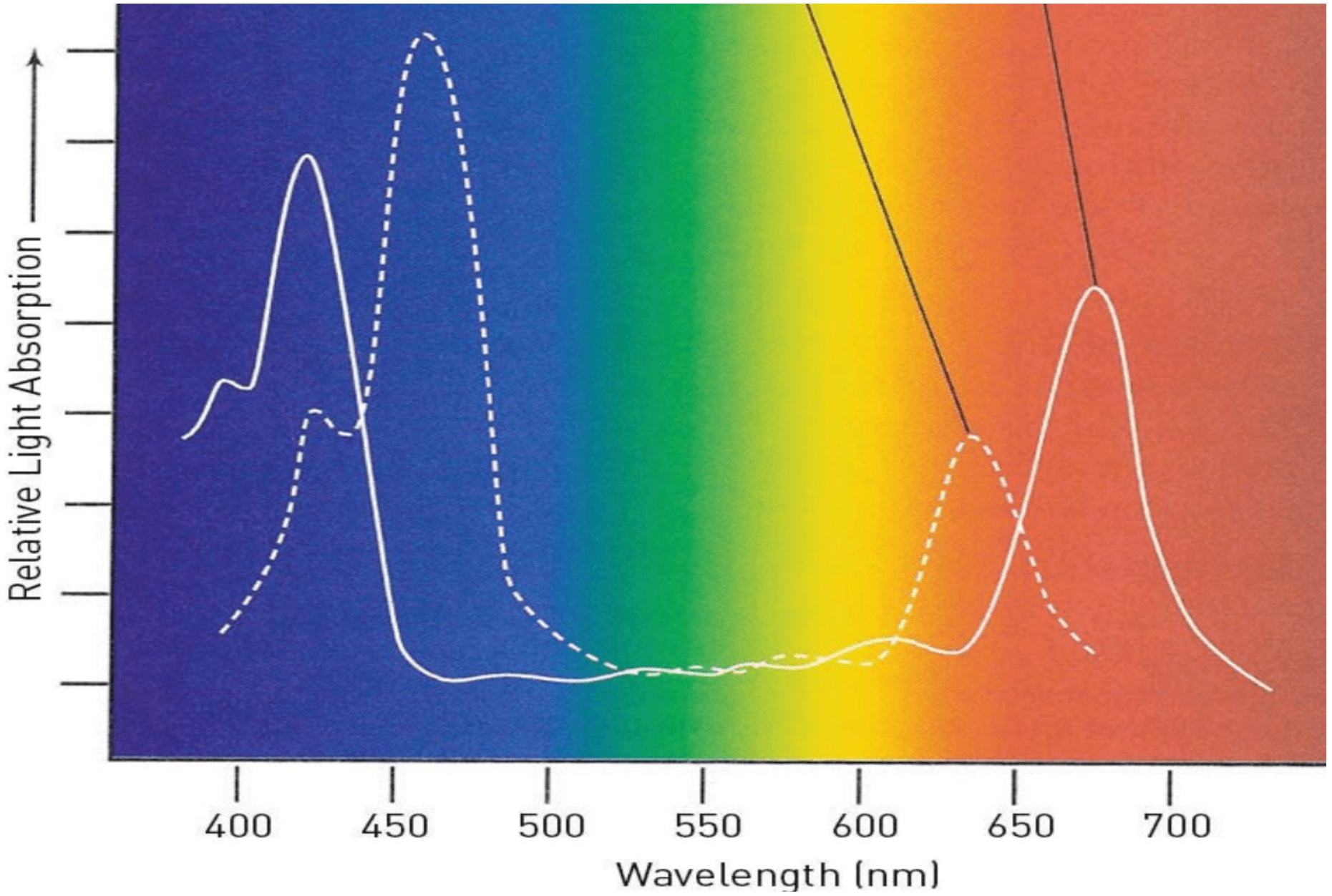
# Methods of absorption spectroscopy

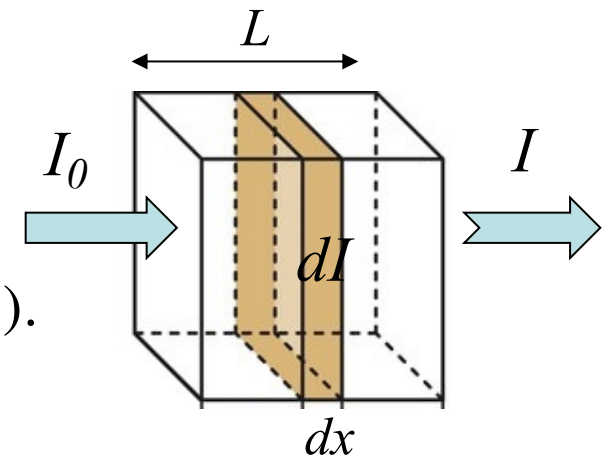


# Beer Lambert Law

$$dI(\tilde{\nu}) = -\sigma(\tilde{\nu}) \cdot I(\tilde{\nu}) \cdot n_1 \cdot dx, \quad \text{Loss of intensity}$$

$$\ln I = -\sigma(\tilde{\nu}) \cdot L + const \quad \Rightarrow$$

$$I(\tilde{\nu}) = I_0(\tilde{\nu}) \exp(-\sigma(\tilde{\nu}) \cdot n_1 \cdot L) = I_0(\tilde{\nu}) \exp(-\alpha(\tilde{\nu}) \cdot L).$$




$\tilde{\nu}$ – frequency in wavenumbers [$cm^{-1}$] (can be $\nu$, $\lambda$ as well);

$I(\tilde{\nu})$ – spectral brightness of light; [ Watt/($cm^{-1} \cdot m^2$) ];

$\alpha(\tilde{\nu})$ – differential absorption coefficient (sample): sample spectrum [$cm^{-1}$];

$\sigma(\tilde{\nu})$ – differential absorption cross-section [$cm^2$]: molecular spectrum.

For an isolated transition one must account for its lineshape:

$$\int_0^\infty \sigma(\tilde{\nu}) d\tilde{\nu} = \sigma_0 \int_0^\infty g(\tilde{\nu}) d\tilde{\nu} = \sigma_0 \quad \text{Integral absorption cross section [cm]}$$

$$\int_0^\infty \alpha(\tilde{\nu}) d\tilde{\nu} = \alpha_0 \int_0^\infty g(\tilde{\nu}) d\tilde{\nu} = \alpha_0 \quad \text{Absorption coefficient [cm}^{-2}\text{]}$$

What do we measure in experiment?

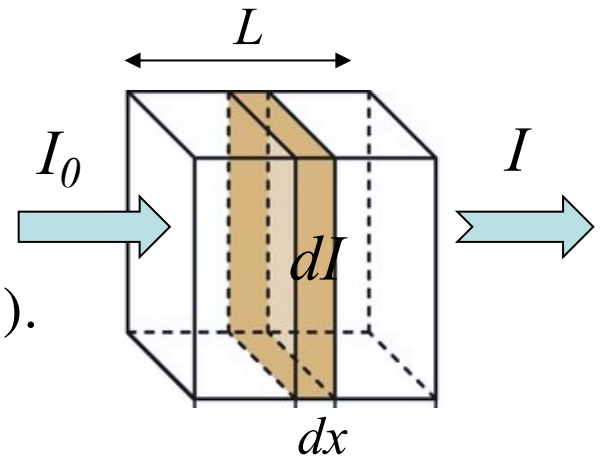
# Beer Lambert Law

$$dI(\tilde{\nu}) = -\sigma(\tilde{\nu}) \cdot I(\tilde{\nu}) \cdot n_1 \cdot dx, \quad \text{Loss of intensity}$$

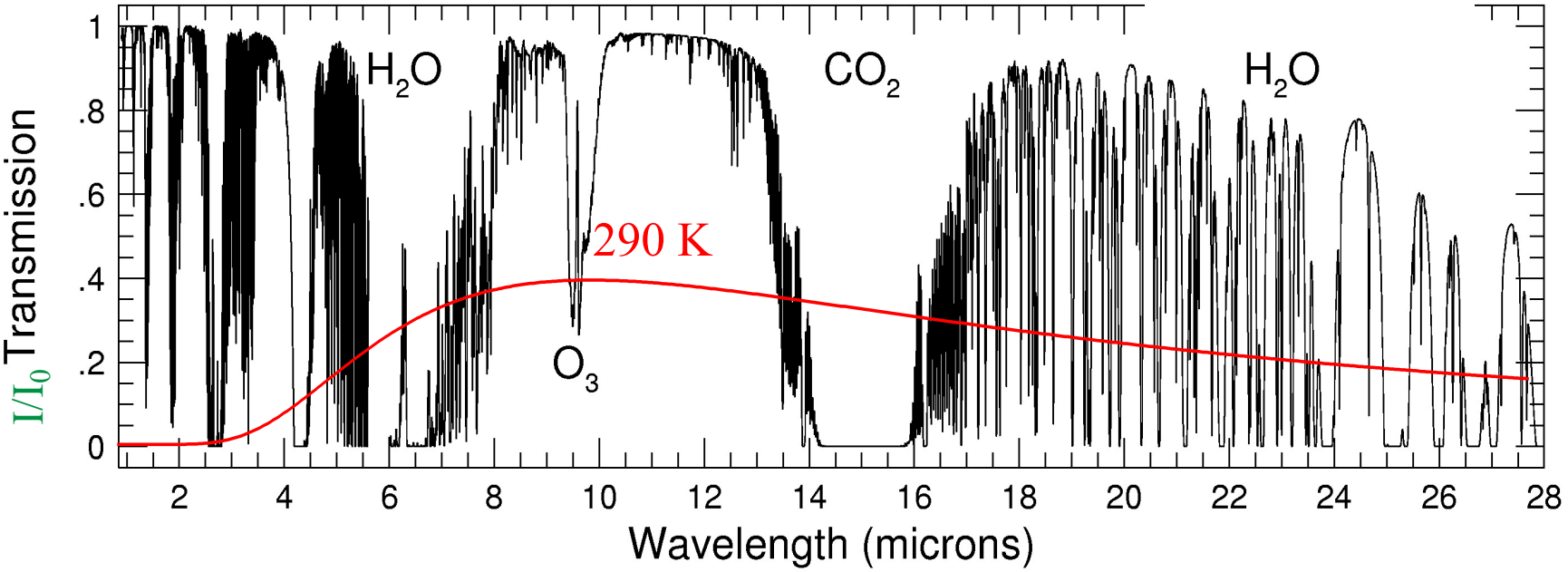
$$\ln I = -\sigma(\tilde{\nu}) \cdot L + const \quad \Rightarrow$$

$$I(\tilde{\nu}) = I_0(\tilde{\nu}) \exp(-\sigma(\tilde{\nu}) \cdot n_1 \cdot L) = I_0(\tilde{\nu}) \exp(-\alpha(\tilde{\nu}) \cdot L).$$

$$\sigma(\nu) = \frac{\ln(I_0 / I(\tilde{\nu}))}{n \cdot L}$$




Earth atmosphere




$T_{av}$=290K

$$T(\lambda_p) = \frac{2900}{\lambda_p(\mu m)}; \quad T(6) = 480K; \quad T(15) = 193K; \quad T(25) = 120K.$$

# Beer Lambert Law

Detector measures light intensity integrated over frequency-range

$$P = \int_0^\infty I(\tilde{\nu})d\tilde{\nu} = \int_0^\infty I_0(\tilde{\nu})\exp(-\alpha(\tilde{\nu})\cdot L)\cdot d\tilde{\nu}.$$

For $\alpha(\tilde{\nu})\cdot L << 1$ (optically thin):

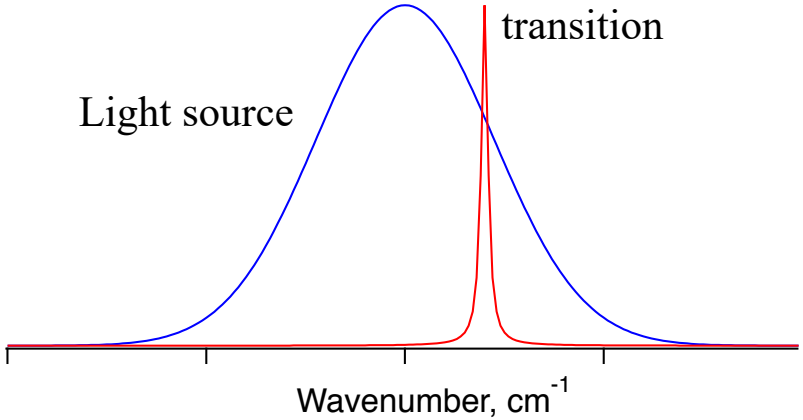
$$I(\nu) = I_0(\tilde{\nu})\exp(-\alpha(\tilde{\nu})\cdot L) \simeq I_0(\tilde{\nu})\cdot(1-\alpha(\tilde{\nu})\cdot L.$$

1) $\Delta\nu_I \gg \Delta\nu_g$ (broad light source):

$$P = \int_0^\infty I(\tilde{\nu})d\tilde{\nu} \simeq \int I_0(\tilde{\nu})\cdot(1-\alpha(\tilde{\nu})\cdot L)\cdot d\tilde{\nu}$$

$$P \simeq P_0 - I_0(\tilde{\nu}_g)\cdot L\cdot\int_0^\infty \alpha(\tilde{\nu})\cdot d\tilde{\nu}$$

$$\Delta P(\tilde{\nu}_g) = -I_0(\tilde{\nu}_g)\cdot L\cdot\alpha_0;$$




The spectrum will reflect spectral profile of the source, $I_0(\tilde{\nu})$, not of the molecule !

# Beer Lambert Law

Detector measures light intensity integrated over frequency-range

$$P = \int_0^\infty I(\tilde{\nu})d\tilde{\nu} = \int_0^\infty I_0(\tilde{\nu})\exp(-\alpha(\tilde{\nu})\cdot L)\cdot d\tilde{\nu}.$$

For $\alpha(\tilde{\nu})\cdot L << 1$ (optically thin):

$$I(\nu) = I_0(\tilde{\nu})\exp(-\alpha(\tilde{\nu})\cdot L) \simeq I_0(\tilde{\nu})\cdot(1-\alpha(\tilde{\nu})\cdot L.$$

2) $\Delta\nu_I << \Delta\nu_g$ (narrow band light source, e.g., laser):

$$P = \int_0^\infty I(\tilde{\nu})d\nu \simeq \int I_0(\tilde{\nu})\cdot(1-\alpha(\tilde{\nu})\cdot L)\cdot d\tilde{\nu}$$

$$\Delta P(\tilde{\nu}_I) = -P_0\cdot L\cdot\alpha(\tilde{\nu}_I) \propto \sigma(\tilde{\nu}_I);$$

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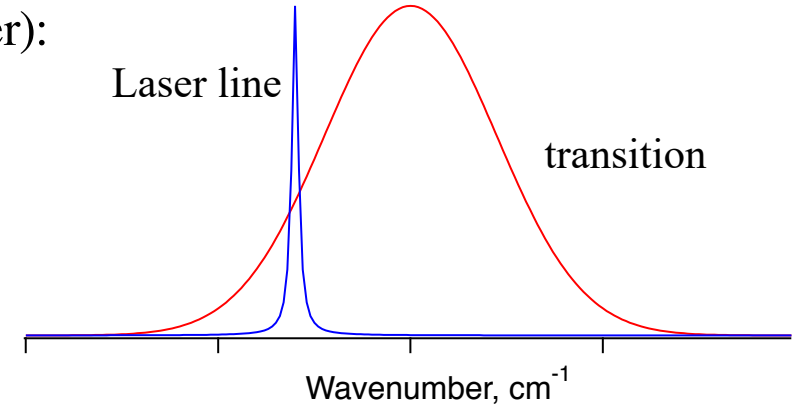



This is the only truly measurements of molecular spectra

The condition $\Delta\nu_I << \Delta\nu_g$ allows for spectral resolution

# Einstein coefficient B, cross section and TDM

B and σ are empirical, TDM comes from QM.
All three reflect probability for a transition

$$\sigma_0 = \frac{h\tilde{\nu} B_{12}}{c^2} \qquad [B_{12}]=(\mathrm{cm}\cdot\mathrm{cm}^2\cdot\mathrm{s}^{-2})/\mathrm{J}=\mathrm{cm}^3/(\mathrm{J}\cdot\mathrm{s}^2)$$

$$\mathrm{A}_{21} = \frac{8\pi \mathrm{h}}{\mathrm{c}^3}\cdot\nu_{12}^3\,\mathrm{B}_{21} = 8\pi \mathrm{h}\cdot\tilde{\nu}_{12}^3 B_{21} \Rightarrow B_{21} = \frac{\mathrm{A}_{12}}{8\pi \mathrm{h}\cdot\tilde{\nu}_{12}^3};$$

$$\sigma_0 = \frac{h\tilde{\nu} B_{21}}{c^2} = \frac{h\tilde{\nu}}{c^2}\frac{\mathrm{A}_{12}}{8\pi \mathrm{h}\cdot\tilde{\nu}_{12}^3} = \frac{1}{8\pi c^2\cdot\tilde{\nu}_{12}^2}\mathrm{A}_{12} \Rightarrow \tau_{sp} \propto \frac{1}{\sigma_0};$$

- The stronger is a transition the shorter is the lifetime of excited state

$$\sigma_0 = M_{21}^2\frac{\pi\cdot\tilde{\nu}}{3\varepsilon_0\cdot h\cdot c} \Rightarrow A_{21} \propto \tilde{\nu}^3\cdot M_{21}^2 \Rightarrow \tau_{12} \propto \frac{1}{\tilde{\nu}^3};$$

- Lifetime of excited state reduces quickly with its energy

# Spectroscopic techniques

1. Direct absorption (frequency and abs. intensity):
   - ✓ Intracavity spectroscopy (IC),
2. Indirect absorption (frequency only):
   - ✓ Photoacoustic spectroscopy (PA),
   - ✓ Laser induced fluorescence (LIF),
   - ✓ Photodissociation spectroscopy (UV/IR-PD).
3. Fourie-transform IR (FTIR)
4. (Stimulated) Raman scattering (RS or SRS)

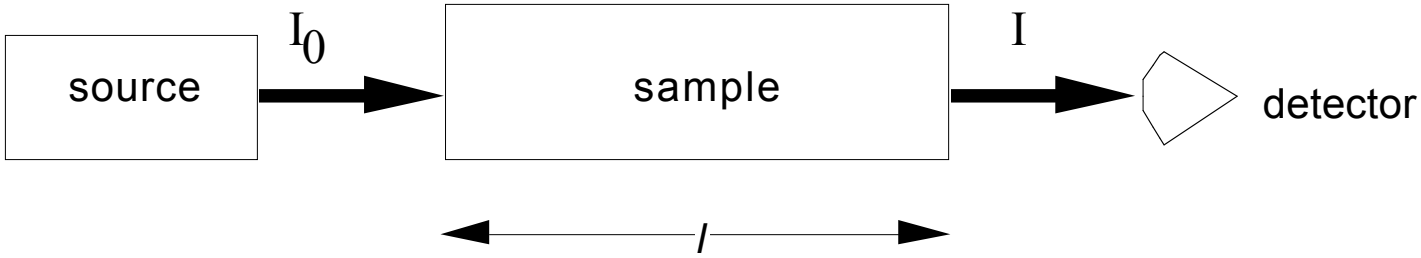
# *What one can do?*

- Measure frequencies and intensities of transitions to calculate structure and energy levels;
- Detect presence of different chemical species by detecting specific transitions;
- Measure concentration of chemical species, including short-living intermediates;
- Study dissociation/chemical kinetics;
- Study intramolecular ultra-fast processes:

  a) by time-resolved spectroscopy with ps/fs lasers,

  b) from frequency resolved spectra.

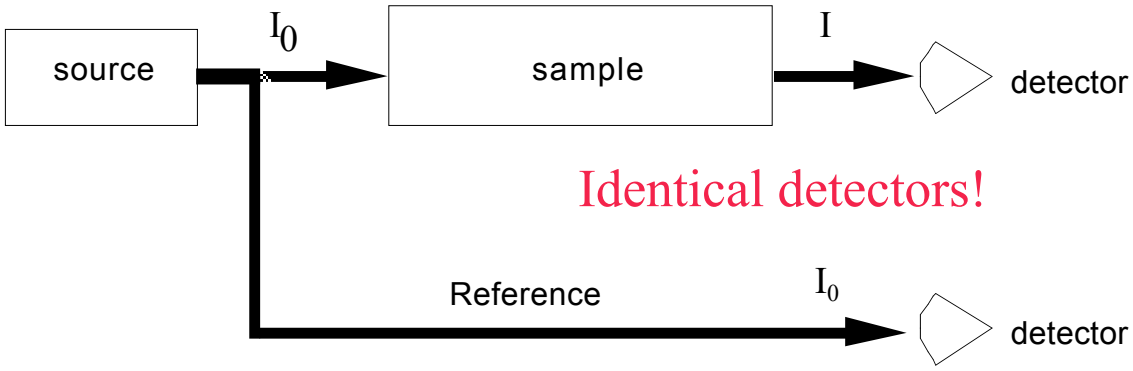
# *Absorption Spectroscopy*




$$I(\nu) = I_0\, e^{-nl\sigma(\nu)} \qquad \Delta I(\nu) \simeq I_0 nl\sigma(\nu)$$

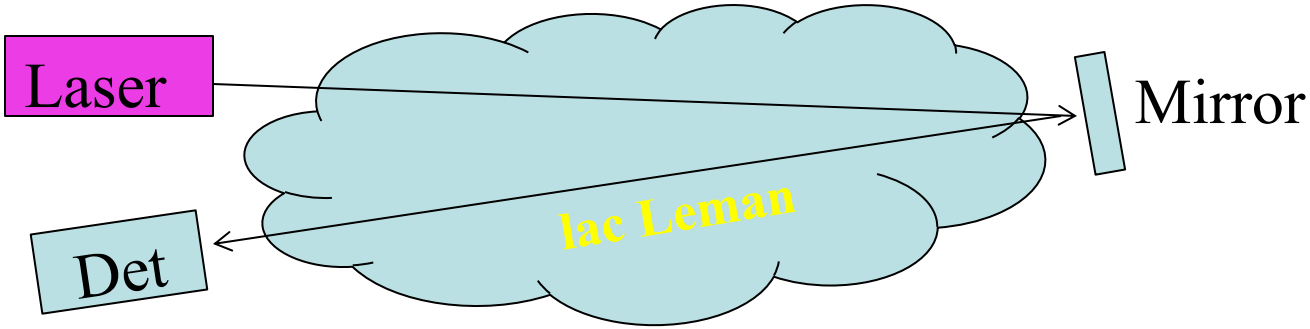
$CF_3H$ ($\nu_{CH}$=3): p=1mBar ($n=3\cdot10^{16}$ $cm^{-3}$), l=10cm, $\sigma=10^{-21}$ $cm^2$

$$\Delta I(\nu)/I_0 = 3\cdot10^{-4} = 0.03\%$$



# Direct laser absorption methods

1. Single long pathway: ($(H_2O)_2$ above lake, L=8 km)
2. Multipath cells;
3. Intra-cavity spectroscopy;



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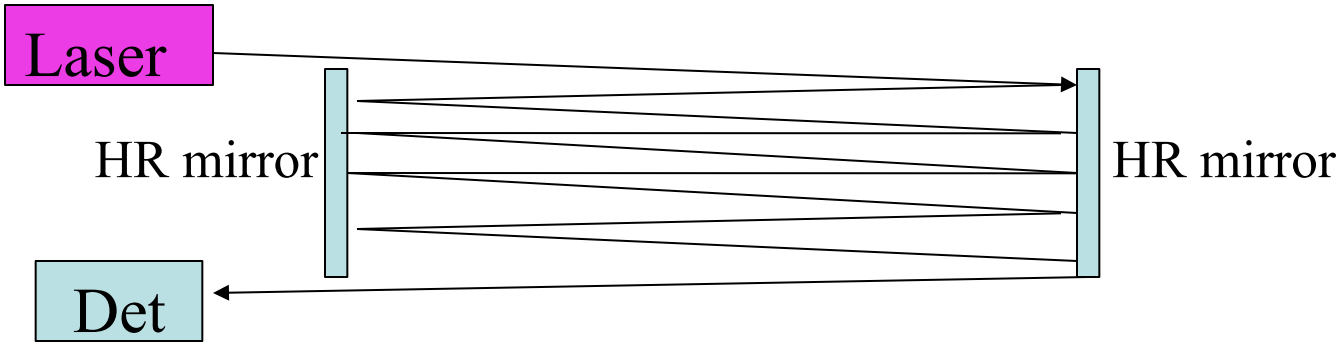

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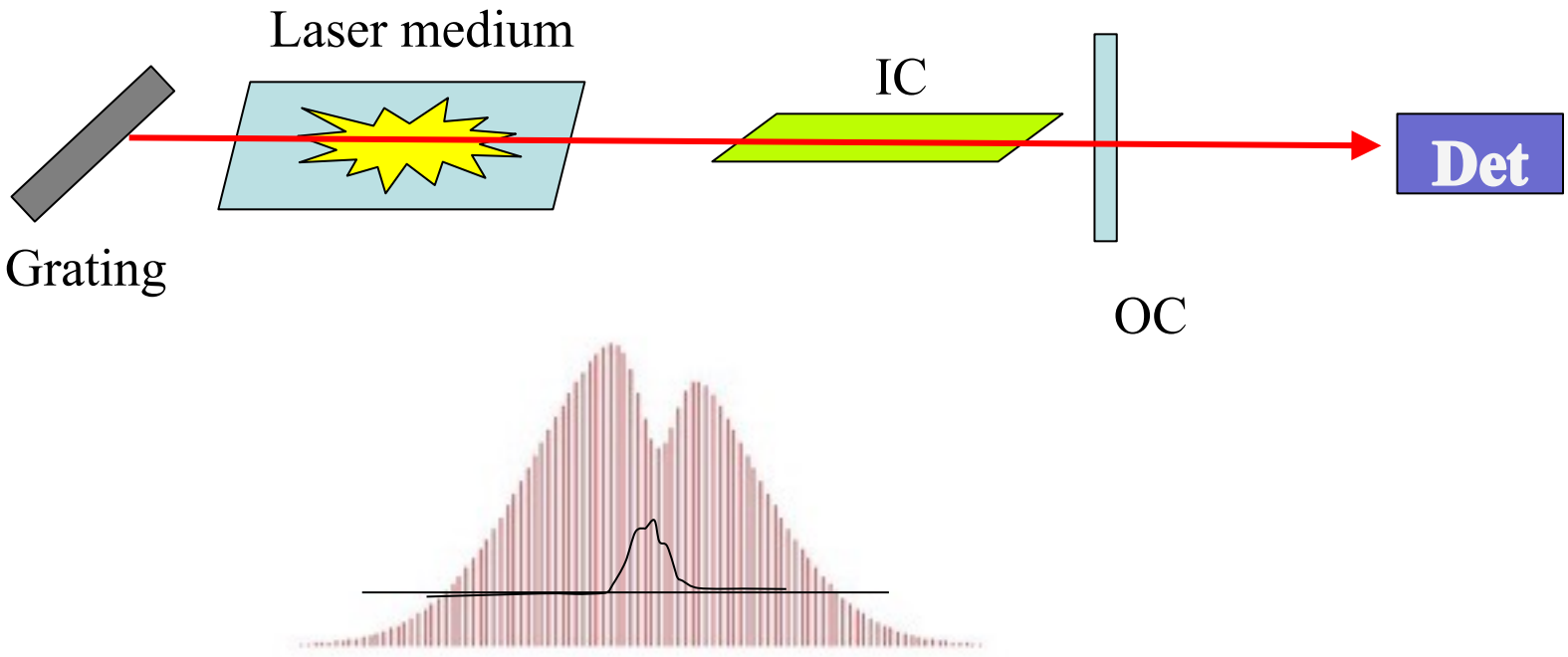
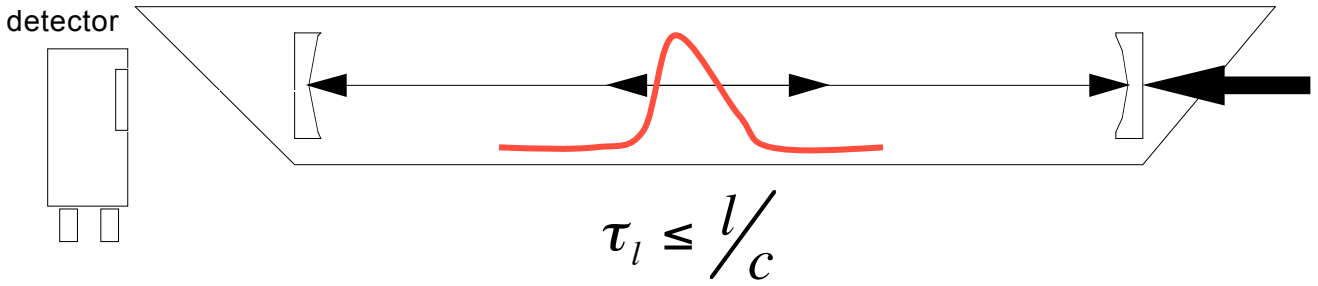
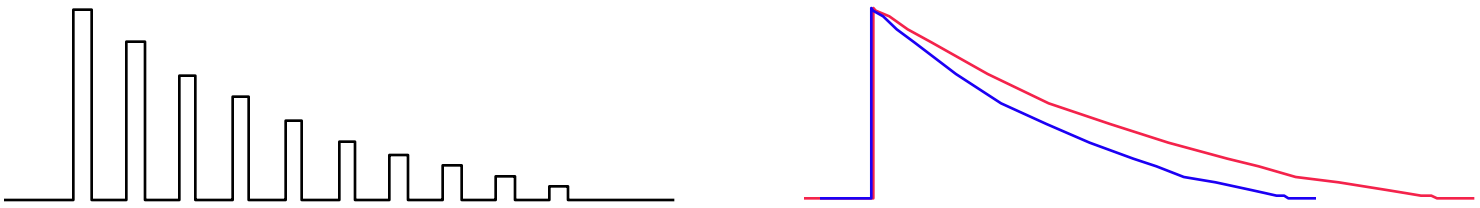


# Direct absorption methods

1. Single long pathway: ($(H_2O)_2$ above lake, L=8 km)
2. Multipath cells;
3. Intra-cavity spectroscopy;
4. Cavity ring-down spectroscopy:




$$\tau_l \leq l/c$$



$$I = I_0 \exp(-\alpha(\lambda) \cdot t)$$

# *Application of absorption spectroscopy*

- Concentration of chemical species;
- Frequencies and intensities of transitions.

## Advantages:

- Absolute measurements of concentration/absorption cross section;
- Simplicity and universality.

## Drawbacks:

- Low sensitivity, limited by laser power stability;
- Low selectivity.
- Significant thermal broadening (T>300 K).

# *Indirect Absorption Methods*

## Photoacoustic spectroscopy:

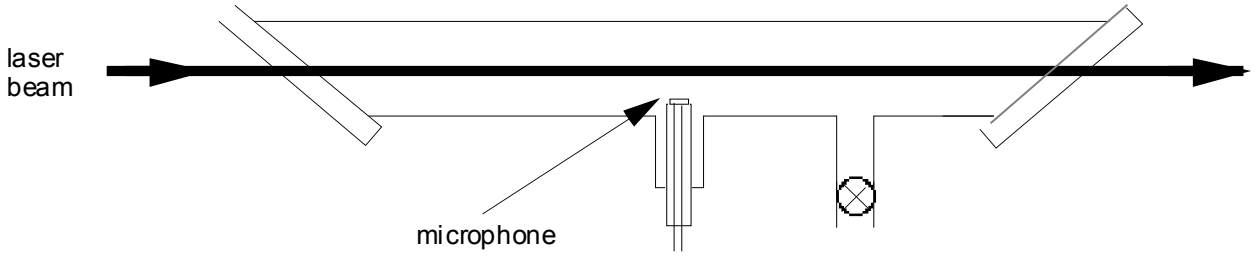
Thunderstorm:
Lightning followed by **Thunder**

Why Thunder?

1. Heating of air inside the discharge channel,
2. Acoustic shockwave

# *Indirect Absorption Methods*

## Photoacoustic spectroscopy:




$$h\nu \rightarrow el \rightarrow V \rightarrow rot \rightarrow trans$$

Direct absorption: $S_a = I_0 \cdot (1 - n \cdot l \cdot \sigma), \quad n \cdot l \cdot \sigma \ll 1;$

$Baseline: I_0.$

Photo acoustic signal: $S_{pa} = \alpha \cdot I_0 \cdot n \cdot l \cdot \sigma,$

*Zero baseline*!

## Photoacoustic spectroscopy:

$$d \gg \frac{1}{n \cdot \sigma}$$

### *Advantages:*

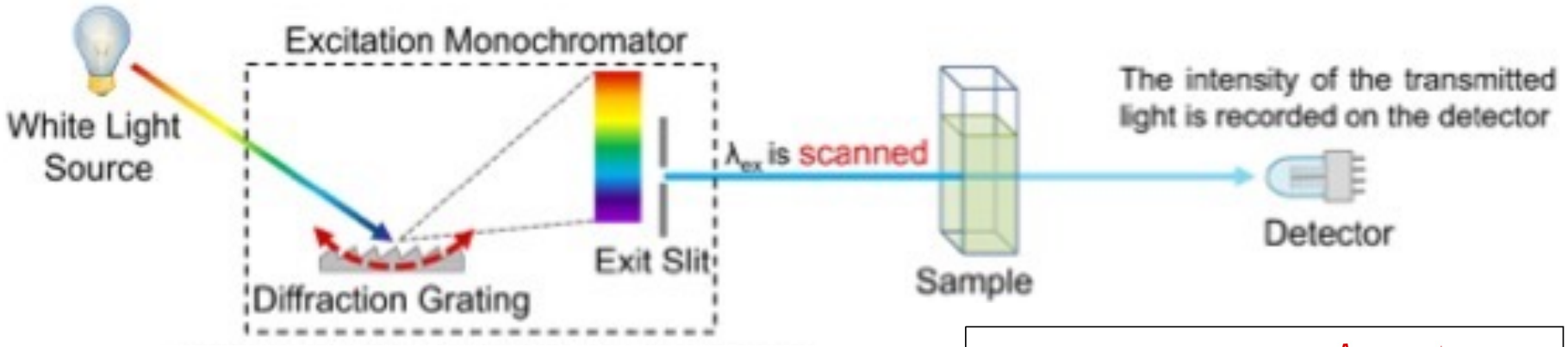
1) Extremely high sensitivity;
2) Simple and inexpensive;
3) Universal.

### *Disadvantage:*

1) Collisional =>
   - Pressure broadening,
2) No absolute intensity
3) Requires pulsed tunable laser
4) Requires a vacuum pump

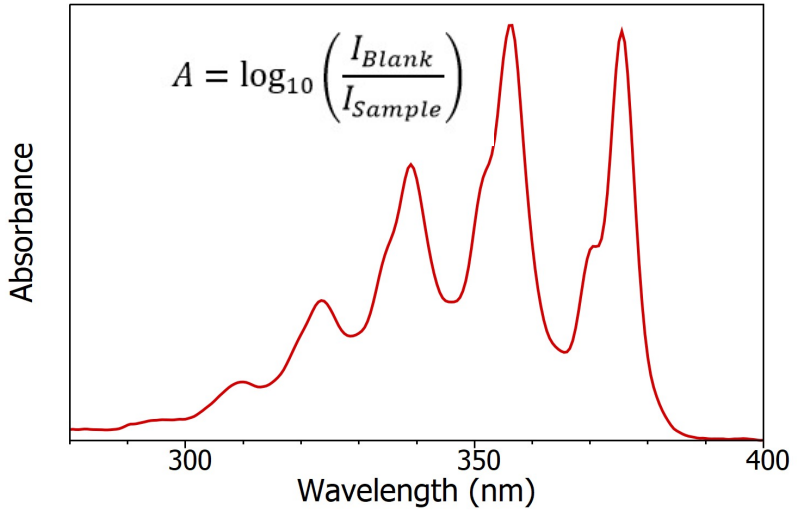
Used for laboratory studies/detections

# Direct absorption spectrometers



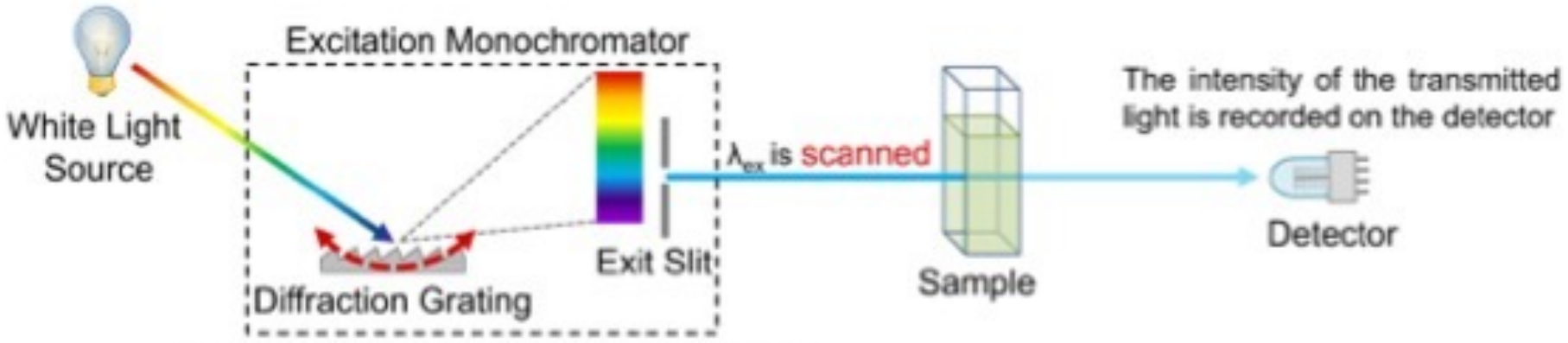

UV-Vis or IR absorption:
"Blanc" spectrum with no sample, $\boldsymbol{I}_0$
"Sample" spectrum with sample, $\boldsymbol{I}$.

$$A = \log_{10}\left(\frac{I_o}{I}\right) = \epsilon c l$$




Typically: the spectrum is fit by a linear combination of the library spectra to get concentrations of the analytes in solution

# Direct absorption spectrometers




+ Low cost, reliable
+ Universal, suitable for multi compound samples
+ Direct determination of concentration.
– Low sensitivity (solution; high concentration of sample)
– Non-selective
– Small dynamic range (=min to max concentration)
– Sensitive to sample T

# Emission spectroscopy

$$I = \alpha \cdot \left\langle \varphi_{el}^{i} \left| \overrightarrow{\mu_{el}} \right| \varphi_{el}^{f} \right\rangle \left\langle \varphi_{vib}^{i}(r) \middle| \varphi_{vib}^{f}(r) \right\rangle;$$

Excitation + emission =>
Compared with absorption:
higher selectivity.

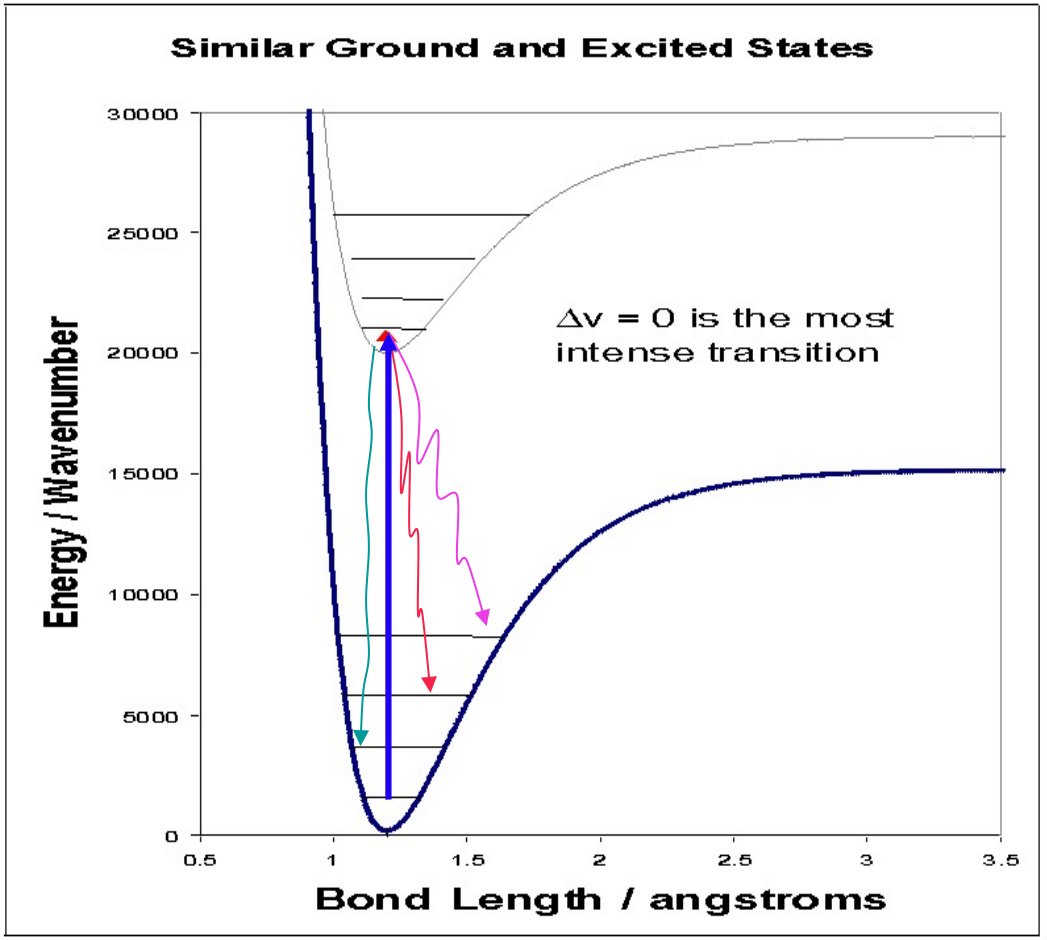
$$\lambda_{em} > \lambda_{exc}$$

- Lines positions
<=> Energy levels;

- Lines intensities
<=> Franck-Condon factor

Background free:

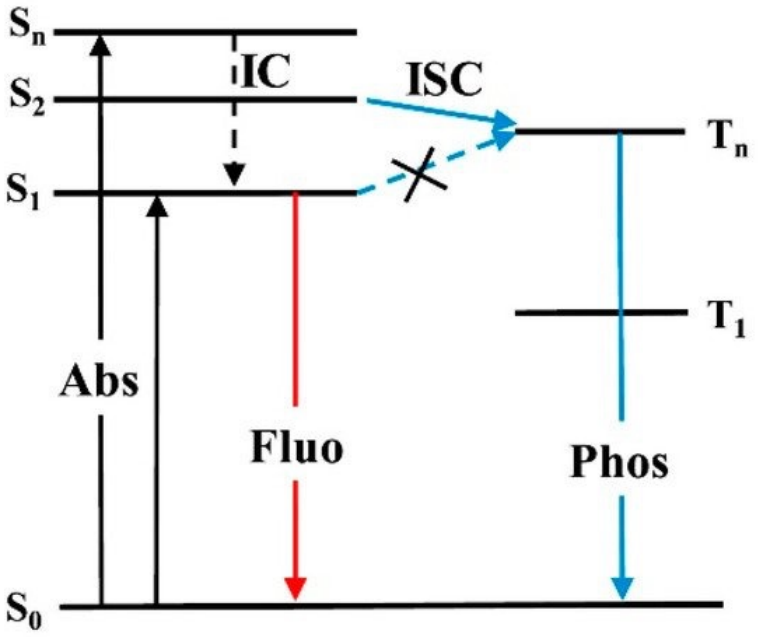
- high sensitivity
- high dynamic range



# Induced Fluorescence/Phosphorescence

**Kasha's/Vavilov rule:**

In many polyatomics in solution an emission spectrum often is nearly independent of the excitation wavelength.



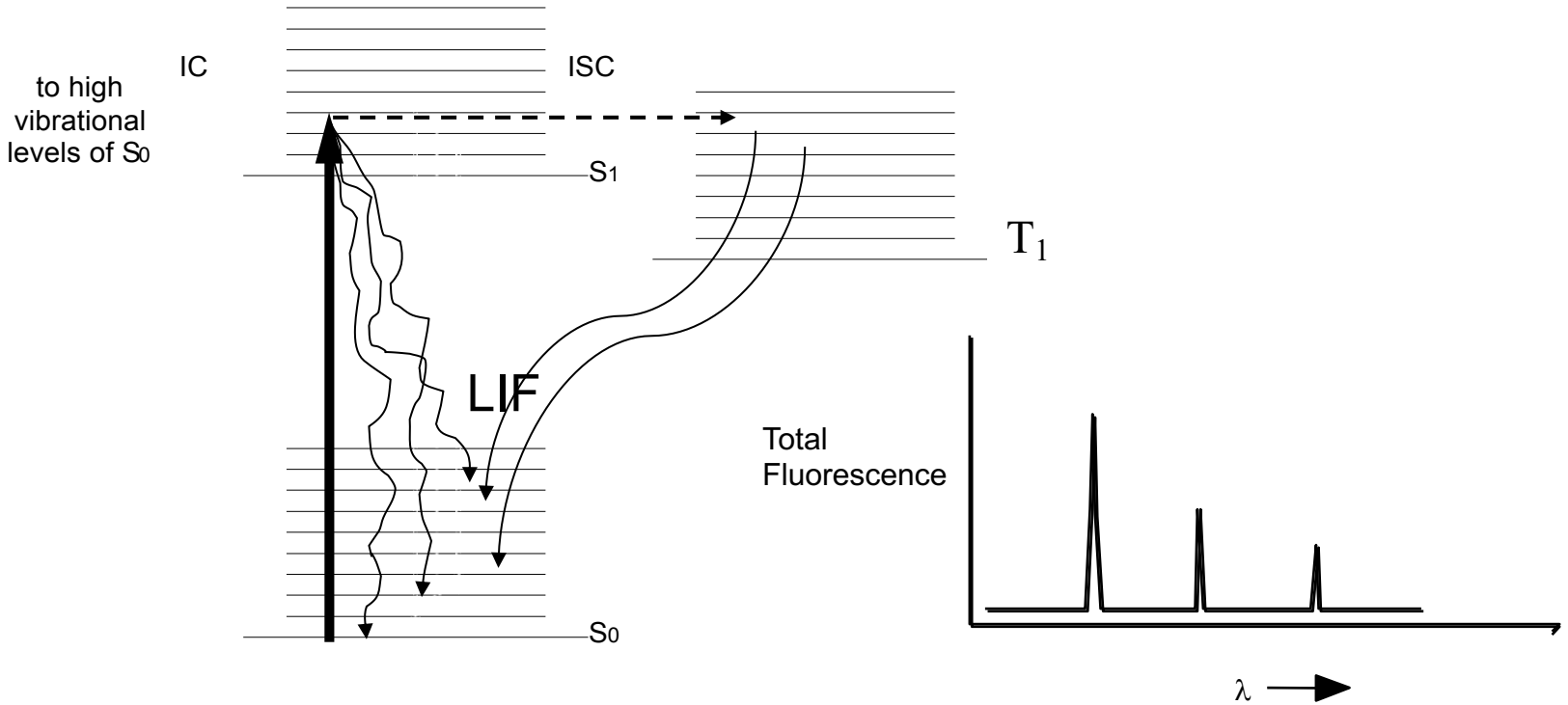

**When K-V rule is obeyed:**

vibrational levels of $S_0$;
if, in addition $S_1$ and $S_0$ are similar:
IF/IP spectrum~ Absorption

Excitation to $S_2$, $S_3$, … often is followed by fast internal conversion to $S_1$ and, subsequently, by fast vibrational relaxation to v=0 in $S_1$

*This rule has many exceptions.*
*There is no vibrational relaxation in the gas phase.*

# Induced Fluorescence/Phosphorescence




$S_0 \leftarrow S_1$: Fluorescence (10-100 ns in UV/Vis, 10-100 μs in IR)

$$\frac{1}{\tau_{21}} = A_{21} = \frac{8\pi h \nu_{12}^3 B_{21}}{c^3}$$

$S_0 \leftarrow T_1$: Phosphorescence (formally forbidden; ms to s)

# Emission spectroscopy

**Case (1):**

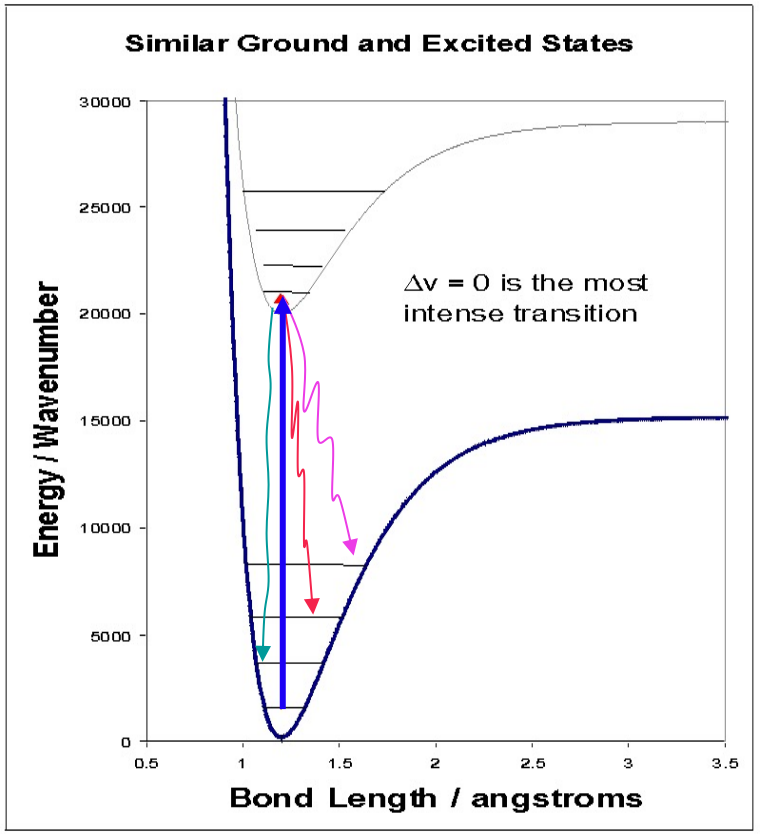
Excitation wavelength is scanned, while total fluorescence is collected (LIF): (rovibronic structure of $S_1$ and FC factor)

**Case (2):**

Excitation wavelength is scanned, emission at a specific transition only is detected (rovibronic structure of $S_1$ and additional selectivity)

**Case (3):**

Excitation wavelength is fixed, emission is detected as a function of wavelength (rovibronic structure of $S_0$, FC factor )



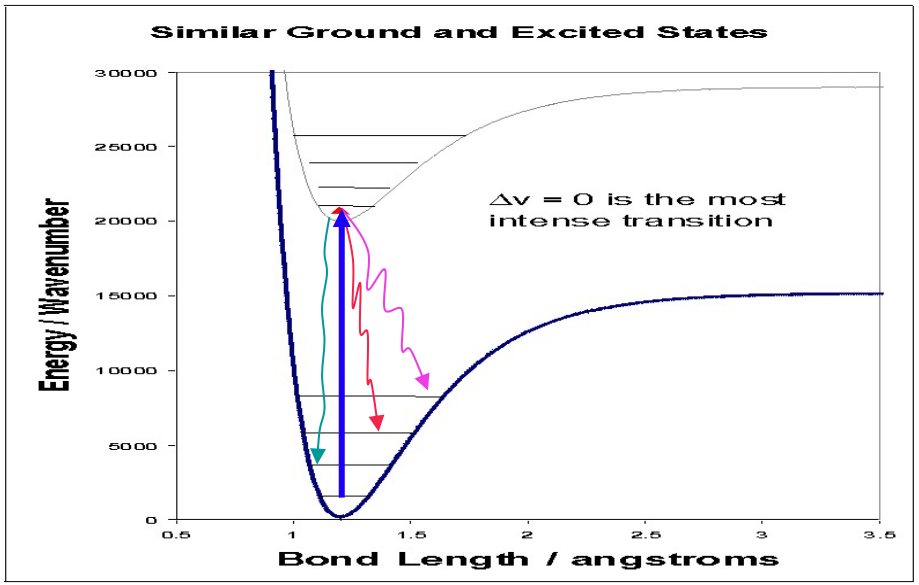
# Emission spectroscopy

## *Advantages:*

1) Extremely sensitive (1);
limited by quantum yield and
design of light collection system
2) Cases (2) and (3) are less sensitive
but highly selective.

## *Disadvantages:*

1) Require high fluorescence
quantum yield;
2) Scattered light discrimination;
3) Difficult for triplet states and for
vibrational spectroscopy

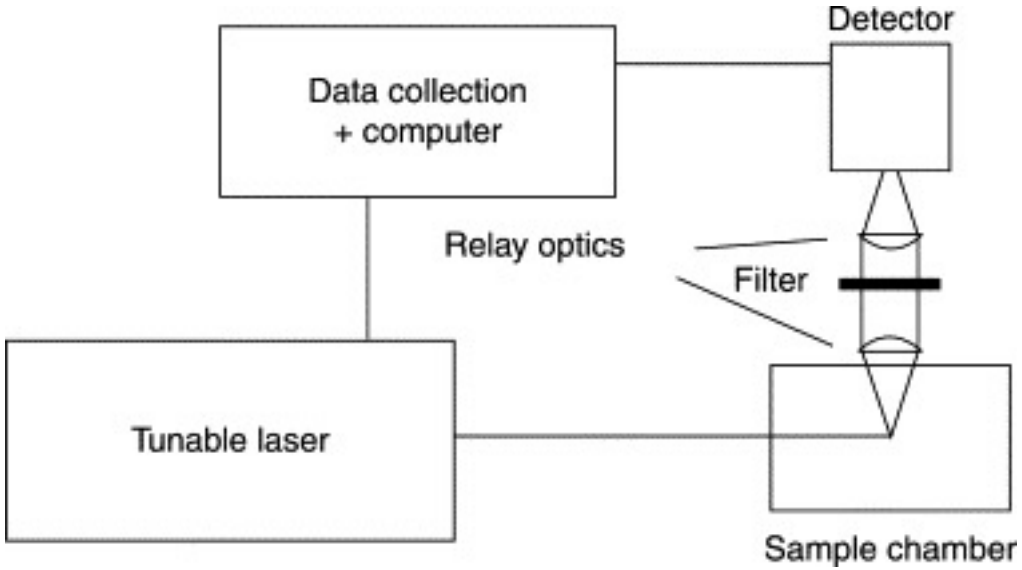



$$\frac{1}{\tau_{21}} = A_{21} = \frac{8\pi h\nu_{12}^3 B_{21}}{c^3}$$

# Laser-induced fluorescence spectroscopy

(**Case 1**. Research only)

High spectral resolution =
Selectivity
High spectral brightness and directionality =>
Sensitivity

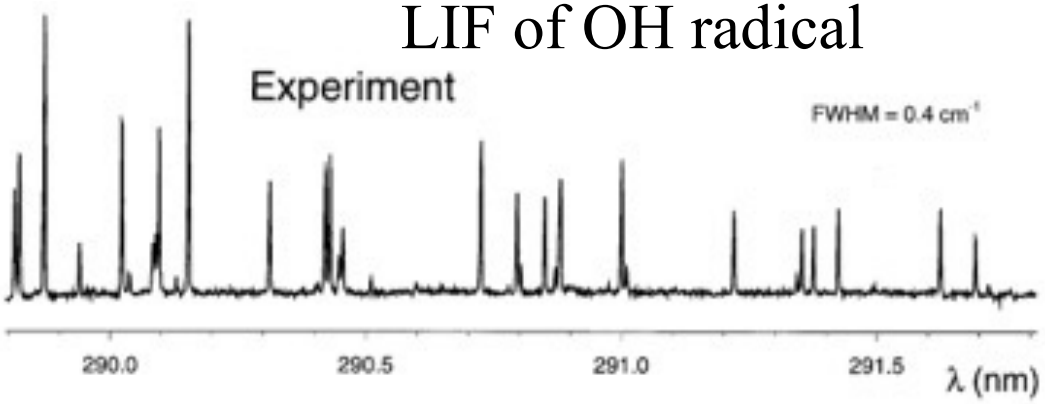



- Optimized geometry of optics to reduce scattered light (baffles, cut-off glass filters).

$$\lambda_{LIF} > \lambda_{Laser}$$

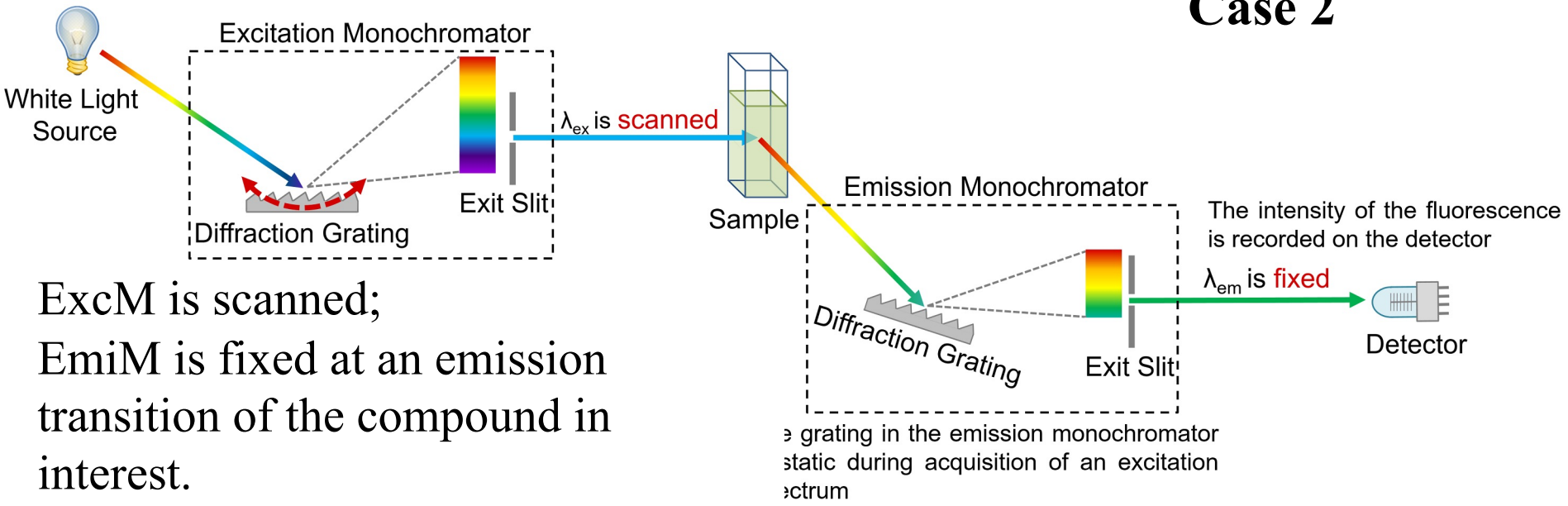
- Requires a tunable laser

LIF of OH radical



# Excitation spectra with spectrofluorometer

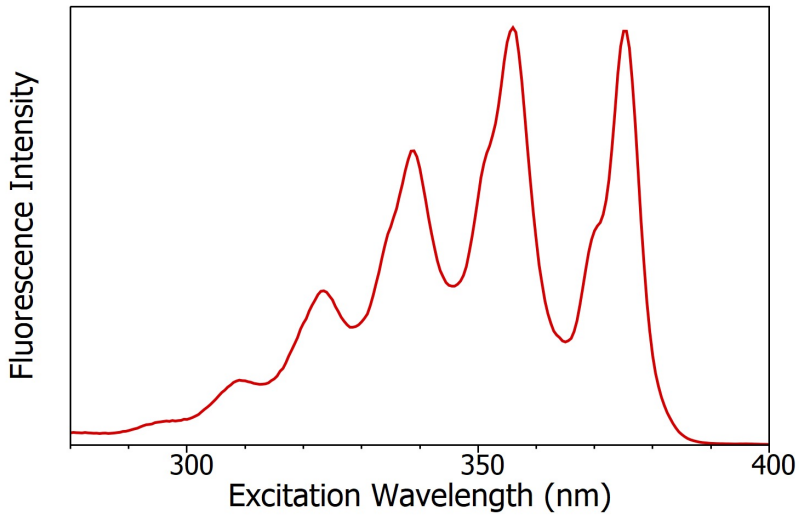
**Case 2**




ExcM is scanned;
EmiM is fixed at an emission transition of the compound in interest.

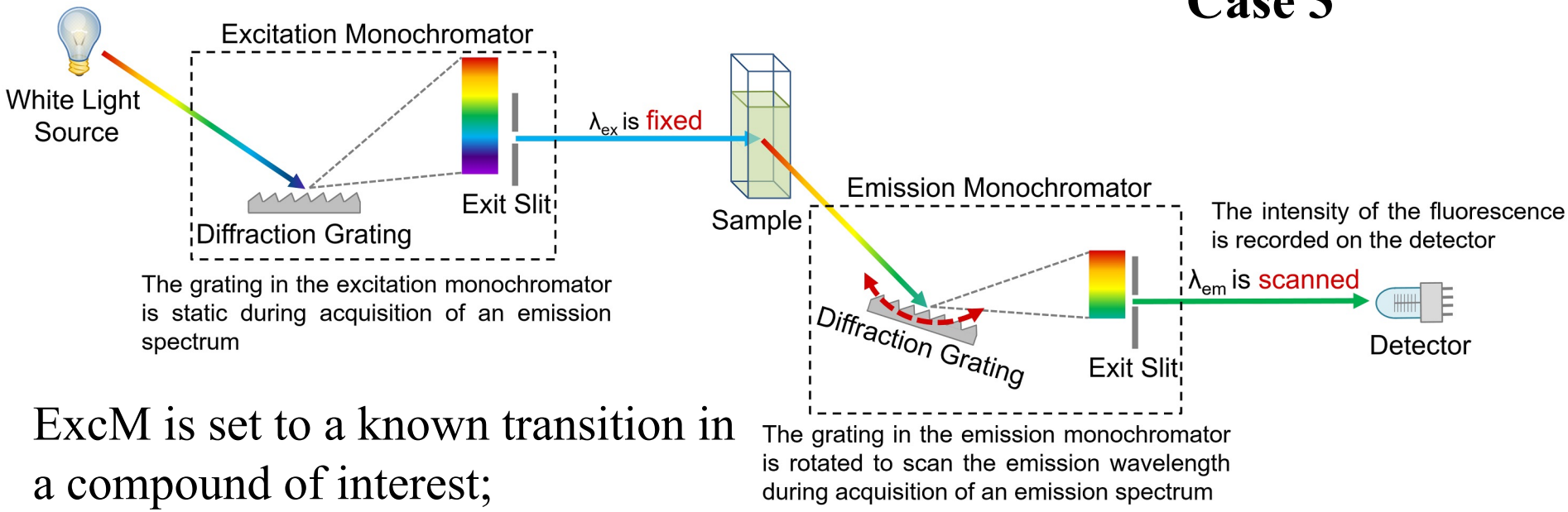
*Often (K-V rule) yields nearly absorption spectrum*

+ High selectivity
+High sensitivity
+High dynamic range
– One molecule at time
– Technical complexity



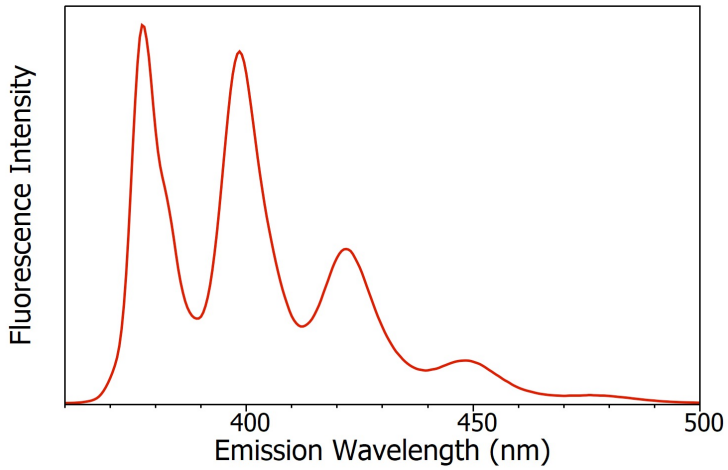
# Emission spectra with spectrofluorometer

**Case 3**




ExcM is set to a known transition in a compound of interest;
EmiM is scanned across the region of emission from the excited state of the compound in interest.

+ High selectivity
–High sensitivity
– One molecule at time
– Technical complexity




Fluorescence emission spectrum of anthracene in cyclohexane

# Photodissociation action spectroscopy

$$M + h\nu \rightarrow M^* \rightarrow A+B$$

The more light is absorbed the more fragments appear

A or B fragment is detected; the number of fragments $\propto \sigma_{MA}$

*Background-free technique* => *highly* ***sensitive***

**Photofragmentation techniques:**

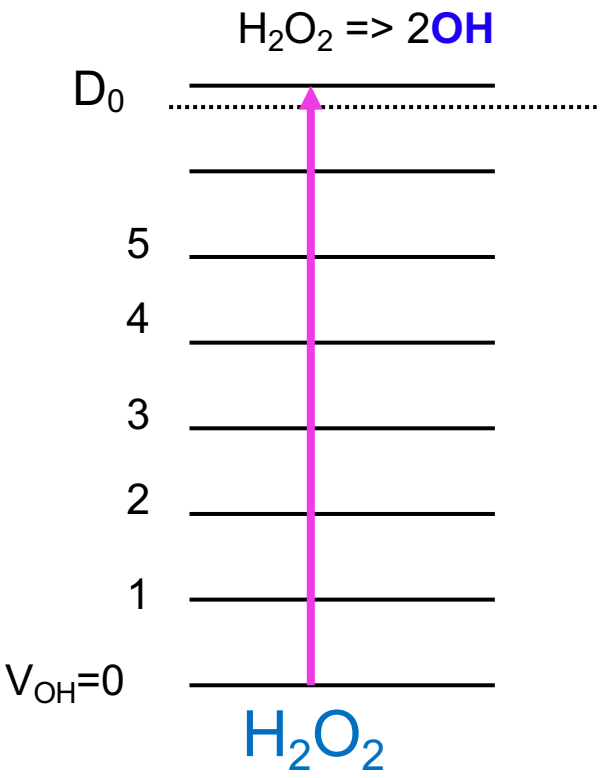
- Overtone excitation
- UVPD direct
- Vibrationally mediated UVPD
- IRMPD

**Detection techniques:**

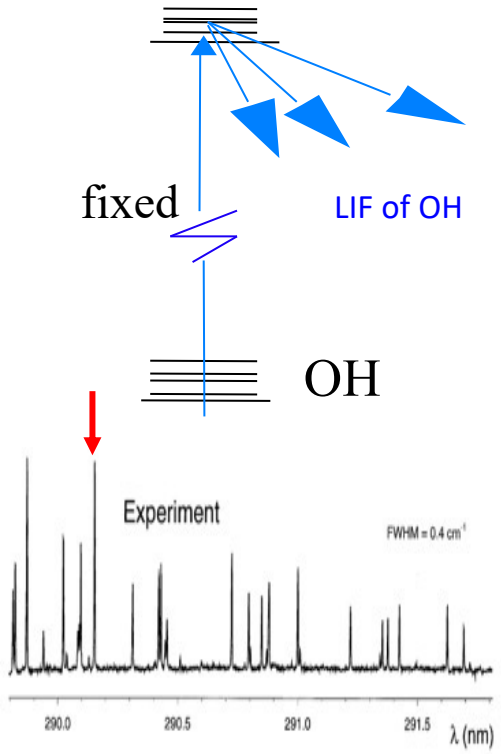
- LIF
- Mass spectrometry

# Photodissociation action spectroscopy

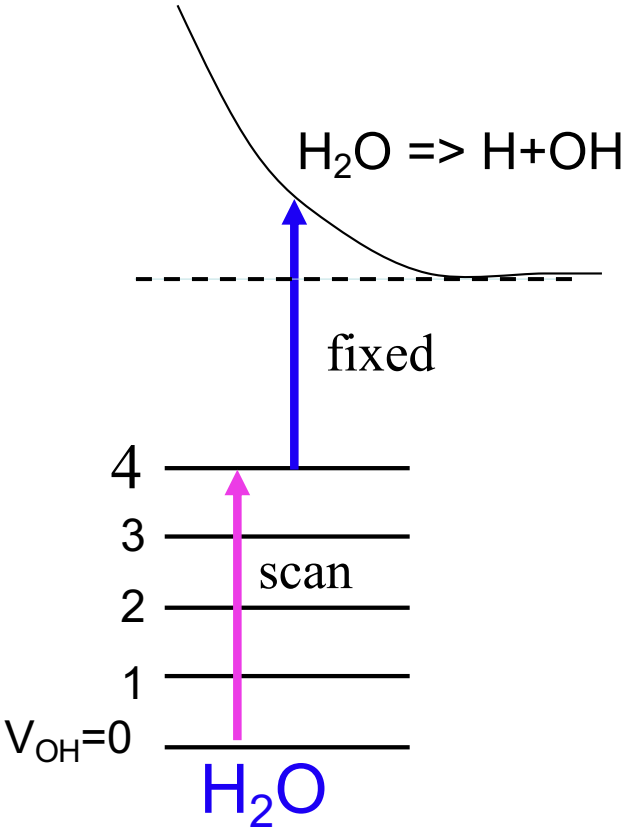
Vibrational overtone photodissociation




LIF detection

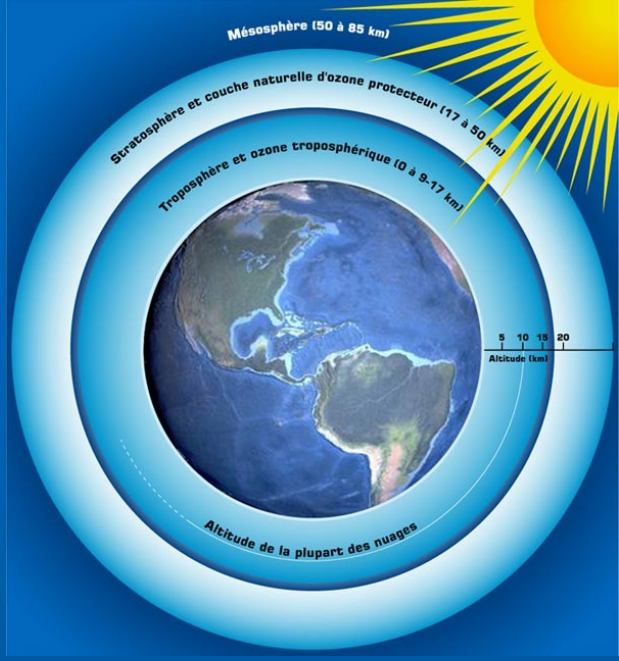



Vibrationally mediated UV dissociation

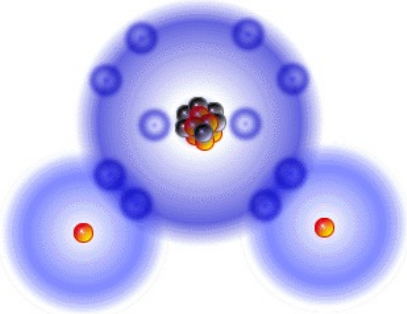


# Atmospheric water vapor :

- **Main absorber (70 %) of the incoming sunlight;**
- **Strong green house gas (IR absorption);**



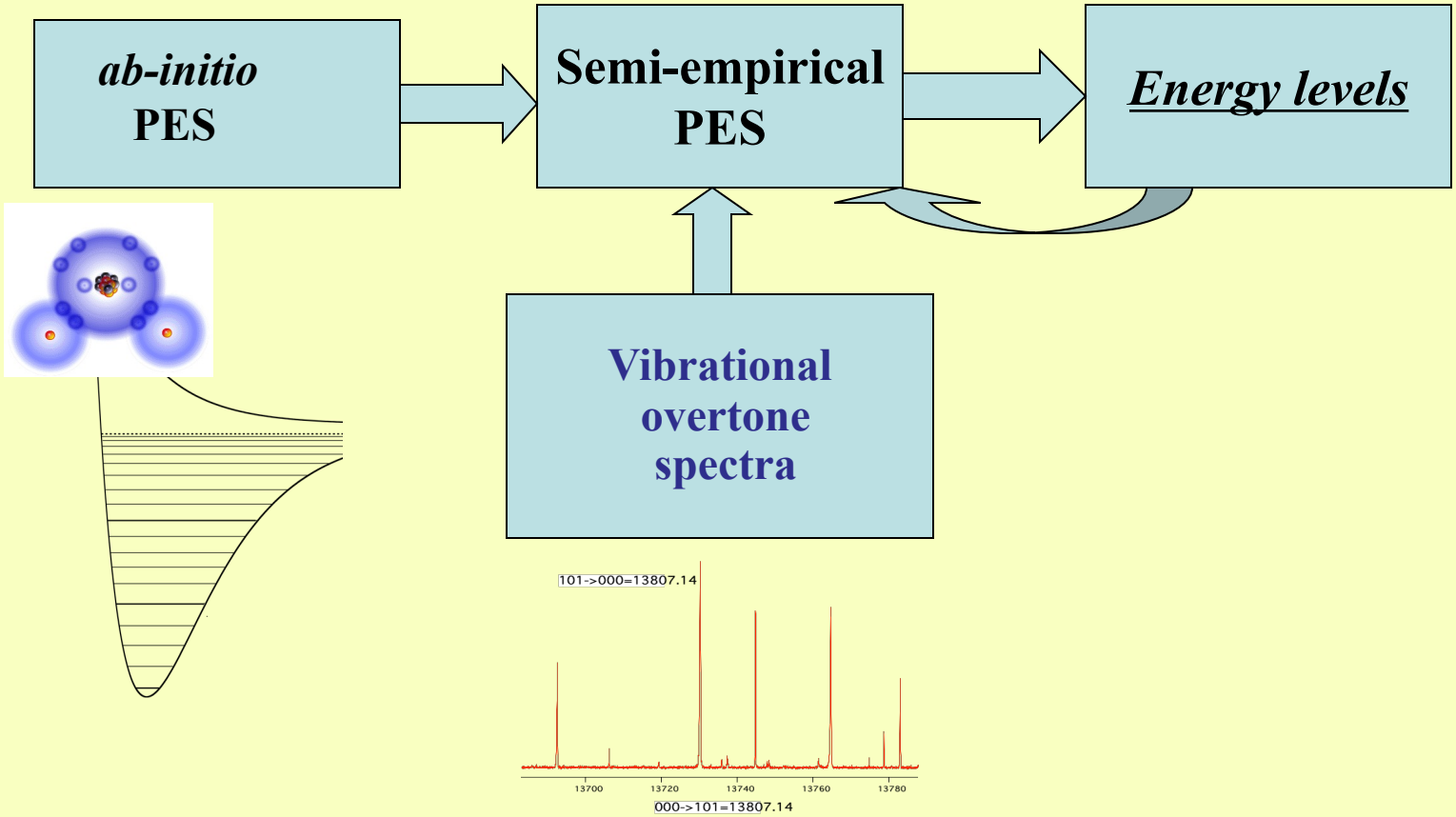

***Water vapor absorption must be well modeled!***



**Fundamental to $H_2O$ molecule:**

- Ro-vibrational energy levels,
- Intensity of transitions.

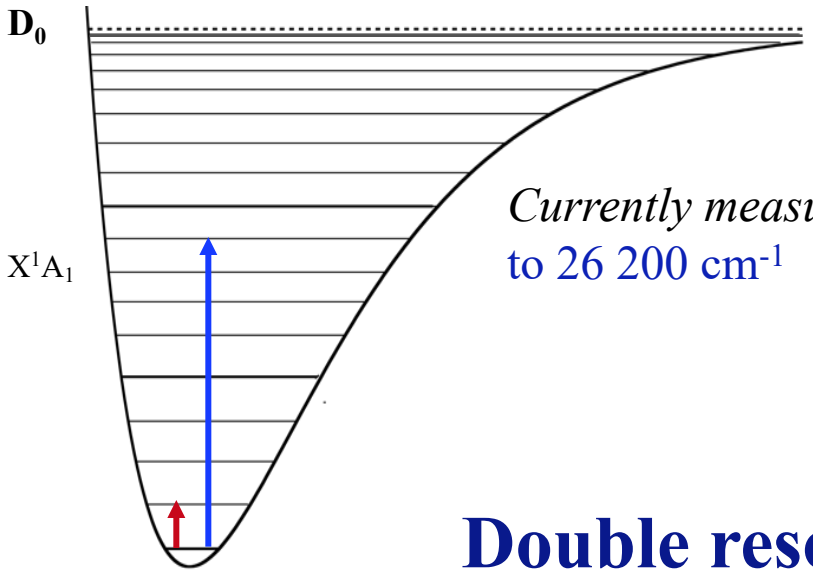
# Obtaining overtone transitions



# Problems and solutions

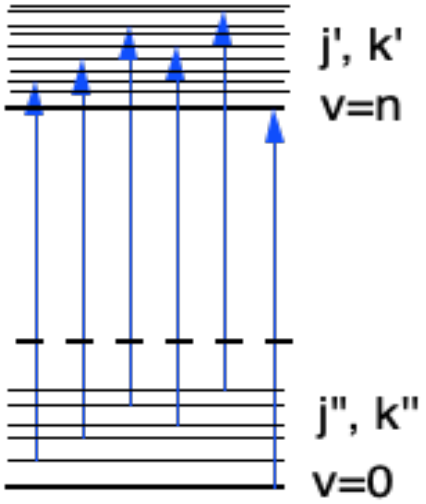
- Very low intensity of high vibrational overtone transitions:

$$\frac{\sigma(n \leftarrow 0)}{\sigma(1 \leftarrow 0)} \approx 10^{n+1}$$



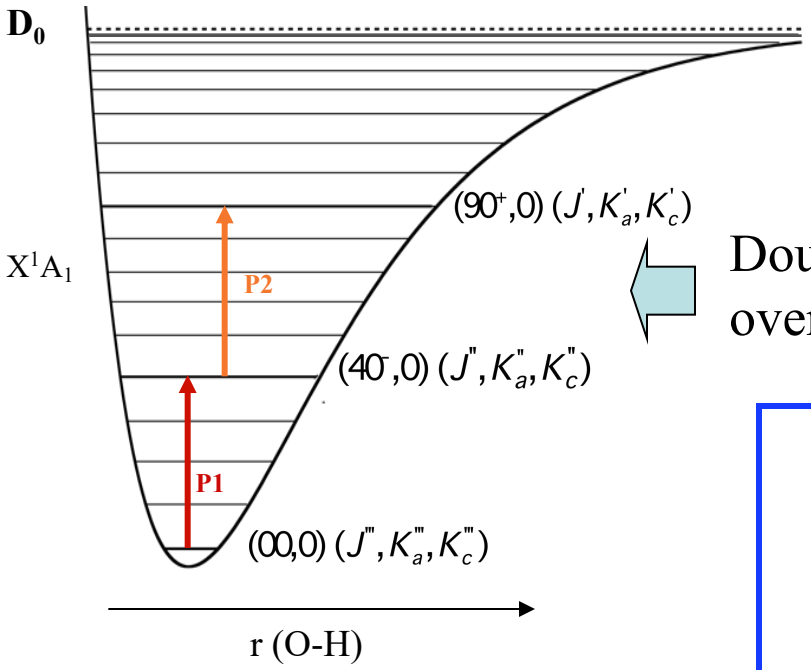

*Currently measured*: up to 26 200 $cm^{-1}$

- Rotational congestion due to thermal distribution




**Double resonance overtone excitation combined with photofragment detection**

# Energy Level Diagram

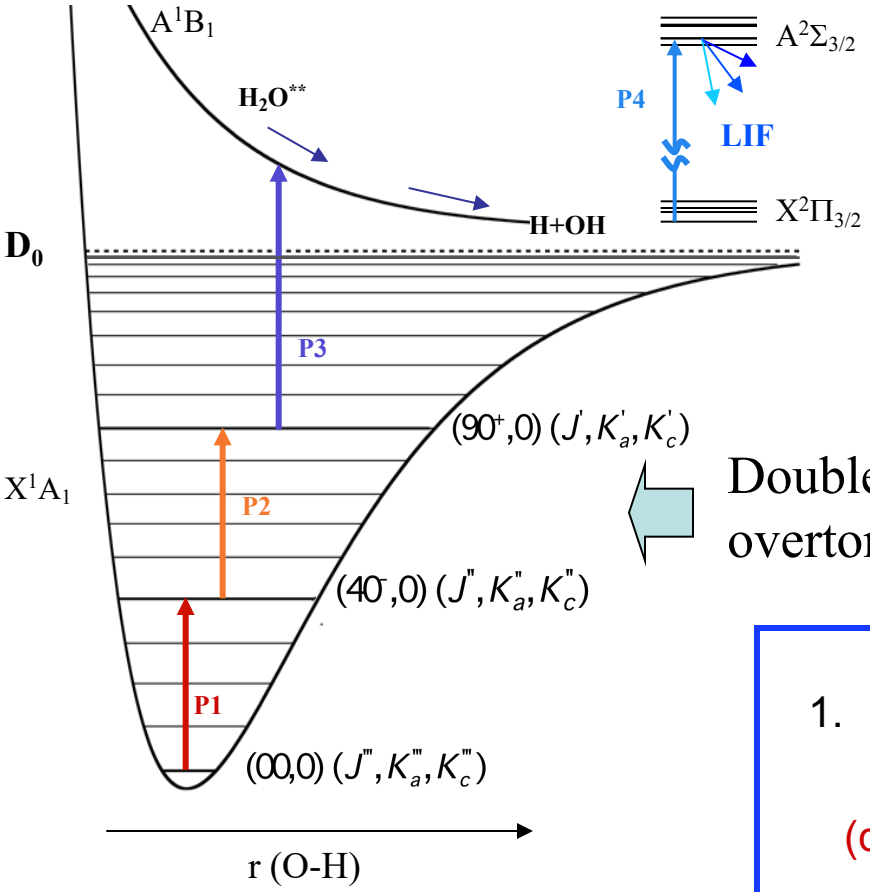



Double resonance
overtone excitation

1. Gain in excitation efficiency:
   $0.1 * 0.1 = 10^{-2}$ **vs** $10^{-5}$-$10^{-6}$
   (double resonance) (direct excitation)

2. Rotational pre-selection => simpler assignment

# Energy Level Diagram



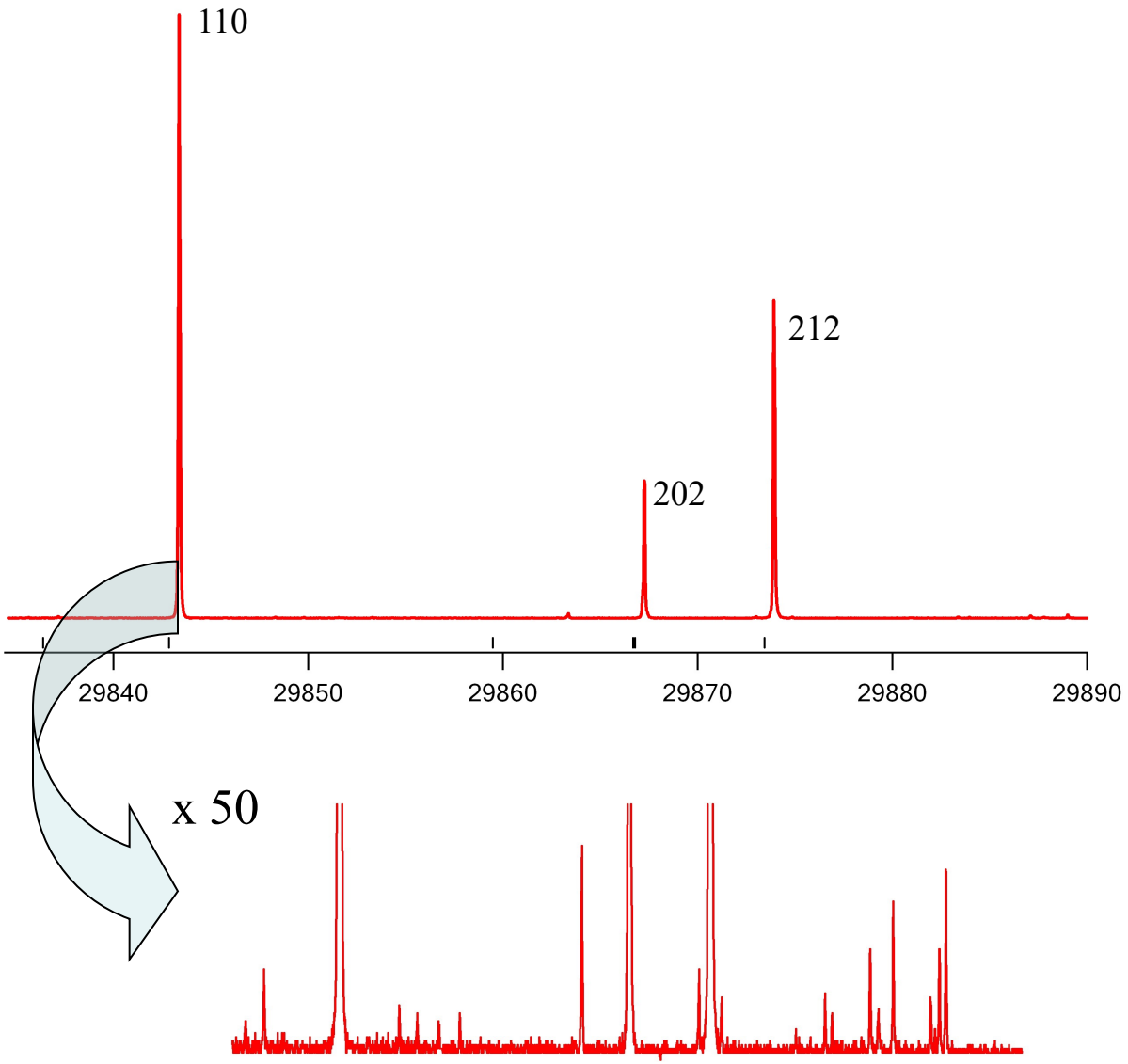

Photofragmentation detection

High selectivity and sensitivity

Double resonance overtone excitation

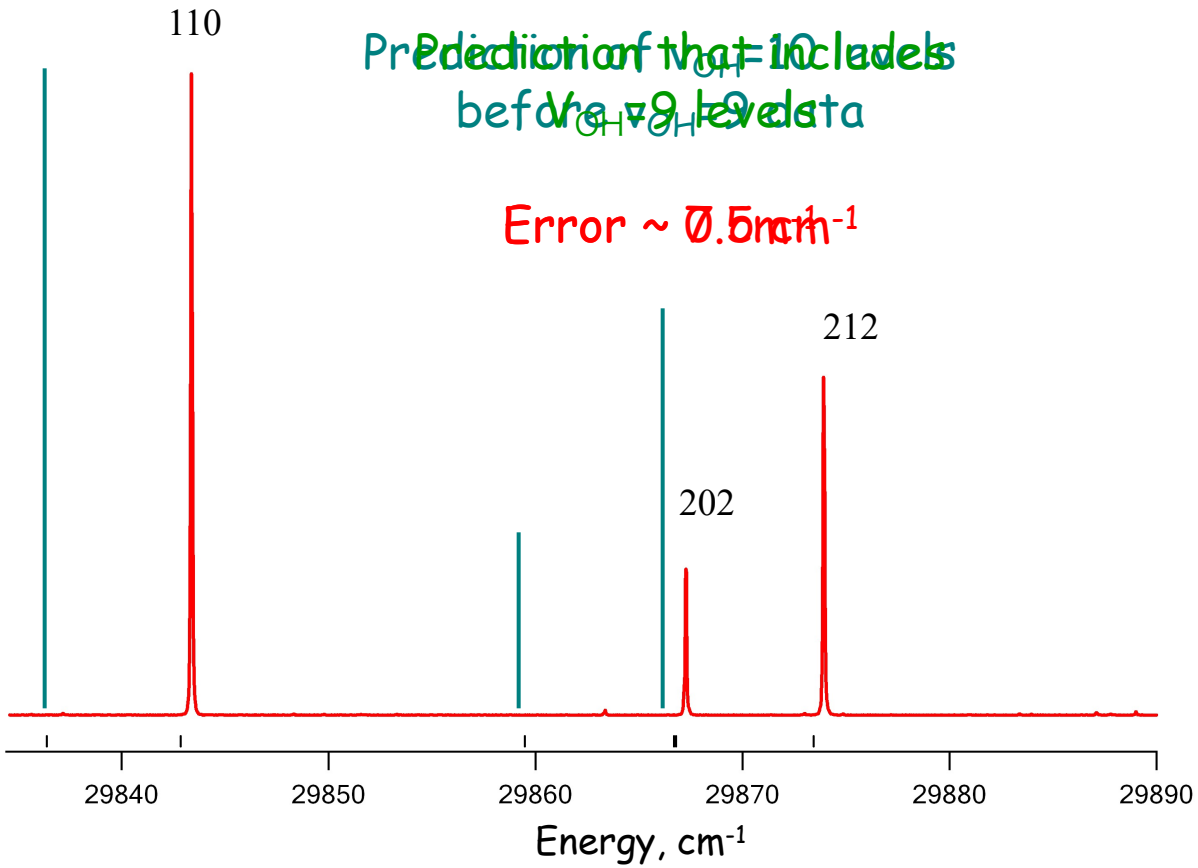
1. Gain in excitation efficiency:
   $0.1 * 0.1 = 10^{-2}$ **vs** $10^{-5}$-$10^{-6}$
   (double resonance) (direct excitation)
2. Rotational pre-selection => simpler assignment

# 9th OH-stretch overtone

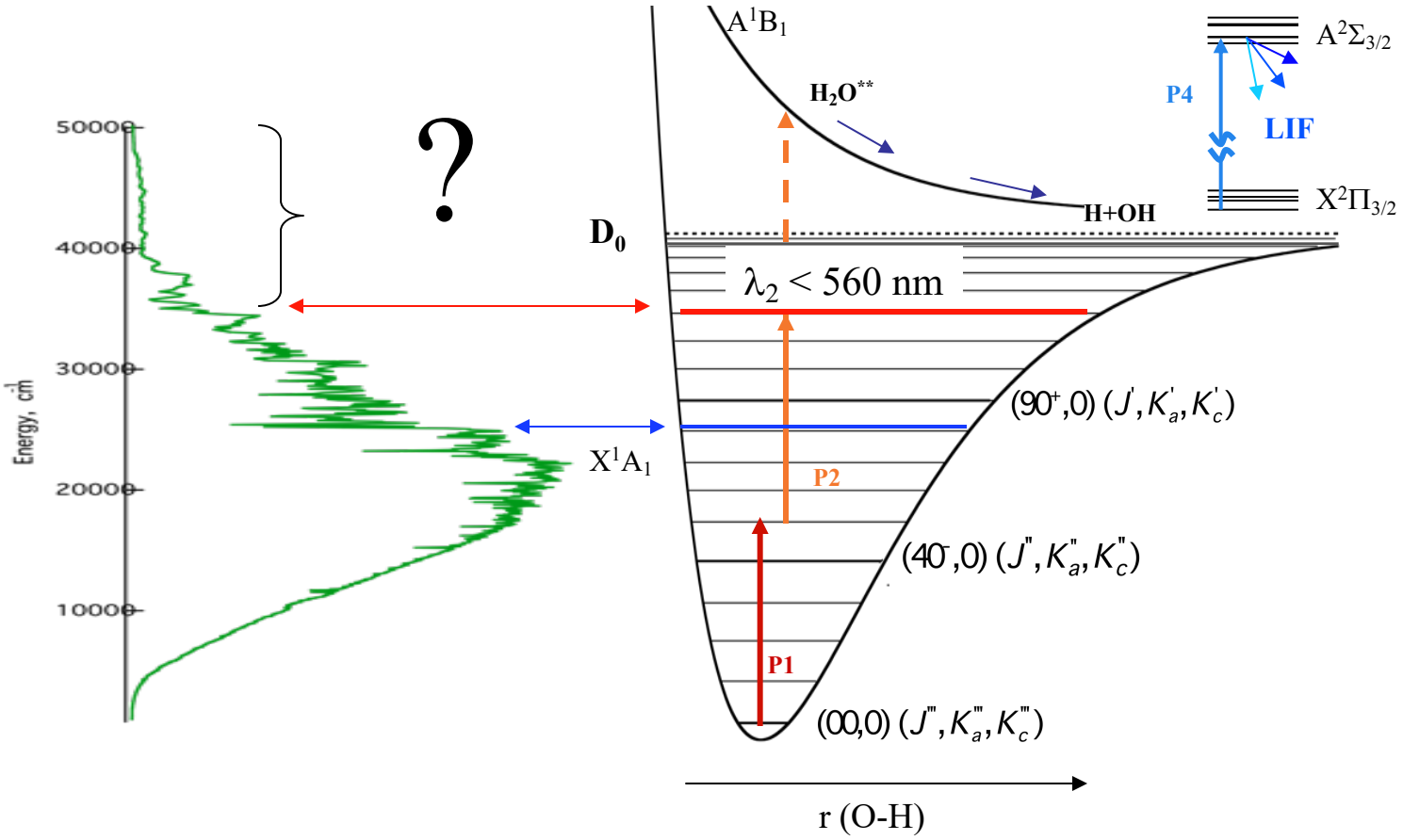



S/N >3000

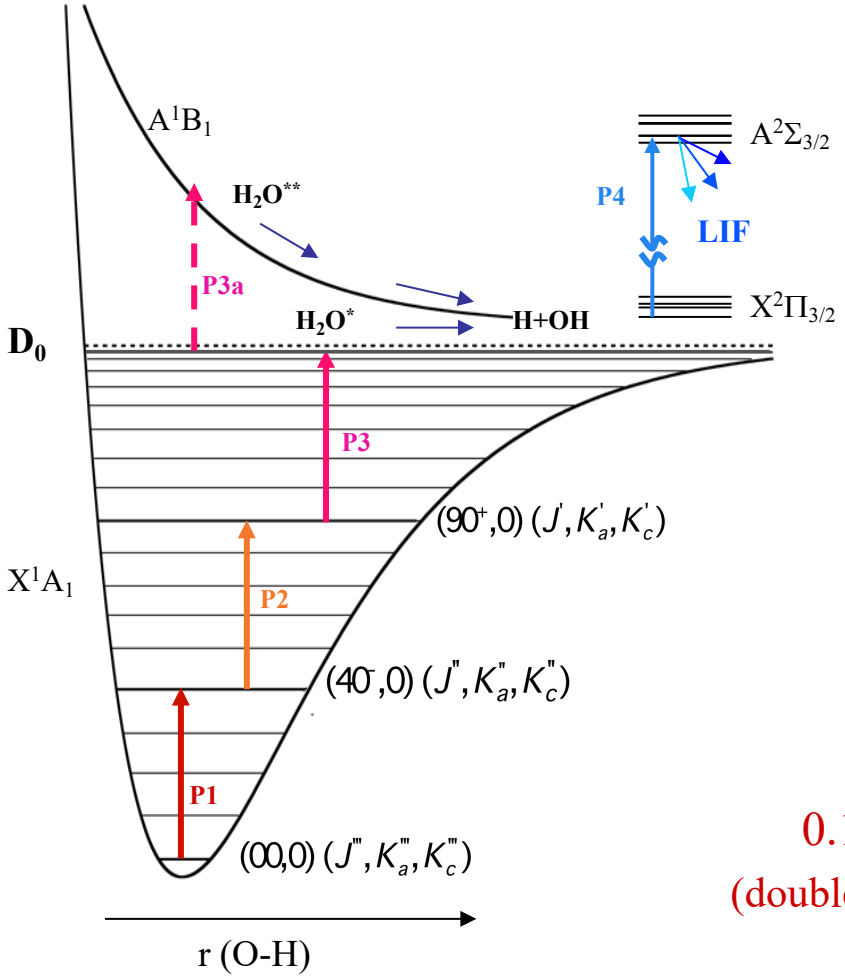
# 9th OH-stretch overtone



# Solar irradiance spectrum



# Triple-Resonance Excitation

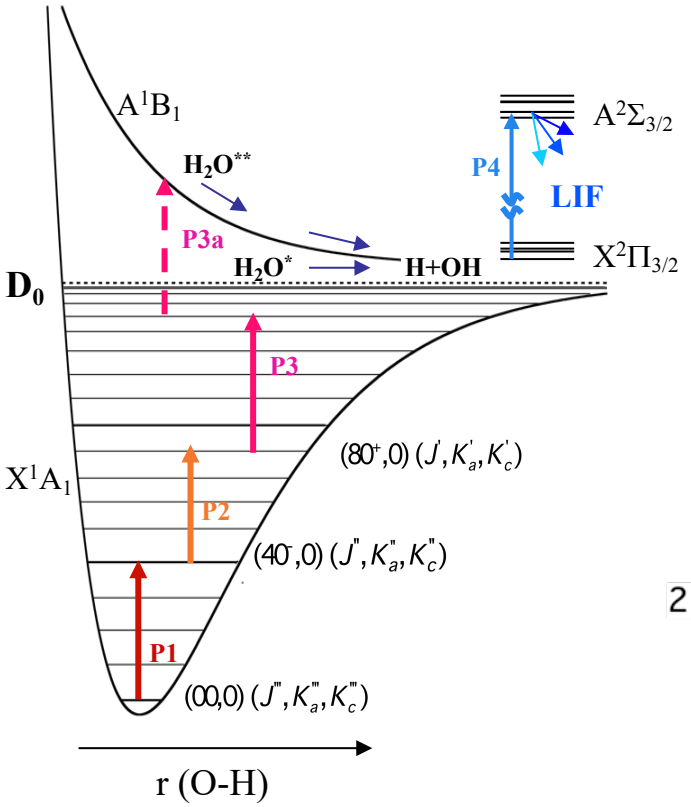


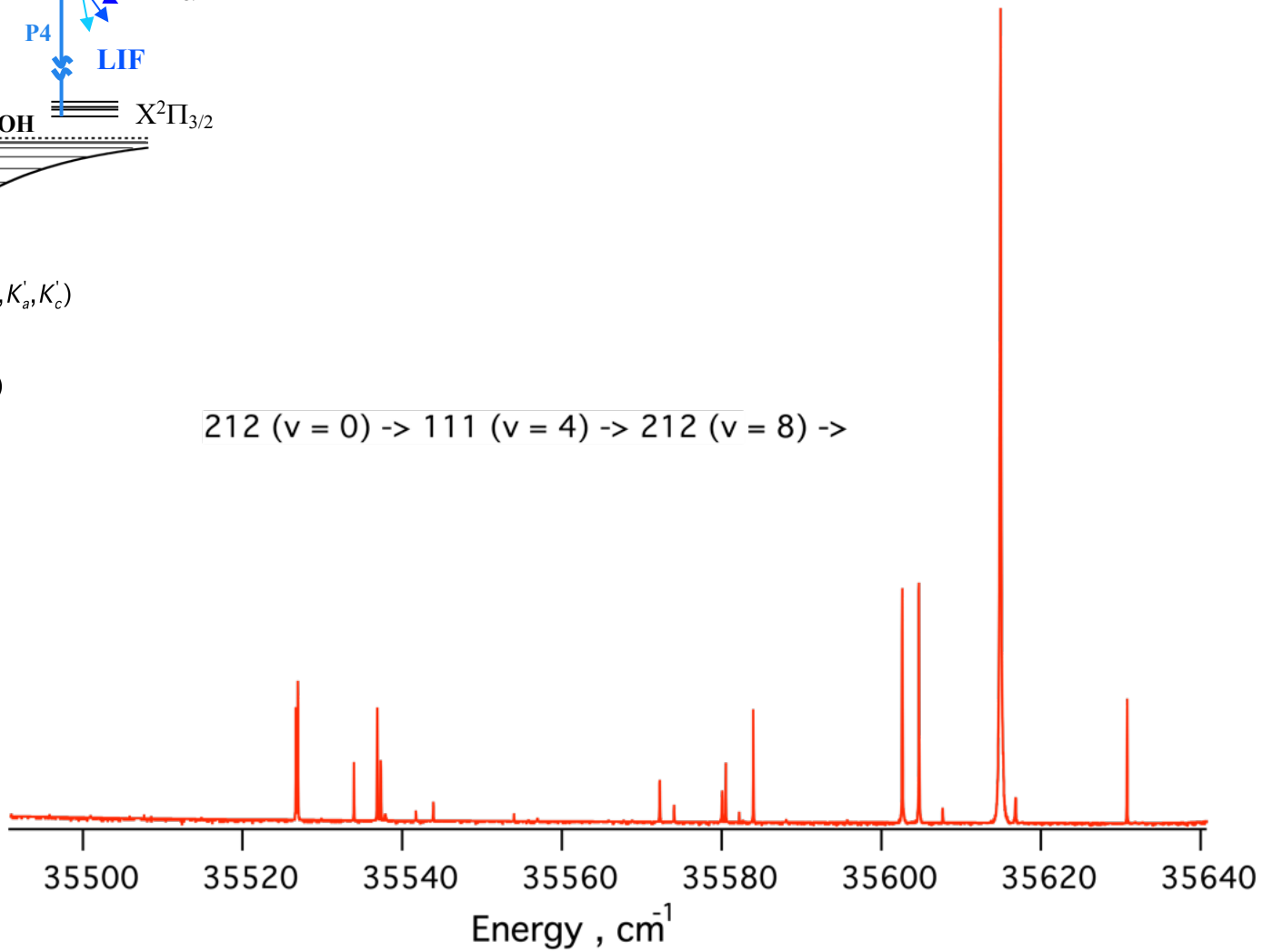

Gain in excitation efficiency:

$0.1 * 0.1 * 0.1 = 10^{-3}$ **vs** $10^{-15}$-$10^{-16}$

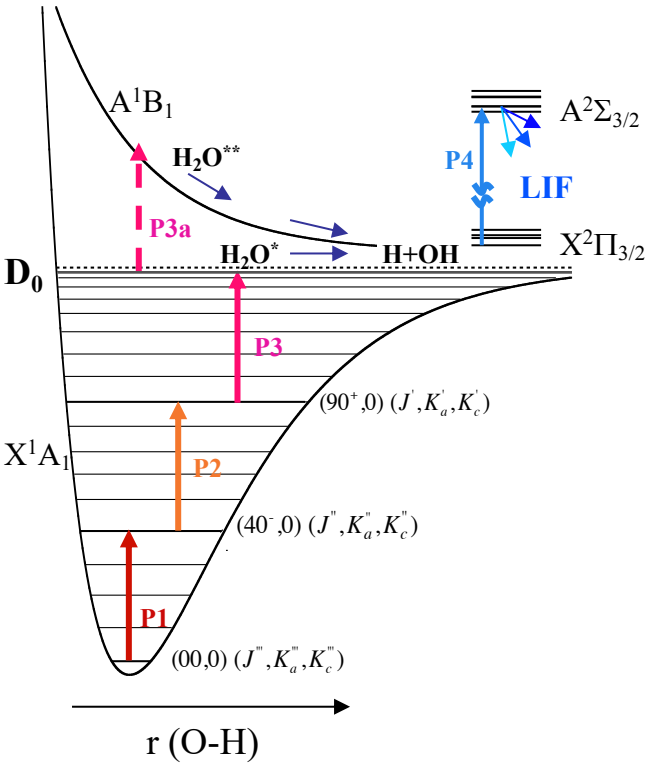
(double resonance) (direct excitation)

# 129th OH-stretch overtone



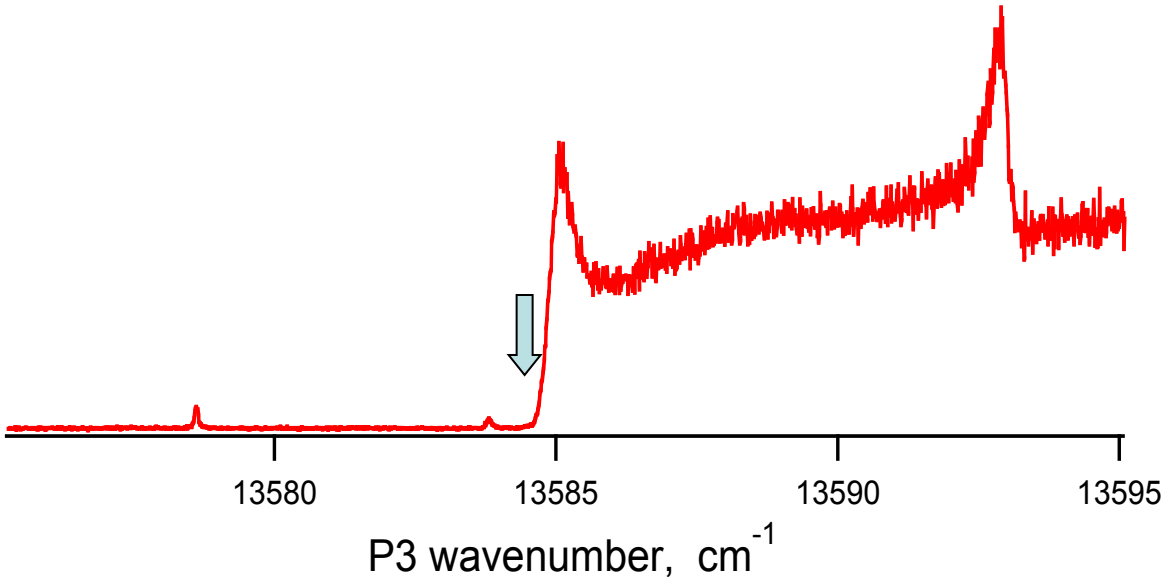



# *Precise determination of $D_0$ in water*




Triple resonance overtone excitation

- Start from rotationaless state of $H_2O$
- Prepare $H_2O$ with no rotational energy
- Detect OH with no rotational energy

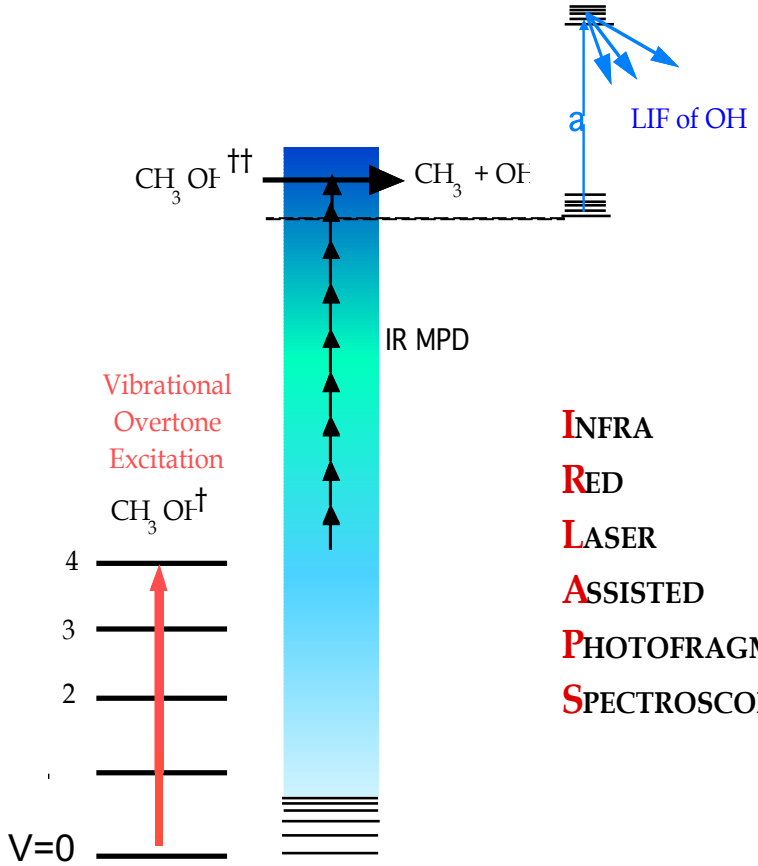



**$D_0$= 41 145.94 ± 0.15 cm$^{-1}$**

**Made in EPFL**

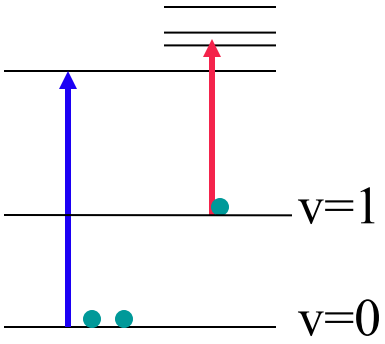
# Photofragmentation

Energy diagram of double resonance overtone IRLAPS:




**I**NFRA
**R**ED
**L**ASER
**A**SSISTED
**P**HOTOFRAGMENT
**S**PECTROSCOPY

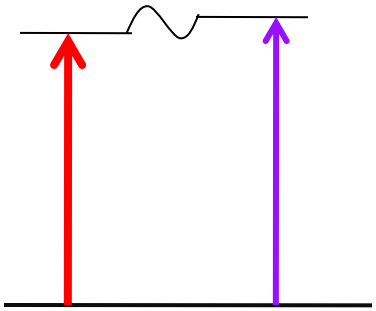
# State-resolved laser Spectroscopy

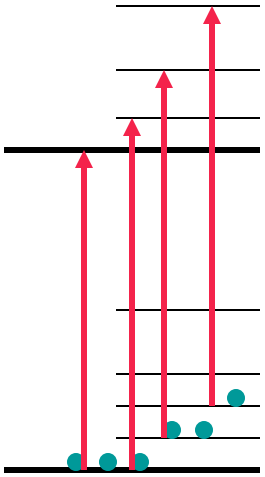



*Spectral congestion:*

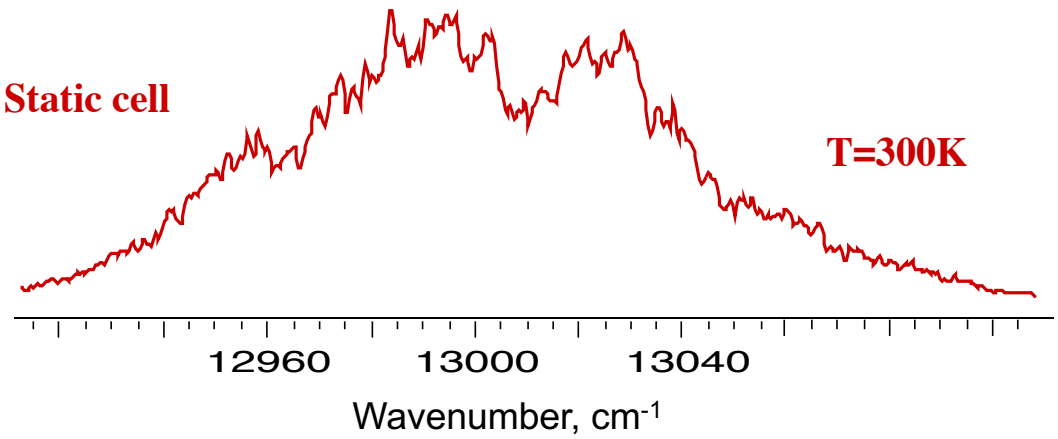
1. Hot bands,
2. Rotational structure,
3. Anharmonic couplings,…

$$E_{vib}(5OH) \approx E_{vib}(4OH + CH)$$





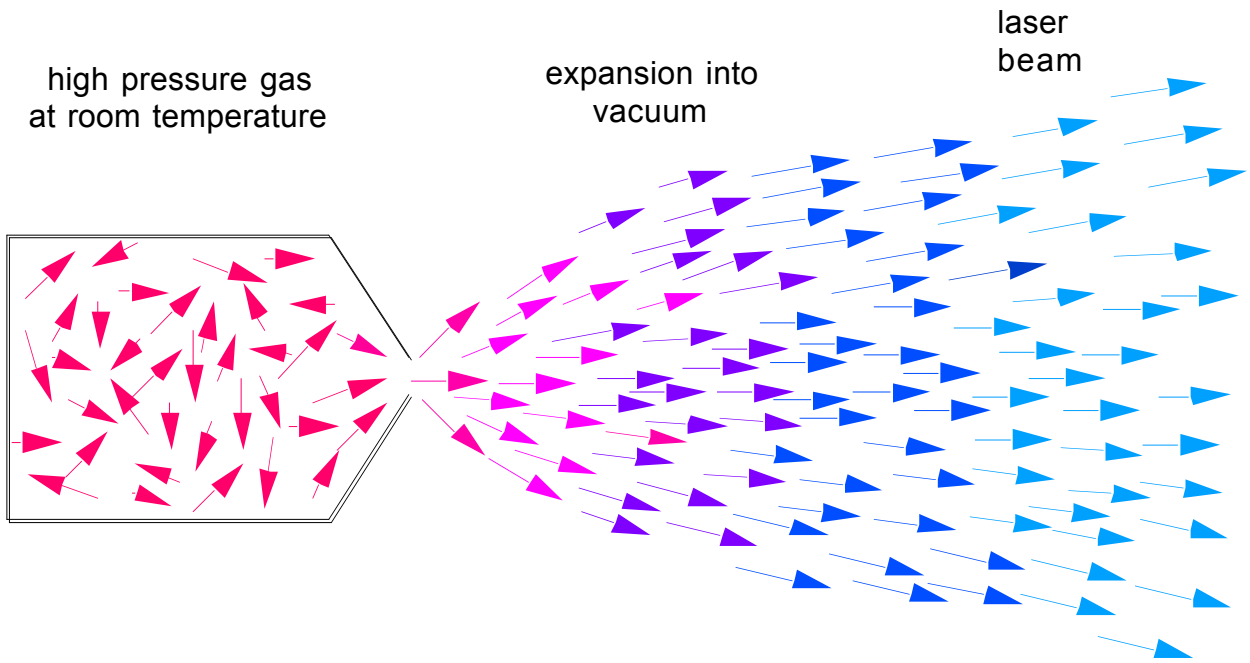
**$CH_3OH$** **$5\nu_1$**

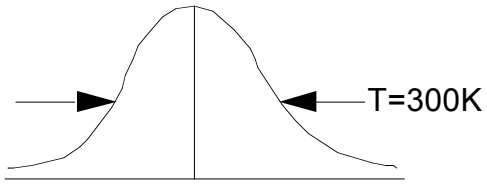


# Spectral Simplification Techniques

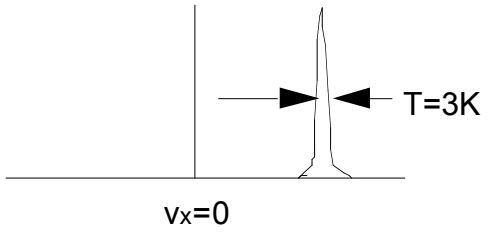
## Supersonic cooling

$T_{translational}$ = 1-3 K
$T_{rotational}$ = 3-15 K
$T_{vibrationoal}$ = 10 - 100 K




speed distribution
in x direction

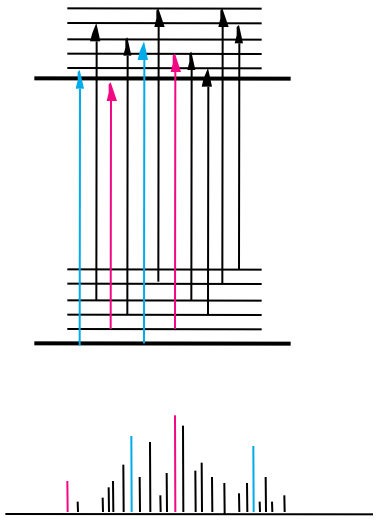



speed distribution
in x direction

# Supersonic cooling

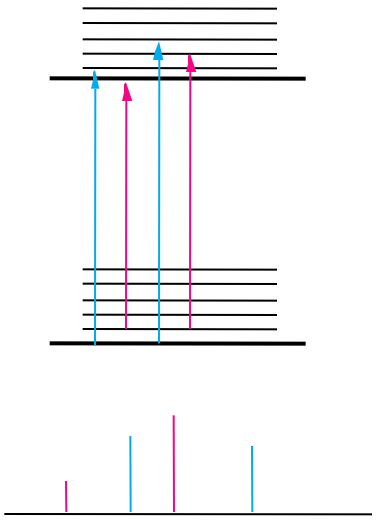
Spectral Simplification via Supersonic Expansion

Room temperature experiment



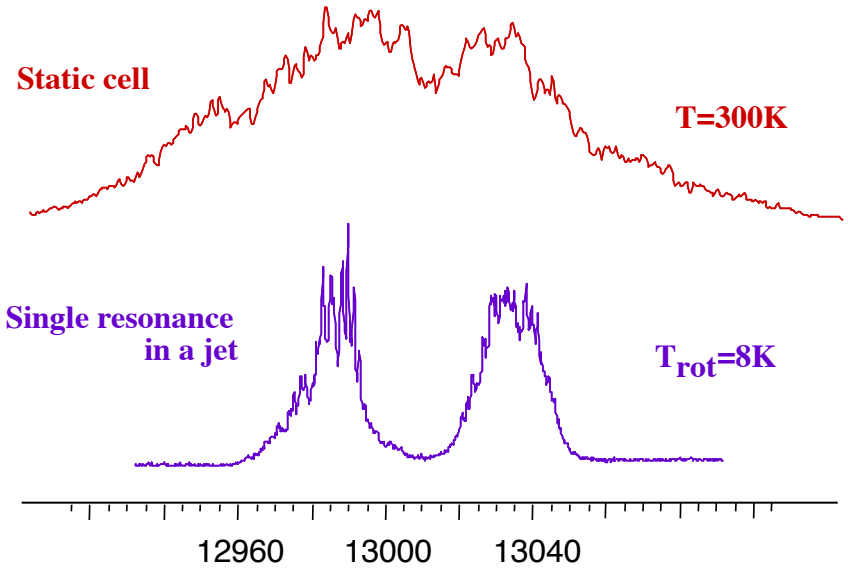
spectrum

In supersonic expansion



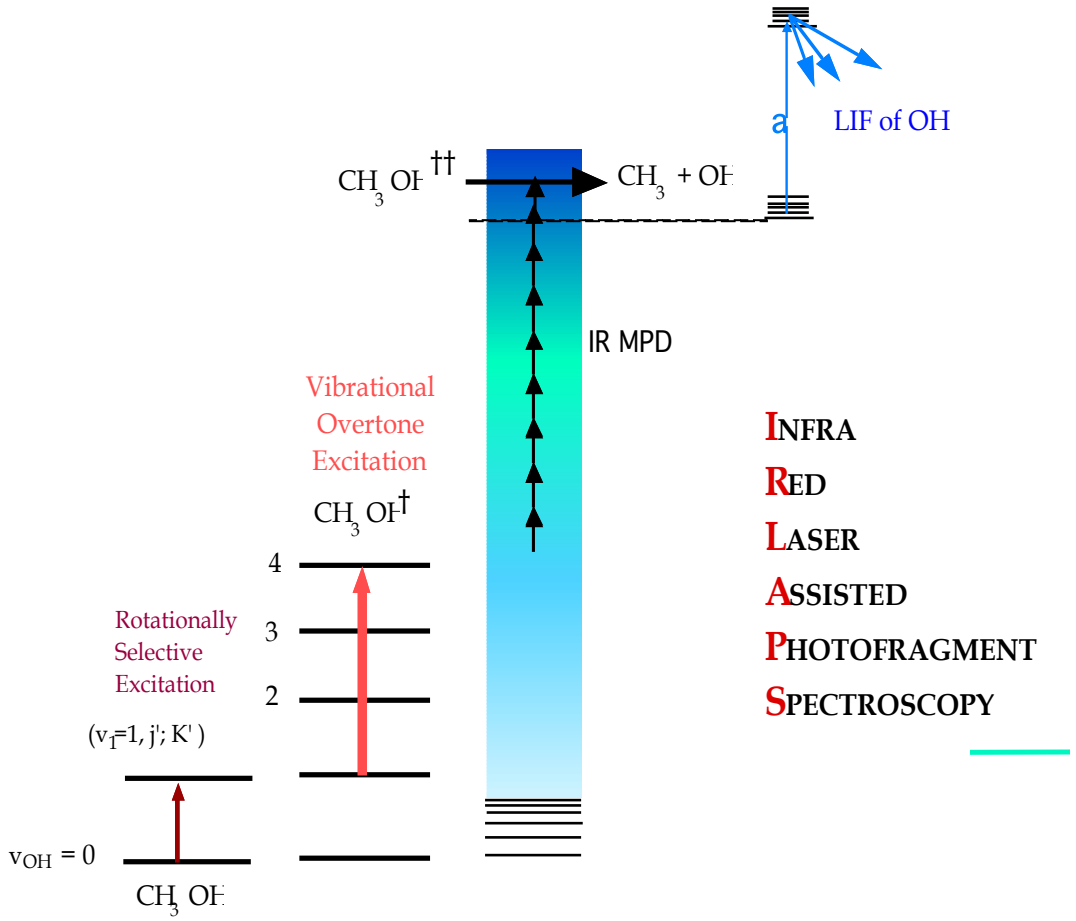
spectrum

$CH_3OH$ $5\nu_1$



# Photofragmentation

Energy diagram of double resonance overtone IRLAPS:

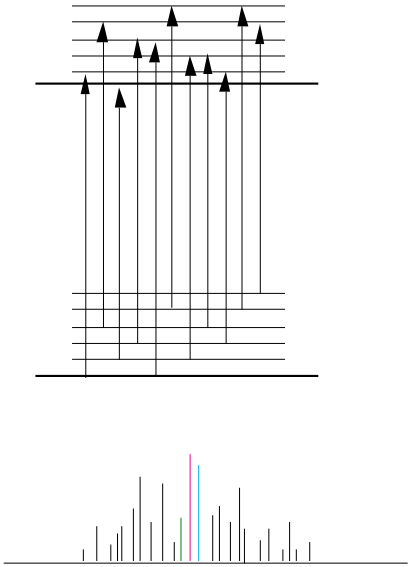



**I**NFRA
**R**ED
**L**ASER
**A**SSISTED
**P**HOTOFRAGMENT
**S**PECTROSCOPY

# Double resonance

## Spectral Simplification via Double Resonance Techniques

Single laser experiment




Double resonance experiment