

10.1 Term Symbols for Diatomic Molecules

Term symbols, introduced in the previous chapter, are the notation used to characterize key features of electron spin and orbital angular momentum.

For an atom, the term symbol is: $^{2S+1}L_J$

For a diatomic, the term symbol is: $^{2S+1}\Lambda_\Omega$

Important terms to define are \vec{S} , $\vec{\Sigma}$, $\vec{\Lambda}$, and $\vec{\Omega}$:

$\vec{\Lambda}$ projection of orbital angular momentum on the internuclear axis
Its magnitude is $|\vec{\Lambda}| = \Lambda\hbar$, where Λ is an integer, and the symbols associated with different values of Λ are shown in the table below.

Λ	0	1	2
Symbol	Σ	Π	Δ

\vec{S} total electronic spin angular momentum (the net sum of electron spin in unfilled shells). The magnitude is $|\vec{S}| = S\hbar$, where S will have 1/2-integer values.

$\vec{\Sigma}$ projection of \vec{S} onto the internuclear axis (only defined when $\Lambda \neq 0$). The magnitude of this projection is $|\vec{\Sigma}| = \Sigma\hbar$, and the allowed values of Σ are

$$\Sigma = S, S - 1, \dots, -S \quad (2S + 1 \text{ values})$$

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

$$\vec{\Omega} = \vec{S} + \vec{L}$$

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

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 cm^{-1}
- 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 with no influence from electrons. Easiest case!
- O₂** The ground state for O₂ is $X^3\Sigma_g^-$.
 $S = 1, \Lambda = 0$
 The $^-$ and $_g$ are notations about symmetric properties of wave functions. This is an example of a molecule that is modelled by Hund's case *b*, discussed below.

10.2 Common Molecular Models for Diatomics

There are four common molecular models that are used to describe diatomic electronic spectra:

Rigid rotor $\Lambda = 0, S = 0$

Symmetric top $\Lambda \neq 0, S = 0$

Hund's *a* $\Lambda \neq 0, S \neq 0$

Hund's *b* $\Lambda = 0, S \neq 0$

The rigid rotor and symmetric top models have no spin, and thus their multiplicity ($2S + 1$) is one; these states are called "singlets." For the Hund's cases, the influence of spin on the electronic state structure must be considered through interactions of Λ and Σ .

10.2.1 Rigid Rotor ($^1\Sigma$)

The simplest model for molecular rotation assumes that electron motions do not contribute to the rotational energy. Rotation of the nuclei occurs about an axis perpendicular to the *A*-axis (i.e., the *B*-axis). Recall that $I_A \approx 0$ and $I_B = I_C$ (Fig. 10.1).

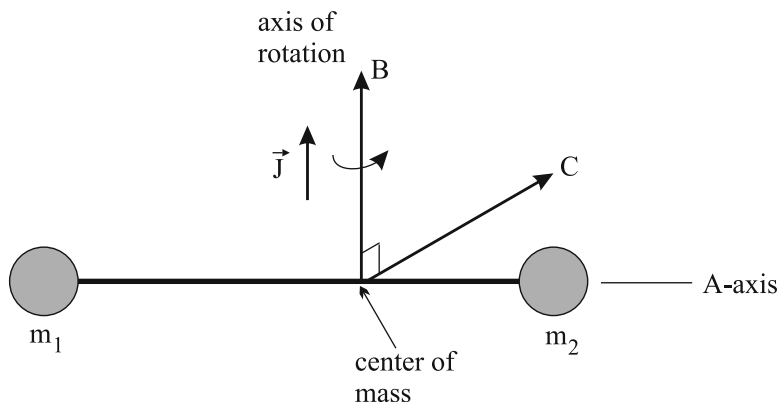


Fig. 10.1 Rigid rotor model for molecular motion

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

Rotational Energy

The total rotational energy for a rigid rotor, including centrifugal distortion is, as before,

$$F(J) = B_v J(J + 1) - D_v J^2(J + 1)^2 \quad (10.1)$$

Total Energy

Rovibronic transitions (those that include electronic, vibrational, and rotational changes in quantum number) have a total energy that includes contributions from each mode, i.e. $\Delta E = \Delta T_e + \Delta G + \Delta F$

$$\text{where } E(T_e, v, J) = T_e + G(v) + F(J). \quad (10.2)$$

Selection Rules

The selection rules for these transitions, as described before, are:

$$\begin{array}{ll} \text{Rotational spectra:} & \Delta J = J' - J'' = +1 \\ \text{Rovibrational spectra:} & \Delta v = v' - v'' = +1 \\ & \Delta J = \pm 1 \\ \text{Rovibronic spectra:} & \Delta v \text{ determined by Franck-Condon factors} \\ & \Delta J = \pm 1 \end{array}$$

Note: An alternate form for the selection rules is used in some texts, i.e. $\Delta\alpha = \alpha_{\text{final}} - \alpha_{\text{initial}}$ where ($\alpha = J$ or v).

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 branches), known as the Hönl–London factor (defined later in this chapter). Similarly, 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 (a manifestation of the Franck–Condon principle). The relative total emission or absorption from v_{initial} (i.e., to all values of v_{final}) depends directly on the Boltzmann fraction in that level, i.e. $n_{v_{\text{initial}}}/n$, and also on an overall Einstein coefficient or oscillator strength for the specific electronic system (i.e., a specific pair of lower and upper electronic states), as presented in Sect. 10.3.

Examples

Most stable diatomics, including CO, Cl₂, Br₂, N₂, H₂ are Rigid Rotors. Exceptions are NO ($X^2\Pi$) and O₂ ($X^3\Sigma$). (Note that there are no $X\Delta$ states for the diatomics listed in Herzberg—all X states are Σ or Π !) Some linear polyatomics such as CO₂ ($\tilde{X}^1\Sigma_g^+$) and both HCN and N₂O ($\tilde{X}^1\Sigma^+$) are Rigid Rotors with $^1\Sigma$ ground states. Remember, however, that nuclear spin can have an impact on the statistics of homonuclear diatomic molecules.

10.2.2 Symmetric Top

Symmetric tops have a non-zero projection of orbital angular momentum on the internuclear axis and zero spin ($\Lambda \neq 0, S = 0$). Thus, its ground states are $^1\Pi$, $^1\Delta$ (although, as mentioned in the previous section, there are no known $X^1\Delta$ ground states for diatomics) (Fig. 10.2).

The important components are

- \vec{N} angular momentum of nuclei
- $\vec{\Lambda}$ A-axis projection of electron orbital angular momentum
- \vec{J} total angular momentum; $\vec{J} = \vec{N} + \vec{\Lambda}$

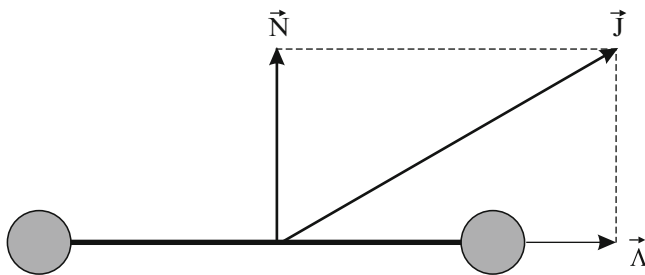


Fig. 10.2 Symmetric top model for molecular motion

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.

Rotational Energy

The total rotational energy for a symmetric top is

$$F(J) = BJ(J + 1) + (A - B)\Lambda^2 \quad J = \Lambda, \Lambda + 1, \dots \quad (10.3)$$

The constants A and B are given as before by

$$A, B = \frac{h}{8\pi^2 c I_{A,B}} \quad (10.4)$$

Therefore, the symmetric top energy levels have the same spacing as the Rigid Rotor, but with a constant offset. Note, however, that since I_A is small compared to I_B , A is large compared to B . Lines with $J < \Lambda$ are missing, as $J = \Lambda, \Lambda + 1, \dots$

Selection Rules

The selection rules for symmetric top electronic spectra are

$$\begin{aligned} \Delta\Lambda = 0 & \quad \Delta J = \pm 1, 0 & (\Delta J = 0 \text{ may be weak}) \\ \Delta\Lambda = \pm 1 & \quad \Delta J = \pm 1, 0 \end{aligned}$$

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.

Spectra

The spectra for the case where $\Delta\Lambda = 0$ are discussed here. The upper- and lower-state energies are described by the following equations:

$$T' = B'J'(J' + 1) + (A' - B')\Lambda^2 + G(v') + T'_e \quad (10.5)$$

$$T'' = B''J''(J'' + 1) + (A'' - B'')\Lambda^2 + G(v'') + T''_e \quad (10.6)$$

$$\bar{\nu}_\infty = \text{upper (for } J' = 0) - \text{lower (for } J'' = 0) = \text{constant} \quad (10.7)$$

$T''_e = 0$ for the ground state. Then, for the three branches, the line positions are as follows:

$$P(J'') = \bar{\nu}_\infty - (B' + B'')J + (B' - B'')J^2 \quad (10.8)$$

$$Q(J'') = \bar{\nu}_\infty + (B' - B'')J + (B' - B'')J^2 \quad (10.9)$$

$$R(J'') = \bar{\nu}_\infty + (B' + B'')(J + 1) + (B' - B'')(J + 1)^2 \quad (10.10)$$

Using the rotational number m for the three branches,

$$\begin{aligned} m_P &= -J \\ m_Q &= +J \\ m_R &= J + 1 \end{aligned}$$

the line positions for the P and R branches become

$$\bar{\nu} = \bar{\nu}_\infty + am + bm^2, \quad (10.11)$$

where $a = B' + B''$ and $b = B' - B''$, and the line positions for the Q branch become

$$\bar{\nu} = \bar{\nu}_\infty + bm + bm^2 \quad (10.12)$$

Note that the three branches now can lead to two bandheads (see the Fortrat parabola plot below for the case of a ${}^1\Delta \leftarrow {}^1\Delta$ band) (Fig. 10.3).

The Fortrat parabola shows the bandheads in the Q and R branches for the typical case of $B' < B''$. For the ${}^1\Delta \leftarrow {}^1\Delta$ case, $J_{\min} = 2$ and therefore $m_{\min} = 3$ for the R branch, $m_{\min} = 2$ for the Q branch and $m = -3$ is the first line in the P branch, resulting in multiple missing lines near the origin.

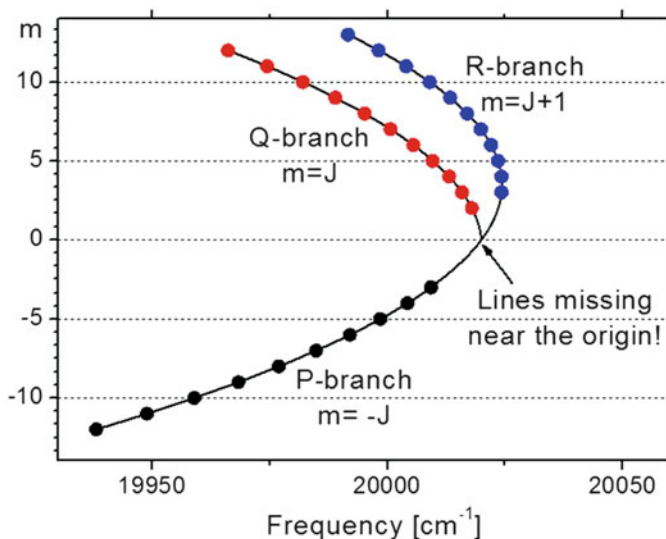


Fig. 10.3 Symmetric top model for molecular motion, ${}^1\Delta \leftarrow {}^1\Delta$ case

Intensity Distribution

Actual relative intensities depend on n_J/n and “relative intensity factors/line strengths,” also known as Hönl–London factors, denoted below by $S_J^{P,Q,R}$. Differences in Hönl–London factors indicate the breakdown of the principle of equal probability [1].

Example: Hönl–London factors for symmetric top (p. 208 of [1])

For $\Delta\Lambda = 0$

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

- Note:**
1. $\sum S_J = 2J+1$, the total degeneracy!
 2. The R-branch line, for a specified J , is approximately $(J+1)/J$ times as strong as the P branch line.
 3. For $\Delta\Lambda = \pm 1$, and $J \gg \Lambda$

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

The Q branch lines are thus twice as strong as the P and R lines! Therefore, the $\Delta\Lambda$ value is important in determining the relative line and branch strengths of rovibronic spectra.

Example: $X = {}^1\Pi$

If $X = {}^1\Pi$, then the following transitions are possible for changes in Λ of 0 or ± 1 . That is, there are three separate “systems” of bands possible from $X^1\Pi$.

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

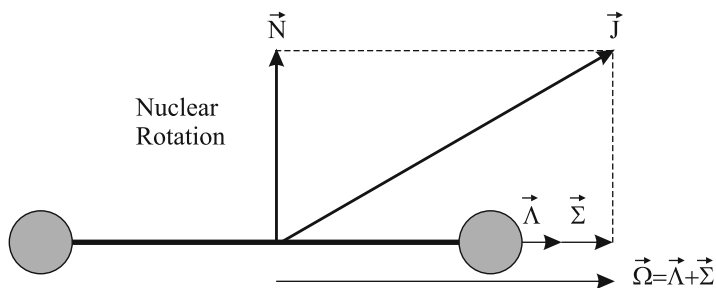


Fig. 10.4 Coupling of Σ and Λ

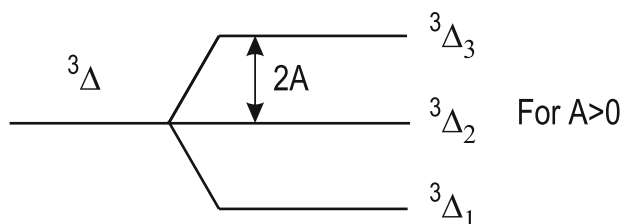


Fig. 10.5 Spin-orbit splitting

10.2.3 Interaction of Λ and Σ

Understanding the interactions and coupling of Λ and Σ is a key to modelling the influence of spin on the electronic state structure. When $\Lambda \neq 0$ and $S \neq 0$, they combine to form a net component of Ω , as shown in Fig. 10.4.

The presence of $\Lambda \neq 0$ implies that there is an associated magnetic field due to net current about the axis. This field interacts with spinning electrons. This effect is known as spin-orbit coupling (or spin-splitting) (Fig. 10.5).

Examples

${}^3\Delta$ has three components (${}^3\Delta_3$, ${}^3\Delta_2$, ${}^3\Delta_1$) corresponding to $S = 1$, $\Lambda = 2$ and $\Omega = 3, 2, 1$ (since $\Sigma = 1, 0, -1$). These states have different electronic energies, which may be represented by

$$T_e = T_0 + A\Lambda\Sigma \quad (10.13)$$

Here, A is the spin-orbit coupling constant (it's not exactly the same A as in the symmetric top, but it is similar; keep in mind that these are *models*). A generally increases with molecular weight and the number of electrons. T_0 is the energy without interaction.

For ${}^3\Delta$, $\Lambda = 2$, $S = 1$, and $\Sigma = 1, 0, -1$. Therefore,

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

Some sample spin-orbit coupling constants are listed below.

$$A_{\text{BeH}} \approx 2 \text{ cm}^{-1} \quad (10.14)$$

$$A_{\text{NO}} \approx 124 \text{ cm}^{-1} \quad (10.15)$$

$$A_{\text{HgH}} \approx 3600 \text{ cm}^{-1} \quad (10.16)$$

$$A_{\text{OH}} \approx -140 \text{ cm}^{-1} \quad (10.17)$$

Note that the spin-orbit coupling constant for OH is negative. (See Herzberg, Vol. I for details; p. 215/216, 232, 558/559, 561.)

Note: 1. $Y = \frac{A}{B_v}$ is the ratio of the spin-orbit constant and B_v
2. Values for A are given in tables in Herzberg, Vol. I

Now, finally, we are ready to consider rotational levels for cases where $S \neq 0$. There are two primary cases: Hund's *a* and Hund's *b*.

10.2.4 Hund's Case *a*

Hund's case *a* is for $\Lambda \neq 0$ and $S \neq 0$ with Σ defined as $\Sigma = S, S - 1, \dots, -S$. Replace Λ with Ω in $F(J)$ for the symmetric top to get [1]

$$\begin{aligned} F(J) &= BJ(J + 1) + (A - B)\Omega^2 & (10.18) \\ \Omega &= \Lambda + S, \Lambda + S - 1, \dots, |\Lambda - S| \\ J &= \Omega, \Omega + 1, \dots \end{aligned}$$

Remember that A for the equation above is $A = h/8\pi^2 I_A c$; it is *not* the spin-orbit constant.

There are *P*, *Q*, and *R* branches for each value of Ω . For example, with ${}^2\Pi$, we have $\Omega = 3/2$ and $1/2$, i.e. two electronic sub-states, giving a total of $2 \times 3 = 6$ branches.

10.2.5 Hund's Case *b*

Hund's case *b* applies when spin is *not* coupled to the *A*-axis [1] (Fig. 10.6), e.g.:

1. for $\Lambda = 0$ (so $\vec{\Sigma}$ is not defined, and we must use \vec{S})
2. at high J , especially for hydrides, even with $\Lambda \neq 0$

The allowed J are $J = N + S, N + S - 1, \dots, N - S$, and $J \geq 0$ only. For this case, \vec{S} and \vec{N} couple directly.

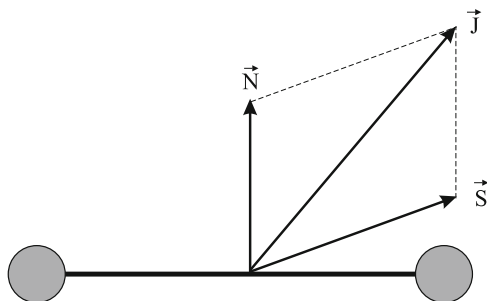
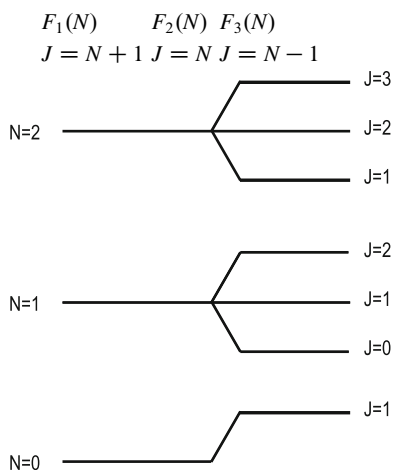


Fig. 10.6 Molecular model for Hund's *b*

Example: O_2

The ground state $X^3\Sigma$ has three J 's for each N except $N = 0$. These energy levels are labelled $F_1(N)$, $F_2(N)$ and $F_3(N)$.



There are split rotational levels for $N > 0$, and each level has a degeneracy of $2J + 1$ and a sum of Hönl–London factors of $2J + 1$. The minimum J is $|N - S|$.

Note: In the $N = 0$ level, since only spin is active and is not equal to zero (i.e., $S = 1$), the minimum value of J is 1.

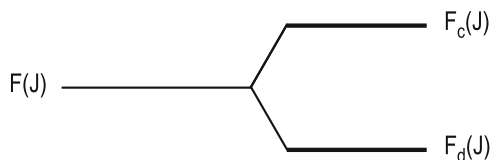


Fig. 10.7 Lambda-doubling results in two different energy levels

10.2.6 Λ -Doubling

There is further complexity in the energy levels resulting from a phenomenon known as Λ -doubling. The two orientations of $\vec{\Lambda}$ ($\pm\Lambda$ along the A-axis) have slightly different energies, owing to different coupling with nuclear rotation (i.e., \vec{N} and $\vec{\Lambda}$ interaction). The result is

$$F(J) \rightarrow F_c(J) \text{ and } F_d(J)$$

That is, there are two components to the energy, $F(J)$ (Fig. 10.7).

By definition, $F_c(J) > F_d(J)$,¹ i.e. the c state is the higher-energy state.

Lambda doubling usually results in a very small change in energy, thus affecting the Boltzmann fraction only slightly (other than adding a state). A more important aspect is found in the change of parity between Λ -doubled states, which reduces the accessible fraction of molecules for a given transition (due to selection rules).

10.2.7 Comment on Models

1. Models are only approximations to real molecules; don't think of them as exact!
2. Coupling may change as J ranges from low to high values.

10.3 Quantitative Absorption

This section is a review of Beer's Law and spectral absorption as interpreted for molecules with multiplet structure.

$$\text{Beer's Law } \left(\frac{I}{I^0}\right)_\nu = \exp(-k_\nu L) \quad (10.19)$$

For a two-level system, we had

$$k_\nu = S_{12}\phi(\nu) = \left(\frac{\pi e^2}{m_e c}\right) n_1 f_{12} (1 - \exp(-h\nu/kT)) \phi(\nu), \quad (10.20)$$

¹Note that the subscripts c and d are replaced by e and f , respectively, in some literature.

where S_{12} is the integrated absorption intensity with units of $\text{cm}^{-1} \text{s}^{-1}$ [see Eq. (7.48)]. How do we evaluate n_1 and f_{12} in a complex, multiple level system? There are two issues:

1. The Boltzmann fraction, and
2. The oscillator strength for a specific transition

10.3.1 Boltzmann Fraction

$$n_1 = n_i \frac{n_1}{n_i} \quad (10.21)$$

where n_i = the total number density of species i and

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

The state/level is specified through the quantum numbers, e.g. n (elec), v (vib), Σ (spin), Λ (orbital), J (total angular momentum), N (nuclear rotation), c or d (Λ -component).

$$\frac{n_1}{n_i} = \frac{N_i(n, v, \Sigma, \Lambda, J, N)}{N_i} \quad (10.22)$$

Λ gives the orientation and distinguishes Λ -doubling.

10.3.2 Oscillator Strength

It is common to denote the oscillator strength of a *specific*, single transition (i.e., from *one* of the J'' substates to a specific J' substate) by $f_{J''J'}$, and to view this transition strength as the product of a system strength, vibrational factor (fraction) and rotational factor (fraction), i.e.,

$$f_{12} = f_{(m,v'',J'')(n,v',J')} \quad (10.23)$$

$$= f_{J''J'} \quad (10.24)$$

$$= \underbrace{f_{\text{el}}}_{\text{“system” osc. strength}} \times \underbrace{q_{v''v'}}_{\text{Franck-Condon factor}} \times \underbrace{\frac{S_{J''J'}}{2J''+1}}_{\text{normalized H-L factor or line strength}} \quad (10.25)$$

We will show later that the sum of line strengths from a specific substate of J'' (i.e., with a specific N and Λ component (c or d)) to all possible J' is simply $2J'' + 1$; further, $\sum_{v'} q_{v''v'} = 1$. **Thus, the effective total oscillator strength (i.e., for the sum of all radiative transitions) for each of the substates, i.e. with specific values of J'' , N'' , Λ'' and v'' , is f_{el} .**

- Note:**
1. $\sum_{J'} S_{J''J'} = (2J'' + 1)[(2S + 1)\delta]$
 $\sum_{J'} S_{J''J'}$ is the sum over all allowed J' (upper states) for the *combined* lower substates with specific $J = J''$. $\delta = 1$ for $\Sigma - \Sigma$, otherwise $\delta = 2$ (to account for Λ -doubling!). The term $[(2S + 1)\delta] = 4$ for OH's $A^2\Sigma \leftarrow X^2\Pi$ system, since there are four substates with a given J'' .
 2. $\sum_{v', J'} f_{J''J'} = [(2S + 1)\delta]f_{el}$
 where $\sum_{v', J'}$ is the sum over v' and all the substates in J'' . This sum is f_{el} for a *single* J'' substate.

Remarks

1. It is common to use band oscillator strengths (available in the literature).

$$f_{v''v'} = f_{el}q_{v''v'}$$

e.g., $f_{00} = 0.001$ (OH; $A^2\Sigma \leftarrow X^2\Pi$)

2. Then

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

e.g., if only P and R are allowed,

$$S_{J''J'}^P = J'' \tag{10.26}$$

$$S_{J''J'}^R = J'' + 1 \tag{10.27}$$

Therefore, the intensities for R and P transitions from a specific J'' are similar, except for small J'' , but the R-branch transitions are stronger than the P-branch transitions by the ratio $(J'' + 1)/J''$.

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

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

where $T_{J''J'}$ is always near 1.

4. In terms of A -coefficients, we may also write

$$f_{v''v'} = \left(\frac{m_e c \lambda^2}{8\pi^2 e^2} \right) A_{v''v'} \left(\frac{g_{e'}}{g_{e''}} \right)$$

5. And recalling Eq. (7.54) we may write

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

We now know enough to tackle a real (and important) molecule, OH; see Chap. 14.

10.4 Exercises

1. A rovibronic transition in nitric oxide (NO) occurs at 226 nm. The oscillator strength for the transition between states 1 and 2 is given by

$$f_{12} = f_{\text{el}} \times q_{v''v'} \times \frac{S_{J''J'}}{2J'' + 1} = f_{21} \frac{g'}{g''}$$

where f_{el} is the oscillator strength for transitions between the lower and upper electronic states, $q_{v''v'}$ is the Franck–Condon factor and $S_{J''J'}/(2J'' + 1)$ is the normalized Hönl–London factor. For this transition of NO,

$$\begin{aligned} f_{\text{el}} &= 3.0 \times 10^{-3} \\ q_{v''v'} &= 1.673 \times 10^{-1} \\ \frac{S_{J''J'}}{2J'' + 1} &= 0.5 \end{aligned}$$

Consider a gas mixture at 1000 K and 2 atm, with an effective collisional broadening coefficient for this NO transition of $2\gamma = 0.09 \text{ cm}^{-1} \text{ atm}^{-1}$, and a number density in the absorbing state 1 of $n_1 = 3.7 \times 10^{14} \text{ cm}^{-3}$.

- Determine the peak absorption coefficient k_{v_0} in cm^{-1} at the above temperature and pressure.
- Find the fractional absorption at line center and at a detuning of 0.2 cm^{-1} for path lengths of 1 and 10 cm.
- Determine the spontaneous lifetime of the upper state. You may assume the electronic degeneracies of the upper and lower states are both 2.

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- (d) What is the mole fraction of NO (in ppm) for this gas mixture, assuming an approximate Boltzmann fraction of NO molecules in the absorption state of 4.2 %. (This is a reasonable estimate, if one neglects issues of Λ -doubling and assumes that the absorbing state is in $v'' = 0$ and J'' near the peak of the rotational distribution.) This step requires no spectroscopic calculation, only a simple use of the ideal gas equation of state, but is useful in giving a sense of the species detection sensitivity of spectrally resolved absorption.

Reference

1. G. Herzberg, *Molecular Spectra and Molecular Structure, Volume I. Spectra of Diatomic Molecules*, 2nd edn. (Krieger Publishing Company, Malabar, 1950)