Lecture 2: Optical probes

Overview of the course

<table>
<thead>
<tr>
<th>Date</th>
<th>Instructor(s)</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monday 01/09</td>
<td>Golden / Goedkoop</td>
<td>big introduction &amp; beginning of optical probes</td>
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<tr>
<td>Thursday 04/09</td>
<td>Golden / Goedkoop</td>
<td>optical probes and inelastic electron scattering</td>
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<td>Monday 08/09</td>
<td>Golden / Goedkoop</td>
<td>photoemission and related probes</td>
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<td>Thursday 11/09</td>
<td>Golden / Goedkoop</td>
<td>x-ray spectroscopies</td>
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<td>Friday 12/09</td>
<td>all of us</td>
<td>lab experiments</td>
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<tr>
<td>Monday 15/09</td>
<td>Borgschulte</td>
<td>scanning tunneling microscopy / spectroscopy</td>
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<tr>
<td>Thursday 18/09</td>
<td>all of us</td>
<td>overspill: spectroscopy</td>
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<tr>
<td>Friday 19/09</td>
<td>all of us</td>
<td>lab experiments</td>
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<tr>
<td>Monday 22/09</td>
<td>you guys!</td>
<td>preparing presentations: 'spectroscopy'</td>
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<tr>
<td>Thursday 25/09</td>
<td>all of us</td>
<td>student presentations: 'spectroscopy'</td>
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<tr>
<td>Friday 26/09</td>
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<td>lab experiments</td>
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<tr>
<td>Monday 29/09</td>
<td>Eiser</td>
<td>introduction light/x-ray scattering</td>
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<tr>
<td>Thursday 02/10</td>
<td>Lohstroh</td>
<td>thin film x-ray reflectivity / diffraction</td>
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<td>Friday 03/10</td>
<td>all of us</td>
<td>lab experiments</td>
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<tr>
<td>Monday 06/10</td>
<td>Brück</td>
<td>(3D) crystal structures from x-ray diffraction</td>
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<tr>
<td>Thursday 09/10</td>
<td>Eiser</td>
<td>structure in disordered systems &amp; soft matter</td>
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<td>Friday 10/10</td>
<td>all of us</td>
<td>lab experiments</td>
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<tr>
<td>Monday 13/10</td>
<td>Wegdam</td>
<td>dynamic light scattering and coherent x-rays I</td>
</tr>
<tr>
<td>Thursday 16/10</td>
<td>Wegdam</td>
<td>dynamic light scattering and coherent x-rays II</td>
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<tr>
<td>Friday 17/10</td>
<td>all of us</td>
<td>lab experiments</td>
</tr>
<tr>
<td>Monday 20/10</td>
<td>you guys</td>
<td>preparing presentations: 'scattering'</td>
</tr>
<tr>
<td>Thursday 27/10</td>
<td>all of us</td>
<td>student presentations: 'scattering'</td>
</tr>
</tbody>
</table>
Overview of Lecture 2

**Lecture 2**

- first 45 minutes
  - dealing with the questions from last lecture
  - $h\nu$, electron, neutron:
    - mass
    - equation for $E(\lambda)$
    - $\lambda$ and momentum for $E = 1, 10, 100, 1000$ eV
  - questions (optical) from real life
- from 45-60 minutes = break

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**Lecture 2 continued**

- 60 - 120 minutes (i.e. second hour)
  - theoretical background:
    - basic terms, definitions, useful equations for optical spectroscopies
    - *(not enough time for derivations: see Ibach & Lüth)*

- 120 - 180 minutes (i.e. third hour)
  - mini-break
  - case study: spectroscopy of fullerene $C_{60}$
    - from INS, via IR, Raman, absorption of visible light, inelastic scattering of electrons, x-ray spectroscopy
Lecture 2: Optical probes

- **Optical properties:** absorption, emission, amplification and modification of light

![Optical components: mirror, prism, laser, window, SHG, glass fibre](image)

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**THE ELECTROMAGNETIC SPECTRUM**

- today

pic: courtesy of ALS
Case studies:
'optical' probes
&
(solid) C\textsubscript{60}
Lecture 2: Optical probes

**Fullerenes**

- pure carbon
- the third allotrope of carbon: diamond, graphite, fullerenes
- essentially sp\(^2\) hybridised electronic basis → conjugated
- made of 12 pentagonal faces and the rest = hexagons
- pentagons → pyramidalisation angle → curvature
How many electrons does a carbon atom have?  
How many of them are in valence orbitals?
Conjugated - sp² - carbon systems

- C atom: 1s²2s²2p²
- sp² hybrids have 3 electrons available for σ bonding
- 1 electron remains in a π-orbital (2pₓ)

Lecture 2: Optical probes

**Fullerenes**

- pure carbon
- the third allotrope of carbon: diamond, graphite, fullerenes
- essentially sp² hybridised electronic basis → conjugated
- made of 12 pentagonal faces and the rest = hexagons
- pentagons → pyramidalisation angle → curvature
  - origin = astrophysics question re. interstellar absorption bands
- breakthrough: 1990. Krätschmer & Huffman: carbon arc method of production of g quantities
Why the interest?

Properties of fullerenes as $\pi$-electron systems

**Fundamental challenge**

- How does such a 'simple' system (no d or f electrons) manage to display so many different ground states of quantum electronic matter?

+ storage of gas or charge
Carbon nanostructures: versatile nanoscale building blocks

- field emitters in FPDs
- molecular wires
- field effect transistors
- super strong fibres
- perfect SPM tips
- light emitting diodes
- molecular switches
- photovoltaic devices
- . . . .

Molecular solid

- Non-polar: solid C$_{60}$
- FCC close packing

(111) surface
Close packed structures

.....or nearly close packed

FCC  HCP  BCC

How can we alter the properties of C$_{60}$?

intercalation

interstitial sites
What fits into the interstitial sites of solid $C_{60}$?

$C_{60}$

$d = 0.7 \text{ nm}$

- Li$^+$ 0.076 nm
- Na$^+$ 0.1 nm
- K$^+$ 0.15 nm
- Rb$^+$ 0.16 nm
- Cs$^+$ 0.174 nm

Intercalation is only one of three ways to engineer the properties of fullerenes.
Lecture 2: Optical probes

**π - electronic structure of solid C\textsubscript{60}**

- LUMO
- HOMO
- Band gap
- Density of states: \( N(E) \)
- No. of allowed energy levels per unit vol. in the range \( E \) to \( E + \delta E \)

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**What should n-type intercalation do?**

- Partially fill the LUMO-derived conduction band
- \( t_{1u} \) - total six electrons

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Satpathy et al., PRB, 1992
Solid $C_{60}$: not just a solid made up of 'fat' atoms.

- very low energy degrees of freedom connected with rotations of the balls
  - librations etc.

- use inelastic neutron scattering to measure these . . . .
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**INS: real data**

- **comparison of** $C_{60}$ and $K_3C_{60}$

  intermolecular
  - low $E$
  - intramolecular
  - high $E$
  - intramolecular


**IR**

- photons of energy 50 - 200 meV

  absorption
  \[ K = \frac{\sigma_1(\omega)}{n(\omega)c_0} \]
  \[ K = \frac{\sigma_2(\omega)}{n(\omega)c_0} \]

  reflectivity
  \[ R = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2} \]
Lecture 2: Optical probes

**IR**

- a 60 atom molecule has \(3n-6 = 174\) internal vibrational modes
  
  \[ T = \frac{1 - R}{1 - R e^{-\frac{\hbar}{k}}}. \]

\(C_{60}\) shows only 4 IR-active modes \((\epsilon_{1u})\)

- consequence of high \(I_\text{h}\) symmetry
- (only 46 modes allowed in total)
- e.g. of selection rules

- proves truncated icosahedral structure

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**Raman**

- inelastic light scattering
  
  - Raman has different (symmetry) selection rules w.r.t. IR
    
    different vibrons visible \((\epsilon_3, \epsilon_6)\)
  
  - incoming laser light can be tuned to an electronic transition: **resonant Raman**
  
  - can be used to extract electron phonon coupling constant (\(\lambda\))
IR

- IR: also dynamics of the conduction electrons

- Insulators: phonons visible at low energies

- Metal: phonons screened out, plasma edge visible here at ca. 300 meV

Note also the huge phonon intensities in the doped systems!

Iwasa & Kanewasu, PRB, 1995

IR of conduction electrons in metals

\[ \omega_p = \sqrt{\frac{ne^2}{\varepsilon_0 m}} \]

- \( n \) generally so high that \( \omega_p \) lies in UV
- Thus metals usually only first transparent in UV range....

Commonly used approach is the Drude dielectric function:

\[ \varepsilon_{Drude}(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega/\tau} \]
Lecture 2: Optical probes

**what does a plasma edge at 0.3 eV mean?**

\[ \omega_p = \sqrt{\frac{ne^2}{\epsilon_0 m}} \]

*K_{3}C_{60} is a 'poor' metal!*

In fact it is very far from a simple, free electron metal.....

Data: Iwasa & Kanewasu, PRB, 1995

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Lecture 2: Optical probes

**Kramers-Kronig analysis: extract the optical conductivity \( \sigma(\omega) \)**

\[ \varepsilon(\omega) = 1 + \frac{i\sigma(\omega)}{\omega\varepsilon_0} \]

Real part of \( \sigma(\omega) \)

Iwasa & Kanewasu, PRB, 1995
Lecture 2: Optical probes

- **IR**
  - Drude-Lorentz fit of optical conductivity $\sigma_1(\omega)$
  - Drude
  - interband transition
  - mid-IR

  Iwasa & Kanewasu, PRB, 1995

- **Inelastic electron scattering**
  - EELS
  - in transmission (bulk sensitive)
  - in reflection (surface sensitive)

(bulk):
\[
\frac{d^2\sigma}{d\Omega dE} = \frac{1}{(\pi a_0)^2} \cdot \frac{1}{q^2} \cdot \text{Im} \left\{ -\frac{1}{\varepsilon(q,\omega)} \right\}
\]
measured quantity: loss function

\[
\frac{d^2 \sigma}{d \Omega dE} = \frac{1}{(\pi e a_0)^2} \cdot \frac{1}{q^2} \cdot \text{Im} \left\{ -\frac{1}{\varepsilon(q, \omega)} \right\}
\]

\[
\text{Im} \left\{ -\frac{1}{\varepsilon(\omega)} \right\} = \frac{\varepsilon_1(\omega)}{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}
\]

Kramers-Kronig analysis (KKA) allows extraction of \(\varepsilon_1(\omega)\) and \(\varepsilon_2(\omega)\)

EELS of \(C_{60}\)

peaks in the loss function are plasmons

caused either by free carriers or by interband transitions

\(\pi\) plasmon at 6eV

\(\pi + \sigma\) plasmon at 26eV

Sohmen & Fink, PRB, 1992
Lecture 2: Optical probes

**EELS of C_{60}**

- comparison of EELS in the solid and gas phase, with vis-UV absorption in solution
- interband transitions between occupied and unoccupied molecular orbitals (MO's)

![EELS of C_{60} graph](image)

Bulliard, Allen & Leach, CPL, 1993

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**C_{60} 'band gap' & excitons**

- LDA band gap ca. 1.5 eV

![C_{60} band gap graph](image)
**Lecture 2: Optical probes**

**C\textsubscript{60} 'band gap' & excitons**

- LDA band gap ca. 1.5 eV
- Onset of optical absorption, EELS etc. ca. 1.5 eV

![Graph showing optical transition and exciton BE]

**OK?**  
**NO!**

**True 'transport' gap**

- \(E_{N-1} \) electrons - \(E_{N+1} \) electrons
- Optical transition is an 'on-ball' (Frenkel) exciton
- Exciton BE \(\sim U = 1.5\) eV

![Graph showing transport gap and PES/IPES]
these were examples of using spectroscopy to get information on the energy ($\omega$) and momentum ($k$ or $q$) dependence of:

- librations
- vibrations (phonons)
- dynamics of 'free' electrons
- electronic transitions between localised levels

that's it for this week

x-ray's and C$_{60}$ will be covered next week
### Lecture 2: Optical probes

#### EXPERIMENTS - spectroscopy:

<table>
<thead>
<tr>
<th>Date</th>
<th>Group</th>
<th>Exp.</th>
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<tbody>
<tr>
<td>5/9</td>
<td>1</td>
<td>optical absorption (WZI)</td>
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<tr>
<td>12/9</td>
<td>2</td>
<td>electron spec. (WZI)</td>
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<tr>
<td></td>
<td>3</td>
<td>STM (VU)</td>
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<td>19/9</td>
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<td>electron spectroscopy (WZI)</td>
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<tr>
<td></td>
<td>3</td>
<td>optical absorption (WZI)</td>
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</table>

1 = Wing
Kiu + Sanne
2 = Anne
Lisa + Jeroen
3 = Tracy,
Sven + Eric

#### EXPERIMENTS - scattering:

<table>
<thead>
<tr>
<th>Date</th>
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<tbody>
<tr>
<td>3/10</td>
<td>1</td>
<td>DLS (WZI)</td>
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Research papers:

des will be distributed in
next week's lectures (should
be Monday)