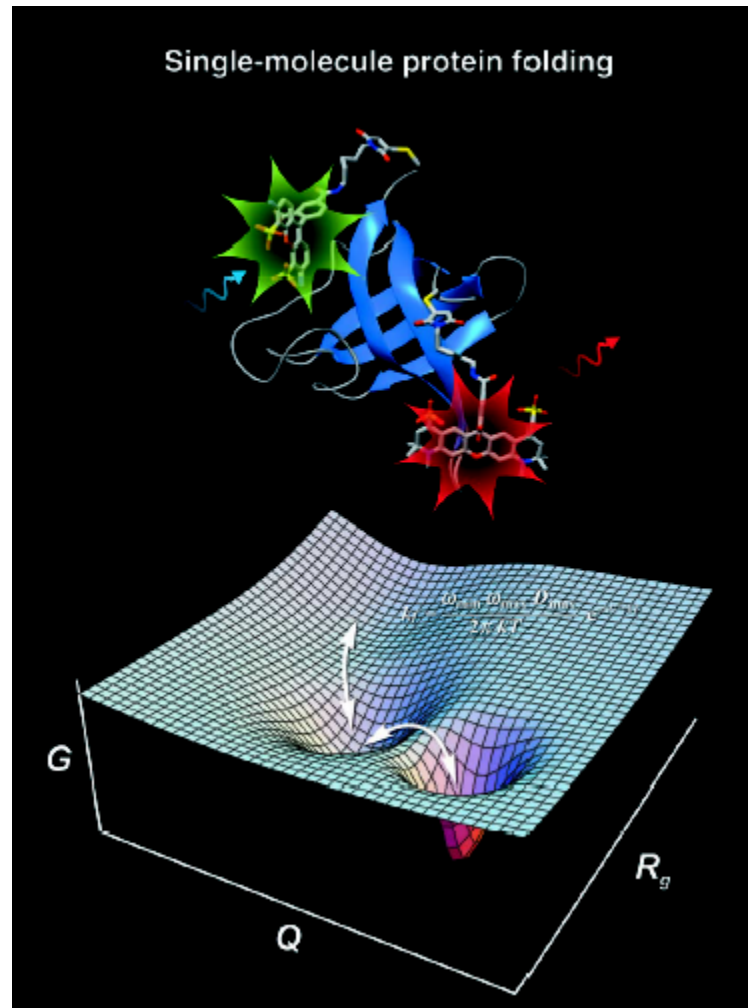


Objective of the course

Lecture 1-2



1: Born – Oppenheimer approximation and various spectroscopies, rotation, vibration, electronic – mention of all spectroscopic tools in this. Microwave, IR, Raman, electronic, ESCA, etc. Breakdown of the approximation.

2. Surface structure, electronic structure, reconstruction, defects

3. Diffraction and spectroscopy to probe surfaces

4-5. Surface chemistry and dynamics

Contents

6. Thermodynamics of surfaces

7. The detection problem in spectroscopy, single molecules, applications in biology

8. Fluorescence and surface enhanced fluorescence – biology - materials

9. Surface enhanced Raman and single molecule Raman measurements – biology - materials

10. Single molecule spectroscopy and modern research

$$\Psi_{\text{tot}}^i(N), E_{\text{tot}}^i(N) \rightarrow \Psi_{\text{tot}}^f(N, K), E_{\text{tot}}^f(N, K)$$

$\Psi_{\text{tot}}^f(N, K) \rightarrow K^{\text{th}}$ final state of N electron system.

Energy conservation equation.

$$E_{\text{tot}}^i(N) + h\nu = E_{\text{tot}}^f(N, K)$$

$$\Psi_{\text{tot}}(N) = \Psi_{\text{tot}}(r_1, \sigma_1, r_2, \sigma_2 \dots r_N, \sigma_N; R_1, R_2 \dots R_P)$$

Nuclear coordinates can be neglected in the resolution scale of electron spectroscopy. In the non-relativistic limit, the Hamiltonian in electrostatic units,

$$\hat{H}_{\text{tot}} = \underbrace{\hbar^2/2m \sum_{i=1}^N \nabla_i^2}_{\text{e-kinetic}} - \underbrace{\sum_{i=1}^N \sum_{l=1}^P Z_l e^2/r_{il}}_{\text{e-n attraction}} + \underbrace{\sum_{i=1}^N \sum_{j>i}^N e^2/r_{ij}}_{\text{e-e repulsion}}$$

$$+ \underbrace{\sum_{l=1}^P \sum_{m>l}^P Z_l Z_m e^2/r_{lm}}_{\text{n-n repulsion}} - \underbrace{\hbar^2/2 \sum_{l=1}^P \nabla_l^2 / M_l}_{\text{Nuclear kinetic}}$$

M – electron mass, Z_l charge of l^{th} nucleus $r_{il} = |r_i - R_l|$, $r_{ij} = |r_j - r_i|$,
 $R_{lm} = |R_l - R_m|$, M_l – mass of l^{th} nucleus.

The total wave function must satisfy the time independent Schrodinger equation,

$$\hat{H}_{\text{tot}} \Psi_{\text{tot}}(\mathbf{N}) = E_{\text{tot}}(\mathbf{N}) \Psi_{\text{tot}}(\mathbf{N})$$

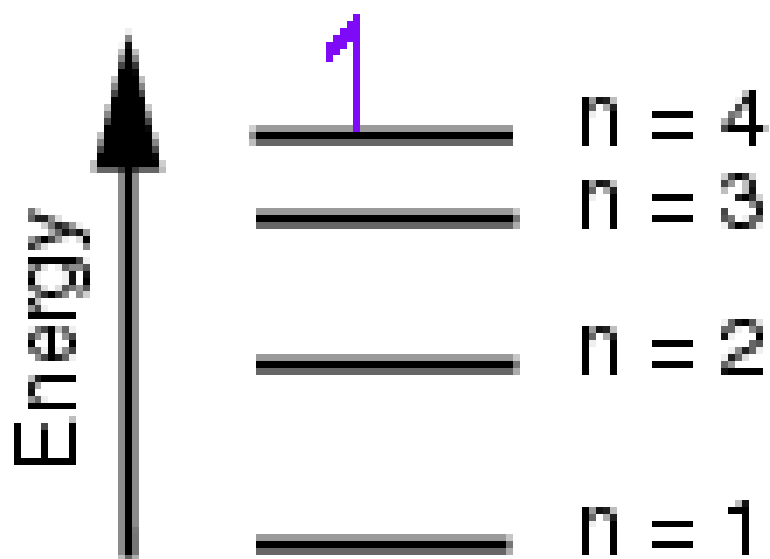
Bohn-oppenheimer approximation permits separation of the total wave function into a product of electronic and nuclear parts.

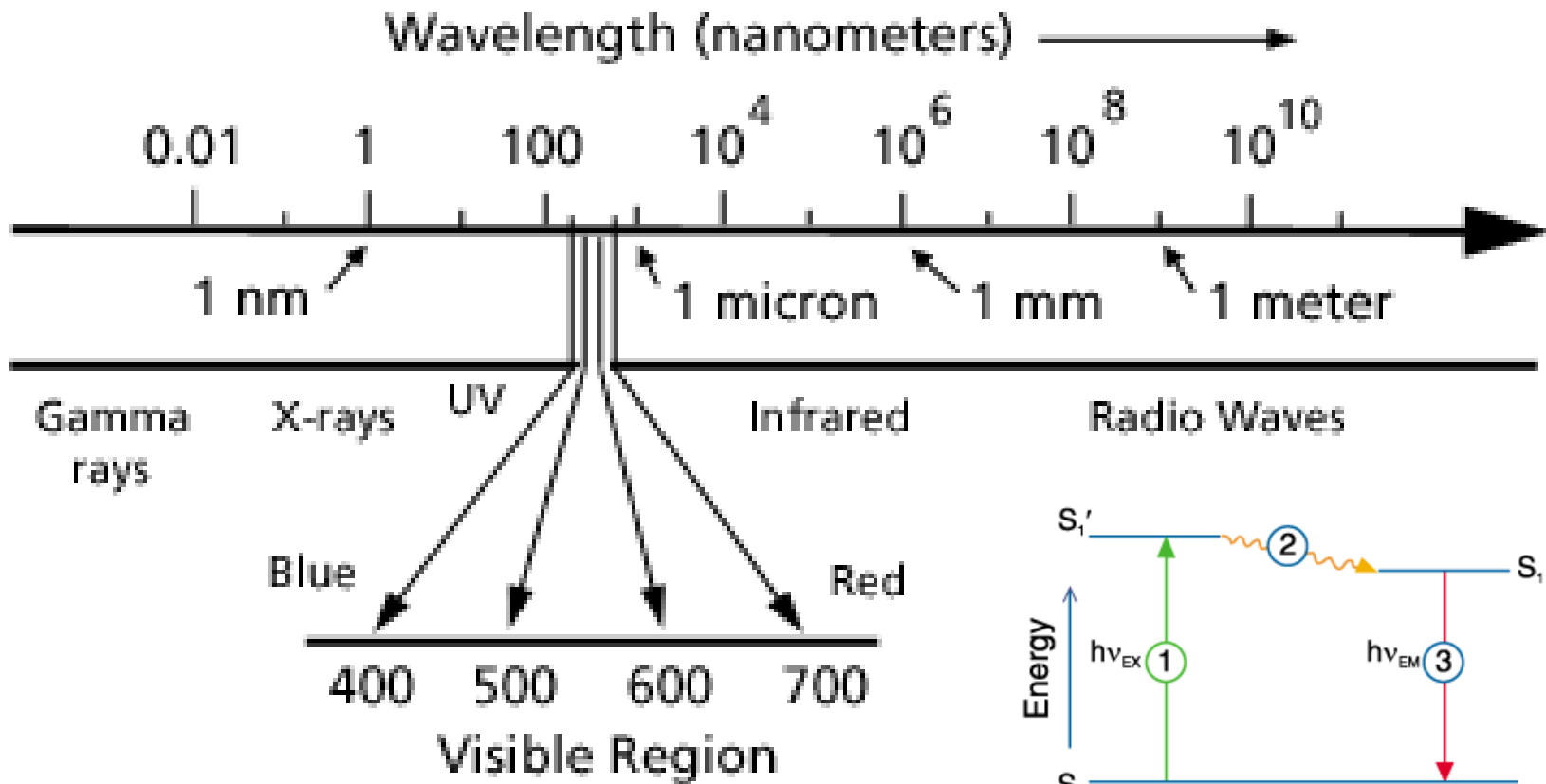
$$\Psi_{\text{tot}}(r_1 \dots r_N; R_1 \dots R_p) = \Psi(r_1, \sigma_1 \dots r_N \sigma_N) \Psi_{\text{nuc}}(R_1 \dots R_p)$$

$\Psi(\mathbf{N})$, the electronic wave function depends on $R_1 \dots R_p$ parametrically through nuclear-nuclear coulombic repulsion.

$$E^{\text{tot}}(\mathbf{N}) = E_e + E_v + E_r + \dots$$

Electronic energy levels





Electromagnetic Spectrum

Jablonski Energy Diagram

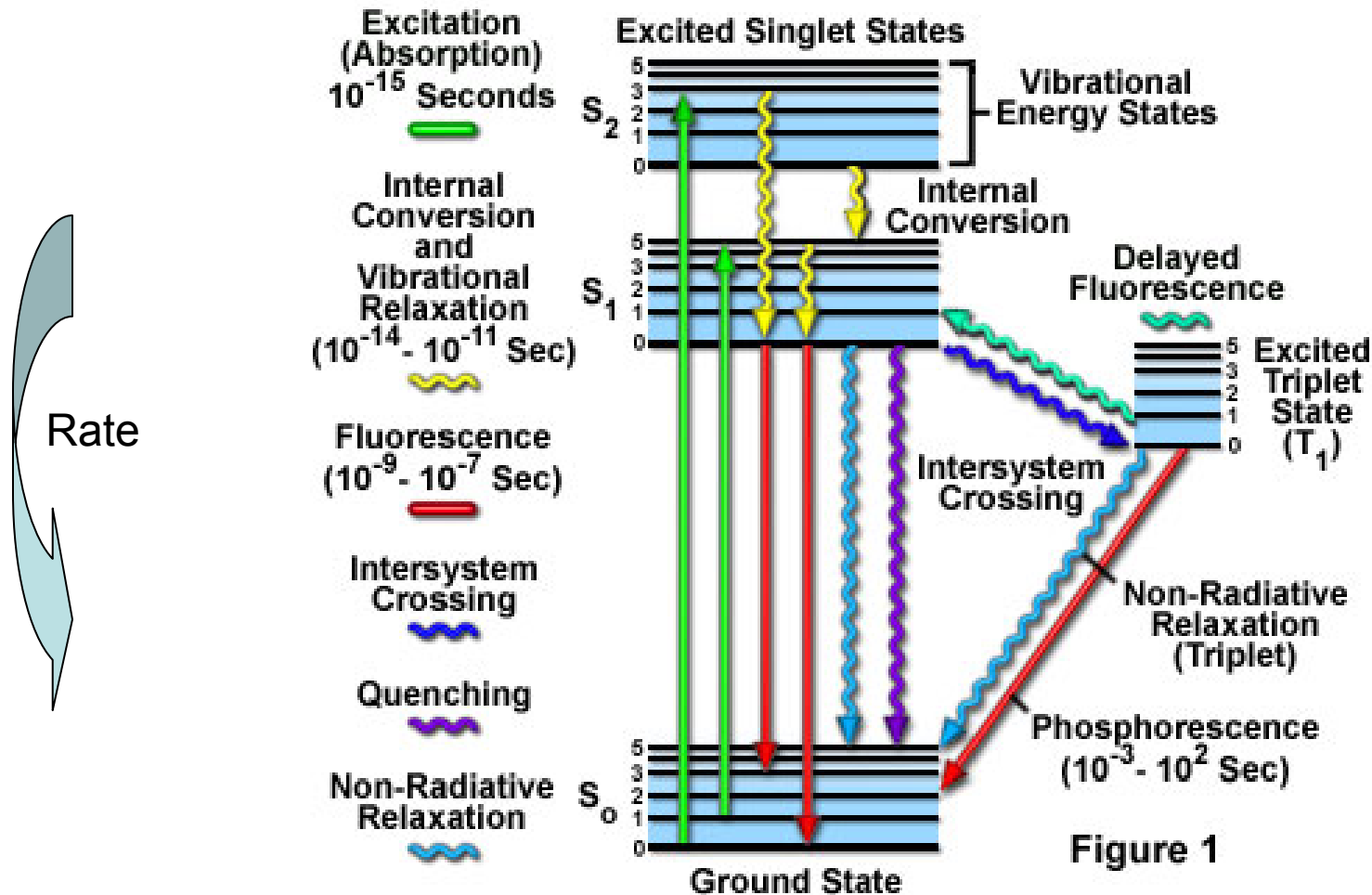
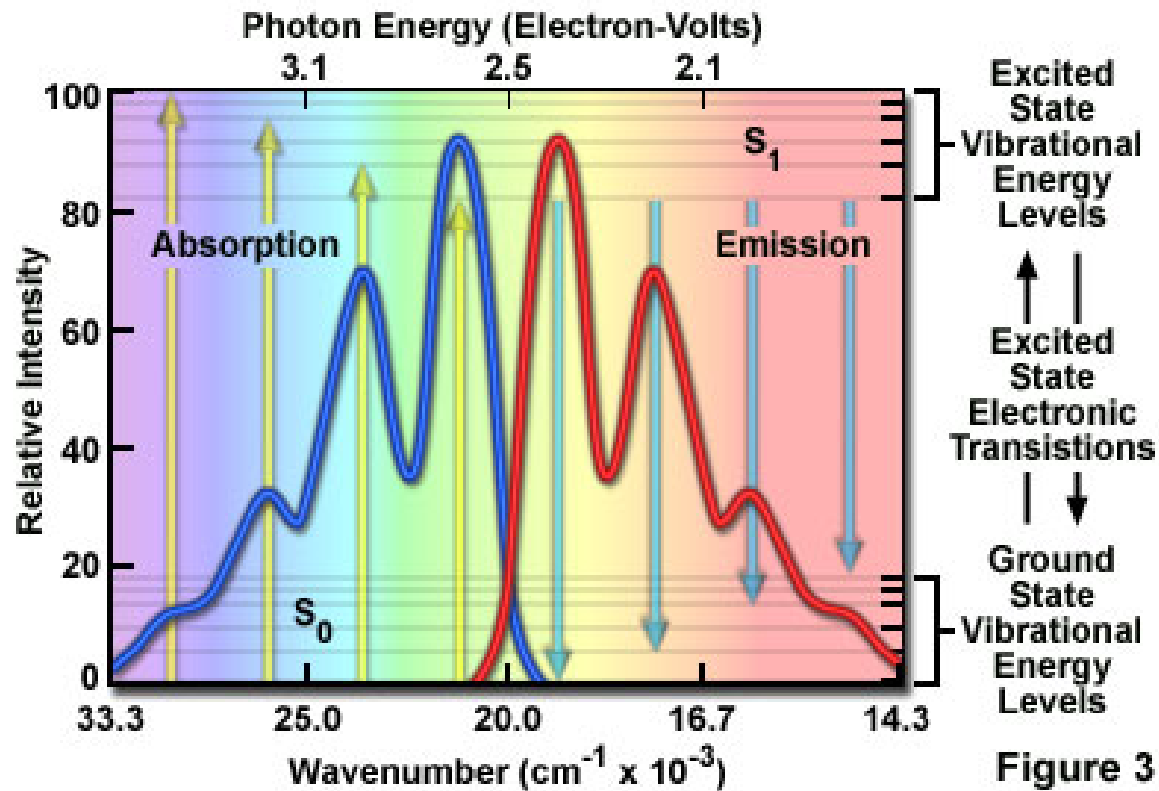


Figure 1

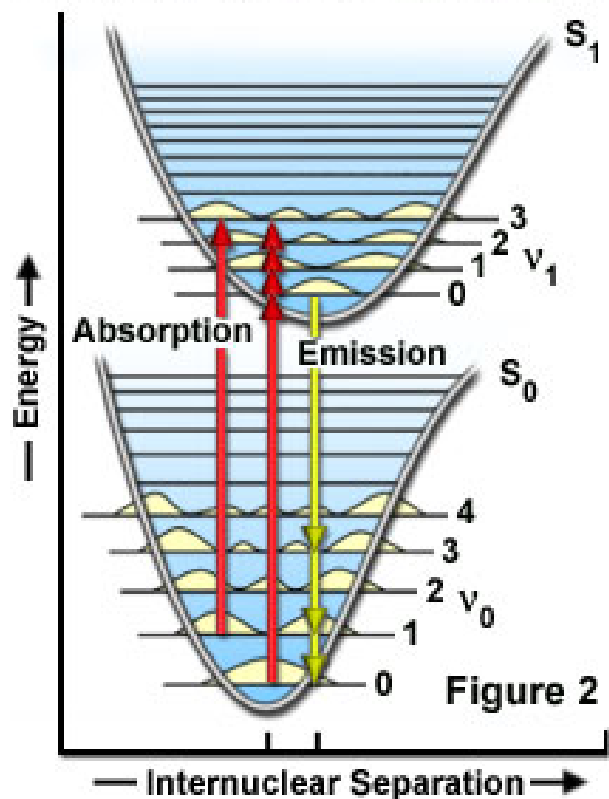
Aleksander Jablonski (1898-1980):

Born in Voskresenovka, Ukraine. Started studying physics at Kharkov University and continued (after the 1st World War at Warsaw under S. Pienkowski. He received his PhD in 1930. In 1935 he suggested the famous diagram, commonly known under his name, which makes it possible to explain both the kinetics and spectra of fluorescence, phosphorescence and delayed fluorescence. In 1931 Jablonski started to work in his second main field of research, namely the pressure broadening of spectral lines. In 1945 he moved to Torun and became the first chairman of the Physics department.

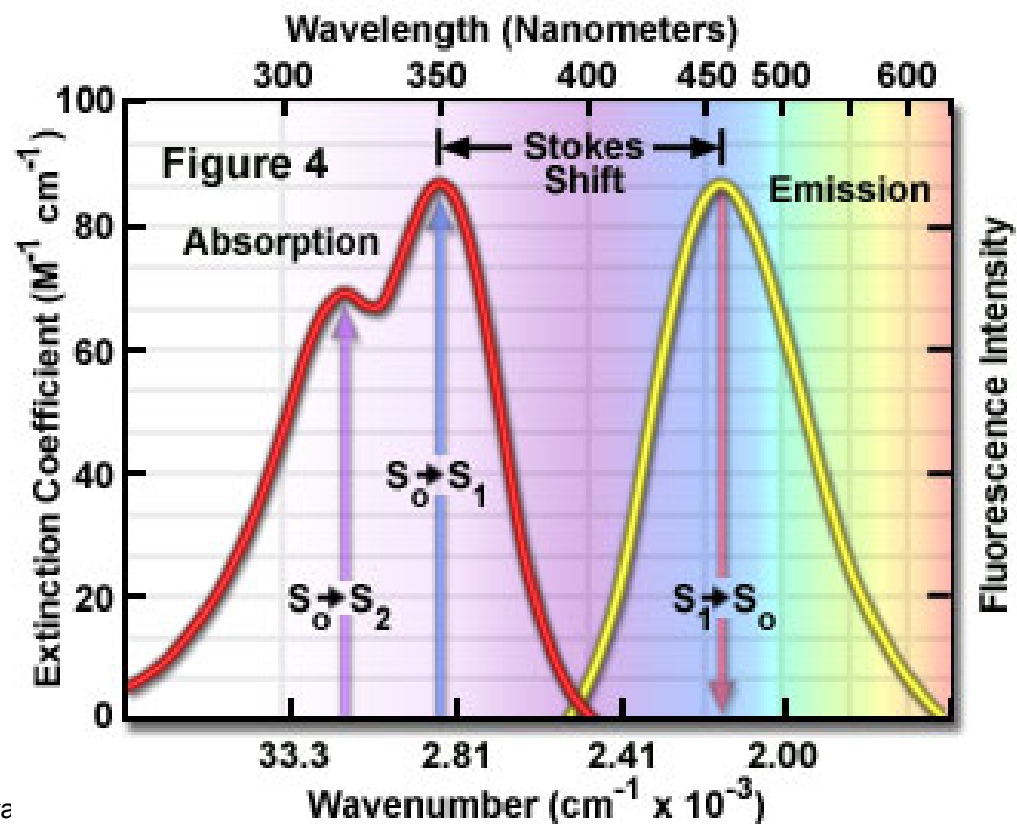
Electronic Absorption and Emission Bands

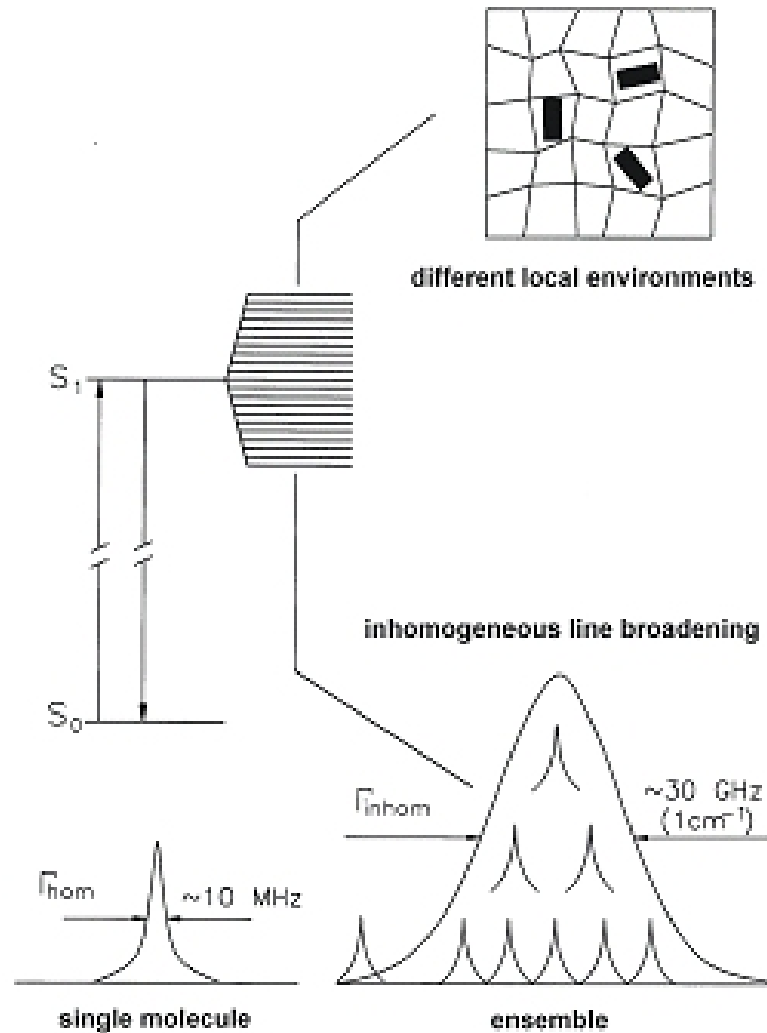


Franck-Condon Energy Diagram



Quinine Absorption and Emission Spectra





Ensemble averaging

