Organic Materials for Energy and Optoelectronics

Materials characterization

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Feb 11, 2022

Reading

Textbooks

- *Koehler* 1.5 UV-Vis, 2.4.4 CV
- *Forrest* by Index
- *Wikipedia* by keyword

Reviews

- R Wu, M Matta, B Paulsen, J Rivnay, Operando Characterization of Organic Mixed Ionic/Electronic Conducting Materials, Chem Rev (2022)

Lecture

- K Stevenson, Spatially-resolved Measurements of Semiconductor Interfaces (2022) – see Canvas/Files

Topics

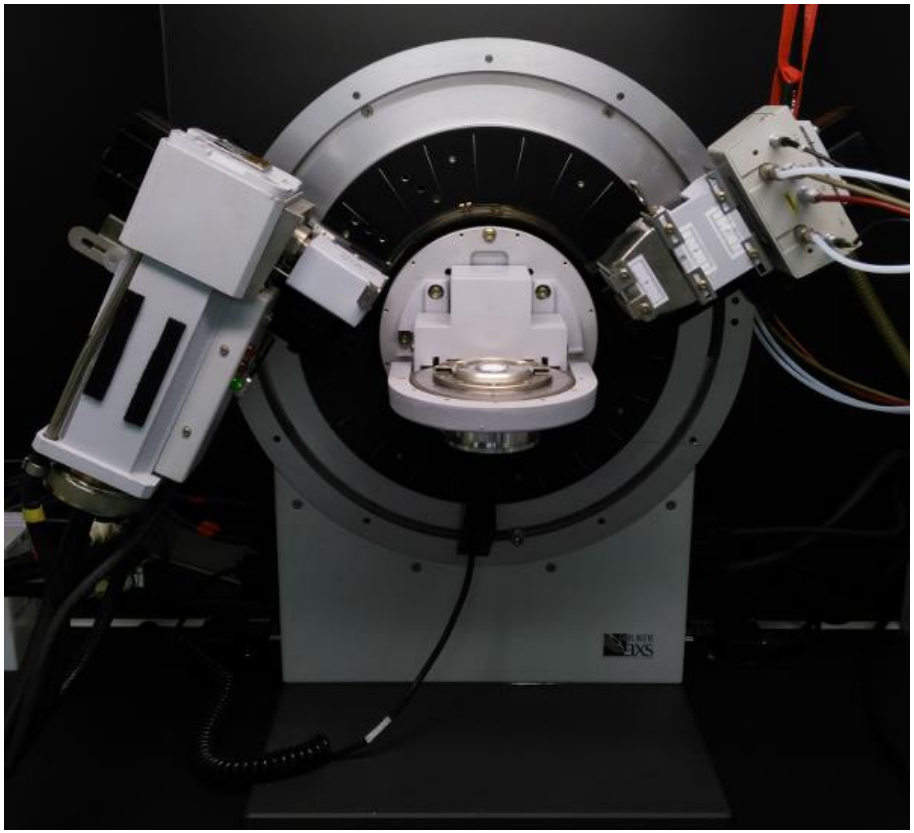
- Skoltech facilities

- Scanning near-field microscopies
- UV-Vis spectroscopy
- IR/Raman spectroscopy
- Cyclic voltammetry
- X-ray crystallography

- XPS
- NMR
- DSC
- Mass spectroscopy

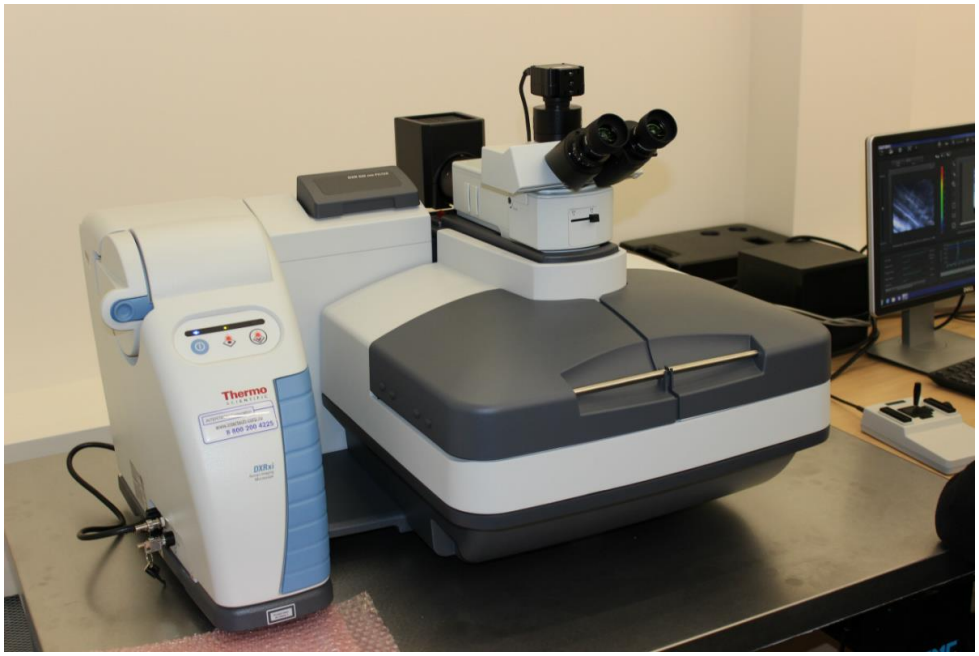
Virtual overview of Skoltech facilities

X-ray Powder Diffractometer
(Huber G670)

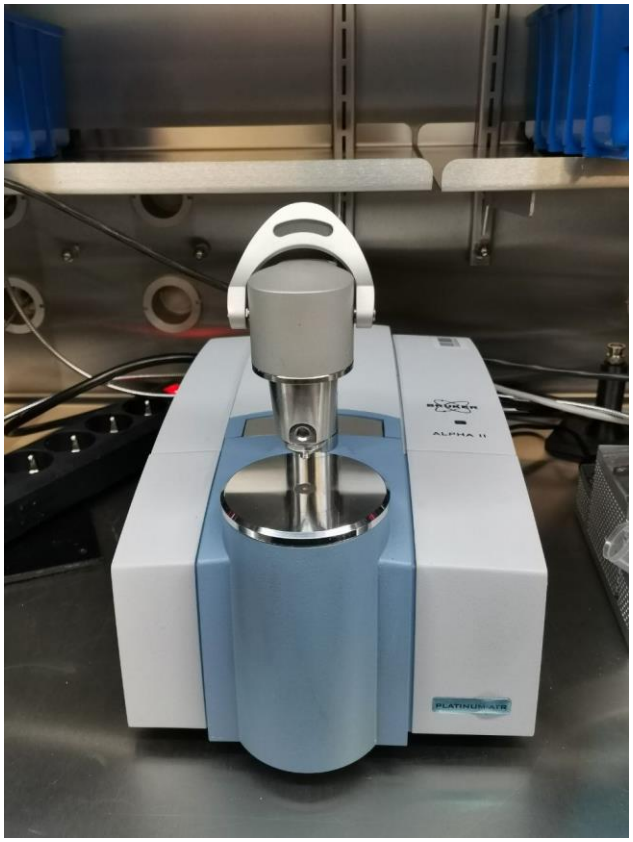


X-Ray Powder Diffractometer
(Bruker D8 Advance)

Virtual overview of Skoltech facilities



DXRxi Raman Imaging Microscope
(Thermo Fisher Scientific)

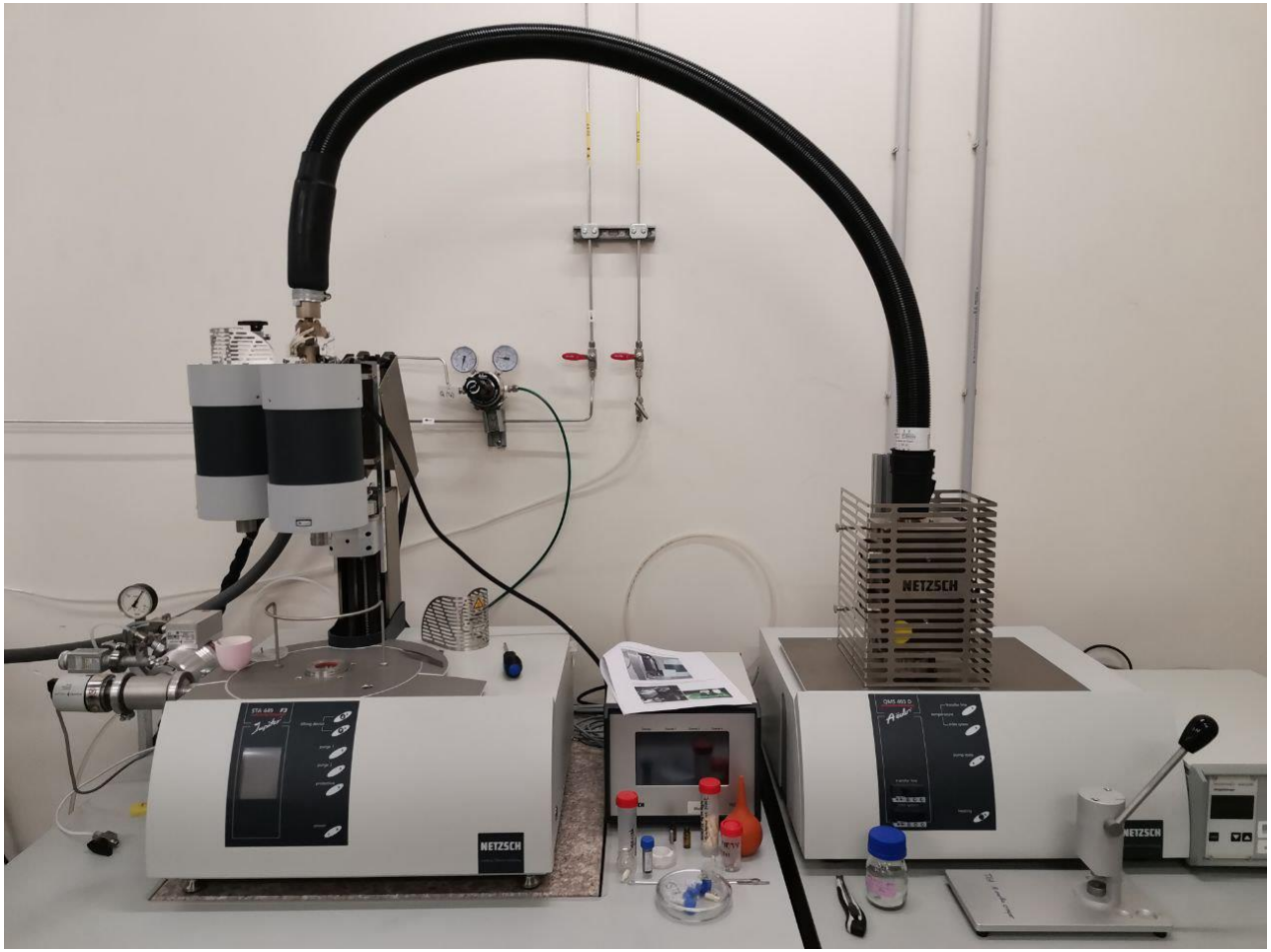


FTIR spectrometer
(Alpha II Bruker)

Virtual overview of Skoltech facilities

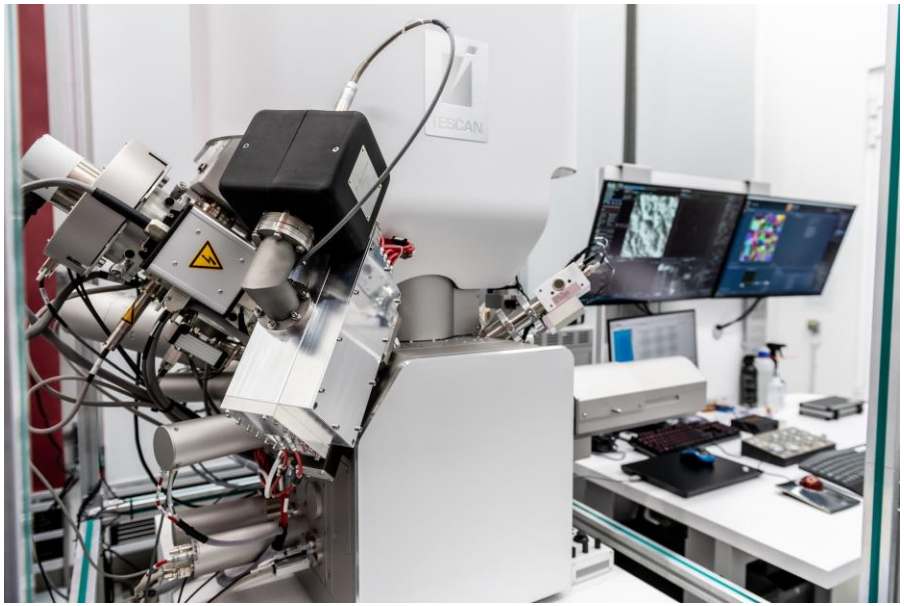
Potentiostat/galvanostat PGSTAT 302N
(Metrohm Autolab)

Virtual overview of Skoltech facilities



Thermogravimetry – Differential Scanning Calorimetry analyzer
(STA 449 F3 Jupiter)
with Quadrupole Mass Spectrometer
(QMS 403 D Aëolos)

Virtual overview of Skoltech facilities



Scanning Electronic Microscope
(Tescan Solaris)

Scanning Electronic Microscope
(Quattro S)

ADVANCED IMAGING CORE FACILITY

AICF

https://www.skoltech.ru/research/en/advanced-imaging-core-facility/

Scanning near-field microscopies

See Lecture of Keith Stevenson in Canvas/Files:

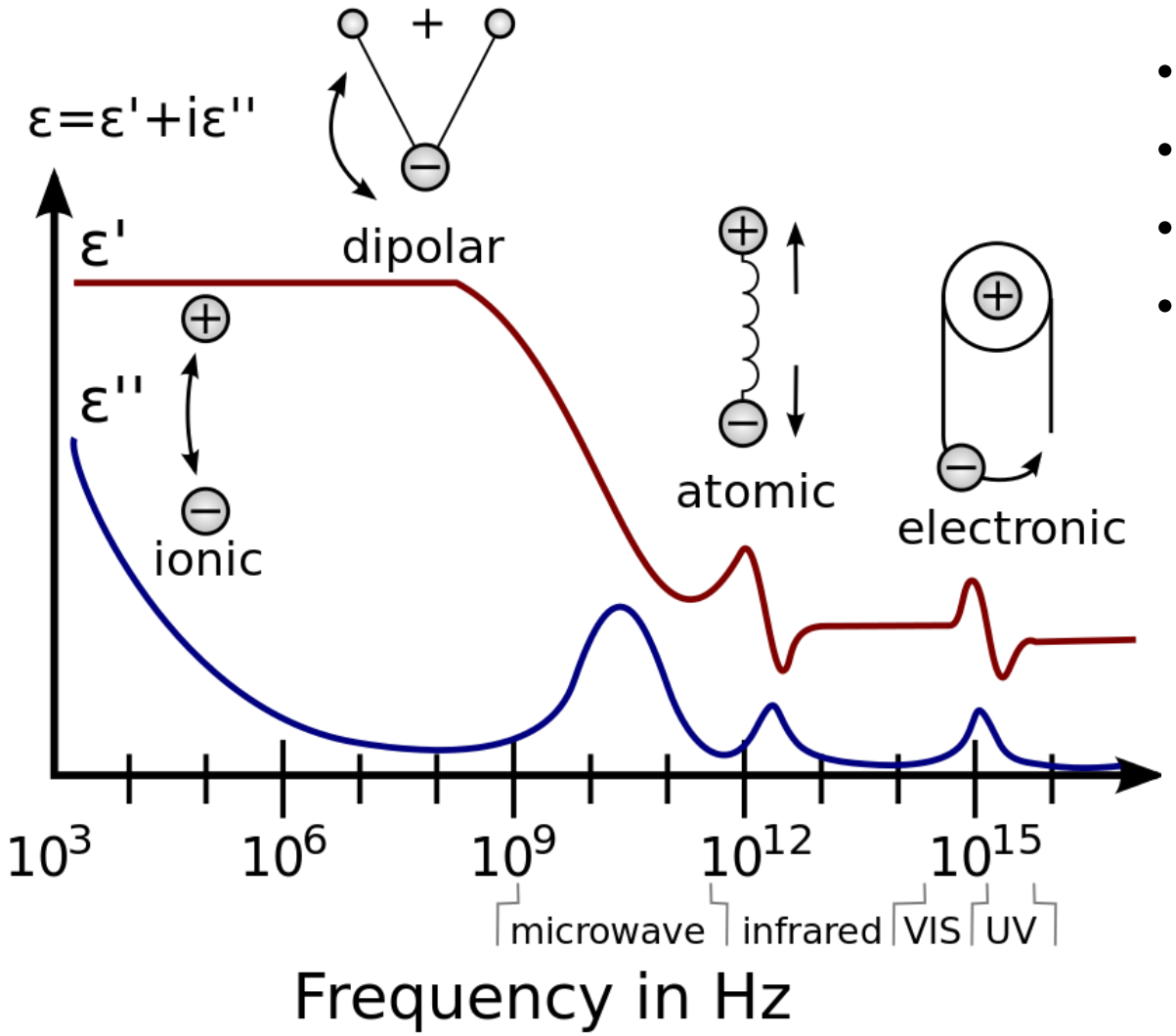
- Atomic Force Microscopy
- Conductive (Probe) Atomic Force Microscopy
- Kelvin Probe Force Microscopy
- Scanning Electron Microscopy and TEM
- Grazing incidence X-ray diffraction and small-angle scattering
- Light Beam Induced Current Imaging
- Time of Flight Secondary Ion Mass Spectrometry
- Raman Microscopy

Discussion: Scanned Probe Microscopy

Several SPM techniques were discussed for characterization of mixed electronic/ionic conductors.

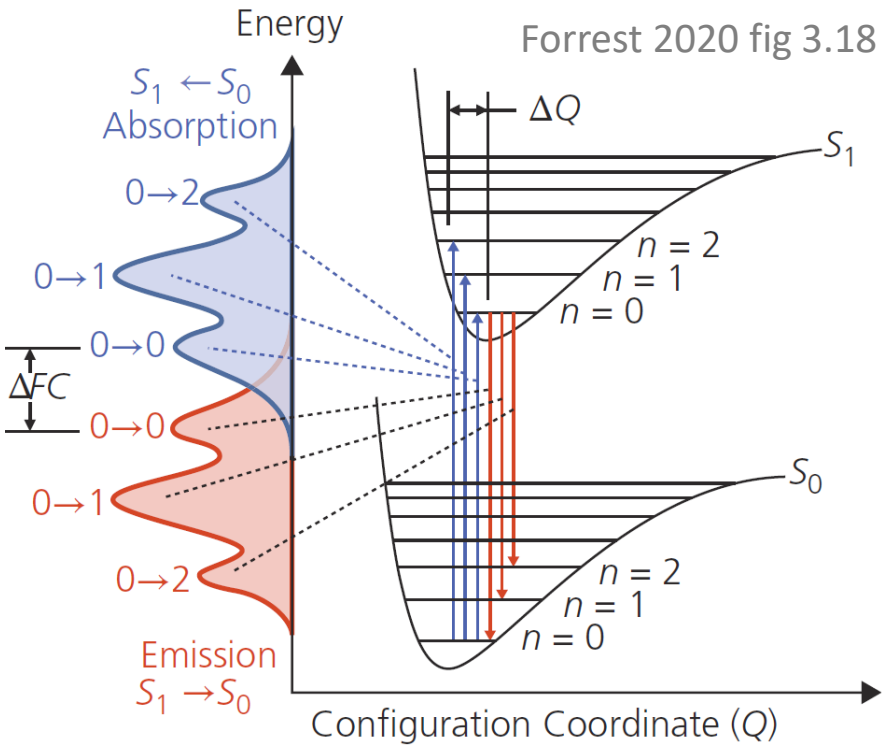
- Which method is best for characterizing local electronic conductivity? Why is it important for resolving spatial distribution of electronic conductivity?
- Which method is best for characterizing structural and morphological heterogeneities?
- Which method is best for characterizing buried interfaces or interfaces at electrode/semiconductor devices?

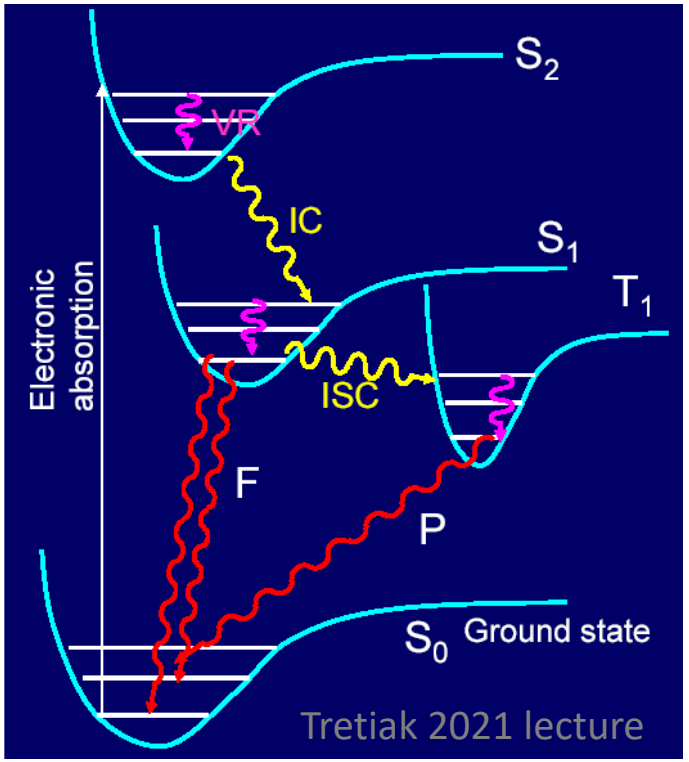
Discussion: dielectric spectroscopy



- UV-Vis
- IR/Raman
- THz spectroscopy
- Electrochemical Impedance Spectroscopy

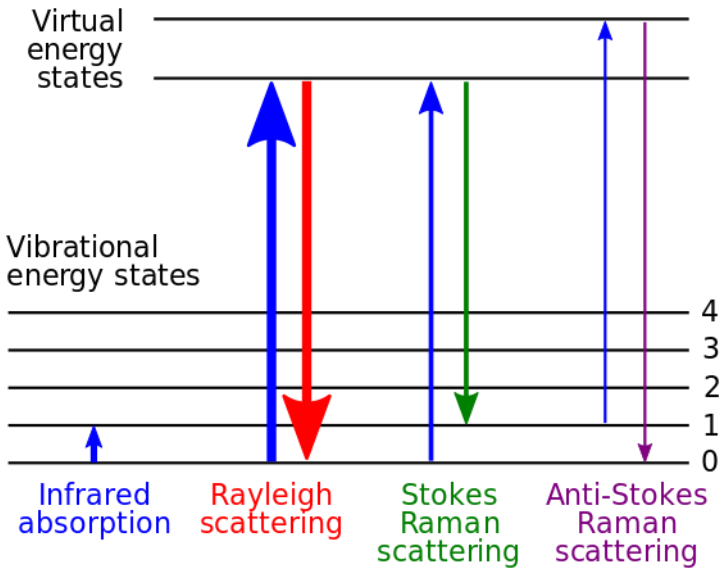
Discussion: UV-Vis spectroscopy

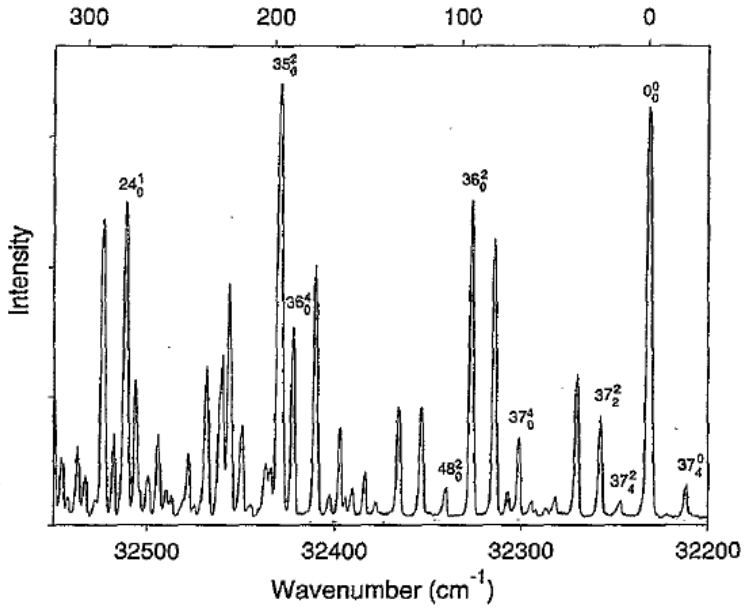




- Why is excitation energy lower for longer and DA molecules?
- Why is this picture not used for inorganic semiconductors?
- Why are spectra of molecules and crystals different?
- Why is there a shift in 0-0 transition? See e.g. JCP 113, 11372 (2000)

Discussion: IR/Raman spectroscopy





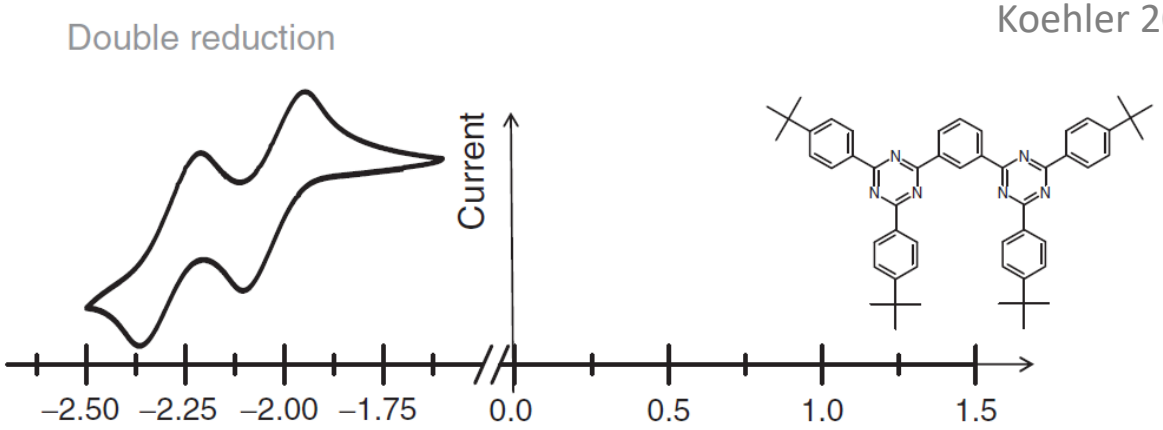
JCP 100, 8755 (1994)

FIG. 3. Fluorescence excitation spectra of jet-cooled *trans*-stilbene.

- Compare sensitivity of IR/Raman spectra to electronic state.
- What types of motions/vibrations are the most important for Raman spectra of organic semiconductors?
- How do anharmonicity, mode mixing, quantum phenomena influence vibrational spectra?

Discussion: Cyclic voltammetry

Koehler 2015 fig 2.67 (d)



- What causes the stepwise redox processes of organic molecules containing two or more identical electroactive pieces?
- How is it possible to investigate redox activity of insoluble organic molecules/polymers? How the corresponding CV curves may look like?
- What effects and side processes may distort the results of HOMO/LUMO level energy evaluation?

Discussion: X-ray crystallography

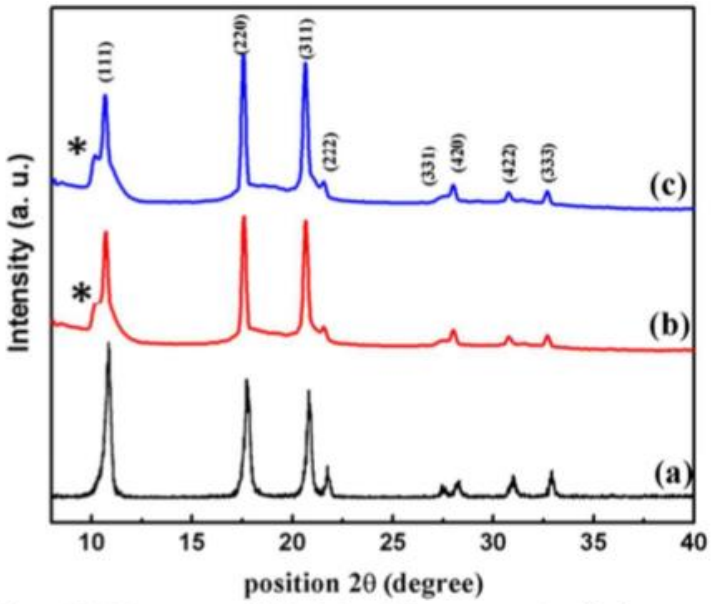
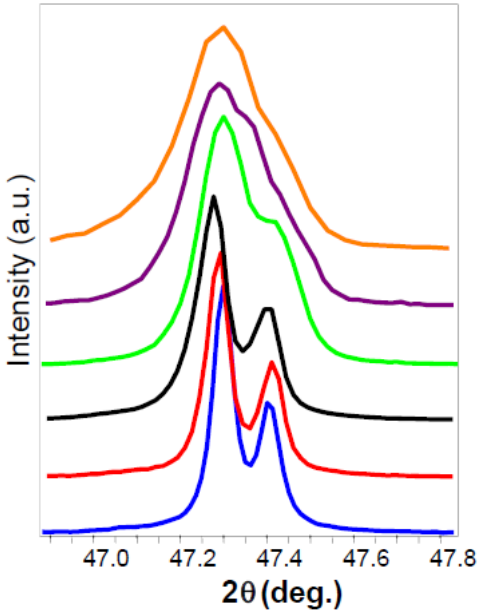


Figure 3. XRD pattern of (a) pristine fullerene powder, (b) flower-like and (c) octahedron-like fullerene crystals.

RSC Adv., 2016, **6**, 78791-78794



XRD spectra of <u>one sample</u> obtained on different-configured diffractometers

- Why could diffraction spectra of organic thin films differ from these materials in powder form? Discuss what additional information can give a comparison of those spectra.
- Suppose which parameters may affect the quality of the XRD spectrum in the right picture.

NMR spectroscopy

Principles of NMR are quite complicated whereas the method is rather routine

^{13}C and ^{1}H nuclei have spin (s = ½);

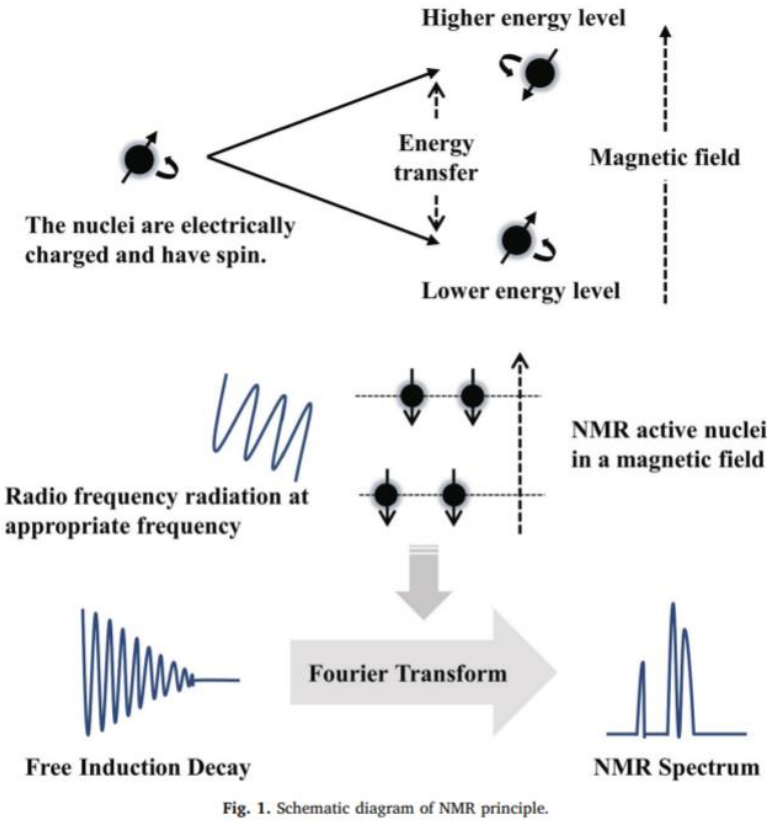


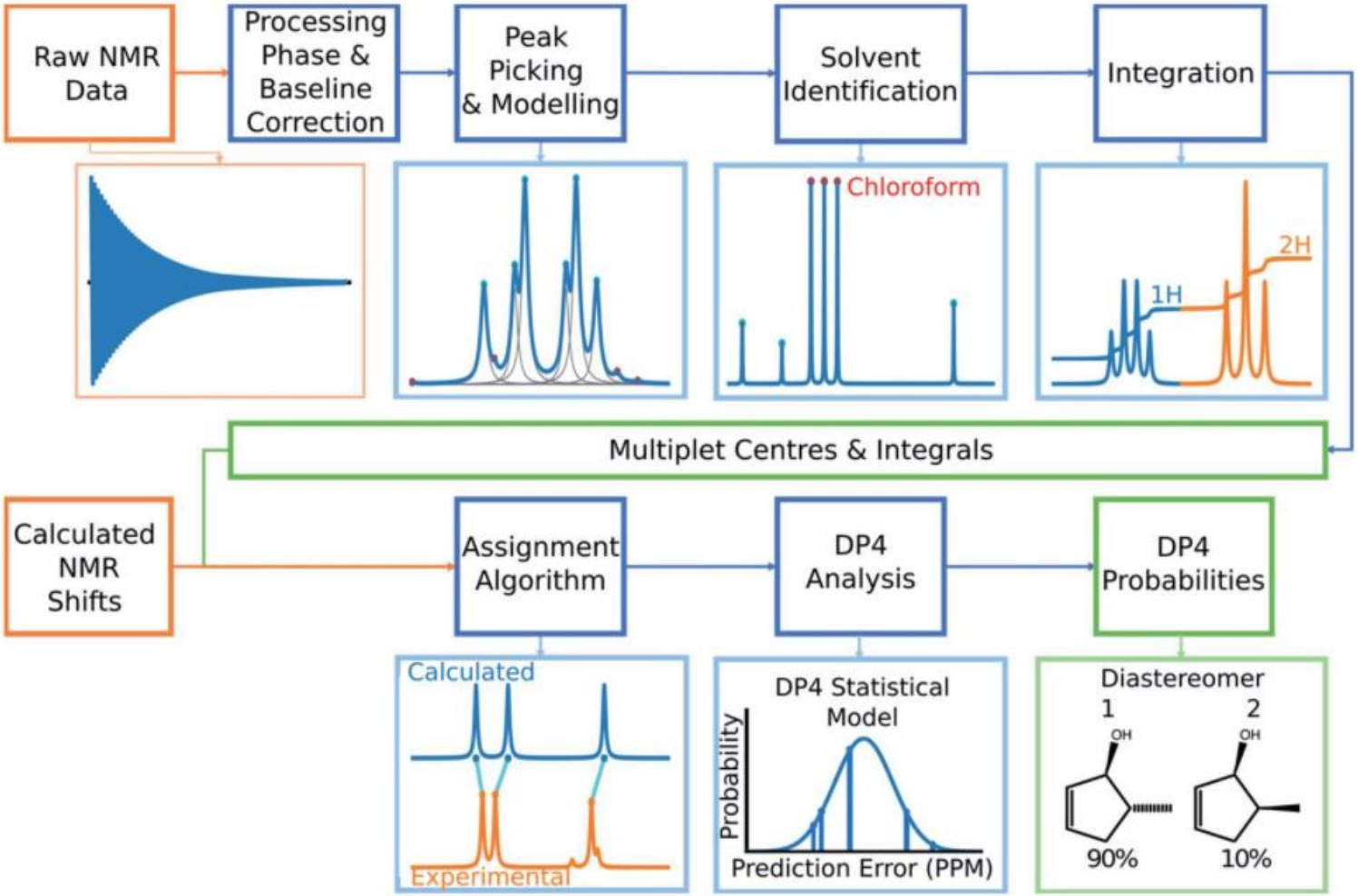
Fig. 1. Schematic diagram of NMR principle.

Food Chemistry, 2021, **342**, 128258

In NMR spectra of organic molecules, each C and H atom has a set of parameters allowing these compounds to be characterized both qualitatively and quantitively

NMR spectroscopy

Source: © Jonathan Goodman/University of Cambridge



AIST Database

SDBS Compounds and Spectral Search

Compound Name:
match partial

Molecular Formula:
C, H, then the other elements are alphabetical order, "%,*" for the wild card

Molecular Weight:
to
Numbers between left and right columns
Up to the first place of a decimal point

CAS Registry No.:
"%,*" for the wild card.

SDBS No.:
"%,*" for the wild card.

Atoms:

C(Carbon)		to	
H(Hydrogen)		to	
N(Nitrogen)		to	
O(Oxygen)		to	
F(Fluorine)		to	
Cl(Chlorine)		to	
Br(Bromine)		to	
I(Iodine)		to	
S(Sulfur)		to	
P(Phosphorus)		to	
Si(Silicon)		to	

Numbers between left and right columns.

Spectrum:
Check the spectra of your interest.
MS, IR, ^{13}C NMR, Raman, ^{1}H NMR, ESR

IR Peaks(cm^{-1}): Allowance ± 10
"," or space is the separator for multiple peaks.
Use "-", to set a range:. eg. 550-750,1650 3000-
Transmittance < 80 %

^{13}C NMR Shift(ppm): Allowance ± 2.0
"," is the separator for multiple shifts, eg. 129.3,18.4,...
No shift regions:
Range defined by two numbers separated by a space, eg. 110 78,...

^{1}H NMR Shift(ppm): Allowance ± 0.2
No shift regions:

MS Peaks and intensities:
Mass and its intensity are a set of data separated by a space, eg. 110 22,..

Search | Clear | Hit: 20hit | Sort by: Molecular Weight | Ascending Order | Result Display type: with Structures

http://sdbs.riodb.aist.go.jp/sdbs/cgi-bin/cre_search.cgi