Chapter 15 - Electronic Spectroscopy

diatomic molecules

ignoring spin-orbit coupling, the good quantum #'s are m_L, S, m_S.

$$m_L = \sum_i m_{\ell_i} \quad , \quad m_S = \sum_i m_{s_i}$$

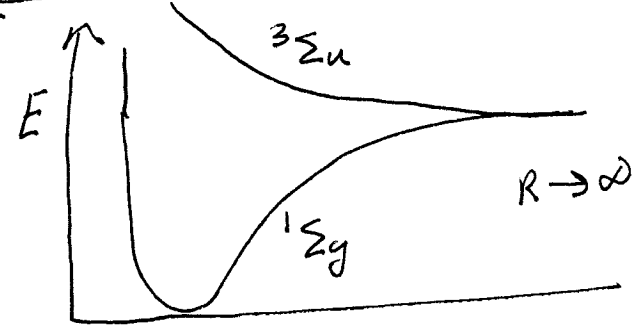
term symbols: $^{2S+1}\Lambda$, $\Lambda = |m_L|$

Λ	0	1	2	3
Symbol	Σ	Π	Δ	Φ

g, u subscripts if there is an inversion center.

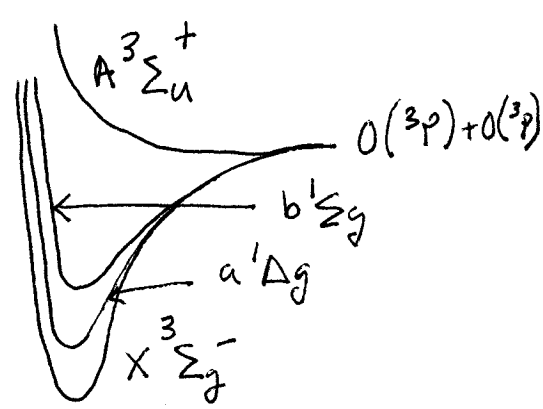
H_2 $\quad 1\sigma_g^2 \rightarrow {}^1\Sigma_g$

$1\sigma_g 1\sigma_u \rightarrow {}^3\Sigma_u, {}^1\Sigma_u \leftarrow$ excited states



+, - symmetry
Σ states only
depends on whether Ψ changes sign upon reflection through a plane containing the molecular axis

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



Selection rules

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

$\Delta S = 0$

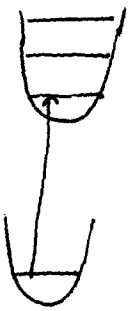
$u \leftrightarrow g \qquad + \rightarrow +; - \rightarrow -$

First two transitions of O_2 are forbidden.
If allowed, the earths atmosphere would not be transparent.

Photodissociation $O_2 \xrightarrow{h\nu} 2O$.

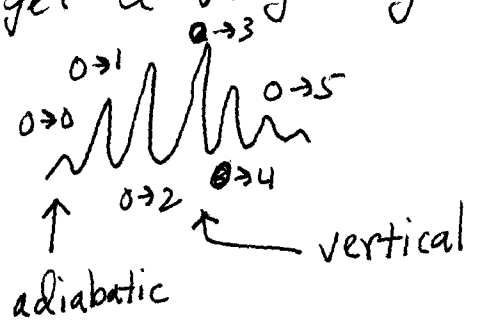
$$O + O_2 + M \longrightarrow \underline{\underline{O_3}} + M^*$$

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.



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

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

$$|\langle \phi_f^{vib} | \phi_i^{vib} \rangle|^2 = \text{Franck-Condon factor}$$

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