7. Introduction to rotational spectroscopy

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

Diatomic molecules

\[ COM \equiv \text{center of mass (or inertia): } m_1r_1 = m_2r_2 \]

\[ I = \frac{r^2m_1m_2}{(m_1 + m_2)^2} + \frac{r^2m_1^2m_2}{(m_1 + m_2)^2} = r^2 \frac{m_1m_2}{m_1 + m_2} = \mu r^2, \text{ where } \mu \text{ is the reduced mass (for rotation, in this case).} \]

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, \( I_i = \int r_i^2dm_i \), where \( r_2 \) 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., \( I_{xy} = I_{yx} = -\sum_i m_ix_iy_i \). 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 \( L = I\omega \), or, \( E = \frac{L^2}{2I} \). However, quantum mechanics says that \( L \) must be quantized in units of \( \hbar = \frac{h}{2\pi} \), where \( h \) is Planck’s constant:

\[ L = \frac{\hbar}{2\pi}; \quad E = \left(\frac{\hbar/2\pi}{2I}\right)^2 \]

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 \[ \frac{j^2 \Psi}{2I} = E\Psi = \frac{J(J+1)h^2\Psi}{2I} \] and

\[ E = BJ(J+1), \quad \text{where} \quad B = \frac{\hbar^2}{2I} = \frac{\hbar^2}{8\pi^2I}. \]

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 (H₁³Cl) | 10.59 | ← hydrogenic |
| B (HF)    | 20.94 | ← hydrogenic |
| B (OH)    | 18.87 | ← hydrogenic |
| B (O₂)    | 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 \( \sigma^3 \) factor in the blackbody expression. These are NOT hydrides. In hydrides, the hydrogen atom has a formal negative charge (e.g., NaH, LiH, LiAlH₄).

\[ \frac{j^2 \Psi}{2I} = E\Psi \] has the set of solutions \( \Psi = P_m \cos \theta e^{iM\phi} \), which are spherical harmonics, where \( J = 0, 1, 2, \ldots \) and \( |M| \leq J \)

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

\[
\begin{array}{c|c|c|c|c}
J & g_J & M = -1, 0, 1 & M = 0 \\
2 & 5 & & \\
1 & 3 & & \\
0 & 1 & & \\
\end{array}
\]

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 \( R_\sigma d\sigma = \frac{2\pi h^2 \sigma^3 d\sigma}{e^{hc\sigma/kT} - 1} \)
The radiation density \( \rho(\sigma) = \frac{8\pi \hbar c \sigma^3}{e^{\frac{\hbar c \sigma}{kT}} - 1} \) erg cm\(^{-3}\)/cm\(^{-1}\) = erg cm\(^{-2}\).

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

**Intensities** (without quantum mechanics)

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

Dipole moment: \( \mu = \int e_z dx \), \( \mu_x, \mu_y \) (usually a sum over charges)

The unit of \( \mu \) is the Debye (D) \( \equiv 1 \) esu-Å. One Debye:

\[
\begin{array}{c}
-1 \\
\hline
+1
\end{array}
\quad 1\text{Å} \quad \begin{array}{c}
\rightarrow \\
\text{COM}
\end{array}
\]

The intensity of a transition is proportional to \( \mu^2 \):

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

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

\( \mu_0 \) (HCl) = 1.1 D

\( \mu_0 \) (OH) = 1.7 D

\( \mu_0 \) (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,

\[
\left| \mu_{J \rightarrow J+1} \right|^2 = \mu_0^2 \frac{J+1}{2J+1}; \quad \left| \mu_{J+1 \rightarrow J} \right|^2 = \mu_0^2 \frac{J+1}{2J+3}
\]

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 \( \Delta E = 2B, 4B, 6B \). ….
Transition dipole moment:
\[ R_{mn} \propto \int \Psi_m \mu \Psi_n d\Omega. \]
It is independent of degeneracy as defined:
\[ |R_{mn}|^2 = |\mu_{J\rightarrow J\pm 1}|^2 (2J + 1) = |\mu_{J\rightarrow J\pm 1}|^2 (2J + 3). \]

Then, quantum mechanics gives:
\[ A_{mn} = \frac{64\pi^4 \sigma^3}{3h} |R_{mn}|^2 / g_m = \frac{64\pi^4 \sigma^3}{3h} \mu_{mn}^2, \]
\[ B_{mn} = \frac{8\pi^3}{3h^2 c} |R_{mn}|^2 / g_m = \frac{8\pi^3}{3h^2 c} \mu_{mn}^2, \]
\[ B_{nm} = \frac{8\pi^3}{3h^2 c} |R_{mn}|^2 / g_n = \frac{8\pi^3}{3h^2 c} \mu_{mn}^2. \]

The standard definition of intensity, \( S \)

\[ u \]  
\[ l \]  

Treating the induced absorption and emission (for now):

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

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

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

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

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 steradiancy, the result is
\[ S = \frac{8\pi^3}{3hc} (e^{c_l \sigma / T} - 1) f_u \mu_{ul}^2. \]

In general:
\[ S = \frac{8\pi^3}{3hc} \sigma \left( \frac{e^{c_l \sigma / T} - e^{c_u \sigma / T}}{Q} \right) |R|^2. \]
\( f_l \) is the fraction of molecules in the lower state and \( f_u \) in the upper state. \( S \) is in cm (my preference), or in cm\(^{-1}\)/(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,

\[
S \times l(\sigma) = \text{the cross section } \Sigma(\sigma) \text{ in cm}^2
\]

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

Then, we get the actual equivalent width after applying the Beer-Lambert law and integrating over the whole line.

\[
W = \int (1 - e^{-\tau(\sigma)}) d\sigma, \text{ for absorption. What is it for emission?}
\]