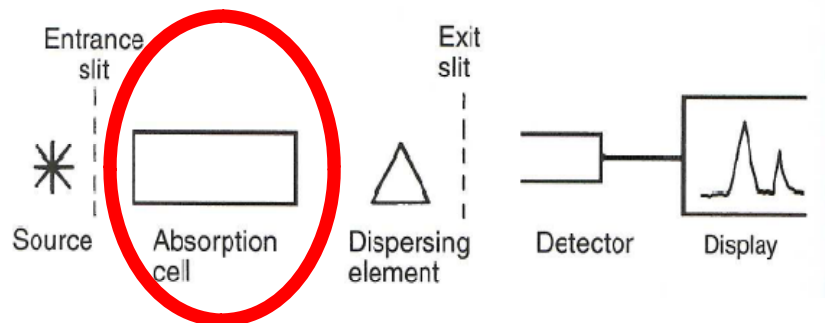


Radiative processes of use in analytical spectroscopy



- Absorption
- Photoluminescence
- Scattering

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CHEM 5161

Multiplicity of an electronic state

- Multiplicity = $2s + 1$ ($s = \sum m_s$)
- S = Singlet State
 - Paired spins: $\uparrow\downarrow \Leftrightarrow s = 0$
 \Leftrightarrow multiplicity = 1
- T = Triplet
 - unpaired spins: $\uparrow\uparrow \Leftrightarrow s = 1$
 \Leftrightarrow multiplicity = 3

Radiative processes #1

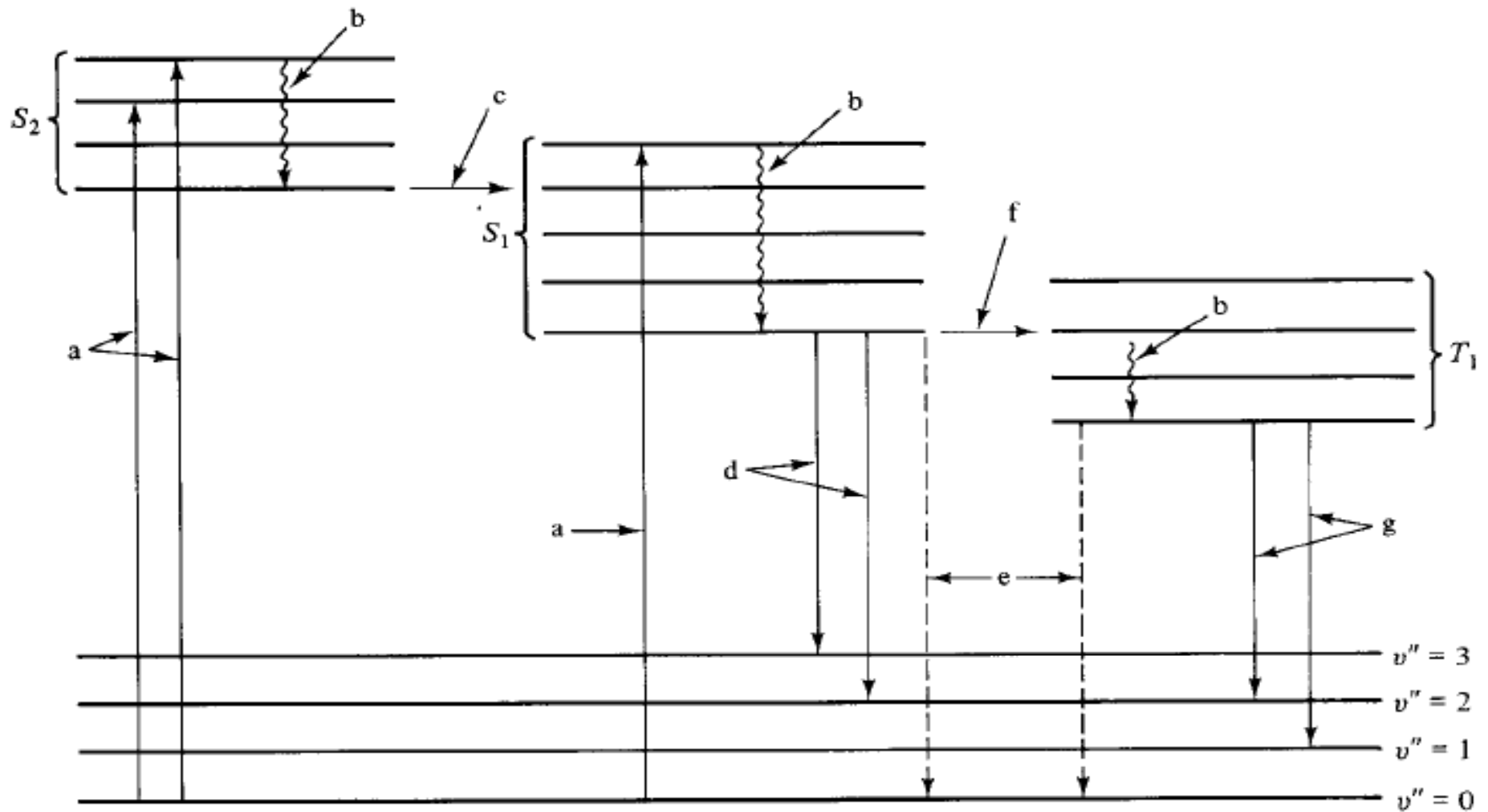


FIGURE 12-7 Deactivation processes for an excited molecule. a, absorption; b, vibrational relaxation; c, internal conversion; d, fluorescence; e, external conversion; f, intersystem crossing; g, phosphorescence.

Associated time scales

	timescale [s]	Selection Rule
A) Absorption:	$>10^{-15}$	same multiplicity
B) Vibrational relax.:	$10^{-10} - 10^{-12}$	$\Delta v = 1$
C) Internal conversion:	10^{-12}	same multiplicity
D) Fluorescence:	$10^{-6} - 10^{-10}$	same multiplicity
E) External conversion (quenching)		
F) Intersystem crossing:	$10^{-4} - 10^{-12}$	spin forbidden
G) Phosphorescence:	$10^{-4} - 10$	spin forbidden
H) Scattering:	$<10^{-15}$ (instantaneous)	

Photoluminescence: any radiative process that produces a photon !

Example

- Assume an internal conversion process from $S_2 \rightarrow S_1$, that produces the third overtone of S_1 .
- Assume further a vibrational constant of 2100 cm^{-1}
- What is the corresponding shift expected in the fluorescence spectrum ?

Absorption vs Luminescence

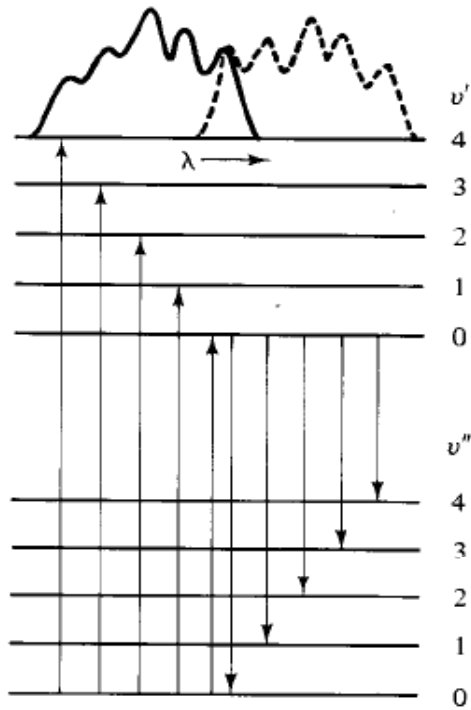
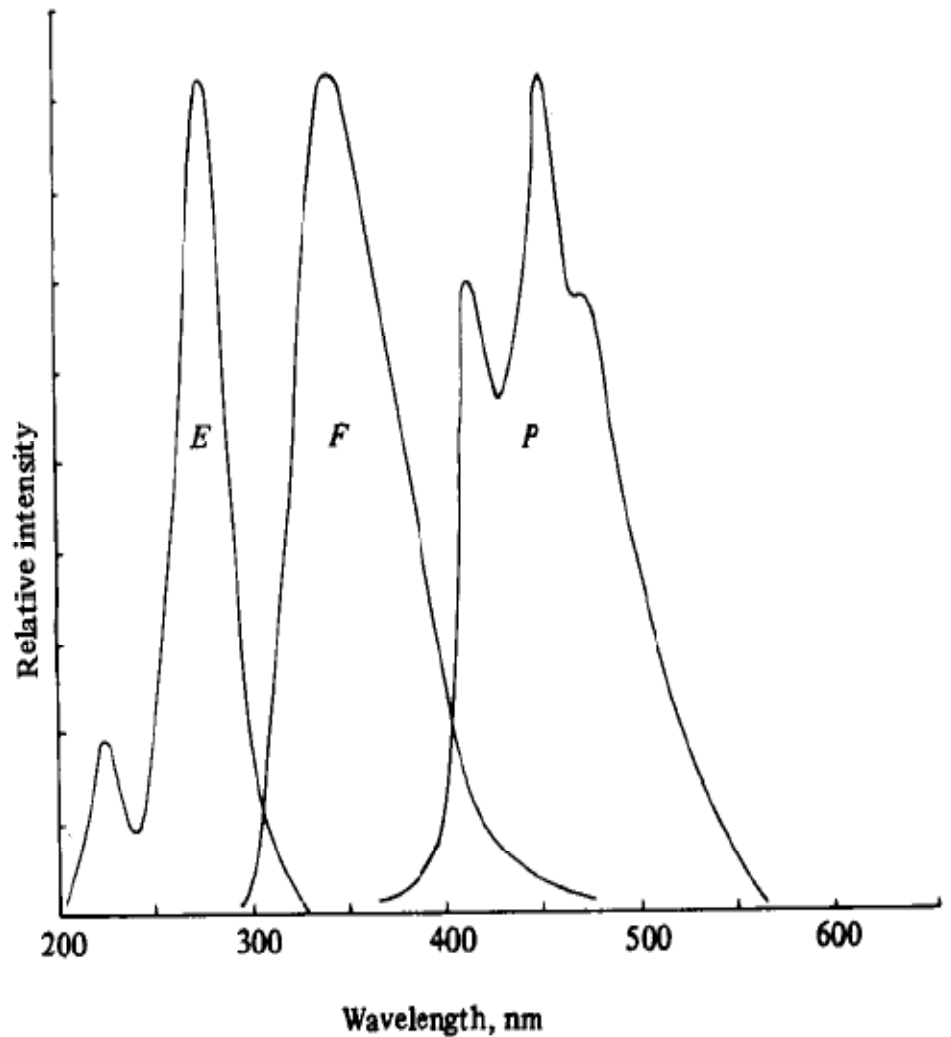


FIGURE 12-8 Relationship between absorption and fluorescence. The absorption and fluorescence emission spectra are represented by the solid and dashed lines, respectively. The fluorescence transitions occur generally at longer wavelengths because the energy differences are less. In solution the vibronic detail is often not present and only a broad band is observed.



Radiative processes #2

- Scattering
 - Rayleigh scattering: $I \sim \lambda^4$
 - Debye scattering
 - Mie scattering
- Raman Effect
 - Inelastic scattering
 - Polarizability of electron cloud