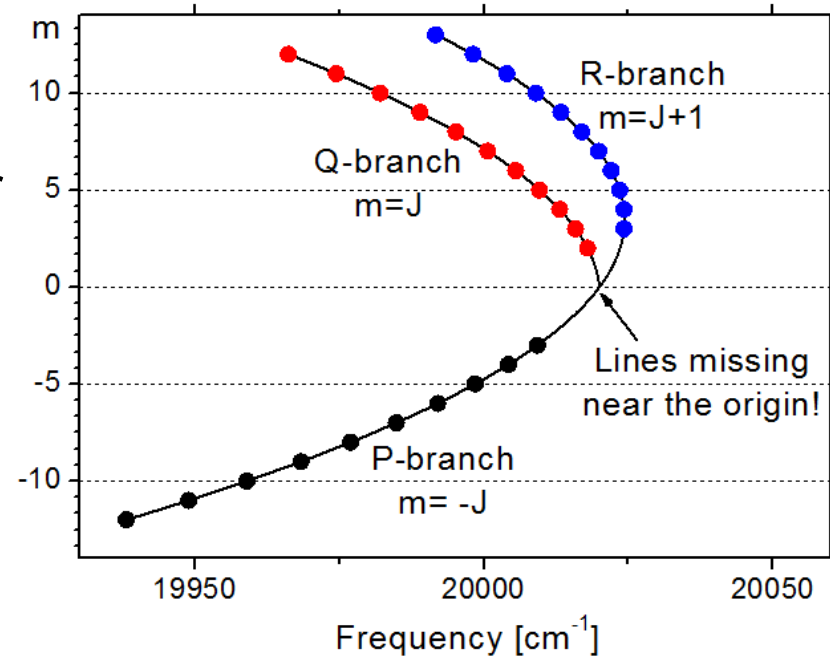


# Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

## 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: 

$\Lambda$	0	1	2
Symbol	$\Sigma$	$\Pi$	$\Delta$

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:  $121\text{cm}^{-1}$

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

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

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

$\text{O}_2$  The ground state for  $\text{O}_2$  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

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

- This lecture:

**Rigid Rotor**

**Symmetric Top**

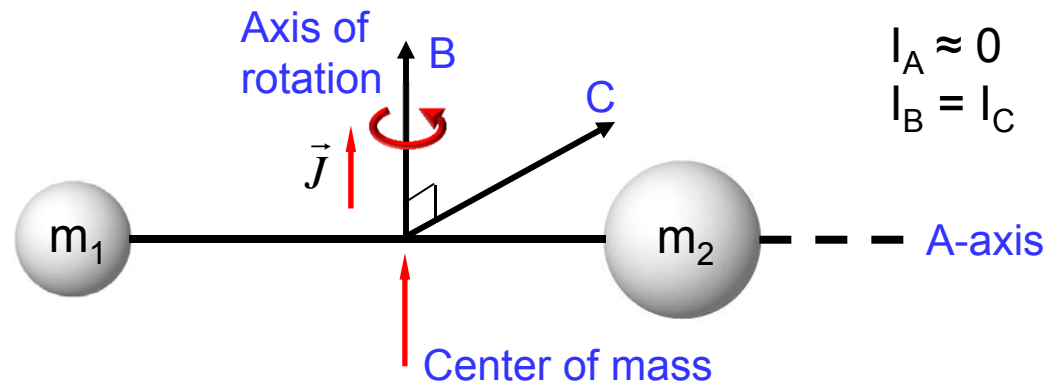
Followed by:

**Hund’s *a***

**Hund’s *b***

## 2. Common molecular models for diatomics

- Rigid rotor ( ${}^1\Sigma$ )



- $\Lambda = 0, S = 0 \Rightarrow {}^1\Sigma$  type,  $\Omega$  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  $E(T_e, v, J) = T_e + G(v) + F(J)$

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

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

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

$$\Delta J = \pm 1$$

Rovibronic spectra:  $\Delta v$  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 ( $^1\Sigma$ )

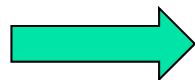
**Intensity Distribution** Within each band ( $v'$ ,  $v''$ ), the intensity distribution follows the Boltzmann distribution for J modified by a J-dependent branching ratio (i.e., for the P and R branch), known as the **Hönl-London factor**.

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

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

**Examples** Most stable diatomics: CO, Cl<sub>2</sub>, Br<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub> are rigid rotors  
Exceptions: NO ( $X^2\Pi$ ), O<sub>2</sub>( $X^3\Sigma$ )

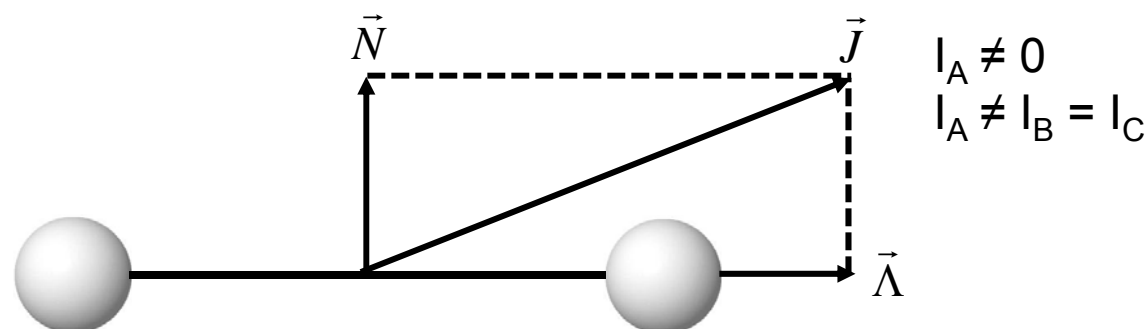
Note: no  $X\Delta$  states for diatomics – all X states are  $\Sigma$  or  $\Pi$ !  
Some linear polyatomics: CO<sub>2</sub>( $\tilde{X}^1\Sigma_g^+$ ), HCN and N<sub>2</sub>O ( $\tilde{X}^1\Sigma^+$ ) are rigid rotors with  $^1\Sigma$  ground states.



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  $^1\Delta \leftarrow ^1\Delta$ )

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

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

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

→

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

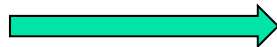
$$Q(J'') = \bar{\nu}_\infty + (B' - B'')J + (B' - B'')J^2$$

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

$$m_P = -J$$

$$m_Q = +J$$

$$m_R = J + 1$$



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:

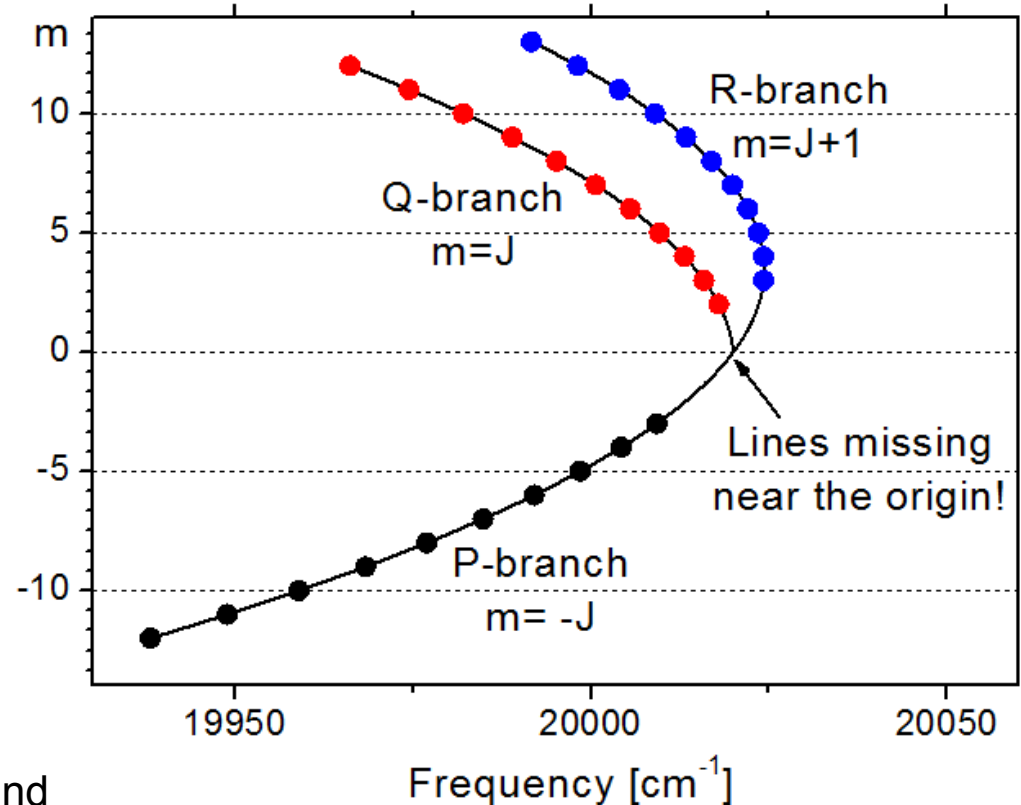
- **Band heads** in the Q and R branches for the typical case of  $B' < B''$ .
- $m_P = -J, m_Q = +J, m_R = J+1$
- $J_{\min} = 2$  for  ${}^1\Delta \leftarrow {}^1\Delta$ 
  - ➔  $m_{\min} = 3$  for R branch
  - $m_{\min} = 2$  for Q branch
  - $|m_{\min}| = 3$  for P branch
- ➔ **missing lines near 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  $\Delta\Lambda = 0, \pm 1$ )

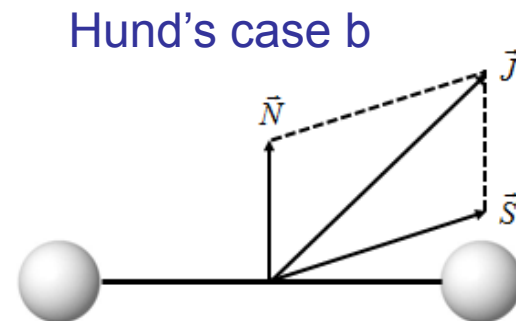
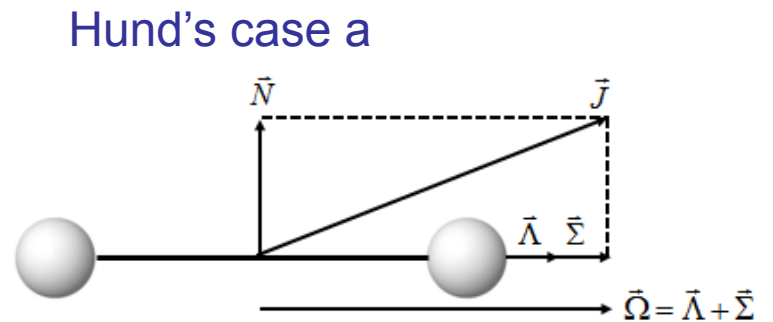
${}^1\Pi \leftarrow {}^1\Pi$	${}^1\Delta \leftarrow {}^1\Pi$	${}^1\Sigma \leftarrow {}^1\Pi$
$\Delta\Lambda = 0$	$\Delta\Lambda = 1$	$\Delta\Lambda = -1$



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  $\Lambda$  and  $\Sigma$
3. Hund's case a ( $\Lambda \neq 0, S \neq 0$ )
4. Hund's case b ( $\Lambda = 0, S \neq 0$ )
5.  $\Lambda$ -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  $\Lambda \neq 0$

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

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

$\Lambda$	0	1	2
Symbol	$\Sigma$	$\Pi$	$\Delta$

Projection of electron orbital angular momentum on A axis

- 4 models

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

## 3.1. Review of angular momentum

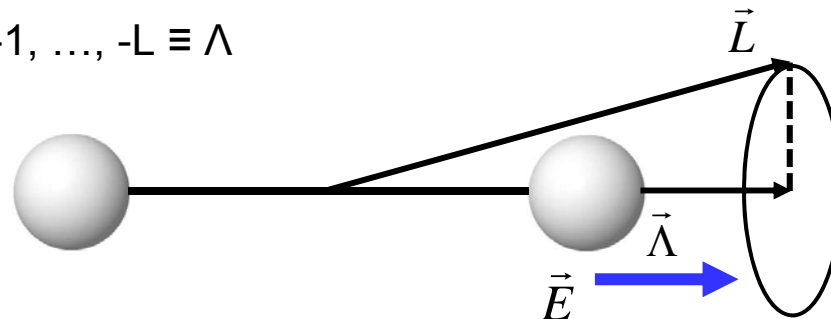
- Electronic angular momentum for molecules

- 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

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



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





## 3.1. Review of angular momentum

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- 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 ( $\Sigma$  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

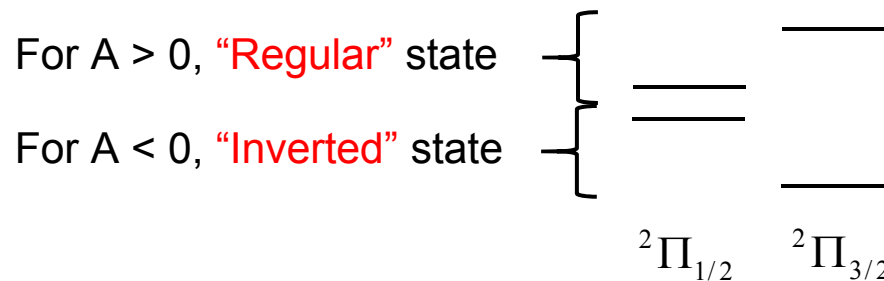
$$\Omega = |\Lambda + \Sigma|$$

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

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

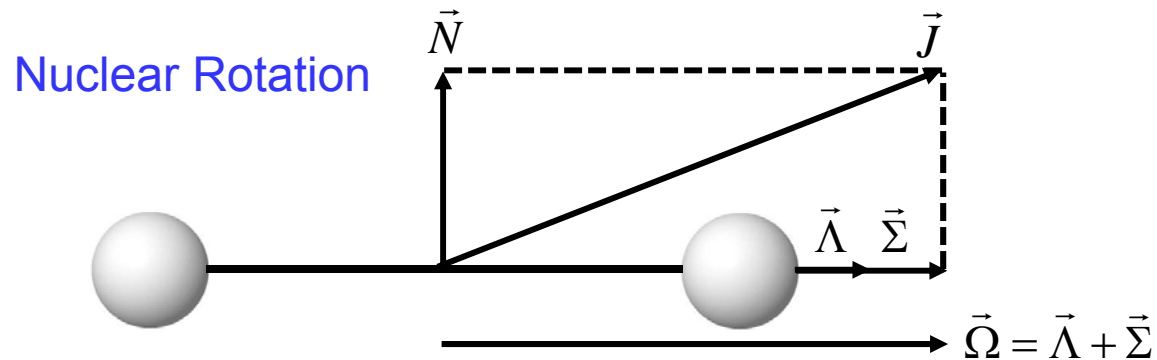
So interaction energy is proportional to  $E \sim \mu H \sim \Lambda \Sigma$ , or

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



## 3.2. Interaction of $\Lambda$ and $\Sigma$

- 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  $\Omega$ .

$\Lambda \neq 0$  ➔ 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 $\Lambda$ and $\Sigma$

### Examples

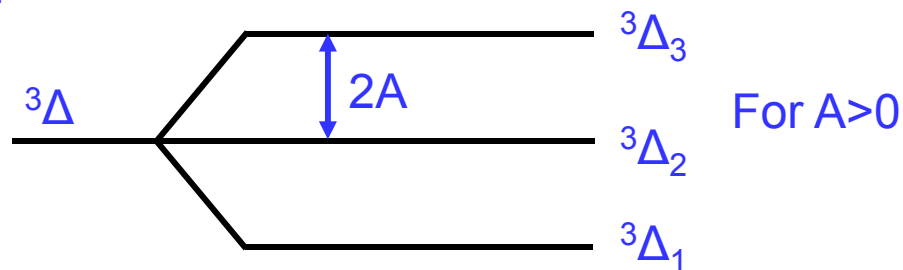
$${}^3\Delta \begin{cases} {}^3\Delta_3 \leftarrow S = 1, \Lambda = 2, \Omega = 3 (\Sigma = 1) \\ {}^3\Delta_2 \leftarrow S = 1, \Lambda = 2, \Omega = 2 (\Sigma = 0) \\ {}^3\Delta_1 \leftarrow S = 1, \Lambda = 2, \Omega = 1 (\Sigma = -1) \end{cases}$$

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

$\uparrow$  Energy without interaction       $\nwarrow$  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

$$\begin{aligned} A_{\text{BeH}} &\approx 2 \text{ cm}^{-1} \\ A_{\text{NO}} &\approx 124 \text{ cm}^{-1} \\ A_{\text{HgH}} &\approx 3600 \text{ cm}^{-1} \\ A_{\text{OH}} &\approx -140 \text{ cm}^{-1} \leftarrow \text{Negative!} \end{aligned}$$



### 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  $\Omega$ .

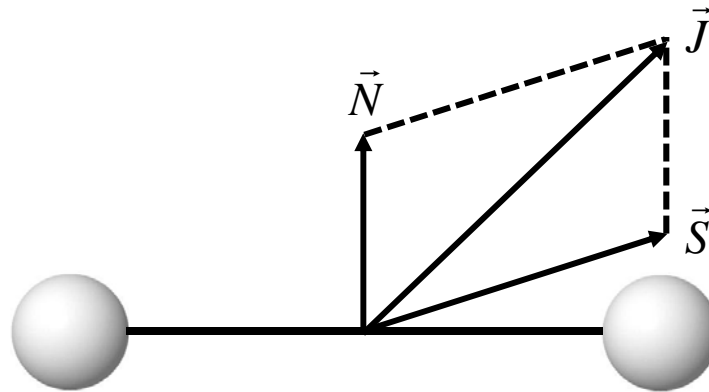
Example:

${}^2\Pi \rightarrow \Omega = 3/2$  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  $\Lambda \neq 0$

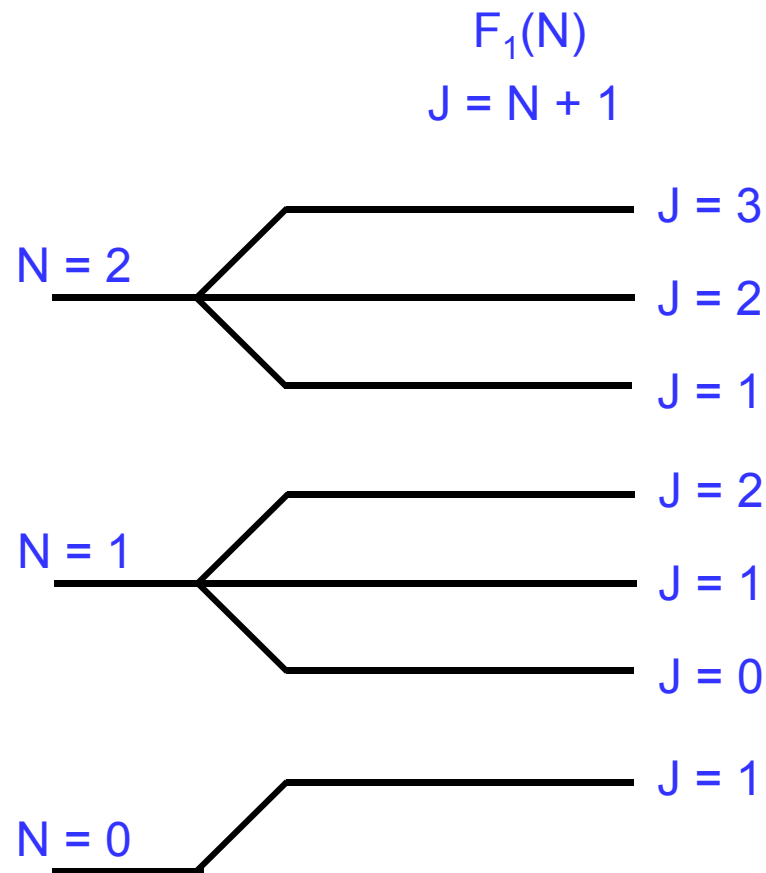


Allowed J:  $J = N+S, N+S-1, \dots, N-S, J \geq 0$  only

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!



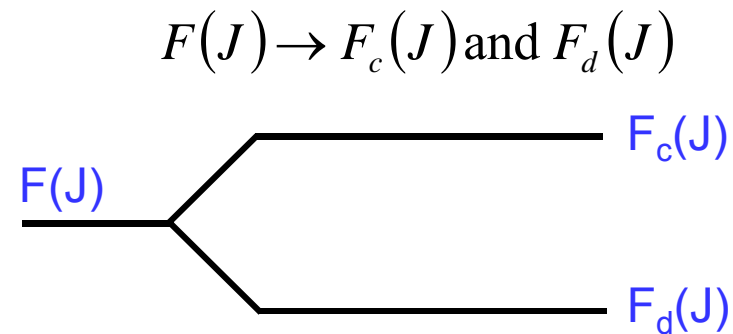
✍ Notes:

- 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. $\Lambda$ – doubling

- Further complexity in the energy levels resulting from  $\Lambda$ -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  $\Lambda$ -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

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- 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

**$\Sigma$**  – spin

**$\Lambda$**  – orbital

**J** – total angular momentum

**N** – nuclear rotation

**c or d** –  $\Lambda$ -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  $\Sigma$ - $\Sigma$ , otherwise  $\delta = 2$  ( $\Lambda$ -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

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- ❖ Ultraviolet: OH