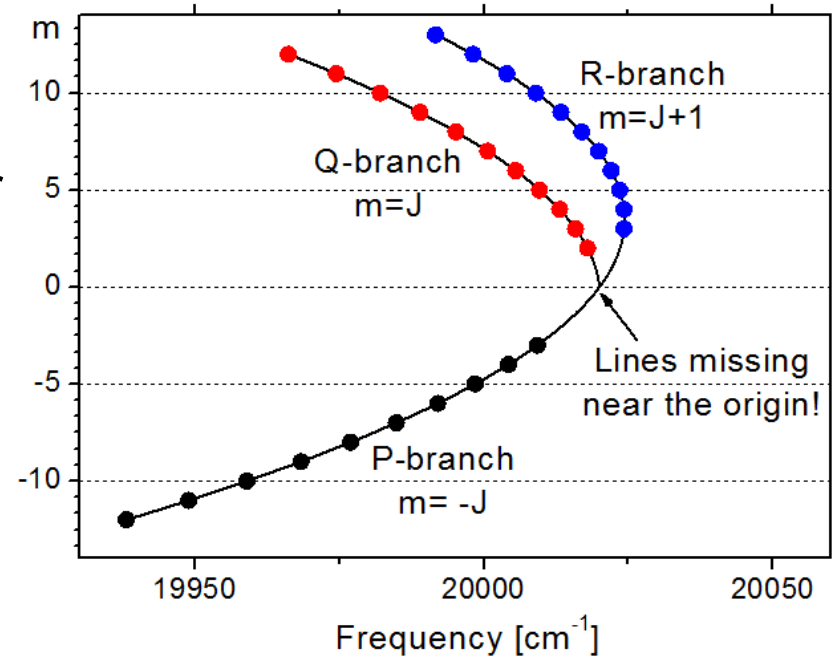


Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

Lecture 7: Electronic Spectra of Diatomics

1. Term symbols for diatomic molecules
2. Common molecular models for diatomics
3. Improved treatments
4. Quantitative absorption

Fortrat parabola, ${}^1\Delta \leftarrow {}^1\Delta$ (Symmetric Top)



1. Term symbols for diatomic molecules

- Term symbols characterize key features of electron spin and orbital angular momentum

For an atom: $^{2S+1}L_J$

For a diatomic: $^{2S+1}\Lambda_{\Omega}$

Important terms

$\vec{\Lambda}$ projection of orbital angular momentum onto the internuclear axis.

Magnitude: $|\vec{\Lambda}| = \Lambda\hbar$

Symbols:

Λ	0	1	2
Symbol	Σ	Π	Δ

Atoms	L	0	1	2
Symbol	S	P	D	

\vec{S} total electronic spin angular momentum (the sum of electron spin in unfilled shells)

Magnitude: $|\vec{S}| = S\hbar$, S will have 1/2-integer values

$\vec{\Sigma}$ projection of \vec{S} onto the internuclear axis (only defined when $\Lambda \neq 0$).

Magnitude: $|\vec{\Sigma}| = \Sigma\hbar$

Allowed values: $\Sigma = S, S-1, \dots, -S$ ($2S+1$ values)

$\vec{\Omega}$ sum of projections along the internuclear axis of electron spin and orbital angular momentum

$$\vec{\Omega} = \vec{\Sigma} + \vec{\Lambda}$$

$$\Omega = \Lambda + S, \Lambda + S - 1, \dots, |\Lambda - S| \quad (2S + 1 \text{ values for } \Lambda \geq S)$$



1. Term symbols for diatomic molecules

- Examples

NO The ground state for NO is $X^2\Pi$

$S = 1/2, \Lambda = 1, \Omega = 3/2, 1/2$

There are two **spin-split** sub-states: $^2\Pi_{1/2}, ^2\Pi_{3/2}$

Separation: 121cm^{-1}

For a diatomic: $^{2S+1}\Lambda_{\Omega}$

CO The ground state for CO is $X^1\Sigma^+$

$S = 0$ and $\Lambda = 0$, therefore Ω is unnecessary. This is a **rigid rotor molecule**. Easiest case!

O_2 The ground state for O_2 is $X^3\Sigma_g^-$

$S = 1, \Lambda = 0$

The $-$ and $_g$ are notations about symmetry properties of wave functions. This is an example of a molecule that is modeled by **Hund's case b**

2. Common molecular models for diatomics

- Four common molecular models

Rigid Rotor	$\Lambda = 0, S = 0$	} $2S+1 = 1 \Rightarrow$ “singlets” no influence of electron spin on spectra
Symmetric Top	$\Lambda \neq 0, S = 0$	
Hund’s <i>a</i>	$\Lambda \neq 0, S \neq 0$	} Spin important through interaction of Λ and Σ
Hund’s <i>b</i>	$\Lambda = 0, S \neq 0$	

- This lecture:

Rigid Rotor

Symmetric Top

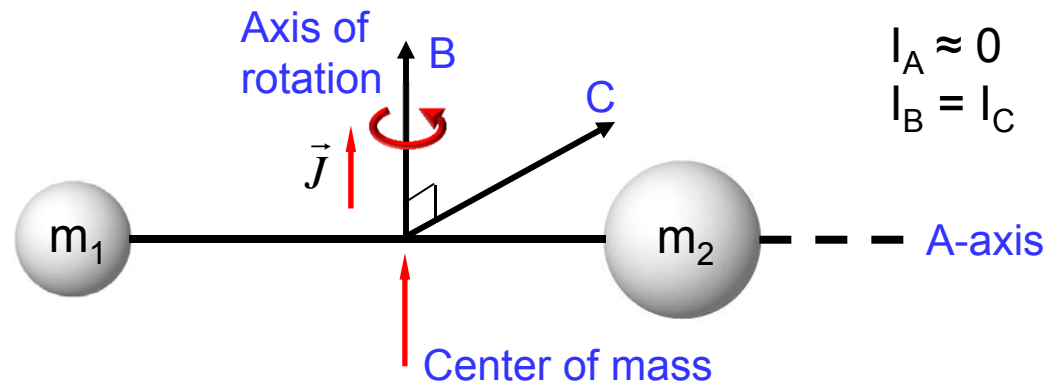
Followed by:

Hund’s *a*

Hund’s *b*

2. Common molecular models for diatomics

- Rigid rotor ($^1\Sigma$)



- $\Lambda = 0, S = 0 \Rightarrow ^1\Sigma$ type, Ω is not defined
- $\Lambda = 0$ means the projection of the orbital angular momentum onto the A-axis is zero, and rotation must thus be around the B-axis



2. Common molecular models for diatomics

- Rigid rotor ($^1\Sigma$)

Rotational Energy $F(J) = B_v J(J+1) - D_v J^2(J+1)^2$

Total Energy $\Delta E = \Delta T_e + \Delta G + \Delta F$

$$E(T_e, v, J) = T_e + G(v) + F(J)$$

Selection Rules Rotational spectra: $\Delta J = J' - J'' = +1$

Rovibrational spectra: $\Delta v = v' - v'' = +1$

$$\Delta J = \pm 1$$

Rovibronic spectra: Δv determined by Frank-Condon factors

$$\Delta J = \pm 1$$

 Note: an alternate form is sometimes used

$$\Delta \alpha = \alpha_{\text{final}} - \alpha_{\text{initial}}$$

$$\alpha = J \text{ or } v$$



2. Common molecular models for diatomics

- Rigid rotor ($^1\Sigma$)

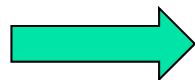
Intensity Distribution Within each band (v' , v''), the intensity distribution follows the Boltzmann distribution for J modified by a J-dependent branching ratio (i.e., for the P and R branch), known as the **Hönl-London factor**.

The relative intensities among all the vibrational bands originating from a single initial level v_{initial} to all possible final levels v_{final} are given by **Franck-Condon factors**.

The relative total emission or absorption from v_{initial} depends directly on the **Boltzmann fraction** in that level, i.e., $n_{v_{\text{initial}}}/n$

Examples Most stable diatomics: CO, Cl₂, Br₂, N₂, H₂ are rigid rotors
Exceptions: NO ($X^2\Pi$), O₂($X^3\Sigma$)

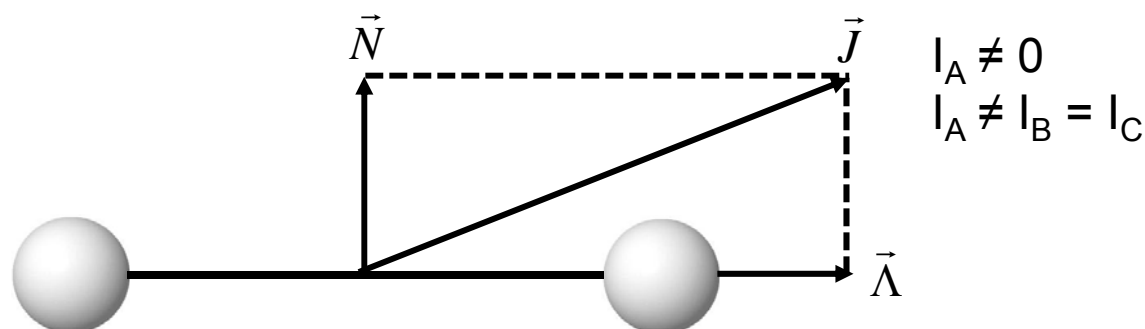
Note: no $X\Delta$ states for diatomics – all X states are Σ or Π !
Some linear polyatomics: CO₂($\tilde{X}^1\Sigma_g^+$), HCN and N₂O ($\tilde{X}^1\Sigma^+$) are rigid rotors with $^1\Sigma$ ground states.



Nuclear spin will have an impact on the statistics of homonuclear diatomic molecules

2. Common molecular models for diatomics

- Symmetric top



- $\Lambda \neq 0, S = 0$ (non-zero projection of orbital angular momentum on the internuclear axis and zero spin) \rightarrow ground states $^1\Pi, ^1\Delta$
- Important components

\vec{N} angular momentum of nuclei

$\vec{\Lambda}$ A-axis projection of electron orbital angular momentum

\vec{J} total angular momentum; $\vec{J} = \vec{N} + \vec{\Lambda}$

Only the axial component of orbital angular momentum is used, because only $\vec{\Lambda}$ is a “good” quantum number, i.e., a constant of the motion

2. Common molecular models for diatomics

- Symmetric top ($\Lambda \neq 0, S = 0$)

Rotational Energy $F(J) = BJ(J+1) + (A-B)\Lambda^2, J = \Lambda, \Lambda+1, \dots$

$$A, B = \frac{h}{8\pi^2 c I_{A,B}}$$

➡ Same spacing as the rigid rotor, but with a constant offset

Since $I_A < I_B, A > B$, lines with $J < \Lambda$ are missing, as $J = \Lambda, \Lambda+1, \dots$

Selection Rules $\Delta\Lambda = 0, \Delta J = \pm 1, 0$ ($\Delta J = 0$ is weak)

$$\Delta\Lambda = \pm 1, \Delta J = \pm 1, 0$$

As a result of having a **Q branch** (i.e., $\Delta J = 0$), the bands for a symmetric top will be **double-headed**, in contrast to the single-headed character of rigid rotor bands

2. Common molecular models for diatomics

- Symmetric top ($\Lambda \neq 0, S = 0$)

Spectra for $\Delta\Lambda = 0$ ($^1\Pi \leftarrow ^1\Pi$ or $^1\Delta \leftarrow ^1\Delta$)

$$T' = B' J'(J'+1) + (A' - B')\Lambda^2 + G(v') + T_e' = 0 \text{ for ground state}$$

$$T'' = B'' J''(J''+1) + (A'' - B'')\Lambda^2 + G(v'') + T_e''$$

$$\bar{\nu}_\infty = \text{upper (for } J' = 0) - \text{lower (for } J'' = 0) = \text{constant}$$

➔

$$P(J'') = \bar{\nu}_\infty - (B' + B'')J + (B' - B'')J^2$$

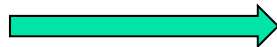
$$Q(J'') = \bar{\nu}_\infty + (B' - B'')J + (B' - B'')J^2$$

$$R(J'') = \bar{\nu}_\infty + (B' + B'')(J + 1) + (B' - B'')(J + 1)^2$$

$$m_P = -J$$

$$m_Q = +J$$

$$m_R = J + 1$$



P and R branches: $\bar{\nu} = \bar{\nu}_\infty + am + bm^2$

Q branch: $\bar{\nu} = \bar{\nu}_\infty + bm + bm^2$

where $a = B' + B''$, $b = B' - B''$

2. Common molecular models for diatomics

- Symmetric top ($\Lambda \neq 0, S = 0$)

Spectra for $\Delta\Lambda = 0$

P and R branches: $\bar{\nu} = \bar{\nu}_\infty + am + bm^2$

Q branch: $\bar{\nu} = \bar{\nu}_\infty + bm + bm^2$

where $a = B' + B'', b = B' - B''$

 Notes:

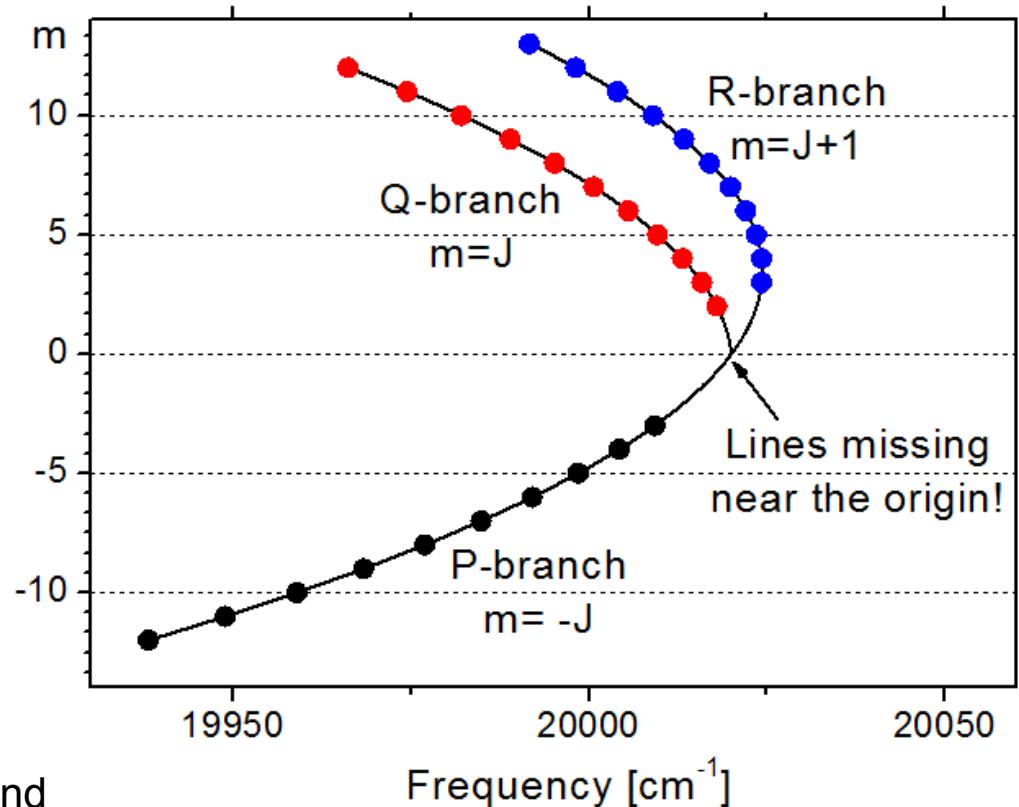
- **Band heads** in the Q and R branches for the typical case of $B' < B''$.
- $m_P = -J, m_Q = +J, m_R = J+1$
- $J_{\min} = 2$ for ${}^1\Delta \leftarrow {}^1\Delta$
 - ➔ $m_{\min} = 3$ for R branch
 - $m_{\min} = 2$ for Q branch
 - $|m_{\min}| = 3$ for P branch
- ➔ **missing lines near the origin**

Intensity Distribution

Relative intensities depend on $\left\{ \begin{array}{l} n_J/n, \text{ and} \\ \text{Hönl-London factors } (S_J^{P,Q,R}) - \text{“relative intensity factors / line strengths”} \end{array} \right.$

➔ breakdown of the principle of equal probability

Fortrat parabola, ${}^1\Delta \leftarrow {}^1\Delta$



2. Common molecular models for diatomics

- Example – 1: Hönl-London Factors for Symmetric Top (see Herzberg)

For $\Delta\Lambda = 0$

$$\left. \begin{aligned} S_J^R &= \frac{(J+1+\Lambda)(J+1-\Lambda)}{J+1} \approx J+1 \quad (J \gg \Lambda) \\ S_J^Q &= \frac{(2J+1)\Lambda^2}{J(J+1)} \approx \frac{2\Lambda^2}{J} \approx 0 \\ S_J^P &= \frac{(J+\Lambda)(J-\Lambda)}{J} \approx J \end{aligned} \right\} \text{for large } J \left. \begin{array}{l} \\ \\ \end{array} \right\} \sum S_J = 2J+1$$



Notes:

- $\sum S_J = 2J+1$, the total degeneracy!
- The R-branch line for a specific J , is $\sim J+1/J$ times as strong as the P-branch line
- For $\Delta\Lambda = \pm 1$, $J \gg \Lambda$

$$\left. \begin{aligned} S_J^R &= \frac{(2J+1)}{4} \\ S_J^Q &= \frac{(2J+1)}{2} \\ S_J^P &= \frac{(2J+1)}{4} \end{aligned} \right\} \sum S_J = 2J+1$$



Q branch lines are twice as strong as P and R lines!

$\Delta\Lambda$ value is important in determining the relative line and branch strengths of rovibronic spectra.

2. Common molecular models for diatomics

- Example – 2: Symmetric Top Ground State

If $X = {}^1\Pi$, possible transitions (Recall $\Delta\Lambda = 0, \pm 1$)

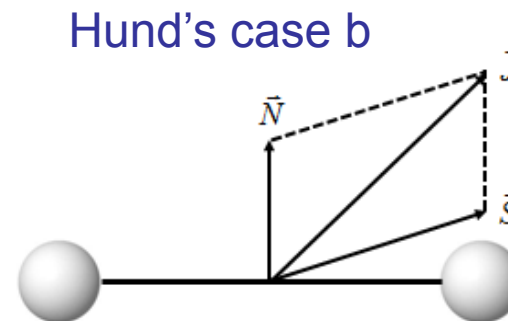
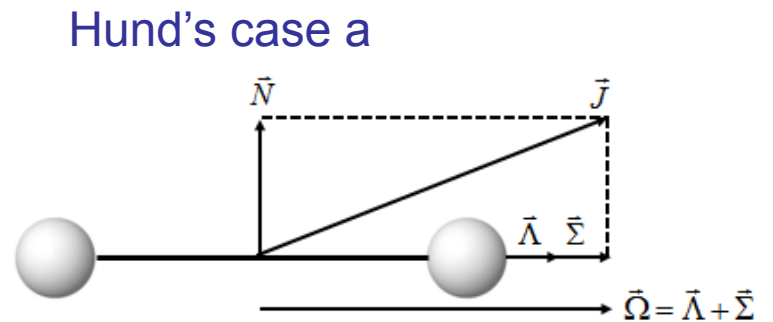
${}^1\Pi \leftarrow {}^1\Pi$	${}^1\Delta \leftarrow {}^1\Pi$	${}^1\Sigma \leftarrow {}^1\Pi$
$\Delta\Lambda = 0$	$\Delta\Lambda = 1$	$\Delta\Lambda = -1$



1. Three separate “systems” of bands possible from $X^1\Pi$
2. Hönl-London factors for $\Delta\Lambda = \pm 1$ differ from for $\Delta\Lambda = 0$ (see previous page)

3. Electronic Spectra of Diatomic Molecules: Improved Treatments (add Spin)

1. Review of angular momentum
2. Interaction of Λ and Σ
3. Hund's case a ($\Lambda \neq 0, S \neq 0$)
4. Hund's case b ($\Lambda = 0, S \neq 0$)
5. Λ -doubling



3.1. Review of angular momentum

- Review – then add spin
 - Term symbol

“Multiplicity” of state

$$\text{Term Symbol} = {}^{2S+1}\Lambda_{\Omega}$$

Sum of projections on A axis when $\Lambda \neq 0$

$$\vec{\Omega} = \vec{\Lambda} + \vec{\Sigma}$$

$$\Omega = \Lambda + S, \Lambda + S - 1, \dots, |\Lambda - S|$$

Λ	0	1	2
Symbol	Σ	Π	Δ

Projection of electron orbital angular momentum on A axis

- 4 models

- | | |
|----------|---|
| | <ul style="list-style-type: none"> Rigid Rotor $\Lambda = S = 0$ e.g., $\text{N}_2, \text{H}_2: X^1\Sigma$ Symmetric Top $\Lambda \neq 0; S = 0$ e.g., ${}^1\Pi$ |
| Add spin | <ul style="list-style-type: none"> Hund's a $\Lambda \neq 0; S \neq 0$ e.g., OH, NO (both $X^2\Pi$) Hund's b $\Lambda = 0; S \neq 0$ e.g., $\text{O}_2: X^3\Sigma$ |

3.1. Review of angular momentum

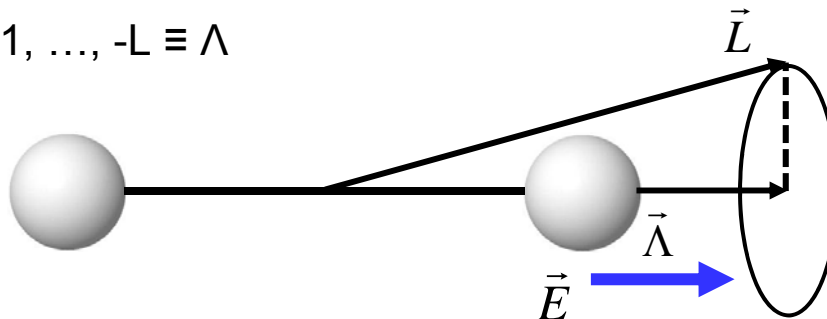
- Electronic angular momentum for molecules

- Orbital angular momentum of electrons

1. Separate from spin and nuclear rotation
2. Strong electrostatic field exists between nuclei.

So \vec{L} precesses about field direction (internuclear axis) with “allowed” components along axis

➔ $m_l = L, L-1, \dots, -L \equiv \Lambda$



3. If we reverse direction of electron orbit in \vec{E} field, we get the same energy but $\Lambda \rightarrow -\Lambda$ (Λ doubling)



3.1. Review of angular momentum

- Electronic angular momentum for molecules

- Spin of electrons

1. To determine L and S for molecule, we usually sum l & s for all electrons. e.g., $S = \sum_i s_i$

So **even** number of electrons \Rightarrow **integral** spin

odd number of electrons \Rightarrow **half-integral** spin

2. For $\Lambda \neq 0$, precession of L about internuclear axis \Rightarrow magnetic field along axis. So m_s is defined. $m_s \equiv \Sigma = S, S-1, \dots -S$.

Note for change of orbital direction, energy of electron spinning in magnetic field changes \Rightarrow no degeneracy \Rightarrow **2S+1** possibilities (multiplets)

3. For $\Lambda = 0$, no magnetic field exists and the projection of S on the nuclear axis is not conserved (Σ not defined)

3.1. Review of angular momentum

- Electronic angular momentum for molecules

- Total electronic angular momentum

1. Total electronic angular momentum along internuclear axis is $\vec{\Omega} = \vec{\Lambda} + \vec{\Sigma}$

But since all in same direction, use simple addition

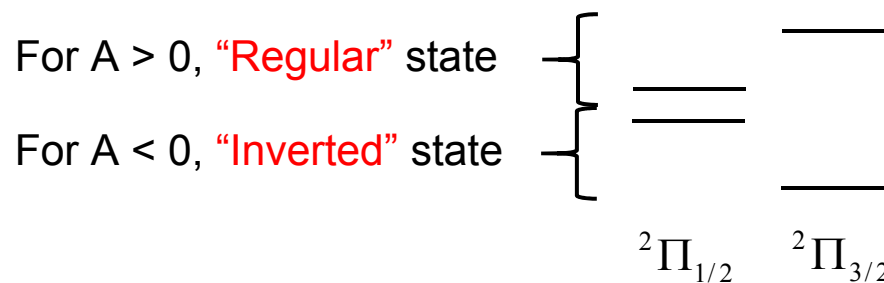
$$\Omega = |\Lambda + \Sigma|$$

2. For $\Lambda \neq 0$, magnetic field $H \propto \Lambda$.

Magnetic moment of “spinning” electron $\mu_H \propto \Sigma$.

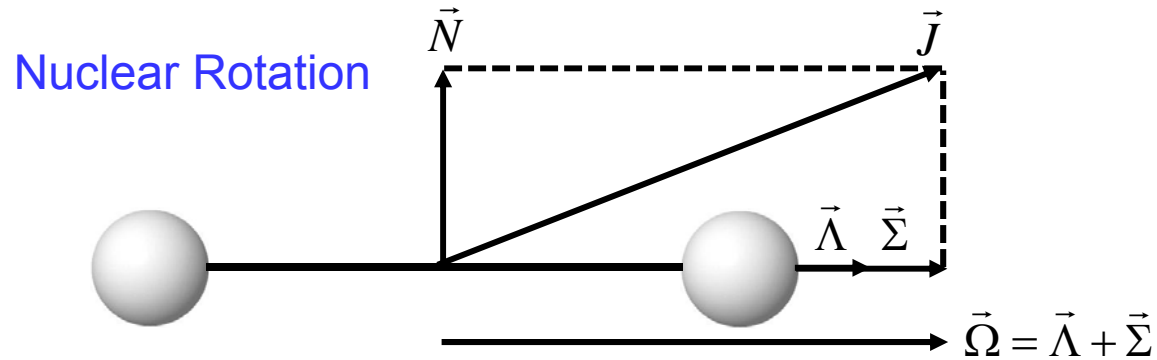
So interaction energy is proportional to $E \sim \mu H \sim \Lambda \Sigma$, or

$$T_e = T_0 + A\Lambda\Sigma \text{ (more on this later)}$$



3.2. Interaction of Λ and Σ

- This interaction is key to modeling the influence of spin on the electronic state structure.



When $\Lambda \neq 0$, $S \neq 0$, they combine to form a net component of Ω .

$\Lambda \neq 0$ ➔ an associated magnetic field due to net current about the axis. This field interacts with spinning electrons.

➔ Spin-orbit coupling (spin-splitting of energy levels)

Comments:

- Models are only approximations.
- Coupling may change as J ranges from low to high values

3.2. Interaction of Λ and Σ

Examples

$${}^3\Delta \begin{cases} {}^3\Delta_3 \leftarrow S = 1, \Lambda = 2, \Omega = 3 (\Sigma = 1) \\ {}^3\Delta_2 \leftarrow S = 1, \Lambda = 2, \Omega = 2 (\Sigma = 0) \\ {}^3\Delta_1 \leftarrow S = 1, \Lambda = 2, \Omega = 1 (\Sigma = -1) \end{cases}$$

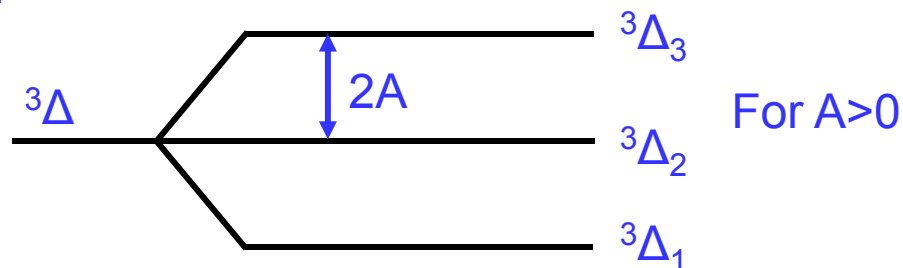
Electronic energies $T_e = T_0 + A\Lambda\Sigma$

T_0 ↑
Energy without interaction

A ↑
Spin-orbit coupling constant, generally increases with molecular weight and the number of electrons

$${}^3\Delta \rightarrow S = 1, \Lambda = 2, \Sigma = 1, 0, -1$$

$$T_e = T_0 + A(2) \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$$



Sample constants

$$A_{\text{BeH}} \approx 2 \text{ cm}^{-1}$$

$$A_{\text{NO}} \approx 124 \text{ cm}^{-1}$$

$$A_{\text{HgH}} \approx 3600 \text{ cm}^{-1}$$

$$A_{\text{OH}} \approx -140 \text{ cm}^{-1} \leftarrow \text{Negative!}$$



Notes:

1. The parameter Y is often specified, where $Y = A/B_v$
2. Values for A given in Herzberg, Vol.I

Now, consider Hund's cases where $S \neq 0$



3.3. Hund's case a

- $\Lambda \neq 0, S \neq 0, \Sigma = S, S-1, \dots, -S$

$$F(J) = BJ(J+1) + (A-B)\Omega^2$$

$$\Omega = \Lambda + S, \Lambda + S - 1, \dots, |\Lambda - S|$$

$$J = \Omega, \Omega + 1, \dots$$

- Recall

$$A = \frac{h}{8\pi^2 I_A c}, B = \frac{h}{8\pi^2 I_B c}$$

Not to be confused
with spin-orbit constant

P, Q, R branches for each value of Ω .

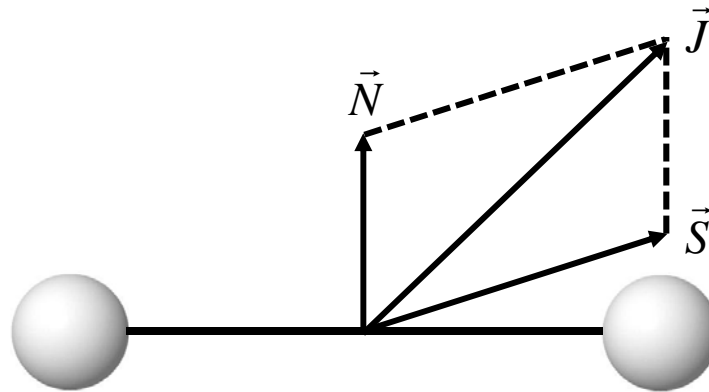
Example:

${}^2\Pi \rightarrow \Omega = 3/2$ and $1/2$, two electronic sub-states

\rightarrow a total of $2 \times 3 = 6$ branches

3.4. Hund's case b

- Applies when spin is *not* coupled to the A-axis
 - E.g.,
 1. For $\Lambda = 0$, $\vec{\Sigma}$ is not defined, must use \vec{S}
 2. At high J, especially for hydrides, even with $\Lambda \neq 0$

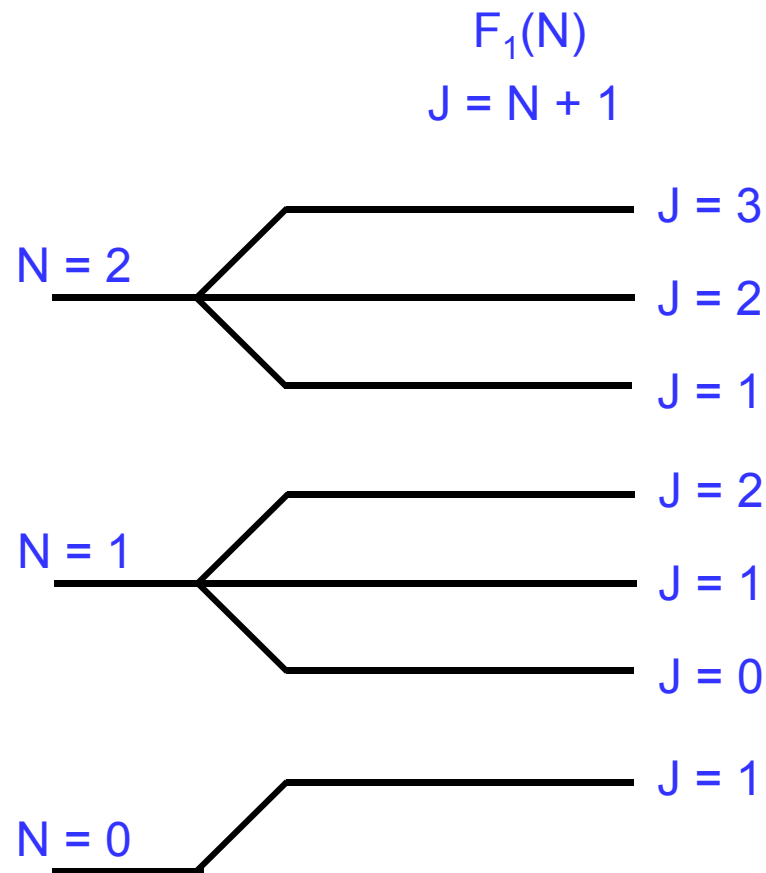


Allowed J: $J = N+S, N+S-1, \dots, N-S, J \geq 0$ only

For this case, \vec{S} and \vec{N} couple directly,

3.4. Hund's case b

- Example – O_2
 - Ground state $X^3\Sigma$ has **three** J's for each N!



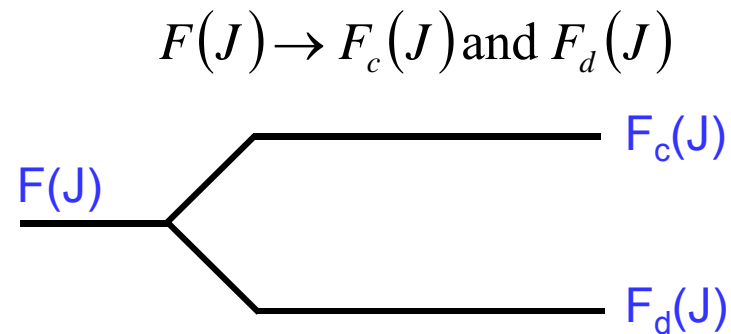
✎ Notes:

- Split rotational levels for $N > 0$
- Each level has a degeneracy of $2J + 1$, and a sum of Hönl-London factors of $2J + 1$
- Minimum J is $|N-S|$
- In $N = 0$ level, only spin is active ($S = 1$), this is the minimum value of J



3.5. Λ – doubling

- Further complexity in the energy levels resulting from Λ -doubling
 - Different coupling with nuclear rotation (\vec{N} and $\vec{\Lambda}$ interaction)
 - ➔ The two orientations of $\vec{\Lambda}$ ($\pm \Lambda$ along the A-axis) have **slightly different energies**



- By definition, $F_c(J) > F_d(J)$ (c,d replaced by e,f in some literature)
- Lambda doubling usually results in a **very small change in energy**, affecting Boltzmann distribution only slightly.
- **Change of parity** between Λ -doubled states – reduces the accessible fraction of molecules for a given transition (due to selection rules)

4. Quantitative absorption

- Review of Beer's law and spectral absorption as interpreted for molecules with multiplet structure

- Beer's Law

$$\left(\frac{I}{I^0}\right)_\nu = \exp(-k_\nu L)$$

- For two-level system

$$k_\nu = S_{12} \phi(\nu) = \left(\frac{\pi e^2}{m_e c}\right) n_1 f_{12} (1 - \exp(-h\nu/kT)) \phi(\nu)$$

↑
↑
↑

Integrated absorption
intensity [$\text{cm}^{-1}\text{s}^{-1}$]

$n_1 = \frac{n_1}{n_i} n_i$
 $f_{ij}, i - \text{initial}, j - \text{final}$

For a complex, multiple level system, we have 2 quantities to specify:

- Boltzmann fraction?*
- Oscillator strength for a specific transition?*



4. Quantitative absorption

- Boltzmann fraction

- $$n_1 = n_i \frac{n_1}{n_i}$$

n_i = the total number density of species I

n_1/n_i = the fraction of species i in state/level 1

- $$\frac{n_1}{n_i} = \frac{N_i(n, v, \Sigma, \Lambda, J, N)}{N_i}$$

Quantum numbers:

n – electronic

v – vibrational

Σ – spin

Λ – orbital

J – total angular momentum

N – nuclear rotation

c or d – Λ -component

We will illustrate this in the next lecture!

4. Quantitative absorption

- Oscillator strength
 - Strength of a *specific*, single transition (i.e., from *one* of the J'' substrates to a specific J' substrate), $f_{J''J'}$

$$\begin{aligned}
 f_{12} &= f_{(m,v'',J'')(n,v',J')} = f_{J''J'} \\
 &= \underbrace{f_{el}}_{\text{"system" osc. strength}} \times \underbrace{q_{v''v'}}_{\text{Franck-Condon factor}} \times \underbrace{\frac{S_{J''J'}}{2J''+1}}_{\text{normalized H-L factor or line strength}}
 \end{aligned}$$



Notes:

- $\sum_{v'} q_{v''v'} = 1$
- $\sum_{J'} S_{J''J'} = (2J''+1)[(2S+1)\delta]$ $\delta = 1$ for Σ - Σ , otherwise $\delta = 2$ (Λ -doubling).
 $[(2S+1)\delta] = 4$ for OH's $A^2\Sigma \leftarrow X^2\Pi$ system.
- $\sum_{v',J''} f_{J''J'} = [(2S+1)\delta] f_{el}$ sum is f_{el} for a single J'' substate.

4. Quantitative absorption

- Oscillator strength

Remarks

1. Band oscillator strength $f_{v''v'} = f_{el} q_{v''v'}$ → often is tabulated
e.g., $f_{00} = 0.001$ (OH $A^2\Sigma \leftarrow X^2\Pi$)

2.
$$f_{J''J'} = f_{v''v'} \left(\frac{S_{J''J'}}{2J''+1} \right)$$

e.g., if only P and R are allowed $S_{J''J'}^P = J''$, $S_{J''J'}^R = J''+1$

3. In some cases, an additional “correction term” $T_{J''J'}$ is used, e.g., in OH

$$f_{J''J'} = f_{v''v'} \left(\frac{S_{J''J'}}{2J''+1} \right) T_{J''J'}, T_{J''J'} \text{ always near 1}$$

4. In terms of A-coefficient
$$f_{v''v'} = \left(\frac{m_e c \lambda^2}{8\pi^2 e^2} \right) A_{v'v''} \left(\frac{g_{e'}}{g_{e''}} \right)$$

$$= \frac{g_{e'}}{g_{e''}} f_{v'v''}$$



Next: Case Study of Molecular Spectra

- ❖ Ultraviolet: OH