## What is non-linear optical spectroscopy?

molecular motion (dynamics) in „real" time

relevant timescales

$\boxed{\text{10ths of fs}}$ $10^{-15}$ s = fs

experimental tool – set of tools

~ a lot of theory

classical light (coherent pulsed light from laser)

requires quantum theory for description of matter (molecules, electronic states molecular vibrations)

molecules come in ensembles

– not individualy
– not in gas phase

open quantum systems

## Why non-linear spectoscopy?

– not for study of non-linearities

– using non-linearities to study time-evolution

⇙

Time-resolved spectroscopy ≃ non-linear spectr.

Paradigmatic example: **pump-probe spectroscopy**

## Observing quantum systems?

### Macroscopic observation

1878 Eedweard Muybridge

sychronizing observation with the motion

### Microscopic observation

- first we have to start the dynamics

  → photo-induced dynamics

  ↑ pump

- then observe ← probe

We do start and observation by light

≡ non-linearity

Laser light ↗

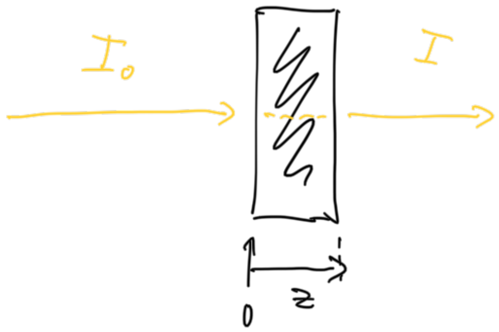
$$\vec{E}(t)$$

Response of molecules to $\vec{E}(t), \vec{E}^2(t), \vec{E}^3(t), \dots$

# Perturbation theory

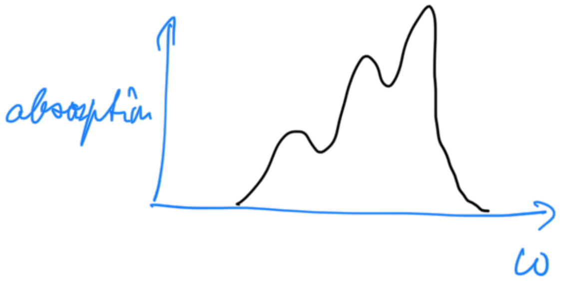
- not as approximation to effects
- observed effects ARE of certain order of perturbation in $\vec{E}(t)$

## Example: Linear absorption



Lambert-Beer law

$$I = I_0 e^{-\alpha(\omega) z}$$



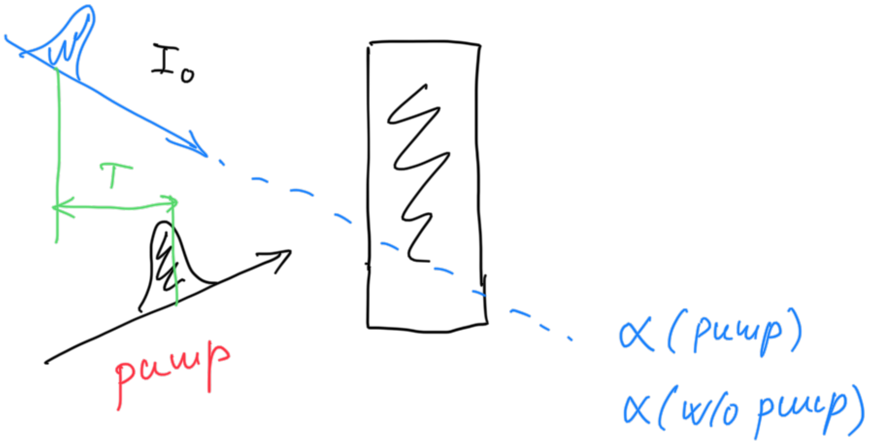
$$\frac{I}{I_0} = e^{-\alpha z}$$

↖ does not depend on intensity

$$\alpha z = \ln \frac{I_0}{I}$$

$$\boxed{\frac{\Delta I}{I_0} = \frac{I_0 - I}{I_0} = 1 - \frac{I}{I_0} = 1 - e^{-\alpha z} \approx 1 - 1 + \alpha z = \alpha z}$$

# Example: Pump-probe

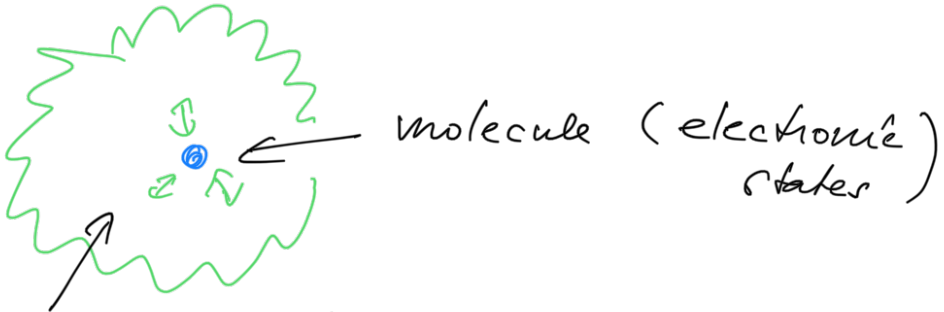


Difference between two absorption

$$\frac{\Delta I_{pu}}{I_0} - \frac{\Delta I_{w/o}}{I_0} = \beta(I_{pu})$$

# Molecules as Open Quantum Systems

Quantum systems embedded in environment



environment – solvent
- proteint
- intramolecular vibrations

||

bath @ definite temperature

The whole system – Schrödinger equation

$$\hat{H} = \hat{H}_B + \boxed{\hat{H}_s} + \underline{\underline{\hat{H}_{s-B}}}$$

$$\frac{\partial}{\partial t} |\Psi(t)\rangle = -\frac{i}{\hbar} \hat{H} |\Psi(t)\rangle$$

# Reduced description ?

Liouville - von Neuman equation

$$\boxed{\hat{W}(t) = |\Psi(t)\rangle\langle\Psi(t)|} \Longrightarrow \boxed{\hat{\rho}(t) = \mathrm{tr}_B\{\hat{W}(t)\}}$$

Reduced statistical operator

$$\boxed{\langle\hat{A}\rangle = \mathrm{tr}\{\hat{A}\hat{\rho}(t)\}}$$

$$\boxed{\frac{\partial}{\partial t}\hat{\rho}(t) = \quad ?}$$

Does spectroscopy depend only on $\hat{\rho}(t)$ ?

- in general NO!
- as a good approximation often YES!