

# Introduction to Raman Spectroscopy

Day 1: The Basics

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This is the tersest description I can think of...

- Hardware & methods a lot like photoluminescence measurement
- Raman Spectroscopy looks at light inelastically scattered off materials
  - Inelastic because of loss (gain) to molecular and lattice vibrations
- Frequency and intensity of peaks → which bonds are present (and more!)
  Most common use is materials ID (fingerprint)

Let's look closer at these statements...



#### Raman Spectroscopy Looks at Scattered Light





Here's a cartoon of a minimalist setup for measuring Raman spectra. A laser illuminates a sample, and a little bit of the incoming light is scattered off the sample at longer wavelength (lower energy)



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#### Raman Spectroscopy Looks at Scattered Light



- Raman Spectroscopy looks at scattering, not absorption (e.g. infrared absorption spectroscopy)
- Works at any wavelength, typically visible or NIR
- It can piggyback on optical tools like:



Microscopes





# **Discovery of the Raman Effect**

OXFORD ANDOR

- Discovered by the eponymous C.V. Raman in 1928
- The story is surprising and interesting <u>see a brief</u> <u>history here</u>
- Experimentally demonstrated with telescopeconcentrated sunlight aimed at various liquids (how could that possibly work – let's revisit later?)
- Why did it take until 1928 if fluorescence was discovered in 1852 (if not earlier)?
  - Raman scattering is \*weak\*
  - How to distinguish from weak fluorescence?





#### Raman Spectroscopy vs. Photoluminescence





- <u>This is also how you could measure photoluminescence...</u>
- What makes Raman different?
  - PL is STRONG, Raman is WEAK (10<sup>6</sup>-10<sup>8</sup> difference?)
    - PL always "wins" when present\*
  - Raman is relative to laser line, PL at set energy
  - Raman scattering is "faster" than PL lifetime
  - Raman scattering carries much more info!



#### Raman Spectroscopy vs. Photoluminescence









Kneipp, Janina, et al. "Optical prol based on surface-enhanced indocyanine green on gold chemistry 77.8 (2005): 2381-238



Jonak, Constanze, et al. "Intradermal indocyanine green for in vivo fluorescence laser scanning microscopy of human skin: a pilot study." PLoS One 6.8 (2011): e23972.

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### A Note About Units

- Raman involves the loss (and sometimes gain) of small amounts of energy
- Typical unit is cm<sup>-1</sup> (aka wavenumber, inverse centimeter, rarely: Kayser)

•  $E = \frac{hc}{\lambda}$ 



Here's one of Raman's original spectra of benzene

Excitation (aka Rayleigh) wavelength is 435.83 nm

We convert to wave numbers (cm<sup>-1</sup>): 10<sup>7</sup>/(435.83 nm) = 22944 cm<sup>-1</sup>

Unknown band is at ~ 457.4 nm 10<sup>7</sup>/(457.4 nm) = 21862 cm<sup>-1</sup>

Difference is  $V_0$ -V1 = 22944 – 218





Excitation – 435.8nm from mercury lamp



### More on Units







# A More Concrete Example



- We hit a drop of cyclohexane with **monochromatic** 514 nm light from a laser
- Collect scattered light with a lens
- Remove residual laser light with strong edge/long-pass filter
- Focus collected light into \*high resolution\* spectrometer
- Record emission/scattering spectrum with \*high-sensitivity\* camera
- And we'd get something like this...



#### Raman Spectroscopy vs. Photoluminescence



- Raman and PL "coexist", but Raman normally *hidden* by much, much brighter PL
- At left top (green) spectrum is PL spectrum of fluorescent polymer
- As PL-quenching dopant is added, PL intensity drops proportionally, and Raman can slowly be resolved (spectra are normalized)



#### Kerr Gating to Uncover PL-Swamped Raman



- If you can measure quickly (picosecond), you can grab the Raman signal before PL arrives!
- Not usually practical (yet?) but extremely cool



# A Closer Look at a Raman Spectrum



- Raman peaks correspond to molecular (or lattice) vibrations that symmetrically changes the polarizability
- Benzene has two strong Ramanactive vibrations
- Light interacts with these molecular vibrations, losing a little bit of energy and shifting to a slightly-longer wavelength
- If we can measure disperse and measure the light fro with a spectrometer, the type and quantity active molecular bor



**ANDOR** 

Animations from https://www.chemtube



- How do map Raman peaks  $\rightarrow$  vibrations  $\rightarrow$  molecules?
- For unknown substances, usually paying someone to do linear algebra



 Tables can provide a good starting point though... (e.g., <u>https://www.chem.uci.edu/~dmitryf/manuals/Raman%20correlations.pdf</u>)

| RAMAN Band Correlation Table |                     |           |
|------------------------------|---------------------|-----------|
| Approximate                  | Group               | Intensity |
| Wavenumber Range (cm-1)      |                     |           |
| 100–210                      | Lattice vibrations  | Strong    |
| 150-430                      | Xmetal-O            | Strong    |
| 250-400                      | C-C aliphatic chain | Strong    |
| 295–340                      | Se-Se               | Strong    |
| 425–550                      | S-S                 | Strong    |
| 460–550                      | Si-O-Si             | Strong    |
| 490–660                      | C-I                 | Strong    |
| 505-700                      | C-Br                | Strong    |



# (More) Limitations of Raman



- Vibrational frequencies mostly shared between molecules
- Must disentangle mixtures with overlapping peaks
- Not a fool-proof ID
- "Unique" bonds in e.g. explosives often targeted



Raman spectroscopy is not this



# Raman vs. Infrared Absorption Spectroscopy OXFORD ANDOR

- Raman and IR Absorption (i.e. FTIR) are both vibrational spectroscopies
- That is, IR and Raman bands come from light interacting with vibrating parts of molecules
- IR and Raman are complementary "Raman active" vibrations are weak in IR and vice versa



# A Hand-Wavy Mechanism for Raman





Imagine we have a cartoon "jellyium" molecule



It's polarizable – it shifts a little bit in response to an electric field, creating a little temporary dipole



# A Hand-Wavy Mechanism for Raman

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ectric

Dipole



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- Now imagine this molecule vibrates at some frequency  $\omega$
- Charges move symmetrically no change in dipole just from vibrating (no IR activity)

What if the polarizability changed a tiny bit as the molecule vibrated?

Φ



ectio

#### A Hand-Wavy Mechanism for Raman

Rayleigh

• The induced dipole  $\mu$  is equal to the polarizability a times the electric field E...

And the polarizability  $\alpha$  is changing as the molecule vibrates at frequency  $\omega$ 

1)  $\mu = \alpha E$ 

2)  $\alpha = \alpha_0 + \alpha_1 \cos(\omega_v t)$ 

• And the electric field of our laser light oscillates at  $\omega_{ extsf{L}}$ 

3) E =  $E_o cos(\omega_L t)$ 

• Then the induced dipole will mix both frequencies

4)  $\mu = \alpha E = (\alpha_0 + \alpha_1 \cos(\omega_v t))^* E_0 \cos(\omega_t t)$ 

• Multiply this out, and the relevant part is

5)  $\alpha_1 E_0 \cos(\omega_v t) \cos(\omega_t t)$ 

Idea taken from "Spectra of Atoms and Molecules" by Peter F Bernath – definitely a good book worth checking out

**Anti-Stokes** 

Which through a trig identity gives us three components

6)  $\mu = \alpha_o E_o \cos(\omega_L t) + \alpha_1 E_o \cos((\omega_L - \omega_v)t)/2 + \alpha_1 E_o \cos((\omega_L + \omega_v)t)/2)$ 

**Stokes** 

#### A Hand-Wavy Mechanism for Selection Rules





- Now imagine we had a stretch that was asymmetric...
- Now the two "extremes" of the stretch are the same (but flipped)
- One could (charitably?) imagine a weak or non-existent Raman effect here
- The lopsided movement of charge back and forth *could* make absorb or emit lowfrequency light ... (IR activity)



# A Note about Resolution



Raman spectroscopy demands a reasonably high resolution spectrometer (and grating)



## **Next Time**



- Raman measurements in practice
  - Experimental Concerns & Details
- Applications
  - What do people \*do\* with Raman?





# Thank for your attention!