Chapter 14 – Electronic Spectroscopy

Diatomic molecules

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

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

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

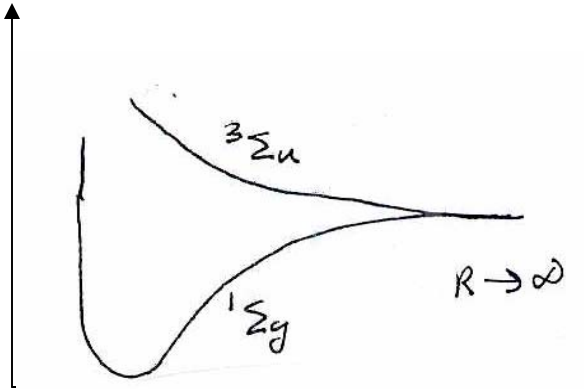
Λ	0	1	2	3
symbol	Σ	Π	Δ	Φ

g, *u* subscripts if there is an inversion center

$H_2 \quad 1\sigma_g^2 \rightarrow {}^1\sum_g$

$1\sigma_g 1\sigma_u \rightarrow {}^3\sum_u, \quad {}^1\sum_u$ excited states

$\pi^2 \rightarrow {}^1\sum^+, \quad {}^3\sum^-, \quad {}^1\Delta$



+, - symmetry

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

Selection rules

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

$\Delta S = 0$

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

Electronic states of O_2

First two transitions of O_2 are forbidden.

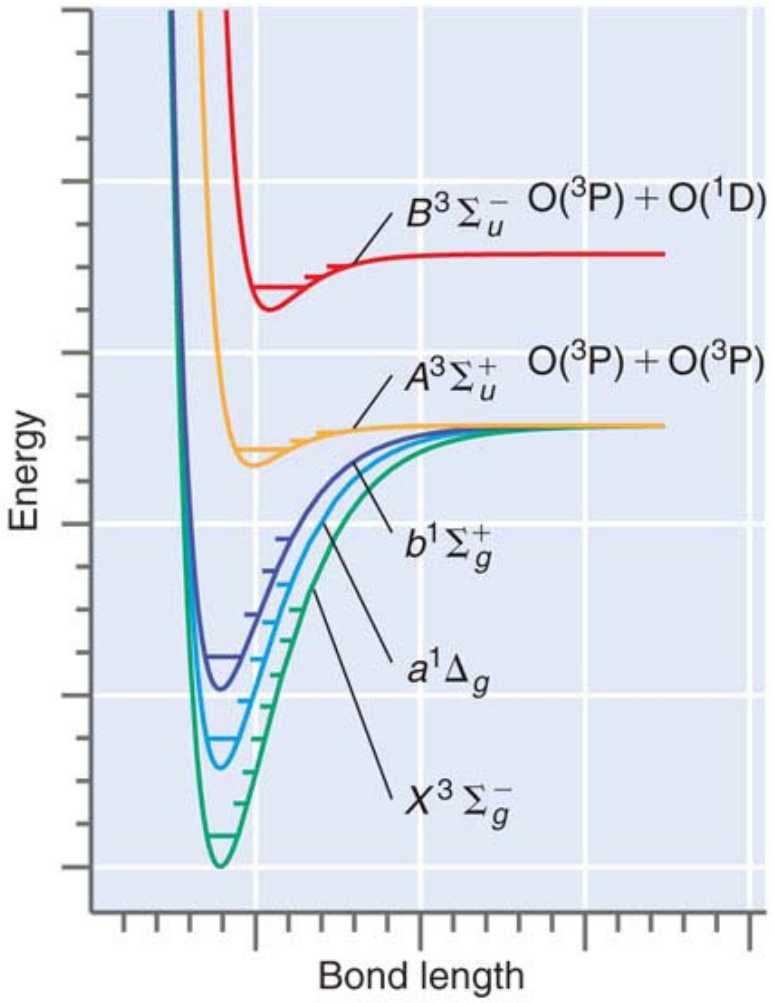
If allowed, the earth's atmosphere would not be transparent!

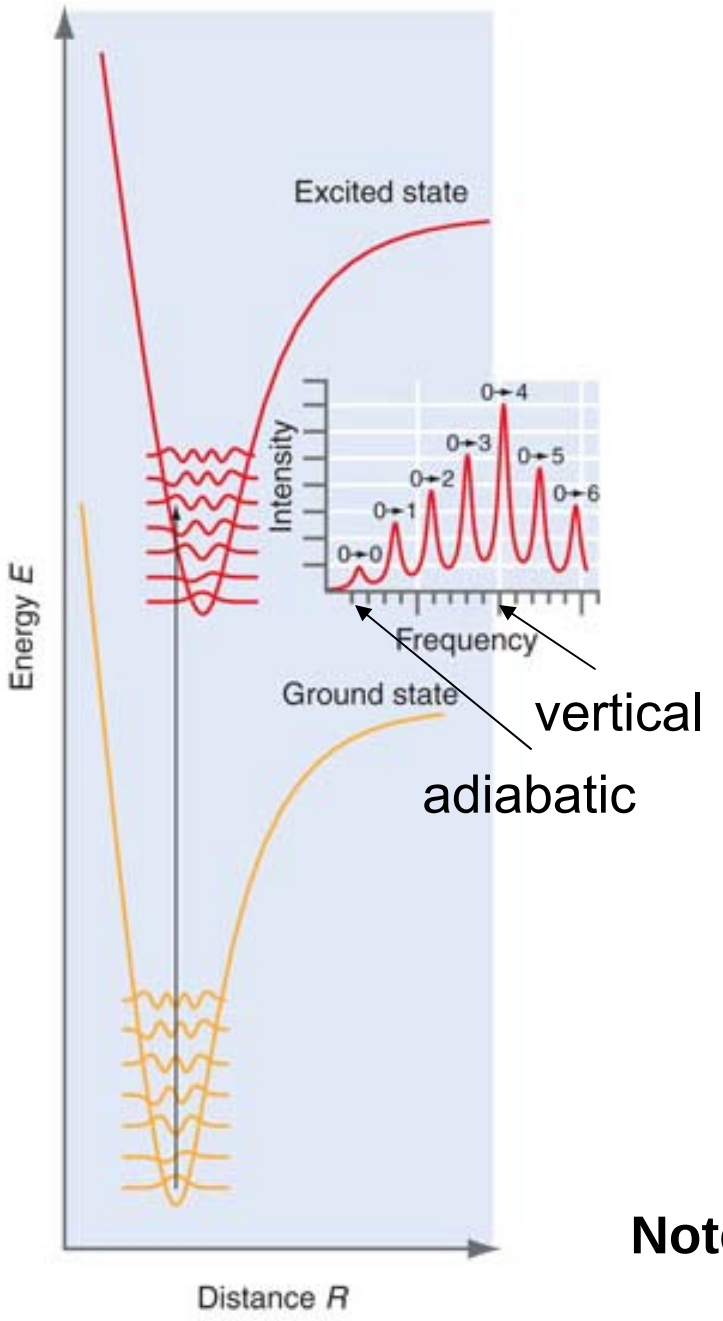
Photodissociation

$$O_2 \xrightarrow{h\upsilon} 20$$ Requires 5.1 eV

$$O + O_2 + M \rightarrow O_3 + M^*$$

filters UV radiation





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

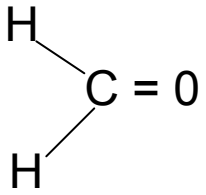
$$\mu_{fi} = \left\langle \psi_f \left| \hat{\mu} \right| \psi_i \right\rangle, \qquad \hat{\mu} = -e\sum_i \vec{r}_i$$

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

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

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

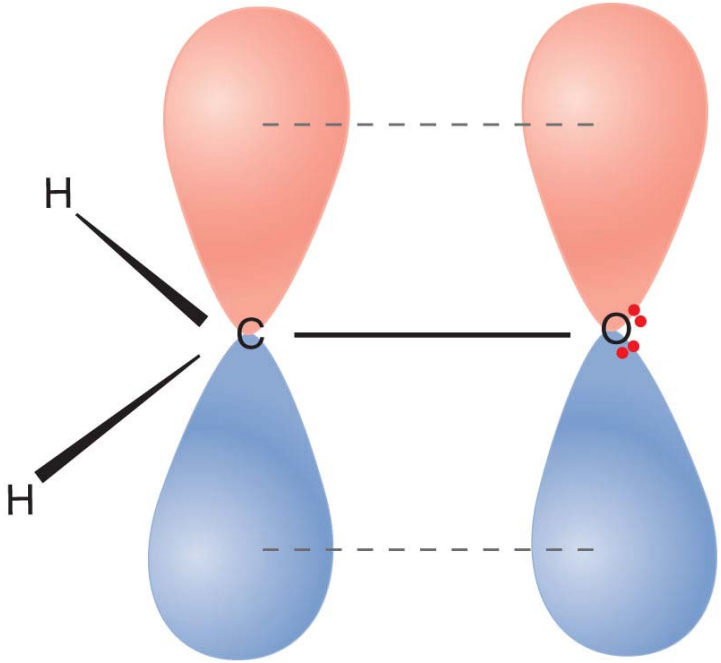
Formaldehyde



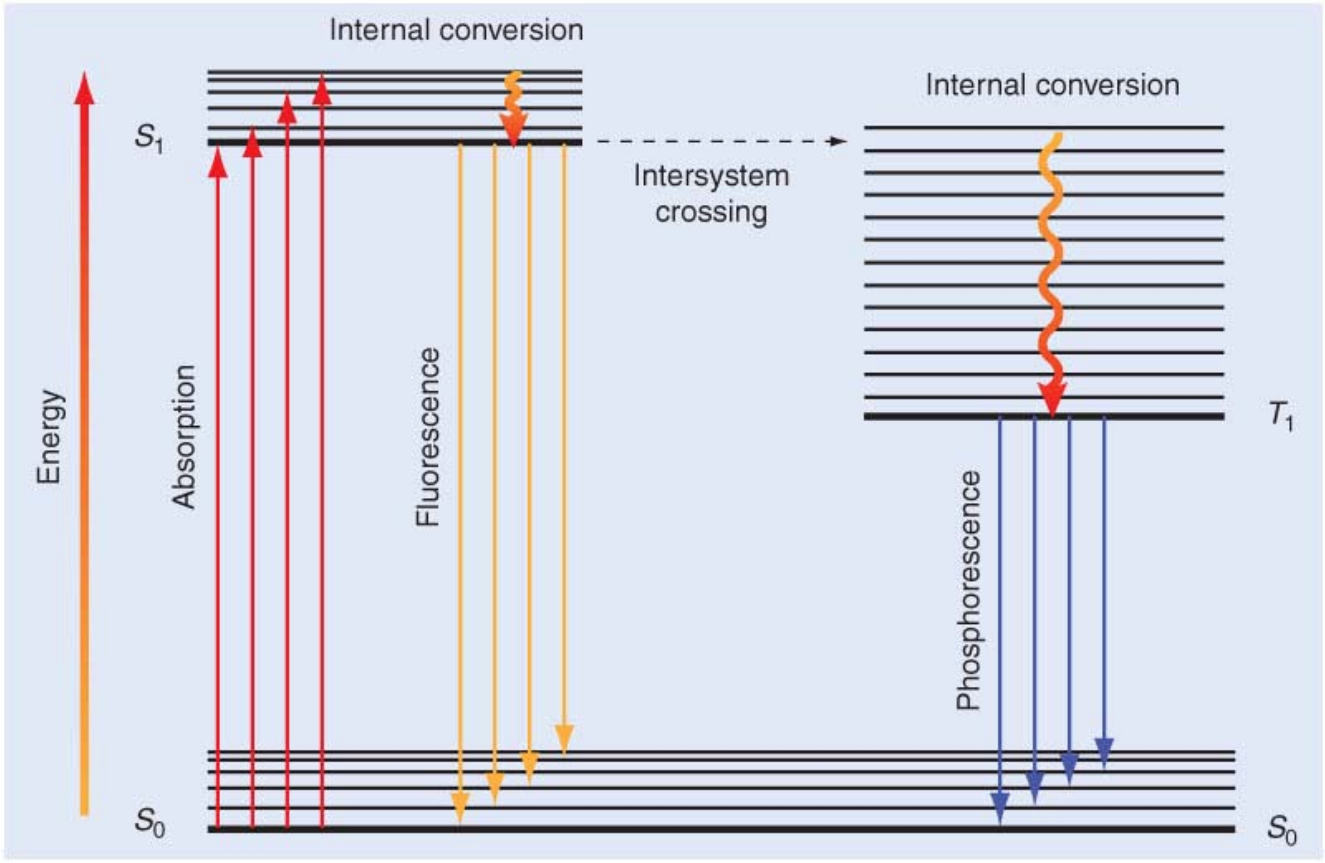
$$1s_0^2 1s_c^2 \sigma_{CH}^2 \sigma_{CH'}^2 \sigma_{CO}^2 \pi_{CO}^2 n_0^2 \pi_{CO}^{*0}$$

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	$BO = 1$



Radiative Transitions

absorption
fluorescence
phosphorescence

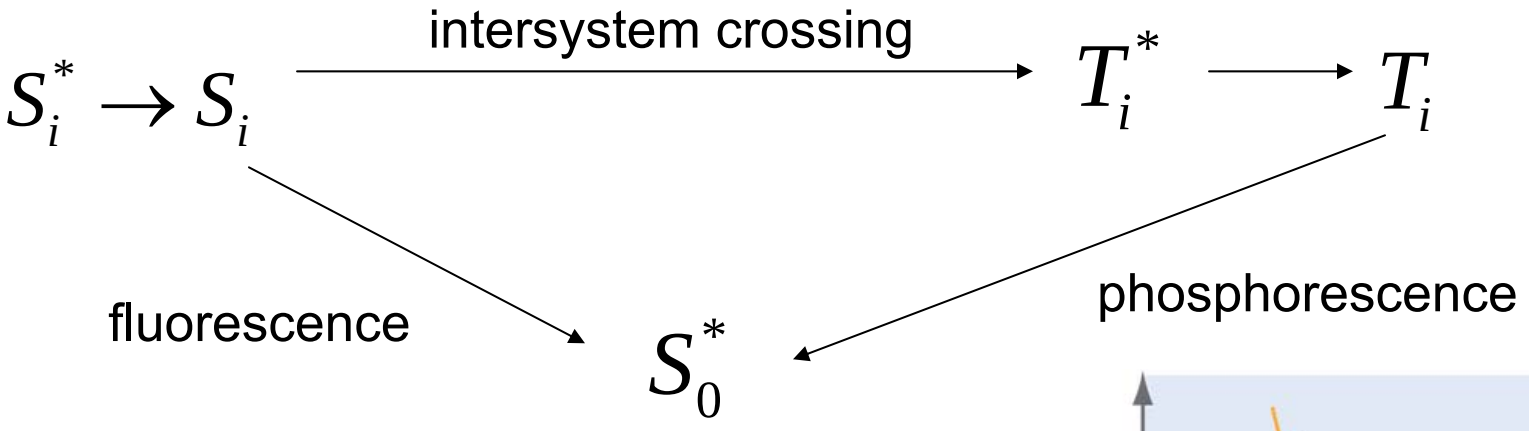
Non-Radiative Transitions

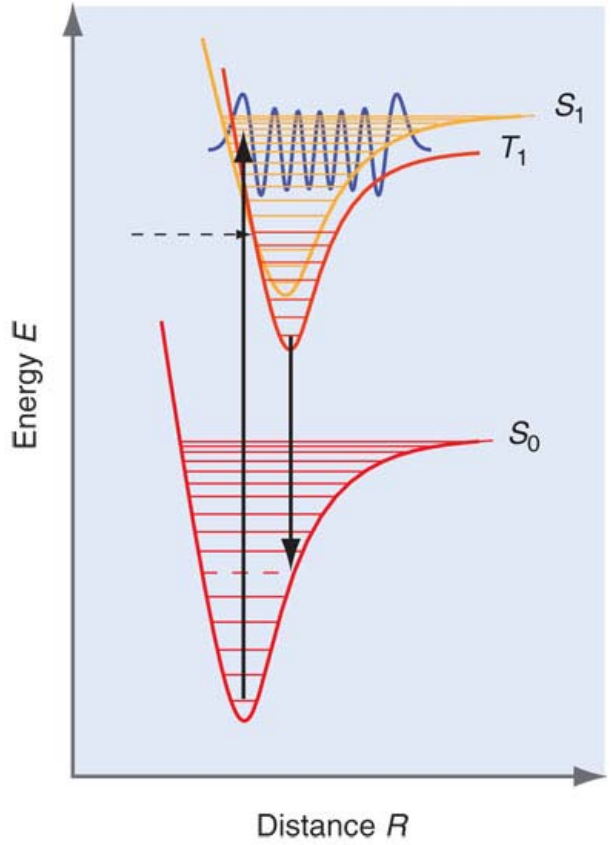
internal conversion
intersystem crossing

↑

collisions usually important

Internal conversion is generally fast compared to fluorescence

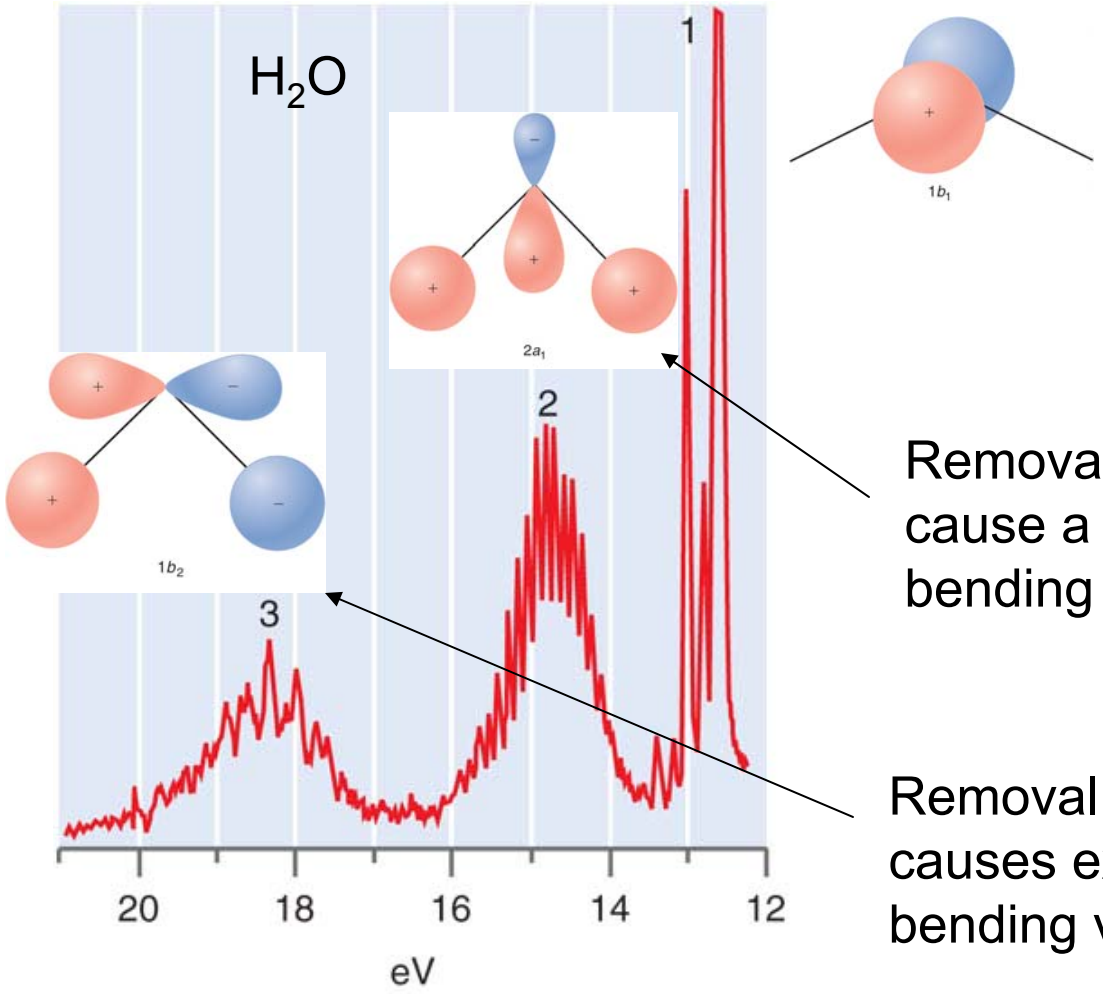




fluorescence $\tau \approx 10^{-7}\, s$

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

UV Photoelectron Spectroscopy

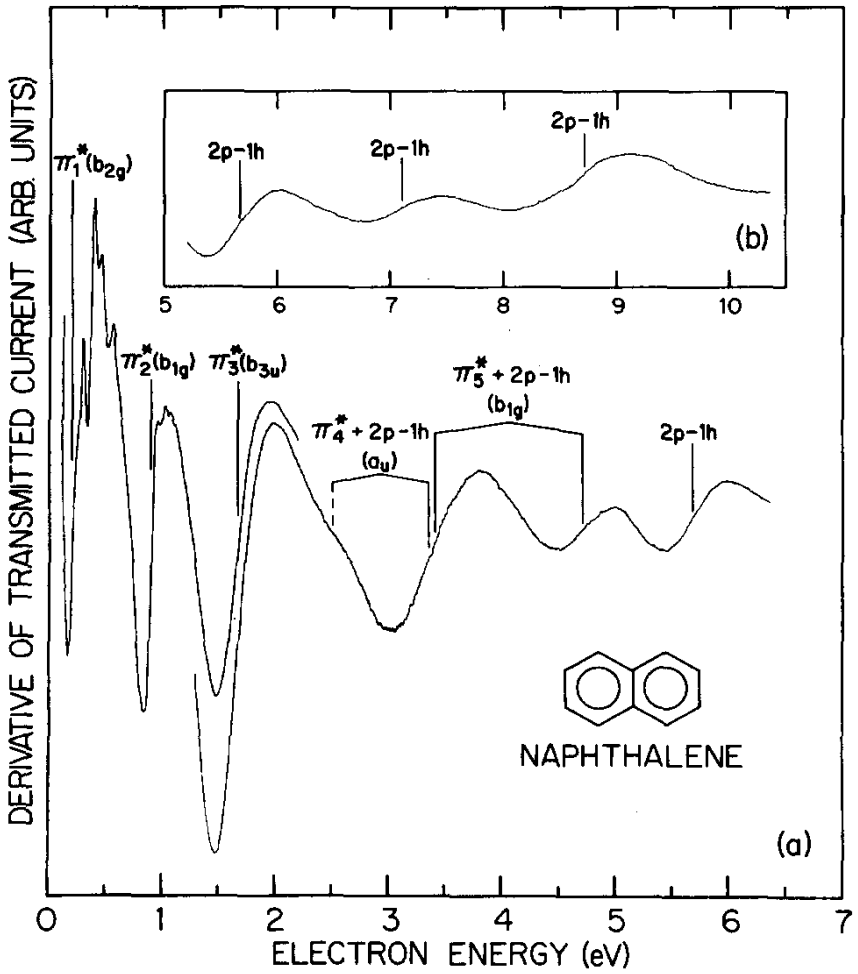


Removal of an electron from this orbital has little impact on the bonding → not a very wide FC envelope

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

Electron transmission spectroscopy –
measures energies of unfilled orbitals.



ETS of naphthalene (Jordan, Michejda, and Burrow, J. Chem. Phys. 1987)