Physical Chemistry

14: Electronic spectroscopy
spin multiplicity
\[ = 2S + 1 \]
S is the total spin quantum number for the molecule

**Diatomic molecular term symbols**

\[ \Omega = \Lambda + \Sigma \]
Here, \( \Sigma \) is the projection of S on the internuclear axis

\[ \Sigma \] for \( \lambda = 0 \)
\[ \Pi \] for \( \lambda = \pm 1 \)
\[ \Delta \] for \( \lambda = \pm 2 \)
Diatomic molecular term symbols

Angular momentum about the internuclear axis ($\lambda$)

Example: $p_z$-orbitals form molecular orbitals.

$m_l = 0$

$\sigma$ (g)

$\sigma^*$ (u)

$\Sigma^-$  $\Sigma^+$  $\Sigma$ terms  $\lambda = 0$
Diatom molecular term symbols

Angular momentum about the internuclear axis ($\lambda$)

Example: $p_x$, $p_y$-orbitals form molecular orbitals.

$m_l = \pm 1$

$\pi^* (g)$

$\Pi (u)$

To get $\Lambda$, sum over all $e^-$.  

$\Pi$ terms $\lambda = \pm 1$
Franck-Condon factors: diagram

I. If the bonding character of the two states is similar:

\[ R_e' \sim R_e'' \]

Best overlap \((v' = 0) - (v'' = 0)\)

II. If the bonding character of the two states is very different:

\[ R_e' \neq R_e'' \]

Best overlap \((v' > 0) - (v'' = 0)\)

http://mackenzie.chem.ox.ac.uk/teaching/Molecular%20Electronic%20Spectroscopy.pdf
Dissociation energies

Morse oscillator:

\[ \tilde{G}_\nu = \left( \nu + \frac{1}{2} \right) \omega_e - \left( \nu + \frac{1}{2} \right)^2 \omega_e x_e \]

\[ \nu = 0, 1, 2 \ldots \nu_{\text{max}} \]

\[ \frac{d\tilde{G}_\nu}{d\nu} = \omega_e - 2 \omega_e x_e \left( \nu + \frac{1}{2} \right) = 0 \]

at the dissociation limit \[ \left( \nu + \frac{1}{2} \right)_{\text{max}} \]

\[ \nu_{\text{max}} = \frac{\omega_e}{2 \omega_e x_e} - \frac{1}{2} \]

\[ \tilde{G}_{\nu_{\text{max}}} = D_e = \frac{\omega_e^2}{4 \omega_e x_e} \]

http://mackenzie.chem.ox.ac.uk/teaching/Molecular%20Electronic%20Spectroscopy.pdf
I₂ spectrum
$I_2$ spectrum

![Graph showing $I_2$ spectrum with peaks at different wavelengths marked with $v'' = 0$ and $v'' = 1$.]
$I_2$ spectrum - analysis

$(\nu' + 1) \text{ vs. } \Delta\tilde{\nu}(\nu')$

Birge-Sponer plot
Birge-Sponer plot

y-intercept \[ = \tilde{\nu}_e' \]
slope \[ = 2 \tilde{x}_e' \tilde{\nu}_e' \]
x-intercept = convergence limit

\[ \Delta \tilde{\nu}(\nu') = \tilde{\nu}_e - 2 \tilde{x}_e' \tilde{\nu}_e' (\nu' + 1) \]

\[ D_0' = \Delta \tilde{\nu}(\nu' = 0) + \Delta \tilde{\nu}(\nu' = 1) + ... = A \]

\[ De = D_0' + E_{vib}(\nu' = 0) = D_0' + \frac{1}{2} \tilde{\nu}_e' + \frac{1}{4} \tilde{\nu}_e' \tilde{x}_e \]

\[ E^* = \tilde{\nu}(\nu' = b) + A = D_0' + E(I^*) \]

\[ \tilde{T}_e = D_e'' + E(I^*) - D_e' \]
$I_2$ energy levels

$\nu = \text{vibrational quantum number}$

$\tilde{\nu} = \text{vibrational frequency}$

$D_0 = \text{dissociation energy}$

$D_e = \text{equilibrium dissociation energy}$

$T_e' = \text{electronic energy}$

$\tilde{x}_e' = \text{anharmonicity constant}$

$(\nu' = b)$ convergence limit
Photoelectron spectroscopy

Excite with high-energy photons at fixed wavelength.

Measure kinetic energy of ejected electrons.
Photoelectron spectra
Photoelectron spectrum of $N_2$

A: weakly bonding electron ($2p\sigma_g$)
B: strongly bonding electron ($2p\pi_u$)
C: weakly anti-bonding electron ($2s\sigma_u$)

http://mackenzie.chem.ox.ac.uk/teaching/Molecular%20Electronic%20Spectroscopy.pdf
X-ray crystallography

In our experience, matter seems to be composed of particles.

For a photon:

\[ m = \frac{h}{\lambda} \]

For a particle with velocity \( v \):

\[ m = \frac{h}{\lambda v} \]

\[ \lambda = \frac{h}{mv} \]
X-ray crystallography

Molecules in a regular crystal lattice can diffract X-rays.

Crystal Structure of Rhodopsin: A G Protein-Coupled Receptor
Krzysztof Palczewski et al.
Science 289, 739 (2000);
DOI: 10.1126/science.289.5480.739
X-ray crystallography

Diffraction patterns can be used to solve molecular structures.

crystal  diffraction pattern  structure