Outline

- Instrumentation
  - Frequency domain spectroscopy (dispersive spectrometers): UV-Vis-NIR
  - Fourier transform infrared (FTIR) spectroscopy: NIR-MIR-FIR/THz
  - Raman scattering and Photoluminescence
- CW optical spectroscopy at Maglab
- Introduction to Lab Practicals
Optical spectroscopy – What?

Study of **interaction** of **matter** with **light** (or photons)
Spectrum: response of matter to EM radiation as a function of energy

**Light** (or photon) has:
- Energy (or frequency)
- Momentum
- Polarization (helicity)
- Intensity (or flux)
- Coherence time and length

\[ E = h \nu = \hbar \omega \quad \vec{p} = \hbar \vec{k} \quad s_z = \pm \hbar \]
Optical spectroscopy – What?

Study of interaction of matter with light (or photons)

Spectrum: response of matter to EM radiation as a function of energy

Electromagnetic spectrum, after a diagram from SURA (D. Tanner, Optical Effects in Solids)
Optical spectroscopy – Why?

Study of interaction of matter with light (or photons)

Spectrum: response of matter to EM radiation as a function of $E$ (or $\text{wn}$, or $\lambda$)

\[ \text{wn} = \lambda^{-1} = c/\nu \]
\[ h\nu = eV = k_B T \]
Study of **interaction** of **matter** with **light** (or photons)

Spectrum: response of matter to EM radiation as a function of $E$ (or $\omega n$, or $\lambda$)

---

**Spectroscopist’s take on life’s development on Earth**

- Proto-ocean protected early life from the Sun’s UV
- Photosynthesis harvesting Vis range photons
- Vision in the visible range
Optical spectroscopy – Why?

Probe various structural, electronic and magnetic states/excitations in matter

Basov et al., Rev. Mod. Phys., 83, 471 (2011)
Optical spectroscopy – Why?

Probe various structural, electronic and magnetic states/excitations in matter
introduce tunable length scale

\[ l_m = \sqrt{\frac{\hbar}{eB}} = \frac{25.6}{\sqrt{B}} \text{nm} \]

1T \rightarrow 25 \text{ nm}  
10T \rightarrow 8 \text{ nm}  
40T \rightarrow 4 \text{ nm}

... tunable orbital and electron spin energy scales

Cyclotron energy:

\[ \hbar \omega_c = \hbar \frac{eB}{m^*} \sim 1 \text{ meV/T} \]

\[ m^*/m_0 \sim 0.1 \]

Zeeman energy:

\[ E_Z = g\mu_B B \sim 0.1 \text{ meV/T} \]

... interaction energy scale

\[ E_{e-e} = \frac{e^2}{\varepsilon l_B} \approx \frac{50 \text{meV}}{\varepsilon} \sqrt{B} \]

10T \rightarrow 15 \text{ meV} 
\[ \varepsilon=10 \]

breaks time-reversal symmetry

Magneto-Optics: CP \( \neq \)
High magnetic fields in condensed matter physics

Magnetic field reduces the effective dimensionality

\[ l_m = \sqrt{\frac{\hbar}{eB}} = \frac{25.6}{\sqrt{B}} \text{nm} \]

1T → 25 nm
10T → 8 nm
40T → 4 nm

... tunable orbital and electron spin energy scales

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10T → 15 meV
\[ \epsilon = 10 \]

breaks time-reversal symmetry

Magneto-Optics: CP ≠ 0
Optical spectroscopy – How?

- Reflection and Transmission: Uv, Vis, IR, THz
  \[ \nu_{in} = \nu_{out} \]
- Raman scattering
  \[ \nu_{in} \neq \nu_{out} \]
- Photo-Luminescence (PL)
  Photoconductivity, electroluminescence, ...
Optical spectroscopy – How?

**Broad-band spectroscopy**

- Transmission
- Reflectivity

**Excitation spectroscopy**

- Photo-Luminescence
- Inelastic Light Scattering (Raman)
**Broad-band spectroscopy – How?**

**Transmission**

- Broad-band light source: UV/Viz/IR/THz
- Sample
- Broad-band detector

Transmission experiment:
- shine light $I_0(\nu)$ on a sample
- measure what is going through $I_T(\nu)$
- calculate transmittance $T(\nu)$

$$T(\nu) = \frac{I_T(\nu)}{I_0(\nu)}$$

**Reflectivity**

- Broad-band detector
- Sample

Reflectivity experiment:
- shine light $I_0(\nu)$ on a sample
- measure what is what is coming back $I_R(\nu)$
- calculate transmittance $R(\nu)$

$$R(\nu) = \frac{I_R(\nu)}{I_0(\nu)}$$

**Transparent samples:**
- insulators
- semiconductors
- thin films of good conductors

**Highly reflecting samples:**
- good conductors
- reflectance bands (phonons)
Low-energy states
- vibrational
- spin

High energy states
- electronic states or bands
- impurities

\[ \nu_{in} = \nu_{out} \]

Vis spectroscopy
- Transmission
- \( \Delta E \sim 1-2 \text{ eV} \)
- \( \hbar \omega \)

IR spectroscopy
- Transmission
- \( \omega_0 \)
- \( \Delta E \sim (1-100) \text{ meV} \)
- \( \hbar \omega \)
Excitation spectroscopy – How?

**Photo-Luminescence**

- E\(_3\)
- non-radiative relaxation
- E\(_2\)
- E\(_1\)

\(\nu_{\text{in}} \neq \nu_{\text{out}}\)

\(\omega_0\)

**Raman scattering**

- virtual state
- scattered

\(\omega_0\)

- S
- \(\omega_L\)
- aS

\(\Delta E \sim 1\text{eV}\)

\(\Delta E \sim (1-100)\text{meV}\)
Physics: spectroscopic probe of structural, electronic and magnetic states or excitations

Chemistry: analytical tool to determine composition, structure, ...

Biology: ...
Optical spectroscopy – How?

**SELECTION RULES**

IR activity: Induced dipole moment due to change in atomic position

\[
\left( \frac{\partial \mu}{\partial Q} \right)_0 \neq 0 \quad \mu \text{ is dipole moment}
\]

\( Q \) is the normal coordinate at the equilibrium configuration

IR modes: “Asymmetrical” (\( E_u, A_{1u} \) etc.,)

Raman Activity: Induced dipole moment due to deformation of electron shell

\[
\text{Induced polarization } P = \alpha E
\]

\[
\left( \frac{\partial \alpha}{\partial Q} \right)_0 \neq 0 \quad \alpha \text{ – Polarizability}
\]

\( E \) – Electric Field

Raman modes: “Symmetrical” (\( E_g, A_{1g} \) etc.,)

**RULE OF MUTUAL EXCLUSION**

In a centrosymmetric molecule (i.e., one with a center of inversion symmetry) a vibrational mode may be either IR active or Raman active but not both.
Optical spectroscopy – How?

SELECTION RULES – CO$_2$

- $v_1$: Symmetric C-O Stretch
  - IR Inactive
  - Raman Active

- $v_2$: Bend
  - IR Active
  - Raman Inactive

- $v_3$: Asymmetric C-O Stretch
  - IR Active
  - Raman Inactive
Raman and Hyper-Raman scattering

<table>
<thead>
<tr>
<th>Topic</th>
<th>Description</th>
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<tbody>
<tr>
<td>SAM</td>
<td>Spectral Active Modes (IR, RAMAN and HYPER-RAMAN Selection Rules).</td>
</tr>
<tr>
<td>RAMAN AND HYPER-RAMAN TENSORS</td>
<td>Raman and Hyper-Raman tensors in any orientation</td>
</tr>
<tr>
<td>POLARIZATION SELECTION RULES</td>
<td>Polarization Selection Rules for Raman and Hyper-Raman Scattering processes</td>
</tr>
<tr>
<td>TWINS TENSORS</td>
<td>Raman or Hyper-Raman Tensors for Different Orientation Domains</td>
</tr>
<tr>
<td>CORRELATIONS POINTS</td>
<td>Relation between the symmetry modes in a high and low symmetry phases and</td>
</tr>
<tr>
<td>RAMAN CORRELATIONS SPACE</td>
<td>their activity.</td>
</tr>
<tr>
<td>MORPHIC EFFECTS</td>
<td>IR and Raman activity under a symmetry break for a given structures.</td>
</tr>
<tr>
<td></td>
<td>Correlation relations for point groups under the action of an electric or</td>
</tr>
<tr>
<td></td>
<td>magnetic field</td>
</tr>
</tbody>
</table>
Mulliken symbols

A, B: 1D representations ↔ non-degenerate (single) mode
    only one set of atom vector displacements \( (u_1, u_2, ..., u_n) \) for a given wavenumber \( \omega \)
    A: symmetric with respect to the principle rotation axis \( n \, (C_n) \)
    B: anti-symmetric with respect to the principle rotation axis \( n \, (C_n) \)

E: 2D representation ↔ doubly degenerate mode
    two sets of atom vector displacements \( (u_1, u_2, ..., u_n) \) for a given wavenumber \( \omega \)

T (F): 3D representation ↔ triply degenerate mode
    three sets of atom vector displacements \( (u_1, u_2, ..., u_n) \) for a given wavenumber \( \omega \)

subscripts \( g, u \) \( (X_g, X_u) \): symmetric or anti-symmetric to inversion \( \bar{1} \)
superscripts \( ', '' \) \( (X', X'') \): symmetric or anti-symmetric to a mirror plane \( m \)
subscripts \( 1, 2 \) \( (X_1, X_2) \): symmetric or anti-symmetric to add. \( m \) or \( C_n \)
IR and Raman spectroscopy: selection rules

Example: $\text{Al}_2\text{O}_3$ (aka corundum, ruby, sapphire)

Space group: R-3c
Atomic (Wyckoff) coordinates:
- O: 18e
- Al: 12c

Crystal structure of $\alpha$-$\text{Al}_2\text{O}_3$ (●, Al; ○, O).

http://www.cryst.ehu.es
IR and Raman spectroscopy: selection rules

http://www.cryst.ehu.es

Example: Al$_2$O$_3$ (aka corundum, ruby, sapphire)

- Space group: R-3c
- Atomic (Wyckoff) coordinates:
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  - Al: 12c

### IR Active Modes

$$\Gamma_{\text{acoustic}} = A_{2u} + E_u$$

<table>
<thead>
<tr>
<th>WP</th>
<th>$A_{1g}$</th>
<th>$A_{1u}$</th>
<th>$A_{2g}$</th>
<th>$A_{2u}$</th>
<th>$E_u$</th>
<th>$E_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12c</td>
<td>·</td>
<td>·</td>
<td>·</td>
<td>1</td>
<td>2</td>
<td>·</td>
</tr>
<tr>
<td>18e</td>
<td>·</td>
<td>·</td>
<td>·</td>
<td>2</td>
<td>3</td>
<td>·</td>
</tr>
</tbody>
</table>

### Raman Active Modes

<table>
<thead>
<tr>
<th>WP</th>
<th>$A_{1g}$</th>
<th>$A_{1u}$</th>
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<th>$A_{2u}$</th>
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<tr>
<td>12c</td>
<td>1</td>
<td>·</td>
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<td>·</td>
<td>·</td>
<td>2</td>
</tr>
<tr>
<td>18e</td>
<td>1</td>
<td>·</td>
<td>·</td>
<td>·</td>
<td>·</td>
<td>3</td>
</tr>
</tbody>
</table>

- Raman active modes: 7
  - $2 \ A_{1g} + 5 \ E_g$

- IR active modes: 6
  - $2 \ A_{2u} + 4 \ E_u$

Crystal structure of $\alpha$-Al$_2$O$_3$ (●, Al; ○, O).
Optical spectroscopy – Techniques

- **Frequency domain spectroscopy (dispersive spectrometers)**
  
  UV-Vis-NIR spectral region: ~ 1 eV scale

- **Fourier transform infrared (FTIR) spectroscopy**
  
  IR-THz spectral region: ~ 1-1000 meV

- **Raman spectroscopy**
  
  UV-Vis-NIR (~ 1 eV) probe of low energy excitations (~meV)
Conventional (dispersive) optical spectrometer based on a broadband source and dispersive elements (prism, grating)

"I procured me a triangular glass prism to try therewith the celebrated phenomena of colors."
(Newton, 1665)
Frequency domain spectroscopy (UV-VIS-NIR)

Conventional (dispersive) optical spectrometer based on a broadband source and dispersive elements (prism, grating)

"I procured me a triangular glass prism to try therewith the celebrated phenomena of colors."

(Newton, 1665)
$s(\omega)$ - complex transmission/reflection coefficient

Frequency domain spectroscopy (UV-VIS-NIR)

\[ I_{sample}(\omega) \propto |s(\omega)|^2 |E(\omega)|^2 \]

\[ |s(\omega)|^2 = \frac{I_{sample}(\omega)}{I_{ref}(\omega)} \]
Czerny-Turner spectrometer for Vis spectroscopy, Raman scattering and PL

Main factors affecting the spectral resolution:
- slit
- diffraction grating
- focal length
- detector (CCD: pixel size, number of pixels)
- laser linewidth (for Raman spectroscopy)
Birth of IR spectroscopy

William Herschel, February 11th 1800

XIII. Investigation of the Powers of the prismatic Colours to heat and illuminate Objects; with Remarks, that prove the different Refrangibility of radiant Heat. To which is added, an Inquiry into the Method of viewing the Sun advantageously, with Telescopes of large Apertures and high magnifying Powers.

By William Herschel, LL.D. F.R.S.

F.W. Herschel, Phil. Trans. Royal Soc. London 90, 49 (1800).
Infrared spectroscopy

What is special about IR spectroscopy?

- Broadband IR spectroscopy – Not a one source/detector system!
- Brightness of sources
- Sensitivity of Detectors
- Optical components – All materials have absorption in IR
- Vacuum needed for even RT measurements
- Delivery losses
- Working close to diffraction limit in FIR
Fourier transform infrared (FTIR) spectroscopy

Light source

Fixed mirror

Beamsplitter

Sample position

Movable mirror

Detector

$B(\nu)$

$\nu_0$

Spectrum

Interferogram

$\delta/2$

$0$, $\lambda/4$, $\lambda/2$, $3\lambda/4$
Fourier transform infrared (FTIR) spectroscopy

1. Interferogram

\[ I(\tau) = \int d\omega |s(\omega)|^2 |E(\omega)|^2 (1 + \cos \omega \tau) \]

2. Fourier transform

\[ I(\omega) \propto |s(\omega)|^2 |E(\omega)|^2 \]

3. Referencing

\[ T(\nu) = \frac{S_{\text{air}}(\nu)}{S_{\text{vac}}(\nu)} \]
Fourier transform infrared (FTIR) spectroscopy

1. Interferogram

\[ I(\tau) = \int d\omega |s(\omega)|^2 |E(\omega)|^2 (1 + \cos \omega \tau) \]

\[ T(\nu) = \frac{S_{air}(\nu)}{S_{vac}(\nu)} \]
What is special about IR spectroscopy?

- From a pure optics point of view: **nothing is special!**
  
  Same physics, same formulas, same approaches ...
  
  (geometrical optics, electrodynamics, diffraction, interference, QM,...)

- In real life: **everything is special!**

  1. **IR sources** (MUCH lower intensity compared to Vis)
  2. **IR detectors** (MUCH lower sensitivity compared to VIS)
  3. **IR optics** (almost all materials have strong absorption bands in the IR)
  4. **Air IR absorption** (the whole system has to be in vacuum of ~1mbar)
  5. **IR light delivery losses**
Raman spectroscopy

Timeline

1923 – Inelastic light scattering is predicted by A. Smekel
1928 – Landsberg and Mandelstam see unexpected frequency shifts in scattering from quartz
1928 – C.V. Raman and K.S. Krishnan see “feeble fluorescence” from neat solvents
1930 – C.V. Raman wins Nobel Prize in Physics

"A new type of Secondary Radiation", *Nature*, 1928

C₆H₆ scattering
Hg arc lamp

1960 – Invention of laser made Raman experiments more effective and meaningful
1964 – Townes, Basov, Prochorov win Nobel Prize in Physics for the invention of the maser and the laser

Here again, Ted Maiman was the first to have a first working laser!
What is special about Raman spectroscopy?

1 in $10^7 - 10^{14}$ photons is scattered inelastically. Very low signal!

Devereaux and Hackl, RMP. 79, 175 (2007)
What is special about Raman spectroscopy?

• **Deliver the high-quality** (narrow, stable) excitation laser beam to the sample
  - Low power loss through the system
  - Clean up excitation beam (narrow-band clean-up filter)

• **Efficiently collect the scattered light** \((I_{\text{Raman}} < 10^{-7} I_{\text{exc}})\)
  - Efficient collection optics (high numerical aperture)
  - High level of rejection of the scattered laser (filters)

• **Efficiently disperse the scattered light**
  - Long focal, high dispersion spectrometers
CW Magneto-Optical Spectroscopy at MagLab
CW optical magneto-spectroscopy @ MagLab

FTIR Magneto-Spectroscopy

SPECTROMETERS:
- Bruker Vertex 80v
- Bruker IFS 66v/s
- Bruker IFS 113

MAGNETS:
18 T SCMs
31 T-35 T Resistive Magnets
**CW optical magneto-spectroscopy @ MagLab**

**FTIR Magneto-Spectroscopy**

**Interaction-induced Shift of the CR in Monolayer Graphene**

![Graphene Image](image)

Henriksen et al., PRL 104 (6), 067404 (2010)
Spatially resolved PL and Raman spectroscopy

CW optical magneto-spectroscopy @ MagLab

Sample plate

Piezo-stages
x-y travel: ~2.5mm
z travel: ~3mm

Excitation fiber

Collection fiber

Working distance: ~1.5mm
### Spatially resolved PL and Raman spectroscopy

<table>
<thead>
<tr>
<th>Magnet</th>
<th>Temperatures</th>
<th>Techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>45T</td>
<td>1.5K-300K</td>
<td>PL, Raman,</td>
</tr>
<tr>
<td>35T</td>
<td>1.5K-300K</td>
<td>PL, Raman,</td>
</tr>
<tr>
<td>31T (cell#9)</td>
<td>300mK-70K, 1.5K-300K</td>
<td>PL, Raman, spatially resolved</td>
</tr>
<tr>
<td>18T (SCM2)</td>
<td>300mK-70K, 1.5K-300K</td>
<td>PL, Raman, spatially resolved</td>
</tr>
<tr>
<td>17.5T (SCM3)</td>
<td>4K-100K</td>
<td>PL, Raman, spatially resolved</td>
</tr>
<tr>
<td>14.5T (EMR)</td>
<td>4.5K-300K</td>
<td>PL, Raman, spatially resolved</td>
</tr>
</tbody>
</table>
Spatial resolved micro-PL: Examples

Excitons in monolayer semiconducting TMDs

Extraordinary valley Zeeman shift of charged excitons in monolayer WSe$_2$

Magnetic Brightening of dark excitons in monolayer WSe$_2$

Ground state of neutral and charged excitons in monolayer MoSe$_2$ and WSe$_2$
Spectroscopy of excitons in monolayer semiconducting TMDs (MoSe₂, WSe₂)
Semiconducting monolayer TMDs

Photoluminescence (PL)

Neutral exciton

Charged exciton (trion)

TMDs: Strongly bond excitons!

\[ E_{PL} = E^c - E^v \]

\[ E_{PL} = E^c - E^v - E_{X0}^b - E_{X-}^b \]

\( E_{X0} \): ~ 500 meV

\( E_{X-} \): ~ 30 meV
Neutral and charged excitons in WSe2

PL process

Neutral exciton configurations

Bright $X^0$

Dark $X^0$

Charged exciton configurations (bright $X^-$ only)
Charged excitons: MoSe$_2$ vs. WSe$_2$

**MoSe$_2$: intervalley**

![Diagram of MoSe$_2$ intervalley excitons](image1)

**WSe$_2$: intravalley**

![Diagram of WSe$_2$ intravalley excitons](image2)
Magnet-Raman spectroscopy: Examples

Charge-lattice-spin coupling in $\text{Co[N(CN)}_2\text{]}_2$

LAB PRACTICALS - Optical spectroscopy of Al₂O₃

Al₂O₃: Fe, Ti
Natural blue sapphire (this is not your sample)

Al₂O₃: Cr
Natural ruby (this is not your sample)

Al₂O₃
Synthetic sapphire ...
This is your sample!
Probing phonons by Raman and IR spectroscopy

Phonon modes (1st order, Γ-point):

\[ \Gamma = A_{2u} + E_u + 2A_{1g} + 5E_g + 2A_{2u} + 4E_u + 3A_{2g} + 2A_{1u} \]

- acoust.
- Raman
- IR
- silent

Two \( \text{Al}_2\text{O}_3 \) groups per unit cell

Crystal structure of \( \alpha\)-\( \text{Al}_2\text{O}_3 \) (\( \bullet \), Al; \( \bigcirc \), O).
Raman scattering

Raman active modes: 7

\[ 2A_{1g} + 5E_g = A_{1g} + A_{1g} + 5E_g \]

\( \perp c \) \( \parallel c \) \( \perp c \)
IR spectroscopy

IR active modes: 6
2 $A_{2u}$ + 4 $E_u$

$\parallel c$ $\perp c$

Restrahlen band
LAB PRACTICALS - Optical spectroscopy of Al₂O₃

Photoluminescence

Ruby PL (and laser !!!)

E₄ \[\rightarrow\] Cr⁺ E₂

E₃ \[\rightarrow\] E₂

blue

R₂

R₁ (694nm)

E₁

green

LASER EMISSION

R₁ (693nm)

intensity (counts/sec)

wavenumber (cm⁻¹)

4300 4350 4400 4450 4500

250x10³

200

150

100

50

0

Cr⁺

532nm excitation
Excitation spectroscopy: PL vs. Raman

532nm excitation
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