Lecture 18 Rotations and Vibrations

Topics
1. Vibrations of Polyatomic Molecules
2. Rotational Motion
3. Ro-vibrational Transitions

References
• Steinfeld, *Molecules and Radiation* (Dover 1985)
• Townes & Schawlow, *Microwave Spectroscopy* (Dover 1975)
• Herzberg, “Free Radicals” (Cornell, 1971)
• Herzberg, *Molecular Spectra & Molecular Structure II: Infrared and Raman Spectra of Polyatomic Molecules* (van Nostrand 1945)

1. Vibration of Polyatomic Molecules

Dense gas ⇒ Cool gas ⇒ Long wavelengths ⇒ Observations across spectrum from NIR to cm ⇒ Rotational and vibrational transitions (*not* electronic)

• Transitions involve at least a unit change in vibrational quantum number, as in: *(upper) v’ → (lower) v’’*.

• Many transitions occur since each vibrational level has a manifold of rotational transitions, i.e. “band” structure. Transitions involve changes in *both* vibrational and rotational quantum numbers: *(upper) v’ J’ → (lower) v’’ J’’*, so-called “rotational-vibrational” transitions or ro-vibrational or just *ro-vib transitions*.

• There are usually no rules for ro-vib transitions against any change v’ → v’’, although the strength decreases with increasing | v’-v’’ |. The change J’ → J’’ is governed by the usual angular momentum selection rules for dipole (or quadrupole) transitions.
Vibrational Modes of Polyatomic Molecules

Let \( N > 2 \) be the number of nuclei in a polyatomic molecule with \( 3N \) degrees of freedom. With 3 for the center-of-mass and 3 for rotation (or 2 for a linear molecule with two rotational degrees), there are \( 3N-6 \) (or \( 3N-5 \)) vibrational degrees of freedom, e.g., three for \( N = 3 \) and six for \( N = 4 \), etc.

We consider the vibrational frequencies as given. Once the equilibrium configuration is known, this is a problem in classical Lagrangian mechanics. Of course high vibrational levels are subject to anharmonic corrections, as discussed in Lec. 17. See Ch. 8 of Seinfeld for a discussion of Lagrangian and more elegant methods, with explicit solutions for \( N = 3 \) and 4.

The ultimate source of accurate frequencies is spectroscopic measurements, presumably compiled and up to date at: [http://physics.nist.gov/PhysRefData/MolSpec/index.html](http://physics.nist.gov/PhysRefData/MolSpec/index.html)

N.B. Vibrational frequencies are in the NIR. Recall that 2 microns corresponds to 5000 cm\(^{-1}\) or \( ~7500\)K

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Vibrations of \( XY_2 \) Molecules, e.g., \( H_2O \) and \( C_2H \)

![Diagram of Vibrations of \( XY_2 \) Molecules](image)

Fig. 25 from Herzberg, Vol. II: Normal vibrations of bent and linear \( XY_2 \)
**Vibrations of Planar XYZ\textsubscript{2}**

The two panels represent reflections in the symmetry plane through XY and \perp to the plane of the molecule.

In mode 6, nucleus Y moves out of the plane while the others move into the plane.

XYZ\textsubscript{2} can also have other isomeric forms

Fig. 24 from Herzberg, Vol. II: Normal vibrations of bent and linear XYZ\textsubscript{2}

**Vibrational Levels of H\textsubscript{2}**

14 vibrational levels of the ground electronic state of H\textsubscript{2} included in CLOUDY (Shaw et al. ApJ, 624, 674, 2005)
Vibrational Levels of the OH Ground State

\[ \Delta E_{ul} \text{ (cm}^{-1}\text{)} \]

Fig. 32 Herzberg’s “Radicals”

\[ E_{ul} \text{ (cm}^{-1}\text{)} \]

\[ X^2 \Pi_{1/2,3/2} \]

\[ S = 1/2, \Lambda = 1 \]

\[ J = 1/2, 3/2 \]

\[ 1 \text{ cm}^{-1} = 1.4883K \]

\[ 1 \text{ eV} = 11604K \]

Ro-vibrational Transition Probabilities

The transition probability is determined by the matrix element of the electric dipole moment, which varies with the inter-nuclear separation \( R \). Expand \( \mu(R) \) about the minimum in the potential \( R_0 \):

\[ \mu(R) = \mu(R_0) + \mu'(R_0)(R - R_0) + \frac{1}{2} \mu''(R_0)(R - R_0)^2 + \cdots \]

Evaluating the matrix element with oscillator wave functions yields:

\[ \langle v | \mu(R_0) | v' \rangle \propto \delta(v', v) \] (pure rotational)

\[ \langle v | \mu'(R_0)(R - R_0) | v' \rangle \propto \delta(v', v \pm 1) \] (rovib fundamental)

\[ \langle v | \frac{1}{2} \mu''(R_0)(R - R_0)^2 | v' \rangle = \delta(v', v \pm 2) \] (rovib first overtone)

1. Ro-vib transition probabilities are determined by the derivatives of the dipole moment, and not on the permanent moment.
2. Fundamental ro-vib transitions are much stronger than overtone.
3. Molecules with small permanent dipole moments can have large ro-vib transition moments, e.g., CO.
2. Rotational Motion

The rotational motion of a molecule is determined by the moments of inertia and the angular momenta.

- Classically, any object has three orthogonal principal moments of inertia (diagonals of the inertia tensor) with corresponding simple expressions for the rotational energy and angular momentum.
- This carries over directly to quantum mechanics.
- It is customary to classify the rotational properties of molecules according to the values of the principle moments of inertia.

*The principle moments of inertia are usually designated \( I_a, I_b, \) and \( I_c \) in order of increasing magnitude.*

**Nomenclature for Rotating Molecules**

A molecule with rotational symmetry is a **symmetric top**, and either \( I_c = I_b > I_a \) or \( I_c > I_b = I_a \):

- **prolate symmetric tops** \( (I_c = I_b > I_a) \)
  - example: \( \text{NH}_3 \), linear molecules \( (I_a = 0) \)
- **oblate symmetric tops** \( (I_c > I_b = I_a) \)
  - example: planar benzene

A molecule with equal moments is a **spherical top**.
  - example: \( \text{CH}_4 \)

A molecule with unequal moments \( I_c \neq I_b \neq I_a \) is an **asymmetric top**, example: \( \text{H}_2\text{O} \)

- benzene
- methane
- water
Rotational Energy of a Symmetric Top

Classically the energy of rotation is

$$E = \frac{1}{2} I_x \omega_x^2 + \frac{1}{2} I_y \omega_y^2 + \frac{1}{2} I_z \omega_z^2 = \frac{J_x^2}{2 I_x} + \frac{J_y^2}{2 I_y} + \frac{J_z^2}{2 I_z}$$

The symmetry axis is \( z \). For an oblate rotor \( I_x = I_y = I_b \), and since \( J^2 = J_x^2 + J_y^2 + J_z^2 \)

$$E = \frac{J^2}{2 I_b} + \frac{J_z^2}{2 I_c} \left( \frac{1}{2 I_a} - \frac{1}{2 I_b} \right) \quad \text{(oblate)}$$

Similarly for a prolate rotor, \( I_x = I_y = I_b \) still holds and

$$E = \frac{J^2}{2 I_b} + \frac{J_z^2}{2 I_c} \left( \frac{1}{2 I_a} - \frac{1}{2 I_b} \right) \quad \text{(prolate)}$$

The next step is to quantize these classical expressions.

Rotational Energy of Symmetric Tops

The square of the angular momentum and its projection on the symmetry axis are good quantum numbers.

NB The projection on a fixed axis is also conserved; it is usually denoted \( M_z \) and enters into the Zeeman effect.

$$J^2 = J(J + 1) \hbar^2 \quad \text{and} \quad J_z = K \hbar$$

\( J = 0, 1, 2 \cdots \quad K = 0, 1, 2 \cdots \)

$$E = \frac{\hbar^2}{2 I_b} J(J + 1) + \left( \frac{\hbar^2}{2 I_c} - \frac{\hbar^2}{2 I_b} \right) K^2 = BJ(J + 1) + (C - B)K^2 \quad \text{(oblate)}$$

$$E = \frac{\hbar^2}{2 I_b} J(J + 1) + \left( \frac{\hbar^2}{2 I_a} - \frac{\hbar^2}{2 I_b} \right) K^2 = BJ(J + 1) + (A - B)K^2 \quad \text{(prolate)}$$

in terms of the rotational constants, \( A = \frac{\hbar^2}{2 I_a}, \quad B = \frac{\hbar^2}{2 I_b}, \quad C = \frac{\hbar^2}{2 I_c} \)
Rules of the Game for Symmetric Tops

- \(J\) can have any integral value
- As a projection of \(J\), \(K\) has \((2J+1)\) values, 
  \(+J, J-1, \ldots -J+1, -J\)
- The energy depends on \(|K|\), so there are only 
  \(J+1\) distinct values, and the levels start at \(J = K\)
- For a prolate top (cigar) \(A > B\): levels increase with \(K\)
  For an oblate top (pancake) \(C < B\): levels decrease 
  with \(K\) -- see the diagram on the next slide
- The simple rotational ladder of a linear molecule is 
  recovered for \(K = 0\) (slide 27)

For asymmetric tops (all unequal moments): Only \(J\) and \(E\) are 
conserved. The states are labeled by \(J\) and \((K,K_z)\) -- conserved 
projections in the limit of prolate & oblate symmetric tops.
To be discussed later in connection with the water molecule.

Energy Levels of a Symmetric Top

Prolate, \(A > B\)

Oblate, \(C < B\)

Allowed transitions are up and down fixed \(K\) ladders.
Order of Magnitude of the Rotational Energy

The rotational energy is determined by the moments of inertia, e.g., for an oblate asymmetric top

\[ E = \frac{\hbar^2}{2I_b} J(J+1) + \left( \frac{\hbar^2}{2I_c} - \frac{\hbar^2}{2I_b} \right) K^2 = BJ(J + 1) + (C - B)K^2 \]

And \( I \sim ma^2 \) where \( m \) is a typical atomic mass and \( a \) is a typical nuclear separation. The order of magnitude of the rotational energy is, using these constants for a hydride,

\[ \frac{\hbar}{2\pi} = 1.05 \times 10^{-27} \text{ erg s, } \quad m \sim 2 \times 10^{-24} \text{ g, } \quad a \sim 10^{-8} \text{ cm,} \]

\[ (\hbar/2\pi)^2/2I \sim 5 \times 10^{-15} \text{ erg } \sim 3 \times 10^{-3} \text{ eV} \]

Converting to Kelvins, this rough estimate gives \( \sim 40 \text{ K} \) for \( \text{H} \) and smaller values for heavier atoms. Recall from Lec. 17 that \( B(\text{H}_2) = 85\text{K} \) and \( B(\text{CO}) = 2.77\text{K} \)

Radiative Transitions

Rotational Transitions – Molecules with a \textit{permanent dipole moment} can generate a strong pure rotational spectrum.
Symmetric molecules like \( \text{H}_2, \text{C}_2, \text{O}_2, \text{CH}_4 \) and \( \text{C}_2\text{H}_2 \) have weak rotational spectra generated by the electric quadrupole moment.
For \( \text{H}_2 \), the \( \Delta J = 2 \) transitions start at \( \lambda(2 \rightarrow 0) = 28 \mu\text{m} \).

Selection Rules – The general rules apply, albeit in new forms dictated by molecular symmetry.

For a \textit{symmetric top}, the dipole moment lies along the symmetry axis. The radiation field cannot exert a torque along this axis, so the selection rule for a pure rotational transition is \( \Delta K = 0 \) (and \( \Delta J = \pm 1 \)). Levels with \( J=K \) are metastable.
Observed Rotational Transitions

607-725 GHz (415-490 µm) line survey of Orion-KL (Kleinman-Low Nebula) dominated by CO, CS, SO, SO₂ and CH₃OH. Note the relatively high transparency in this FIR/submm band.

1 GHz slice of the spectrum from the 607-725 GHz line survey of Orion-KL (Schilke et al. 2001) centered on the strongest line, CO(J=6-5).
For the Odin satellite observations of this spectral region, see Olofsson et al. A&A, 476, 791 & 807, 2007
A-value for Dipole Radiation From a Simple Rotor

The standard atomic formulae are slightly changed:

\[ A(v'J' \rightarrow v''J'') = \frac{64\pi^4}{3h} \left( \frac{\nu}{c} \right)^3 \frac{S(J', J'')}{2J'+1} |(v''J''| M | v'J')|^2 \]

The upper level is \( (v'J') \) and the lower level is \( (v''J'') \).
\( S(J', J'') \) is the Honl-London factor.
\( (v''J''|M|v'J') \) is the dipole matrix element

\[ S(J', J'') = \frac{1}{2} | J'(J'+1) - J''(J''+1) | 
= J' \text{ for } J' = J''+1 \ (R) \text{ and } J'+1 \text{ for } J' = J''-1 \ (P) \]

The absorption cross section is

\[ \sigma(v'J', v''J'') = f(v'J', v''J'') \frac{\pi \epsilon^2}{m_c} \rho(\Delta \nu) \]

\[ f(v'J', v''J'') = \frac{2J'+1}{3(2J''+1)} \left( \frac{\lambda(v'', J'', v', J')}{\lambda(00,01)} \right)^2 \frac{A(v'J', v''J'')}{A(01,00)} \]

### 3. Ro-Vibrational Transitions

Convention: lower level has double, upper level has single prime.

\[ v', J' \]
\[ v', 0' \]
\[ v', 0' \rightarrow 1\text{st level in } v' \text{ band} \]
\[ v''J'' \]
\[ v'', 0'' \]
\[ v'', 0'' \rightarrow 1\text{st level in } v'' \text{ band} \]

N.B. \( v' \) and \( v'' \) may be in different electronic states

The standard dipole transition selection rule, \( \Delta J = 0, \pm 1 \) allows three possibilities:

- **P-transitions**: \( J' = J''-1 \), i.e., 0-1, 1-2, etc.
- **Q-transitions**: \( J' = J'' \), i.e., 1-1, 2-2, etc.
- **R-transition**: \( J' = J''+1 \), i.e., 1-0, 2-1, etc.
Ro-Vibrational Energies for a Diatomic Molecule

The energy in a ro-vibrational transition of a diatomic molecule is, ignoring the centrifugal terms discussed in Lec. 17 (slide 27),

$$\Delta E(v', J', v'', J'') = \Delta E(v', v'')_{\text{vib}} + B' J' (J' + 1) - B'' J'' (J'' + 1)$$

Keeping $v'$ and $v''$ fixed (and also the first term, denoted $E_0$ below), the energy changes for the three types of ro-vibrational transitions are,

- P branch - $J'' = J' - 1$
  $$\Delta E(J)_P = E_0 - (B' + B'')J + (B' - B'')J^2$$
- Q branch - $J'' = J'$
  $$\Delta E(J)_Q = E_0 + (B' - B'')J(J + 1)$$
- R branch - $J'' = J' + 1$
  $$\Delta E(J)_R = E_0 + 2B' + (3B' - B'')J + (B' - B'')J^2$$

where now everywhere $J$ stands for $J''$

Unlike pure rotational transitions, ro-vib transitions depend quadratically on rotational quantum number.

Ro-vibrational Progression for a Diatomic Molecule

Unlike rotational transitions within the same vibrational band, the ro-vibrational transitions have an additional quadratic dependence $(B' - B'')J^2$. Since $B' < B''$ usually, this means that:

- P transition frequencies are a monotone decreasing function of $J$ and start at $v_0$
- Q transitions also start at $v_0$ and crowd around this frequency.
- R transitions start $2B'$ above $v_0$ and increase with $J$ for small $J$.

For large $J$, the quadratic term cuts in and changes the frequency from an increasing to a decreasing function of $J$. The maximum frequency for the P branch is given by

$$J^* = \frac{3B' - B''}{2(B'' - B')}$$

Because this is a stationary point, many transitions crowd around this point, which is called the bandhead.
Caveat on Selection Rules

We used a diatomic molecule to illustrate P, Q, and R branches, even though they rarely have Q branches in the ground electronic state. A more complete statement of the selection rules governing rotation-vibration transitions (c.f. Rybicki & Lightman, Sec. 11.5) helps clarify the situation:

\[ \Delta J = 0, \pm 1 \text{ but not } J=0 \rightarrow J=0 \]
\[ \Delta \Lambda = 0, \pm 1 \]
\[ \Delta J = 0 \text{ is not allowed for } \Lambda=0 \rightarrow \Lambda=0 \]
\[ \Delta v = \text{any positive or negative integer} \]

Most diatomic molecules are in \( \Lambda = 0 \) (\( \Sigma \)) ground electronic states and therefore do not have Q branches. An important exception is the OH radical, to be discussed in Lec. 20.

Q branches are more commonly found in polyatomic molecules and in electronic transitions such as the \( ^1\Pi \rightarrow ^1\Sigma \) transition of AlH shown in the previous side.
P, Q, and R Branches for C$_3$

$B' \neq B''$ because the moment of inertia, proportional to $<v|1/R^2|v>$, depends on $v$. However $B'$ is only a little smaller than $B''$ so that the quadratic terms are small.

**Summary:** P and R are linear in $J$ for small $J$ and quadratic for large $J$; $Q \propto (B'-B'')$ so the transitions crowd around $E_0$.

![Diagram of P, Q, and R branches for C$_3$.](image)

Interstellar absorption spectrum of C$_3$ for the X $^1\Sigma_g$ $\rightarrow$ A $^1\Pi_u$ transition.

Top: synthetic spectrum ($T = 80$ K) for spectral resolution of $10^5$.

Noticing locations of P, Q, and R in accord with previous formulae.


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CO($v = 2-0$) First Overtone Bandhead

WL16 is a young stellar object with a broad and distorted bandhead near 2.3 $\mu$m providing information about its accretion disk.

The inset shows the intrinsic line shape assumed in modeling the spectrum (solid curve) that generates the broad feature.

In 1992, the sensitivity was insufficient to detect individual ro-vib lines. The pile up of lines at the bandhead generates enough flux to have made this measurement possible.

Example of the Rigid Rotor

For the pure rotational spectrum of a rigid rotor, the energy emitted in the transition \( J' = J \rightarrow J'' = J - 1 \) is (\( J \) is upper level)
\[
\Delta E_J = E(J) - E(J - 1) = 2BJ
\]
and leads to the sequence 2B, 4B, 6B ... .

For the ro-vibrational spectrum, with \( B' = B'' \) (\( J \) is always the lower level), the transition energies are

- **P branch** - \( J'' = J' - 1 \equiv J \)
  \[
  \Delta E(J)_P = E_0 - 2BJ
  \]
- **R branch** - \( J'' = J' + 1 \equiv J \)
  \[
  \Delta E(J)_R = E_0 + 2B(J + 1)
  \]
- **Q branch** - \( J'' = J' \equiv J \)
  \[
  \Delta E(J)_Q = E_0
  \]

In order of increasing energy or frequency:

\[
\ldots -6B -4B -2B 0 2B 4B 6B \ldots
\]

P branch      Q      R branch

Brief Summary

1. Vibrational frequencies are well known in most cases.
2. Ro-vib transition probabilities depend on the derivatives of the dipole moment function \( \mu(R) \).
3. Moments of inertia are conventionally ordered \( I_a < I_b < I_c \) with \( I_c = I_b > I_a \) for prolate symmetric tops and \( I_c > I_b = I_a \) for oblate symmetric tops
4. The selection rules for symmetric tops, \( \Delta K = 0, \Delta J = \pm 1 \).
   imply that transitions are up and down “K-ladders”
5. Ro-vib transitions depend quadratically on \( J' - J'' \) and lead to the crowding near the bandhead frequency of P and Q branch transitions.