

Chapter 15 – Electronic Spectroscopy

Diatomic molecules

ignoring spin-orbit coupling, the good quantum #s are M_L , S , M_S .

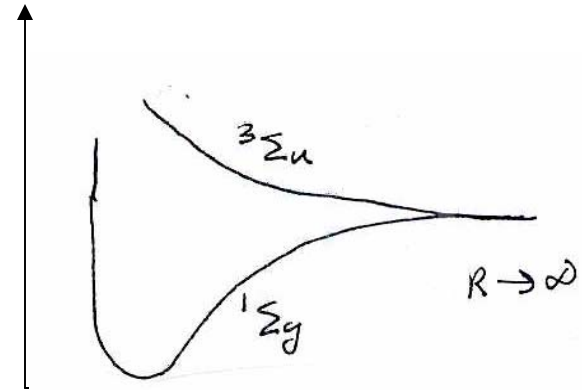
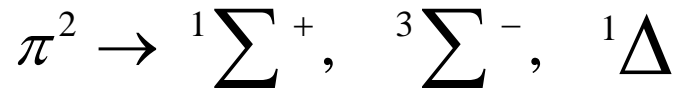
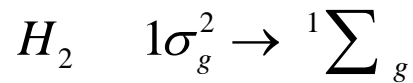
$$M_L = \sum_i M_{\ell_i}, \quad M_S = \sum_i M_{S_i}$$

Term symbols: $^{2S+1}\Lambda$, $\Lambda = |M_L|$

Λ 0 1 2 3

symbol Σ Π Δ Φ

g , u subscripts if there is an inversion center



+, - symmetry

Σ states only depends on whether ψ changes sign upon reflection through a plane through the molecular axis

Selection rules

$$\Delta\Lambda = 0, \pm 1$$

$$\Delta S = 0$$

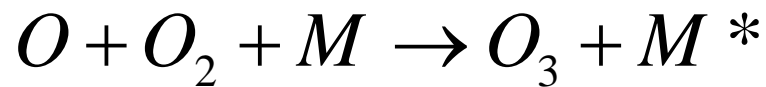
$$u \leftrightarrow g \quad + \rightarrow +; \quad - \rightarrow -$$

Electronic states of O₂

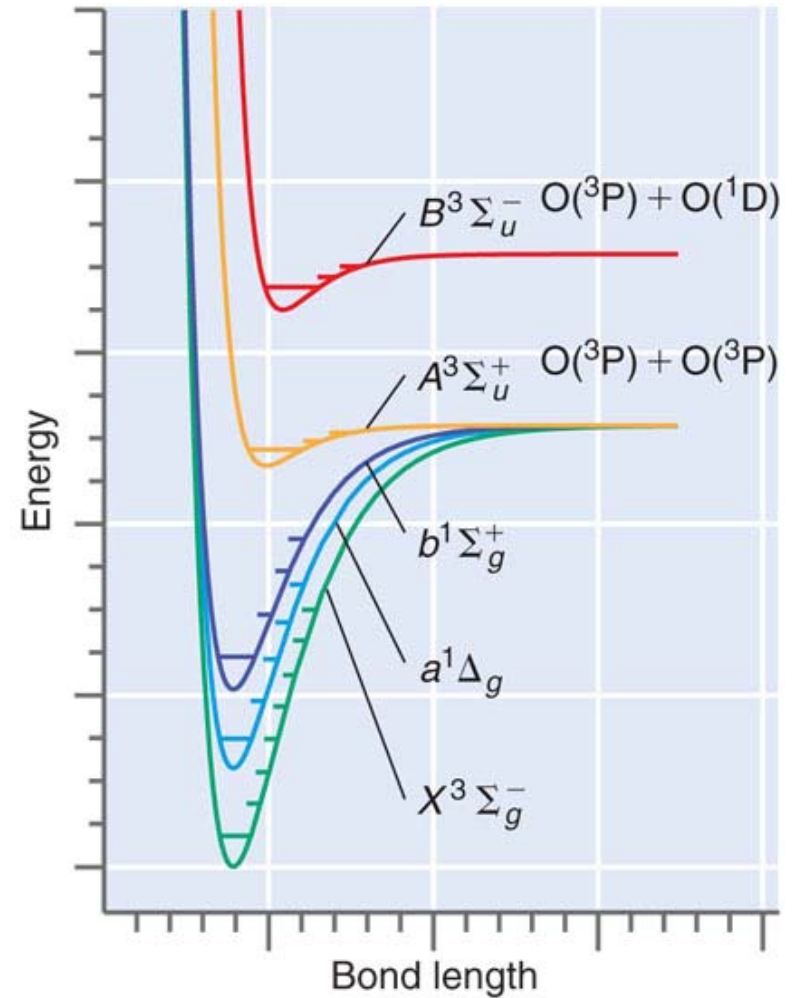
First two transitions of O₂ are forbidden.

If allowed, the earth's atmosphere would not be transparent!

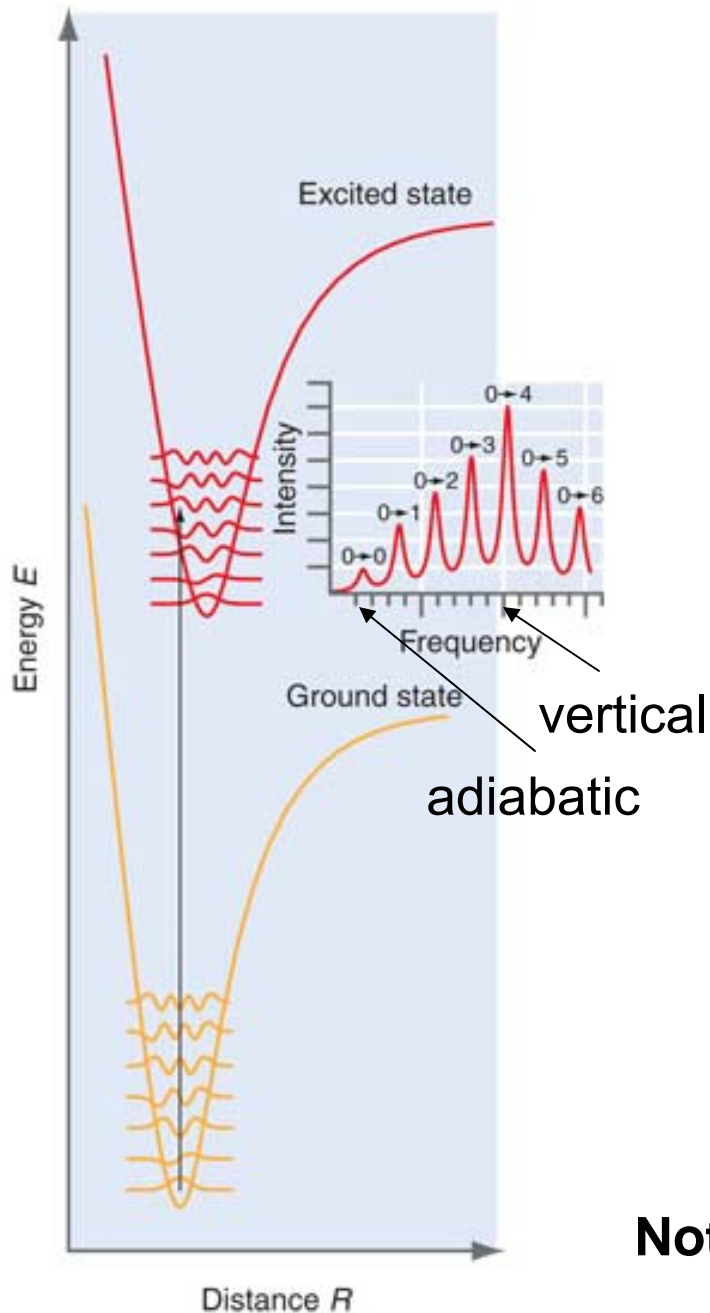
Photodissociation



↑
filters UV radiation



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If ground + excited states had the same potential energy curves, would get a single line

If excited state potential is displaced, can get a very long progression.

Intensities of vibrational peaks

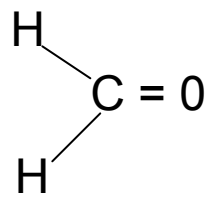
$$\mu_{fi} = \langle \psi_f | \hat{\mu} | \psi_i \rangle, \quad \hat{\mu} = -e \sum_i \vec{r}_i$$

$$\approx \langle \psi_f^{el} | \hat{\mu} | \psi_i^{el} \rangle \langle \phi_f^{vib} | \phi_i^{vib} \rangle$$

$$\left| \langle \phi_f^{vib} | \phi_i^{vib} \rangle \right|^2 = \text{Frank-Condon Factor}$$

Note: vibrational structure is seen in the electronic transitions of molecules such as H_2 , N_2 , O_2 .

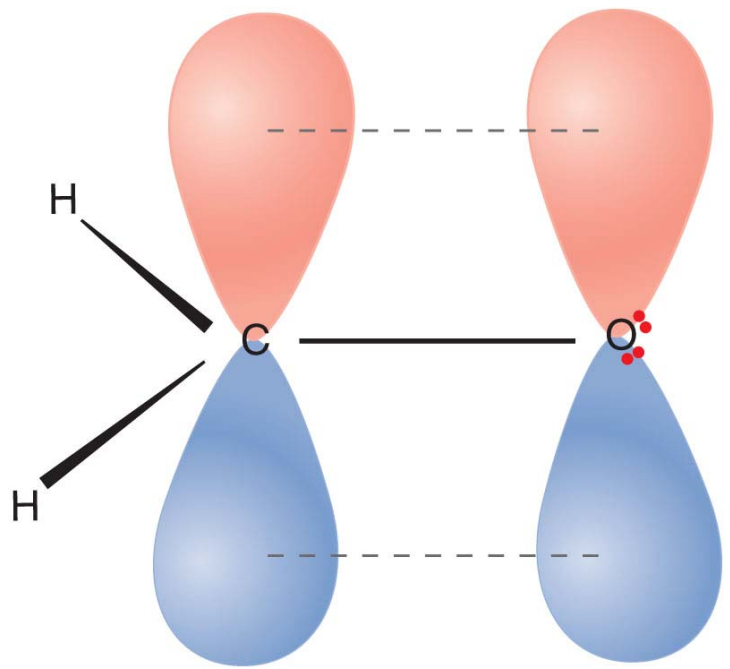
Formaldehyde



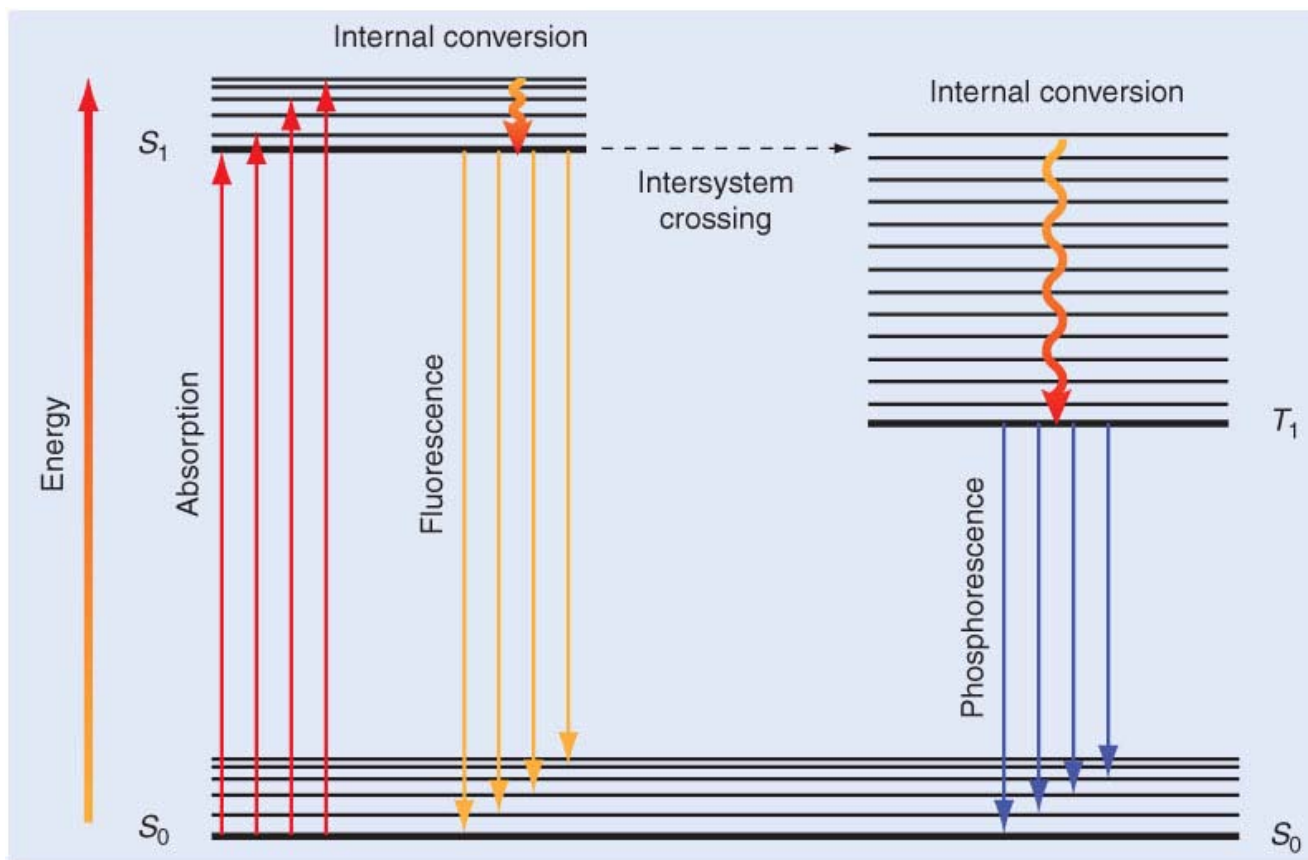
$$1s_0^2 1s_c^2 \sigma_{CH}^2 \sigma_{CH}^2 \sigma_{CO}^2 \pi_{CO}^2 n_0^2 \pi_{CO}^{*0}$$

using localized orbitals

σ, π not really valid symmetries for a nonlinear molecule



Excited states		C — O
$n \rightarrow \pi^*$	triplet	$BO = 3/2$
$n \rightarrow \pi^*$	singlet	$BO = 3/2$
$\pi \rightarrow \pi^*$	triplet	$BO = 1$
$\pi \rightarrow \pi^*$	singlet	$BO = 1$



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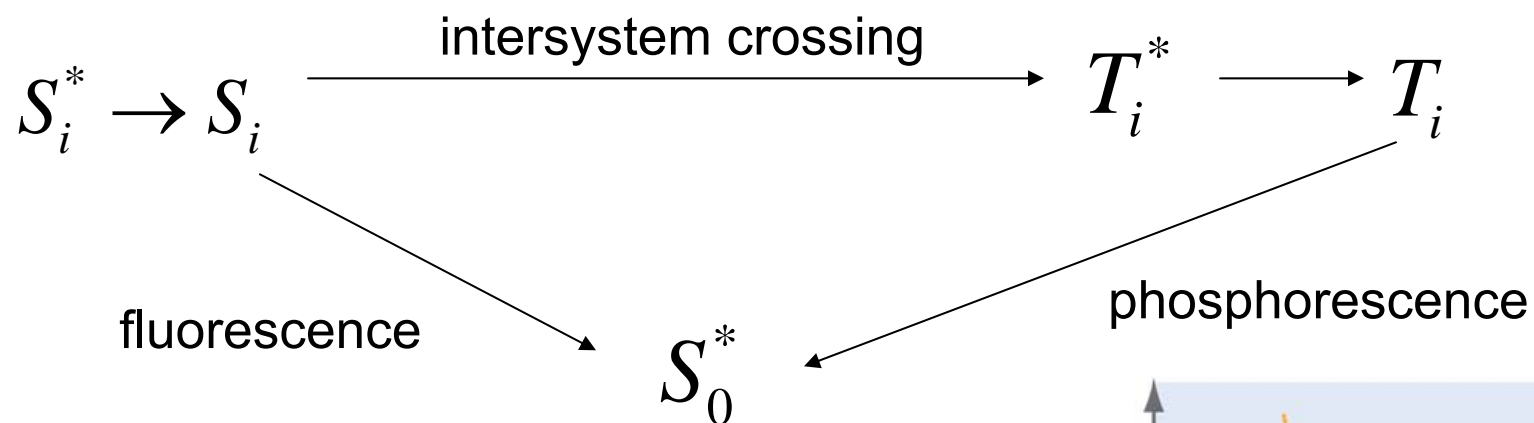
Radiative Transitions

absorption
fluorescence
phosphorescence

Non-Radiative Transitions

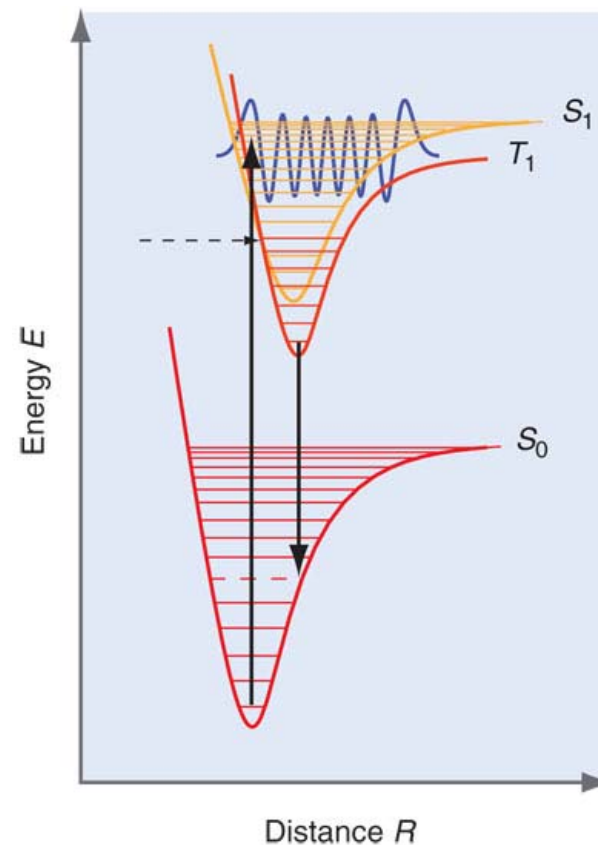
internal conversion
intersystem crossing
↑
collisions usually
important

Internal conversion is generally fast compared to fluorescence

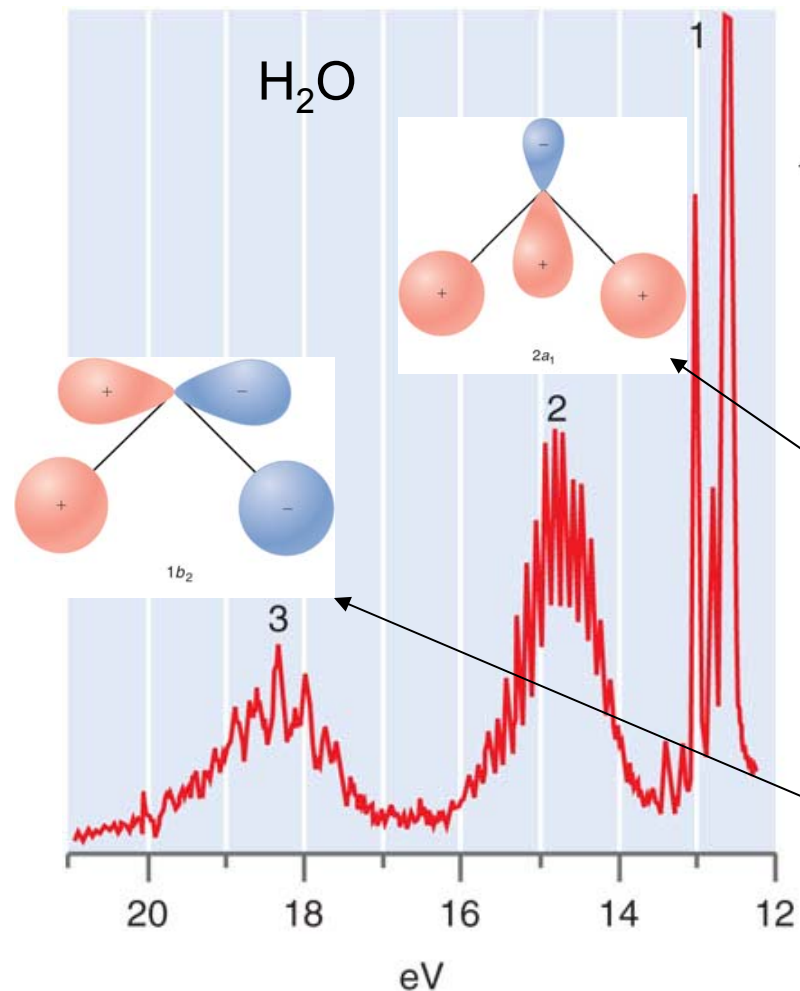


fluorescence $\tau \approx 10^{-7} s$

phosphorescence $\tau \gtrsim 10^{-3} s$



UV Photoelectron Spectroscopy



Removal of an electron from this orbital has little impact on the bonding \rightarrow not a very wide FC envelope

Removal of an e^- from this orbital will cause a long progression in the bending vibration

Removal of an e^- from this orbital causes excitation of both stretch and bending vibrations