

Time-dependent quantum mechanics

2

Transition probability

CH: 3-1, 3-2, 3-4 ∂ HB

4, 5 ∂ SR

Time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = [H_0 + V(x, t)] \Psi(x, t)$$

stationary Hamiltonian,
does not depend on time time-dependent perturbation

Stationary states : $H_0 \Phi_n(x) = E_n \Phi_n(x)$

We assume that at $t=0$ the system is
at state Φ_0 : $\Psi(x, 0) = \Phi_0(x)$

Linear combination of stationary states :

$$\Psi(x, t) = \sum_n c_n(t) \Phi_n(x) e^{-iE_n t/\hbar}$$

$$\begin{aligned} i\hbar \frac{\partial \Psi}{\partial t} &= i\hbar \sum_n \left[\dot{c}_n - \frac{i}{\hbar} E_n c_n \right] \Phi_n(x) e^{-\frac{iE_n t}{\hbar}} = \\ &= \sum_n c_n(t) (E_n + V(x, t)) \Phi_n(x) e^{-\frac{iE_n t}{\hbar}} \end{aligned}$$

$\langle \Phi_e |$

$$i\hbar \dot{c}_e = \sum_n e^{i(E_e - E_n) \frac{t}{\hbar}} c_n(t) V_{E_n}(t)$$

First-order time-dependent perturbation theory

Suppose V_{kn} is small (e.g., electric field of light is much weaker than the atomic electric field).

To a first approximation, $c_n(t)$ can be replaced by $c_0(0) = 1$

$$\dot{c}_k^{(1)} = -\frac{i}{\hbar} V_{ko} e^{i\omega_{ko} t}$$

stands for the first order perturbation

$$c_k^{(1)}(t) = c_k(0) - \frac{i}{\hbar} \int_0^t V_{ko}(t') e^{i\omega_{ko} t'} dt'$$

$$c_k(0) = \delta_{ko}$$

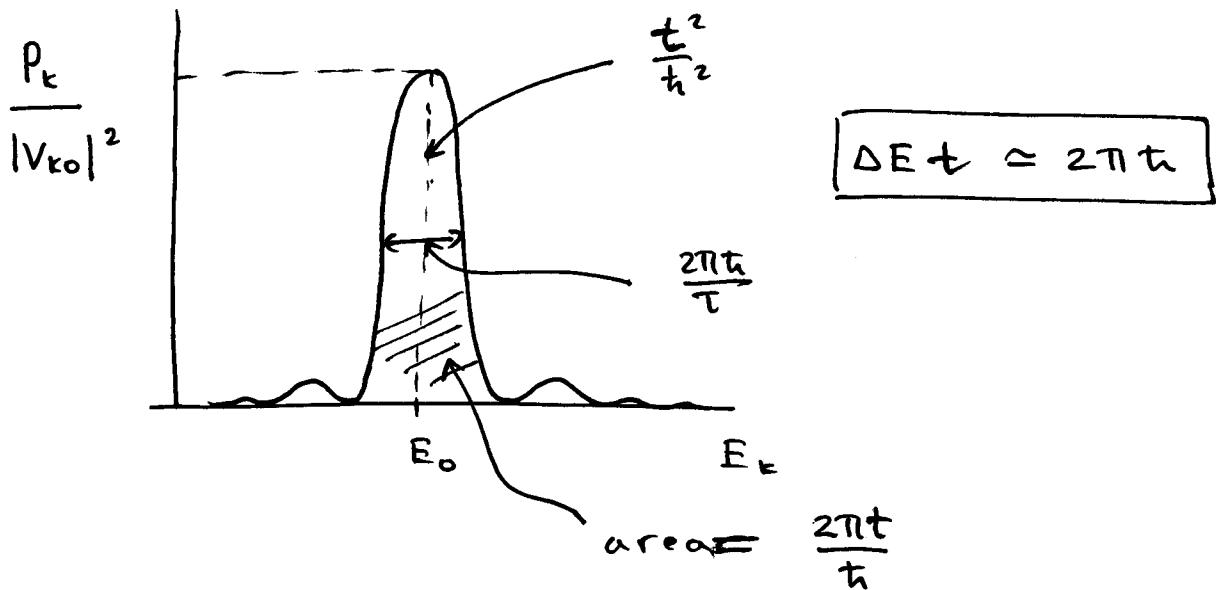
The probability P_k of finding the system in state k at time t :

$$P_k(t) = |c_k^{(1)}(t)|^2 = \frac{1}{\hbar^2} \left| \int_0^t dt' V_{ko}(t') e^{i\omega_{ko} t'} \right|^2$$

When $V_{ko} = \text{const}$ (constant interaction potential):

$$P_k = |V_{ko}|^2 \frac{\sin^2 \left[\frac{(E_k - E_0)t}{2\hbar} \right]}{\left[(E_k - E_0)/2 \right]^2} \quad (*)$$

Homework: Derive eq (*).

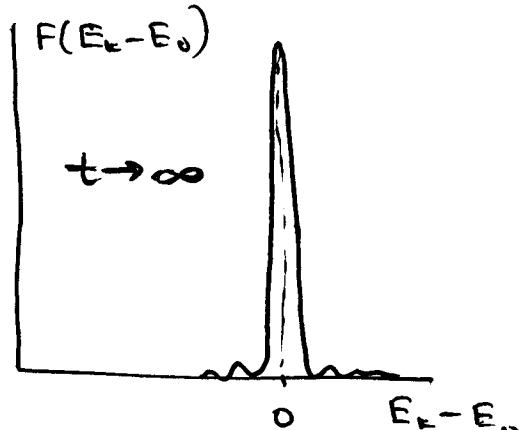


Fermi's Golden Rule :

$$F(E_k - E_0) = \frac{P_k}{t |V_{k0}|^2} = \frac{\sin^2 \frac{\omega_{k0} t}{2}}{\hbar^2 t (\omega_{k0}/2)^2}$$

$$\int_{-\infty}^{\infty} F(E_k - E_0) d(E_k - E_0) = \frac{2\pi}{\hbar}$$

$$\lim_{t \rightarrow \infty} F(E_k - E_0) = \frac{2\pi}{\hbar} \delta(E_k - E_0)$$



$$P_k(t) = \frac{2\pi t}{\hbar} |V_{k0}|^2 \delta(E_k - E_0)$$

The rate of transition :

$$\omega_{k0} = \frac{P_k(t)}{t} = \frac{2\pi}{\hbar} |V_{k0}|^2 \delta(E_k - E_0)$$

at $t \rightarrow \infty$ only transitions which obey energy conservation can be caused by a time-independent interaction .

Periodic Interactions

For $V(+)=V^{(0)} e^{\pm i\omega t}$

$$C_k(t) = -\frac{i}{\hbar} \int_0^t dt' V_{k0}^{(0)} e^{i(\omega_{k0} \pm \omega)t'} \\ = -V_{k0}^{(0)} \frac{e^{i(\omega_{k0} \pm \omega)t} - 1}{\hbar(\omega_{k0} \pm \omega)}$$

The Fermi's golden rule becomes :

$$\omega_{k0} = \frac{2\pi}{\hbar} |V_{k0}^{(0)}|^2 \delta(E_k - E_0 \pm \hbar\omega)$$

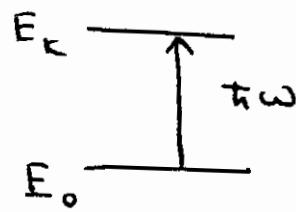
Transitions occur at the frequencies:

$$\hbar\omega = E_k - E_0 \leftarrow \text{absorption } (E_0 < E_k)$$

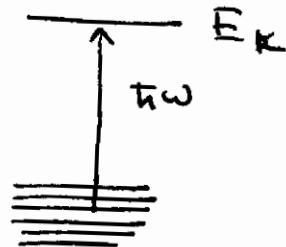
$$\hbar\omega = E_0 - E_k \leftarrow \text{emission } (E_0 > E_k)$$

Multiple states

Two states :



Continuum of states :



$$|c_k(t)|^2 = \sum_m P_{mk} = \sum_m |V_{mk}^{(0)}|^2 \frac{\sin^2((E_k - E_m)t/2\hbar)}{[(E_k - E_m)/2]^2}$$

$$= \int dE_m \left(\frac{dk}{dE_m} \right) \frac{\sin^2((E_k - E_m)t/2\hbar)}{(E_k - E_m)^2/4}$$

Density of states,
number of distinct
states in the energy
interval dE_m

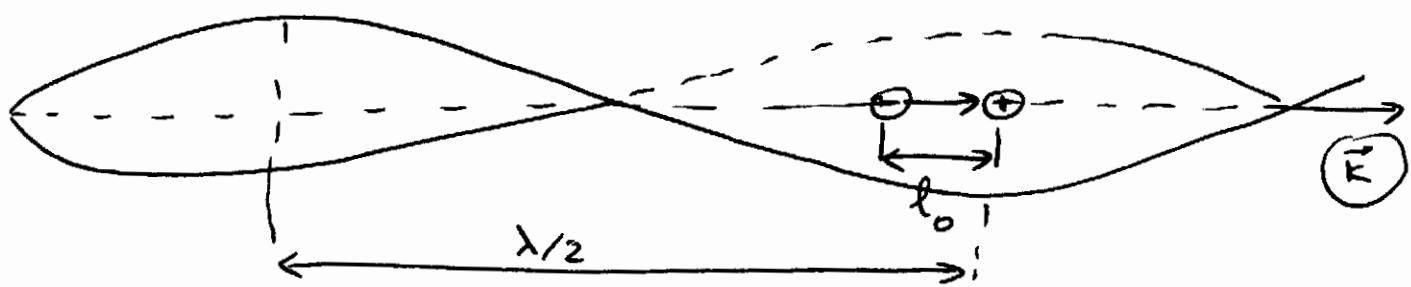
$$\rho(E_m)$$

$$|c_k(t)|^2 = \frac{2\pi t}{\hbar} \rho(E_0) |V_{k0}^{(0)}|^2$$

$$\omega = \frac{|c_k(t)|^2}{t} = \frac{2\pi}{\hbar} |V_{k0}^{(0)}|^2 \rho(E_0)$$

Interaction of matter with radiation

Dipole approximation: assumes that the light intensity is constant over the length of the molecule



l_0 is the characteristic length of the molecule
(e.g., bond distance for a diatomic molecule)

$$\lambda \gg l_0, \quad k l_0 = \frac{2\pi l_0}{\lambda} \ll 1$$

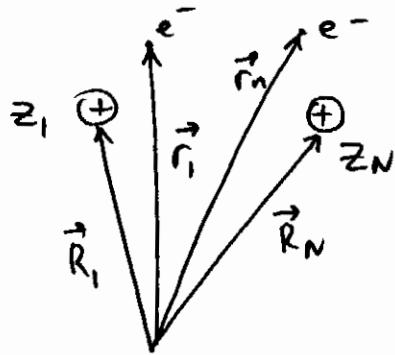
$$V(t) = V_0 \sqrt{\omega} \vec{\epsilon} \cdot \hat{\vec{\mu}} \cos(\vec{k} \cdot \vec{r} - \underline{\omega} t)$$

wavenumber circular
 frequency

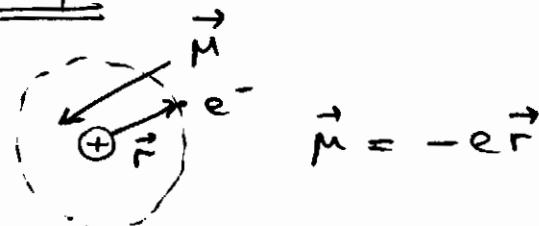
Electric dipole

Electric dipole of a molecule is defined as

$$\vec{\mu} = \sum_i z_i \vec{r}_i = e \sum_i^{nuclei} z_i \vec{r}_i - e \sum_i^{electrons} \vec{r}_i$$



Example:



Since \vec{r} is an operator, $\vec{\mu}$ is also an operator.

Observables are matrix elements of operators.

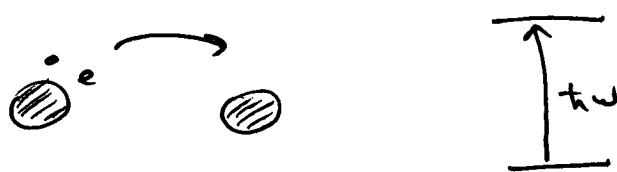
Diagonal matrix elements of $\vec{\mu}$ are called
the dipole moment of a molecule

$$\vec{\mu}_i = \langle i | \vec{\mu} | i \rangle$$

Off-diagonal matrix elements are transition dipoles

$$\vec{\mu}_{ik} = \langle i | \vec{\mu} | k \rangle$$

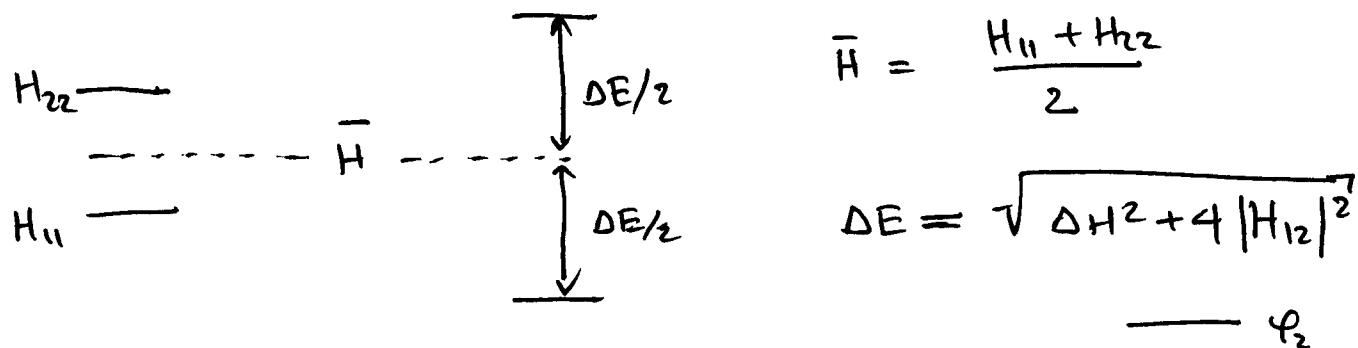
Two-state model for the transition dipole



φ_1 and φ_2 are atomic states

Linear combinations of φ_1 and φ_2 should generate two MOs. The energies are solutions of the secular equation:

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0 \quad E = \bar{H} \pm \frac{\Delta E}{2}$$



$$(*) \quad \Psi_1 = \sqrt{1-f} \varphi_1 + \sqrt{f} \varphi_2 \quad n=1 \quad \text{LCAO} \quad \downarrow$$

$$\Psi_2 = -\sqrt{f} \varphi_1 + \sqrt{1-f} \varphi_2$$

$f \ll \varphi_2$

$$f = \frac{1}{2} - \frac{\Delta H}{2\Delta E}$$

$$\frac{1-f}{2} \quad \text{LCAO} \quad \downarrow$$

Homework: Prove eq (*).

States E_1 and E_2 are often called adiabatic states with adiabatic wavefunctions φ_1 and φ_2

Transition dipole

The observed transition dipole is the off-diagonal matrix element of the dipole moment operator taken between states Ψ_1 and Ψ_2

$$\vec{\mu}_{12} = \langle \Psi_1 | \vec{\mu} | \Psi_2 \rangle = (1-f) \langle \Psi_1 | \vec{\mu} | \Psi_2 \rangle + \\ + \sqrt{f(1-f)} \left(\langle \Psi_2 | \vec{\mu} | \Psi_2 \rangle - \langle \Psi_1 | \vec{\mu} | \Psi_1 \rangle \right)$$

$\overset{''}{\Delta \vec{\mu}}$

If the atomic states Ψ_1 and Ψ_2 are well localized, the overlap $\langle \Psi_1 | \vec{\mu} | \Psi_2 \rangle$ is small and, in the first approximation, $\langle \Psi_1 | \vec{\mu} | \Psi_2 \rangle = 0$.

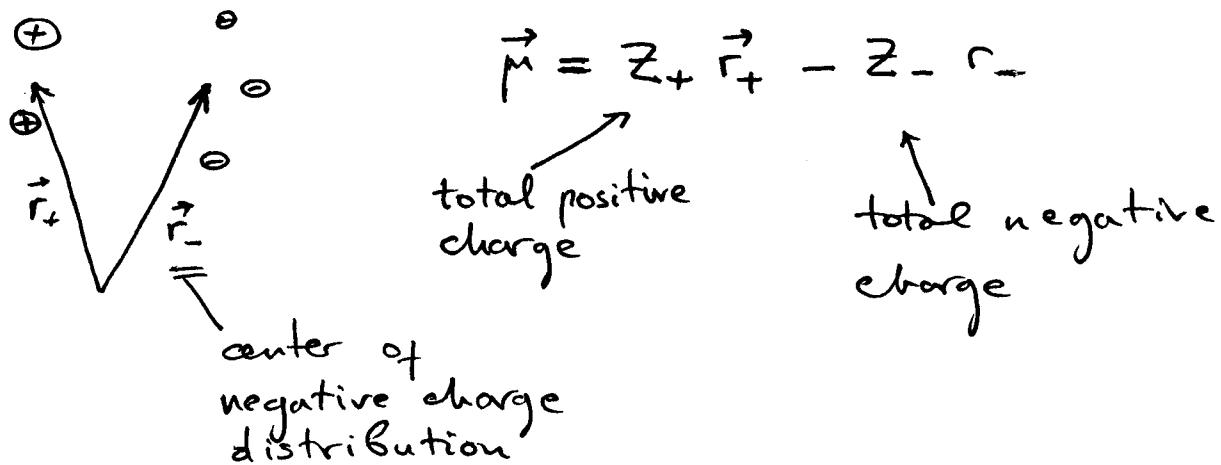
$$\sqrt{f(1-f)} = \sqrt{\frac{1}{4} - \frac{\Delta H^2}{4\Delta E^2}} = \frac{\Delta H_{12}}{\Delta E}$$

The Mulliken-Hush relation

$$\vec{\mu}_{12} = \Delta \vec{\mu} \frac{\Delta H_{12}}{\Delta E}$$

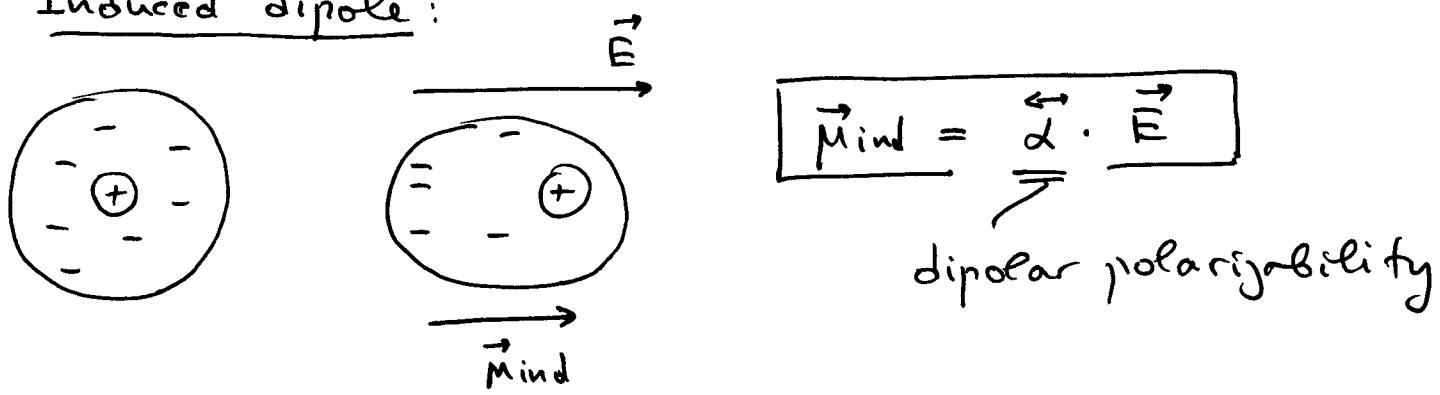
Induced dipole and polarizability

Permanent dipole: $\vec{\mu} = \sum z_i \vec{r}_i$



Molecules with a center of inversion have $\vec{\mu} = 0$

Induced dipole:



α is a 3×3 matrix:

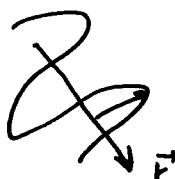
$$\alpha = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}$$

Polarizability usually reported in handbooks refer to the trace

$$\alpha = \frac{1}{3} \text{Tr}(\alpha) = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

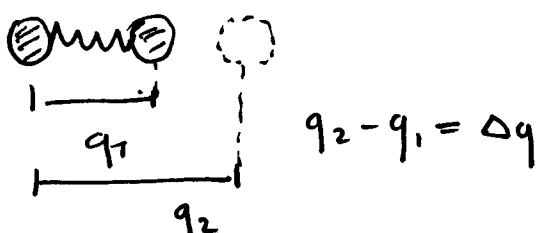
If $\alpha_{xx} = \alpha_{yy} = \alpha_{zz}$ and off-diagonal elements are zero
 { The molecule is called isotropically polarizable.

Qualitative description of light scattering



$$E(t) = E_0 \cos \omega t$$

$$\vec{\mu}_{ind}(t) = \alpha \vec{E}_0 \cos \omega t$$



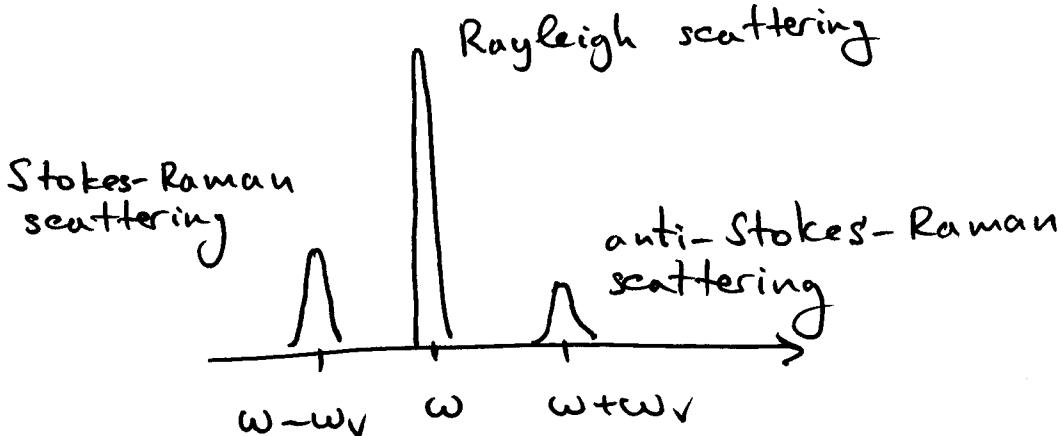
If molecular vibrations are excited the polarisability α become time-dependent

$$\alpha = \alpha_0 + \frac{\partial \alpha}{\partial q} (q - q_0), \quad \alpha_0 = \alpha(q_0)$$

For a vibration with the vibrational frequency ω_v

$$q - q_0 = \Delta q \cos \omega_v t$$

$$\vec{\mu}_{ind}(t) = \alpha_0 \vec{E}_0 \cos \omega t + \frac{\partial \alpha}{\partial q} \Delta q E_0 \underbrace{\cos \omega t \cos \omega_v t}_{\frac{1}{2} [\cos(\omega + \omega_v)t + \cos(\omega - \omega_v)t]}$$



Dipole approximation

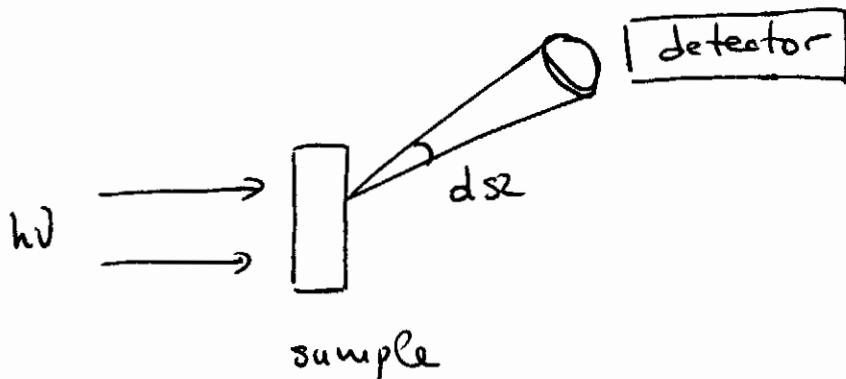
$$V_{k0}^{(0)} = \langle k | \nu_0 V_0 \vec{\epsilon} \cdot \vec{\mu} | 0 \rangle = \nu_0 \sqrt{\omega} \vec{\epsilon} \cdot \vec{\mu}_{k0}$$

transition dipole between states 0 and k

Density of states of radiation

$$p(E) \propto \omega^2 \frac{d\Omega}{\Omega}$$

angle of a 3-D vector



$$\omega_{k0} = \frac{2\pi}{\hbar} V_0^2 \omega^3 \int |\vec{\epsilon} \cdot \vec{\mu}_{k0}|^2 d\Omega$$

number of absorbing molecules

$\omega_{k0} = \frac{\omega_{\text{abs}}}{\Omega} = N \frac{4}{3\hbar} \left(\frac{\omega}{c}\right)^3 |\mu_{k0}|^2$

absorption rate

Interaction Between field and induced dipole

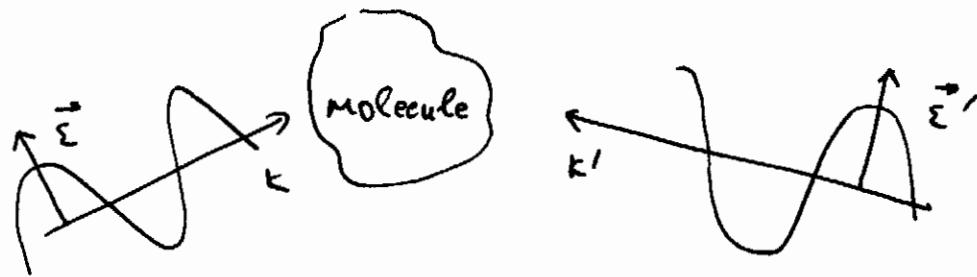
Two electric fields

$$\frac{\vec{E}_\omega}{\text{electric field}} = E_0 \vec{\epsilon} \sin \omega t$$

of the wave
with frequency ω

$$\frac{\vec{E}_{\omega'}}{\text{electric field of}} = E'_0 \vec{\epsilon}' \sin \omega' t$$

the wave with
frequency ω'



$$\vec{\mu}_{\text{ind}} = \vec{\alpha} \cdot \vec{E}_\omega$$

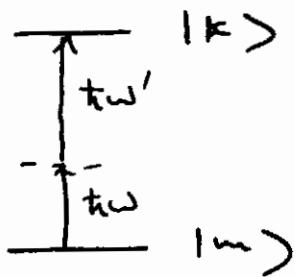
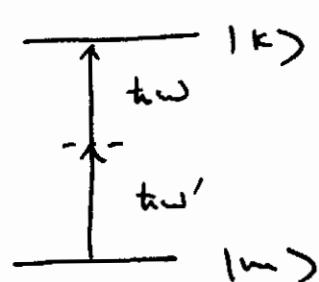
$$V(+) = - \vec{E}_{\omega'} \cdot \vec{\alpha} \cdot \vec{\mu}_{\text{ind}} = - \vec{E}_{\omega'} \cdot \vec{\alpha} \cdot \vec{E}_\omega$$

$$\begin{aligned} V(+) &= - E_0 E'_0 (\vec{\epsilon}' \cdot \vec{\alpha} \cdot \vec{\epsilon}) \frac{1}{2i} (e^{i\omega't} - e^{-i\omega't}) \frac{1}{2i} (e^{i\omega' t} - e^{-i\omega' t}), \\ &= V \left(e^{i(\omega+\omega')t} + e^{-i(\omega+\omega')t} - e^{i(\omega-\omega')t} - e^{-i(\omega-\omega')t} \right), \end{aligned}$$

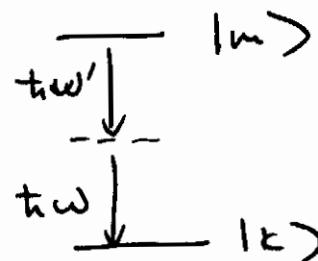
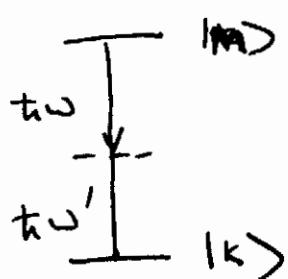
$$V = \frac{1}{4} E_0 E'_0 (\vec{\epsilon}' \cdot \vec{\alpha} \cdot \vec{\epsilon})$$

$$V(t) = U(e^{i(\omega+\omega')t} + e^{-i(\omega+\omega')t} - e^{i(\omega-\omega')t} - e^{-i(\omega-\omega')t})$$

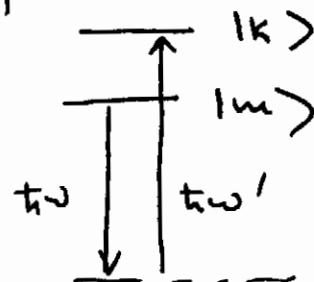
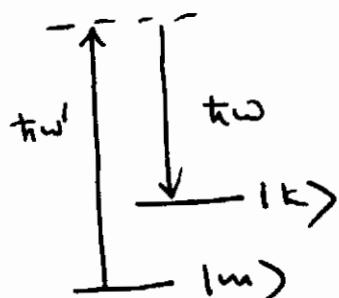
$e^{-i(\omega+\omega')t}$ ← two-photon absorption



$e^{i(\omega+\omega')t}$ ← two-photon emission



$e^{i(\omega-\omega')t}$ ← emission of a photon of frequency ω
absorption of ω'



Stokes - Raman
scattering

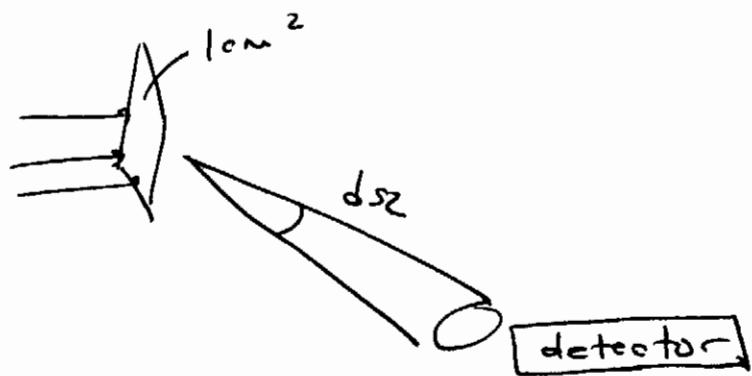
anti-Stokes - Raman
scattering

Rate of Stokes-Raman scattering

$$w_{km} = \frac{2\pi}{h} \rho |V_{km}|^2 \propto \omega \omega' |\vec{\epsilon}' \cdot \vec{\alpha}_{km} \cdot \vec{\epsilon}|^2 \rho$$

Raman cross-section:

$$d\sigma = \frac{\text{scattering rate into } d\Omega}{\text{photon flux}}$$



Differential cross-section:

$$\frac{d\sigma}{d\Omega} \propto \omega^3 \omega' |\vec{\epsilon}' \cdot \vec{\alpha}_{km} \cdot \vec{\epsilon}|^2$$

$$\frac{d\sigma}{d\Omega} \propto \underline{\underline{\omega}}^4$$

responsible for blue sky