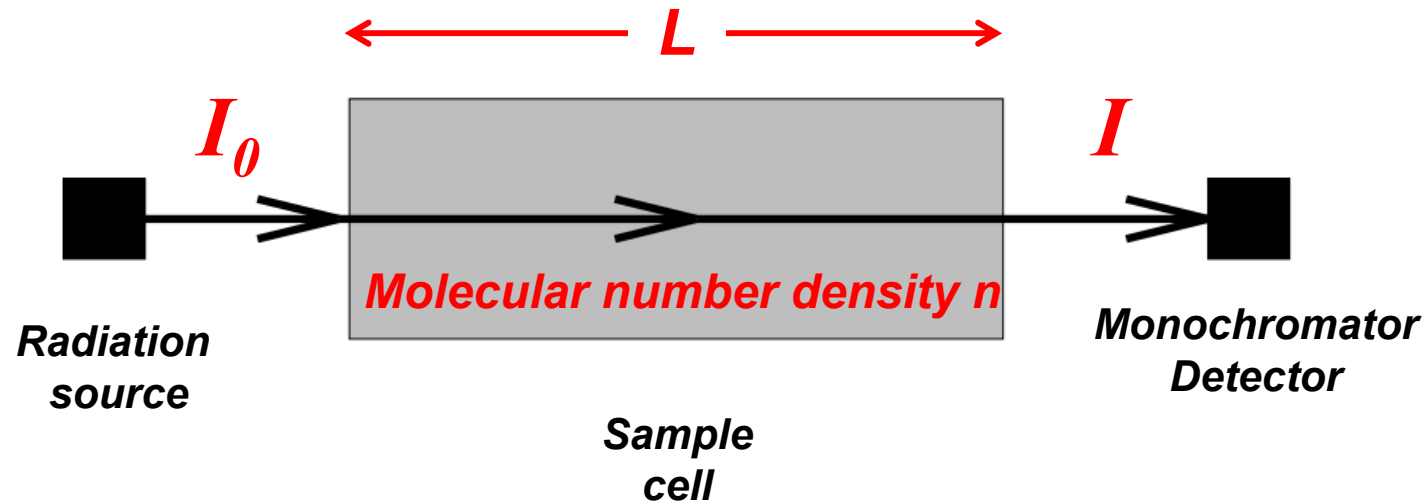


Basic quantitative spectroscopy

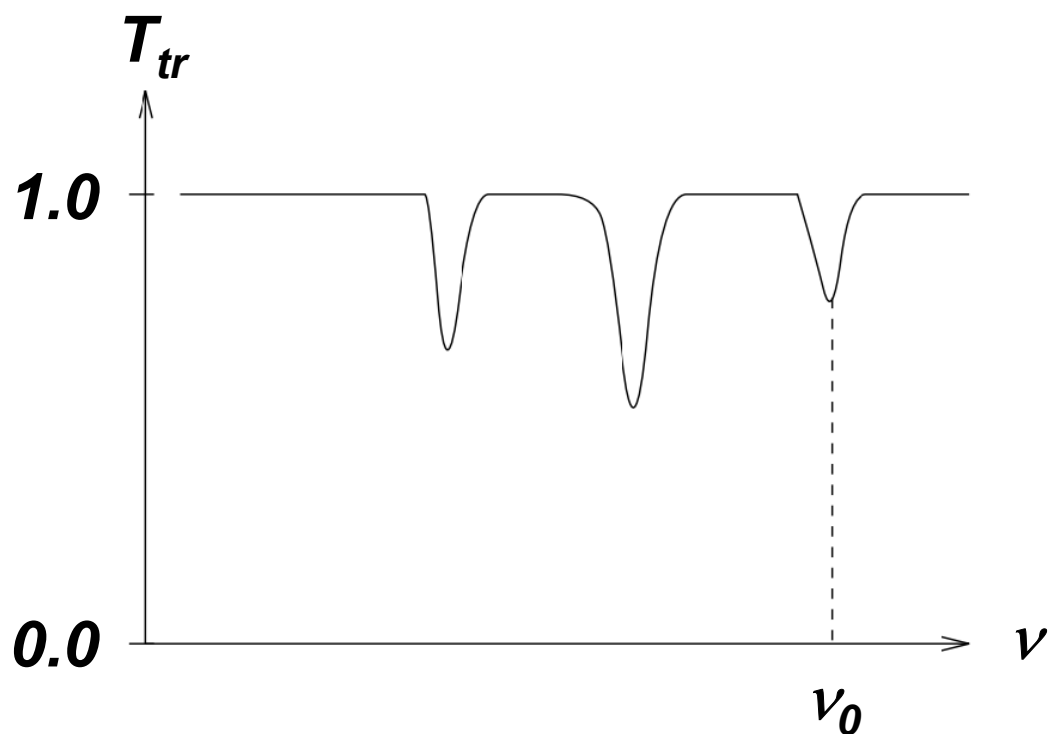


Lambert-Beer law:

$$\text{Transmittance } T_{\text{tr}} = \frac{I}{I_0} = \exp(-nL\epsilon(\nu))$$

$\epsilon(\nu)$: Absorption coefficient

Transmission spectrum



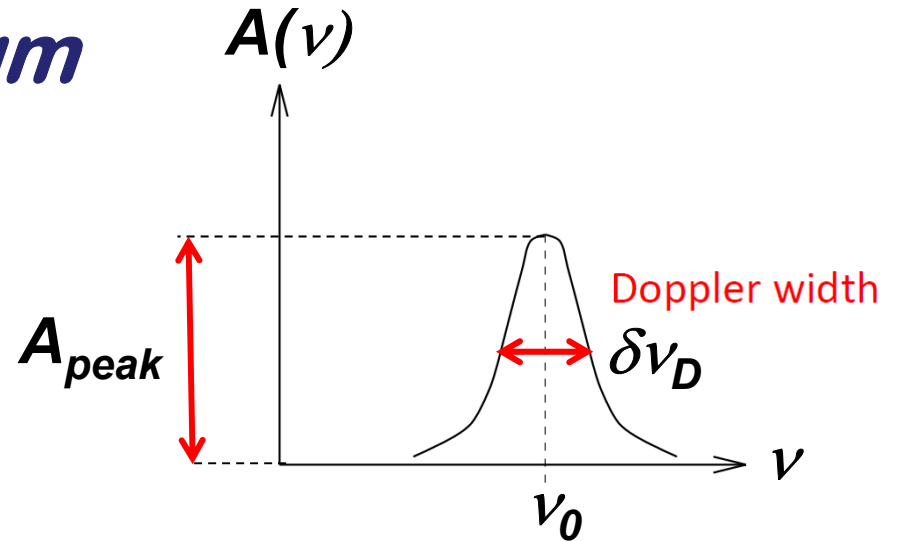
Absorbance

$$A = -\ln(T_{tr}) = -\ln\left(\frac{I}{I_0}\right) = nL\varepsilon$$

Absorbance spectrum

$$A = -\ln(T_{\text{tr}}) = -\ln\left(\frac{I}{I_0}\right) = nL\varepsilon$$

$$\varepsilon = A/(nL)$$



Basic CES equation

$$A_{\text{peak}} = L\alpha_{\text{peak}}(T) = \frac{nL}{Q} \frac{8\pi^3}{3ch} (1 - e^{-h\nu_0/kT}) S_{ij} \mu^2 e^{-E_l/kT} \sqrt{\frac{\ln(2)}{\pi}} \frac{\nu_0}{\Delta\nu_D}$$

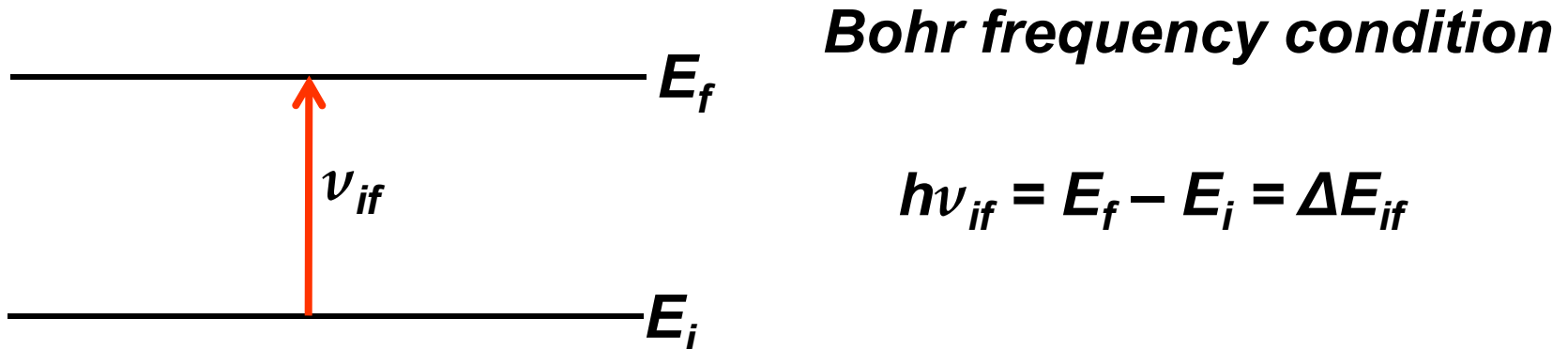
Q: Partition function

E_l : Energy of lower state

T: Temperature

$S_{ij}\mu^2$: Line strength

The positions of spectral lines



Divide by hc to get wavenumber version ($\tilde{\nu} = 1/\lambda = \nu/c$)

$$\tilde{\nu}_{if} = \nu_{if}/c = E_f/hc - E_i/hc = \Delta E_{if}/hc$$

Assignment of upper and lower levels of each spectral line to their position in the energy level ladder is one of the tasks of spectroscopy.

Now to intensities and line shapes

Intensities of spectral lines

Integrated absorption coefficient (weak radiation)

$$I(f \leftarrow i) = \frac{8\pi^3 N_A \nu_{if}}{(4\pi\epsilon_0)3hc^2} F(E_i) R_{\text{stim}}(f \rightarrow i) S(f \leftarrow i) = \int_{\text{Linie}} \epsilon(\tilde{\nu}) d\tilde{\nu}.$$

**Fraction of molecules
In level E_i**

$$F(E_i) = \frac{g_i e^{-E_i/kT}}{\sum_j g_j e^{-E_j/kT}}$$

$$\epsilon = A/(nL)$$

**Resonant
stimulated
emission**

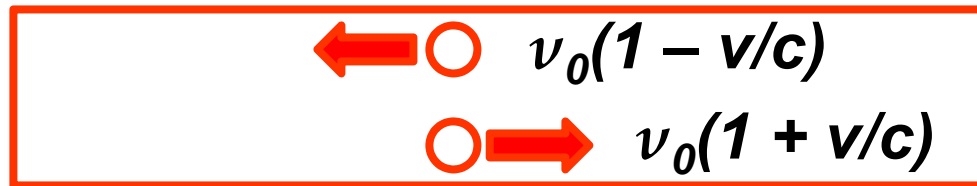
$$R_{\text{stim}}(f \rightarrow i) = 1 - \exp(-h\nu_{if}/kT)$$

Line strength

$$S(f \leftarrow i) = \sum_{A=X, Y, Z} \left| \int \Phi_f^* \mu_A \Phi_i d\tau \right|^2$$

Line shapes

Doppler effect



Where ν_0 is central frequency.

Using $P(v) = 4\pi(M/2\pi kT)^{3/2} v^2 e^{-Mv^2/2kT}$

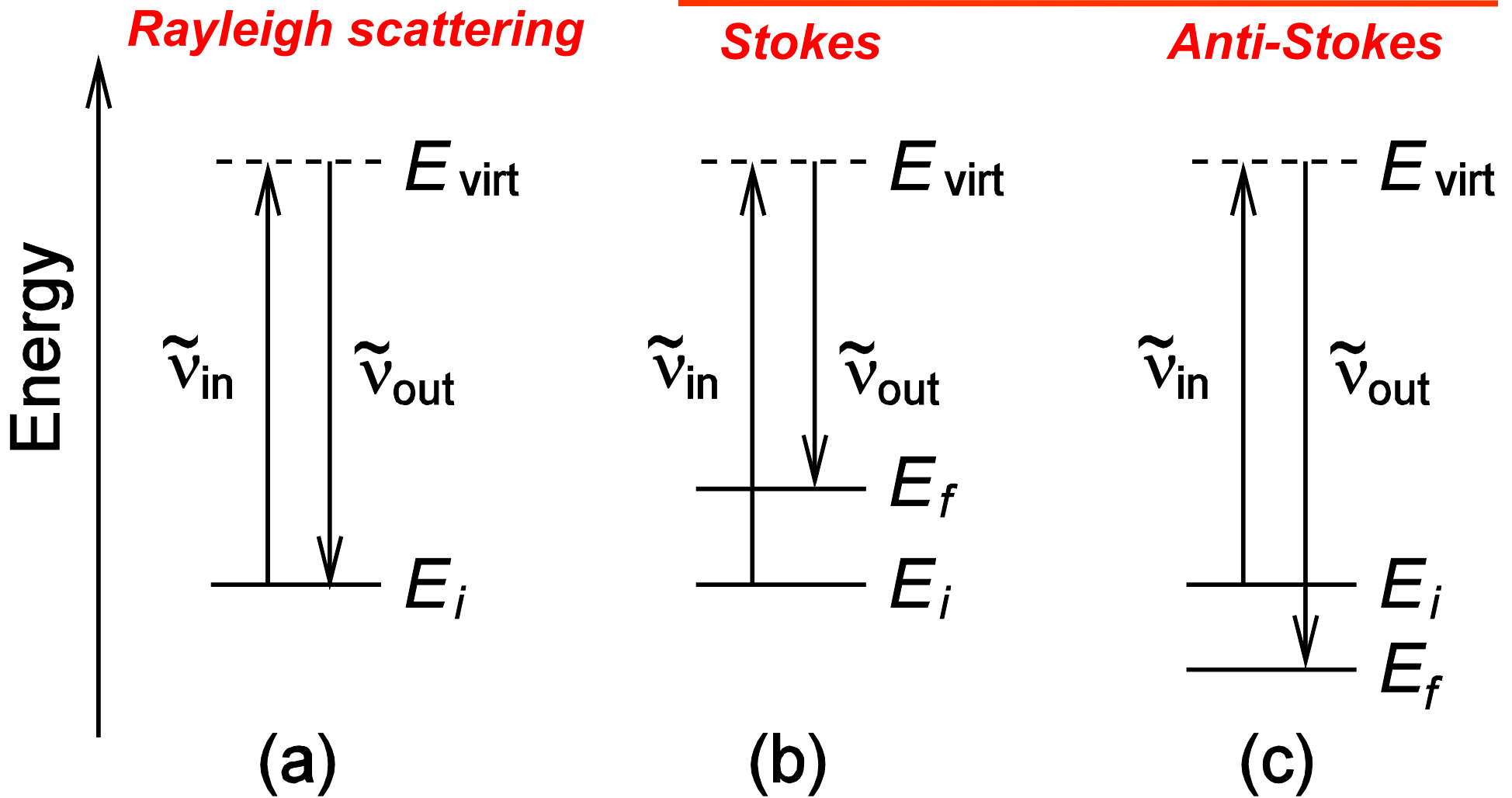
lineshape function is $S(\nu) = S(\nu_0) \exp \left[\frac{Mc^2(\nu - \nu_0)^2}{2kT \nu_0^2} \right]$

Lifetime effect

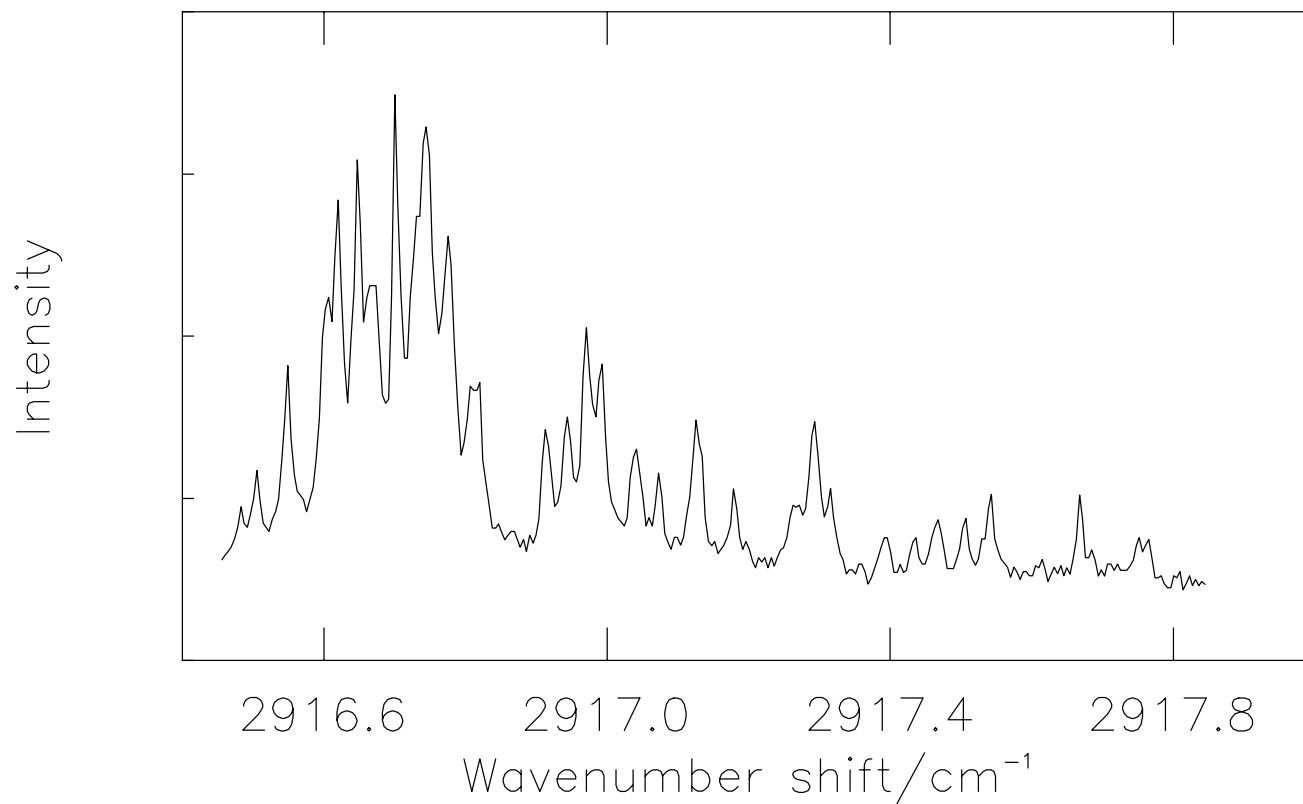
Lineshape function is $S(\nu) = \frac{1}{\pi} \left[\frac{(1/2\pi\tau)}{(\nu - \nu_0)^2 + (1/2\pi\tau)^2} \right]$

Finite τ : Spontaneous emission, collisions, predissociation

Raman scattering (10^{-7})

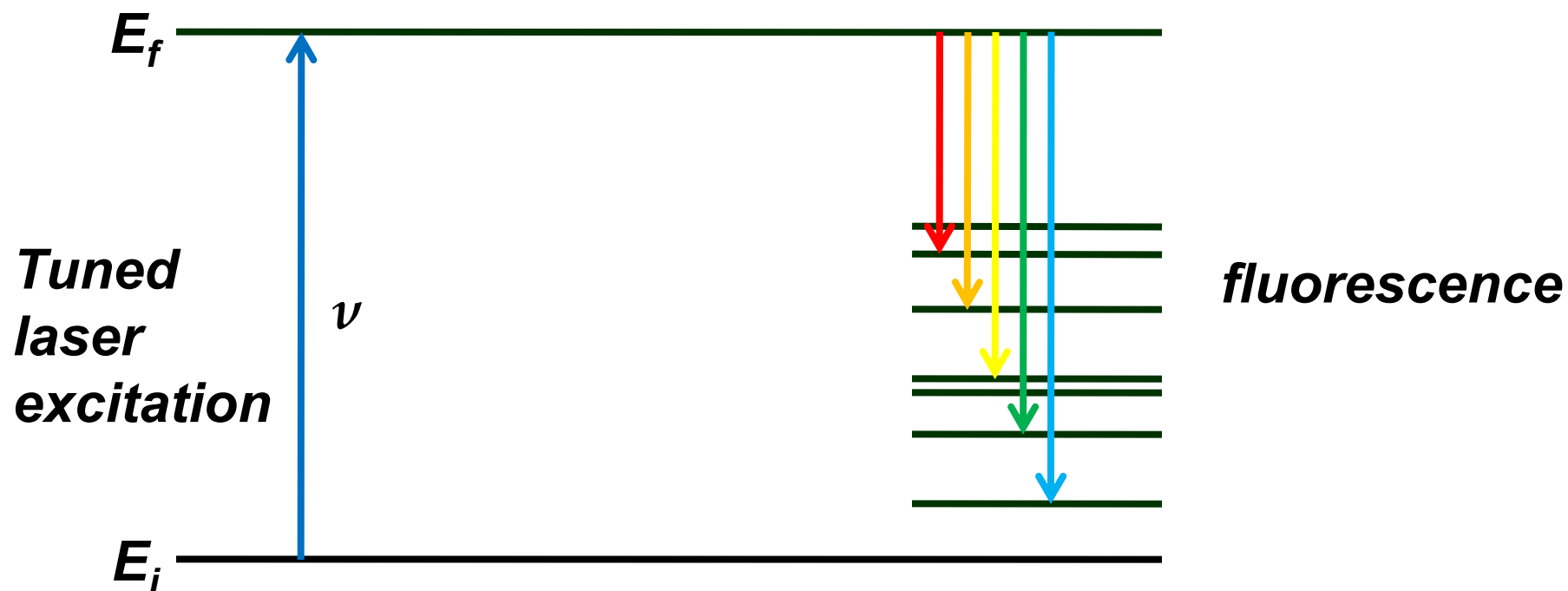


$$\text{Raman shift} = \tilde{\nu}_{\text{in}} - \tilde{\nu}_{\text{out}} = (E_f - E_i)/hc$$



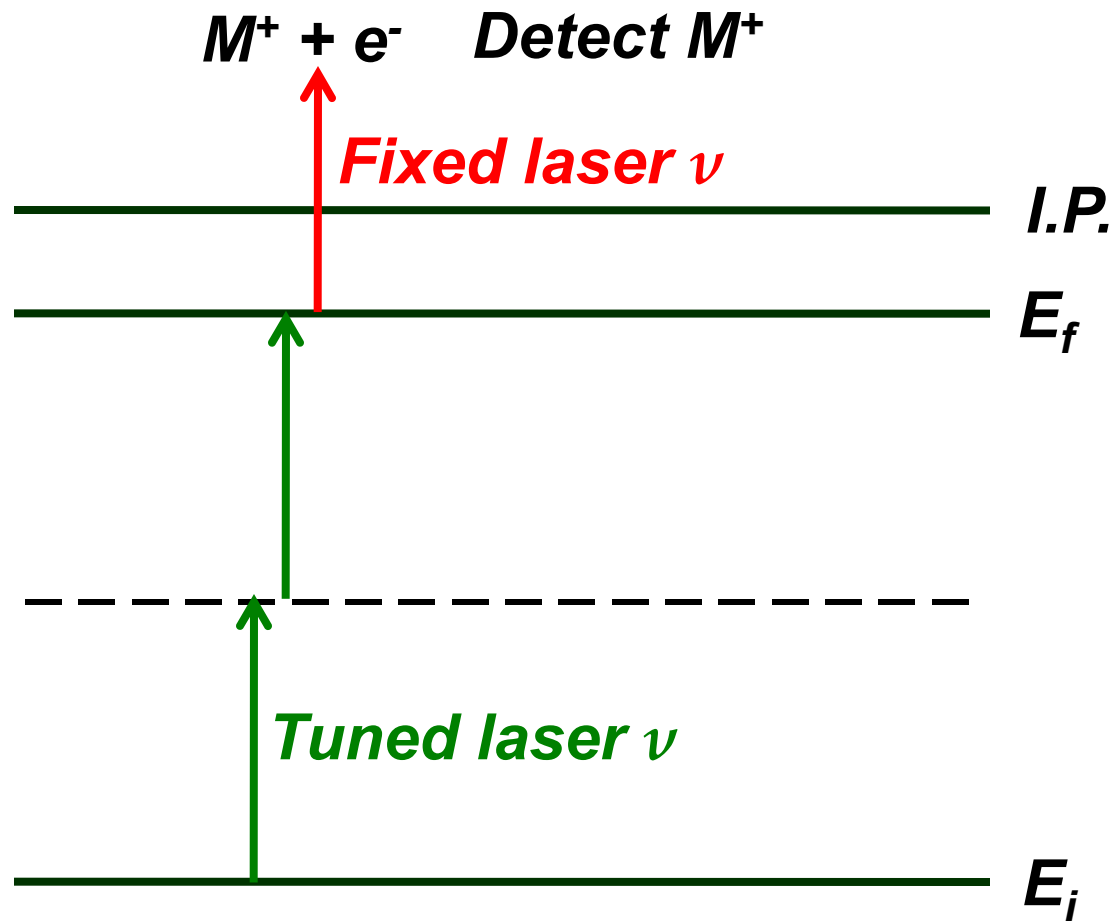
***Part of the Raman spectrum of methane.
Owyong et al., CPL 59, 156 (1978).***

Laser Induced Fluorescence (LIF) Spectroscopy



- 1. Measure total fluorescence as $f(\nu)$ to get E_f***
- 2. Disperse fluorescence to get ground state ΔE .***

Resonance Enhanced Multi-Photon Ionization (REMPI)



$$2h\nu = E_f - E_i \quad (\text{hence 'Resonance'})$$

Quantum Mechanics

QUASAAR Winter School 2008

Electronic Structure Methods

Walter Thiel

Max-Planck-Institut für Kohlenforschung, Mülheim, Germany



A famous statement by Dirac in 1929

Paul Andre Maurice Dirac
1902-1984

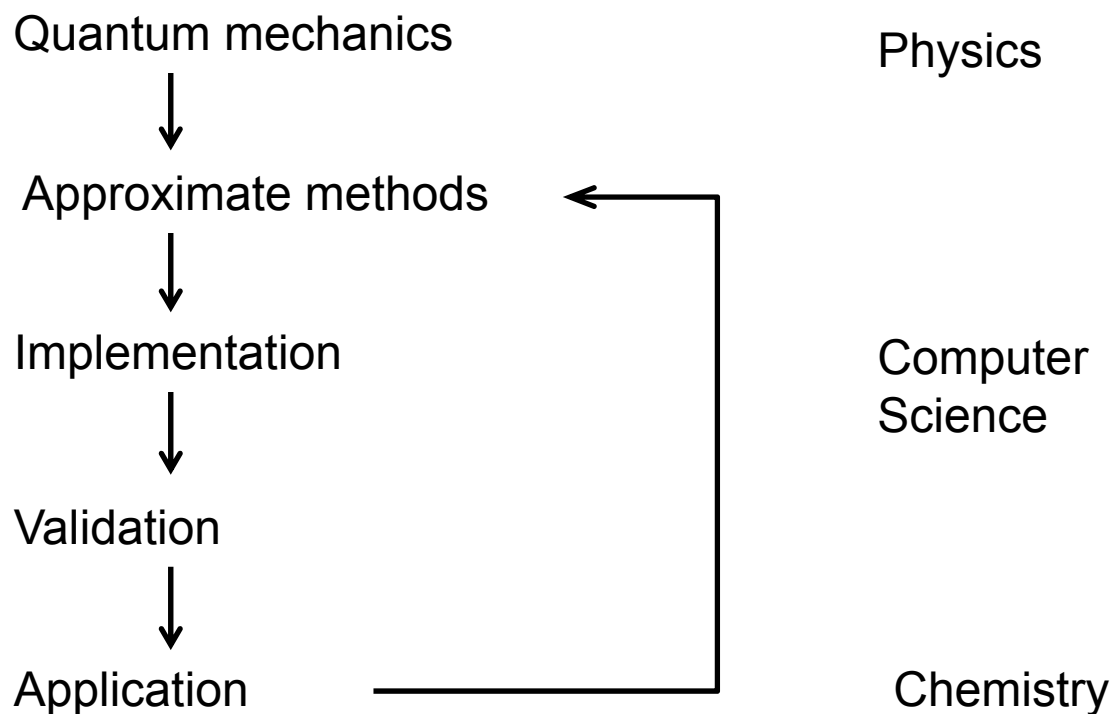


The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known,

and the difficulty is only that the exact application of these laws leads to equations much too complicated to be solved.

P.A.M. Dirac, Proc. Roy. Soc. (London) 123, 714 (1929) .

Quantum chemistry and the vision of Dirac



The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be solved.

Postulates of quantum mechanics

Postulate 1: wavefunctions

Every possible state of a system is described completely by a wave function Ψ , with $\Psi^*\Psi$ giving the probability density distribution in the system.

Postulate 2: operators

Every physical observable A is represented by an operator \hat{A} .

We have: $\hat{\mathbf{r}} = \mathbf{r}$, $\hat{\mathbf{p}} = -i\hbar \frac{\partial}{\partial \mathbf{r}}$ and $\hat{E} = i\hbar \frac{\partial}{\partial t}$.

The operator of other observables are obtained by writing them as classical functions of spatial and linear momentum coordinates and replacing these coordinates by the given operators.

Postulates of quantum mechanics

Postulate 3: eigenvalues and eigenfunctions

The only possible values that can result from measurements of the observable A are the eigenvalues a_n corresponding to the eigenfunctions Ψ_n of the associated operator \hat{A} : $\hat{A}\Psi_n = a_n\Psi_n$

Postulate 4: expectation values

For a system in state Ψ_n , the expectation value $\langle A \rangle$ of an observable corresponding to the operator \hat{A} is defined for a sequence of measurements as:

$$\langle A \rangle = \int \Psi_n^* \hat{A} \Psi_n d\tau$$

One-particle systems (I)

We consider a particle of mass m moving with kinetic energy T in a **time-independent** potential $V(\mathbf{r})$.

Classically, the total energy is:

$$(1) \quad E = T + V(\mathbf{r}) = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) + V(x, y, z)$$

Quantum-mechanically, the associated Hamiltonian \hat{H} is obtained by replacing the spatial and linear momentum coordinates in (1) by the corresponding operators:

$$(2) \quad \hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x, y, z)$$