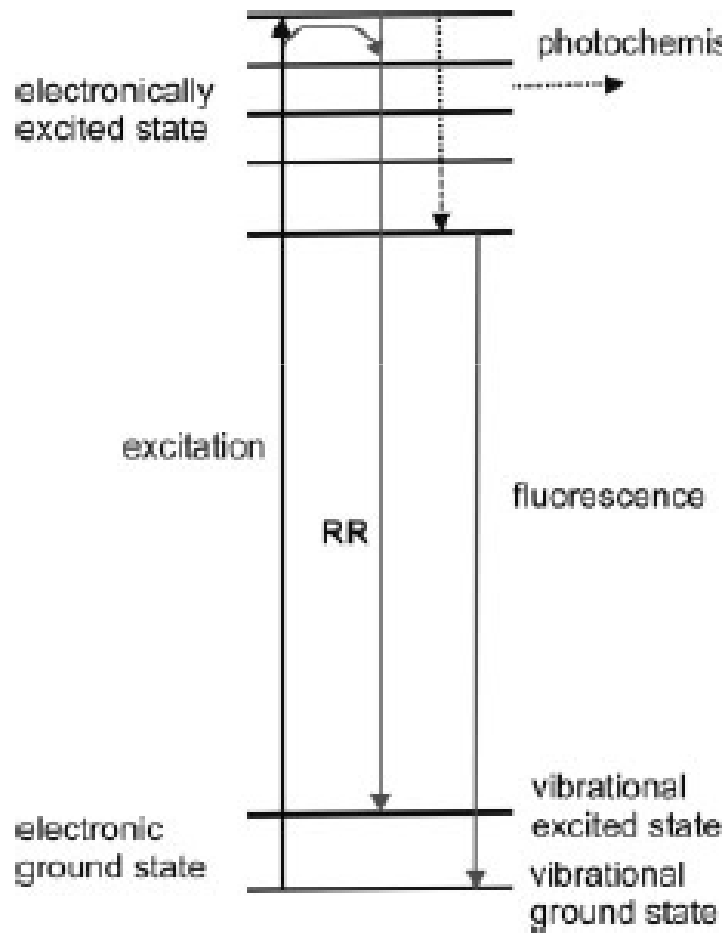
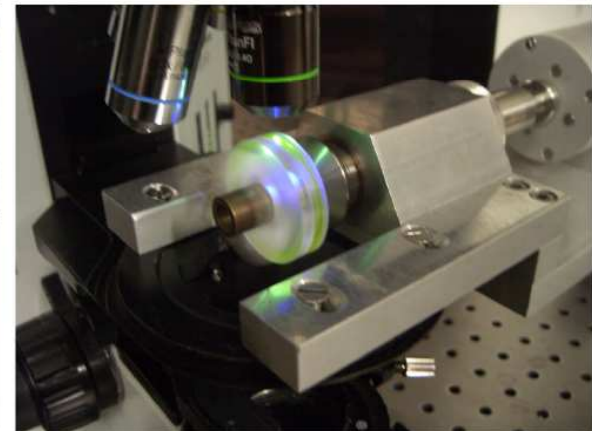
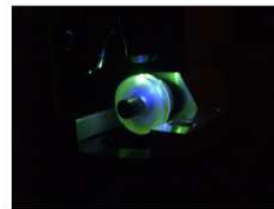


# Drawbacks of Resonance Raman Spectroscopy



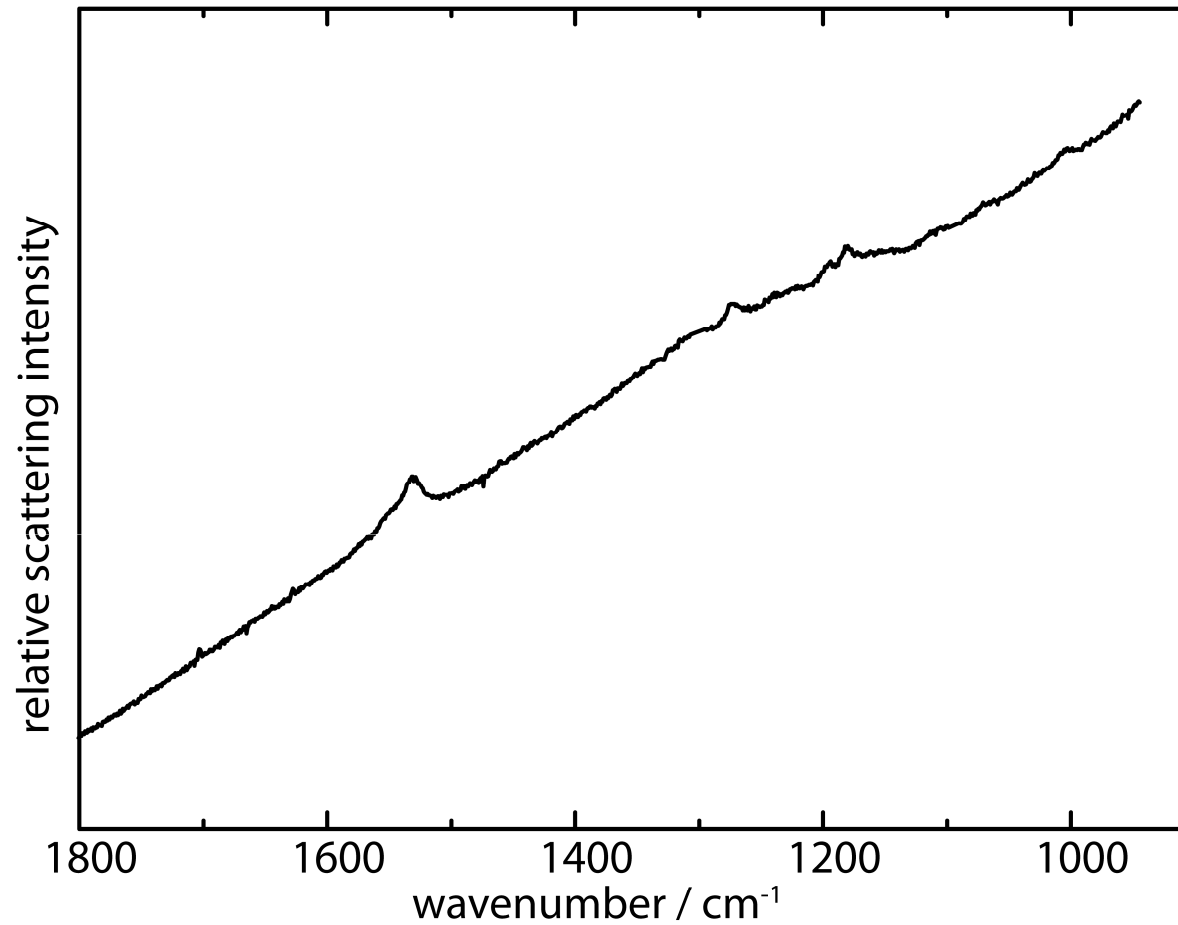
- photochemistry
- laser-induced thermal degradation

## Rotation cell



- fluorescence

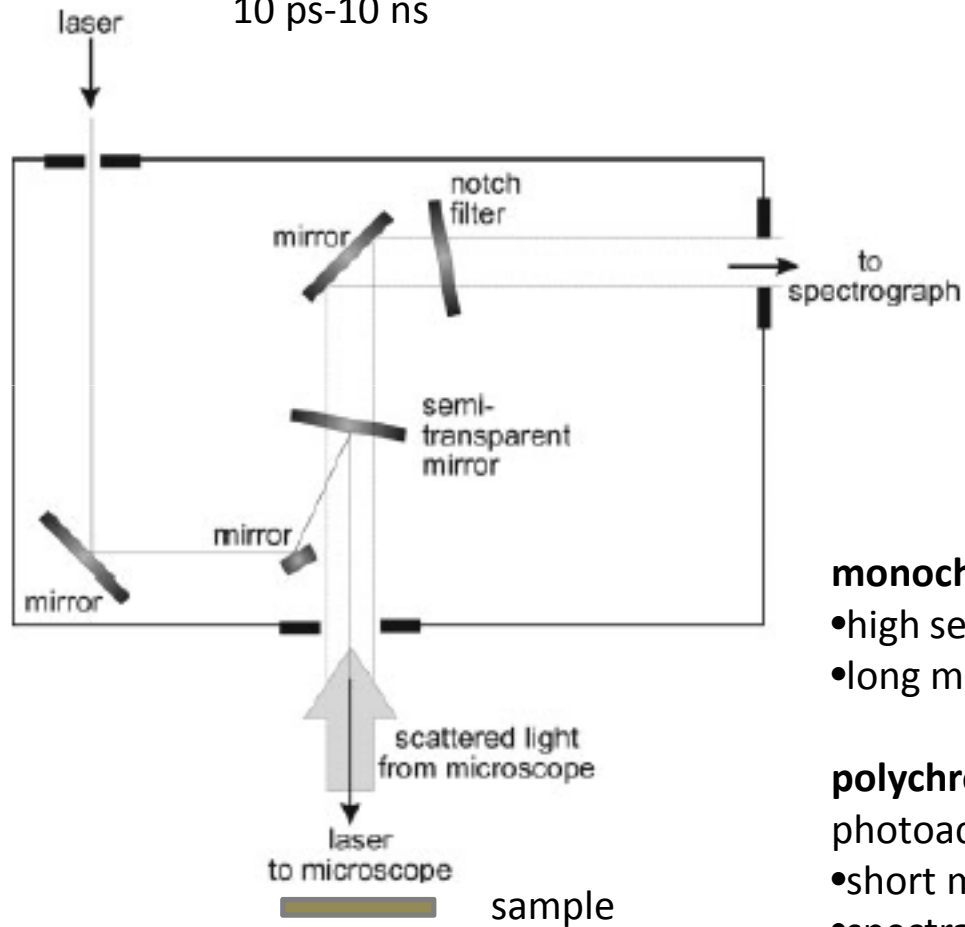
# Fluorescence and Resonance Raman Scattering



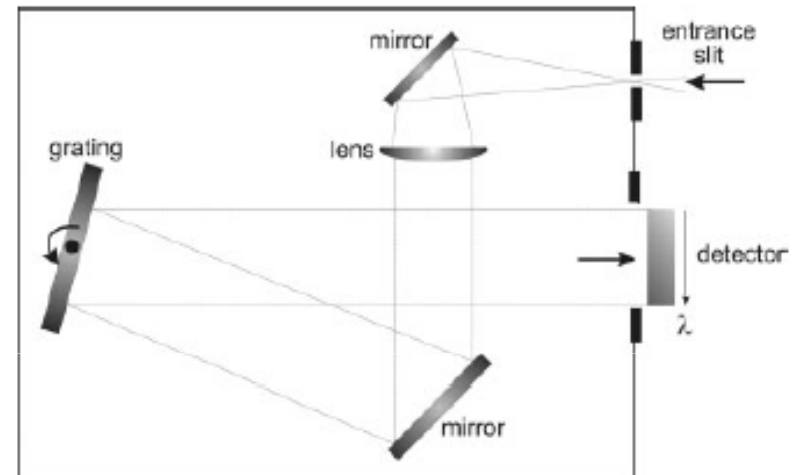
- The excitation line can be shifted to lower / higher energy sides of the fluorescing transition.
- quenching molecules : iodide

# Experimental Set-Up

cw-laser: 240 – 1064 nm  
pulsed laser: 180-1064 nm  
10 ps-10 ns



spectral resolution: entrance slit + grating



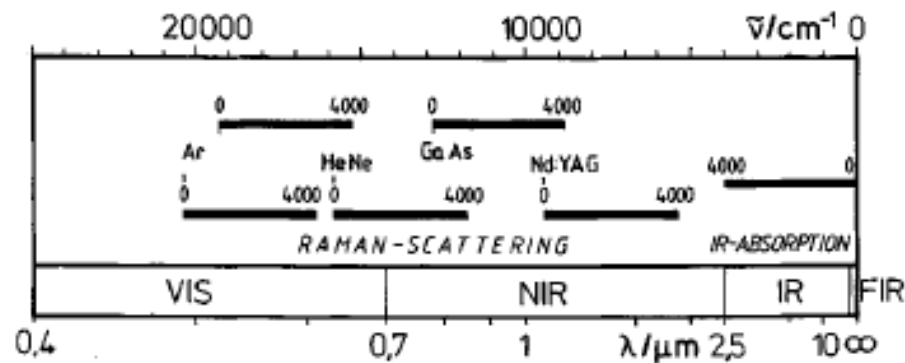
**monochromatic detection (PMT):**

- high sensitivity
- long measuring time

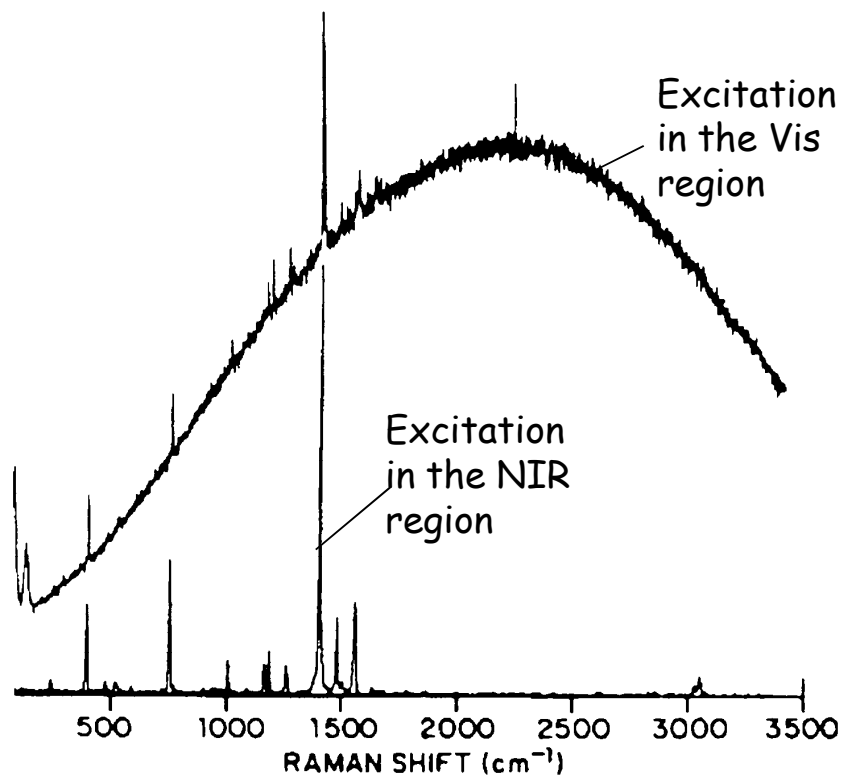
**polychromatic detection (CCD):** 25 mm length/ 1000 photoactive elements

- short measuring time
- spectral range increases with decreasing nr. of lines of the grating
- lack sensitivity at wavelengths above 1000 nm

# FT-Raman spectroscopy



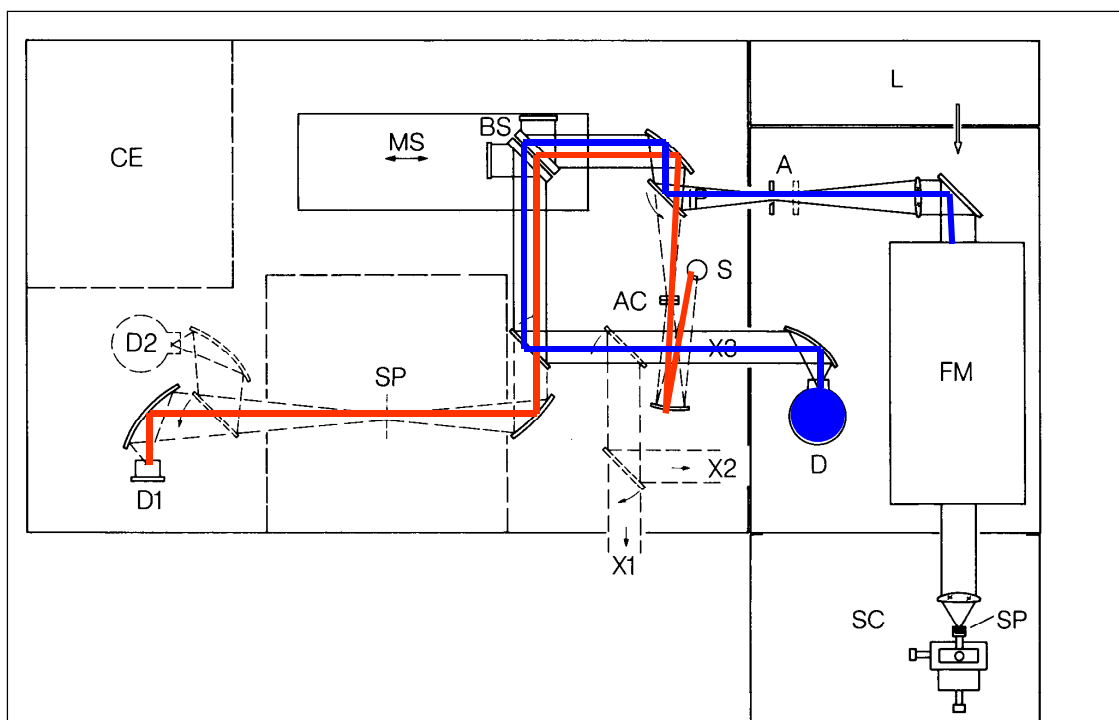
Excitation with Nd:YAG laser (1064 nm)  
⇒ no fluorescence background !



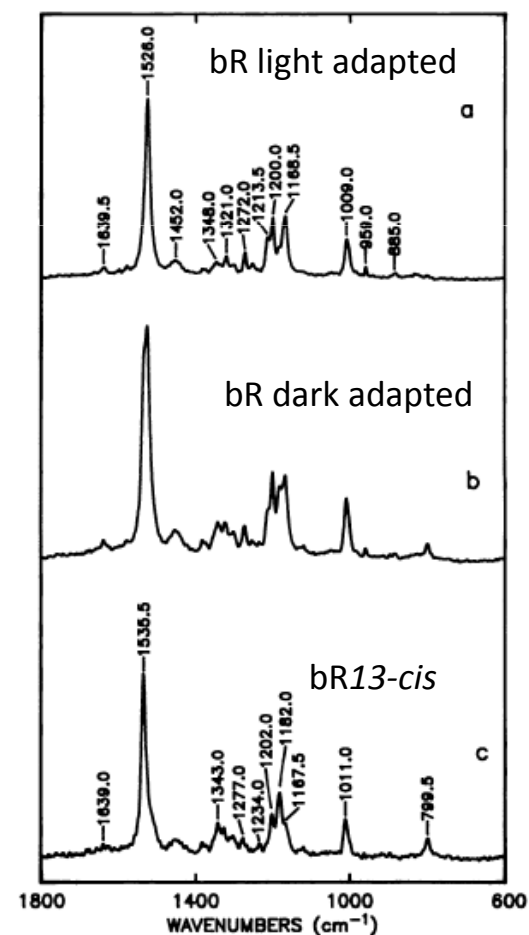
## Integration of FT-IR and FT-Raman

Jacquinot advantage compensates for weaker pre-resonance enhancement and low intensity ( $\nu^4$ ) of Raman scattering.

FT-Raman detectors: InGaAs and Ge



**Figure 3.4-1** Optical diagram of a commercial Michelson interferometer for infrared and Raman spectroscopy (Bruker IFS 66 with Raman module FRA 106). CE control electronics, D1/D2 IR detectors, BS beamsplitter, MS mirror scanner, IP input port, S IR source, AC aperture changer, X1 — X3 external beams, A aperture for Raman spectroscopy, D detector for Raman spectroscopy, FM Rayleigh filter module, SC sample compartment with illumination optics, L Nd:YAG laser, SP sample position.



# Time-resolved resonance Raman spectroscopy

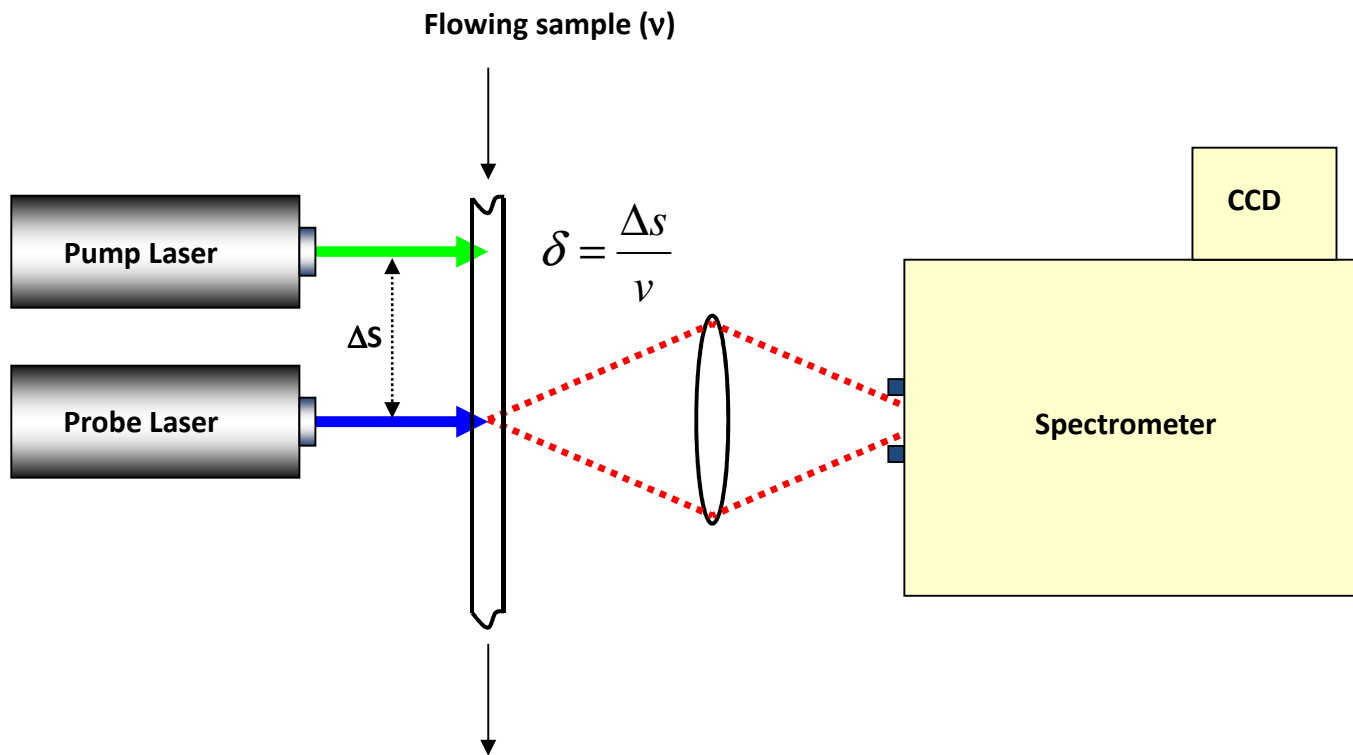
Pump-Probe RR Spectroscopy: pump laser initiates the reaction and probe beam monitors the RR spectrum of the photoactive cofactor

- cw laser excitation with time resolution of ns-ms
- pulsed laser excitation with time resolution of ps-ns

## CW Laser Excitation

energy flux of pump laser +  $\Delta t_p$  : degree of photoconversion as high as possible

$$\Delta t_p = \frac{2r_p}{\nu}$$



**Time resolution:**

$$\Delta t = \delta + \Delta t_r = \frac{\Delta s}{\nu} + \frac{2r_r}{\nu}$$

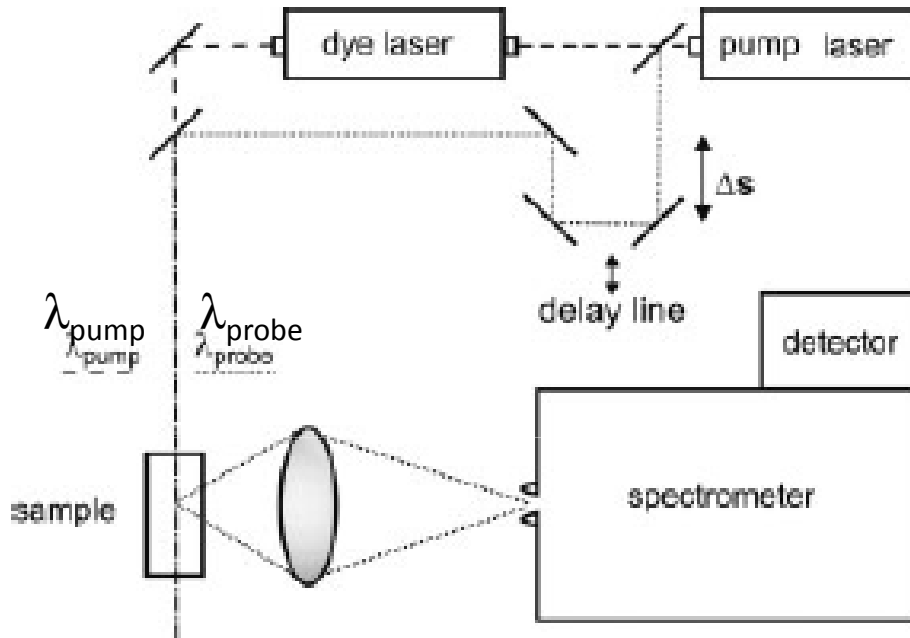
$$\Delta s_{\min} \sim 2(r_p + r_r)$$

$$\Delta t_{\min} \sim 100 \text{ ns}$$

energy flux of probe laser +  $\Delta t_r$  : degree of photoconversion as low as possible

$$\Delta t_r = \frac{2r_r}{\nu}$$

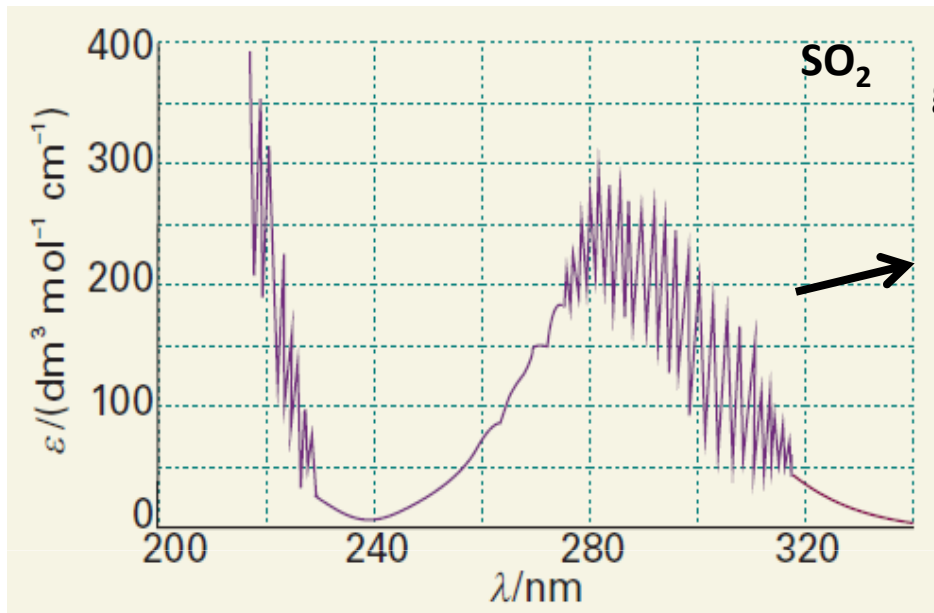
## Pulsed Laser Excitation



Time resolution: 
$$\Delta t = \frac{\Delta s}{c}$$

$\Delta s = 0.3 \text{ cm}$   $\Delta t = 10 \text{ ps}$

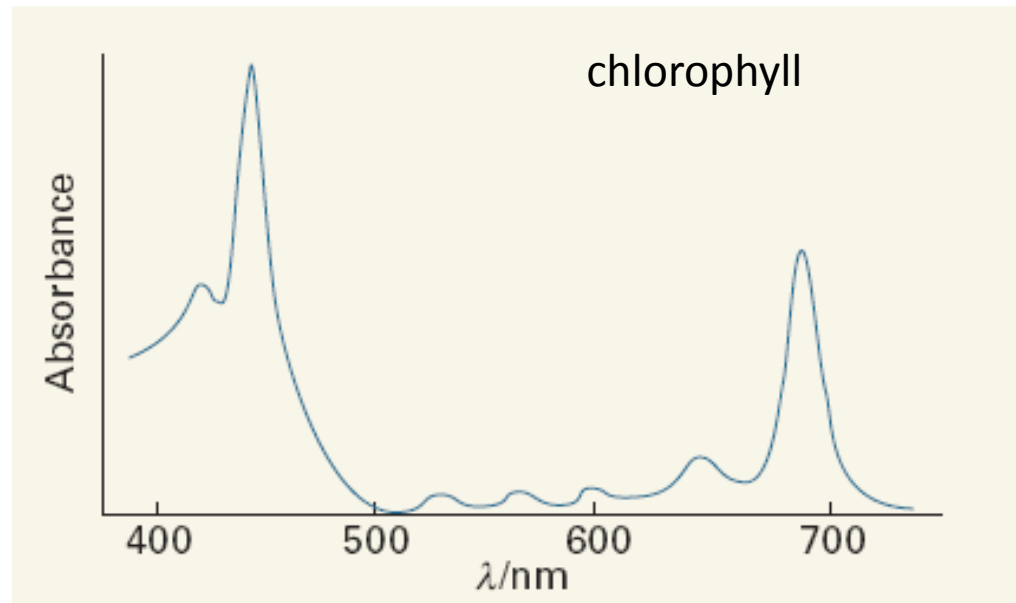
# Electronic transitions: Vibronic structure



gaseous sample

vibrational structure

liquid sample

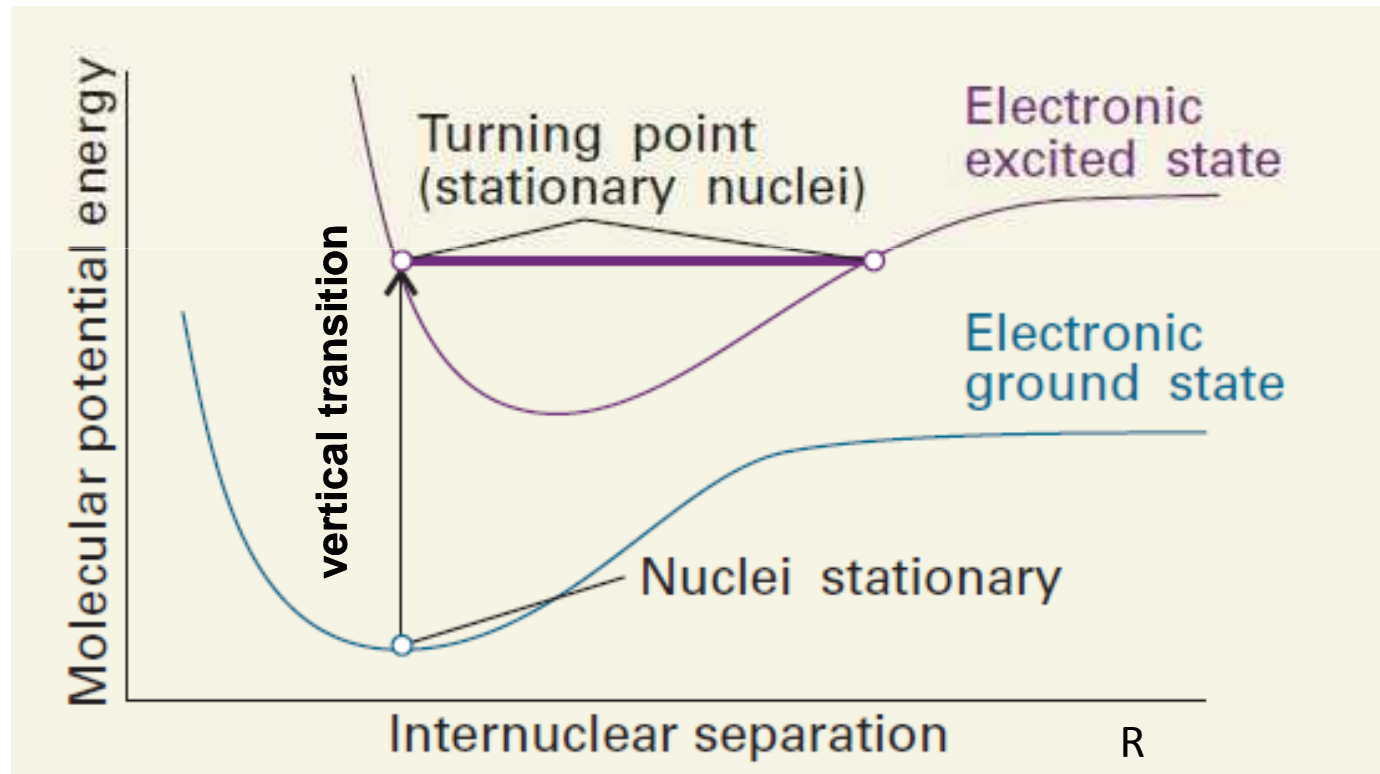


chlorophyll

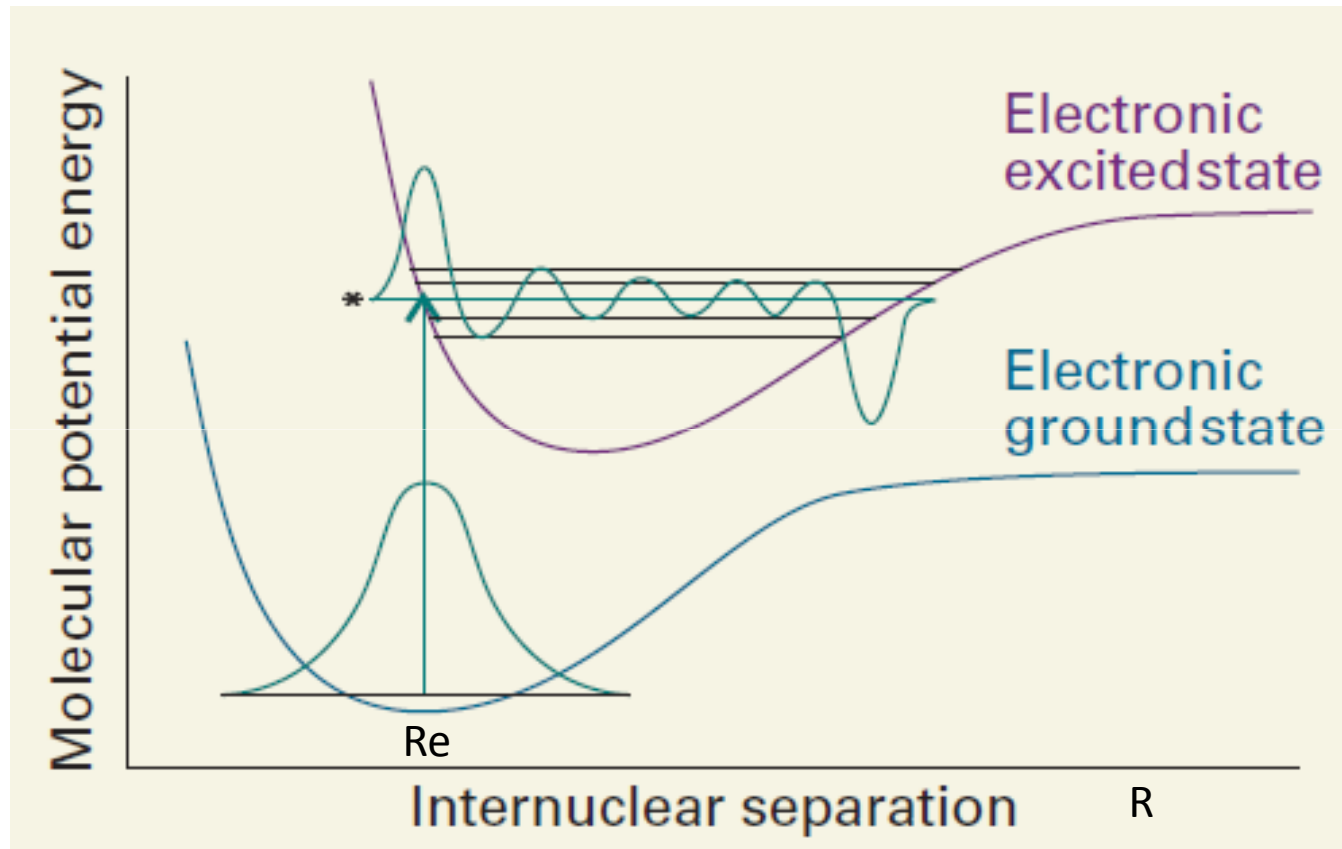


## Franck-Condon principle

Because the nuclei are more massive than the electrons, an electronic transition takes place much faster than the nuclei can respond.



## Franck-Condon principle



Electronic absorption spectra may be used to assess the force fields and dissociation energies of electronically excited molecules.

## Franck-Condon factors

$$\mu_{fi} = \langle f | \mu | i \rangle \quad f = |\varepsilon\nu\rangle \quad i = |\varepsilon'\nu'\rangle \quad (7)$$

$\downarrow$   
 $\psi_\varepsilon(r; R)\psi_\nu(R)$

Electric dipole moment of the molecule:

$$\mu = -e \sum_i r_i + e \sum_s Z_s R_s = \mu_e + \mu_N \quad (8)$$

Transition dipole moment :

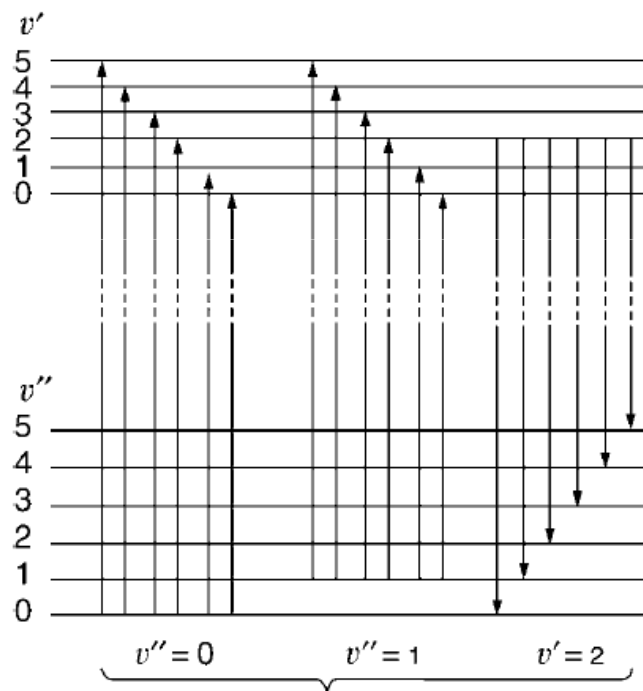
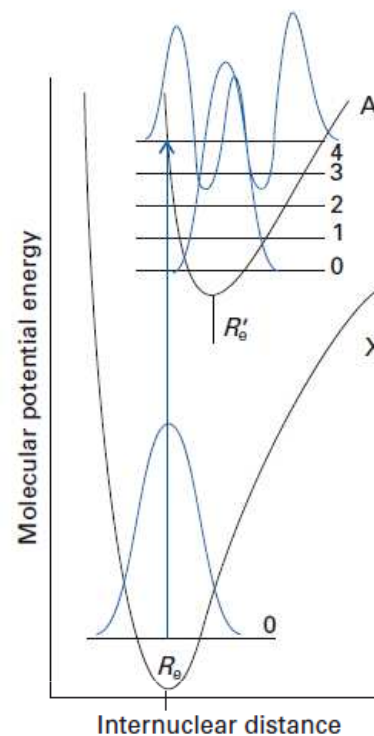
$$\begin{aligned} \langle \varepsilon'\nu' | \mu | \varepsilon\nu \rangle &= \int \psi_{\varepsilon'}^*(r; R)\psi_{\nu'}^*(R) (\mu_e + \mu_N) \psi_\varepsilon(r; R)\psi_\nu(R) d\tau_e d\tau_N \quad (9) \\ &= \int \psi_{\nu'}^*(R) \left\{ \int \psi_{\varepsilon'}^*(r; R) \overbrace{\mu_e \psi_\varepsilon(r; R)}^{\mu_{\varepsilon\varepsilon'}} d\tau_e \right\} \psi_\nu(R) d\tau_N \\ &\quad + \int \psi_{\nu'}^*(R) \mu_N \left\{ \int \psi_{\varepsilon'}^*(r; R) \underbrace{\psi_\varepsilon(r; R)}_0 d\tau_e \right\} \psi_\nu(R) d\tau_N \end{aligned}$$

The overall electric dipole:

$$\langle \epsilon' v' | \mu | \epsilon v \rangle = \mu_{\epsilon' \epsilon} \int \psi_{v'}^*(\mathbf{R}) \psi_v(\mathbf{R}) d\tau_N = \mu_{\epsilon' \epsilon} S(v', v) \quad (10)$$

Overlap integral between the two vibrational states:

$$S(v', v) = \int \psi_{v'}^*(\mathbf{R}) \psi_v(\mathbf{R}) d\tau_N \quad (11)$$



Progressions

Relative intensities of vibrational progression lines: ~

$$|S(v', v)|^2 = \left| \int \psi_{v'}^* \psi_v d\mathbf{R} \right|^2$$

Frank Condon factor