Measurement of vibrational spectra in microworld and nanoworld – far field and near field techniques

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Nanospectroscopy and microspectroscopy

- Chemical images of samples
  - Generate from peak heights, areas, peak ratios, correlation, results of principal component analysis etc.
  - Useful for monitoring changes in chemical composition in a sample
    - inhomogeneities, defects, composite materials...

Nanospectroscopy and microspectroscopy

- Chemical images of sample
  - Group of points collected over the entire area of interest
    - Points can be collected in series (mapping – scanning the surface) or in parallel (imaging – multichannel detection)
- Chemical images of sample
- IR imaging – multichannel detection
Chemical images of sample

IR imaging – multichannel detection

- Selected bands
- PCA
Nanospectroscopy vs. microspectroscopy

- **Microspectroscopy** – techniques of far field
- **Nanospectroscopy** – techniques of near field
  - “coupling of a probe and surface”
Nanospectroscopy vs. microspectroscopy

- **Microspectroscopy** – techniques of far field
  - The maximum spatial resolution in a properly designed microscope is limited by the **diffraction** of light.

- **Nanospectroscopy** – techniques of near field
  - The maximum spatial resolution is under diffraction limit, it is limited mostly **by probe aperture** (probe diameter).
Microspectroscopy

Spatial Resolution
- the ability to view two closely spaced points as distinct objects

Diffraction
- the bending (or “scattering”) of light/energy by an opening of an optical element (lens, aperture)
Microspectroscopy

**Diffraction**

- the bending of light by an opening of an optical element
- occurs when the wavelength of the light approaches the size of the opening
- for infrared spectroscopy $\sim 10 \mu m$
  - (1000 cm$^{-1}$ is 10 $\mu m$)
- for Raman spectroscopy better than 1 $\mu m$
  - excitation in visible range
Microspectroscopy

Diffraction

\[ d = \frac{1.22 \lambda}{\text{NA obj. } + \text{NA cond.}} \]

For 1469 cm\(^{-1}\),

\( (1469 \text{ cm}^{-1} = 6.8 \mu\text{m}) \)

\[ d = \frac{1.22 (6.8 \mu\text{m})}{0.58 + 0.71} = 6.4 \mu\text{m} \]
Microspectroscopy

**Diffraction, resolution, sample size**

- Large sample (>100 μm)
  - No apparent diffraction
- Small sample (<100 μm)
  - Diffraction Present

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**Diagram:**

- Full field
- Sample area
- Diffracted radiation
Microspectroscopy

Minimize Diffraction Effect - Dual Remote Aperture

- First aperture placed between infrared source and sample, limiting IR beam to desired sample area

- Second aperture placed between sample and detector to reduce amount of diffracted light detected
IR Microspectroscopy Sampling Modes

Transmission

Reflection

Transmission Mode

Reflection Mode
IR Microspectroscopy Sampling Modes

Transmission
- transparent samples, thin layers

Reflection
- ATR
- reflection - absorption, specular reflection, grazing angle
IR Microspectroscopy Sampling Modes

Transmission

- transparent samples, thin layers
  - 5 - 15 \( \mu \text{m} \) thickness
  - large and uniform surface

- mounting in compression cell between windows makes ideal transmission sample
IR Microspectroscopy Sampling Modes

Reflection - ATR

- simplifies sample preparation
- simplifies sample thickness problem
  (0.4 - 2.0 μm penetration depth)
- position sample on stage
- adjust for contact alert – contact sensor
IR Microspectroscopy Sampling Modes

**Reflection - ATR**

- objective crystals - ZnSe, Ge, Si, Diamond

- Contaminant on Analgesic Tablet by Micro ATR
- Surface of Analgesic Tablet by Micro ATR

- 40 μm defect
IR Microspectroscopy Sampling Modes

Reflection – grazing angle
Raman Microspectroscopy Modes

Raman Microspectroscopy
- dispersive
  - visible excitation
  - possibility of confocal mode to enhance spatial resolution
- FT Raman
  - near-infrared excitation
  - lower spatial resolution
Original Concepts of Raman Microscope

Initial goal was to produce a picture of the sample through its Raman signal in order to promote the development to the Raman community.

Laser spot scanned across sample - image reconstructed from PMT signal

Laser spot scanned along line and imaged thru stigmatic mono onto multichannel detector

Global laser illumination - sample imaged onto detector thru λ-selection filter
Raman Microspectroscopy - dispersive

Microscope lenses 1

NOTCH or EDGE FILTER

FILTER plasma lines

Sample on sample stage

Microscope lenses 2

Pinhole

SPECTROGRAPH

HeNe Laser

CCD camera
Raman Microspectrometers

Renishaw

Kaiser Optical

Chromex

Nicolet

Jobin-Yvon
Raman Microspectroscopy

- mapping of surfaces - Gram-Schmidt

Au – target

after deposition of 4-aminothiophenole
Raman Microspectroscopy

- mapping of surfaces – PCA (RGB)

**Au – target**

- red – value of 1-st principal component (PC)
- green – value of 2-nd PC
- blue – value of 3-rd PC

after deposition of 4-aminothiophenole
Microspectroscopy Applications

- Small samples
- Large Samples
- Plastics
- Packaging materials
- Pharmaceuticals
- Fibers
- Trace evidence
- Contaminants
- Forensic analysis
- Failure analysis
- Coatings & inks
- Electronic materials
- Migration, diffusion and aging studies
- Reverse engineering
- Art conservation
- Geology
- Archaeology
- ...
Optical nanospectroscopy and nanomicroscopy (or nanoscopy ?)

- Nanospectroscopy
  - non-destructive approach
  - easy sample preparation
  - vacuum is not required (compared to SEM)
Nanospectroscopy

- Near-field techniques
  - probe near the surface („near field“)

- Near-field spectroscopy
- Near-field microscopy (nanoscopy) – AFM, STM
  - SNOM (NSOM) – scanning near-field optical microscopy
  - UV-vis, IR (IR-SNOM), Raman spectroscopy (Raman SNOM, TERS)
  - photoluminiscence, fluorescence
    - resolution better than 50 nm
    - spectroscopy of single molecule
Infrared nanospectroscopy

- Near-field techniques
  - construction of spectroscopic image by punctual “mapping” of the surface
  - probe scans the surface – point by point
  - critical parameter – probe aperture and its distance from surface
Infrared nanospectroscopy

- distance of probe – $\approx 10$ nm
- aperture of probe – 10 – 100 nm
- optical modes of spectra collection
  - transmission (only for transparent samples)
  - reflection – narrow tip – transmitter, receiver
Infrared nanospectroscopy

- distance of probe – $\approx 10$ nm
- aperture of probe – $10 - 100$ nm

- optical coupling of the tip of the probe and the sample surface

- the probe responses on changes of dielectric function in its surroundings
Infrared nanospectroscopy
Advantages and problems of SNOM

• ADVANTAGES
  ➢ OVERCOME of diffraction limit – „nanoresolution“
  ➢ non-destructive method
  ➢ flexible modes of data collection

• PROBLEMS
  ➢ technological demands on design and construction of SNOM probe
  ➢ low intensity of detected radiation
  ➢ demands on sensitivity of a detector
Advantages of IR SNOM

- combination of SNOM and IR radiation
  - spatial resolution of SNOM – nanometers
  - chemical resolution - chemical specificity of IR spectra

- chemical characterization of nanomaterials
  - nanodomains
Examples

- organic nanocomposite materials

  - domains
    - polystyrene
    - poly-2-vinylpyridine
Examples

- organic nanocomposite materials

- domains
  - polystyrene
  - poly-2-vinylpyridine
Examples
  – cellular culture

• 20 x 20 μm IR SNOM images
  – 1515 cm\(^{-1}\)

  – 1440 cm\(^{-1}\)
Examples

- NIR SNOM
Examples
– NIR SNOM

Vulnerable Atherosclerotic Plaque

stained section
adjacent IR mapped section
Examples

– NIR SNOM

Analysis of Hyperspectral Images
Combination
– MicroRaman, SNOM enhanced Raman, AFM

Parallel imaging of a Silicone Semiconductor

AFM image – 9 x 7 μm
Raman instensity image – 520 cm⁻¹, the same area