Rotational spectroscopy

ver. 20191201

Interaction of materials with microwave light

Microwave (and far infrared) light excites the rotational motion of molecules.

(Remember, that higher energy light (IR, VIS, UV) excites the rotation, too,
but for that case this is a „minor/side” effect.)

The most practical application of microwave radiation.

https://fsmedia.imgix.net/b6/e2/4a/ff/72a0/4d2d/a08a/599db2e4d90a/toshiba-microwave.jpeg?crop=edges&fit=crop&auto=format%2Ccompress&h=485.5&w=971

Mechanical basics

Physical quantities of linear and rotational motions are **analogous** to each other.

linear	rotational
force	torque
mass	moment of inertia
acceleration	angular acceleration
momentum	angular momentum

Torque: a twisting force that tends to cause rotation.
Moment of inertia: measures how difficult to rotationally accelerate a body.
Angular acceleration: time derivative of the angular velocity.
Angular momentum: $\vec{L} = m\vec{p}$, the rotational equivalent of the momentum ($\vec{p} = m\vec{v}$)

Note: the dimension of the analogous quantities are not the same!

Moment of inertia, angular momentum

Moment of inertia (*I*): measures how difficult to rotationally accelerate a body.

$$I = \frac{L}{\omega}$$

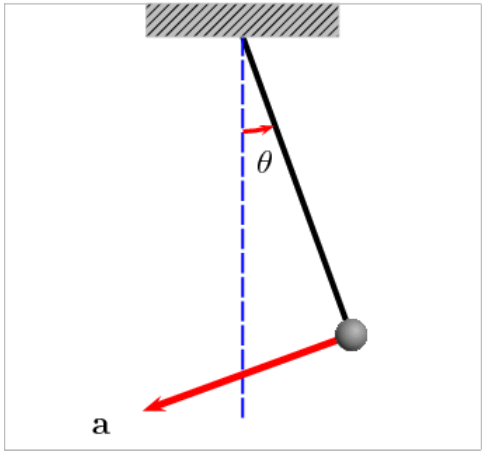
where L is the angular momentum, ω is the angular velocity around a principal axis.

Angular momentum is a conserving quantity (Video of rotating chair experiment, illustrating moment of inertia. When the spinning professor pulls his arms, his moment of inertia decreases; to conserve angular momentum, his angular velocity increases.)

For a simple pendulum: $I = m \cdot r^2$
where m is the mass, r is the distance from the pivot point

The moment of inertia of a body is the sum of the induvidual terms:

$$I = \sum_{\mathrm{i}} m_{\mathrm{i}} \cdot r_{\mathrm{i}}^2$$



Moment of inertia of molecules

The moment of inertia of a body is the sum of the induvidual terms:

$$I = \sum_{\mathrm{i}} m_{\mathrm{i}} \cdot r_{\mathrm{i}}^2$$

In molecules the moment of inertia **depends** on both the **mass of the atoms** and the **geometry of the molecule**, the rotational spectroscopy will provide us with information about bond lengths and bond angles.

Physics of rotations
The rigid rotor model

Rigid rotor is an arbitrary 3D rigid object.
To represent a **diatomic molecule** a much simpler version, the **linear rigid rotor** is used.

The moment of inertia for this two point system:

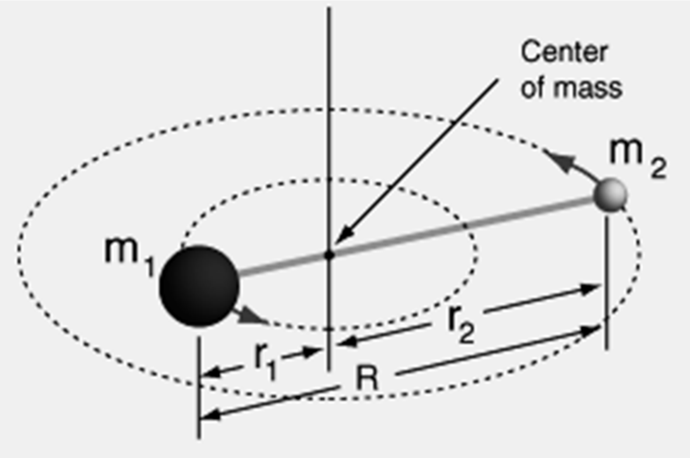
$$I = m_1 \cdot r_1^2 + m_2 \cdot r_2^2$$

r_1, r_2 distances can be replaced by the bond length:

$$I = \frac{m_1 m_2}{m_1 + m_2} \cdot R^2$$

and $\frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass, μ:

$$I = \mu \cdot R^2$$



R: bond length
r_1, r_2: distances from the pivot point
m_1, m_2: masses of atoms

Rotational axis

A 3D body has 3 rotational axis. In general, the rotational properties of any molecule can be expressed using the moments of inertia about three mutually perpendicular axes (I_a, I_b, I_c).

Classification of rigid rotors:

Spherical rotors have three equal moments of inertia (e.g. CH_4, SF_6).

Symmetric rotors have two equal moments of inertia (e.g. CH_3Cl, NH_3, C_6H_6).

Linear rotors have one moment of inertia (that around the molecular axis) equal to zero (e.g. CO_2, HCl, CH≡CH).

Asymmetric rotors have three different moments of inertia (e.g. IBrCFCl).

Rotational energy

The rotational energy can be similarly calculated as the linear kinetic energy:

$$E = \frac{1}{2} I\omega^2$$

It is often expressed by the angular momentum:

$$E = \frac{1}{2} L\omega \quad \text{or} \quad E = \frac{1}{2}\frac{L^2}{I}$$

In the quantum mechanical description the rotational energy can only have **discrete values**:

$$E = J(J+1)\frac{h^2}{8\pi^2 I}$$

where *J* is the rotation quantum number.

In wavelengths: $E = hc\tilde{v} = J(J+1)\frac{h^2}{8\pi^2 I}$, therefore $\tilde{v} = J(J+1)\frac{h}{8\pi^2 Ic} = J(J+1)B$

$B = \frac{h}{8\pi^2 Ic}$ is called rotational constant.

Selection rule

The rotation quantum number can be only non-negative number (J = 0, 1, 2, …).

The rotation quantum number can change only by one: $\Delta J = \pm 1$

Only dipole molecules absorb microwave radiation (the molecule must have a permanent dipole moment, $\mu \neq 0$).

Practical consequences: water absorbs microwave radiation in the MW oven quite well. More salty parts of the food can be heated much easier then less salty ones. Apolar molecules (e.g. hexane) do not absorb microwave radiation and can not be heated in MW oven (less important piece of information from the cooking point of view).

Absorbtion energies

The rotational energy differences can simply be expressed:

$\Delta J = J_2 - J_1 = 1$, therefore $J_2 = J_1 + 1$

$$\Delta\tilde{v} = J_2(J_2 + 1)B - J_1(J_1 + 1)B = (J_2^2 + J_2 - J_1^2 - J_1)B = (J_2^2 - J_1^2 + J_2 - J_1)B$$

$$= \left(\underbrace{(J_2 - J_1)}_{=1}\underbrace{(J_2 + J_1)}_{=2J_1+1} + \underbrace{J_2 - J_1}_{=1}\right)B = (2J_1 + 2)B = 2B(J_1 + 1)$$

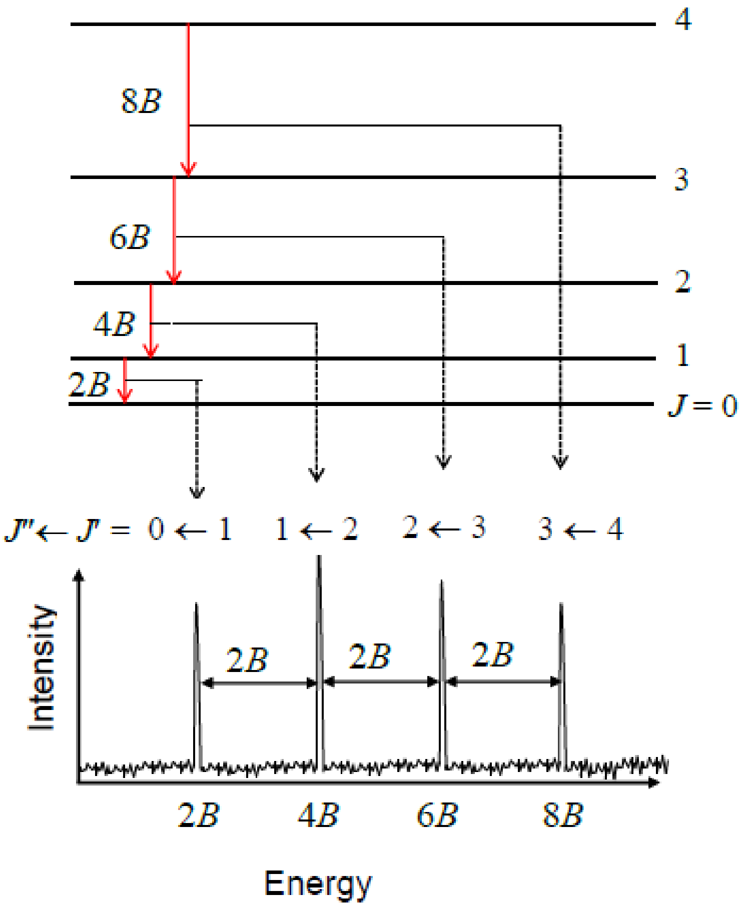
$$\Delta\tilde{v} = 2B(J_1 + 1) \text{ or } \Delta\tilde{v} = 2BJ_2$$

Absorption peaks appear at these wavelengths.

Energy levels and absorption peaks

The distances between the rotation energy levels are not the same, but increases by 2*B*.

This leads to that the adjacent transitions are separated by 2*B* in the spectrum.



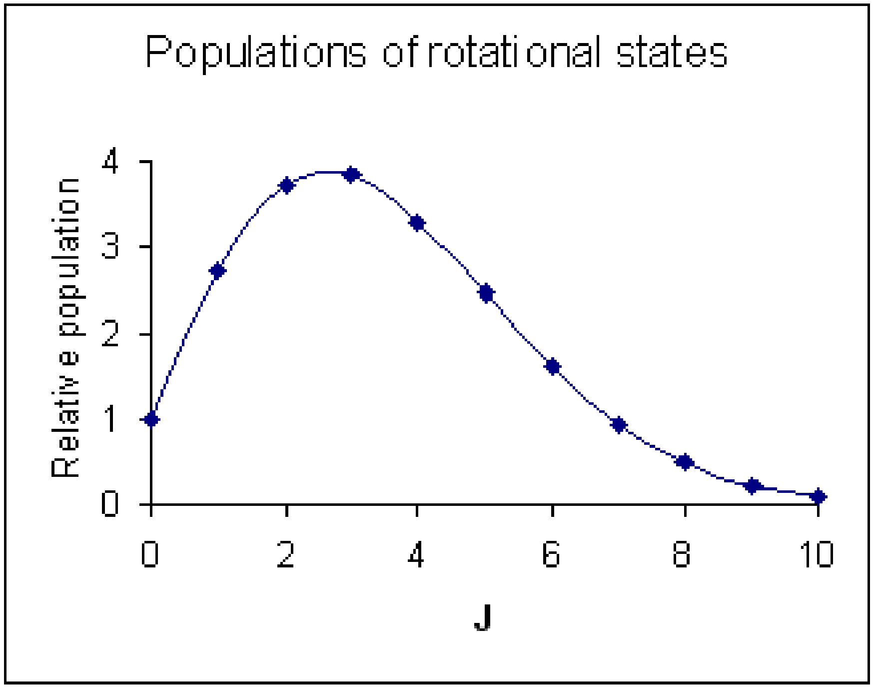
https://en.wikipedia.org/wiki/File:Rotational_spectrum_example.png

The intensities of the rotational lines

The probability of a transition os proportional to the population of the initial state involved.

The rotatinal energies are quite low, therefore many rotationally excited states are accessible even at room temperature.

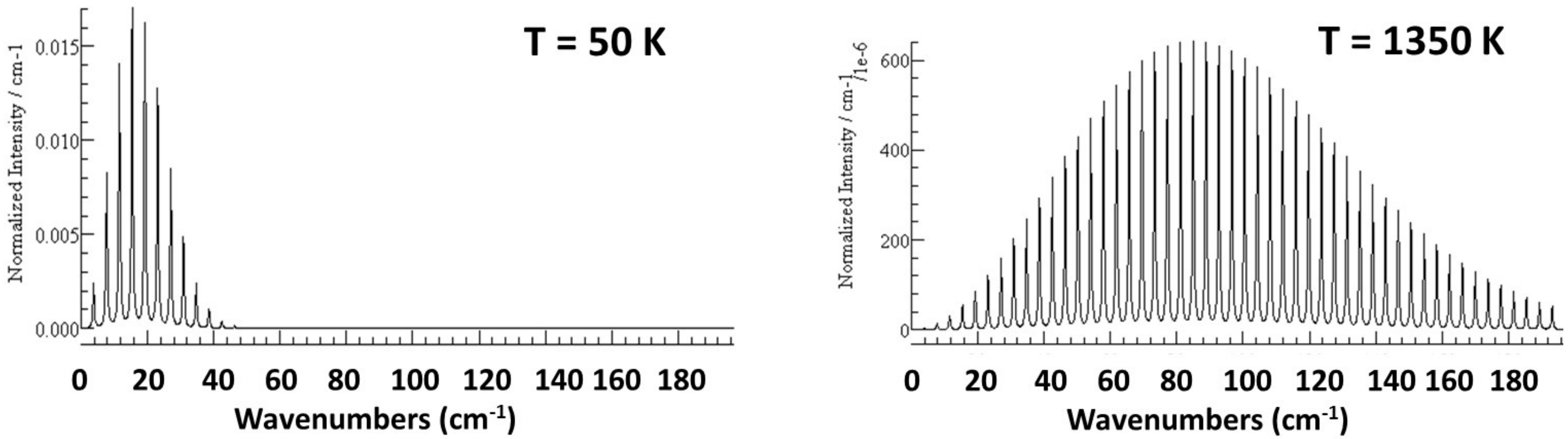
The population distribution can be calculated using the Boltzman distribution.



Rotational level populations with $Bhc/kT = 0.05$.

https://en.wikipedia.org/wiki/File:Rotational_spectrum_example.png

Temperature dependence of the rotational spectra



The temperature dependence of the pure CO rotational spectrum.

http://stemed.site/NCSU/CH331/module/lec5/lec5_images/pure_rot.jpg

Calculation of the bond length from the rotational constant

Problem: Given the rotational constant of nitrogen molecule ($B = 1.99\ \mathrm{cm}^{-1}$) calculate the bond length! $M_\mathrm{N} = 14.0067\ \mathrm{g/mol}$

Let us combine two equations: $I = \mu \cdot R^2$ and $B = \frac{h}{8\pi^2 Ic}$

Rearranging them: $R = \sqrt{\frac{I}{\mu}}$ and $I = \frac{h}{8\pi^2 Bc}$, and substituting: $R = \sqrt{\frac{h}{\mu 8\pi^2 Bc}}$

The reduced mass of N_2: $\mu = \frac{m_\mathrm{N} m_\mathrm{N}}{m_\mathrm{N}+m_\mathrm{N}} = \frac{m_\mathrm{N}}{2} = \frac{\frac{0.0140067\ \frac{\mathrm{kg}}{\mathrm{mol}}}{6.02214076 \cdot 10^{23}\ \mathrm{mol}^{-1}}}{2} = 1.1629 \cdot 10^{-26}\ \mathrm{kg}$

$$R = \sqrt{\frac{6.62607004 \cdot 10^{-34}\ \frac{\mathrm{m}^2\mathrm{kg}}{\mathrm{s}}}{1.1629 \cdot 10^{-26}\ \mathrm{kg} \cdot 8\pi^2 \cdot 1.99\ \mathrm{m}^{-1} \cdot 2.99792458 \cdot 10^8\ \mathrm{m/s}}} = 1.100 \cdot 10^{-10}\ \mathrm{m}$$

$= 1.100\ \text{Å}$