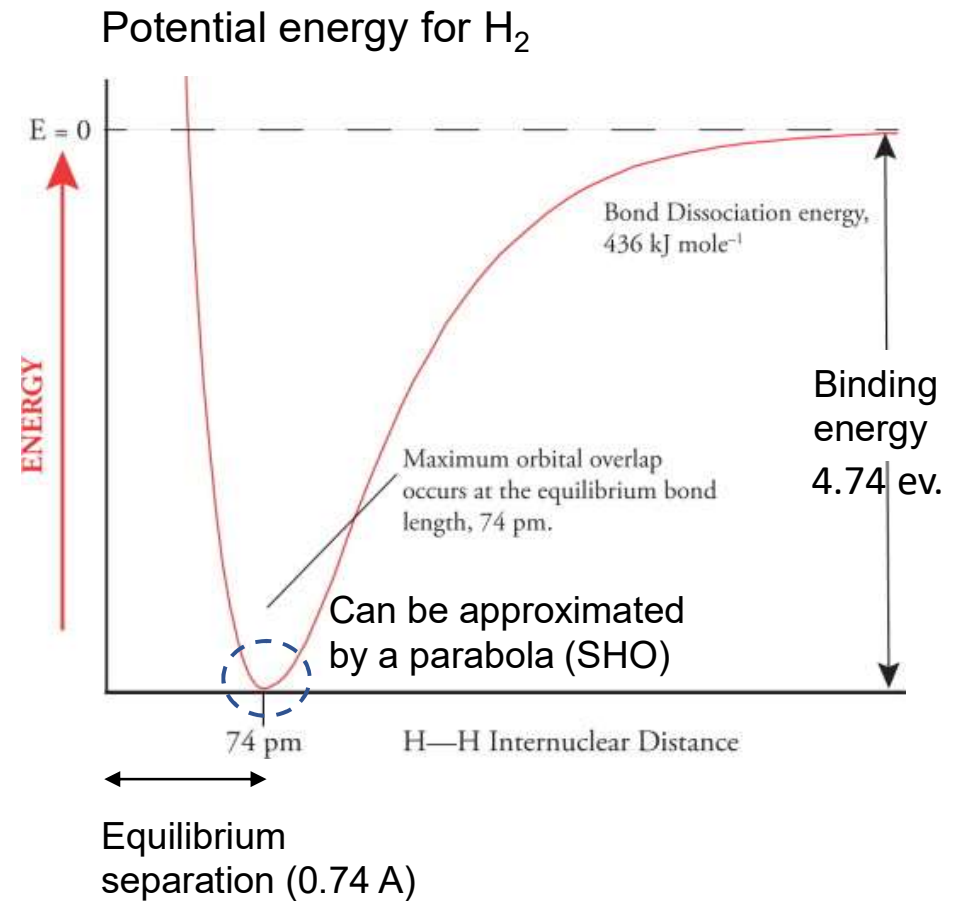Chap 10

Molecules and solids

- Molecular bonding and spectra

- Raman spectroscopy

- Stimulated emission and laser

- Structural properties of solids (skip)

- Thermal and Magnetic properties of solids (skip)

- Superconductivity (>> chap 9)

Chemical bonding is the attractive force that holds various constituents (atoms, ions, etc.) together and stabilizes them through the overall loss of energy. Below are some typical chemical bonds.

- **Covalent bonds**:

**Ex**: Diatomic molecules (H_2, N_2, O_2) formed by 2 identical atoms tend to be covalent.

Atoms share electrons to achieve a stable electron configuration.

Potential energy for H_2

E = 0

ENERGY

Bond Dissociation energy, 436 kJ mole^{-1}

Maximum orbital overlap occurs at the equilibrium bond length, 74 pm.

Can be approximated by a parabola (SHO)

74 pm

H—H Internuclear Distance

Binding energy 4.74 ev.

Equilibrium separation (0.74 A)

- **Ionic bonds**:

Ex: Sodium readily gives up its 3s electron to become Na$^+$, while chlorine readily gains an electron to become Cl$^-$. That forms the NaCl molecule.   NaCl
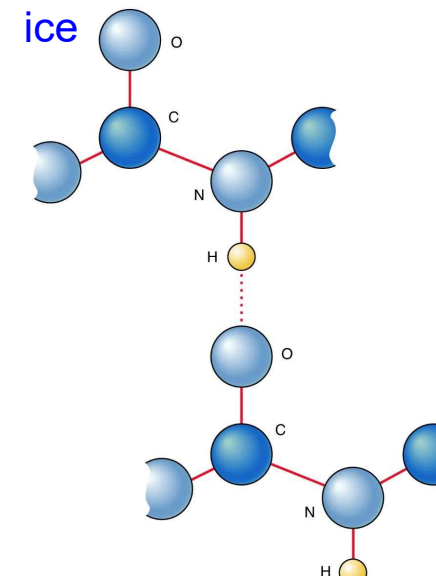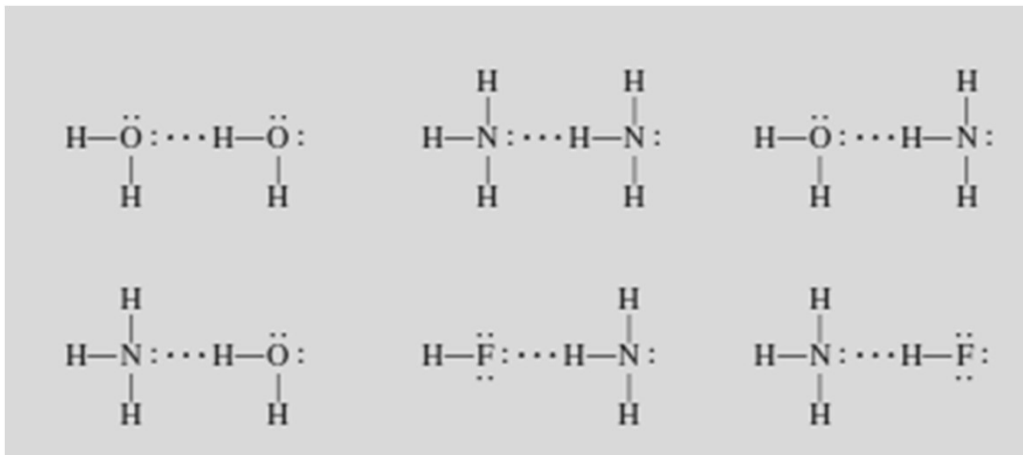
The resulting oppositely charged ions are held together by electrostatic forces.
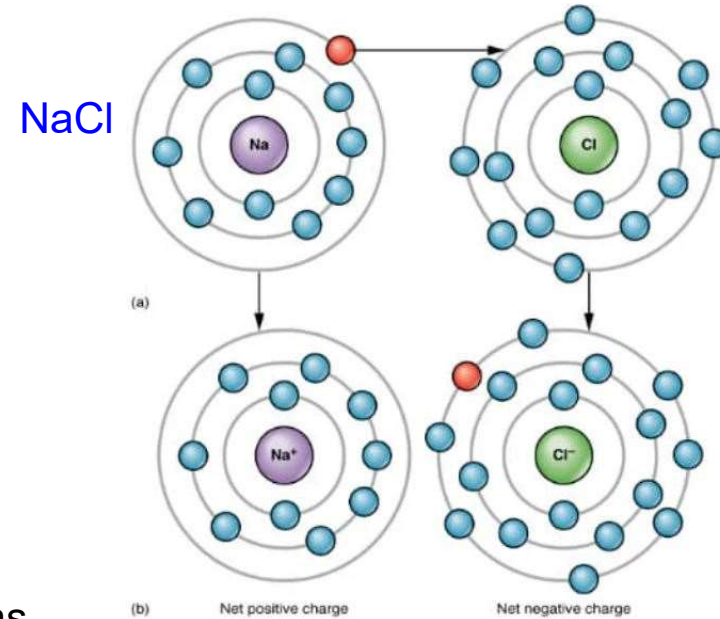
- **Hydrogen bond**:

Ex: H_2O. In general, between H and N/O/F atoms of another molecule.

A hydrogen bond is a dipole-dipole force between a slightly positive hydrogen on one molecule and a slightly negative atom on another molecule.
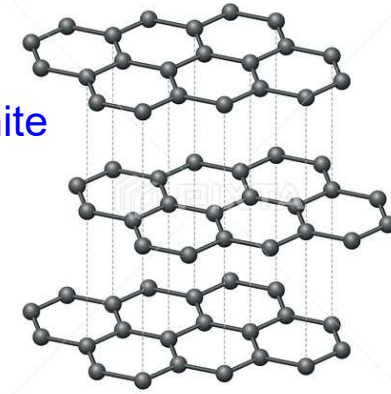
ice

- **Van der Waals bond**:

Ex: In graphite, the van der Waals bond holds together adjacent sheets of carbon atoms.

Van der Waals force is a result of temporarily induced dipoles.

graphite

- Dipole electric field

$$E = \frac{1}{4\pi\epsilon_0}\left[\frac{p}{r^3} - \frac{3(p \cdot r)}{r^5}r\right]$$

- Induced dipole moment

$$p' = \alpha E$$

- Interaction energy

➡ $$U = -p' \cdot E = -\alpha E \cdot E$$

$$= -\frac{\alpha}{(4\pi\epsilon_0)^2}(1 + 3\cos^2\theta)\frac{p^2}{r^6}$$

Van der Waals force $\sim \dfrac{1}{r^7}$

instantaneous dipole on A induces a dipole on B
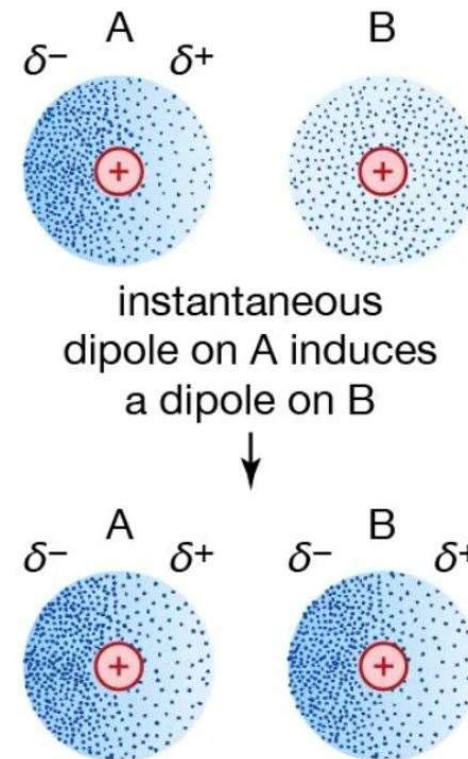
Molecular spectroscopy: diatomic molecule
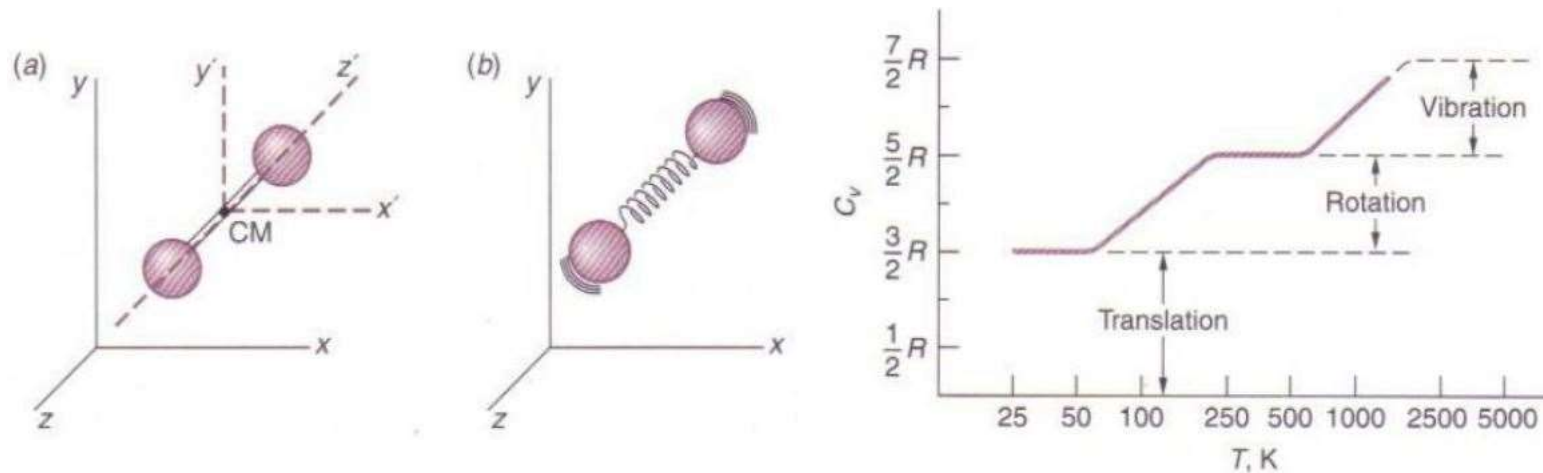
3 types of motion:

- Rotation: $f \sim 10^{11} - 10^{13}$ (far infrared to microwave)

- Vibration: $f \sim 10^{13} - 10^{14}$ (infrared)

- Electronic transition: $f \sim 10^{14} - 10^{16}$ (visible and ultraviolet)

To simplify, "assume" these 3 motions decouple from each other.

1. Rotational states

- Moment of inertia $I = \mu R_0^2$

  Reduced mass $\dfrac{1}{\mu} = \dfrac{1}{m_1} + \dfrac{1}{m_2}$

- Energy of rotation

  $$H_{rot} = \frac{L^2}{2I} = \frac{L^2}{2\mu R_0^2}$$

- Schrödinger eq.

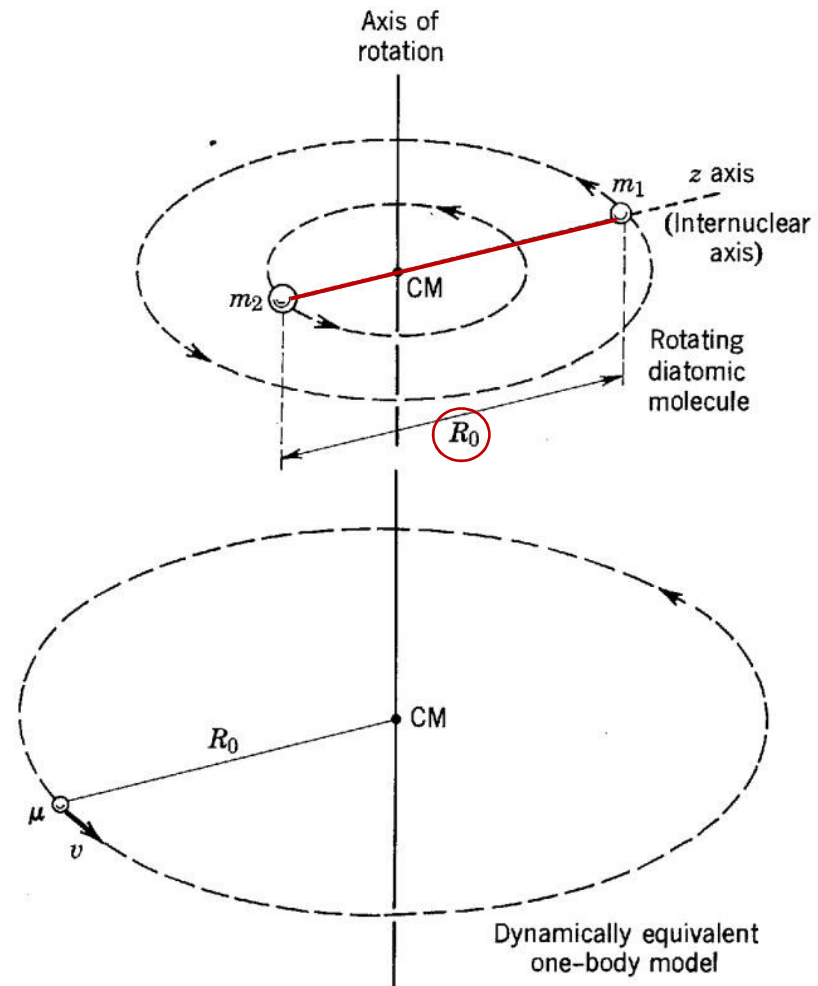 $$\frac{\hat{L}^2}{2I}\psi = E\psi$$

  Quantization of angular momentum

  $$L^2 = \ell(\ell+1)\hbar^2$$

  $$\Rightarrow \quad E_\ell^{\text{rot}} = \frac{\hbar^2 \ell(\ell+1)}{2I}$$

- $E^{\text{rot}} \sim 10^{-3}$ - 10^{-4} eV ($\lambda \sim 1$ mm - 1cm)

  $E^{\text{tran}} \sim 10^{-2}$ eV, so collision can cause rotation

Axis of rotation

z axis (Internuclear axis)

CM

Rotating diatomic molecule

R_0

R_0 CM

μ

v

Dynamically equivalent one-body model

Ex 10.1: Estimate the value of E_{rot} for the lowest rotational energy state of N_2, which has a bond length 0.110 nm.

Solution

For nitrogen, $m = 2.33 \times 10^{-26}$ kg, and $R = 1.10 \times 10^{-10}$ m. Thus,
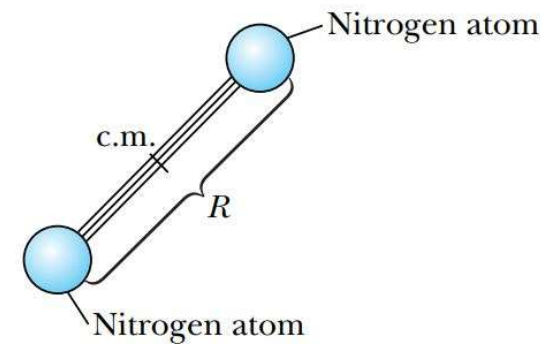
$$I = \frac{(2.33 \times 10^{-26} \text{ kg})(1.10 \times 10^{-10} \text{ m})^2}{2}$$

$$= 1.41 \times 10^{-46} \text{ kg} \cdot \text{m}^2$$

For $\ell = 1$,

$$E_{rot} = \frac{2\hbar^2}{2I} = \frac{\hbar^2}{I} = \frac{(1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{1.41 \times 10^{-46} \text{ kg} \cdot \text{m}^2}$$
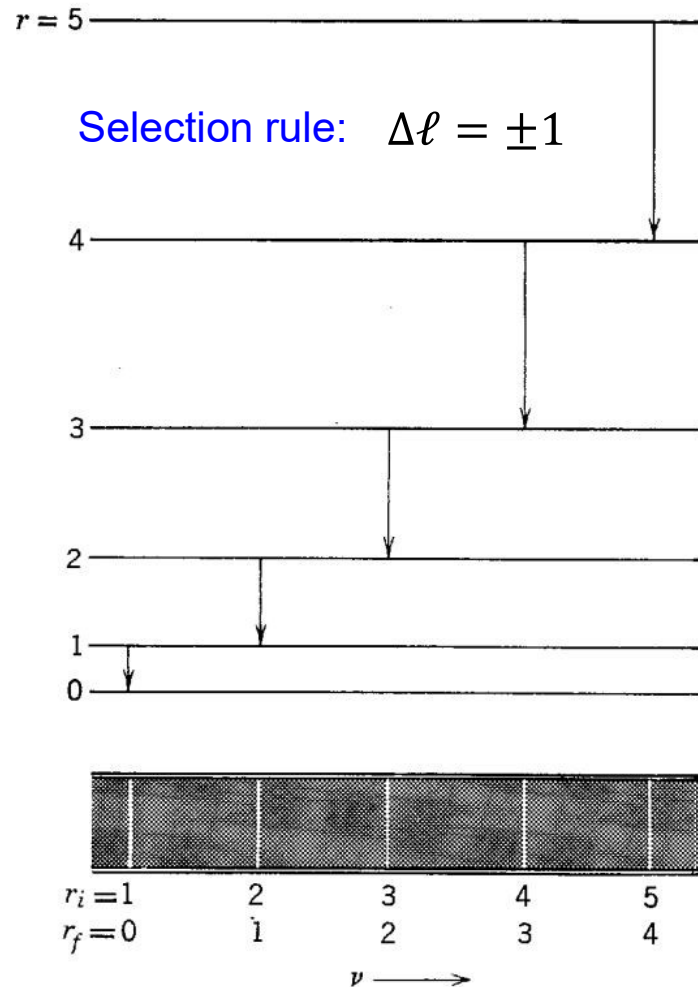
$$= 7.89 \times 10^{-23} \text{ J} = 4.93 \times 10^{-4} \text{ eV}$$

Molecule	R_0(Å)	v_0 (cm^{-1})	$\dfrac{\hbar^2}{2I}$ (eV)
H_2	0.74	4395	7.56×10^{-3}
HD	0.74	3817	5.69×10^{-3}
D_2	0.74	3118	3.79×10^{-3}
Li_2	2.67	351	8.39×10^{-5}
N_2	1.09	2360	2.48×10^{-4}
O_2	1.21	1580	1.78×10^{-4}

Transitions between rotational energy levels

(emission/absorption of light is possible *only for molecules with*

permanent electric dipoles)   e.g., HCl, but not O_2

Selection rule: $\Delta \ell = \pm 1$

$$\Delta E_\ell = E_\ell - E_{\ell-1} = \frac{\hbar^2}{I}\ell = \frac{hc}{\lambda}$$

$$\rightarrow \Delta\left(\frac{c}{\lambda}\right) = \frac{\hbar}{2\pi I} = \text{const.} \ (6.2 \times 10^{11} \ \text{Hz for HCl})$$

For HCl, reduced mass

$$\rightarrow I = 2.66 \times 10^{-47} \ kg \cdot m^2$$

$$\mu = 1.63 \times 10^{-2} \ \text{kg} \quad \text{(see Ex 10.2 later)}$$
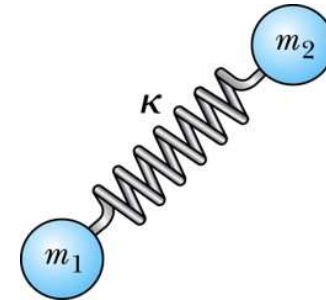
$$\rightarrow R_0 = 1.27 \times 10^{-10} \ m$$

2. Vibrational states

- Small vibrations are approximately simple harmonic motion

  Energy levels:

  $$E_m^{\text{vibr}} = \left(m + \frac{1}{2}\right)\hbar\omega \qquad \omega = \sqrt{\frac{\kappa}{\mu}}$$

  For HCl, ΔE=0.36 eV, so it's harder to be excited by collisions

- Total energy of a vibration-rotation system

  (suppose two motions are independent):

  $$E = E_\ell^{\text{rot}} + E_m^{\text{vibr}} = \frac{\hbar^2 \ell(\ell+1)}{2I} + \left(m + \frac{1}{2}\right)\hbar\omega$$

Ex 10.2: (a) Given that the spacing between vibrational energy levels of the HCl molecule is 0.36 eV, calculate the effective force constant. (b) Find the classical temperature associated with this difference between vibrational energy levels in HCl.

(a) $k = \mu\omega^2$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(34.97 \text{ u})(1.008 \text{ u})}{34.97 \text{ u} + 1.008 \text{ u}}$$

$\boxed{1\text{u} = 1.66 \times 10^{-2} \text{ kg}}$

$$= 0.9798 \text{ u} = 1.63 \times 10^{-27} \text{ kg}$$

$$\omega = \frac{\Delta E}{\hbar} = \frac{0.36 \text{ eV}}{6.58 \times 10^{-16} \text{ eV} \cdot \text{s}} = 5.47 \times 10^{14} \text{ rad/s}$$

➡ $$\kappa = \mu\omega^2 = (1.63 \times 10^{-27} \text{ kg})(5.47 \times 10^{14} \text{ rad/s})^2$$
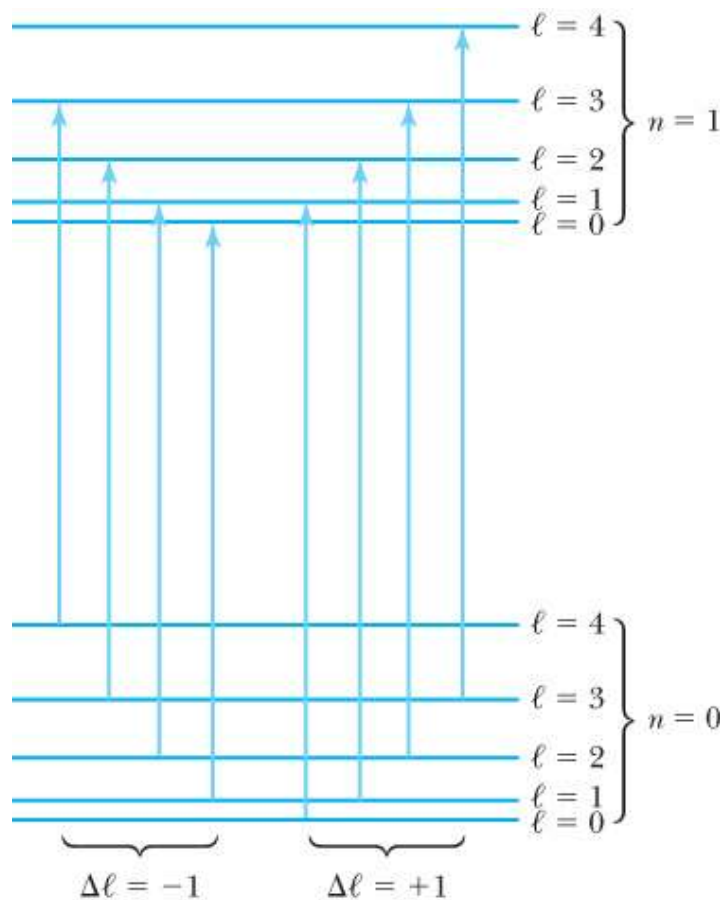
$$= 490 \text{ N/m}$$

(b) Two energies are associated with an oscillator, one is the kinetic energy and the other the potential energy

$$\Delta E = \hbar\omega = 2\left(\frac{kT}{2}\right) = kT \qquad \leftarrow \text{Equipartition theo (Chap 9)}$$

➡ $$T = \frac{\Delta E}{k} = \frac{0.36 \text{ eV}}{8.62 \times 10^{-5} \text{ eV/K}} = 4200 \text{ K}$$
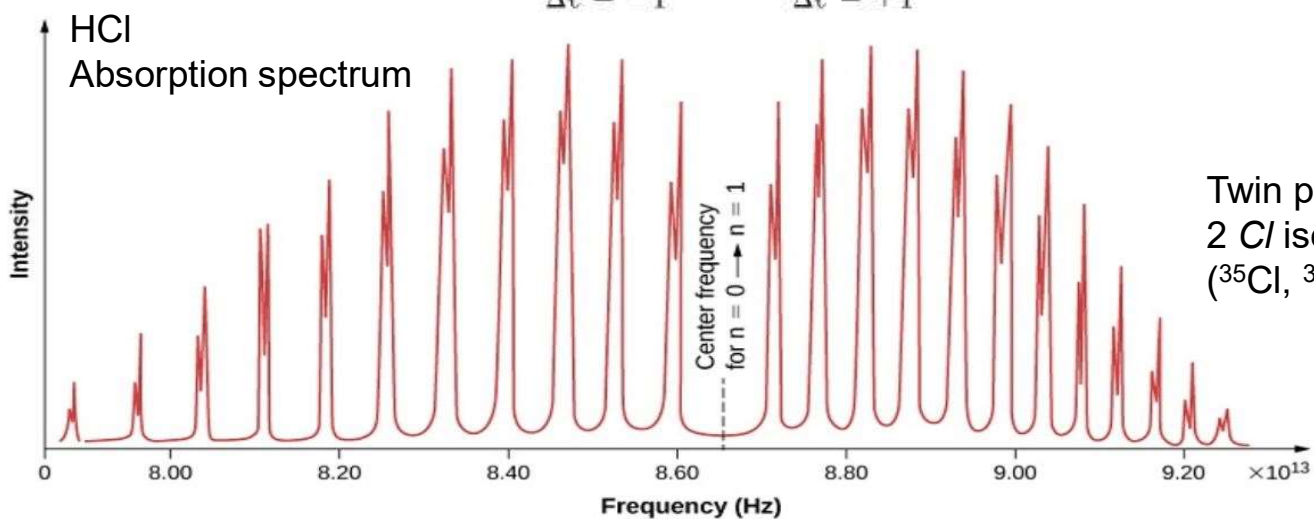
Vibration-rotation
spectrum

Selection rule:

$\Delta m = \pm 1$

$\ell = 4$
$\ell = 3$ $\}\ n = 1$
$\ell = 2$
$\ell = 1$
$\ell = 0$

Due to rotation

Due to vibration

$\ell = 4$
$\ell = 3$ $\}\ n = 0$
$\ell = 2$
$\ell = 1$
$\ell = 0$

Due to rotation

$\Delta \ell = -1$ $\Delta \ell = +1$

HCl
Absorption spectrum

Intensity

Center frequency
for $n = 0 \rightarrow n = 1$

Twin peaks due to
2 *Cl* isotopes
(^{35}Cl, $^{37}Cl \sim 3{:}1$)

0   8.00   8.20   8.40   8.60   8.80   9.00   9.20 $\times 10^{13}$

Frequency (Hz)

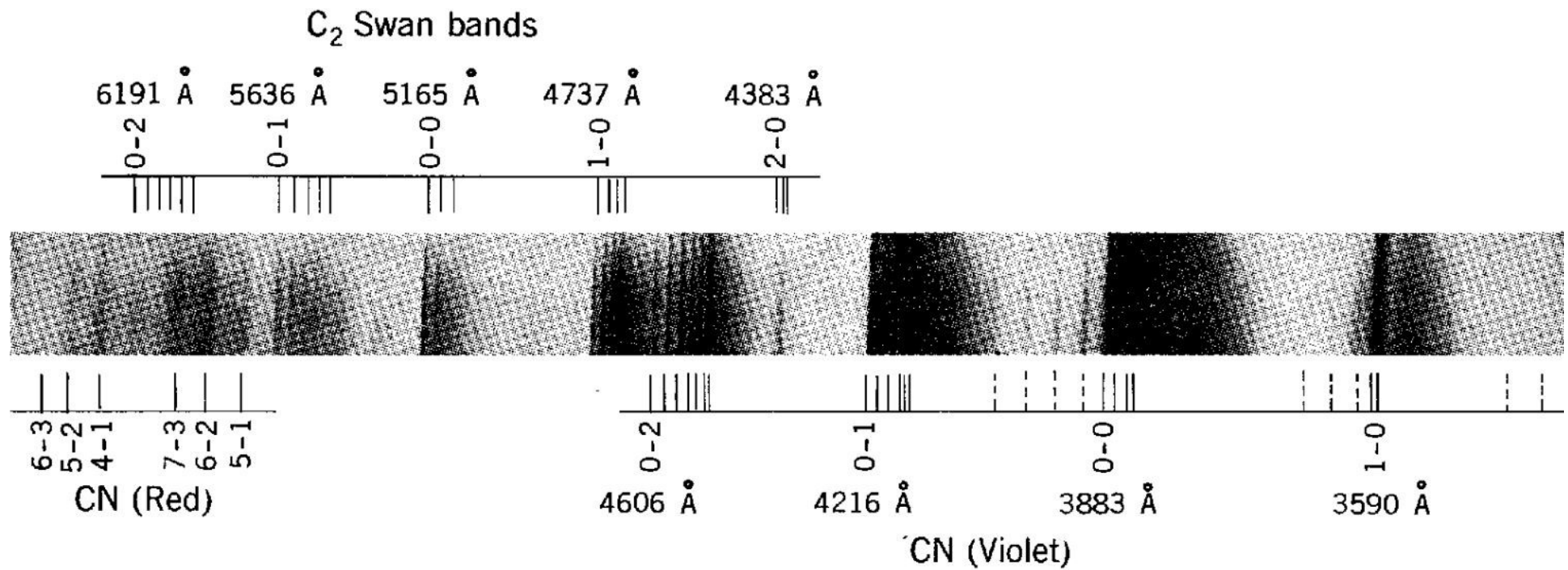After including electronic levels, we have

$$E_{tot} = E_n^{elec} + \frac{\hbar^2}{2I} \ell(\ell + 1) + \hbar\omega_0 \left(m + \frac{1}{2} \right)$$

Electronic   rotation   vibration
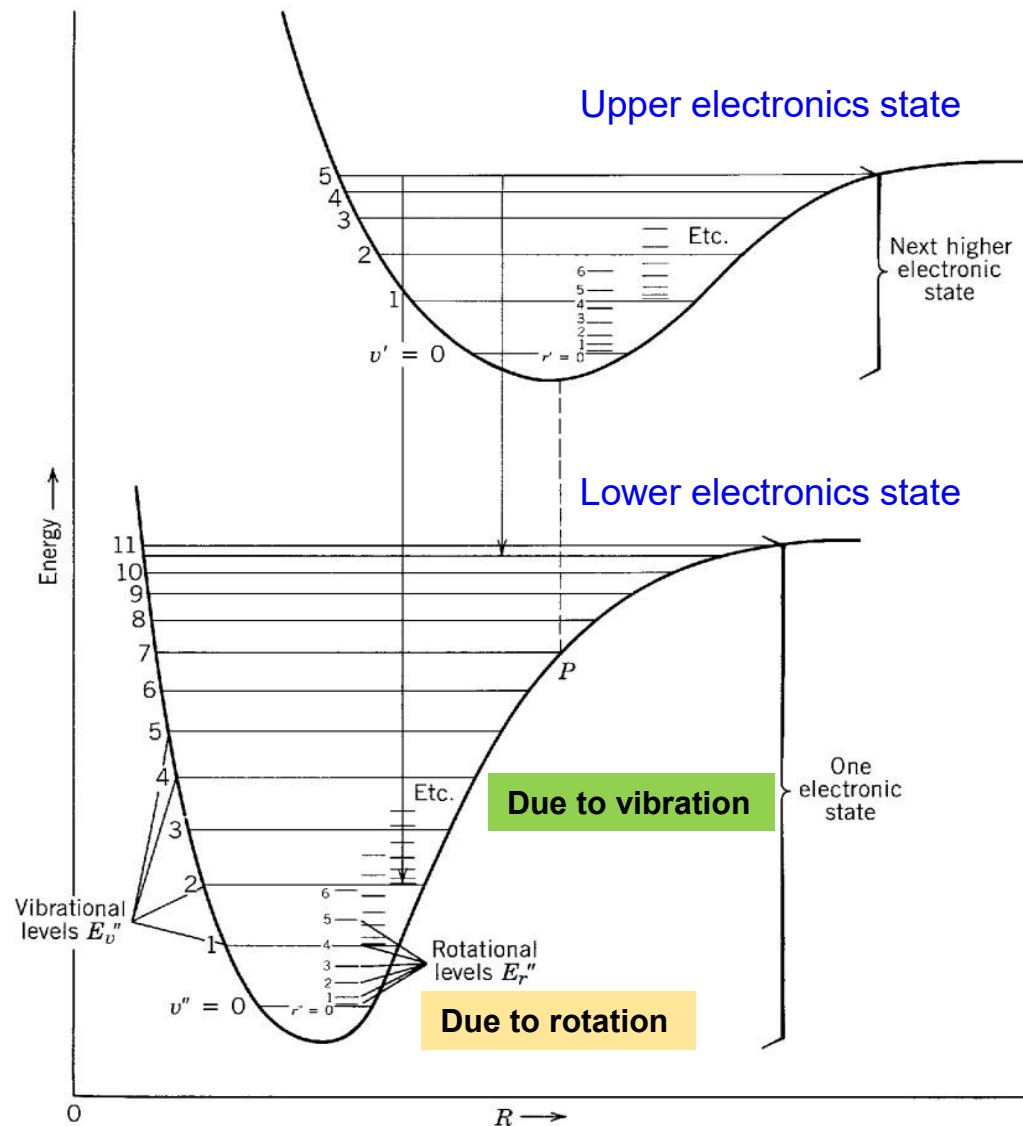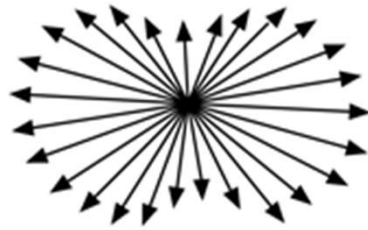
Electronic-vibration spectrum:

Bands of CN and C_2 molecules in a carbon arc in air

Eisberg and Resnick

Next, we talk a different type of light-atom interaction

First, in classical physics: (Elastic) scattering of light by a particle

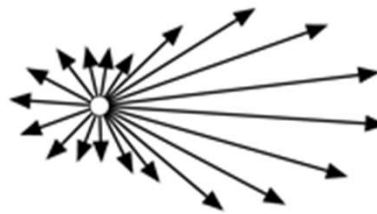1871 Rayleigh Scattering   1908 Mie Scattering   Mie Scattering, larger particles

Direction of incident light

Air molecule (kd<<1)   Aerosol 0.01-10 micron (kd～1)
                            氣膠

Rayleigh scattering (the smoke appears blue)

w/ aerosols   w/o aerosols

Mie scattering
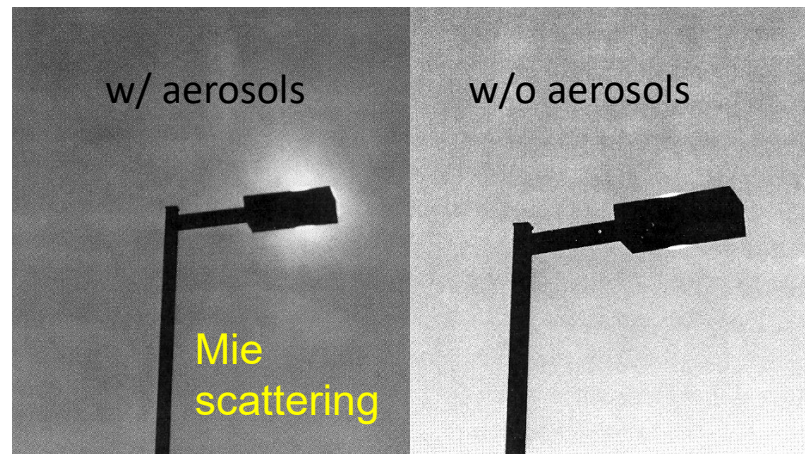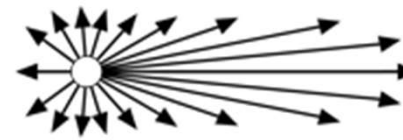
Raman spectroscopy (Raman and Krishnan, 1928)

- Raman's motivation: In the Compton effect, the X-ray photon changes its frequency after being scattered. Could similar thing happens to photons of visible light?

- Around that time, it is reported that the color of sunlight scattered by a

甘油　highly purified glycerine is a brilliant green instead of the usual blue.

- This leads Raman to actively work on this problem, and finally is able

Air molecule
(kd<<1)　　　　to observe the spectral shift of scattered light in several organic liquids

正戊烷　(such as pentane).

- They used arc lamp, so extremely long hours were needed (2-100 hours for liquids and more than 180 hours for vapors).
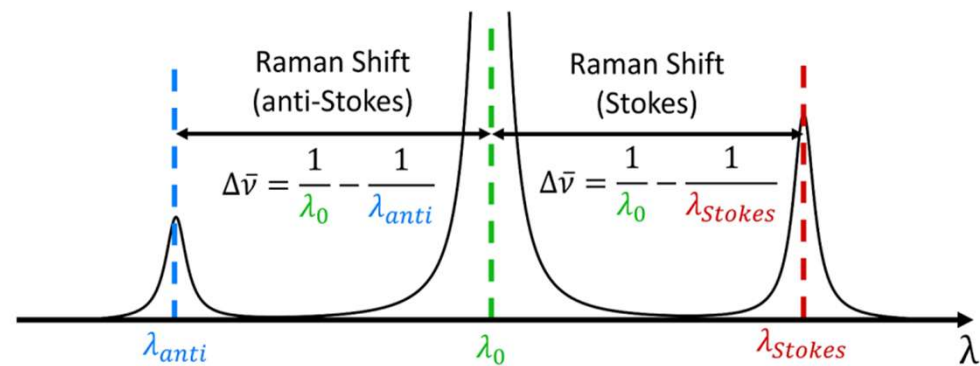
Raman and his effect, by G. Venkataraman

Raman scattering: inelastic photon scattering

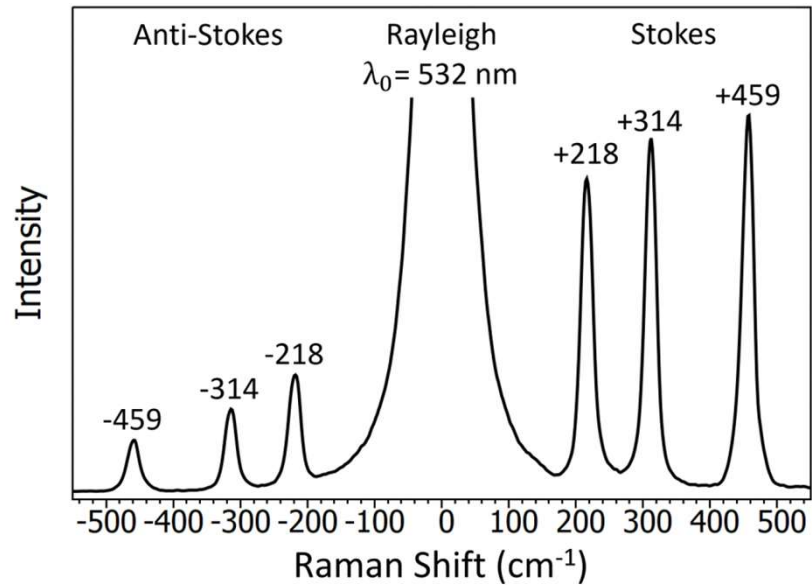## (there are rotational Raman, vibrational Raman etc)

virtual levels
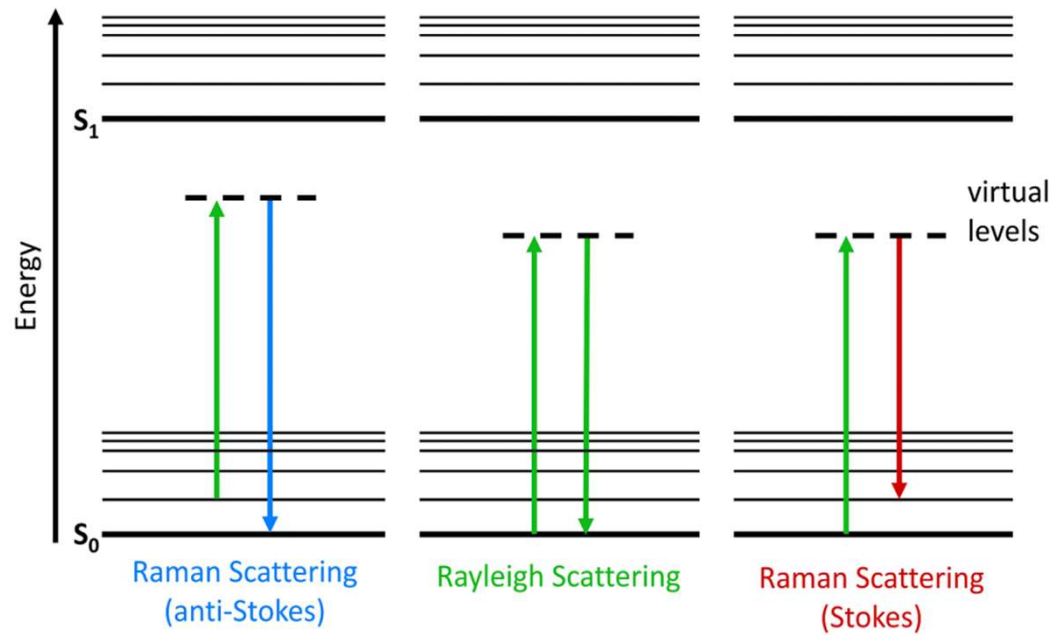
a transient state that exists for an extremely short time (~10^{-15} seconds).

(The Raman scattering involve second order perturbation.)

Raman Scattering (anti-Stokes)

Rayleigh Scattering

Raman Scattering (Stokes)

Raman Shift (anti-Stokes)

Raman Shift (Stokes)

$$\Delta \bar{\nu} = \frac{1}{\lambda_0} - \frac{1}{\lambda_{anti}}$$

$$\Delta \bar{\nu} = \frac{1}{\lambda_0} - \frac{1}{\lambda_{Stokes}}$$

λ_{anti} λ_0 λ_{Stokes} λ

https://www.edinst.com/blog/what-is-raman-spectroscopy/
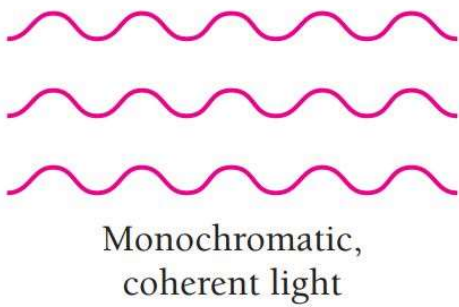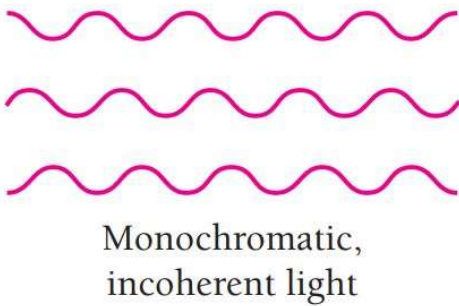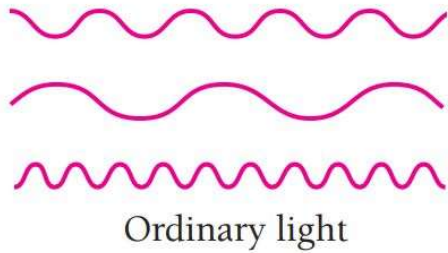
Raman Spectrum of CCl_4

Note:

For molecules without permanent dipoles like O_2, N_2, the rotational/vibration levels can be detected with Raman spectra (because of the induced dipole by EM wave).

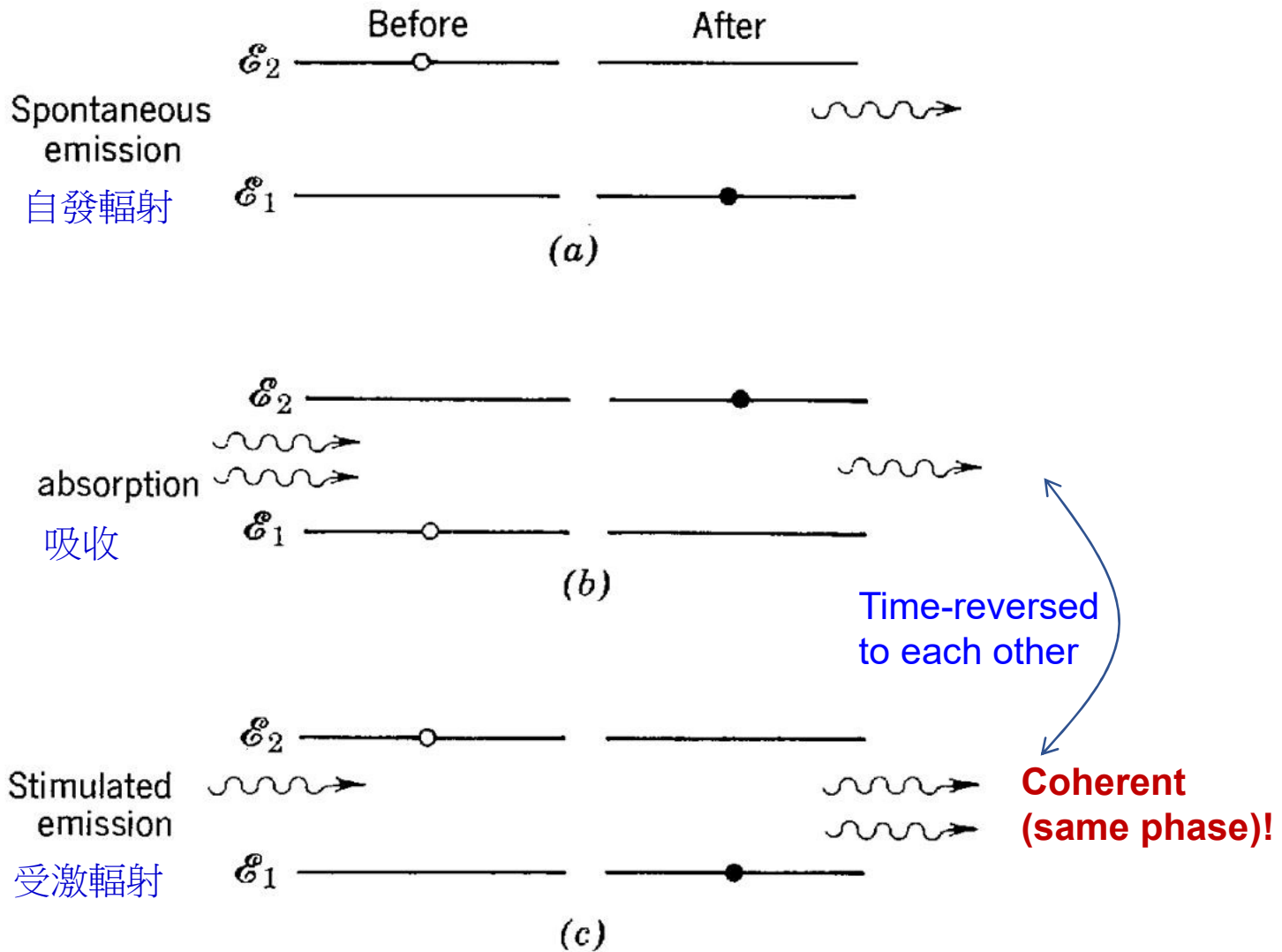Nowadays, Raman spectra can be easily observed with laser.

Ordinary light

Monochromatic, incoherent light

Monochromatic, coherent light
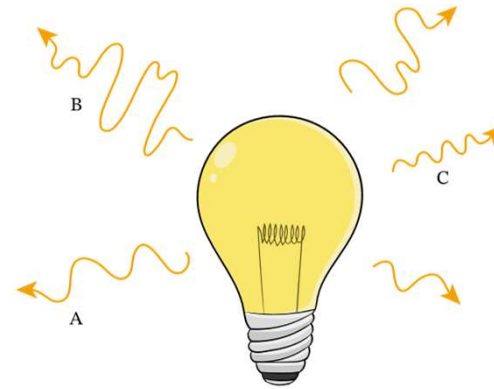
雷射的特性

- 單頻
- 同調
- 強度高
- 準直(方向)性佳

To understand how laser works, we need to learn
3 types of optical transitions:

	Before	After

$\mathscr{E}_2$

Spontaneous emission

自發輻射 $\mathscr{E}_1$

(a)

$\mathscr{E}_2$

absorption

吸收 $\mathscr{E}_1$

(b)

Time-reversed to each other

$\mathscr{E}_2$

Stimulated emission

受激輻射 $\mathscr{E}_1$

(c)

Coherent (same phase)!

Einstein's *A*, *B* coefficients (Einstein, 1917)

Consider transitions between two molecular states
with energies $E_1 < E_2$

Absorption

- The rate that a molecule at E_1 absorbs a photon is $B_{12}u(f)$.
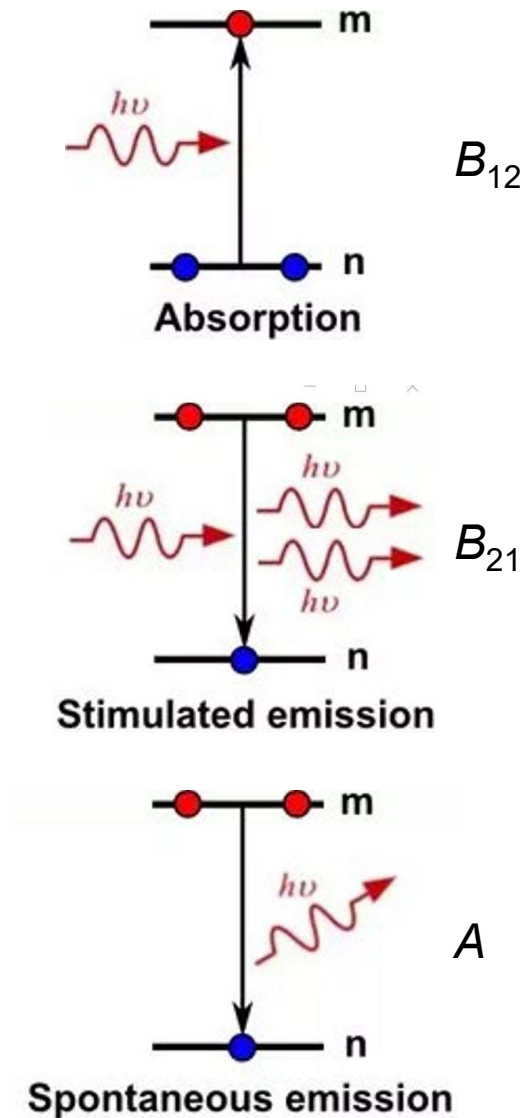 B_{21} is a constant.

Stimulated emission

- The number of molecules in the higher state $= N_2$.
  The energy density of the incoming radiation $= u(f)$.

- The rate of stimulated emissions from E_2 to E_1 is $B_{21}u(f)$.

Spontaneous emission

- The rate of spontaneous emission is A, A is a constant.

$$\Rightarrow \begin{cases} R_{1\to2} = B_{12}u(f) \\ R_{2\to1} = A + B_{21}u(f) \end{cases}$$

B_{12}

Absorption

B_{21}

Stimulated emission

A

Spontaneous emission

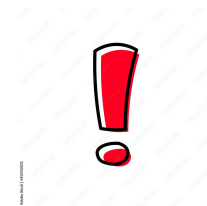Once the system reached a steady state, the total number of downward and upward transitions must be equal.

$$N_1 R_{1 \to 2} = N_2 R_{2 \to 1}$$

➡️ $$B_{12} u(f) N_1 = \left[B_{21} u(f) + A \right] N_2$$

➡️ $$u(f) = \frac{\dfrac{A}{B_{21}}}{\dfrac{N_1}{N_2} \dfrac{B_{12}}{B_{21}} - 1} \qquad \frac{N_1}{N_2} = e^{(E_2 - E_1)/kT} = e^{hf/kT}$$

Compare with $$u(f) = \frac{8 \pi f^2}{c^3} \frac{hf}{e^{hf/kT} - 1}$$

➡️ $$B_{21} = B_{12}, \quad \frac{A}{B_{12}} = \frac{8 \pi h f^3}{c^3} \quad ❗$$

"One major reason that Einstein was so happy with this work, and even called it "the derivation" of Planck's formula, was that it did not at any point use the strange counting of the distribution of energy units that Planck had employed."

Stone, Einstein and the Quantum

Principle of laser (first built by Maiman, 1960)

1) Atoms in the ground state are *pumped* to a higher state
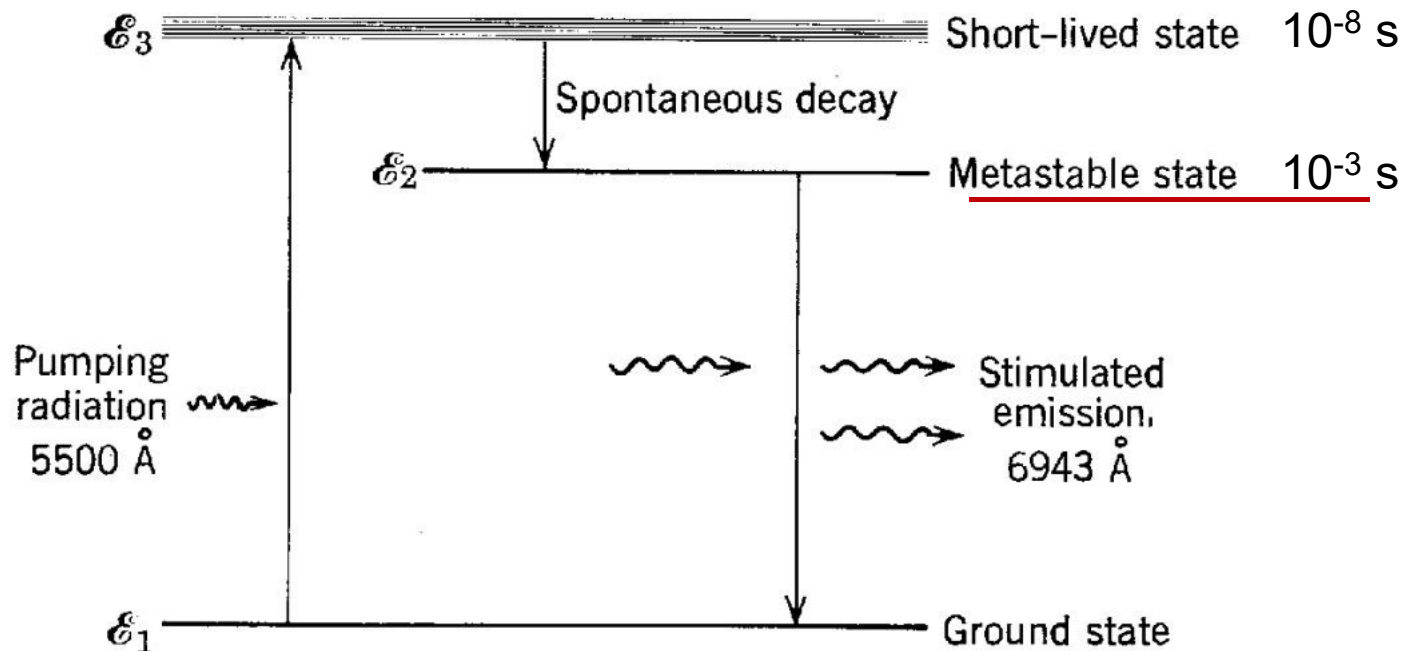
2) The atom decays quickly to E_2.

   The transition from E_2 to E_1 is *forbidden* by selection rule.

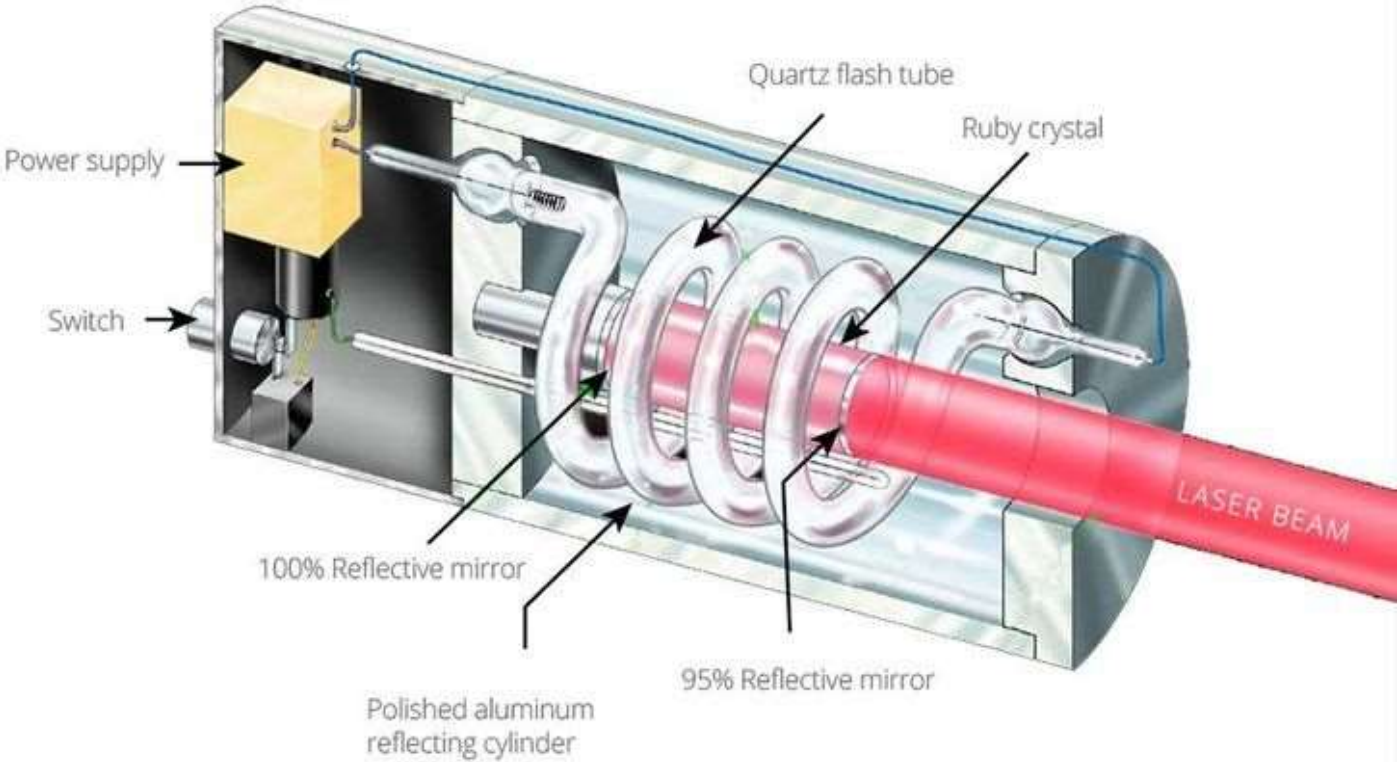亞穩態 E_2 is said to be **metastable**.

粒子數反轉 **3) Population inversion**: more atoms are in the metastable
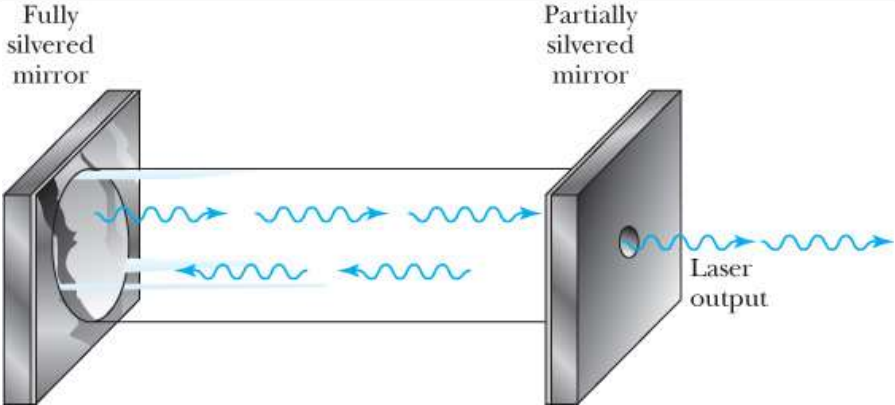
   than in the ground state.

$\mathcal{E}_3$ ══════════════════════════════ Short–lived state 10^{-8} s

                    Spontaneous decay

$\mathcal{E}_2$ ─────────────────── Metastable state 10^{-3} s

Pumping
radiation ∿∿∿➤   ∿∿∿➤   ∿∿∿➤ Stimulated
5500 Å   emission,
                                        6943 Å

$\mathcal{E}_1$ ─────────────────── Ground state

COMPONENTS OF THE FIRST RUBY LASER
Theodore Maiman

Power supply

Switch

Quartz flash tube

Ruby crystal

LASER BEAM

100% Reflective mirror

95% Reflective mirror

Polished aluminum
reflecting cylinder

Resonant cavity
for laser

Fully
silvered
mirror

Partially
silvered
mirror

Laser
output

Scientific application of laser

• Raman spectroscopy
• Holographic techniques for measurement techniques.
• Investigating nonlinear optics phenomena
• Laser based lidar (LIght raDAR) technology has application
in geology, remote sensing and atmospheric physics.
• A wide variety of interferometric techniques (e.g. LIGO)
• Inertial-confinement Nuclear fusion
• Laser cooling for atom gas
•…

Also,

• Telecommunication (Optical fiber…)

• Data storage (DVD player…)

• Material processing (welding, heat treating…)

• Medicine (diagnostics, LASIK, cosmetic…)

• Laser printers, bar-code readers

• …

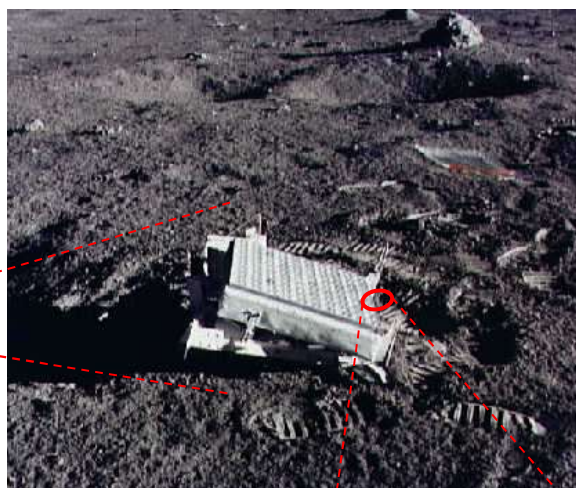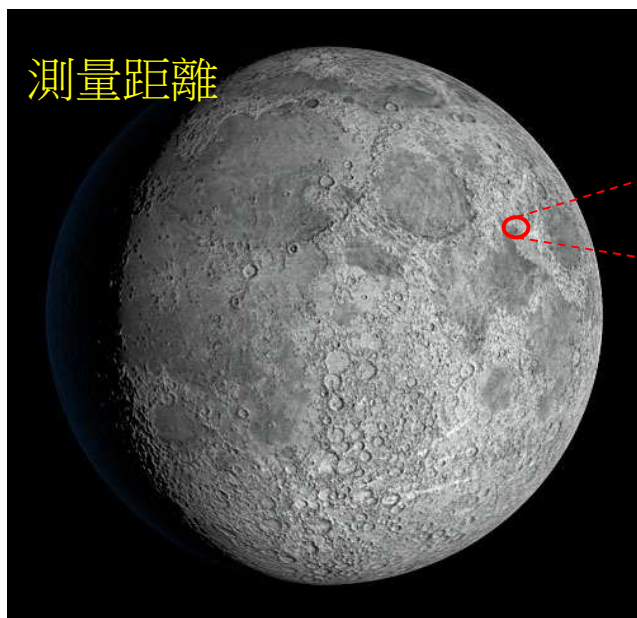https://en.wikipedia.org/wiki/List_of_laser_applications

光纖通訊

原子鐘
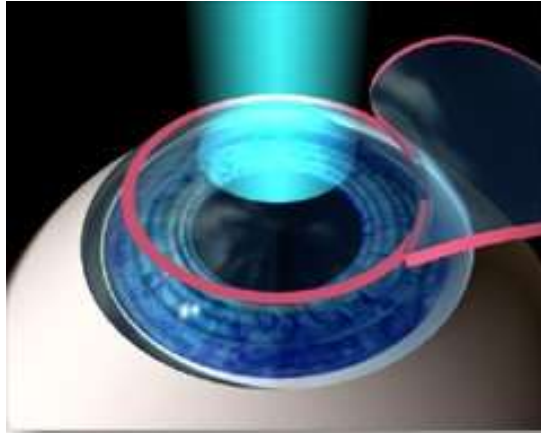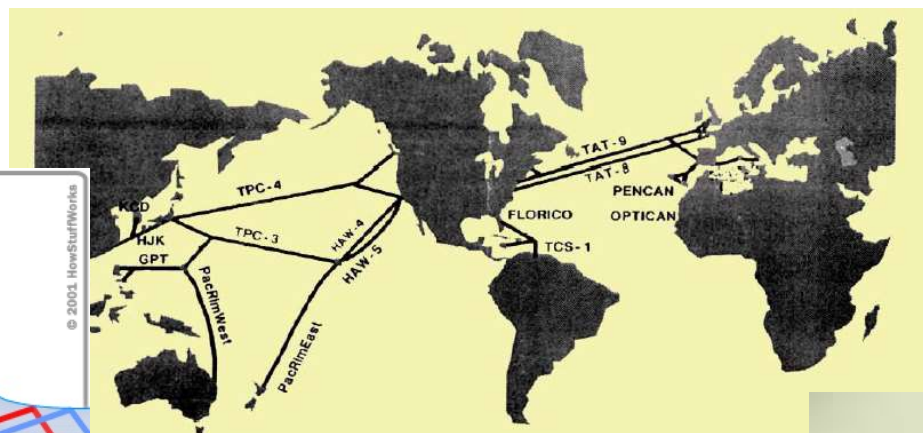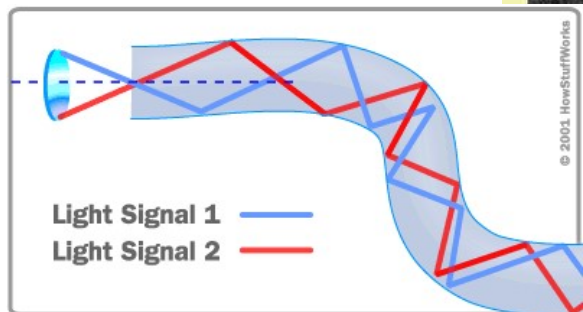
測量距離

AT&T undersea fiber-optic communication network of the 1990

Light Signal 1
Light Signal 2

回射鏡