Fluorescence and Hole Burning

Mike Reppert

October 12, 2020

Previously on CHM676...

Fluorescence

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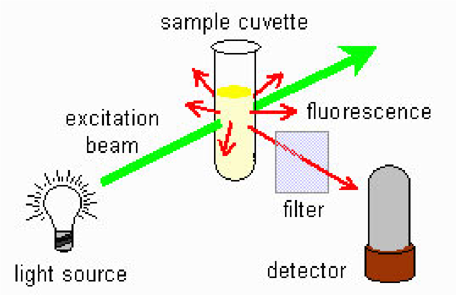

https://www.chromedia.org/dchro/gfx/ZgbwordJmB.jpeg

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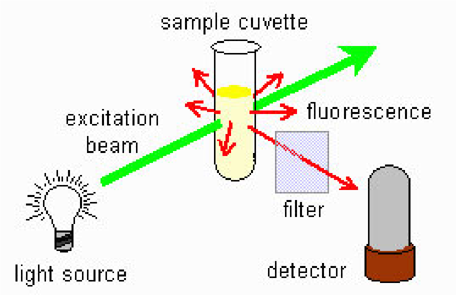

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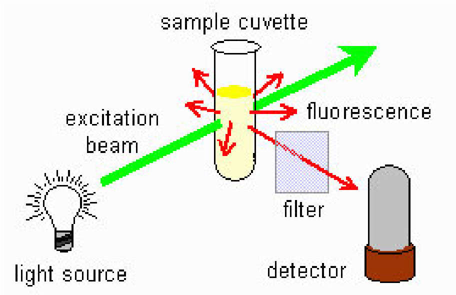

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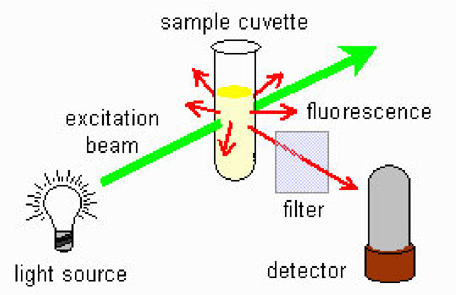

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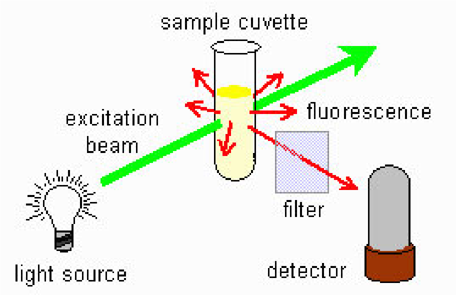

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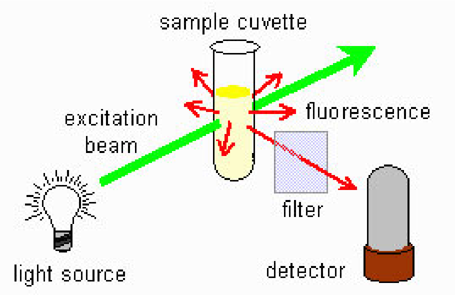

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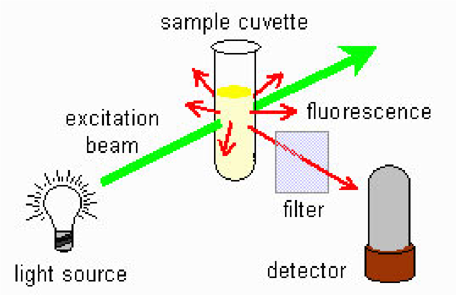

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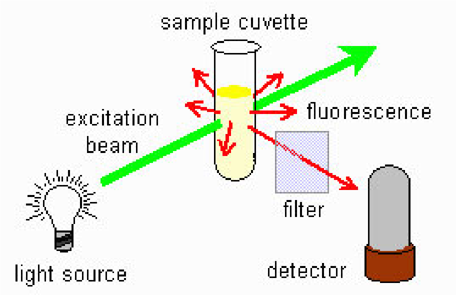

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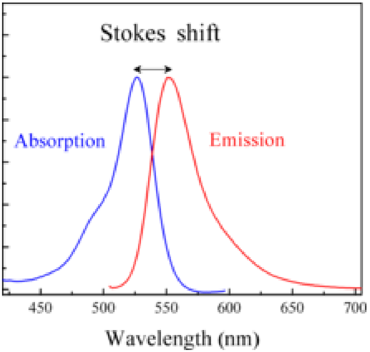
Stokes Shift

Experimentally: Absorption and emission peaks are separated by a **Stokes Shift**.



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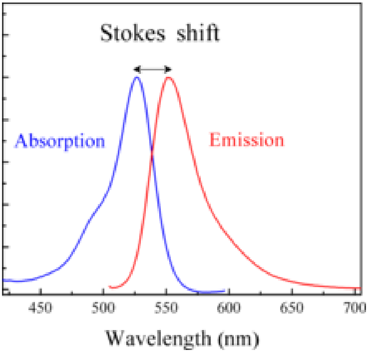

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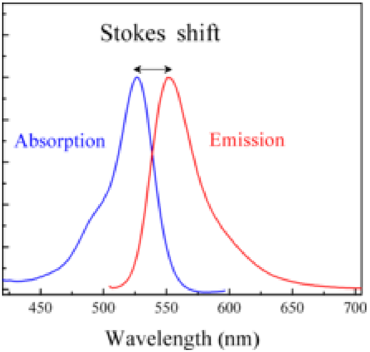

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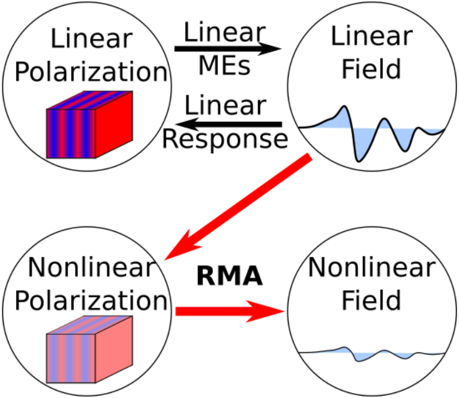
QUANTUM MECHANICS!

Response Theory

Q: So how does fluorescence fit into our response theory framework?



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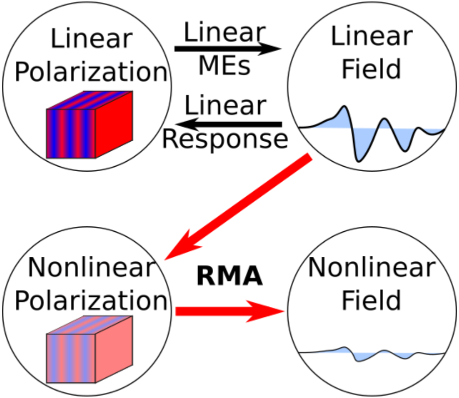


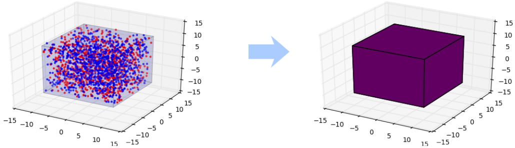
A: It doesn't!

Response Theory: Average Physics

Recall: Response theory works with *macroscopic* fields:

$$\boldsymbol{E}(\boldsymbol{x},t) \equiv \langle \boldsymbol{e}(\boldsymbol{x},t)\rangle_M$$

Microstate Macrostate



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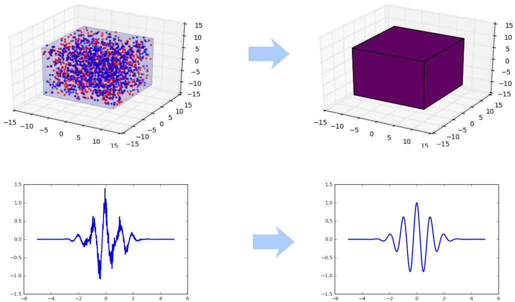

Incoherent Fields

In **incoherent** processes, the average *field* is zero – but the average *intensity* is not!

Fluorescence gives a typical example:

- A *single* dipole emits a *coherent* field with a well-defined phase
- An *ensemble* of dipoles with uncorrelated phases emit an *incoherent field* with a stochastic phase.

Fluorescence: Light after Dephasing

Consider an ensemble of dipoles with the same frequency ω and polarization ϵ but *random phases*:

$$\langle \boldsymbol{E}(t) \rangle = \frac{1}{2\pi} \epsilon \int_0^{2\pi} \sin(\omega t + \phi) = 0.$$

$$\begin{aligned} \langle I(t) \rangle &= \frac{\varepsilon^2}{2\pi} \int_0^{2\pi} \sin^2(\omega t + \phi) \\ &= -\frac{\varepsilon^2}{8\pi} \int_0^{2\pi} \left(e^{2i(\omega t + \phi)} - 2 + e^{-2i(\omega t + \phi)} \right) = -\frac{\varepsilon^2}{2}. \end{aligned}$$

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Take-Home Points

Fluorescence corresponds to radiation of light from a completely *dephased* sample – the phase of each microscopic emitter is random!

This process falls **outside** the scope of *our development* of response theory since the average field is zero. (Though it can be related!)

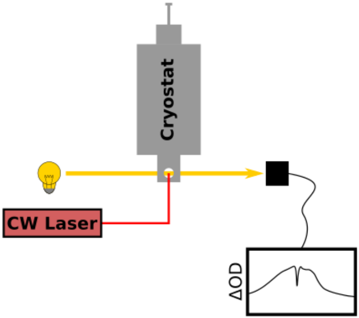
Even though the mean *field* vanishes, the mean *intensity* – and hence the radiant energy – is nonzero.

The **Stokes shift** between absorption and emission spectra results from the quantum population weighting of vibrational energy states.

Hole Burning Spectroscopy

Hole Burning Experiment

1. Sample temperature $\rightarrow \sim 5$ K.
2. Measure absorption spectrum
3. Fry it with a narrow-band laser
4. Measure the spectrum again
5. Signal = Pre-burn absorption - post-burn absorption



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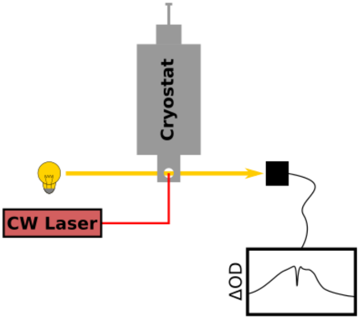
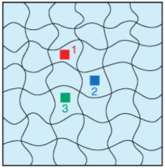


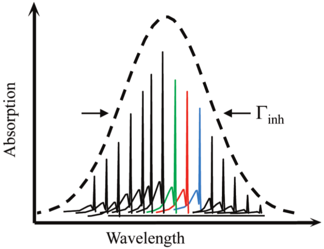
https://www.janis.com/Products/productsoverview/SuperTranContinuousFlowCryostatSystems/ST-100_OpticalCryostat.aspx

Low-Temperature Absorption Spectra

Large low-temperature absorption spectra are determined by two factors:

- **Inhomogeneous broadening:** The distribution of *electronic transition frequencies* (site energies) associated with *different sites* in the material





Chem. Rev. 2011, 111, 4546-4598

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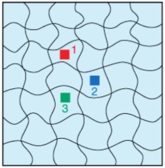

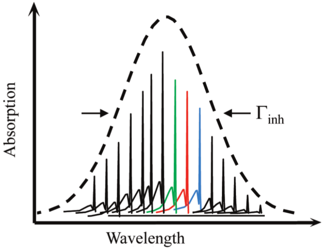

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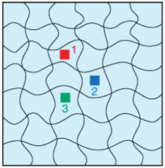
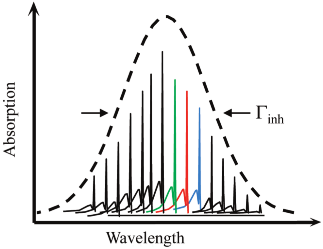
The bulk absorption spectrum is a **convolution** of the *single-site spectrum* and the *probability density*





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Convolutions

A **convolution** is a mathematical operation that combines two functions:

$$f * g(x) = \int dx' f(x')g(x - x')$$

Key Concept: $f * g$ looks like a *weighted average* of *shifted* copies of $g(x)$, where

- The integral dx' runs over all possible *shifts*
- The function $f(x')$ sets the *weight* at each shift.

The Convolution Theorem

A side note: **Fourier Transforms** are still magical:

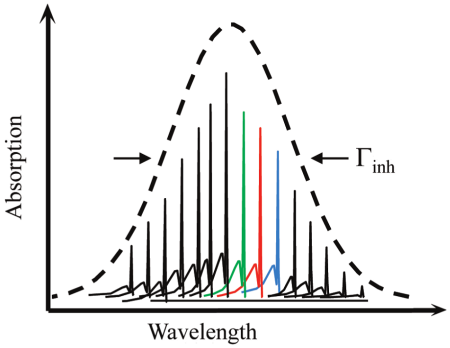
$$f * g(x) = \mathsf{IFT}\left\{\tilde{f} \cdot \tilde{g}\right\}.$$

Convolutions become products in the Fourier domain!

Examples: `https://github.com/mreppert/CHM676/blob/master/FourierTransforms.ipynb`

Back to Hole Burning

Narrow-band excitation creates a “hole” in the site-energy density function



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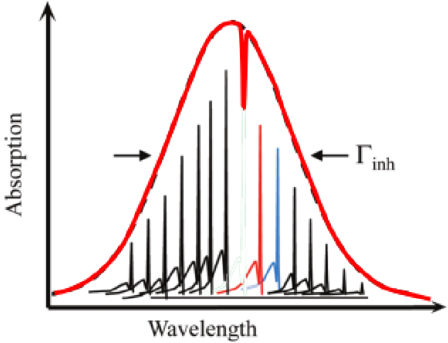

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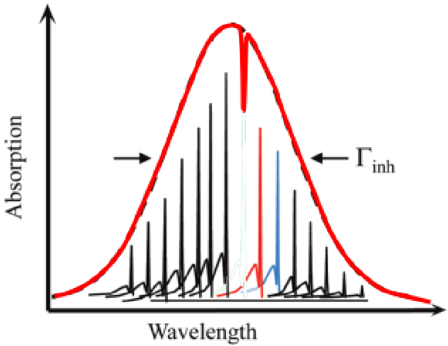

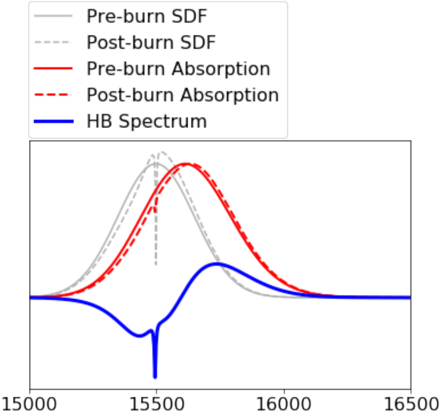

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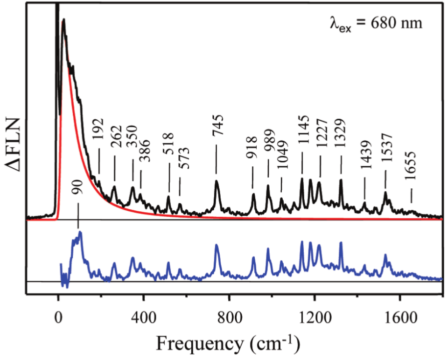
Hole Burning + Fluorescence ⇒ Δ FLN



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Fourier transforms convert convolutions to products:

$$\widetilde{f * g} = \tilde{f} \cdot \tilde{g}$$

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Hole burning can

- Separate homogeneous and inhomogeneous broadening effects
- Provide single-site spectra and site-energy distributions
- Give details on electronic/vibrational interactions
- Uncover excitonic interactions