Chapter 8 - Vibr. + Rotational Spectroscopy - diatomics

rotational → geometries

vibrational → curvature of potential energy surface

absorption emission

$h\nu = |E_2 - E_1|$

gamma rays	$10^{-14} - 10^{-12}$ m		
X rays	$10^{-12} - 10^{-8}$ m		
UV	$10^{-8} - 10^{-7}$ m		> 30,000 cm^{-1}
Visible	$10^{-7} - 10^{-6}$ m	(700 - 400 nm)	14,000 - 24,000 cm^{-1}
IR	$10^{-6} - 10^{-3}$ m		~ 10,000 cm^{-1}
microwave	$10^{-3} - 10^{3}$ m		~ 100 cm^{-1}
radio	$10^{3} - 10^{8}$ m		~ .01 cm^{-1}

NMR

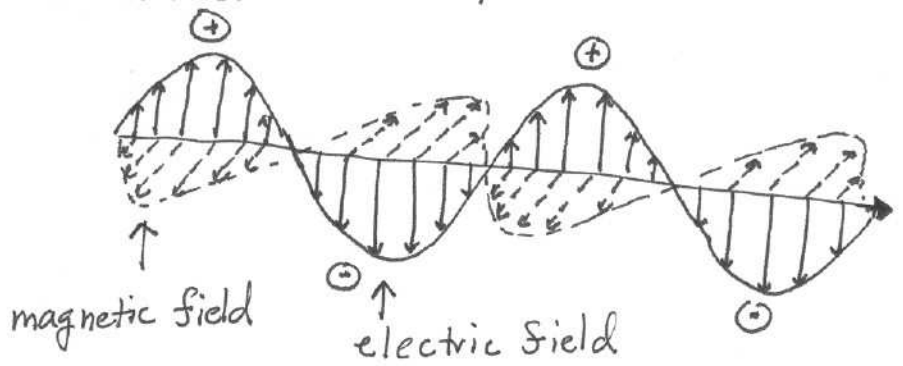
AM radio	530 - 1700 kHz	$\lambda \sim 600 - 200$ m	resonant dipole antenna $\lambda/2$
FM radio	88 - 108 MHz	$\lambda \sim 3.3$ m $- 2.7$ m	
Cell phone wireless network	2.4 GHz	$\lambda \sim 0.125$ m	

Why are X-rays dangerous? How are γ rays formed

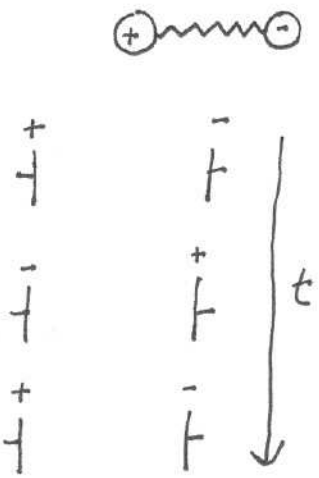
wavenumber units $\tilde{\nu} = \frac{1}{\lambda}$, in cm^{-1}

$\Delta E = h\nu = hc\tilde{\nu}$ (be careful about cm and m)

has to be in cm/s in this case



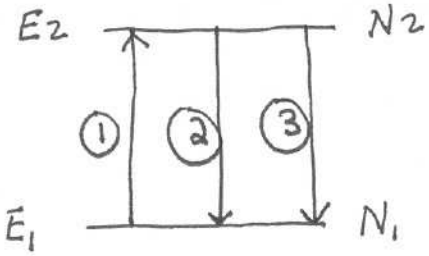
electric + magnetic fields ⊥ to one another and to the propagation direction.



If the frequency of the oscillating field = that of the harmonic oscillator, the oscillator is driven into <u>resonance</u>, i.e. vibrates. Note - the charges are essential for coupling with the field.

For a diatomic molecule treated quantum mechanically, the key is the dynamic (changing) dipole, i.e., $d\mu/dR$.

For rotational spectroscopy, the key is the <u>static</u> dipole



① Absorption: $B_{12}\rho(\nu)N_1$

② Stimulated emission: $B_{21}\rho(\nu)N_2$

③ Spontaneous emission: $A_{21}N_2$

$\rho(\nu)$ = radiation density

$$B_{12}\rho N_1 = B_{21}\rho N_2 + A_{21}N_2$$

N_1, N_2 = # of molecules in each level - given by Boltzman expression.

Einstein showed that $B_{12} = B_{21}$

$$\frac{A_{21}}{B_{21}} = \frac{16\pi^2 h\nu^3}{c^3}$$

using the expression for black-body radiation

spontaneous emission: random, emitted photons incoherent (phases + direction random)

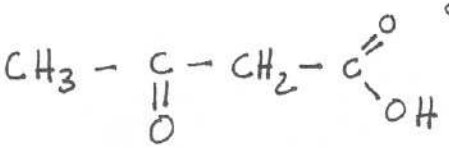
Stimulated emission: emitted photons have same phase + direction as incident photon (coherent)

lasers are based on stimulated emission

A closer look at vibrational spectroscopy

Useful due to <u>characteristic frequencies</u>

group frequencies



CH, C=O, C-O, O-H all have very different frequencies.

In general $\frac{N_1}{N_0} \ll 1$ for vibrational energy levels

So we can assume that only $n=0$ level is populated before photon absorption.

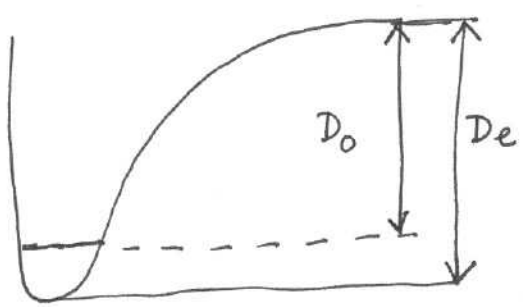
Selection rule $\Delta n = 1$

So usually only have $n=0 \rightarrow n=1$

Actually if the potential is anharmonic, may see weak overtone bands ($\Delta n = 2, 3$)

Realistic potential: $V(R) = D_e\left[1 - e^{-\alpha(R-R_e)}\right]^2$ ← Morse potential

$$E_n = h\nu\left(n+\tfrac{1}{2}\right) - \underbrace{\frac{(h\nu)^2}{4D_e}\left(n+\tfrac{1}{2}\right)^2}_{\text{vibrational anharmonicity}}$$



What does vibration anharmonicity do to the bondlength? R_0 vs. R_e.

transition dipole moment

$$\mu_x^{mn} = \langle m | \mu_x | n \rangle = \int \psi_m^*(x)\, \mu_x(x)\, \psi_n(x)\, dx$$

$$\mu_x = \underbrace{\mu_{0x}}_{\text{permanent dipole in } x \text{ direction}} + x(t)\left(\frac{d\mu}{dx}\right)_{x=0} + \cdots$$

$\langle 0 | \mu_x | 1 \rangle$

only second term in expansion of μ_x contributes $\longrightarrow$ $\Delta n = 1$ selection rule