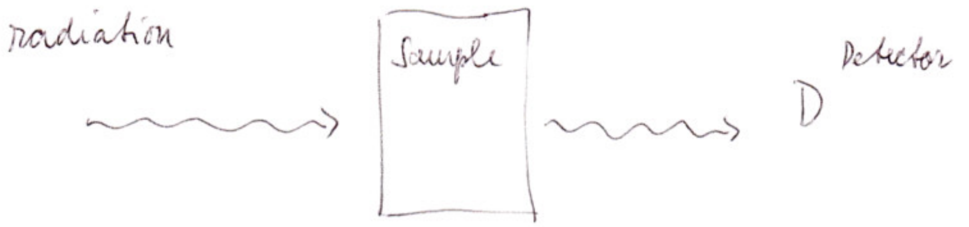
Introduction

Spectroscopy



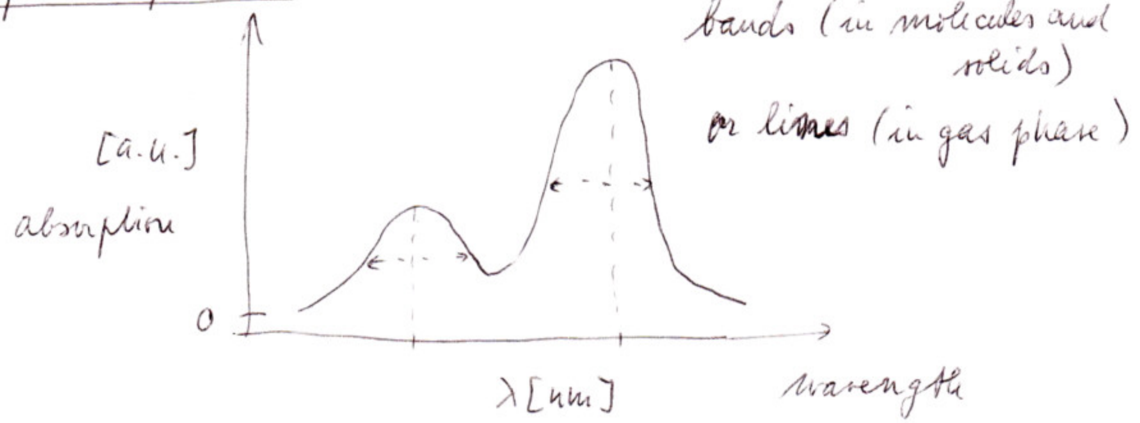
- Response of the sample is frequency (wavelenght) dependent
- Spectroscopic analysis can be performed in the whole range of wavelenght, but we speak about spectroscopy somewhere between terahertz (10^{12} Hz) i.e. for IR to UV
- Special attention will be given to visible region, but the theory is mostly the same for all regions.

Spectrum

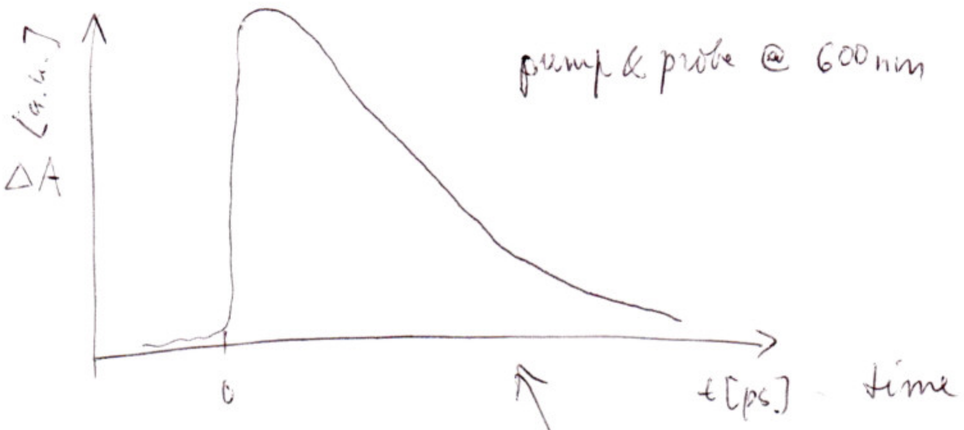
wavelength (frequency) and/or time dependent curve

examples:

(linear) absorption spectrum



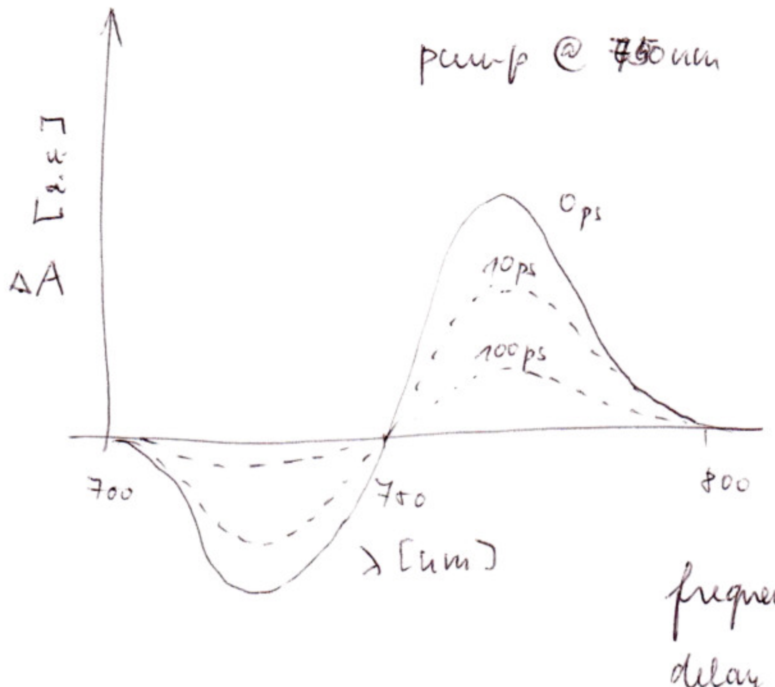
Pump - probe



↙ information about the spectral region

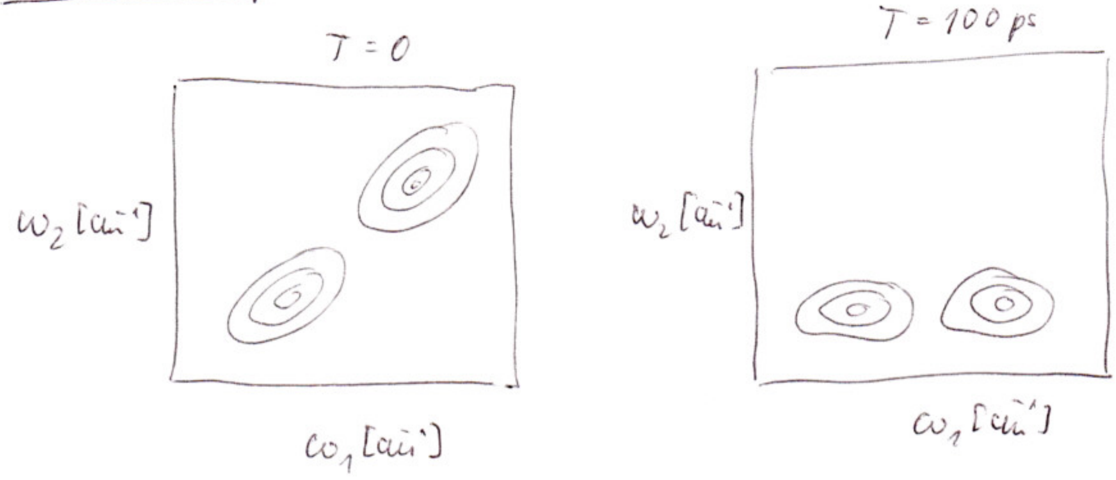
evolution of the absorption change with delay between pump and probe pulses

Frequency resolved pump - probe



frequency resolved spectrum at different delay times pumped at 750 nm
and measured between 700 and 800 nm

Correlation spectra



To read and interpret spectra, one needs to carefully check the units

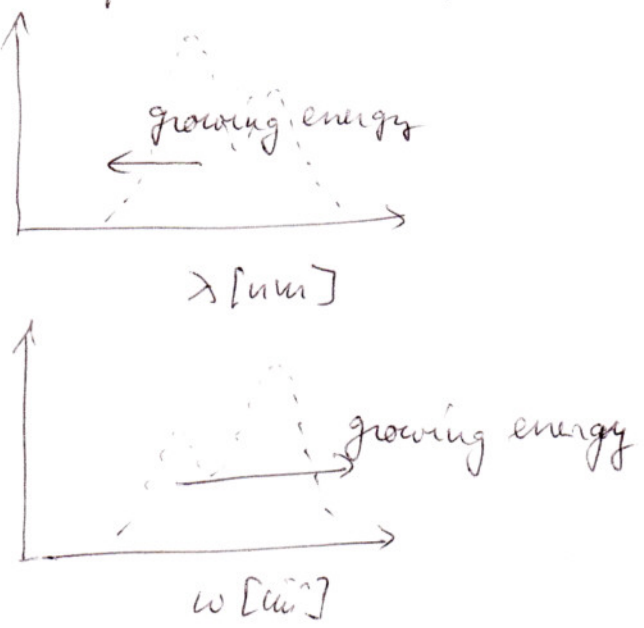
λ ... wavelength [nm]

ω, ν ... frequency [cm^{-1}] [Hz]

E ... energy [eV, cm^{-1}]

t, T, τ ... time [fs, ps, as], today even as

One has to be careful because e.g.

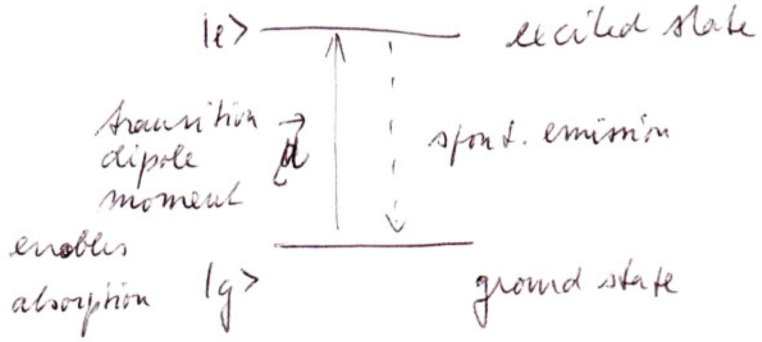


Models for molecular systems

! no ab initio here → we look for models that are capable of capturing essential qualities of the studied system, but are simple to treat

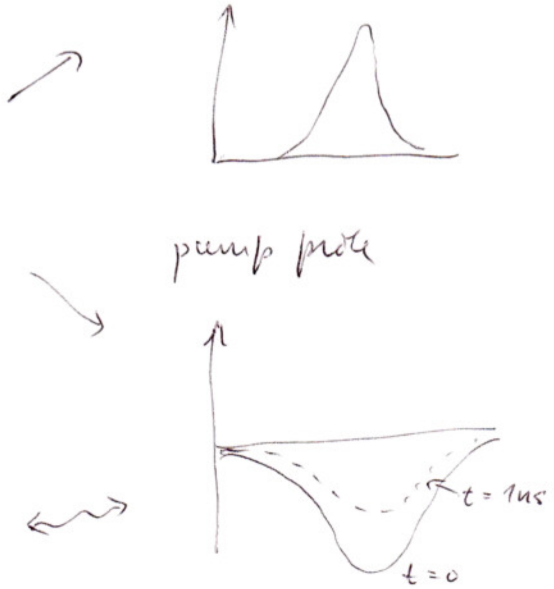
Essence of the molecule are its electronic states

Two state model:



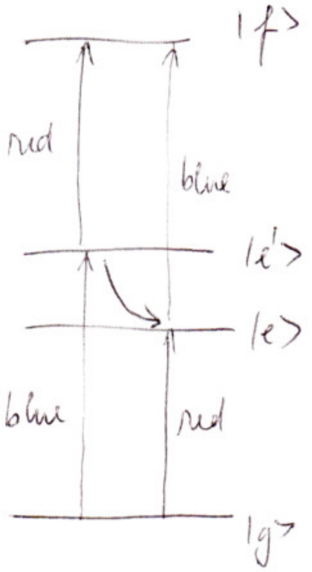
absorption

pump probe

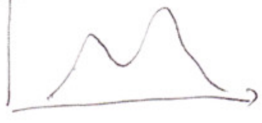


We have less absorption from |g⟩ and we have additional emission – life time can be measured

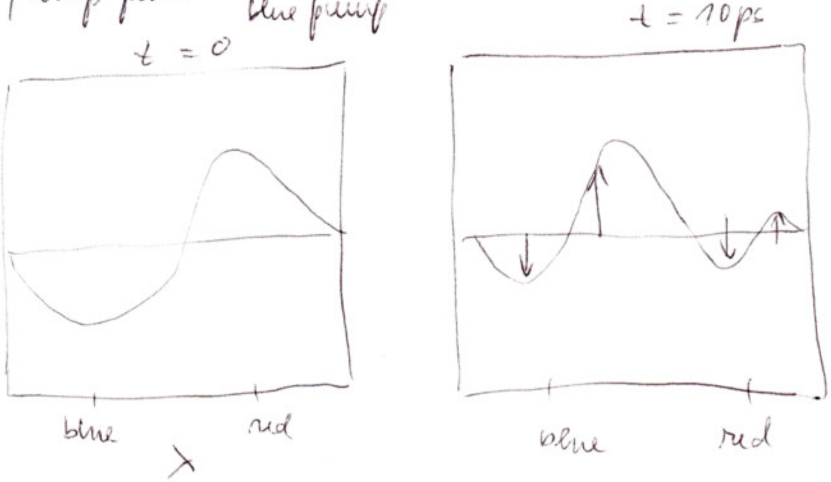
More states:



Absorption



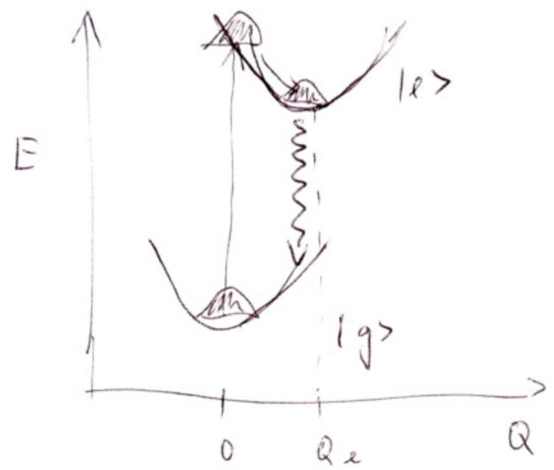
pump probe



Spectra of such simple models would lack any width and relaxation would not be present. There are further degrees of freedom that interact with electronic transitions, cause relaxation and dephasing.

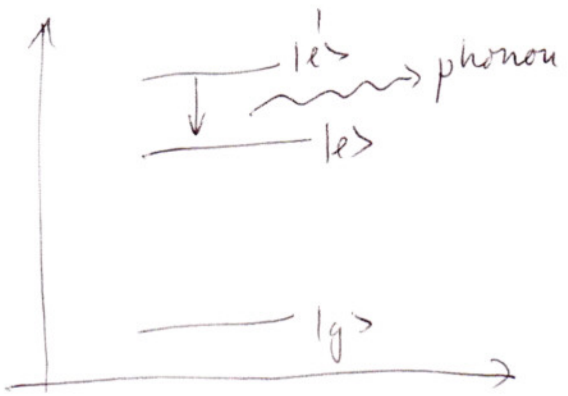
Relaxation

Let us add one degree of freedom to our model



- if Q interacts with bath it will relax to equilibrium
- Spontaneous emission occurs on different wavelength = Stokes shift

... or let us assume more closely spaced electronic states

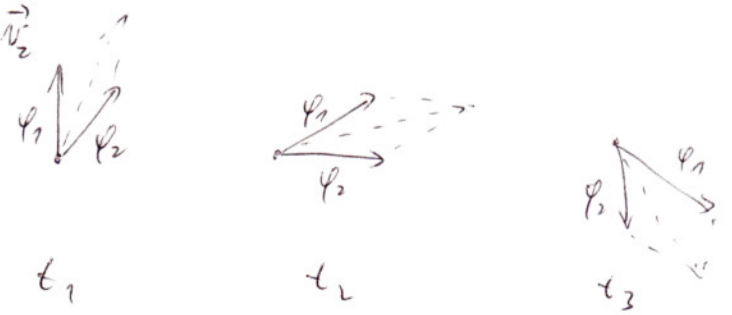


Energy of |e'> will be transferred to nuclear degrees of freedom and the system may relax to |e>

Dephasing

Dephasing is a process in which „something oscillating" is loosing phase relation with something else:

$\vec{v}_1$ a $\vec{v}_2$



$|\vec{v}_1 + \vec{v}_2|$ is constant over the time

$|\vec{v}_1 + \vec{v}_2|$ is changing over time

Two sources of dephasing
- → different frequency
- → random phase jumps

! Polarization is a $\sum_n \vec{\mu}_n$ (sum of all dipoles) and both processes lead to decay of polarization.

If the system relaxes to the ground state, polarization is also deminished = "dephasing" is also caused by relaxation, even though it is not „real dephasing".

! We distinguish <u>homogeneous</u> lineshape ↔ its line shape results from dephasing caused by fluctuations (fast) of the phase of the molecules

<u>Inhomogeneous</u> lineshape ↔ its width is caused by differences in transition energy (i.e. frequency) that are static on the timescale of the experiment.