

Polyatomic Spectroscopy (Sketch): for non-linear molecular $\Psi = \Psi_{el}(\tau, R) \Psi(\alpha, \beta, \gamma) \Psi(v_1, \dots, v_{3N-5})$

$\Psi_{el}(\tau, R)$: all electronic
 $\Psi(\alpha, \beta, \gamma)$: 3 Euler \neq 's
 $\Psi(v_1, \dots, v_{3N-5})$: $3N-5$ vibrational modes
 $\Psi(R_{cm})$: all nuclear, irrelevant

Rotational Motion Notes: (i) ^{"Top"} Energy levels as above

(ii) Selection rules as above; To respect $\left\{ \begin{array}{l} \text{general selection rule: permanent dipole moment} \\ \text{specific selection rule: for symmetric tops,} \end{array} \right.$

$\Delta J = \pm 1, \Delta M = 0, \pm 1, \Delta K = 0$

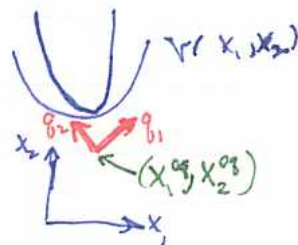
each coordinate spins around principal axis, since no \perp dipole.

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Vibrational Motion: Normal modes (Sketch)

For small oscillation abt. equilibrium in a multidimensional system:

$$V(x_1, x_2) = V(x_1^{eq}, x_2^{eq}) + \frac{1}{2} \sum_{i=1}^2 \sum_{j=1}^2 \frac{\partial^2 V(x_1^{eq}, x_2^{eq})}{\partial x_i \partial x_j} (x_i - x_i^{eq})(x_j - x_j^{eq})$$



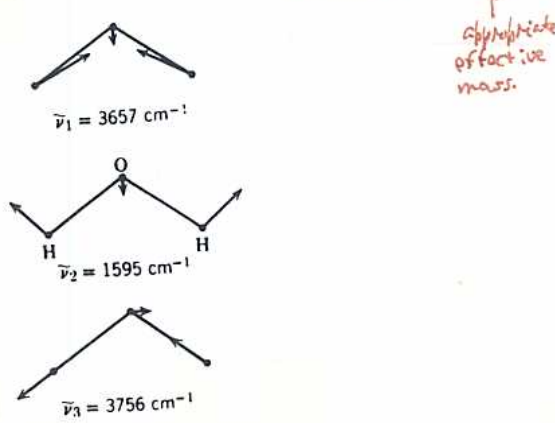
(q_1, q_2) are \rightarrow normal modes

$k_1 q_1^2 + k_2 q_2^2$

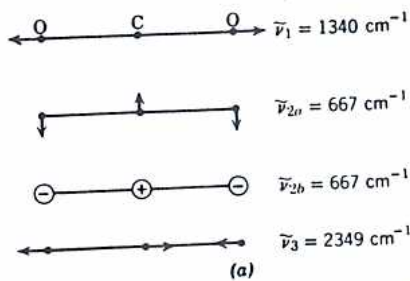
for non-linear molec. $3N-5$

Hence $\Psi_{vib} = \prod_{j=1}^{3N-5} \psi_j(q_j)$ \leftarrow each factor is a 1-d h.o. eigenfn. corresponding to $2\pi \nu_j = \omega_j \sim \sqrt{k_j/m_j}$

(ii) corresponding $E_{vib} = \sum_{j=1}^{3N-5} h \nu_j (v_j + \frac{1}{2})$



NB: for linear molecule $3N-5$ vibrations and 2 rotations $[\psi_{jkm}(\alpha, \beta, \gamma) \rightarrow \psi_{JM}(\theta, \phi)]$



Overview Eq. for Electric Dipole Transitions:

Transition Intensity for $i \rightarrow f$ transition, $I_{i \rightarrow f} = \left| \int \psi_f^* \chi_{e,f} \left(\sum_{j=1}^N \frac{q_j}{M_j} \mu_j(\underline{r}, \underline{R}) \right) \psi_i \right|^2$

$\int \psi_f^* \chi_{e,f} \left(\sum_{j=1}^N \frac{q_j}{M_j} \mu_j(\underline{r}, \underline{R}) \right) \psi_i \int_{\text{elect}} d\tau \int_{\text{vib}} d\tau \int_{\text{rot}} d\tau$

$\mu(\underline{r}, \underline{R}) = \sum_i e \underline{r}_i + \sum_j \frac{q_j}{M_j} \underline{R}_j$

electrons charge on j^{th} nucleus
 nuclei

Consider diatomic for simplicity

From here on, consider electronic transitions, $e_f \neq e_i$:

To understand gross selection rules + trends... integrate d_{elect} in [1]: $\int \psi_f^* \left(\sum_{j=1}^N \frac{q_j}{M_j} \mu_j(\underline{r}, \underline{R}) \right) \psi_i d\tau_{\text{elect}} \equiv \mu_{fi}(\underline{R})$

transition dipole operator

Further, assume $\mu_{fi}(\underline{R})$ is independent of vibrational coordinates. Then

$I_{i \rightarrow f} = \left| \int \psi_f^* \chi_{e,f} \left(\sum_{j=1}^N \frac{q_j}{M_j} \mu_j(\underline{r}, \underline{R}) \right) \psi_i \right|^2 \cdot \left| \int \psi_{\text{vib}}^* \chi_{e,f} \chi_{e,i} \psi_{\text{vib}} \right|^2$

controls rotational selection rules.

Frank-Condon Factor (Controls Intensity of Vibrational Transitions)

Group Selection rules : (1) Transitions between electronic states are allowed/forbidden if $\int \psi_f^*(R) \mu \psi_i(R) dR \neq 0$
 Symmetry plays a critical role here, since

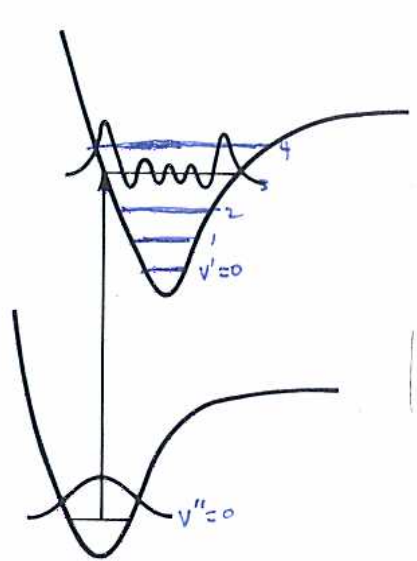
$$\int \psi_f^*(R) \mu \psi_i(R) dR$$

ψ_f^* belongs to particular symmetry species of molecule's point group
 μ belongs to particular symmetry species of molecule's point group
 ψ_i belongs to particular symmetry species of molecule's point group

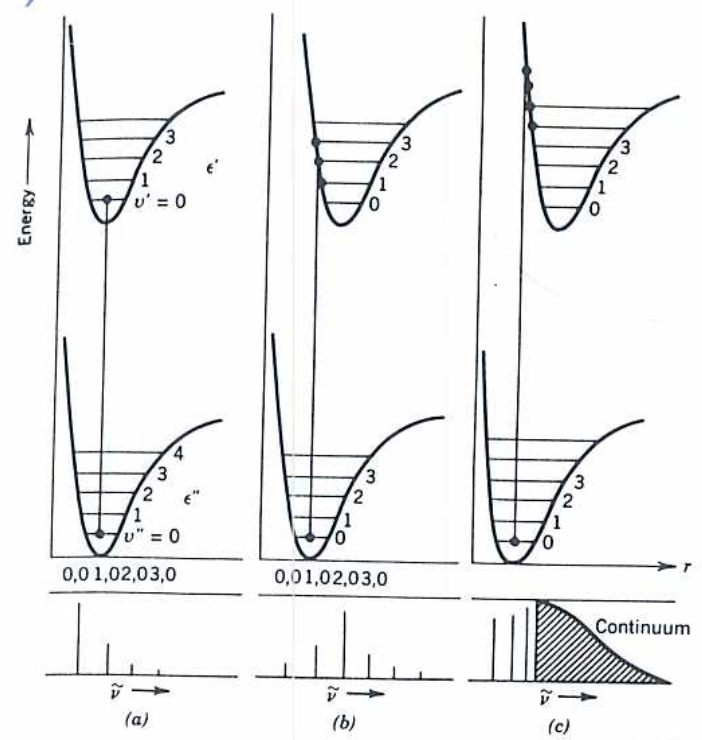
← Group theory can identify many forbidden transitions

(2) Rotational Selection rules depend on symmetry of initial, final electronic states [E.g. in $\Sigma_g^+ \rightarrow \Sigma_g^+$ transition in diatomic, $\Delta J = \pm 1$]

(3) Vibrational transition: Intensity of $v: v' \rightarrow v'': v'''$ transition $\propto \left| \int \psi_{v'''}^*(R) \chi(R) \psi_{v''}(R) dR \right|^2$
 Franck-Condon Factor
 for diatomic



NB: Group Selection rule: no "forbidden" transitions!



} Generic vibrational spectra.

Figure 15.3 Franck-Condon principle. In an electronic transition, the overlap of the ground vibrational wavefunction in the lower electronic state and the various vibrational wavefunctions in the upper electronic state is greatest for the vibrational level whose classical turning point is at the equilibrium separation in the lower state.

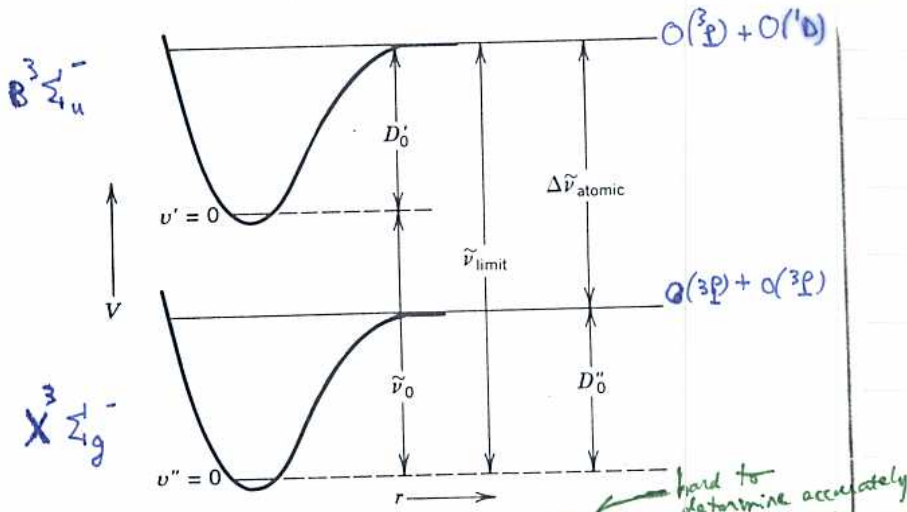
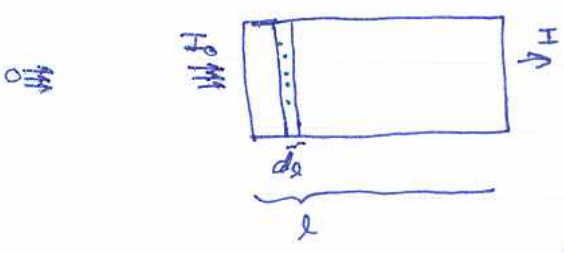


Figure 15.4 Determination of the dissociation energies D_0'' and D_0' of the ground state and the excited state from $\tilde{\nu}_{\text{limit}}$, the wavenumber of the onset of a continuum in a progression.

hard to determine accurately via Birge-Sponer
 (assume know electronic states of dissociated atoms)

NB: \exists Rotational fine structure on each vibronic line!

Measuring Intensities in (UV)-Visible Absorption Spectra: Beer-Lambert Law



$$I(l+dl) = I(l) - I(l) [c \, dl] \epsilon$$

↑ # photons [passes per second] ↓ # photons passing thru
 ↓ # molecules "in the way" ← intrinsic absorption cross sect for each molecule

$$\frac{I(l)}{I_0} = e^{-\epsilon c l} \Rightarrow \ln \frac{I(l)}{I_0} = -\epsilon c l$$

$\xrightarrow{2.303 \log} \left[\frac{I(l)}{I_0} \right]$

Thus:

$$\log_{10} \left(\frac{I_0}{I} \right) = \epsilon c l$$

↑ absorbance
 ↓ molar absorption coef
 depends on λ

NB: $\epsilon(\lambda) \propto$ q.m. transition probability $I_i \rightarrow f = \frac{1}{f_i} \mu_{if}^2$

In particular:

integrate over whole electronic band

oscillator strength $f \equiv (4.32 \times 10^{-9} \text{ L mol}^{-1} \text{ cm}^{-2}) \int_{\text{band}} \epsilon \, d\nu$

If $f \sim 1$, electronic transition allowed; $f \ll 1$ [e.g. 10^{-5}], transition is forbidden [$\mu(R) \equiv 0$ by symmetry]

Electronic Spectra of Polyatomics:

Many instances of absorption in visible / UV region [due to HOMO \rightarrow LUMO transitions]

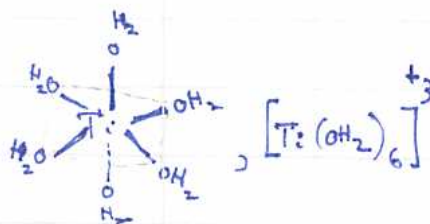
Ex: (1) conjugated hydrocarbons, e.g. "unsaturated" due to $C=C$ bonds



band at 300nm

Red Green Violet
[NB: 700 530 420] nm

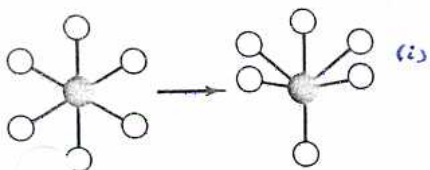
(2) transition metal complexes:



But, note: absorbs in vacuum UV [electron promoted to σ^*]

(3) "chromophores" $C=O$, $-N=N-$, $-N=O$ \leftarrow show characteristic absorption peaks (roughly)
 strong $\pi \rightarrow \pi^*$ transition at 120 nm independent of what they are bound to
 weak $n \rightarrow \pi^*$ " " 270-290 nm

More on Ex. (1), (2): Start w/ transition metal complexes: 2 ways to promote an electron to an un-filled low-lying d orbital on the transition metal



charge-transfer transition [intense color]

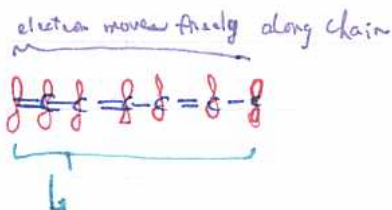
e_g
 t_{2g} } octahedral environment splits d levels

(ii) $t_{2g} \rightarrow e_g$ [low intensity, since $d \rightarrow d$ transitions are forbidden for octahedral symmetry]

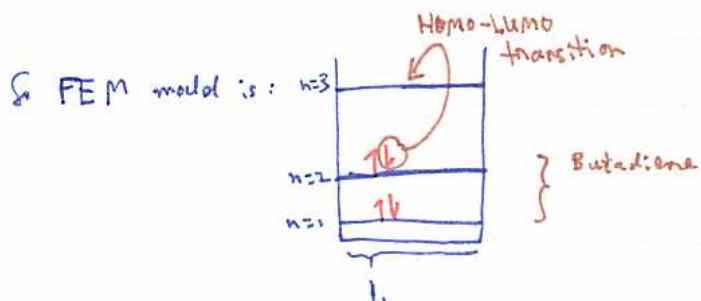
Figure 15.9 Vibrational motion or distortion in an octahedral complex that leads to the destruction of the center of symmetry, thereby making $d \leftarrow d$ transitions allowed.

Conjugated hydrocarbons: pi-orbitals are relatively closely spaced, more so as chain length increases

Study via Free Electron model:



Recall E-levels for particle in a 1-d box, length L: $E_n = \frac{h^2 n^2}{8mL^2}$; $n=1,2,3,\dots$



highest n [doubly occupied] in HOMO

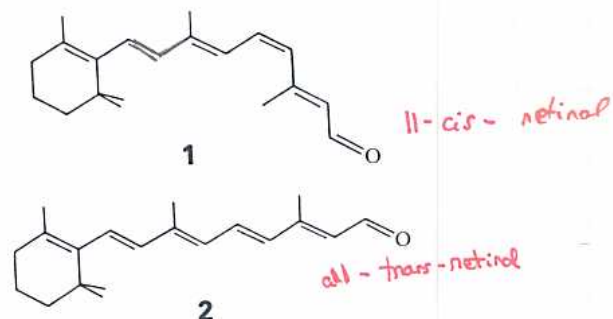
For "completely" conjugated hydrocarbons, $N = \# \text{ pi electrons} = \text{electrons} = 2n$

Thus, $E_{\text{HOMO} \rightarrow \text{LUMO}} = \frac{h^2}{8mL^2} [(n+1)^2 - n^2] = \frac{h^2}{8mL^2} [N+1] = h\nu_{\text{abs}} = hc\tilde{\nu}_{\text{abs}}$

Roughly, $L = \alpha N$ $\Rightarrow \nu_{\text{abs}} \propto \frac{1}{N}$ (for large N)

↑ approximate C-C bond lengths

E.g. retinal [$\tilde{\nu}_{\text{abs}} \sim 500 \text{ nm}$ "in vivo" ← attached to protein]
"visual purple"



Fluorescence + Phosphorescence: Mechanism of Decay for Excited States

- (i) Fluorescence notes: electronic states have same "multiplicity" [spin state]
- (ii) fluorescence is "red-shifted" fr. absorption

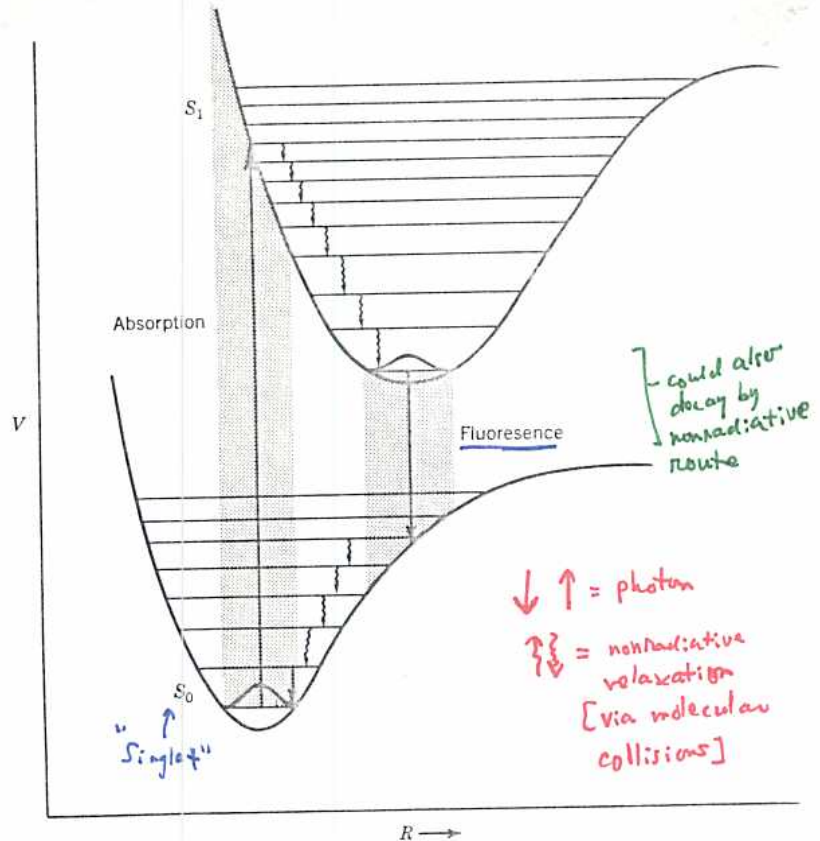


Figure 15.10 Absorption and fluorescence by a diatomic molecule. The shaded areas indicate the transitions to a range of vibrational quantum numbers.

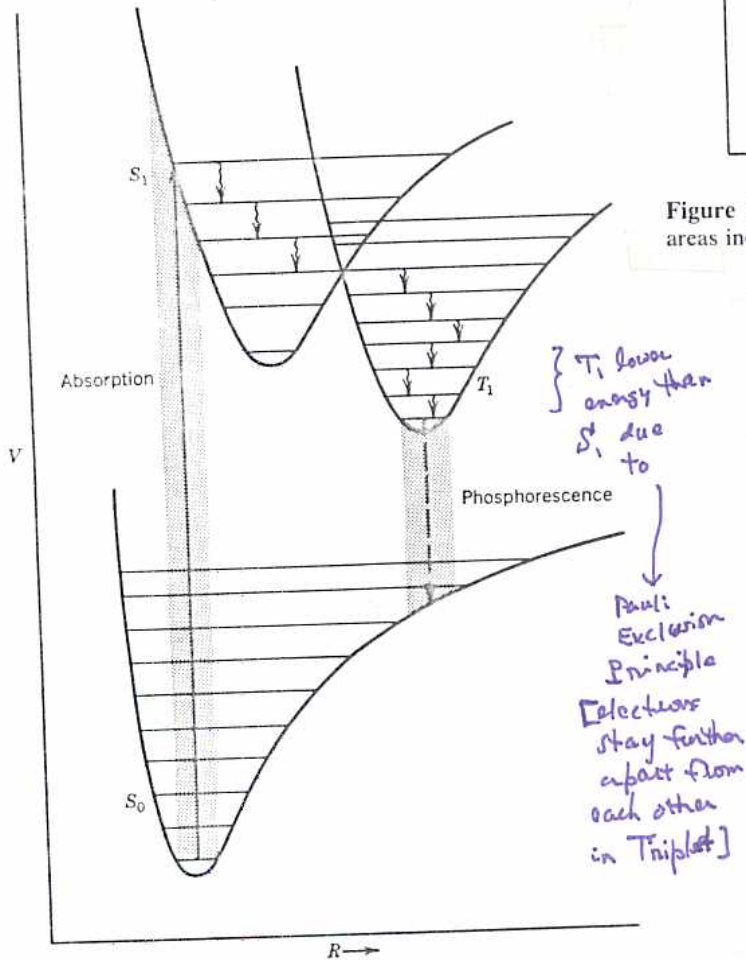


Figure 15.11 Absorption and phosphorescence by a diatomic molecule. The shaded areas indicate transitions to a range of vibrational quantum numbers.

- (i) Phosphorescence notes: T_1 = lowest triplet state is much less strongly coupled, radiatively, to S_0 than is S_1 . This phosphorescence is slow [microseconds + longer]
- (ii) $S_1 \rightarrow T_1$ via nonradiative coupling [called "Intersystem crossing"]

"Final state of affairs, spectrally:"

? Why is: $\nu_{0 \rightarrow 0}^{abs} \neq \nu_{0 \rightarrow 0}^{fluor.}$

Answer: Solute-

solvent effects

equilibration

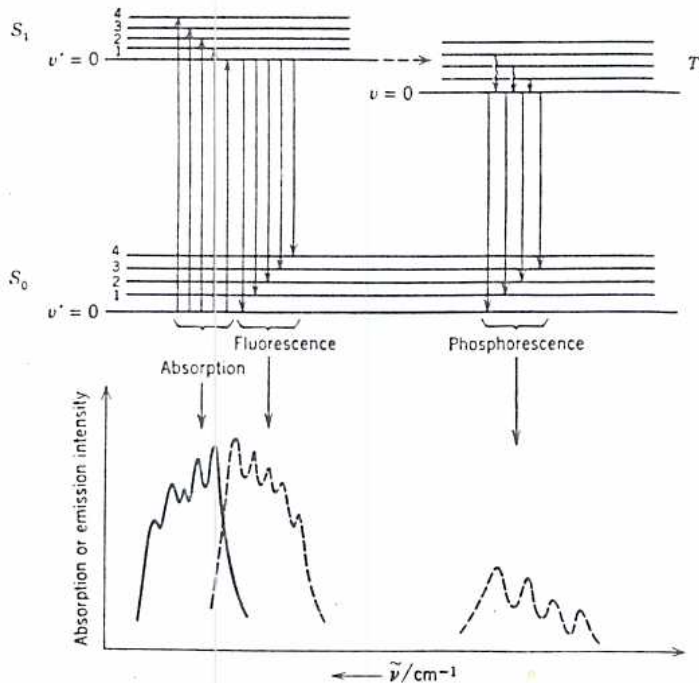


Figure 15.12 Schematic diagram showing absorption, fluorescence, and phosphorescence spectra. (From E. F. H. Brittain, W. O. George, and C. H. J. Wells, *Introduction to Molecular Spectroscopy*. New York: Academic, 1970.)

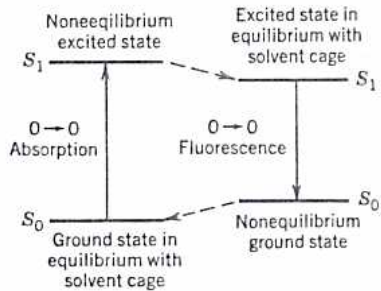


Figure 15.13 Effect of solute-solvent equilibrium in causing a difference in the energy of the 0-0 absorption transition and the 0-0 fluorescence transition. (From C. H. J. Wells, *Introduction to Molecular Photochemistry*. London: Chapman & Hall, 1972. © C. H. J. Wells, 1972.)

Laser: (1) Strategy



← create a "population inversion"

stimulate simultaneous emission of lots of excited molecules.

- (2) Results : (i) high intensity radiation
 (ii) very monochromatic

(3) One technical point: can't create a population inversion in a two-level system; need at least 3 levels.

Ex:

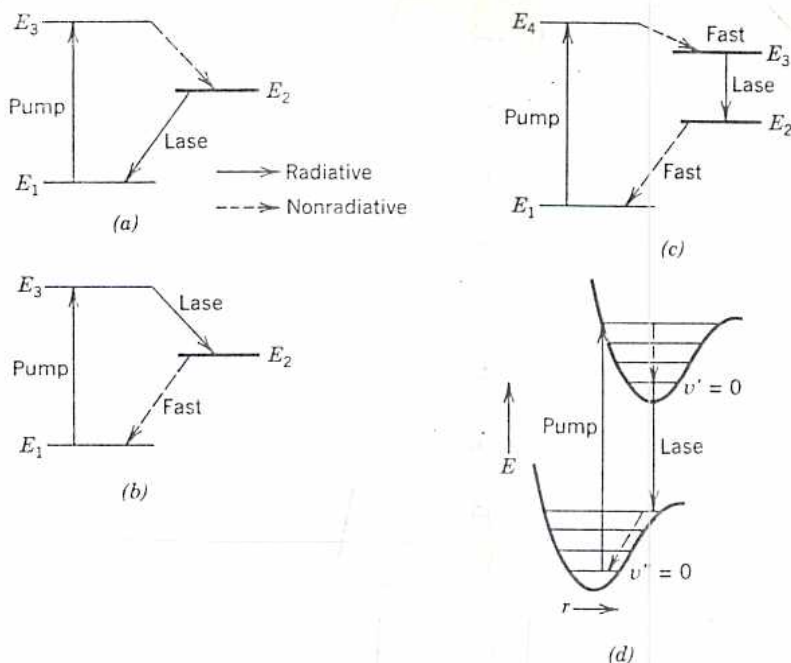
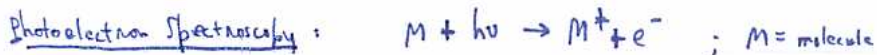


Figure 15.14 Multilevel lasing schemes. (a) and (b) are three-level systems, and (c) and (d) are four-level systems represented in different ways. (From W. F. Coleman, *J. Chem. Educ.* 59:441 (1982).)

- Various types of lasers [see A+S]: (i) Ruby
 (ii) Gas [e.g. CO_2 (+ N_2, He)]
 (iii) dye
 (iv) chemical [e.g. $\text{F} + \text{H}_2 \rightarrow \text{HF}^* + \text{H}$]

- All have advantages/disadvantages w.r.t. : (i) power
 (ii) tunability
 (iii) efficiency
 :

uv or X-Ray photons

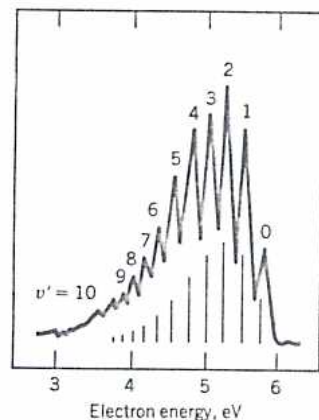


Energy conservation requires

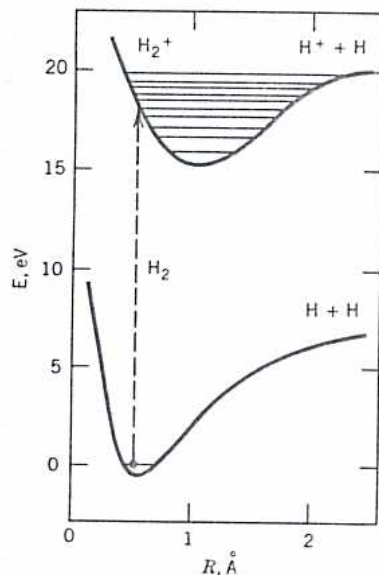
$$E(e^-) = h\nu + E(M) - E(M^+)$$

vib. E levels of neutral molecule vib. E of cation

- Notes: PES (i) gives ^{direct} info about ionization potls
 (ii) gives much info abt. molecular electronic structure
 (iii) X-ray photons can be used to eject core electrons.



note: $\uparrow =$
 vertical ionization potl.
 $[= 15.98 \text{ eV}]$



helium discharge tube

Figure 15.17 (a) Photoelectron spectrum of hydrogen gas excited by helium resonance radiation (58.4 nm or 21.22 eV). (From D. W. Turner and D. P. May, *J. Chem. Phys.* 45:471, 1966.) (b) Potential energies of H_2 and H_2^+ with energy levels involved in spectrum.