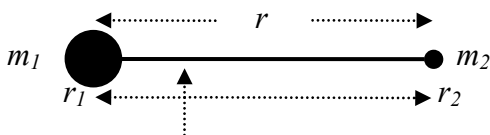


7. Introduction to rotational spectroscopy

See **Bernath** here. For Incredible detail, go to **Herzberg**, *Spectra of Diatomic Molecules* (in all the libraries).

Diatomic molecules



$COM \equiv$ center of mass (or inertia): $m_1 r_1 = m_2 r_2$

I : moment of inertia = $\sum m_i r_i^2 = m_1 r_1^2 + m_2 r_2^2$

$$r_1 = \frac{r m_2}{m_1 + m_2}; r_2 = \frac{r m_1}{m_1 + m_2}.$$

$$I = \frac{r^2 m_1 m_2^2}{(m_1 + m_2)^2} + \frac{r^2 m_1^2 m_2}{(m_1 + m_2)^2} = r^2 \frac{m_1 m_2}{m_1 + m_2} \equiv \mu r^2, \text{ where } \mu \text{ is the reduced mass (for rotation,}$$

in this case). Note the common case of “hydrogenic” reduced mass: For HX molecules (X=F, Cl, Br, I, O, ...) molecules, the reduced mass for rotation is small, similar to the mass of the hydrogen atom.

In general, for axis i of a three-dimensional object, $I_i = \int r_i^2 dm_i$, where r_i is the distance from the axis and dm_i the differential in mass.

The *moment of inertia tensor* has diagonal elements, e.g., $I_{xx} = \sum_i m_i (y_i^2 + z_i^2)$ and off-diagonal elements, e.g., $I_{xy} = I_{yx} = -\sum_i m_i x_i y_i$. The *principal axes* are the choice of axes that diagonalize the moment of inertia tensor for an object: $I_{xy} = I_{xz} = I_{yz} = 0$.

The *rotational energy* $E = I\omega^2 / 2$, classically, and the rotational angular momentum

$$L = I\omega, \text{ or, } E = \frac{L^2}{2I}. \text{ However, quantum mechanics says that } L \text{ must be quantized in}$$

units of $\hbar = \frac{h}{2\pi}$, where h is Planck’s constant:

$$L = \frac{nh}{2\pi}; \quad E = \frac{(nh/2\pi)^2}{2I}$$

The formation of the quantum mechanical *Hamiltonian* operator (total energy operator for a conservative system) for angular momentum problems (developed for atomic spectra, but just as applicable to rotational angular momentum) and its solutions are presented in **Bernath**, Section 5.2.

The Hamiltonian expression for rotation about one axis is $\frac{\hat{j}^2\Psi}{2I} = E\Psi = \frac{J(J+1)\hbar^2\Psi}{2I}$ and

$E = BJ(J+1)$, where $B = \frac{\hbar^2}{2I} = \frac{h^2}{8\pi^2 I}$. B is the *rotational constant*. Nonlinear

polyatomic molecules have 2 or 3 rotational constants, depending on the molecule's symmetry (more later). Expressing B in cm^{-1} :

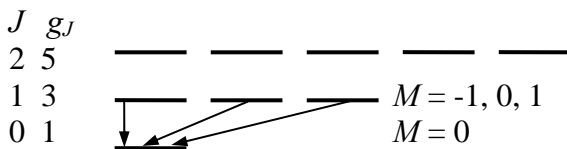
B (H^{35}Cl)	10.59	← hydrogenic
B (HF)	20.94	← hydrogenic
B (OH)	18.87	← hydrogenic
B (O_2)	1.446	← not hydrogenic

The spectroscopic consequences of having small, hydrogenic, moments of inertia, with corresponding large rotational constants, are that such molecules (or the corresponding rotational degrees of freedom in polyatomic molecules having one or more hydrogenic reduced masses about rotational axes) **1.** have smaller rotational partition functions, and thus distribute the rotational spectra into fewer, stronger transitions; **2.** have Boltzmann population distributions that extend to higher energies. This corresponds to the far infrared or submillimeter (or terahertz) region, where intensities are stronger because of the σ^3 factor in the blackbody expression. These are **NOT** hydrides. In hydrides, the hydrogen atom has a formal negative charge (e.g., NaH, LiH, LiAlH_4).

$\frac{\hat{j}^2\Psi}{2I} = E\Psi$ has the set of solutions $\Psi = P_M(\cos\theta)e^{iM\phi}$, which are *spherical harmonics*,

where $J = 0, 1, 2, \dots$ and $|M| \leq J$

There are $2J + 1$ "states" of same energy for each J . The *degeneracy* (in the absence of \vec{m} and \vec{E} .) = $2J + 1$:



This shows why we need to modify our statement from Einstein $B_{nm} = B_{mn}$ to

$g_n B_{nm} = g_m B_{mn}$. The microscopic probabilities are the same but the summed quantities are not. *Detailed balance* requires the above relationship, e.g., $1 \times B_{01} = 3 \times B_{10}$.

Degeneracy in general is given by $2F + 1$, where F is the *total angular momentum* of the state (including rotation, orbital, spin, electronic, nuclear).

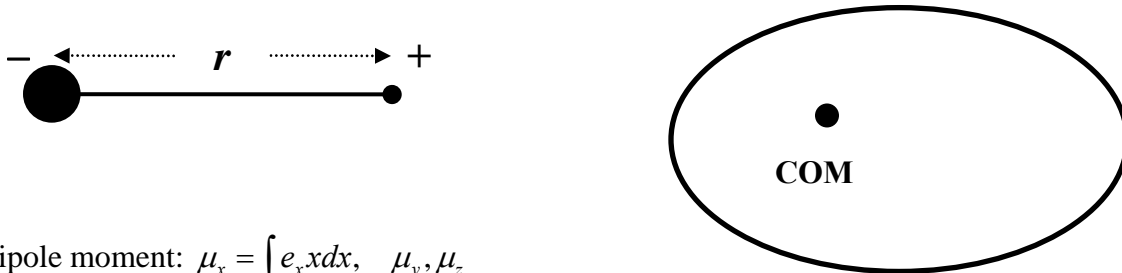
Reminders: Blackbody radiancy $R_\sigma d\sigma = \frac{2\pi hc^2 \sigma^3 d\sigma}{e^{hc\sigma/kT} - 1}$

The radiation density $\rho(\sigma) = \frac{8\pi hc\sigma^3}{e^{hc\sigma/kT} - 1} \text{ erg cm}^{-3}/\text{cm}^{-1} = \text{erg cm}^{-2}$.

Since $\rho(\sigma) = \frac{hc\sigma}{c} F(\sigma)$ (F = flux), $F(\sigma) = \rho(\sigma)/h\sigma$ in $\text{cm}^{-3} \text{ s}^{-1}$.

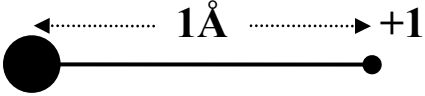
Intensities (without quantum mechanics)

Details on intensities are given in several places in **Bernath** (see Preface to the 2nd Edition). Also, I am very fond of the hard-nosed derivations in **Penner** (especially Chapter 7).



Dipole moment: $\mu_x = \int e_x x dx$, μ_y, μ_z
(usually a sum over charges)

The unit of μ is the *Debye* (D) $\equiv 1 \text{ esu}\cdot\text{\AA}$. One Debye:

-1  $+1$ $(1 \text{ Debye})^2 = 10^{-36} \text{ erg cm}^3$.

The *intensity* of a transition is proportional to μ^2 :

$$\left| \int \Psi_1 \mu \Psi_2 d\Omega \right|^2 = \mu_0^2 \times (\text{direction cosine matrix element})^2$$

For future reference, $(1 \text{ Bohr magneton})^2 = 8.60 \times 10^{-41} \text{ erg cm}^3$

$$\mu_0 (\text{HCl}) = 1.1 \text{ D}$$

$$\mu_0 (\text{OH}) = 1.7 \text{ D}$$

$\mu_0 (\text{O}_2) = 0$, but $\mu_B = 2$. Bohr magnetons (2. means almost exactly 2, with tiny corrections, including a relativistic correction).

For our simple diatomic molecules,

$$|\mu_{J \rightarrow J+1}|^2 = \mu_0^2 \frac{J+1}{2J+1}; \quad |\mu_{J \leftarrow J+1}|^2 = \mu_0^2 \frac{J+1}{2J+3}$$

The usual *selection rules* for rotational transitions of polar diatomics are $\Delta J = \pm 1$ (from the symmetry of $\int \Psi_a \mu \Psi_b$). Then, the rotational lines occur at energies of $\Delta E = 2B, 4B, 6B, \dots$

$$\begin{array}{r}
3 \text{ ————— } 12B \\
2 \text{ ————— } 6B \\
1 \text{ ————— } 2B \\
J = 0 \text{ ————— } E = 0
\end{array}$$

Transition dipole moment:

$\equiv R_{mn} \propto \int \Psi_m \mu \Psi_n d\Omega$. It is independent of degeneracy as defined:

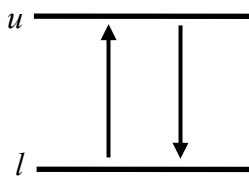
$$|R_{mn}|^2 = |\mu_{J \rightarrow J+1}|^2 (2J+1) = |\mu_{J \leftarrow J+1}|^2 (2J+3).$$

Then, quantum mechanics gives:

$$A_{mn} = \frac{64\pi^4 \sigma^3}{3h} |R_{mn}|^2 / g_m = \frac{64\pi^4 \sigma^3}{3h} \mu_{mn}^2, \text{ where } m \text{ is the upper state.}$$

$$B_{mn} = \frac{8\pi^3}{3h^2 c} |R_{mn}|^2 / g_m = \frac{8\pi^3}{3h^2 c} \mu_{mn}^2, \quad B_{nm} = \frac{8\pi^3}{3h^2 c} |R_{mn}|^2 / g_n = \frac{8\pi^3}{3h^2 c} \mu_{nm}^2.$$

The standard definition of intensity, S



Treating the induced absorption and emission (for now):

$$-\dot{N}_l = N_0 (f_l B_{lu} - f_u B_{ul}) \rho(I_0, \sigma) \text{ in cm}^{-2} \text{ s}^{-1}, \text{ or}$$

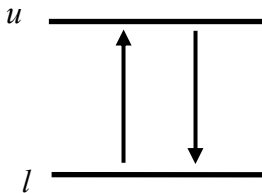
$$-\dot{N}_l = N_0 f_l \frac{8\pi^3}{3h^2 c} \mu_{lu}^2 (1 - e^{-c_2 \sigma / T}) \rho(I_0, \sigma)$$

$$-\dot{N}_l = N_0 f_l \frac{8\pi^3}{3hc} \mu_{lu}^2 \sigma (1 - e^{-c_2 \sigma / T}) F(I_0, \sigma)$$

$$\frac{-\dot{N}_l}{N_0 F} = f_l \frac{8\pi^3}{3hc} \sigma (1 - e^{-c_2 \sigma / T}) \mu_{lu}^2 \equiv S.$$

The above version is in “absorption form.” The entirely equivalent “emission form” can be derived from spontaneous emission using the Einstein A coefficient.

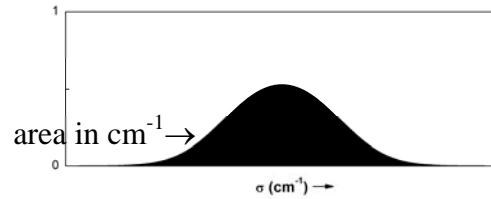
$$\frac{\dot{N}_u}{N_0} = f_u A_{ul}.$$



After normalizing to blackbody sterradiancy, the result is $S = \frac{8\pi^3}{3hc} \sigma (e^{c_2 \sigma / T} - 1) f_u \mu_{ul}^2$.

$$\text{In general: } S = \frac{8\pi^3}{3hc} \sigma \frac{(e^{-c_2 E_l / T} - e^{-c_2 E_u / T})}{Q} |R|^2.$$

f_l is the fraction of molecules in the lower state and f_u in the upper state. S is in cm (my preference), or in $\text{cm}^{-1}/(\text{molecules cm}^{-2})$, which is more standard usage. This is because multiplying S by the *column density* of molecules, in molecules cm^{-2} , gives the line's *equivalent width* (W) in cm^{-1} (ignoring the Beer-Lambert law, for the moment), $W (\text{cm}^{-1}) = S (\text{cm}) \times n (\text{cm}^{-2})$, where n is the column density.



Introduction to line shapes

Given a lineshape $l(\sigma)$ in cm,

$S \times l(\sigma) =$ the *cross section* $\Sigma(\sigma)$ in cm^2 .

$\Sigma(\sigma) \times n (\text{cm}^{-2}) = \tau(\sigma) = S (\text{cm}) \times l (\text{cm}) \times n (\text{cm}^{-2})$ (just as before!)

Then, we get the actual equivalent width after applying the Beer-Lambert law and integrating over the whole line. $W = \int (1 - e^{-\tau(\sigma)}) d\sigma$, for absorption. What is it for emission?