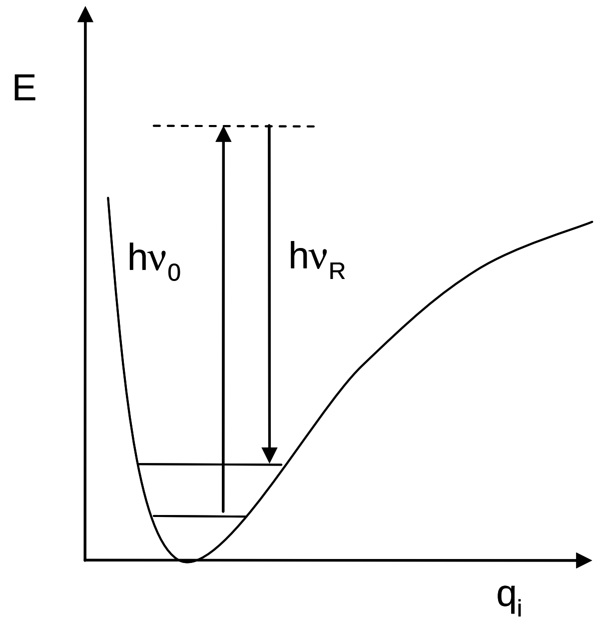
Infrared absorption

Raman scattering

$h\nu_i$



$h\nu_R = h\nu_0 - h\nu_i$



Infrared spectroscopy $\left(\dfrac{\partial \mu}{\partial q_i}\right)_0 \neq 0, \quad \mu \quad \textit{molecular dipole moment}$

Raman scattering $\left(\dfrac{\partial \alpha}{\partial q_i}\right)_0 \neq 0, \quad \alpha \quad \textit{molecular polarizability} \qquad \boldsymbol{\mu}' = \alpha \mathbf{E}$

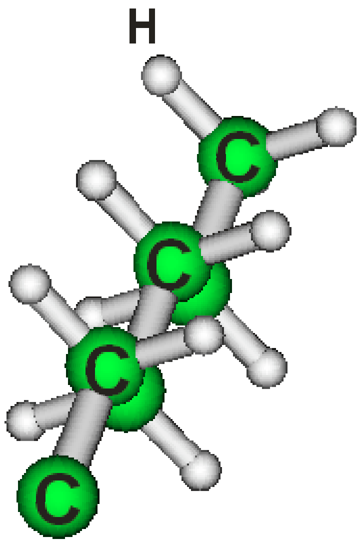
symmetry: selection rules (inversion center - complementary IR, Ra)

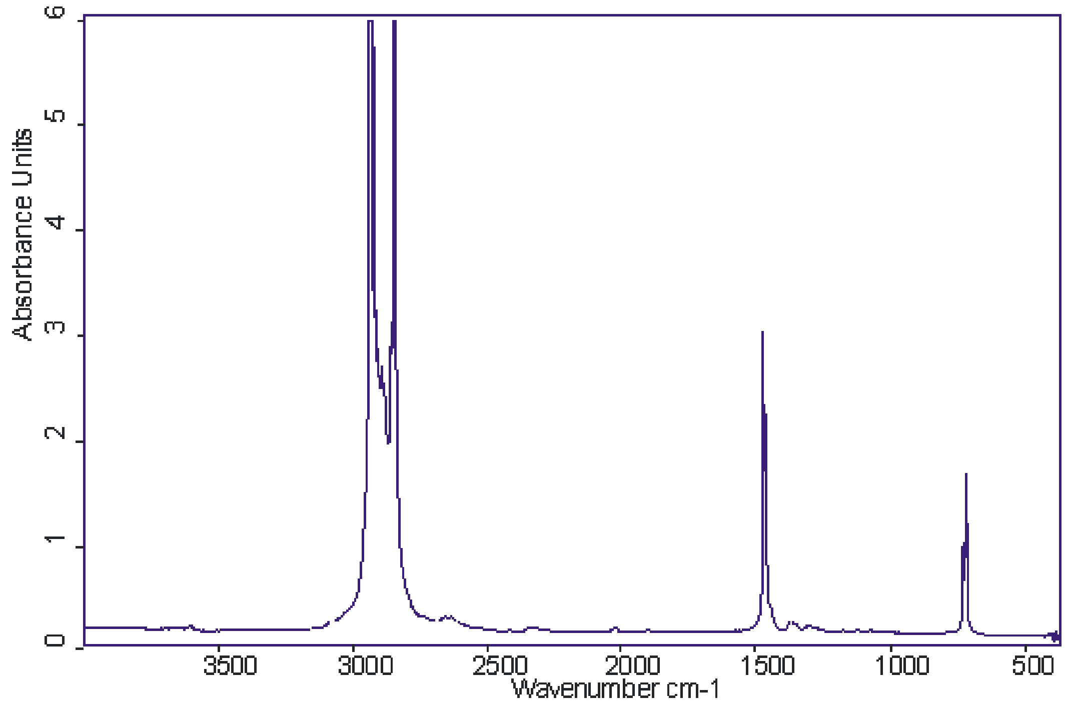
Characteristic frequencies

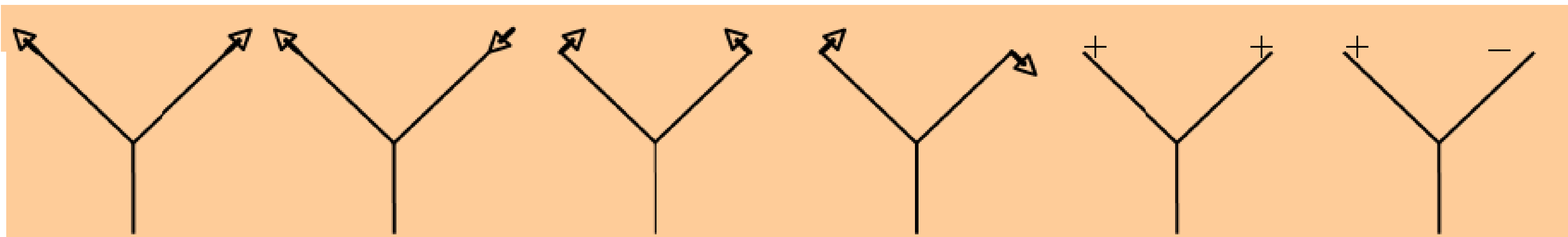
Vibration	Region [cm^{-1}]	Intensity	
		Raman	IR
O-H str	3650-3000	weak	strong
N-H str	3500-3300	medium	medium
=C-H str	3100-3300	weak	strong
-C-H str	3000-2800	strong	medium
C=O str	1820-1680	strong-weak	very strong
C=C str	1900-1500	very strong	very weak
C=N str	1680-1610	strong	medium
CH_2 bend	1470-1410	medium	medium
CH_3 asym. bend	1470-1400	medium	medium
CH_3 sym. bend	1380	medium-weak	strong-medium
C-O-C asym. str	1150-1060	weak	strong
C-O-C sym. str	970-800	strong	weak

Chain molecules

CH_2 groups





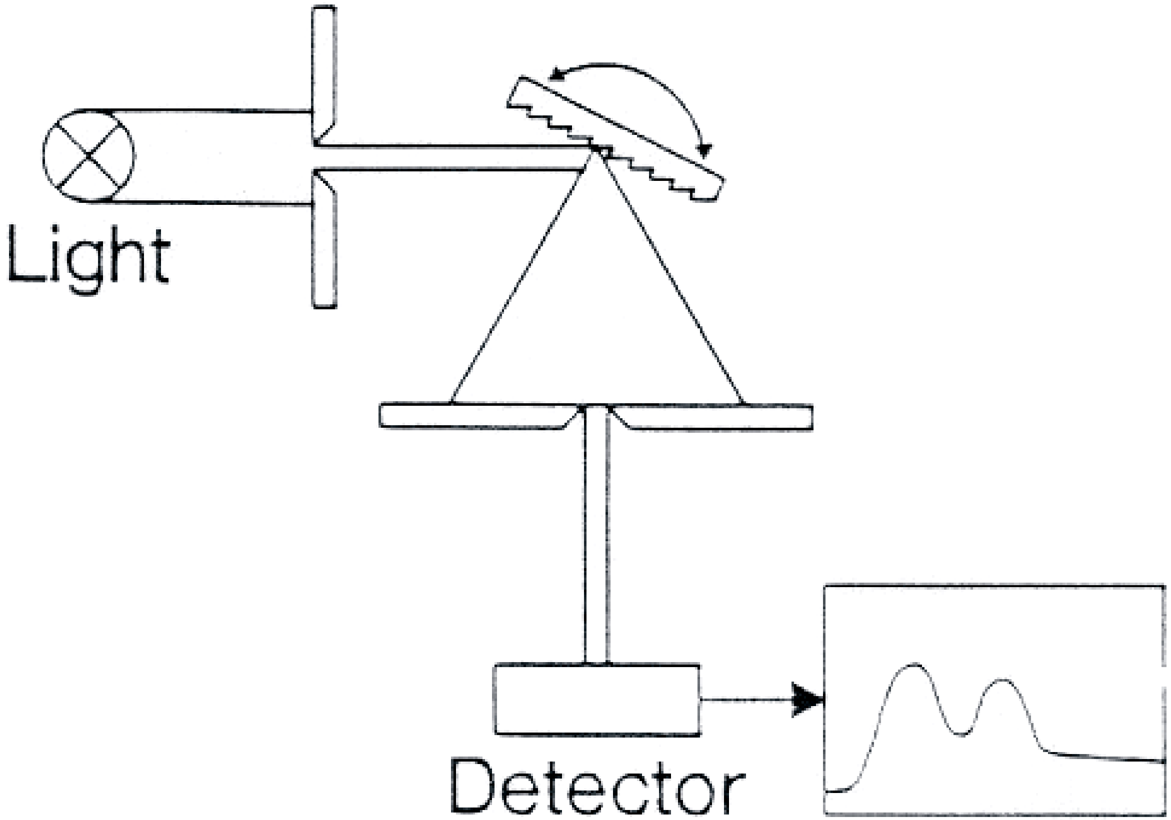


sym. **antisym.**

stretching **deformation** **rocking** **wagging** **twisting**

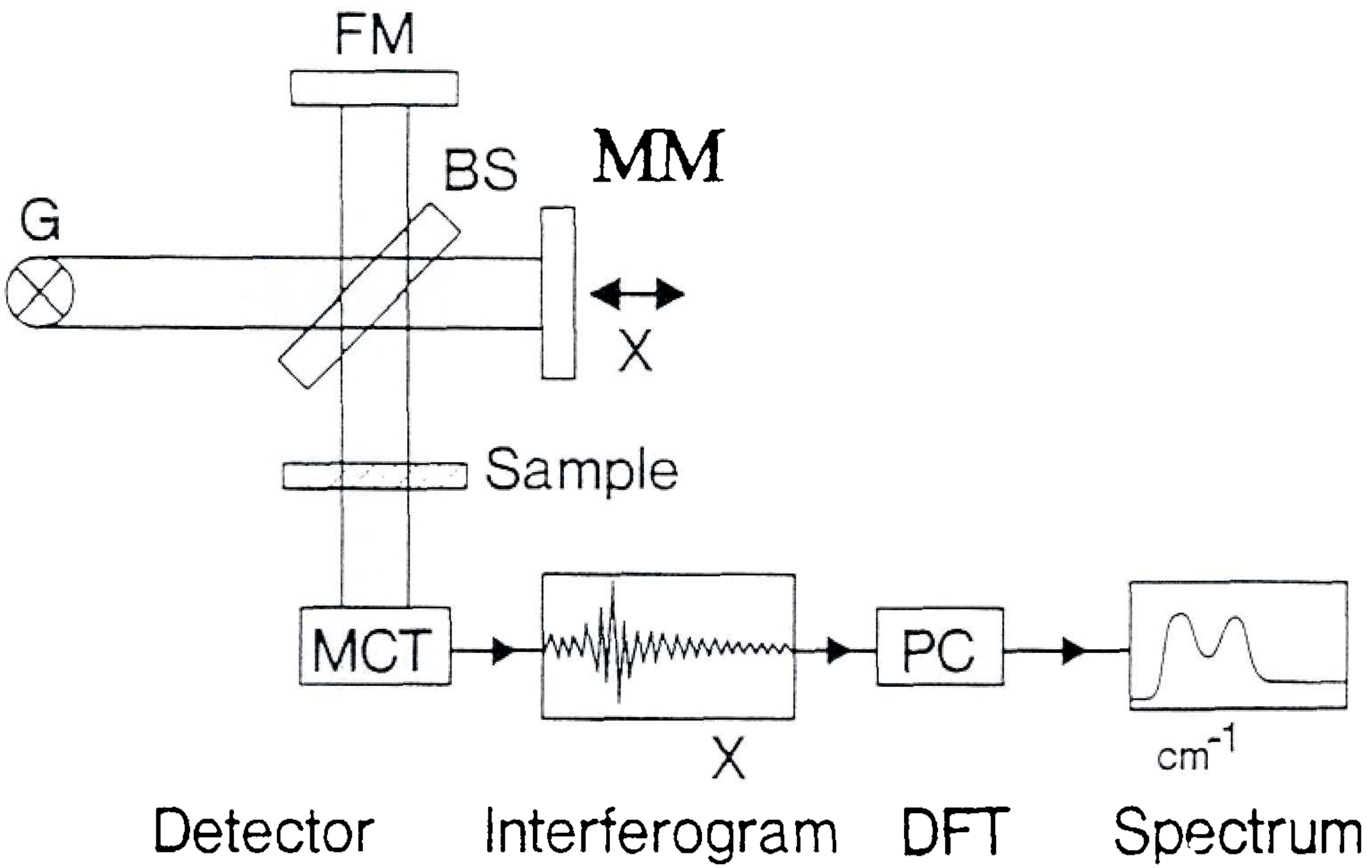
2850 cm^{-1} **2925** **1470** **725** **≈1300** **≈1200**

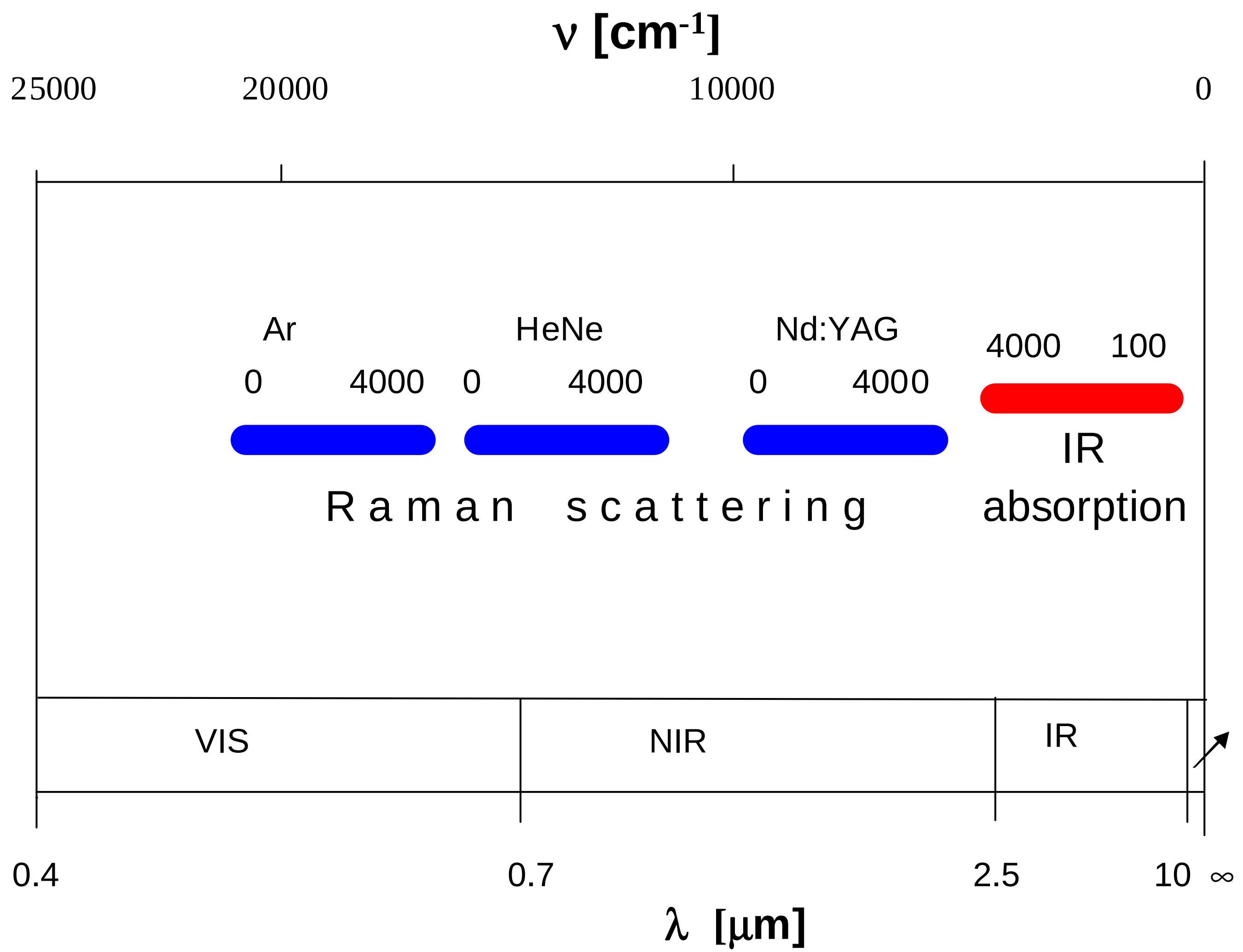
Diagram of an dispersive IR instrument



Raman: CCD detector

Diagram of an FT-IR apparatus



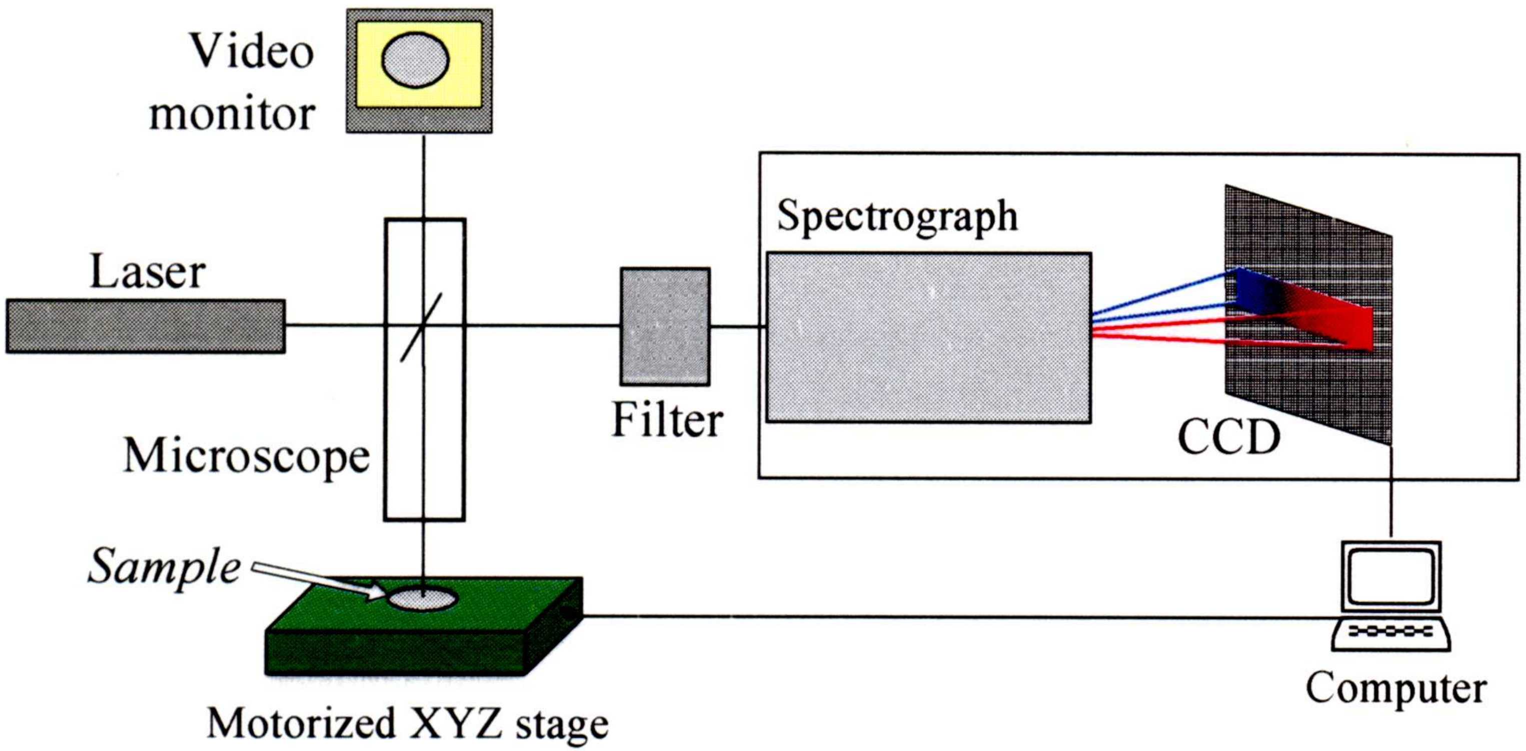


sources, detectors

Renishaw inVia Reflex Raman microscope

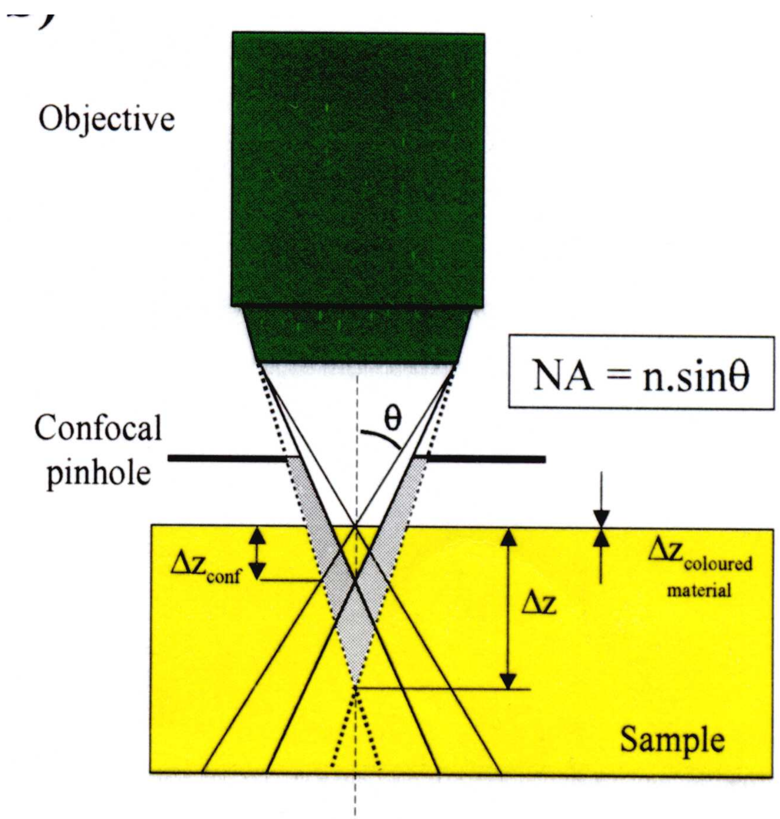
- high efficiency 250 mm focal length spectrograph equipped by 20x50x100 objectives, the resolution of 0.5 cm-1/pixel (grating 3000 lines/mm).
- the HeNe 633 nm and Argon-ion 514 nm lasers are available.
- XYZ maping sample stage with joystick and software control allows scatter, line and area mapping.
- the NExT filtr allows the measurement of the Raman spectrum to 5 cm^{-1}.
- Additional Macro Sampling Kit is available.

Principle of a conventional micro-Raman spectrometer



Principle of a confocal microscope

Observation of a sample through a microscope

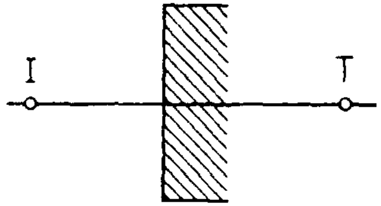


A confocal hole rejects the shadowed light and facilitates a more accurate in-depth analysis (Δzconf < Δz).

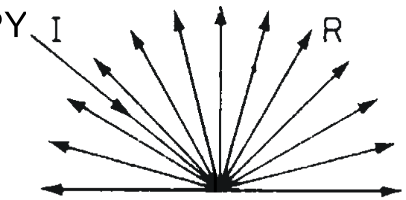
NA: Numerical Aperture
n is the refractive index of the medium separating the objektive from the Hample.

EXPERIMENTAL TECHNIQUES (FT-IR)

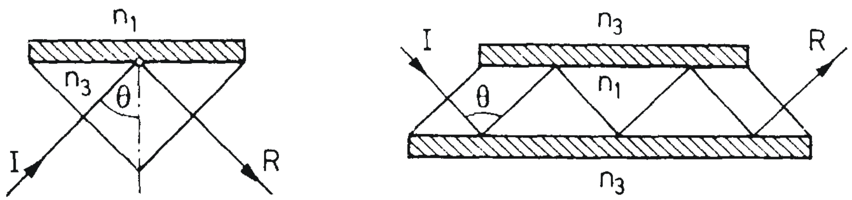
TRANSMISSION MEASUREMENT



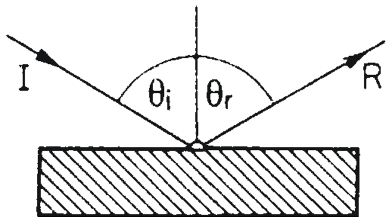
DIFFUSE REFLECTANCE SPECTROSCOPY



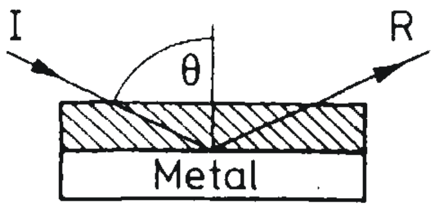
INTERNAL REFLECTION SPECTROSCOPY (ATR, GOLDEN GATE)

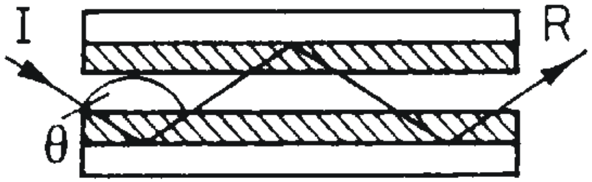


EXTERNAL REFLECTION SPECTROSCOPY

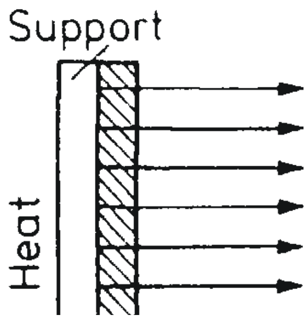


REFLECTION-ABSORPTION INFRARED SPECTROSCOPY



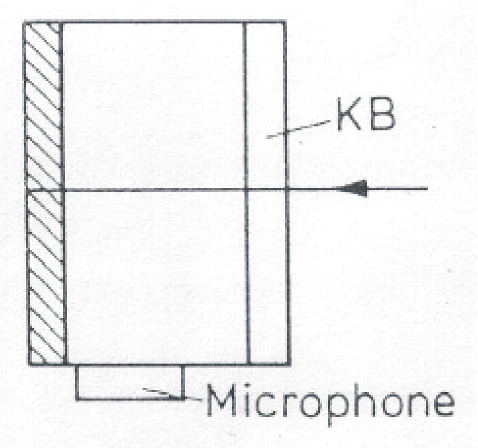


EMISSION SPECTROSCOPY



PHOTOACOUSTIC SPECTROSCOPY

(generation of an acoustic signal by a sample exposed to modulated light, enclosed chamber – helium)

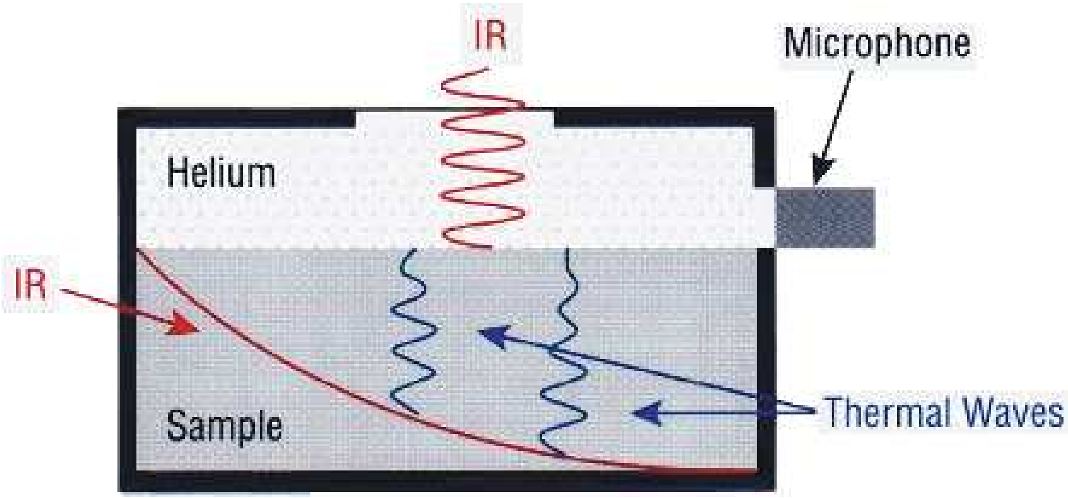


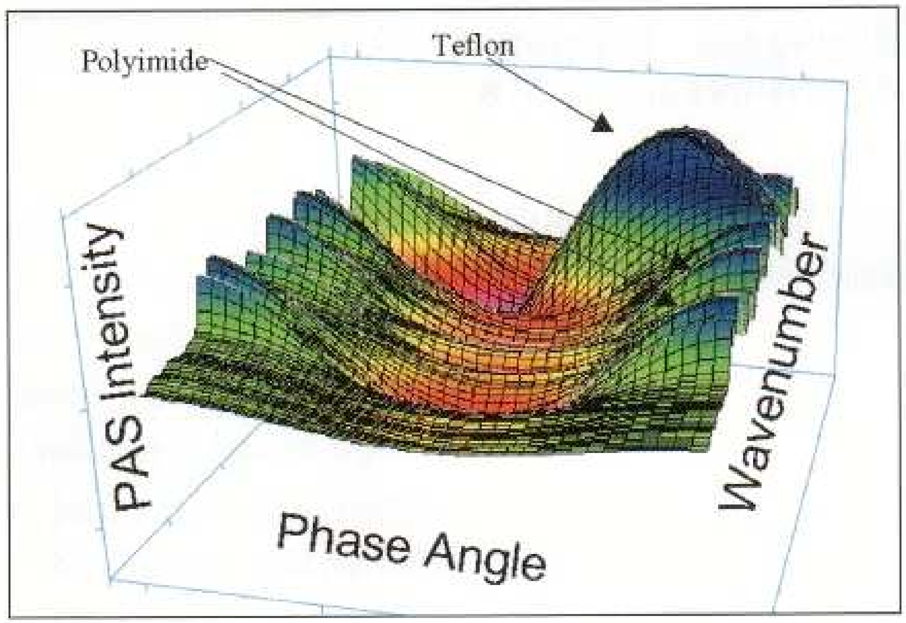
Step-scan application

Photoacoustic Spectral Depth Profiling

phase modulation

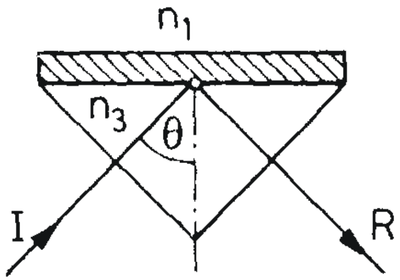
(6 - 80 μm)





Golden Gate

Diamond ATR System



Sensitivity is achieved using high-pressure contact against a type IIa diamond

Applications

Solids, liquids, pastes, powders, pellets
Microsamples, fibers, paint chips
Pharmaceutical preparations
Hard and soft polymer pellets
Forensics
Rocks and geochemicals
Coated wires
Air sensitive samples

Polymer systems

- **Structure analysis** (10^{-11} – 10^{-13} s)

conformational structures (crystallinity)

complexes, aggregation

interactions (hydrogen bonding)

polymer blends

polymer surfaces and interfaces

deformation of polymers

orientation induced by drawing

longitudinal acoustic modes (LAM, Raman) – lamellar structure

Polymer systems

- **Time-dependent phenomena** in polymers

crystallization

curing of polymers

heating effects

dynamic deformation (stress-strain behaviour)

time-resolved spectroscopy (step-scan instruments)

- **Polymer chemistry**

analytical technique (different sample types

variety of environmental conditions)

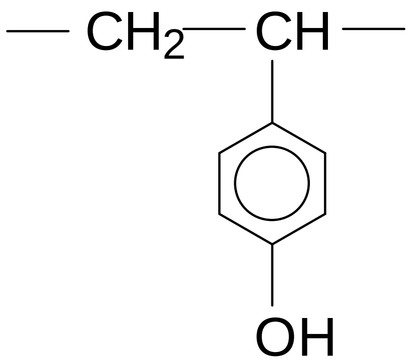
oxidation

irradiation damage

poly(N-methyllaurolactam)/poly(4-vinylphenol) (PNMLL/PVPh)

PNMLL: $-NCH_3-CO-(CH_2)_{11}-$ semicrystalline

PVPh:



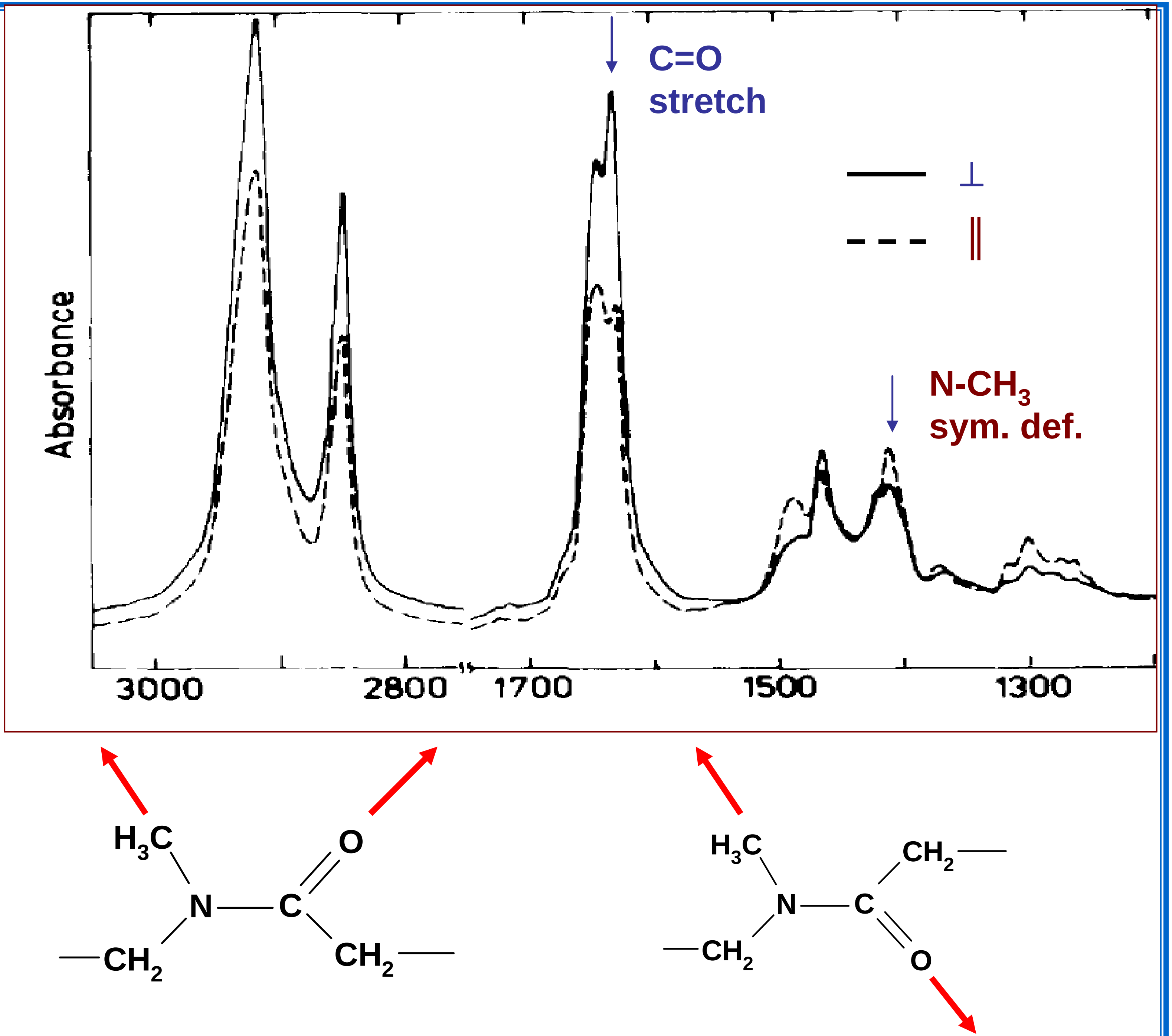
amorphous (atactic)

blends prepared by casting from solutions in THF

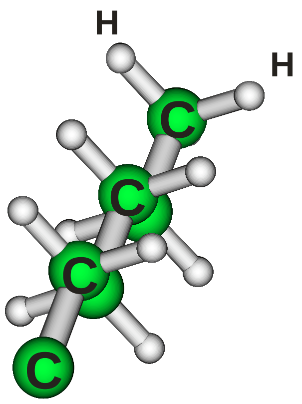
weight ratios:	mol. ratios of monomer units:
88/12	4:1
64/36	1:1
31/69	1:4

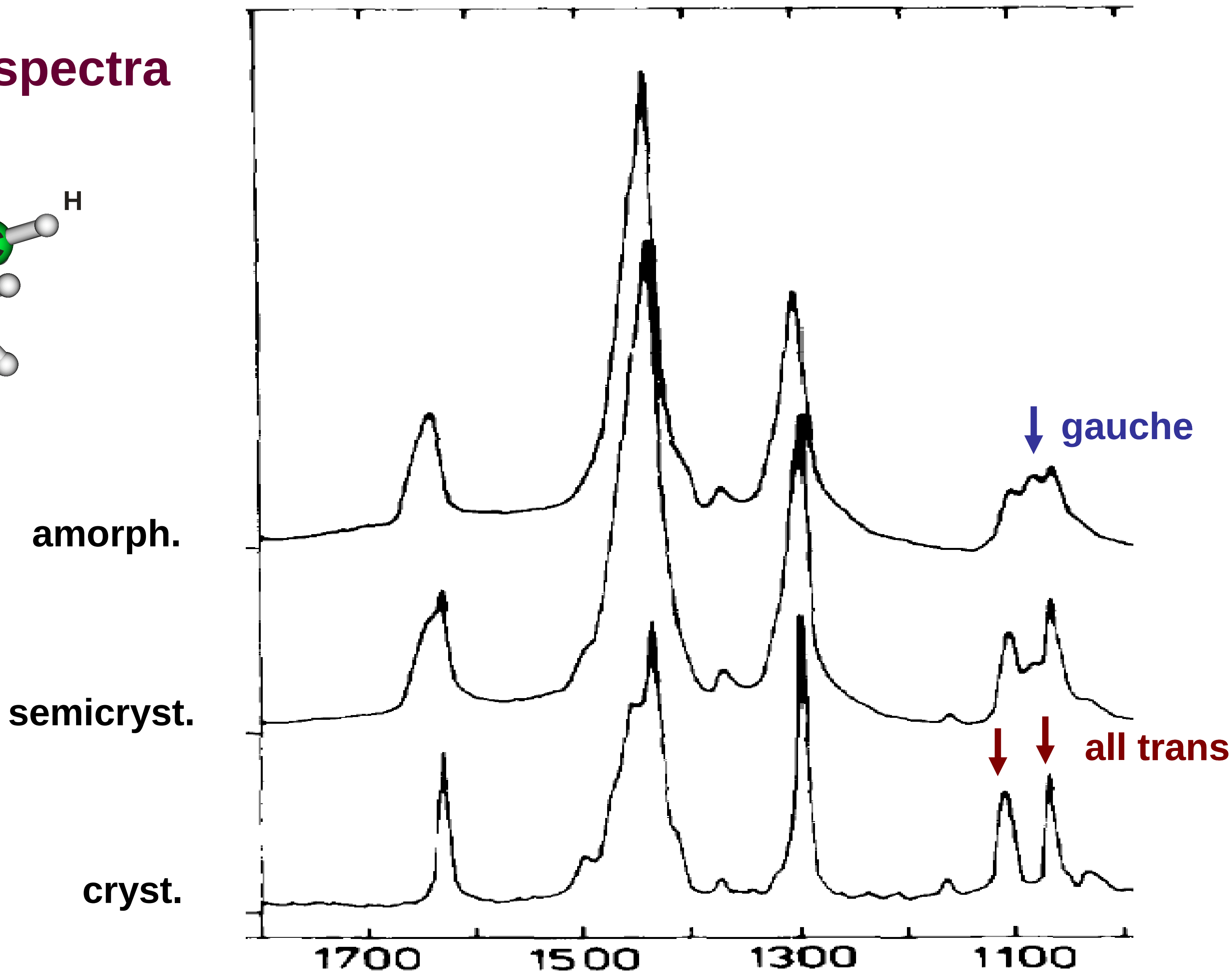
FT-IR spectra

polarized



Raman spectra

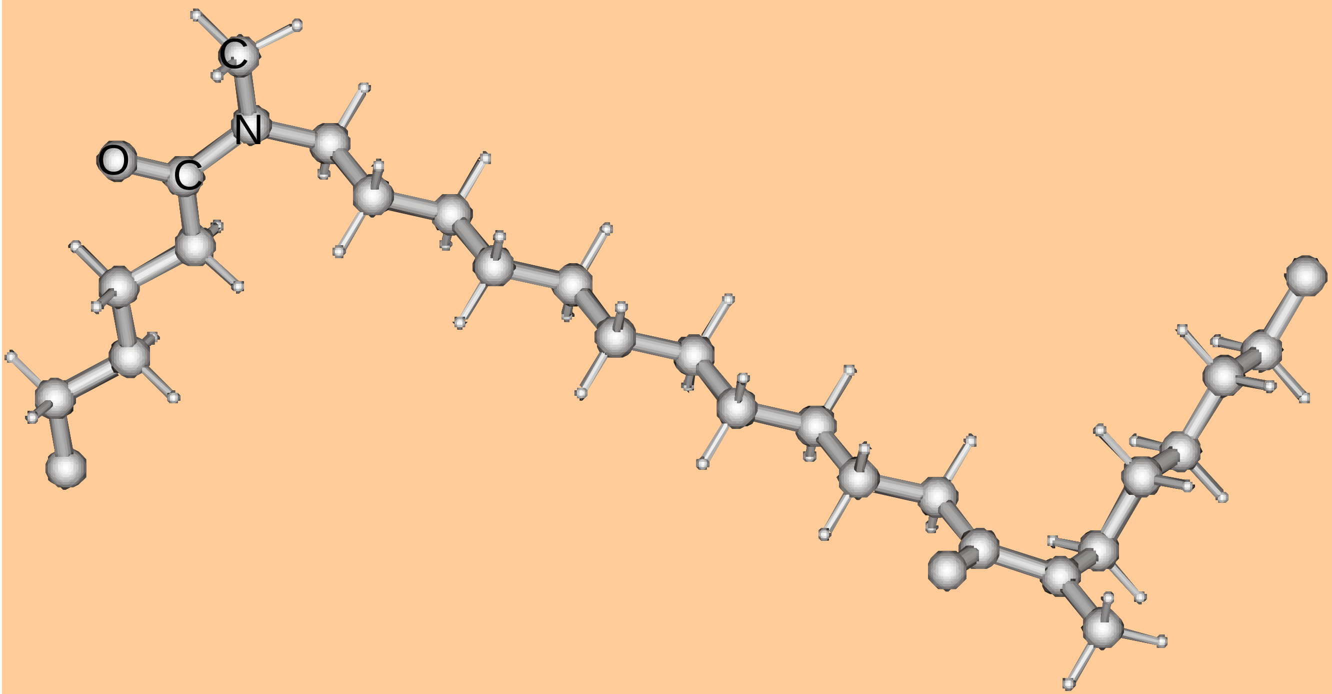




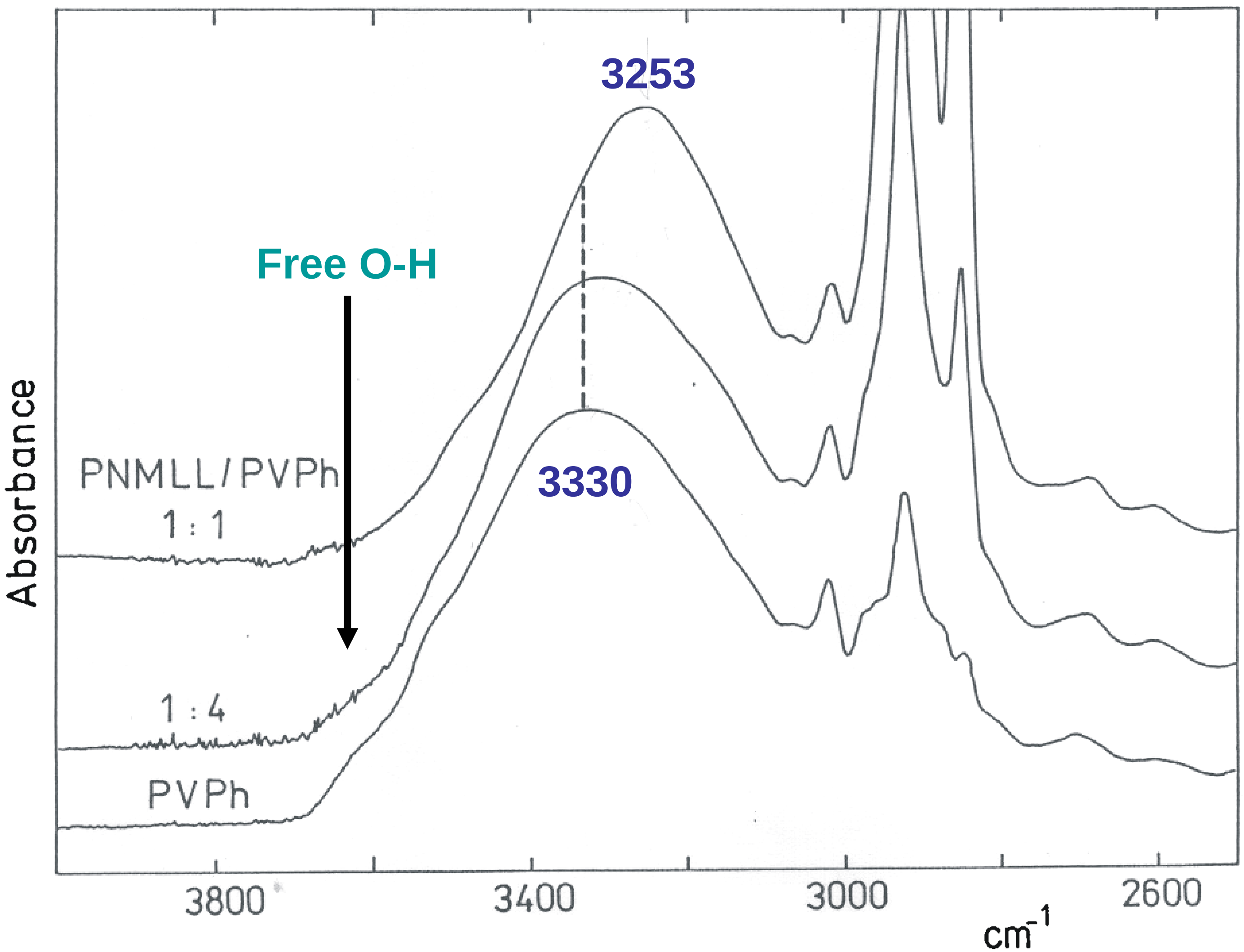
poly(N-methyl laurolactam)

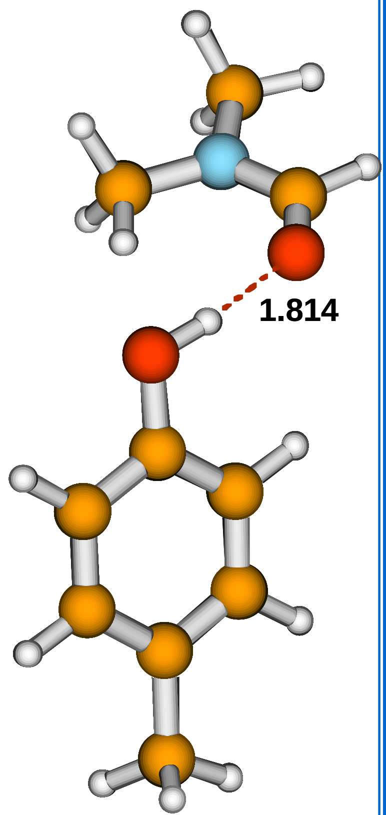
$T_g \sim -35^oC$

$T_m \sim 55^oC, 65^oC$



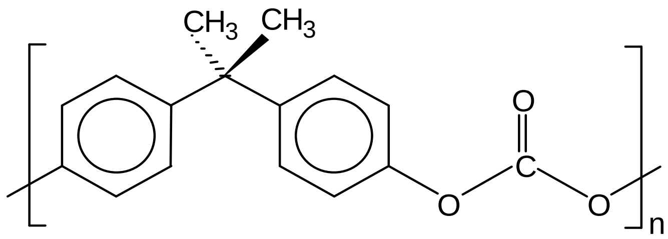
O-H stretching

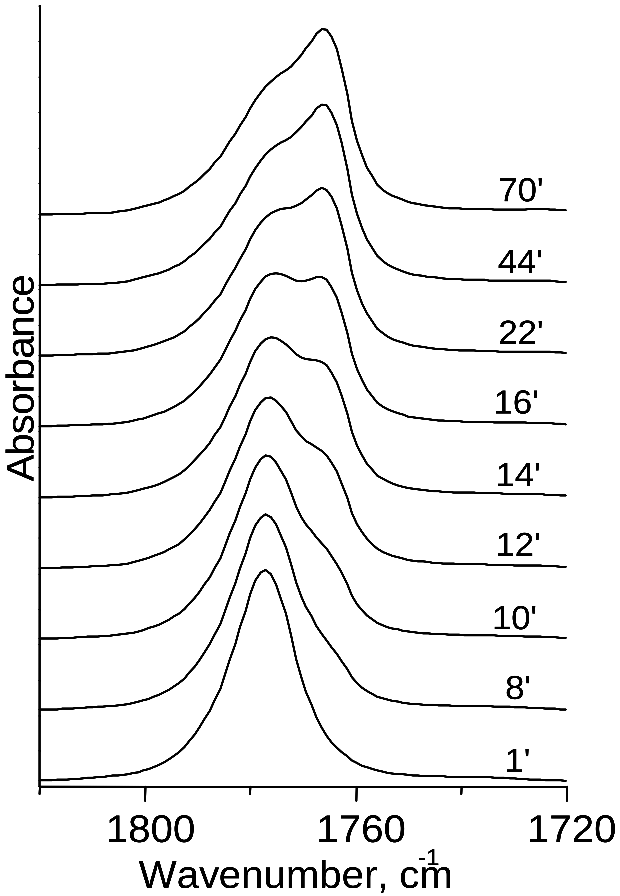


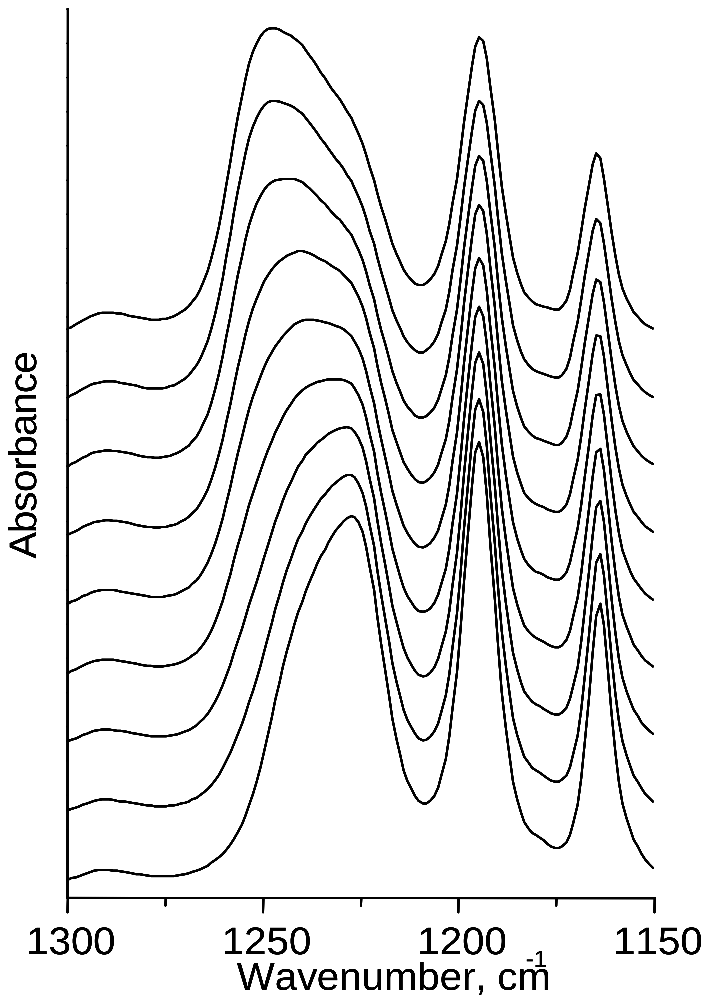


ΔE = -10.9 kcal/mol

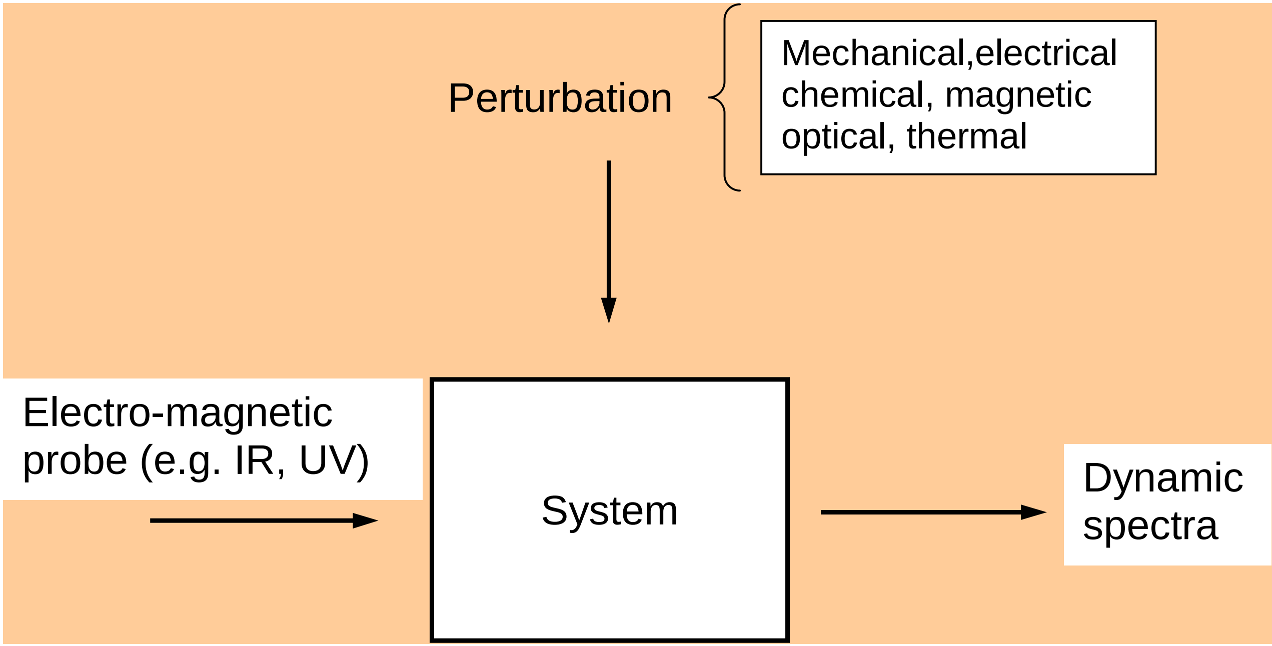
Aggregation of polycarbonate (PC)
in toluene (2% w/w)
FT-IR, room temperature







Two-dimensional spectroscopy



Dynamic spectrum

$$y_s(\nu,t)$$

$$y(\nu,t) = y_s(\nu,t) - y_s(\nu) \qquad \text{for} \qquad -T/2 \le t \le T/2$$

$$= 0 \qquad \text{otherwise}$$

$$y_s(\nu) = \frac{1}{T}\int_{-T/2}^{T/2} y_s(\nu,t)\ \mathrm{d}t \qquad \text{static spectrum}$$

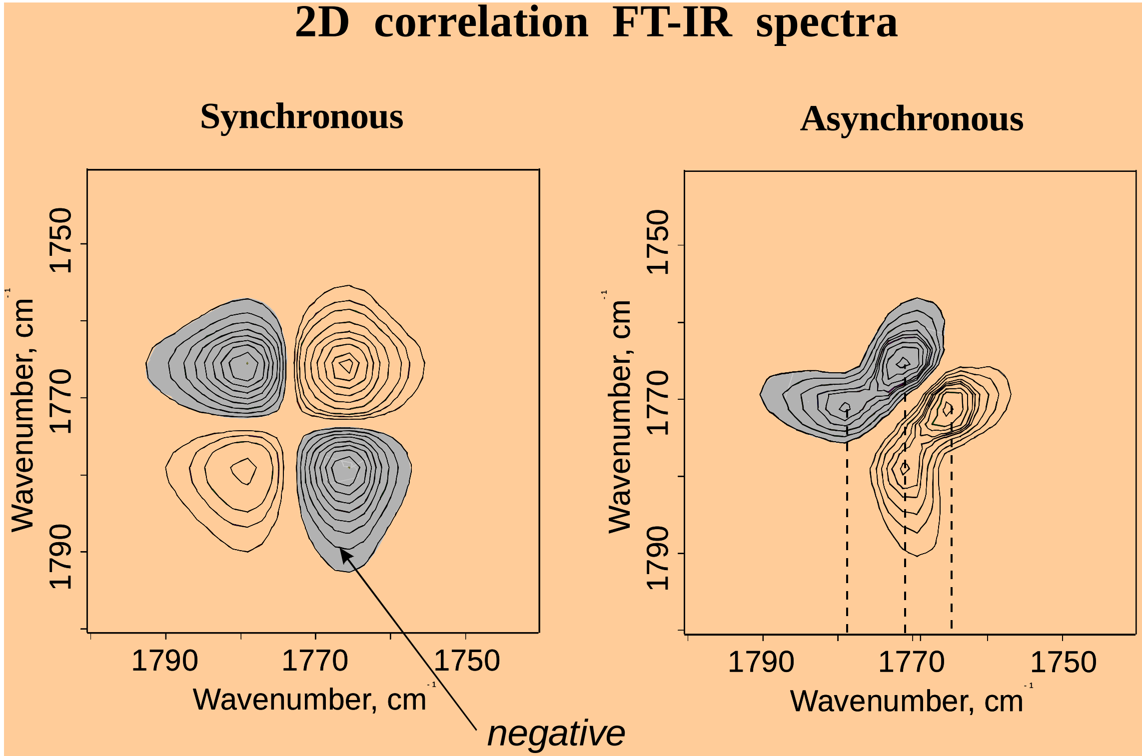
Complex 2D correlation spectrum

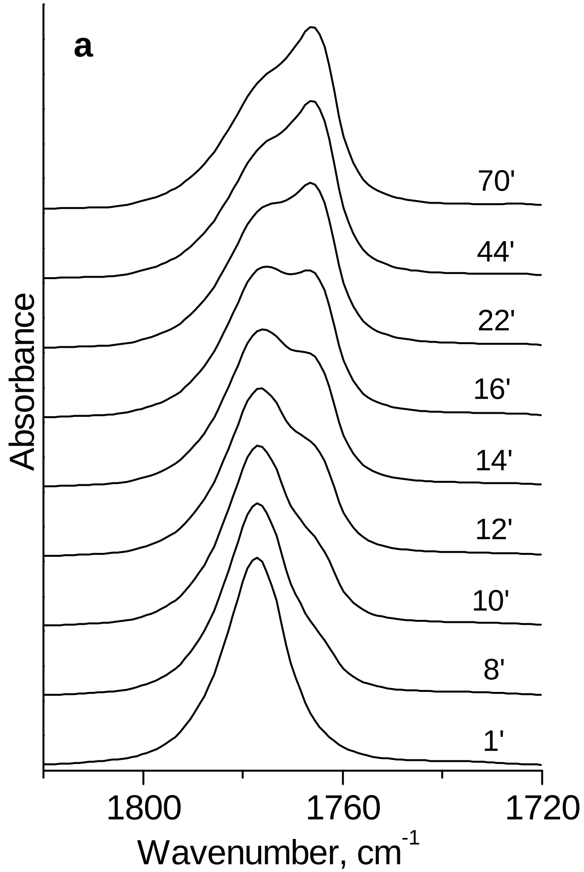
$$Y_1(\omega) = \int_{-\infty}^{\infty} y(\nu_1,t)e^{-i\omega t}\,\mathrm{d}t = Y_1^{\mathrm{Re}}(\omega) + iY_1^{\mathrm{Im}}(\omega)$$

$$Y_2^*(\omega) = \int_{-\infty}^{\infty} y(\nu_2,t)e^{i\omega t}\,\mathrm{d}t = Y_2^{\mathrm{Re}}(\omega) - iY_2^{\mathrm{Im}}(\omega)$$

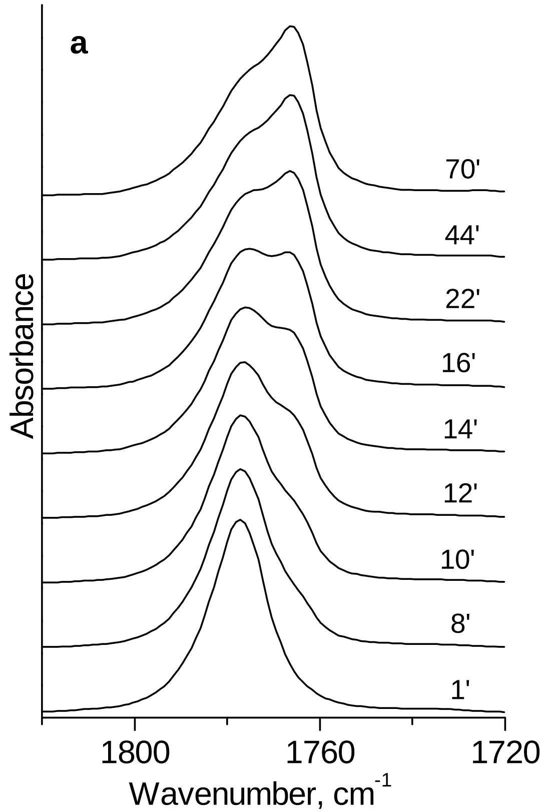
$$\Phi(\nu_1,\nu_2) + i\Psi(\nu_1,\nu_2) = \frac{1}{\pi T}\int_0^{\infty} Y_1(\omega)\cdot Y_2^*(\omega)\,\mathrm{d}\omega$$

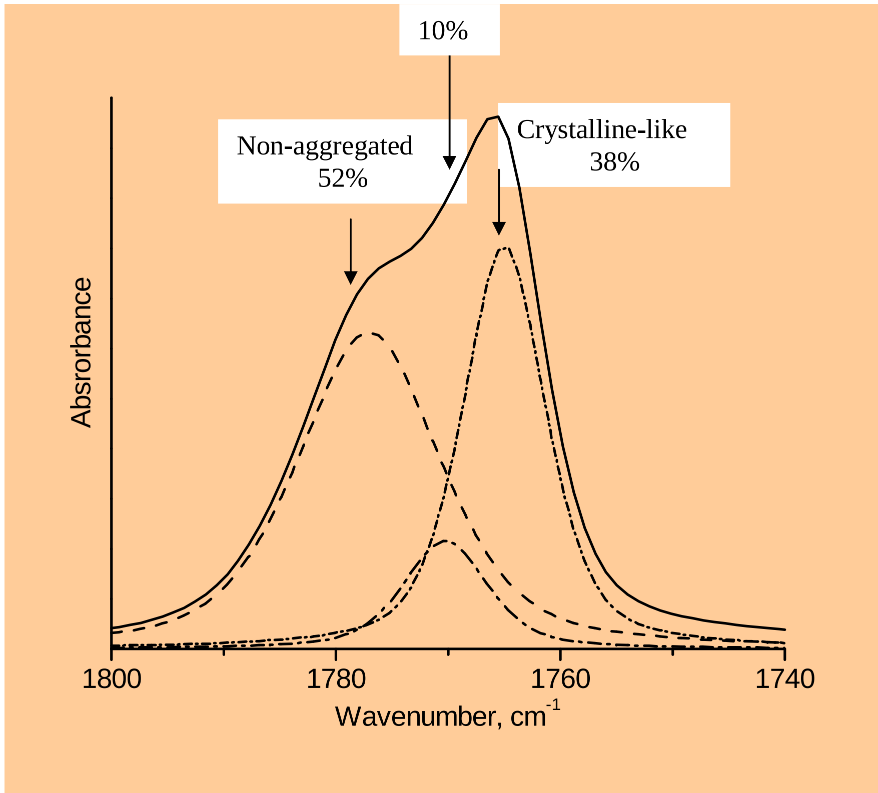
Polycarbonate in toluene





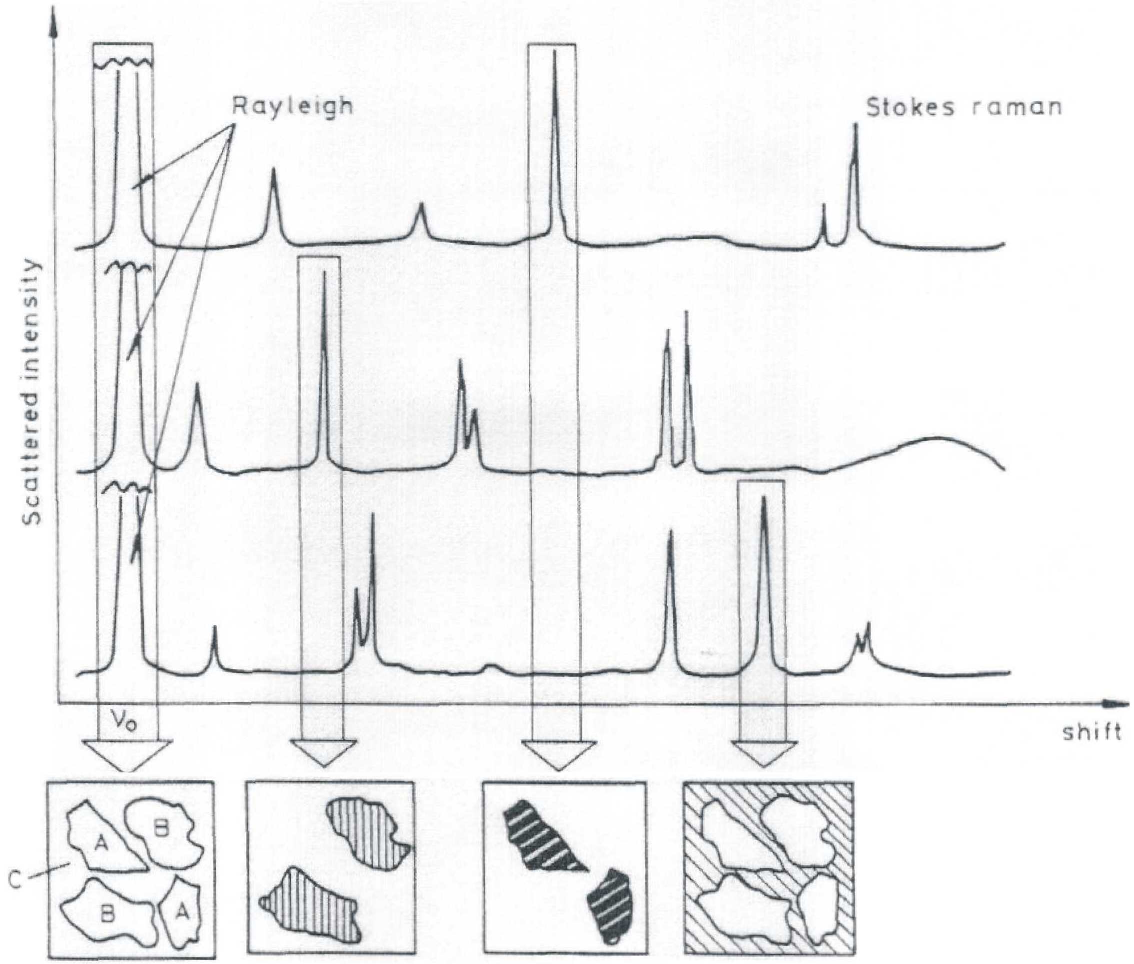
Polycarbonate in toluene





Raman imaging and mapping

	Raman	IR
lateral resolution	1 μm	10 μm
confocal	2.5 μm	-



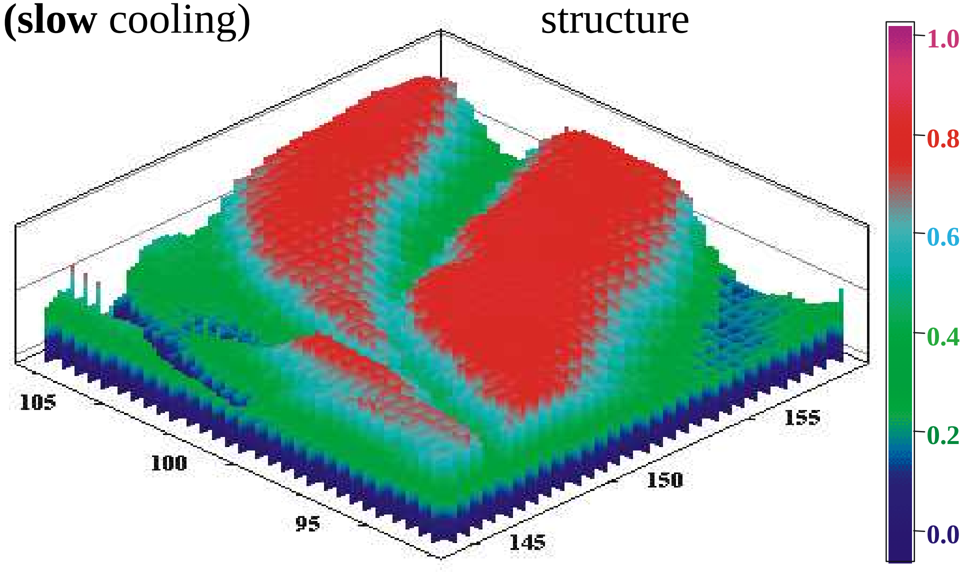
Conventional image

Raman band images

Compositional domain structure of PP/PE blend

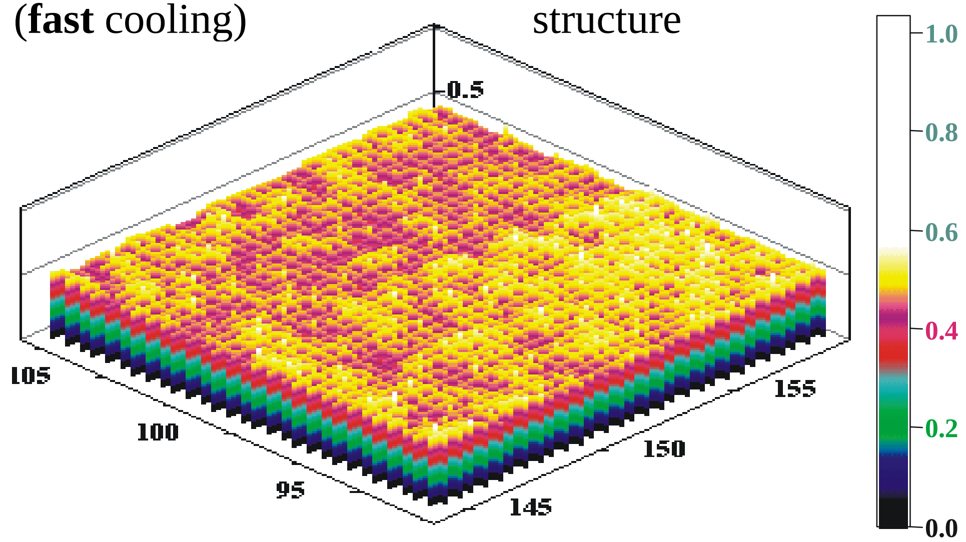
pressed, inner part
(**slow** cooling)

coarse domain
structure



injected, surface
(**fast** cooling)

fine domain
structure



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