Chapter 10. Selection Rules

Notes:
- *Most of the material presented in this chapter is taken from Bunker and Jensen (2005), Chap. 12, and Bunker and Jensen (1998), Chap. 14.*

10.1 Line Strength and Transition Intensity

The selection rules that will be established in this chapter are those applicable to the so-called **electric dipole transitions**. It is known from electrodynamics that the dominant mode of interaction between radiation and (electrically charged) matter happens through their respective electric field and electric dipole moment. Although electric multipole moments of higher orders can be defined (as well as magnetic dipole and multipole moments), and do exist in general, even a small dipole moment, if existent, will dominate. However, it is important to realize that not all charge distributions, and therefore molecules, will have a finite electric dipole. This can be asserted from the definition of the electric dipole moment operator

$$\mu = \sum_i C_i e \mathbf{R}_i, \tag{10.1}$$

where $C_i e$ and $\mathbf{R}_i$ are the charge and the space-fixed position (operator) of particle i, respectively. It should be apparent that *if a molecule has a symmetrical arrangement of charges about the molecular origin, then its dipole moment cancels out*. In cases such as these higher moments can be considered for possible transitions, although we will not carry such analyses in this chapter. Beside the electric dipole, other types of interactions can be of significant importance to explain well-known spectroscopic phenomena. A typical example of these is the interaction of the molecular **magnetic dipole moment** with an external magnetic field, which leads to the **Zeeman effect**.

Electric dipole transitions will be caused by the presence of a perturbation Hamiltonian

$$\hat{H}' = -\mu \cdot \mathbf{E} \tag{10.2}$$

due to the aforementioned electric dipole interaction with the external electric field $\mathbf{E}$ (which is treated classically; i.e., it is not quantized). So, given initial and final molecular states $|i\rangle$ and $|f\rangle$, respectively, we are interested in evaluating the amplitude of the perturbation Hamiltonian matrix elements

$$\begin{aligned} H'_{fi} &= \langle f | H' | i \rangle \\ &= -\int \langle f | \mathbf{r} \rangle \langle \mathbf{r} | \mu \cdot \mathbf{E}(t) | i \rangle d\tau \\ &= -\mathbf{E}(t) \cdot \int \langle f | \mathbf{r} \rangle \langle \mathbf{r} | \mu | i \rangle d\tau \\ &= -E(t) \cos(\varphi) \int \psi_f(\mathbf{r}) \mu \psi_i(\mathbf{r}) d\tau, \end{aligned} \tag{10.3}$$

where φ is the angle made by the dipole moment ($\mu = |\boldsymbol{\mu}|$) with the external electric field. Equation (10.3) makes it clear that we will be concerned with the evaluation of the matrix elements of the electric dipole moment operator between the initial and final states. The vanishing integral rule will be used to determine whether a transition is possible or not.

10.1.1 Einstein Coefficients, Line Strength, and Transition Intensity

Let us consider a system composed of a large number of similar and non-interacting molecules, and denote by N_i the density of molecules in the state $|i\rangle$. We know from statistical mechanics that

$$N_i = \frac{N}{Q} g_i e^{-E_i/kT}, \tag{10.4}$$

where N is the total number of molecules, g_i and E_i are respectively the degeneracy coefficient and the energy associated with state $|i\rangle$, k is the Boltzmann constant, and T is the temperature. The partition function Q is defined with

$$Q = \sum_i g_i e^{-E_i/kT}. \tag{10.5}$$

We also assume that the system is in thermodynamics equilibrium, such that

$$N_i W_{i \to f} = N_f W_{f \to i}, \tag{10.6}$$

where $W_{i \to f}$ is the transition rate from state $|i\rangle$ to $|j\rangle$. We further introduce the **Einstein coefficients** A_{fi}, B_{fi}, and B_{if} for spontaneous emission, stimulated emission, and stimulated absorption (we assume that $E_f > E_i$), respectively, along with $\rho(v_{fi})$ the energy density of the radiation field at frequency $E_f - E_i \equiv h v_{fi}$ to transform equation (10.6) to

$$N_i B_{if} \rho(v_{fi}) = N_f \left[A_{fi} + B_{fi} \rho(v_{fi}) \right], \tag{10.7}$$

and

$$\rho(v_{fi}) = \frac{A_{fi}/B_{if}}{\dfrac{N_i}{N_f} \dfrac{B_{if}}{B_{fi}} - 1}. \tag{10.8}$$

We know, however, that at equilibrium $\rho(v_{fi})$ must equal the Planck function such that

$$\rho\left(v_{fi}\right) = \frac{A_{fi}/B_{if}}{\dfrac{N_i}{N_f}\dfrac{B_{if}}{B_{fi}} - 1} = \frac{8\pi h v_{fi}^3}{c^3}\left(e^{hv_{fi}/kT} - 1\right)^{-1}. \tag{10.9}$$

Inserting equation (10.4) in equation (10.9) we obtain that

$$A_{fi} = \frac{8\pi h v_{fi}^3}{c^3} B_{fi} \quad \text{and} \quad g_i B_{if} = g_f B_{fi}. \tag{10.10}$$

It is important to realize that although these relations were obtained at equilibrium, they truly only pertain to the system under consideration and can be used in any situation, even out of equilibrium. Let us now consider the rate of change in the energy density due to absorption as the radiation travels through the volume containing the molecules

$$\begin{aligned}
\frac{d\rho\left(v_{fi}\right)}{dt} &= -h v_{fi} \rho\left(v_{fi}\right)\left(N_i B_{if} - N_f B_{fi}\right) \\
&= -h v_{fi} N_i B_{if} \rho\left(v_{fi}\right)\left(1 - \frac{N_f}{N_i}\frac{B_{fi}}{B_{if}}\right),
\end{aligned} \tag{10.11}$$

which at equilibrium becomes

$$\frac{d\rho\left(v_{fi}\right)}{dt} = -h v_{fi} \frac{N}{Q} g_i B_{if} \rho\left(v_{fi}\right) e^{-E_i/kT}\left(1 - e^{-hv_{fi}/kT}\right), \tag{10.12}$$

where equation (10.4) was again used. Introducing the intensity of the radiation field $I(v) = c\rho(v)$ we rewrite equation (10.12) as

$$\frac{dI\left(v_{fi}\right)}{cdt} = -\frac{h v_{fi}}{c} \frac{N}{Q} g_i B_{if} e^{-E_i/kT}\left(1 - e^{-hv_{fi}/kT}\right) I\left(v_{fi}\right). \tag{10.13}$$

But by definition, the change in the intensity as it travels through an infinitesimal length dl is

$$dI(v) = -\alpha(v) I(v) dl, \tag{10.14}$$

where $\alpha(v)$ is the **absorption coefficient**. Setting $dl = cdt$ we have

$$\alpha\left(v_{fi}\right) = \frac{h v_{fi}}{c} \frac{N}{Q} g_i B_{if} e^{-E_i/kT}\left(1 - e^{-hv_{fi}/kT}\right), \tag{10.15}$$

and from equation (10.14)

$$\alpha\left(v_{fi}\right)=-\frac{1}{\Delta l}\int_{\Delta l}\frac{dI\left(v_{fi}\right)}{I\left(v_{fi}\right)}. \tag{10.16}$$

Because the absorption coefficient is proportional to the density of molecules, dividing equation (10.16) by the **molar concentration** K will yield a quantity that is more representative of the properties of the molecules. The **molar absorption coefficient** $\varepsilon\left(v_{fi}\right)$ is therefore

$$\begin{aligned}\varepsilon\left(v_{fi}\right)&=-\frac{1}{K\Delta l}\int_{\Delta l}\frac{dI\left(v_{fi}\right)}{I\left(v_{fi}\right)}\\&=\frac{hv_{fi}}{c}\frac{N}{QK}g_iB_{if}e^{-E_i/kT}\left(1-e^{-hv_{fi}/kT}\right).\end{aligned} \tag{10.17}$$

We see from equation (10.14) that we can assume that the intensity will be approximately constant in situations were $\alpha\left(v_{fi}\right)dl\ll1$, and the molar absorption coefficient will equal the relative intensity of the transition line per unit length

$$\varepsilon\left(v_{fi}\right)=-\frac{1}{K\Delta l\,I\left(v_{fi}\right)}\int_{\Delta l}dI\left(v_{fi}\right)=-\frac{1}{K\Delta l}\frac{\Delta I\left(v_{fi}\right)}{I\left(v_{fi}\right)}. \tag{10.18}$$

However, because the different molecules in the system will be moving at different velocities the Doppler effect will establish a molecular distribution as a function of the frequency v_{fi} relative to the space-fixed coordinate system. We introduce the **line profile** $\phi(v)$ that will specify the number of molecule $N(v)$ as a function of frequency with

$$N(v)=N\phi(v)dv, \tag{10.19}$$

and the condition

$$\int\phi(v)dv\equiv1. \tag{10.20}$$

It would be preferable to do away with this velocity dependency if we want to be left with a quantity that is only a function of the molecular properties. Thus, the **line intensity** $I(f\leftarrow i)$ is defined as the frequency integration of the molar absorption coefficient, combined with a summation on all initial and final states

$$I(f\leftarrow i)=\sum_{i,f}\int\varepsilon\left(v_{fi}\right)dv_{fi}, \tag{10.21}$$

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and since it is also usually the case that the width of the line profile is much smaller than the value of the frequency of the transition v_{fi}, we write

$$I(f \leftarrow i) = \sum_{i,f} \frac{hv_{fi}}{c} \frac{N_A}{Q} B_{if} e^{-E_i/kT} \left(1 - e^{-hv_{fi}/kT}\right). \tag{10.22}$$

where equation (10.20) was used and N_A is Avogadro's number. The determination of the Einstein coefficient B_{if} will complete the definition of the line intensity. To do so, we start with **Fermi's Golden Rule**, which states that

$$W_{i \to f} = \hbar^{-2} \left|\langle f|\hat{H}'|i\rangle\right|^2 \rho_s\left(v_{fi}\right). \tag{10.23}$$

where $\rho_s\left(v_{fi}\right)$ is the density of states at the frequency v_{fi}. We already know that

$$\hat{H}' = -E(t)\cos(\varphi)\mu, \tag{10.24}$$

and therefore

$$W_{i \to f} = \hbar^{-2} E^2(t) \cos^2(\varphi) \left|\langle f|\mu|i\rangle\right|^2 \rho_s\left(v_{fi}\right). \tag{10.25}$$

We further average over the ensemble of molecules

$$\langle W_{i \to f}\rangle = \hbar^{-2} \langle E^2(t)\rangle \langle \cos^2(\varphi)\rangle \left|\langle f|\mu|i\rangle\right|^2 \rho_s\left(v_{fi}\right), \tag{10.26}$$

and since the molecules are expected to be randomly oriented then

$$\langle \cos^2(\varphi)\rangle = \frac{1}{3}. \tag{10.27}$$

Moreover, we set

$$E(t) = \mathcal{E}\cos(\omega t), \tag{10.28}$$

which implies that

$$\langle E^2(t)\rangle = \frac{\mathcal{E}^2}{2}, \tag{10.29}$$

with the corresponding electromagnetic energy density $\varepsilon_0 \mathcal{E}^2$, where ε_0 is the permittivity of vacuum (from electromagnetism theory). We can therefore define the energy density of the radiation field at frequency ν_{fi} to be

$$\rho\left(\nu_{fi}\right) = \varepsilon_0 \mathcal{E}^2 \rho_{\mathrm{s}}\left(\nu_{fi}\right), \tag{10.30}$$

which is the same quantity as was introduced in equation (10.7). Inserting equations (10.27), (10.29), and (10.30) in equation (10.26) we get

$$\left\langle W_{i \to f} \right\rangle = \frac{\left|\left\langle f|\mu|i\right\rangle\right|^2}{6\varepsilon_0 \hbar^2} \rho\left(\nu_{fi}\right). \tag{10.31}$$

However, since for a single molecule we must have

$$\left\langle W_{i \to f} \right\rangle = B_{if} \rho\left(\nu_{fi}\right), \tag{10.32}$$

then

$$B_{if} = \frac{\left|\left\langle f|\mu|i\right\rangle\right|^2}{6\varepsilon_0 \hbar^2}. \tag{10.33}$$

Inserting this result in equation (10.22) we finally obtain

$$I(f \leftarrow i) = \frac{\pi \nu_{fi} N_{\mathrm{A}}}{3\varepsilon_0 \hbar c} \frac{e^{-E_i/kT}}{Q}\left(1 - e^{-h\nu_{fi}/kT}\right) S(f \leftarrow i), \tag{10.34}$$

with the **line strength** $S(f \leftarrow i)$

$$\begin{aligned}
S(f \leftarrow i) &= \sum_{i,f}\left|\left\langle f|\mu|i\right\rangle\right|^2 \\
&= \sum_{i,f}\sum_{A=\xi,\eta,\zeta}\left|\left\langle f|\mu_A|i\right\rangle\right|^2,
\end{aligned} \tag{10.35}$$

where μ_A is the component of the electric dipole operator along one of the three space-fixed axes ($A = \xi, \eta$, and ζ).

10.2 The Full Rotation Group

The vanishing integral rule will be used to determine the possible transitions between two states, both generating different irreducible representation of the MS group. It should be clear, however, that the vanishing integral rule is not limited to the MS group, but to any group under which the Hamiltonian is invariant. For example, the CNP and CNPI groups

also satisfy this criterion. The full rotation group K, consisting of all possible rotations about a system of axes originating at the centre of mass of the molecule, is also such a symmetry group for the Hamiltonian. The rotation group is either labeled $K(\text{spatial})$ or $K(\text{mol})$ depending whether the system of axes is space- or molecule-fixed. In particular, *an isolated molecule in free space (i.e., subjected to no external field) has $K(\text{spatial})$ as a symmetry group*.

10.2.1 Irreducible Representations, Classes, and Characters

If we are to make use of this group, we must then determine what are its characters under the different possible irreducible representations it generates. The following two facts will greatly simplify our task:

a. The set of all possible rotations about the space-fixed system of axes can be completely described with the three Euler angles ϕ, θ, and χ and their corresponding axes of rotation.
b. Since all rotations are physically similar they all belong to the same class.

We know that when an irreducible representation is degenerate the set of eigenfunctions that generate this representation must transform into one another. So, let us look at the set of wave functions $D_{mk}^{(J)}(\phi,\theta,\chi)$ introduced in equation (4.88) of Chapter 4 for the angular momentum operators $\hat{J}^2$, $\hat{J}_\zeta$, and $\hat{J}_z$. We know from the material covered in that chapter that

$$D_{mk}^{(J)}(\phi,\theta,\chi) = \Theta_{mk}^{(J)}(\theta)e^{im\phi}e^{ik\chi}. \tag{10.36}$$

with $m = -J, -J+1, \ldots, J-1, J$ and similarly for k. Therefore a rotation $C_\alpha^{(\zeta)}$ by an angle α about the ζ-axis will yield

$$\begin{aligned} C_\alpha^{(\zeta)} D_{mk}^{(J)}(\phi,\theta,\chi) &= \Theta_{mk}^{(J)}(\theta)e^{im(\phi+\alpha)}e^{ik\chi} \\ &= D_{mk}^{(J)}(\phi+\alpha,\theta,\chi), \end{aligned} \tag{10.37}$$

implying that the subset of functions $D_{mk}^{(J)}(\phi,\theta,\chi)$ for $m = -J, -J+1, \ldots, J-1, J$ transform into one another for a fixed value of J. That is, they form a basis for that subspace of J. Moreover, because

$$C_\alpha^{(\zeta)} D_{mk}^{(J)}(\phi,\theta,\chi) = e^{im\alpha} D_{mk}^{(J)}(\phi,\theta,\chi), \tag{10.38}$$

then the character under a rotation is

$$\chi^{(J)}[R_\alpha] = \sum_{m=-J}^{J} e^{im\alpha}, \tag{10.39}$$

where R_α can be any rotation by α about any axis (remember that the possible rotations all belong to same class). Equation (10.39) can easily be transformed as follows

$$
\begin{aligned}
\chi^{(J)}[R_\alpha](e^{i\alpha} - 1) &= e^{i(J+1)\alpha} - e^{-iJ\alpha} \\
&= 2ie^{i\alpha/2}\sin\left[(J+1/2)\alpha\right],
\end{aligned}
\tag{10.40}
$$

and

$$
\chi^{(J)}[R_\alpha] = \frac{\sin\left[(J+1/2)\alpha\right]}{\sin(\alpha/2)}.
\tag{10.41}
$$

The totally symmetric irreducible representation $\Gamma^{(s)} = \Gamma^{(J=0)}$ has a character of 1, as expected.

10.2.2 Coupling of Angular Momenta

When applying the vanishing integral rule, or whenever we combine two wave functions of the angular momenta (i.e., equation (10.36)), generating the irreducible representations, say, $\Gamma^{(J)}$ and $\Gamma^{(J')}$, we will obtain a new reducible representation Γ with

$$
\Gamma = \Gamma^{(J)} \otimes \Gamma^{(J')}.
\tag{10.42}
$$

The character of this new representation is therefore

$$
\chi^\Gamma[R_\alpha] = \sum_{m=-J}^{J} e^{im\alpha} \cdot \sum_{m'=-J'}^{J'} e^{im'\alpha} = \sum_{m=-J}^{J} \sum_{m'=-J'}^{J'} e^{i(m'+m)\alpha},
\tag{10.43}
$$

from equation (10.39). As always, we would like to express this reducible representation as

$$
\Gamma = \sum_{J''} a_{J''} \Gamma^{(J'')}.
\tag{10.44}
$$

To do so, we replace the double summation in equation (10.43) with another on two new indices J'' and m'' as follows

$$
\chi^\Gamma[R_\alpha] = \sum_{J''=|J-J'|}^{J+J'} \sum_{m''=-J''}^{J''} e^{im''\alpha}.
\tag{10.45}
$$

Careful comparison of equations (10.43) and (10.45) should convince the reader of their equality. We can therefore write the important result that

$$\Gamma^{(J)} \otimes \Gamma^{(J')} = \sum_{J''=|J-J'|}^{J+J'} \Gamma^{(J'')}. \tag{10.46}$$

The only way that the totally symmetric representation can result from such a direct-product is if $J = J'$.

10.3 Forbidden and Allowed Transitions

The only knowledge that we still need to acquire before we can determine from the vanishing integral rule which transitions are allowed or forbidden concerns the symmetry properties of the electric dipole moment operator $\boldsymbol{\mu}$ under the MS and K(spatial) groups. This is the question we now consider.

10.3.1 The Transformation Properties of the Electric Dipole Moment Operator

The transformation of the μ_A operators ($A = \xi, \eta$, or ζ) under the MS group is readily determined from equation (10.1). First, it should be clear that the components of the electric dipole will be unaffected by a permutation operation P, as this only exchanges the labels of like particles. If we denote by $\Gamma(\mu_A)$ the representation generated by μ_A, then

$$\chi^{\Gamma(\mu_A)}[P] = 1, \tag{10.47}$$

for any P and A. On the other hand, because the position $\mathbf{R}$ for all particles is inverted under a permutation-inversion operator P^* then it must be that

$$\chi^{\Gamma(\mu_A)}[P^*] = \chi^{\Gamma(\mu_A)}[E^*]\chi^{\Gamma(\mu_A)}[P] = -\chi^{\Gamma(\mu_A)}[P] = -1. \tag{10.48}$$

From this result we conclude that *the irreducible representation* $\Gamma(\mu_A)$ *of any component of the electric dipole operator is the one-dimensional irreducible representation that has the character* +1 *under a permutation operator and the character* −1 *under a permutation-inversion operator.*

The transformation of μ_A under the K(spatial) group is easily determined with the realization that

$$\Gamma(\mu_A) = \Gamma(A), \tag{10.49}$$

with $A = \xi, \eta$, or ζ, from the functional form of equation (10.1). Furthermore, we know that

$$D_{m,0}^{(J)}(\phi,\theta,\chi) = Y_{J,m}(\phi,\theta), \tag{10.50}$$

where $Y_{J,m}(\phi,\theta)$ is a spherical harmonic, and in particular

$$Y_{1,0}(\phi,\theta) \propto \zeta$$
$$Y_{1,-1}(\phi,\theta) - Y_{1,1}(\phi,\theta) \propto \eta \qquad (10.51)$$
$$Y_{1,-1}(\phi,\theta) + Y_{1,1}(\phi,\theta) \propto \xi.$$

It is apparent from this that *the irreducible representation generated by any component of the electric dipole operator under the full rotation group $K(\text{spatial})$ is $\Gamma(\mu_A) = \Gamma^{(1)}$*.

10.3.2 Strictly forbidden Transitions

If we were to use no approximations at all for the internal molecular Hamiltonian $\hat{H}_{\text{int}}$ (i.e., use equation (1.126)) or the wave function Φ_{int}, then all of the angular momenta (orbital and spin) will be coupled into the total angular momentum $\hat{\mathbf{F}}$ (see equation (1.125). The irreducible representations of the $K(\text{spatial})$ group will then be $D^{(F)}_{m_F k_F}(\phi,\theta,\chi)$ (instead of $D^{(J)}_{mk}(\phi,\theta,\chi)$) and the vanishing integral rule corresponding to this group dictates that the electric dipole transitions (see equation (10.35)) allowed between two states Φ_{int} and Φ'_{int} respectively generating the irreducible representations $\Gamma^{(F)}$ and $\Gamma^{(F')}$ are those for which (see equation (7.73))

$$\left[\Gamma^{(F)}\right]^* \otimes \Gamma^{(F')} = \Gamma^{(F)} \otimes \Gamma^{(F')} \supset \Gamma^{(1)}. \qquad (10.52)$$

Alternatively, we can write from equation (10.46) that transitions for which

$$\Delta F = F - F' = 0, \pm 1 \quad \left(F = F' = 0 \text{ is forbidden}\right) \qquad (10.53)$$

are the only ones possible. In the same fashion, if the wave functions Φ_{int} and Φ'_{int} generate the irreducible representations Γ and Γ', respectively, under the MS group, then the vanishing integral rule corresponding to this group dictates that the electric dipole transitions allowed between two states are those for which

$$\Gamma^* \otimes \Gamma' \supset \Gamma(\mu_A). \qquad (10.54)$$

Because of the transformation properties of the electric dipole operator (see the paragraph following equation (10.48)) equation (10.54) implies that Φ'_{int} and Φ''_{int} must have opposing parities. More precisely, the only possible transitions are those for which

$$+ \leftrightarrow - \quad \text{and} \quad - \leftrightarrow +. \qquad (10.55)$$

Any transitions that do not obey equations (10.53) and (10.55) are said to be **strictly forbidden**. It is possible that they may acquire some intensity through other types of perturbations (e.g., electric quadrupole, magnetic dipole, etc.), but they are the weakest of all transitions.

10.3.3 Selection Rules under the Born-Oppenheimer, Harmonic Oscillator, and Rigid Rotator Approximations

Under the Born-Oppenheimer, harmonic oscillator, and rigid rotator approximations the nuclear spin does not enter in the equation for the approximate Hamiltonian. Because of this the irreducible representations of the K (spatial) group will be $D_{mk}^{(J)}(\phi,\theta,\chi)$ and the vanishing integral rule dictates that the electric dipole transitions allowed between two states Φ_{int} and Φ'_{int} respectively generating the irreducible representations $\Gamma^{(J)}$ and $\Gamma^{(J')}$ are those for which

$$\Delta J = J - J' = 0, \pm 1 \quad (J = J' = 0 \text{ is forbidden}). \tag{10.56}$$

Furthermore, because the nuclear spins do not enter the expression for the electric dipole Hamiltonian, and the complete internal molecular state can be written as a product of a nuclear spin and rovibronic vectors

$$\left|\Phi_{\text{int}}\right\rangle = \left|\Phi_{\text{nspin}}\right\rangle\left|\Phi_{\text{rve}}^{0}\right\rangle, \tag{10.57}$$

the **transition moment integral** under the MS group will yield (because of the vanishing integral rule)

$$\begin{aligned} I_{\text{TM},A} &= \left\langle\Phi_{\text{int}}\left|\mu_A\right|\Phi'_{\text{int}}\right\rangle \\ &= \left\langle\Phi_{\text{nspin}}\left|\Phi'_{\text{nspin}}\right\rangle\left\langle\Phi_{\text{rve}}^{0}\left|\mu_A\right|\Phi_{\text{rve}}'^{0}\right\rangle \\ &= \delta_{\text{ns, ns}'}\left\langle\Phi_{\text{rve}}^{0}\left|\mu_A\right|\Phi_{\text{rve}}'^{0}\right\rangle. \end{aligned} \tag{10.58}$$

This implies that the nuclear spin states will not change for an electric dipole transition and

$$\Delta I = 0. \tag{10.59}$$

Similarly, because the electric dipole Hamiltonian does not involve the electronic spins we also have that

$$\Delta S = 0. \tag{10.60}$$

From equation (10.58) we see that the allowed transitions are those for which

$$\Gamma_{\text{rve}}^{*} \otimes \Gamma'_{\text{rve}} \supset \Gamma(\mu_A). \tag{10.61}$$

Still under the same sets of approximations, the rovibronic states are further expressed as a product of electronic, vibrational, and rotational states

$$\left|\Phi_{\text{rve}}^{0}\right\rangle = \left|\Phi_{\text{elec},n}\right\rangle\left|\Phi_{\text{vib},n\upsilon}\right\rangle\left|\Phi_{\text{rot},nr}\right\rangle, \tag{10.62}$$

where labels n, υ, and r stand for the particular electronic, vibrational, and rotational states realized. We know that under the Born-Oppenheimer approximation the electronic state affects the rotational state. It turns out, however, that this dependency is usually negligible, and we can ignore it for our analysis. We therefore write

$$\left|\Phi_{\text{rot},nr}\right\rangle \rightarrow \left|\Phi_{\text{rot},r}\right\rangle, \tag{10.63}$$

i.e., we drop the electronic label for the rotational state.

We now need to modify equation (10.58) for the transition moment integral if we are to make any progress in specifying selection rules. First, we use the Euler matrix to express the space-fixed electric dipole operator as a function of its molecule-fixed counterpart

$$\mu_A = \sum_{\alpha=x,y,z} \lambda_{\alpha A} \mu_\alpha. \tag{10.64}$$

Because $\lambda_{\alpha A}$ is only a function of the Euler angles, while μ_α is solely a function of the vibronic (Cartesian) displacement coordinates $\Delta\alpha$ (and the Cartesian equilibrium coordinates; see below) then the transition moment integral becomes

$$\begin{aligned} I_{\text{TM},A} &= \sum_{\alpha=x,y,z} \left\langle \Phi_{\text{vib},n\upsilon} \left| \left\langle \Phi_{\text{elec},n} \left| \mu_\alpha \right| \Phi'_{\text{elec},n'} \right\rangle \right| \Phi'_{\text{vib},n'\upsilon'} \right\rangle \cdot \left\langle \Phi_{\text{rot},r} \left| \lambda_{\alpha A} \right| \Phi'_{\text{rot},r'} \right\rangle \\ &= \sum_{\alpha=x,y,z} \left\langle \Phi_{\text{vib},n\upsilon} \left| \bar{\mu}_\alpha\left(n,n'\right) \right| \Phi'_{\text{vib},n'\upsilon'} \right\rangle \cdot \left\langle \Phi_{\text{rot},r} \left| \lambda_{\alpha A} \right| \Phi'_{\text{rot},r'} \right\rangle, \end{aligned} \tag{10.65}$$

where

$$\bar{\mu}_\alpha\left(n,n'\right) = \left\langle \Phi_{\text{elec},n} \left| \mu_\alpha \right| \Phi'_{\text{elec},n'} \right\rangle \tag{10.66}$$

is the **electronic transition moment function**, which has a dependency on the normal coordinates. Since μ_α is a linear function of the Cartesian displacement coordinates and it has the same mathematical form as T_α (see equation (9.52)) and we find that

$$\Gamma\left(\bar{\mu}_\alpha\right) = \Gamma\left(T_\alpha\right), \tag{10.67}$$

and when limiting oneself to vibronic transitions equation (10.61) becomes

$$\Gamma^*_{\text{ve}} \otimes \Gamma'_{\text{ve}} \supset \Gamma\left(T_\alpha\right). \tag{10.68}$$

We now simplify equation (10.66) with a Taylor expansion about the normal coordinates of one of the states (we keep only term of zero and first orders here)

$$\bar{\mu}_\alpha(n,n') \simeq \mu_\alpha^e(n,n') + \sum_r \mu_{\alpha,r}(n,n') Q_r, \tag{10.69}$$

where $\mu_\alpha^e(n,n')$ is a constant term that corresponds to the electric dipole moment in the equilibrium configuration and $\mu_{\alpha,r}(n,n')$ is the partial derivative of μ_α relative to Q_r.

10.3.3.1 *Electronic Transitions*

For transitions between different electronic states, we focus our attention on the vibronic transition moment integral

$$I_{\text{vib},\alpha} = \left\langle \Phi_{\text{vib},nv} \middle| \bar{\mu}_\alpha(n,n') \middle| \Phi'_{\text{vib},n'v'} \right\rangle, \tag{10.70}$$

and determine the conditions needed to obtain transitions. It is readily established from the vanishing rule integral and equation (10.67) that the necessary condition is

$$\left(\Gamma_{\text{vib}}^* \otimes \Gamma'_{\text{vib}} \right) \otimes \left(\Gamma_{\text{elec}}^* \otimes \Gamma'_{\text{elec}} \right) \supset \Gamma(T_\alpha). \tag{10.71}$$

Transitions obeying this relation are called **vibronically allowed**. The strongest transitions are those that are further restricted to

$$\Gamma_{\text{elec}}^* \otimes \Gamma'_{\text{elec}} \supset \Gamma(T_\alpha), \tag{10.72}$$

and

$$\Gamma_{\text{vib}}^* = \Gamma'_{\text{vib}}. \tag{10.73}$$

These transitions are called **electronically allowed**. The resulting lines are strong because of the presence of the constant (equilibrium) term in equation (10.69), which significantly contribute (and much more than the higher order terms in equation (10.69)) to

$$\left\langle \Phi_{\text{vib},nv} \middle| \bar{\mu}_\alpha(n,n') \middle| \Phi'_{\text{vib},n'v'} \right\rangle. \tag{10.74}$$

In fact, when calculating the line strength of electronically allowed transitions one will often neglect the higher terms to get

$$\left| \left\langle \Phi_{\text{vib},nv} \middle| \bar{\mu}_\alpha(n,n') \middle| \Phi'_{\text{vib},n'v'} \right\rangle \right|^2 = \left| \mu_\alpha^e(n,n') \right|^2 \left| \left\langle \Phi_{\text{vib},nv} \middle| \Phi'_{\text{vib},n'v'} \right\rangle \right|^2. \tag{10.75}$$

The factor $\left| \left\langle \Phi_{\text{vib},nv} \middle| \Phi'_{\text{vib},n'v'} \right\rangle \right|^2$ is the so-called *Franck-Condon factor*, which gives the relative intensities of vibronic bands for a set of electronic transitions.

10.3.3.2 *Transitions within an Electronic State*

When the initial and final electronic states are the same then equation (10.65) leads to

$$\left(\Gamma_{\text{vib}}^{*}\otimes\Gamma_{\text{vib}}'\right)\otimes\left(\Gamma_{\text{rot}}^{*}\otimes\Gamma\left(\lambda_{\alpha A}\right)\otimes\Gamma_{\text{rot}}'\right)\supset\Gamma\left(T_{\alpha}\right). \tag{10.76}$$

since the direct-product of a electronic representation with itself will generate the totally symmetric representation. If we further focus on the vibronic transition moment integral

$$I_{\text{vib},\alpha}=\left\langle\Phi_{\text{vib},n\upsilon}\left|\bar{\mu}_{\alpha}\left(n,n\right)\right|\Phi_{\text{vib},n\upsilon'}'\right\rangle, \tag{10.77}$$

then equation (10.71) becomes

$$\Gamma_{\text{vib}}^{*}\otimes\Gamma_{\text{vib}}'\supset\Gamma\left(T_{\alpha}\right). \tag{10.78}$$

A **vibrationally allowed** transition will fulfill this requirement for at least one possible value of α (i.e., x, y, or z). Because the first term $\mu_{\alpha}^{e}\left(n,n\right)$ in equation (10.69) for the electronic transition moment function is a constant it will transform as the totally symmetric representation, and from equation (10.67)

$$\Gamma\left(T_{\alpha}\right)=\Gamma^{(\text{s})}. \tag{10.79}$$

On the other hand, the second term $\mu_{\alpha,r}\left(n,n\right)Q_{r}$ in equation (10.69) has the symmetry of Q_{r}, which implies that for transition to occur we must have

$$\Gamma\left(Q_{r}\right)=\Gamma\left(T_{\alpha}\right). \tag{10.80}$$

Inserting equation (10.69) into equation (10.77) yields

$$I_{\text{vib},\alpha}=\mu_{\alpha}^{e}\left(n,n\right)\delta_{\upsilon\upsilon'}+\sum_{r}\mu_{\alpha,r}\left(n,n\right)\left\langle\Phi_{\text{vib},n\upsilon}\left|Q_{r}\right|\Phi_{\text{vib},n\upsilon'}'\right\rangle. \tag{10.81}$$

Obviously, the first term on the left hand side does not correspond to a vibrational transition, as the initial and final states must be the same, but it will allow for pure rotational transitions within one vibrational state (see below). The second term, however, can bring vibrational transitions when

$$\left\langle\Phi_{\text{vib},n\upsilon}\left|Q_{r}\right|\Phi_{\text{vib},n\upsilon'}'\right\rangle\neq0. \tag{10.82}$$

Since, from equation (4.27), a normal mode consists of a linear combination of the ladder operators R^{+} and R^{-} (and vice-versa), and then we have the following vibrational selection rule

$$\Delta\upsilon_{r}=\pm1, \tag{10.83}$$

(see also equations (4.31)) with υ_r the vibrational quantum number associated to Q_r, which must have the symmetry translation T_α, from equation (10.80). Such a normal mode is said to be **infrared active** as the associated transitions happen at infrared wavelengths. Other types of transitions, such as **overtone transitions** (from the vibrational ground state to one state r with $|\Delta\upsilon_r| \geq 2$) and **combination tones** (from the vibrational ground state to more than one state r with $|\Delta\upsilon_r| \neq 0$) are forbidden under our approximations. These transitions could arise from second and higher order terms in the Taylor expansion of equation (10.69).

For example, we know for the previous chapter that for water the three possible normal modes have the $2A_1 \oplus B_2$ symmetry, and from Table 9-1 for the characters of the $C_{2v}(\text{M})$ group T_x has symmetry A_1 and T_z has symmetry B_2. All three modes are thus infrared active, as they verify equation (10.80). This does not have to always be the case; some molecules will have normal modes that are not realized.

Before we can state the selection rules for rotational transitions, we need to consider how the elements of the Euler matrix transform under the MS and $K(\text{spatial})$ groups.

1) Transformation of $\lambda_{\alpha A}$ under the MS group.

The components of the space- and molecule-fixed angular momentum are related through

$$\hat{J}_A = \sum_{\alpha=x,y,z} \lambda_{\alpha A} \hat{J}_\alpha, \tag{10.84}$$

with $A = \xi, \eta,$ and ζ. The space-fixed components $\hat{J}_A$ will remain unchanged under the elements of the MS group and they will therefore transform as the totally symmetric representation of the group. This is because these involve a summation (over the nuclei and electrons) of products of space-fixed coordinates and linear momenta. More precisely, these summations are unchanged by permutations (because the summations are over all particles) or by permutations-inversion (because both coordinates and momenta will change sign). This implies that the representations generated by $\lambda_{\alpha A}$ and $\hat{J}_\alpha$ are related by

$$\Gamma(\lambda_{\alpha A}) \otimes \Gamma(\hat{J}_\alpha) = \Gamma^{(s)}, \tag{10.85}$$

or

$$\Gamma(\lambda_{\alpha A}) = \Gamma(\hat{J}_\alpha). \tag{10.86}$$

That is, *the elements of the Euler matrix $\lambda_{\alpha A}$ transform in the same way as the corresponding molecule-fixed component of the angular momentum $\hat{J}_\alpha$.* Therefore, we define the following combinations of the elements $\lambda_{\alpha A}$

$$T_{\pm 1}^1\left(\lambda_A\right)=\frac{-1}{\sqrt{2}}\left(\lambda_{xA}\pm i\lambda_{yA}\right)$$

$$T_0^1\left(\lambda_A\right)=\lambda_{zA},$$

(10.87)

respectively generate the representations (see equation (4.71))

$$\Gamma\left(T_{\pm 1}^1\right)=\Gamma\left(\hat{J}_m^{\pm}\right)$$

$$\Gamma\left(T_0^1\right)=\Gamma\left(\hat{J}_z\right).$$

(10.88)

Moreover, under the MS group the rotational moment integral

$$I_{\mathrm{rot},A}=\left\langle J,k,m\left|T_p^1\left(\lambda_A\right)\right|J',k',m'\right\rangle$$

(10.89)

will generate the representations (see equation (10.65) and equation (10.102) below)

$$\Gamma_{\mathrm{rot},A}=\left[\Gamma_{km}^{(J)}\right]^{*}\otimes\Gamma\left(\hat{J}_m^{\pm}\right)\otimes\Gamma_{k'm'}^{(J')}$$

(10.90)

for $p=\pm 1$ and

$$\Gamma_{\mathrm{rot},A}=\left[\Gamma_{km}^{(J)}\right]^{*}\otimes\Gamma\left(\hat{J}_z\right)\otimes\Gamma_{k'm'}^{(J')}$$

(10.91)

for $p=0$. We therefore find the important result that

$$\left\langle J,k,m\left|T_p^1\left(\lambda_A\right)\right|J',k',m'\right\rangle=0,$$

(10.92)

unless

$$\Delta k=k-k'=0\text{ or }\pm 1,$$

(10.93)

because of the respective effects of the $\hat{J}_z$ and $J_m^{\pm}$ operators on the quantum number k. In other words, the value of p specifies the value of Δk.

2) *Transformation of $\lambda_{\alpha A}$ under the K(spatial) group.*

Referring to equations (3.2), where the elements $\lambda_{\alpha A}$ are defined, and equations (10.87) we find that the quantities $T_p^1\left(\lambda_A\right)$ have the following dependencies

$$T^1_{\pm 1}(\lambda_\xi) \propto \cos(\theta)\cos(\phi)e^{\mp i\chi} - \sin(\phi)e^{\pm i\chi}$$

$$T^1_0(\lambda_\xi) \propto \sin(\theta)\cos(\phi)$$

$$T^1_{\pm 1}(\lambda_\eta) \propto \cos(\theta)\sin(\phi)e^{\mp i\chi} - \cos(\phi)e^{\pm i\chi}$$

$$T^1_0(\lambda_\eta) \propto \sin(\theta)\sin(\phi)$$

$$T^1_{\pm 1}(\lambda_\zeta) \propto \sin(\theta)e^{\mp i\chi}$$

$$T^1_0(\lambda_\zeta) \propto \cos(\theta).$$

$$(10.94)$$

It will be easy to see from a comparison with equations (4.86) and (4.88) that these functions all belong to the $D^{(1)}$ family. That is, *the functions $T^1_p(\lambda_A)$ transform as the $D^{(1)}$ irreducible representation under the K(spatial) group* (hence their superscript). As a result, the rotational moment integral

$$I_{\mathrm{rot},A} = \langle J,k,m | T^1_p(\lambda_A) | J',k',m' \rangle \qquad (10.95)$$

will generate the representation

$$\Gamma_{\mathrm{rot},A} = \left[\Gamma^{(J)} \right]^* \otimes \Gamma^{(1)} \otimes \Gamma^{(J')}. \qquad (10.96)$$

We therefore find that

$$\langle J,k,m | T^1_p(\lambda_A) | J',k',m' \rangle = 0, \qquad (10.97)$$

unless

$$\Delta J = J - J' = 0, \pm 1 \quad \left(J = J' = 0 \text{ is forbidden} \right), \qquad (10.98)$$

based on equations (10.46) and (10.96). Evidently, this is another statement of the more general derivation leading up to equation (10.56). Also equations (10.94) and (10.95) could be used to derive the Δk rule of equation (10.93), as well as similar one for the quantum number m. That is,

$$\Delta m = m - m' = 0 \text{ or } \pm 1. \qquad (10.99)$$

If we now define a new set of functions

$$T^1_{\pm 1}(\mu) = \frac{-1}{\sqrt{2}}\left(\mu_x \pm i\mu_y \right)$$

$$T^1_0(\mu) = \mu_z, \qquad (10.100)$$

then we can transform equation (10.64) for the space-fixed electric dipole moment

$$\mu_A = \sum_{p=-1,0,1} (-1)^p \, T_p^1(\lambda_A) T_p^1(\mu). \tag{10.101}$$

Using equations (10.65), (10.87), (10.100), and (10.101) we write the transition moment integral as

$$I_{\mathrm{TM},A} = \sum_{\Delta k=-1,0,1} (-1)^{\Delta k} \left\langle \Phi_{\mathrm{vib},n\upsilon} \left| T_{\Delta k}^1(\bar{\mu}) \right| \Phi'_{\mathrm{vib},n\upsilon'} \right\rangle \left\langle J,k,m \left| T_{\Delta k}^1(\lambda_A) \right| J',k',m' \right\rangle, \tag{10.102}$$

where we set $\left| \Phi_{\mathrm{rot},r} \right\rangle = \left| J,k,m \right\rangle$. The line strength of a transition can be evaluated by taking the square of the corresponding term in equation (10.102) and summing over the degeneracy of the states (see equation (10.35)).

Equation (10.102) is perfectly suited to summarize the selection rules for rotational transitions of symmetric tops and linear molecules. In particular, we know from equation (10.81) that there will exist **pure rotational transitions** if for one value of α

$$\Gamma(T_\alpha) = \Gamma^{(s)}. \tag{10.103}$$

This rule actually applies to any type of rigid rotator. For example, methyl fluoride CH_3F ($C_{3v}(M)$, Table B.5 of Bunker and Jensen (2005)) has $\Gamma(T_z) = A_1$, and will therefore show pure rotational lines, while H_3^+ ($D_{3h}(M)$, Table B.8 of Bunker and Jensen, *op. cit.*) will not since $\Gamma(T_\alpha) \neq A_1'$ for all α. But for all types of rotational transitions (i.e., pure or otherwise) equations (10.93), (10.98) and (10.102) give the following selection rules

$$\Delta J = J - J' = 0, \pm 1 \quad \left(J = J' = 0 \text{ is forbidden} \right)$$
$$\Delta k = k - k' = 0 \text{ or } \pm 1. \tag{10.104}$$

The transitions for which $\Delta k = 0$ form the **parallel band**, those for which $\Delta k = \pm 1$ form the **perpendicular bands.** The sets of spectral lines for which $\Delta J = -1, 0$, and 1 are called **P-branch**, **Q-branch**, and **R-branch**, respectively; see Figure 10-1.

It is important to realize that symmetric top rotators verify the pure rotational condition of equation (10.103) only for one value of α, namely $\alpha = z$. This implies that we can only have $\Delta k = 0$ in equation (10.102). Pure rotational (electric dipole) transitions with $\Delta k = \pm 1$ are therefore forbidden for symmetric tops. Furthermore, because pure rotational transitions will not bring (by definition) any changes in the electronic and vibrational states, and that energy must be conserved before and after a transition, then transition with $\Delta J = 0$ are forbidden.

In summary, *for symmetric top pure rotational transitions are only allowed when*

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$$\Delta J = \pm 1 \quad and \quad \Delta k = 0. \tag{10.105}$$

For asymmetric tops, we need to consider the transformation properties of the Hamiltonian under the D_2 molecular rotation group, shown in Table 10-1.

Table 10-1 – The character table for the D_2 molecular rotation group and the species of the asymmetric top vectors $\left| J_{K_a K_c} \right\rangle$ in the group.

D_2 :	E	R_a^π	R_b^π	R_c^π	$K_a K_c$	
A :	1	1	1	1	: ee	
B_a :	1	1	-1	-1	: eo	$\hat{J}_a$
B_b :	1	-1	1	-1	: oo	$\hat{J}_b$
B_c :	1	-1	-1	1	: oe	$\hat{J}_c$

We also recall from Chapter 3 that the asymmetric top Hamiltonian can be expressed as

$$\hat{H}_{\mathrm{rot}}^0 = A_{\mathrm{e}}\hat{J}_a^2 + B_{\mathrm{e}}\hat{J}_b^2 + C_{\mathrm{e}}\hat{J}_c^2. \tag{10.106}$$

The fact the character of $\hat{J}_\alpha$ is ± 1 for any α under any element of the D_2 group implies that the asymmetric top Hamiltonian is invariant under this group (since the Hamiltonian is proportional to $\hat{J}_\alpha^2$). That is, *the D_2 molecular group is a symmetry group for an asymmetric top molecule.*

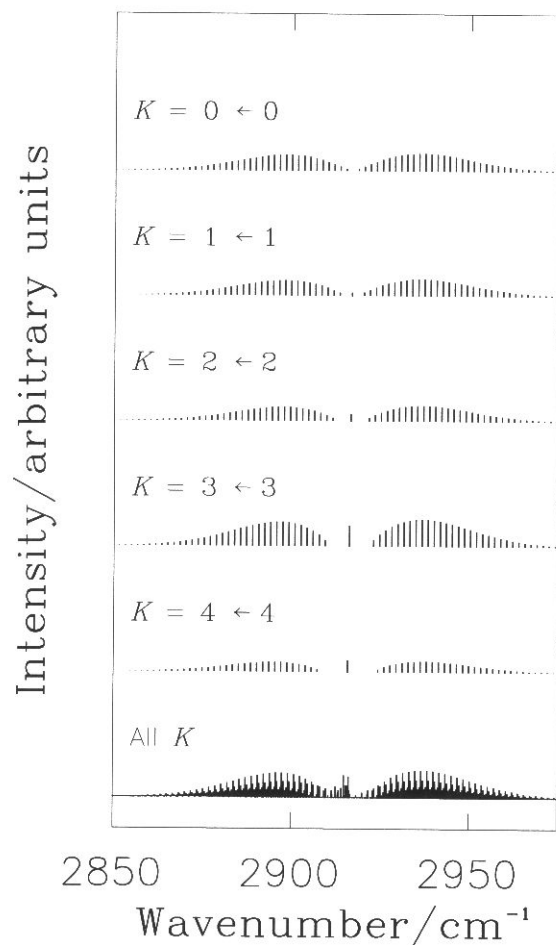The selection rules of the asymmetric top can be determined using

$$I_{\mathrm{TM},A} = \sum_{\alpha=x,y,z} \left\langle \Phi_{\mathrm{vib},n\upsilon} \left| \bar{\mu}_\alpha(n,n) \right| \Phi'_{\mathrm{vib},n\upsilon'} \right\rangle \cdot \left\langle J_{K_a,K_c} \left| \lambda_{\alpha A} \right| J'_{K_a',K_c'} \right\rangle, \tag{10.107}$$

with

$$\bar{\mu}_\alpha(n,n) \simeq \mu_\alpha^{\mathrm{e}}(n,n) + \sum_r \mu_{\alpha,r}(n,n) Q_r, \tag{10.108}$$

the fact that (as was shown earlier, and because of transformation properties of $\hat{J}_\alpha$ under D_2)

$$\Gamma\left(\lambda_{\alpha A}\right) = \Gamma\left(\hat{J}_\alpha\right) = B_\alpha, \tag{10.109}$$

Figure 10-1 – The one-dimensional vibrational υ_1 absorption parallel band ($\Delta k = 0$) for CH_3F. The sets of spectral lines of the left, centre, and right for each sub-bands are the P-branch ($\Delta J = -1$), Q-branch ($\Delta J = 0$), and R-branch ($\Delta J = 1$), respectively.

and the **asymmetric top symmetry rule** enunciated in the previous chapter (also see Table 10-1) and repeated here for convenience

The 'ee' functions will transform as the totally symmetric representation, the 'eo' functions as the representation having $+1$ for R_a^π (and -1 for R_b^π and R_c^π), the 'oe' functions as the representation having $+1$ for R_c^π (and -1 for R_a^π and R_b^π), and the 'oo' functions as the representation having $+1$ for R_b^π (and -1 for R_a^π and R_c^π).

The representation $\Gamma_{rot,\alpha}$ generated by $\left\langle J_{K_a,K_c} \left| \lambda_{\alpha A} \right| J'_{K'_a,K'_c} \right\rangle$ will be

$$\Gamma_{rot,\alpha} = \left[\Gamma_{K_a K_c}^{(J)} \right]^* \otimes B_\alpha \otimes \Gamma_{K'_a K'_c}^{(J')}, \tag{10.110}$$

and this leads to the following selection rules

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$$\Delta K_a = \text{even} \quad \Delta K_c = \text{odd} \quad \text{if } \alpha = a$$
$$\Delta K_a = \text{odd} \quad \Delta K_c = \text{odd} \quad \text{if } \alpha = b \qquad (10.111)$$
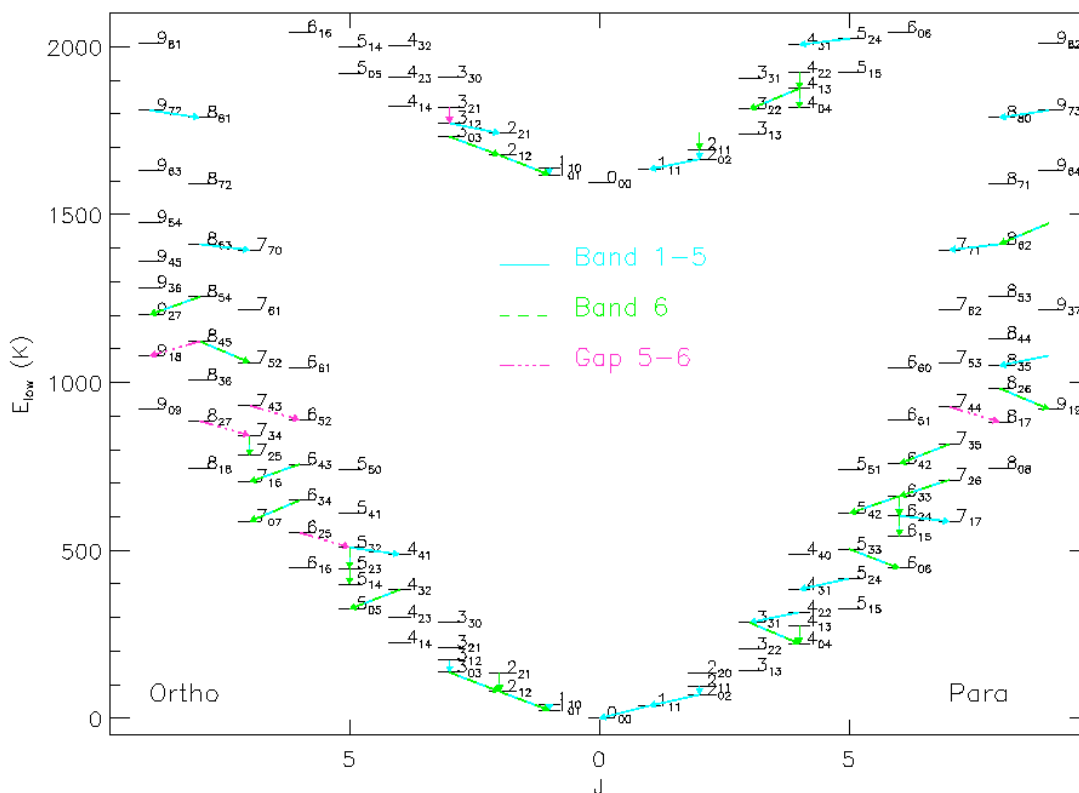$$\Delta K_a = \text{odd} \quad \Delta K_c = \text{even} \quad \text{if } \alpha = c$$

with

$$\Delta J = J - J' = 0, \pm 1 \quad \left(J = J' = 0 \text{ is forbidden} \right), \qquad (10.112)$$

as always.

Finally, the rotational selections rules for spherical tops is simply given by

$$\Delta J = J - J' = 0, \pm 1 \quad \left(J = J' = 0 \text{ is forbidden} \right). \qquad (10.113)$$

The energy of a spherical does not involve k, and the vanishing of the electric dipole moment in the electronic ground state implies that no transitions of this kind can take place.

Figure 10-2 – The ortho and para rotational states and some of the allowed pure rotational transitions (denoted by arrows) for the vibrational ground and first excited states of water. This graph is a courtesy of M. Fich, University of Waterloo, and leader of the Canadian Herschel Space Observatory Consortium.