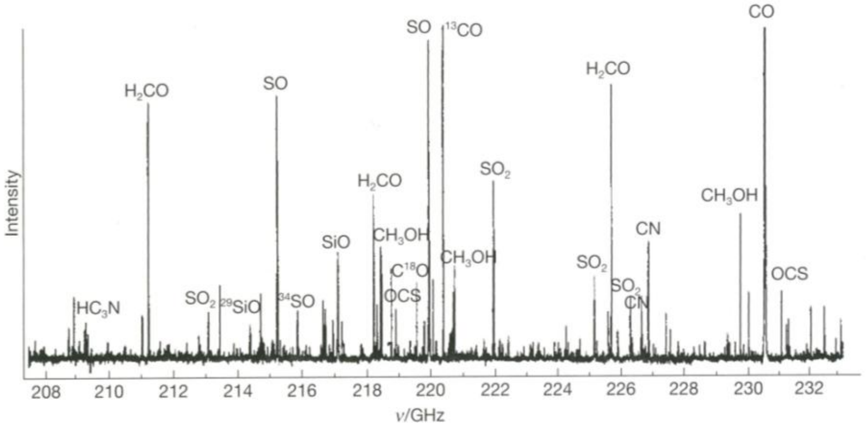
Chapter 12. Spectroscopy 1: rotational and vibrational spectra

-General features of spectroscopy

-Pure rotational spectra

-The vibrations of diatomic molecules

- The vibrations of polyatomic molecules



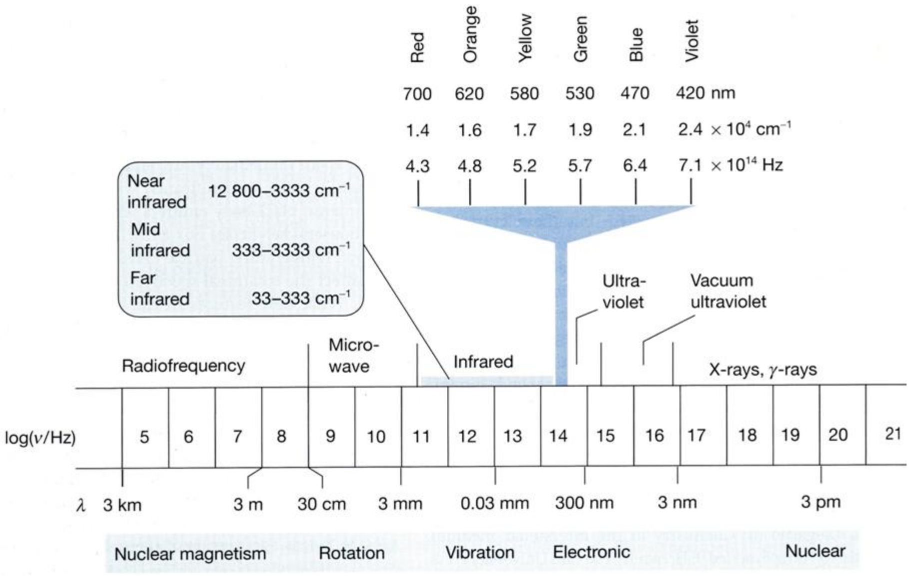
Rotational spectrum of the Orion nebula, showing spectral fingerprints of diatomic and polyatomic molecules present in the interstellar cloud. Adapted from G.A. Blake *et al.*, *Astrophys. J.* **315**, 621 (1987).

General features of molecular spectroscopy

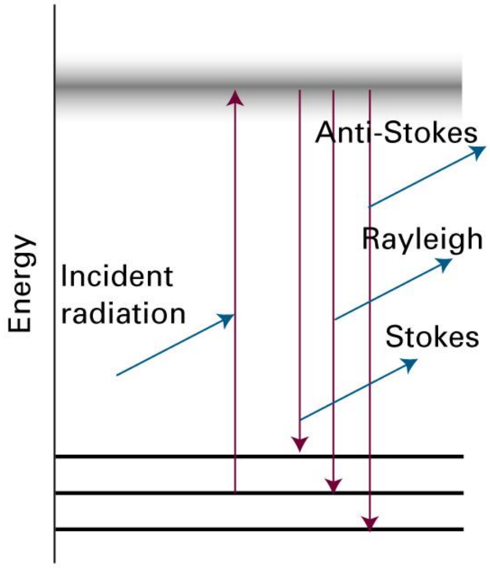
12.1 Experimental techniques
12.2 Selection rules and transition moments

$$\lambda = \frac{c}{\nu}, \tilde{\nu} = \frac{\nu}{c} = \frac{1}{\lambda}$$

- the units of the wavenumber are usually chosen as reciprocal centimeters (cm^{-1})



Raman spectroscopy



Experimental techniques

- Sources of radiation
- The dispersing element
- Fourier transform technique
- Detectors
- Resolution
- Sample

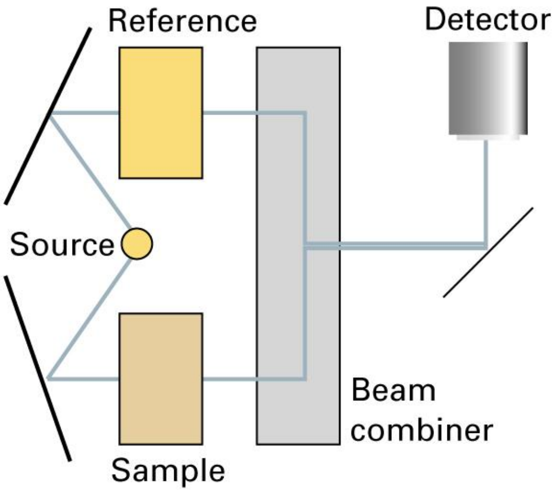
- Emission spectroscopy and absorption spectroscopy are practically the same

- Emission spectroscopy:
  transition from higher E (E_1) to lower E (E_2), and emits excess E as a photon
  -> usually, UV, VIS, near IR, and x-ray spectroscopy

- Absorption spectroscopy
  transition from lower E to higher E
  -> molecular rotations and molecular vibrations

$$h\nu = E_1 - E_2$$

General layout of absorption spectrometer



Sources of radiation

-terminology: polychromatic vs. monochromatic

- commercial spectrometer:
  black-body radiation (wide range of frequencies)

- far-IR: 34~200 cm^{-1}
  mercury arc inside quartz envelope

- mid-IR: 200~4000 cm^{-1}
  Nernst filament (oxide of Zr, Yt, Th …) or globlar (SiC)
  T of filament: 1200~2000K

- W filament: when heat to 3000K
  λ: 320 nm~2500 nm
  quartz-W-halogen lamp is used for the extension of life
  (decompose and replenish W filament)

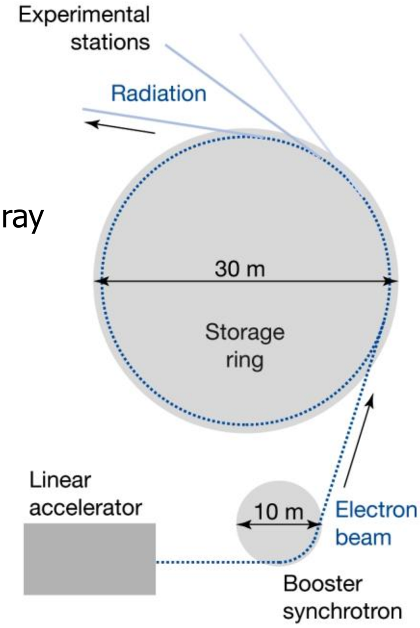
- gas discharge lamp: common source of UV and VIS radiation

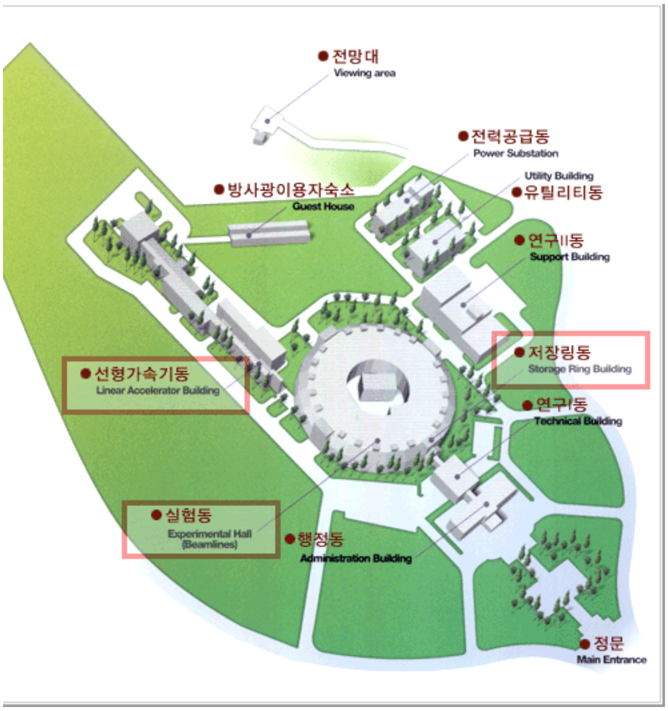
electrical discharges make gas molecules excited
and, the gas molecules emit UV or VIS

ex. Xe lamp or high P Xe lamp…(heated to 6000 K)
D_2 lamp: 200-400nm
Hg, Ne, Kr…

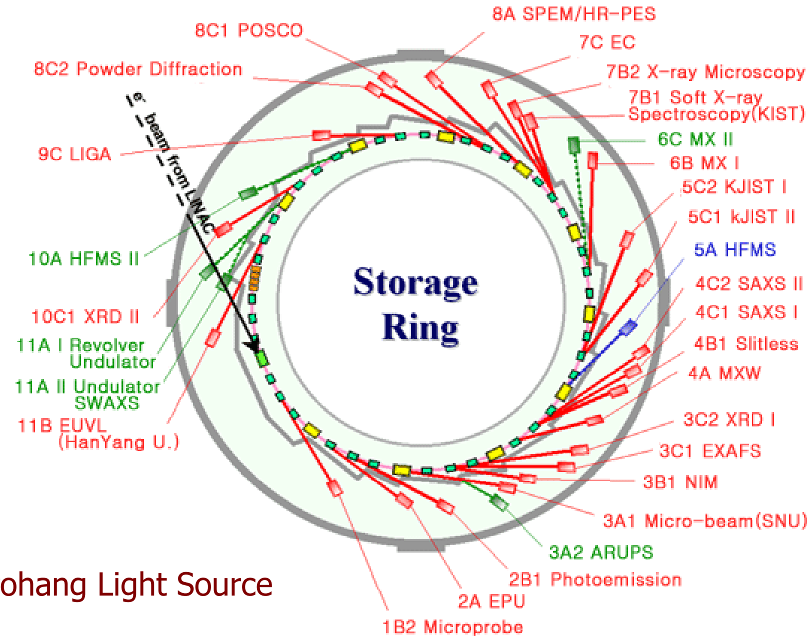
- Klystron and gun diode: microwave radiation

- synchrotron: high flux e-beam
- wide ranges including IR and x-ray





Synchrotron facility

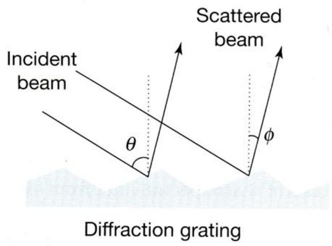


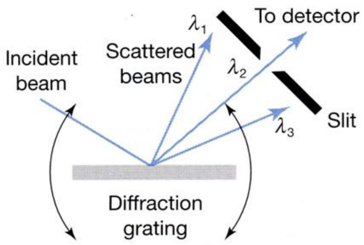
Pohang Light Source

The dispersing element [diffraction gratings]

•diffraction gratings
-glass or ceramic plate into which fine grooves have been cut and covered with a reflective coating

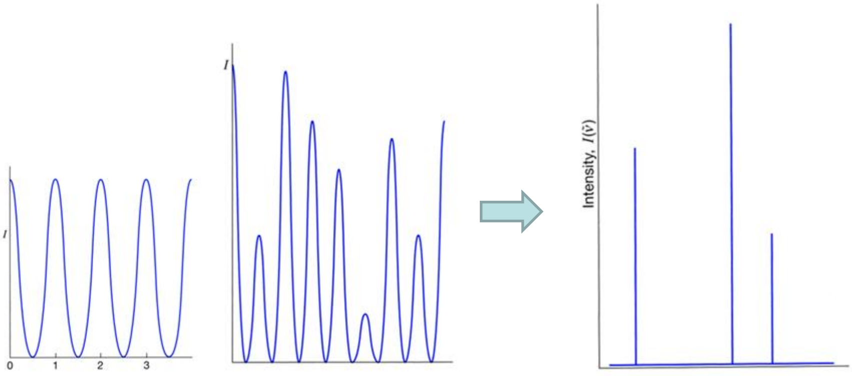
constructive interference ~ Bragg's Law





Fourier transform techniques

- time <-> freq
- real space <-> inverse space



Single freq.

several freq.

Raman spectroscopy

- Stokes radiation:

- 1 out of 10^7 incident photons collide with molecules
  -> lower E -> low freq Stokes shift

- Anti-Stokes radiation:

-other incident photon may collect E
  -> higher E -> high freq anti-Stokes shift

- Rayleigh radiation:

-radiation scattered into forward direction w/o change of freq.

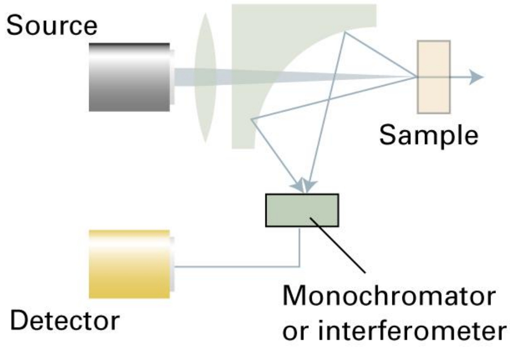
- Lasers need to be used:

1. shift in freq is very small
2. intensity of scattered radiation is low

- FT-Raman: scattered radiation, intensity max at the freq at the Stokes and anti-Stokes shift
- FT-IR: absorbtion

-> both of them are “complementary” due to different selection rules

Arrangement of Raman spectroscopy



Selection rules and transition moments [1]

-as in atomic spectra

$$\boldsymbol{\mu}_{\mathrm{fi}} = \langle \mathrm{f} | \boldsymbol{\mu} | \mathrm{i} \rangle = \int \psi_{\mathrm{f}}^{*} \boldsymbol{\mu} \psi_{\mathrm{i}} \, \mathrm{d}\tau$$

-from the time-dependent perturbation theory

$$\text{transition rate} \propto \left| \mu_{fi} \right|^{2}$$

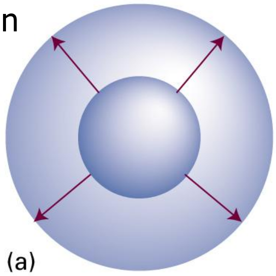
$$\propto \text{stimulated absorption or emission}$$

$$\propto \text{intensity}$$

From 1s to 2s

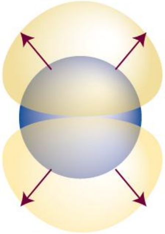
no dipole moment associated
with the charge migration

electric dipole forbidden



(a)

From 1s to 2p



dipole associated with
the charge migration

(b)

Selection rules and transition moments [2]

-gross selection rule

specifies general features of a molecule

-specific selection rule

specifies in terms of quantum number

Detector: radiation -> electric current or V

- photomultiplier tube (PMT): photoelectric effect, very sensitive

- photodiode: not very sensitive,
  light-induced e- transfer rxn create mobile charge carrier

-avalanche photodiode: improving sensitivity by applying large Vdifference
-charge coupled device (CCD):
two dimensional array up to 6 million small photodiode detector

- mercury-cadmium-telluride (MCT) detector:

-photovoltaic device: potential difference changes on IR

- deterated triglycine sulfate (DTGS) detector:

-pyroelectric device: capacitance is sensitive to T

- Crystal diode: microwave detector

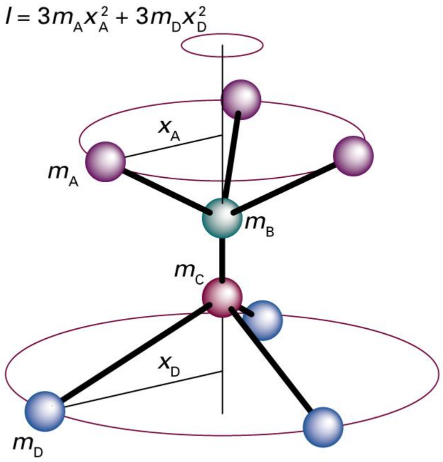
-Ge, Si, GaAs

Pure rotation spectra

12.4 Moments of inertia
12.5 The rotational energy levels
12.6 Rotational transitions
12.7 Rotational Raman spectra
12.8 Nuclear statistics and rotational states

Moments of inertia

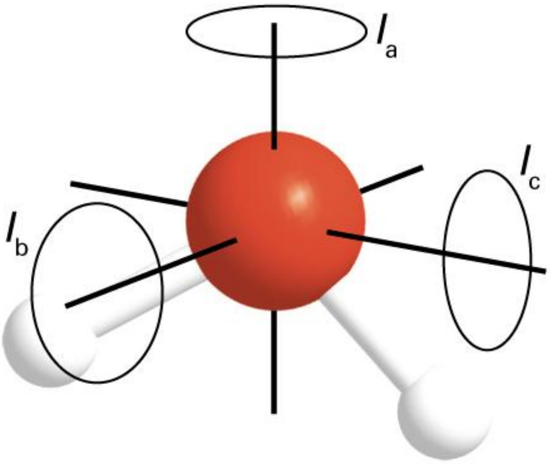
$$I = \sum_i m_i r_i^2$$



12.6 The definition of moment of inertia. In this molecule there are three identical atoms attached to the B atom and three different but mutually identical atoms attached to the C atom. In this example, the centre of mass lies on an axis passing through the B and C atom, and the perpendicular distances are measured from this axis.

Conventionally,

$$I_c \geq I_b \geq I_a$$



12.7 An asymmetric rotor has three different moments of inertia; all three rotation axes coincide at the centre of mass of the molecule.

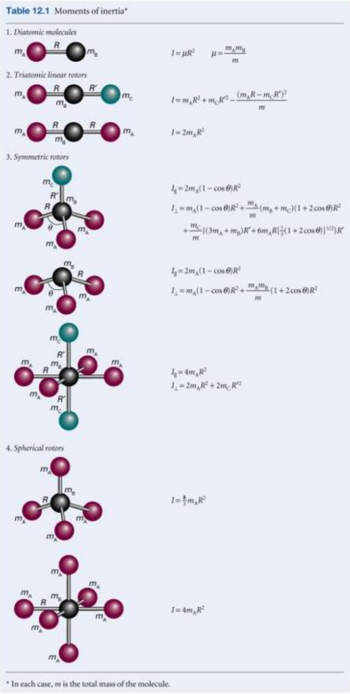


Table 12.1 Moments of inertia*

1. *Diatomic molecules*

$I=\mu R^2 \qquad \mu=\frac{m_A m_B}{m}$

2. *Triatomic linear rotors*

$I=m_A R^2+m_C R'^2-\frac{(m_A R-m_C R')^2}{m}$

$I=2m_A R^2$

3. *Symmetric rotors*

$I_\parallel=2m_A(1-\cos\theta)R^2$

$I_\perp=m_A(1-\cos\theta)R^2+\frac{m_A}{m}(m_B+m_C)(1+2\cos\theta)R^2$
$+\frac{m_C}{m}\{(3m_A+m_B)R'+6m_A R[\frac{1}{3}(1+2\cos\theta)]^{1/2}\}R'$

$I_\parallel=2m_A(1-\cos\theta)R^2$

$I_\perp=m_A(1-\cos\theta)R^2+\frac{m_A m_B}{m}(1+2\cos\theta)R^2$

$I_\parallel=4m_A R^2$

$I_\perp=2m_A R^2+2m_C R'^2$

4. *Spherical rotors*

$I=\frac{8}{3}m_A R^2$

$I=4m_A R^2$

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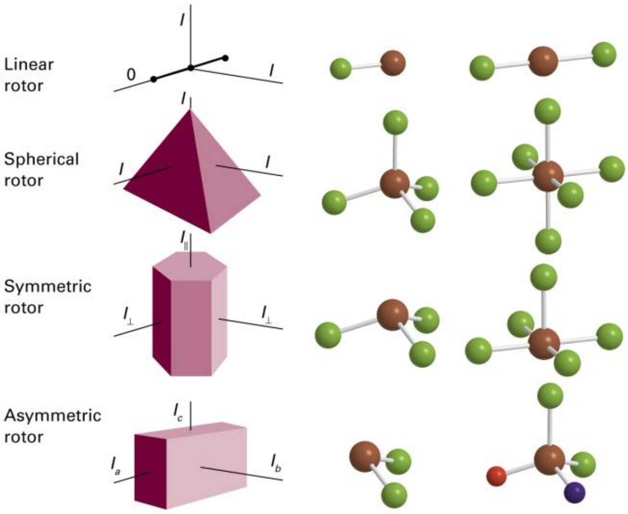
* In each case, m is the total mass of the molecule.

Rigid rotors:

bodies that do not distort under rotation



2 equal
moments of inertia
(3rd zero)

3 equal
moments of inertia

2 equal
moments of inertia
(3rd non-zero)

The rotational E levels

$$E_a = \tfrac{1}{2} I_a \omega_a^2$$

$$E = \tfrac{1}{2} I_a \omega_a^2 + \tfrac{1}{2} I_b \omega_b^2 + \tfrac{1}{2} I_c \omega_c^2$$

$$E = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c}$$

Spherical rotors

all three inertia are equal.

$$E = \frac{J_a^2 + J_b^2 + J_c^2}{2I} = \frac{J^2}{2I}$$

$$J^2 \to J(J+1)\hbar^2 \qquad J = 0, 1, 2, \ldots$$

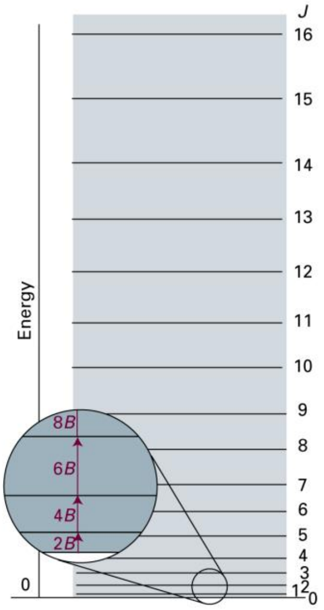
$$E_J = J(J+1)\frac{\hbar^2}{2I} \qquad J = 0, 1, 2, \ldots$$

$hcB = \dfrac{\hbar^2}{2I}$ rotational constant $B = \dfrac{\hbar}{4\pi c I}$

$$E_J = hcBJ(J+1) \qquad J = 0, 1, 2, \ldots$$

rotational term $F(J) = BJ(J+1)$

$$F(J) - F(J-1) = 2BJ$$



12.9 The rotational energy levels of a linear or spherical rotor. Note that the energy separation between neighbouring levels increases as *J* increases.

Symmetric rotors

ex. two inertia are equal.

⇨ principal axis: unique axis, different inertia

oblate: $I_{\parallel} > I_{\perp}$ pancake, C_6H_6
prolate: $I_{\parallel} < I_{\perp}$ cigar, CH_3Cl

$$E = \frac{J_b^2 + J_c^2}{2I_\perp} + \frac{J_a^2}{2I_\parallel} \qquad \mathcal{J}^2 = J_a^2 + J_b^2 + J_c^2$$

$$E = \frac{\mathcal{J}^2 - J_a^2}{2I_\perp} + \frac{J_a^2}{2I_\parallel} = \frac{\mathcal{J}^2}{2I_\perp} + \left(\frac{1}{2I_\parallel} - \frac{1}{2I_\perp}\right) J_a^2$$

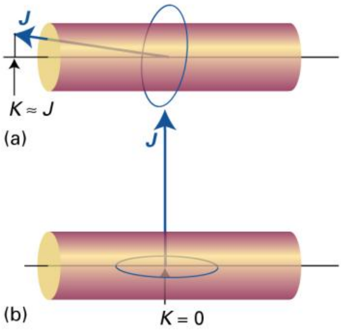
$$A = \frac{\hbar}{4\pi c I_\parallel}, B = \frac{\hbar}{4\pi c I_\perp}$$

$$F(J, K) = BJ(J+1) + (A-B)K^2$$

$$J = 0, 1, 2, \ldots$$
$$K = 0, \pm 1, \ldots, \pm J$$

A=B ->spherical rotor

K=±J,
angular momentum
comes from the principal axis



K=0, no angular momentum
around the principal axis

note) sign of K: opposite direction of rotation -> degeneracy

Linear rotors

-rotation occurs around an axis only perpendicular to the line of atom
('0' angular momentum around the line)

$$F(J) = BJ(J+1) \qquad J = 0, 1, 2, \ldots$$

K=0 $\quad F(J, K) = BJ(J+1) + (A-B)K^2$

Degeneracies

- each level is doubly degenerate due to K (except K=0) (K and –K has the same E.)
- angular momentum of a **symmetric rotor**:

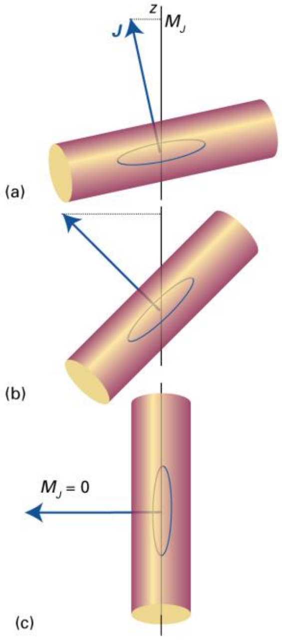
$$M_J\hbar, M_J = 0, \pm 1, \ldots \pm J$$

- all 2J+1 orientations of the rotating molecules have the same E
- in total, 2(2J+1) degeneracy (K≠0)
- (2J+1) degeneracy (K=0)

- for **a spherical rotor:** (A=B)

-(2J+1) degeneracies from orientation in space
-(2J+1) degeneracies from orientation wrt an arbitrary axis of a molecule

overall degeneracy: $(2J+1)^2$



the Stark effect

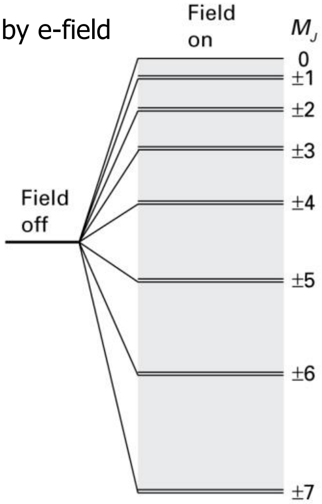
- Splitting of E level due to by an electric field
- degeneracy associated with M_J is partly removed by e-field

- for a linear rotor

$$E(J, M_J) = hcBJ(J+1) + a(J, M_J)\mu^2\mathcal{E}^2$$

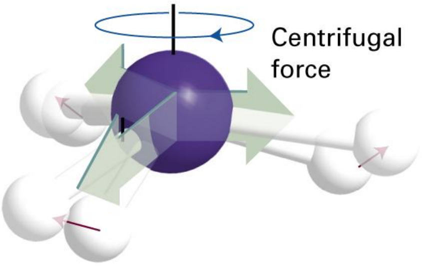
$$a(J, M_J) = \frac{J(J+1) - 3M_J^2}{2hcBJ(J+1)(2J-1)(2J+3)}$$

- E state with M_J is dep on the square of the permanent electric dipole moment (μ) -> μ can be measured due to Stark effect



Centrifugal distortion

- molecules are not really rigid.
- rotation stretches the bond and increases the moment of inertia
- centrifugal distortion reduces B and E level are closer



$$F(J) = BJ(J+1) - D_J J^2 (J+1)^2$$

- Centrifugal distortion constant

-D_J becomes large when the bond is easily stretched.

-for diatomic molecules,

$$D_J \approx \frac{4B^3}{\tilde{\nu}^2}$$

Rotational transitions

by applying oscillating e-field (Stark modulation)
, rotational transition is examined

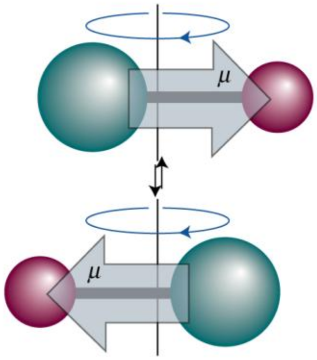
-rotational selection rules

for a pure rot spectrum, a molecule must be polar
(a polar molecule possess a fluctuating dipole when rotating)

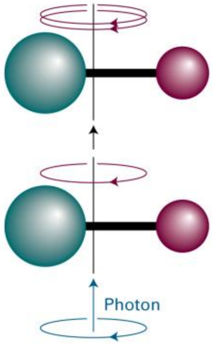
homonuclear diatomic molecule, symmetrical linear molecule, spherical molecule (not distorted by rotation)
-> rotationally inactive

-rotational selection rules

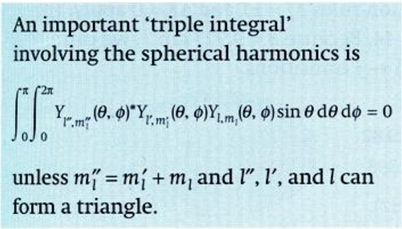
$$\Delta J = \pm 1 \qquad \Delta M_J = 0, \pm 1$$



-Rotating polar molecule
~oscillating dipole
~oscillation of EM filed



-same sense as the spin
of the incoming photon



An important 'triple integral' involving the spherical harmonics is

$$\int_0^{\pi}\int_0^{2\pi} Y_{l'',m_l''}(\theta,\phi)^* Y_{l',m_l'}(\theta,\phi) Y_{l,m_l}(\theta,\phi)\sin\theta\,d\theta\,d\phi = 0$$

unless $m_l'' = m_l' + m_l$ and l'', l', and l can form a triangle.

-transition intensity (J+1 <-> J)

$$|\mu_{J+1,J}|^2 = \left(\frac{J+1}{2J+1}\right)\mu_0^2 \rightarrow \tfrac{1}{2}\mu_0^2 \qquad \text{for} \quad J \gg 1$$

more polar molecules, more intense

for symmetric molecules, ΔK=0 (additional selection rule)
-> when the electric dipole moment // principal axis, the molecule cannot be accelerated.

-The appearance of rotational spectra

$$\tilde{\nu}(J+1 \leftarrow J) = 2B(J+1) \qquad J = 0, 1, 2, \ldots$$

$$\tilde{\nu}(J+1 \leftarrow J) = 2B(J+1) - \underline{4D_J(J+1)^3}$$

very small

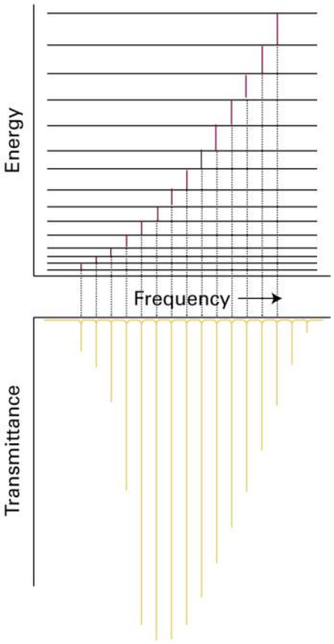
-separation 2B

Population of a rotational E level:
-Boltzmann distribution

$$N_J \propto N g_J e^{-E_J/kT}$$

degeneracy

$$J_{\max} \approx \left(\frac{kT}{2hcB}\right)^{1/2} - \tfrac{1}{2}$$



-Rotational Raman spectra

Gross selection rule for rotational Raman transition:
the molecule must be anisotropically polarizable

polarizability

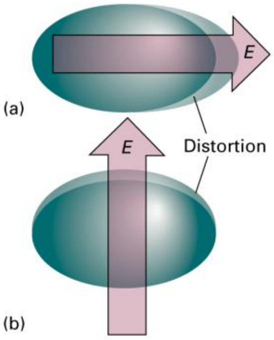
$$\mu = \alpha \mathcal{E}$$

E-field

selection rule

Linear rotors: $\Delta J = 0, \pm 2$

Symmetric rotors: $\Delta J = 0, \pm 1, \pm 2; \qquad \Delta K = 0$



E-filed
~distortion
~dipole moment
~anisotropic polarizability

Justification

gross selection rule

$$\mu_{\text{ind}} = \alpha\mathcal{E}(t) = \alpha\mathcal{E}\cos\omega_{\text{i}}t$$

$$\alpha = \alpha_0 + \Delta\alpha\cos 2\omega_{\text{R}}t \qquad \Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$$

$$\begin{aligned}\mu_{\text{ind}} &= (\alpha_0 + \Delta\alpha\cos 2\omega_{\text{R}}t)\times(\mathcal{E}\cos\omega_{\text{i}}t)\\ &= \alpha_0\mathcal{E}\cos\omega_{\text{i}}t + \mathcal{E}\Delta\alpha\cos 2\omega_{\text{R}}t\cos\omega_{\text{i}}t\\ &= \alpha_0\mathcal{E}\cos\omega_{\text{i}}t + \tfrac{1}{2}\mathcal{E}\Delta\alpha\{\cos(\omega_{\text{i}} + 2\omega_{\text{R}})t + \cos(\omega_{\text{i}} - 2\omega_{\text{R}})t\}\end{aligned}$$

$$\omega_{\text{i}} \pm 2\omega_{\text{R}}$$

$$\Delta J = \pm 2.$$

specific selection rule

$$\begin{aligned}\mu_{\text{ind},x} &= \mu_x\sin\theta\cos\phi\\ \mu_{\text{ind},y} &= \mu_y\sin\theta\sin\phi\\ \mu_{\text{ind},z} &= \mu_z\cos\theta\end{aligned}$$

$$\mathcal{E}_x = \mathcal{E}\sin\theta\cos\phi \qquad \mathcal{E}_y = \mathcal{E}\sin\theta\sin\phi \qquad \mathcal{E}_z = \mathcal{E}\cos\theta$$

$$\mu_{\text{ind}} = \alpha_{\perp}\mathcal{E}_x\sin\theta\cos\phi + \alpha_{\perp}\mathcal{E}_y\sin\theta\sin\phi + \alpha_{\parallel}\mathcal{E}_z\cos\theta = \alpha_{\perp}\mathcal{E}\sin^2\theta + \alpha_{\parallel}\mathcal{E}\cos^2\theta$$

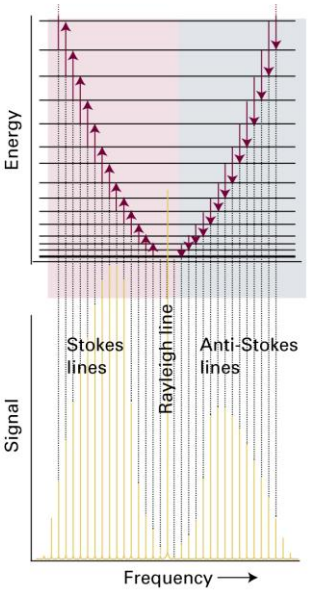
$$\mu_{\text{ind}} = \left\{\tfrac{1}{3}\alpha_{\parallel} + \tfrac{2}{3}\alpha_{\perp} + \tfrac{4}{3}\left(\frac{\pi}{5}\right)^{1/2}\Delta\alpha Y_{2,0}(\theta,\phi)\right\}\mathcal{E}$$

$$\langle Y_{J_{\text{f}},M_{J,\text{f}}}|\mu_{\text{ind}}|Y_{J_{\text{i}},M_{J,\text{i}}}\rangle$$

$$(\tfrac{1}{3}\alpha_{\parallel} + \tfrac{2}{3}\alpha_{\perp})\langle Y_{J_{\text{f}},M_{J,\text{f}}}|Y_{J_{\text{i}},M_{J,\text{i}}}\rangle \qquad \Delta\alpha\langle Y_{J_{\text{f}},M_{J,\text{f}}}|Y_{2,0}Y_{J_{\text{i}},M_{J,\text{i}}}\rangle$$

$$J_{\text{f}} - J_{\text{i}} = 0 \qquad J_{\text{f}} - J_{\text{i}} = \pm 2 \qquad \Delta\alpha \neq 0.$$

-Raman spectroscopy



Stokes line, higher rotational state (ΔJ=+2)

$$\tilde{\nu}(J+2 \leftarrow J) = \tilde{\nu}_i - \{F(J+2) - F(J)\} = \tilde{\nu}_i - 2B(2J+3)$$

anti-Stokes line,
scattered photon with increased E
(ΔJ=-2)

$$\tilde{\nu}(J-2 \leftarrow J) = \tilde{\nu}_i + \{F(J) - F(J-2)\} = \tilde{\nu}_i + 2B(2J-1)$$

separation of adjacent lines
in Stokes and anti-Stokes region: 4B

$\rightarrow I_\perp \longrightarrow$ bond lengths

16.8 Nuclear statistics and rotational states

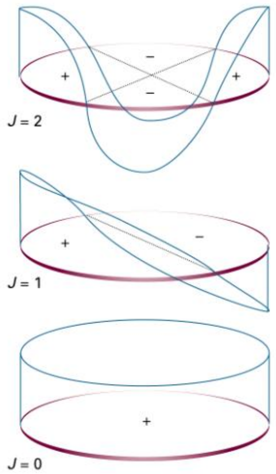
Nuclear statistics:
Selective occupation of rotational states
(from Pauli principle)

ex. rot spectrum of CO_2
2<- 0, 4<- 2, … not 5<- 3, 3<- 1

Pauli principle:
-two identical fermion label exchange -> opposite sign
-two identical boson label exchange -> same sign

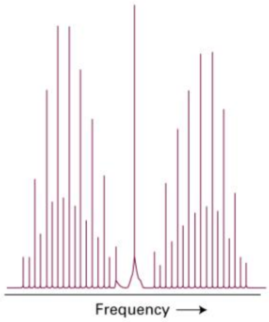
Only even values of Js are permissible since O is boson.

when a CO_2 rotates 180^o, two identical O nuclei (spin 0 boson) are interchanged, overall waveftn are the same. But, rotational waveftn change sign by $(-1)^J$



Symmtries of rotational wavefunctions

alternation in intensity

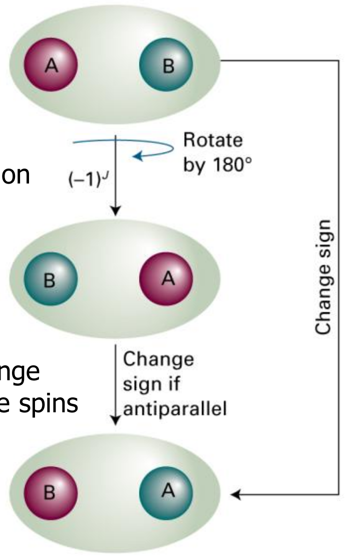


Rotational Raman spectrum of a diatomic molecule with 2 identical spin-1/2 nuclei

for homonuclear diatomic molecule with spin I,

$$\frac{\text{Number of ways of achieving odd } J}{\text{Number of ways of achieving even } J} = \begin{cases} (I+1)/I & \text{for half-integral spin nuclei} \\ I/(I+1) & \text{for integral spin nuclei} \end{cases}$$

The interchange of two identical fermion nuclei

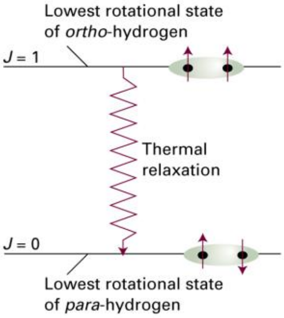


rotation

Change in sign of the overall wavefunction

interchange of unlike spins

When hydrogen is cooled,



parallel nuclear spin:
it cannot exist with J=0
(it just rotates even at low T and
has an effective rotational zero-point E)

not liq.

paired nuclear spin

Slow process, slow release of E

-Making liq hydrogen (from ortho to para)

pass hydrogen over a metal surface:
the molecule adsorb as atoms, and then recombine