Optical and Photonic Glasses

Lecture 31:
Rare Earth Doped Glasses I

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Rare-earth doped glasses

The lanthanide (or **RE**) ions correspond to **4f** wave functions that lie within the closed $5s^2 5p^6$ xenon shell and these electrons shield the 4f electrons from the effects of the environment, causing only small host-induced splittings. The optical transitions between 4f states correspond therefore to weak, sharp absorption and emission lines, with little vibronic structure and weak non-radiative relaxation of the excited states through phonon emission, as opposed to the case of the transition metal ions. In glasses, however, the bands are considerably broadened.

The line strength of a *transition* between two **J** (spin-orbit) multiplets, **a** and **b**, is given by:

$$S_{a,b} = \sum_{i,j} |<b_j |D| a_i>|^2$$

with the summation over all 2J+1 components (for i and j, each) of the a and b multiplets and D being the interaction operator. The *electric* dipole operator is:

$$D = \mu_{ed} = \sum_i e\, r_i$$

where r_i is the position operator for each electron and the sum is over all f electrons of the ion. The probability for *spontaneous emission* from level a $\rightarrow$ b is given by the Einstein coefficient:

$$A_{a,b} = [16\, \pi^3\, n\, (n+2)^2\, /\, (27\, \varepsilon_o\, h\, \lambda_{av}^3)]\, S_{a,b}\, /\, (2J_a+1)$$

where n is the host refractive index, λ_{av} is the mean photon wavelength of the transition and $2J_a+1$ is the degeneracy of the intial state. $A_{a,b}$ expresses the **spontaneous radiative relaxation rate**, in units of s^{-1}.

Transition probabilities (or strengths) are also commonly expressed in terms of the dimensionless *oscillator strength*, f:

$$f_{a,b} = \{9 \, \varepsilon_o \, m_e \, \lambda_{av}^3 / [2 \, \pi \, n \, (n+2)^2 e^2]\} \, A_{a,b}$$

which is proportional to the line strength, $S_{a,b}$.

For fully allowed electric dipole transitions, $f \sim 1$. For magnetic dipole or electric quadrupole allowed (but electric dipole forbidden) transitions, $f \sim 10^{-8}$.

If a is an excited state which decays only by emitting photons, its spontaneous relaxation rate, W_{rad}, is the sum of probabilities for transitions to all possible final states, f, which is the reciprocal of the *excited state lifetime*, τ_a:

$$W_{rad} = \sum_f A_{a,f} = 1 / \tau_a$$

Here, the measured excited state lifetime, τ_a (or τ_{meas}), coincides with the radiative lifetime, τ_{rad}. For fully allowed electric dipole transitions, $\tau_{rad} \sim 10^{-8}$ s. The *branching ratio* for the transition $a \rightarrow b$, $\beta_{a,b}$, is the fraction of all spontaneous decay processes which occur through that channel:

$$\beta_{a,b} = A_{a,b} / \sum_c A_{a,c} = A_{a,b} \, \tau_a \qquad (\sum_b \beta_{a,b} = 1)$$

The branching ratio has a significant impact on the threshold of a laser and the efficiency of an amplifier. For emission from the first excited state, like the 1.5 μm photoluminescence (PL) of Er^{3+}, $\beta = 1$.

On the other hand, the oscillator strength is proportional to the spectral integral of the corresponding cross section, σ:

$$f_{a,b} = [36 \, \varepsilon_o \, m_e \, c \, n / e^2 \, (n+2)^2] \int \sigma_{a,b}(\nu) \, d\nu \sim [\dots] \, \Delta\nu_{eff} \, \sigma_{peak}$$
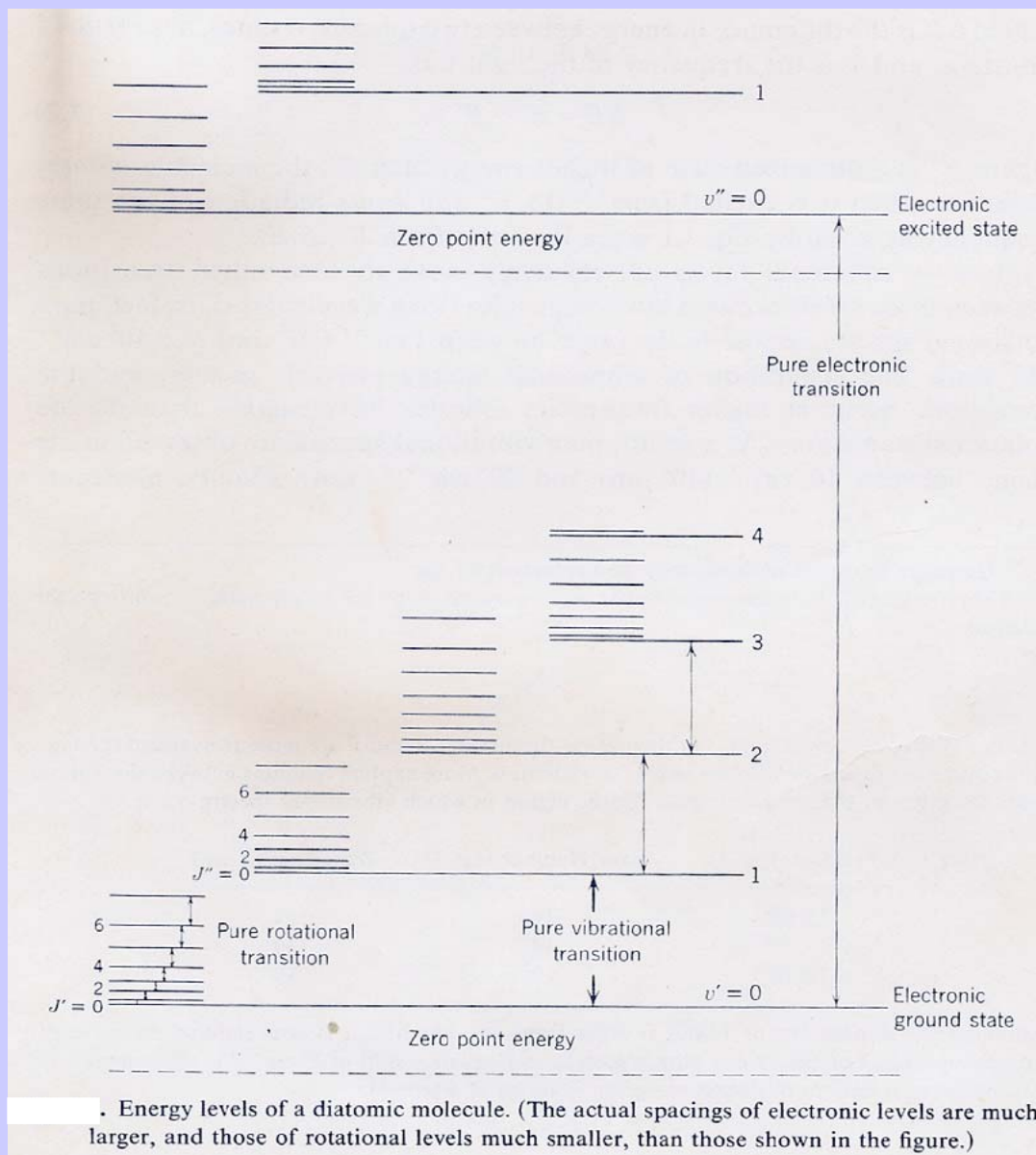
and the integral over the band cross section can thus be replaced by the *peak cross section* times the *effective bandwidth* of the transition, which is often simply taken as the band Full Width at Half Maximum (FWHM), although the exact value of $\Delta\nu_{eff}$ is the integral of the cross section divided by σ_{peak}.

The spontaneous emission cross sections can be obtained from the measured excited state lifetime and emission spectrum as a function of bandwidth (ν) or wavelength:

$$\beta_{a,b} / \tau_a = A_{a,b} = (8\pi n^2/c^2) \int \nu^2 \, \sigma_{a,b}(\nu) \, d\nu = 8\pi n^2 c \int \sigma_{a,b}(\lambda) \, d\lambda / \lambda^4$$

such that, for a given emission cross section, a lower n leads to a longer lifetime. For Er^{3+} at 1.5 μm, for example, $\beta \, (= 1)$ does not need to be measured or calculated, but the measured lifetime, τ_{meas}, may have to be corrected for non-radiative relaxation, including concentration quenching, due to ion-ion interactions.

Different types of intramolecular transitions

. Energy levels of a diatomic molecule. (The actual spacings of electronic levels are much larger, and those of rotational levels much smaller, than those shown in the figure.)
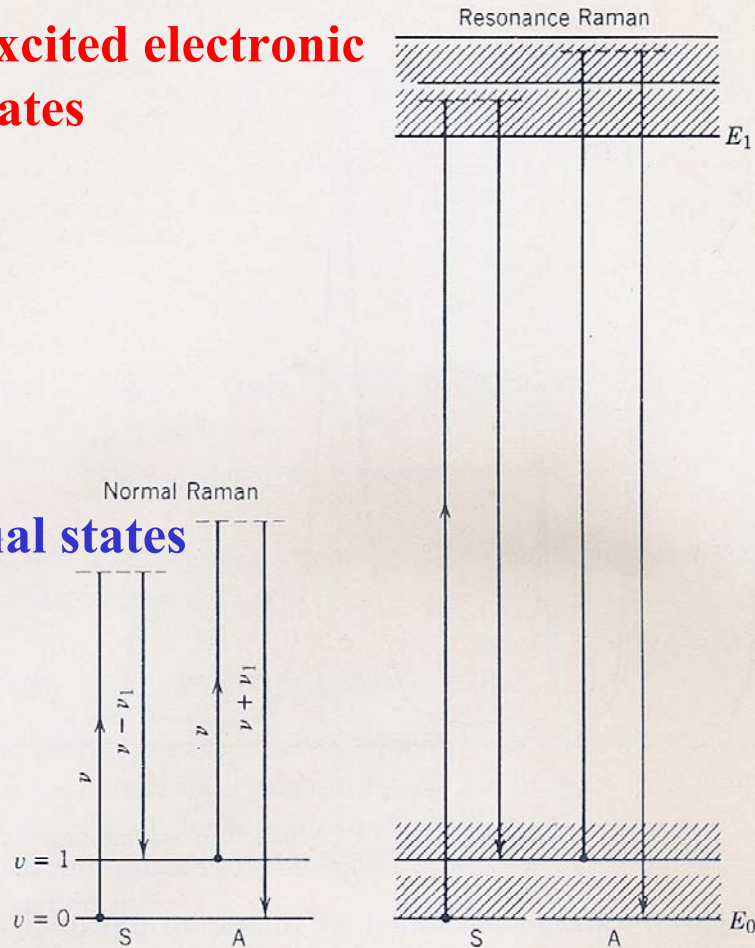
(Adapted from: *Infrared and Raman spectra of inorganic and coordination compounds*, K. Nakamoto, John Wiley, 1986)

# Transitions involved in Raman scattering

Excited electronic states

Virtual states

Resonance Raman

Normal Raman

$v = 1$

$v = 0$

E_1

E_0

S   A   S   A

. Mechanisms of normal and resonance Raman scattering: S, Stokes; A, anti-Stokes. The dashed lines represent the virtual state. The shaded areas indicate the broadening of rotational–vibrational levels.

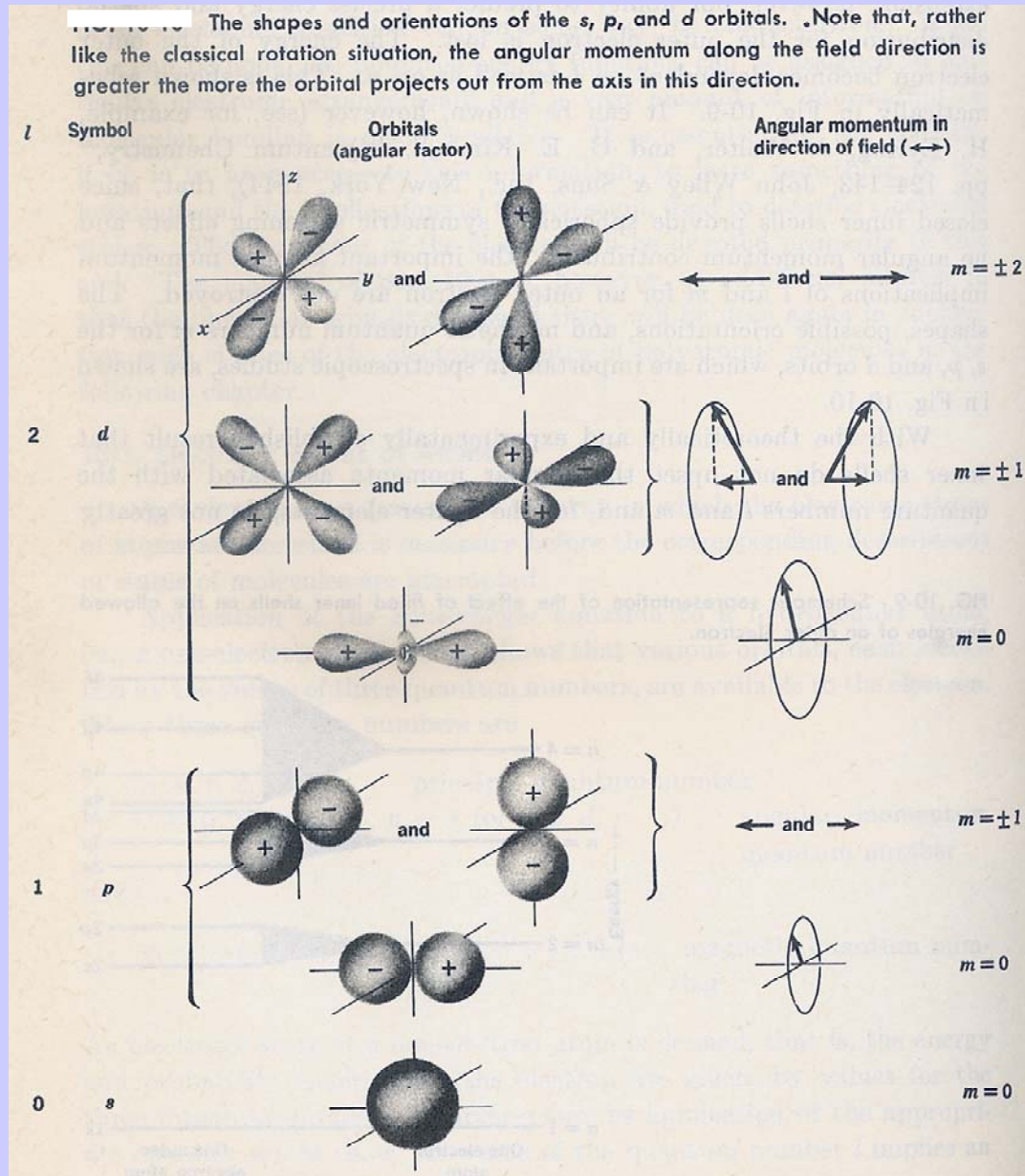(Adapted from: *Infared and Raman spectra of inorganic and coordination compounds,* K. Nakamoto, John Wiley, 1986)

Photoluminescence (PL) processes for a 2-electron system

ΔS = 0

ΔS = 2
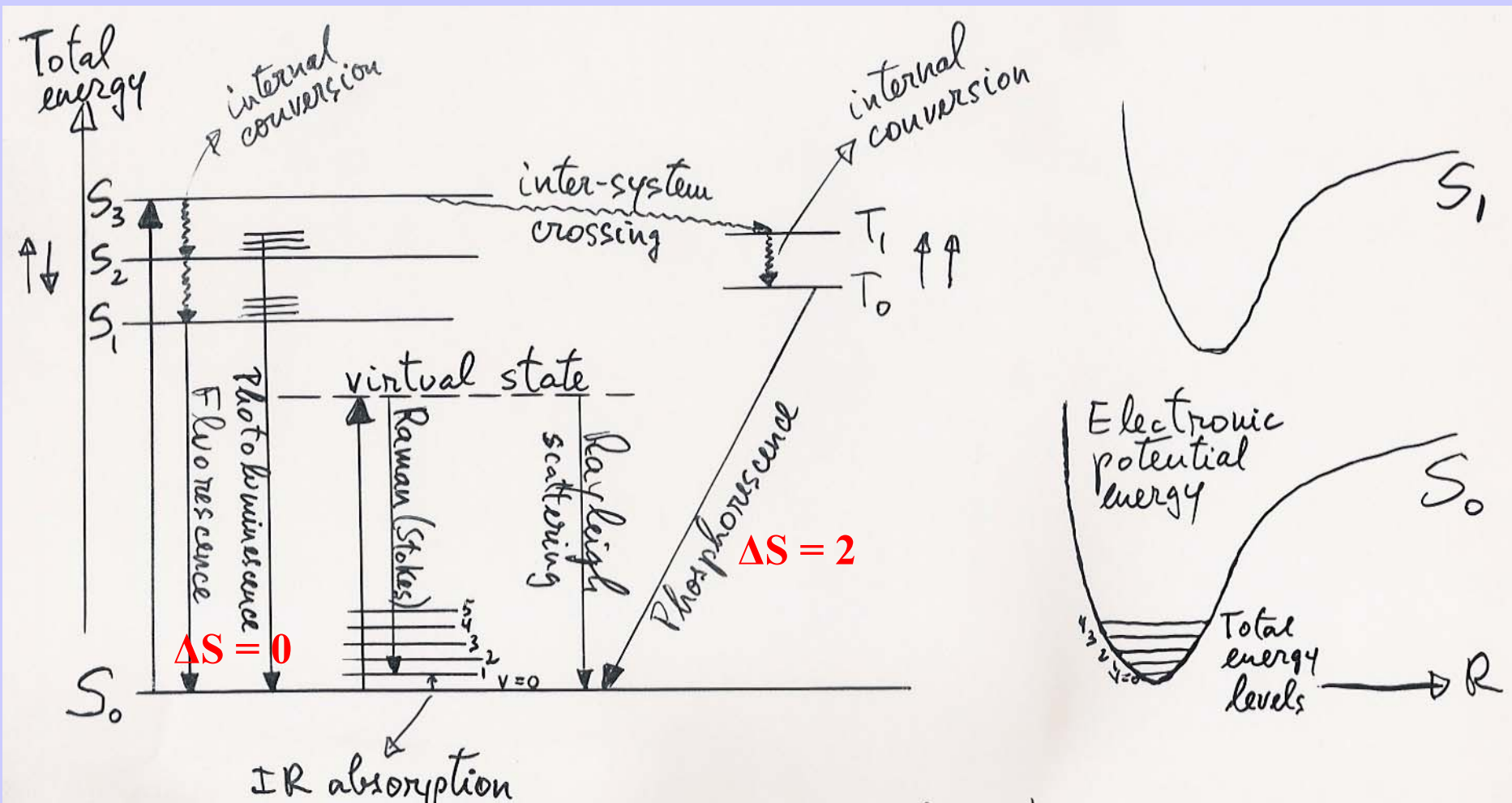
Note: for 2 electrons ($s_1 = s_2 = 1/2$), one has either $S = 0$ ($2S + 1 = 1$, or *singlet, S*), or $S = 1$ ($2S + 1 = 3$, or *triplet, T*). Also, if $(2S+1) = 2$ or 4, one has a *doublet* or a *quadruplet*.

Atomic orbitals
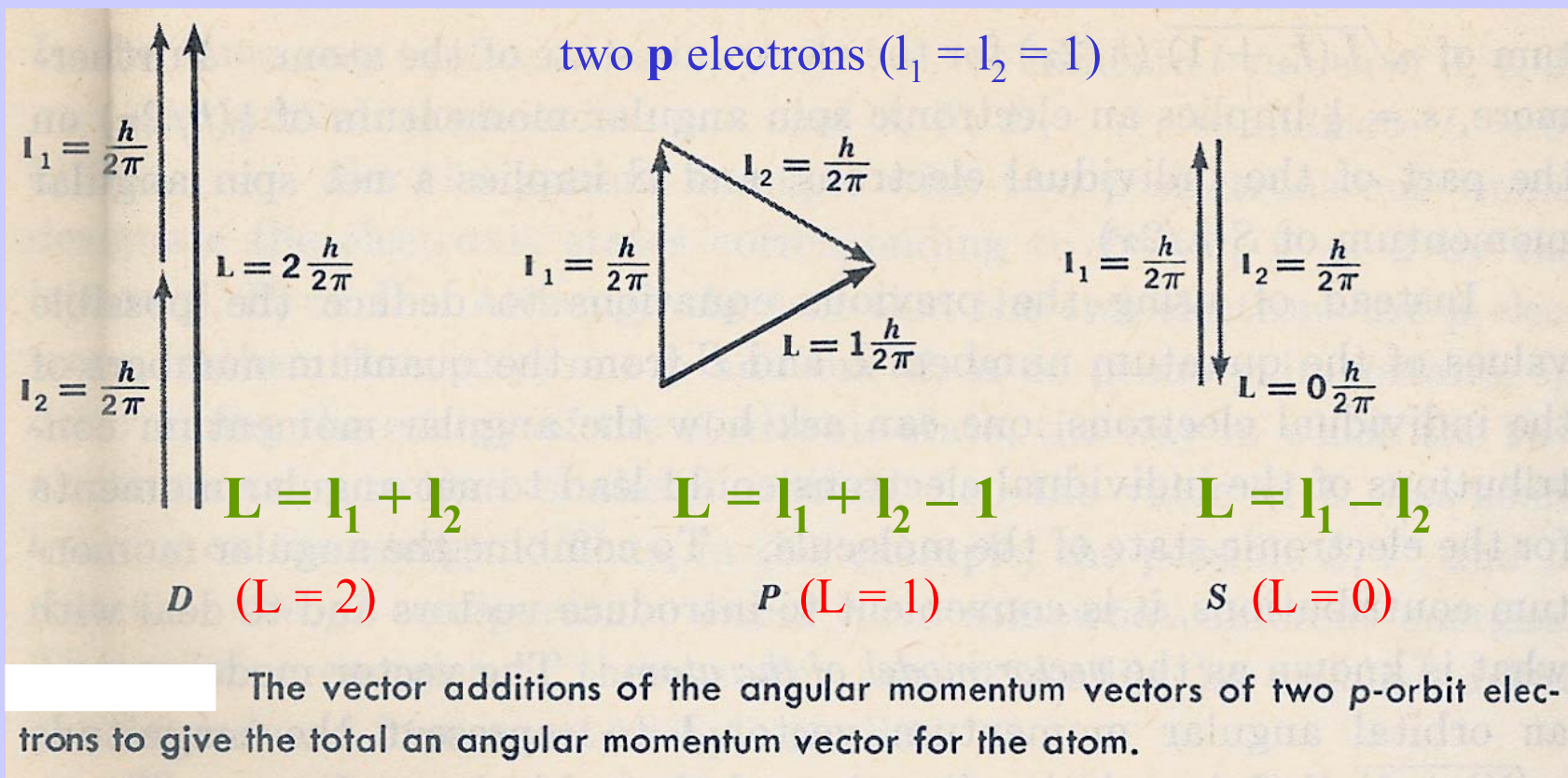

(Adapted from: *Introduction to molecular spectroscopy*, G.M. Barrow, McGraw-Hill, Tokyo, 1962

Vector model of the atom

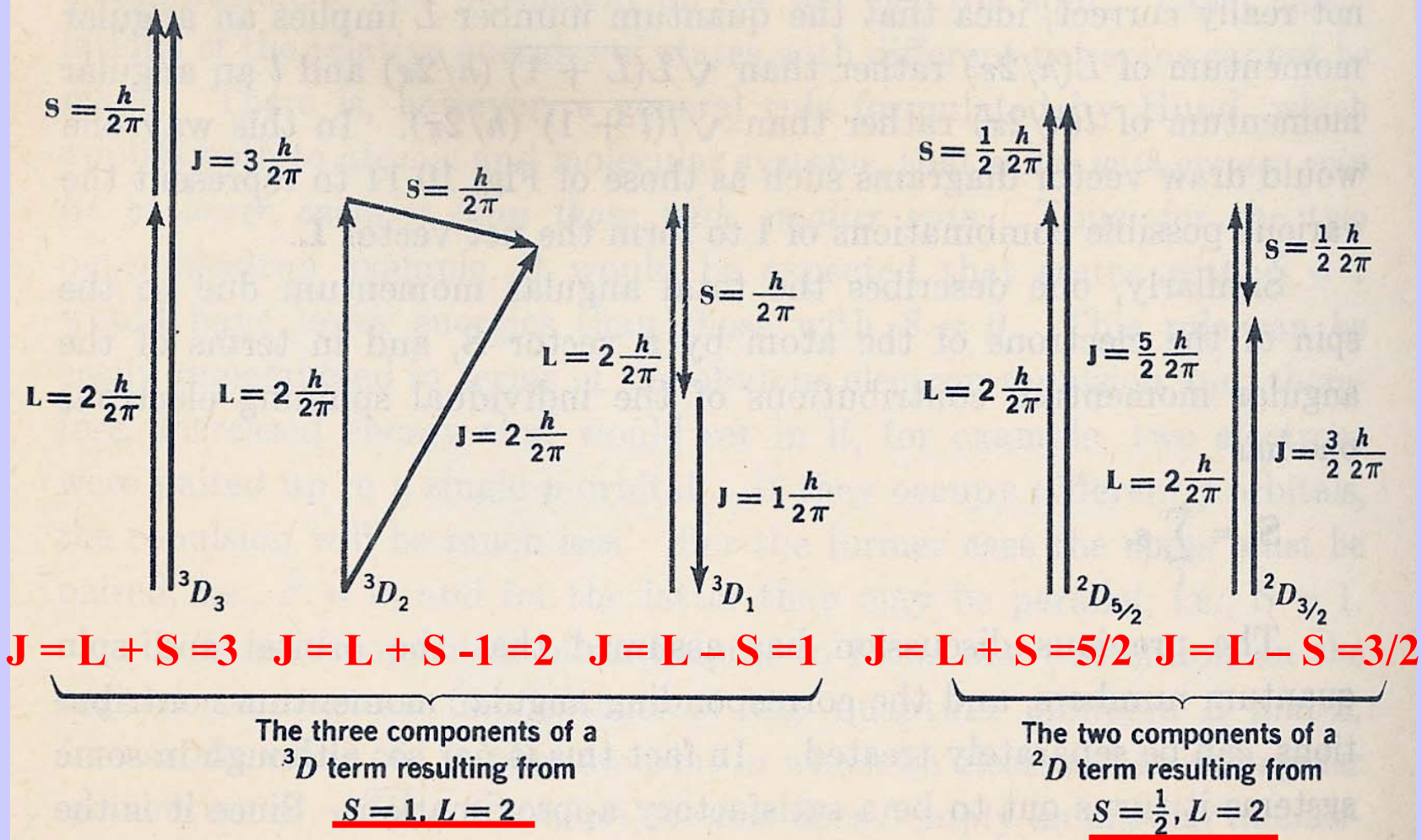## Addition of angular momenta

$$\mathbf{L} = \sum_i \mathbf{l_i}$$

$$L = 0, 1, 2, 3, 4, 5, 6, 7, \ldots \rightarrow S, P, D, F, G, H, I, K, \ldots$$

two **p** electrons ($l_1 = l_2 = 1$)

$l_1 = \dfrac{h}{2\pi}$ $l_2 = \dfrac{h}{2\pi}$ $L = 2\dfrac{h}{2\pi}$ $l_1 = \dfrac{h}{2\pi}$ $L = 1\dfrac{h}{2\pi}$ $l_1 = \dfrac{h}{2\pi}$ $l_2 = \dfrac{h}{2\pi}$ $L = 0\dfrac{h}{2\pi}$

$\mathbf{L = l_1 + l_2}$ $\mathbf{L = l_1 + l_2 - 1}$ $\mathbf{L = l_1 - l_2}$

D (L = 2)   *P* (L = 1)   *S* (L = 0)

The vector additions of the angular momentum vectors of two p-orbit electrons to give the total an angular momentum vector for the atom.

(Adapted from: *Introduction to molecular spectroscopy*, G.M. Barrow, McGraw-Hill, 1962)

$$J = L + S$$

The vector diagrams that represent the ways in which the L and S vectors can be combined to give resulting vectors.

$$J = L + S = 3 \quad J = L + S - 1 = 2 \quad J = L - S = 1 \quad J = L + S = 5/2 \quad J = L - S = 3/2$$

The three components of a ^3D term resulting from $S = 1, L = 2$

The two components of a ^2D term resulting from $S = \frac{1}{2}, L = 2$

(Adapted from: *Introduction to molecular spectroscopy*, G.M. Barrow, McGraw-Hill, 1962)

Energy level splittings for a two 4f electron system: L = 3 (F), 4 (G), 5 (H); S = 0 (2S+1 = 1) or S = 1 (2S+1 = 3); S = 0 and L = 4 => J = 4; S = 1 and L = 3 => J = 4, 3, 2; S = 1 and L = 5 => J = 6, 5, 4; J = 4 => 2J+1 = 9 Stark components of J = 4 multiplet.
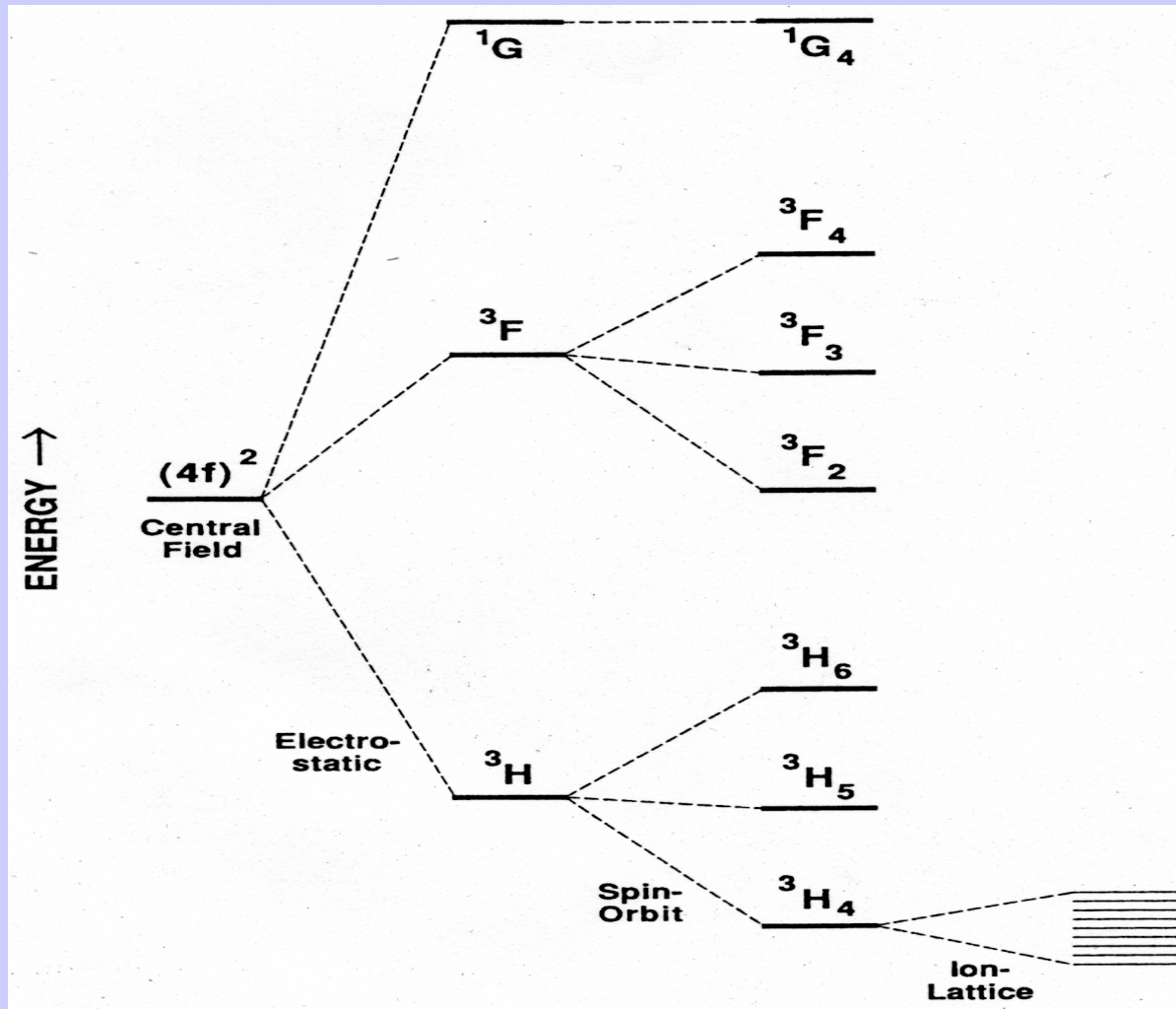
Figure 2 Energy diagram illustrating hierarchy of splittings resulting from electron–electron and electron–host interactions.

(Adapted from: *Rare earth doped fiber lasers and amplifiers*, ed. M.J.F. Digonnet, Marcell-Dekker, 1993)