Physical Chemistry

Chem 131B

13: Electronic Spectroscopy
Molecular term symbols look like

\[ \frac{2S+1}{\Omega,(g/u)} \Lambda^{(+/-)} \]

- **S** = total spin quantum number.
- **\Lambda** = orbital angular momentum along internuclear axis
- **\Omega** = total angular momentum along internuclear axis
- **g/u** = parity (reflection through inversion center)
- **+/−** = reflection symmetry along a plane containing the internuclear axis.
Term symbols for linear molecules

A wavefunction (electronic state) is \( g \) (gerade - even) if it is unchanged under inversion \((x,y,z) \rightarrow (-x,-y,-z)\).

It is \( u \) (ungerade - odd) if it changes sign under inversion.

In centrosymmetric environments, transitions between like orbitals are forbidden.

This is a consequence of the even-odd rule – the dipole moment operator has \( u \) symmetry.

\[
\begin{align*}
g \times u \times g &= u \text{ (forbidden)} \\
g \times u \times u &= g \text{ (allowed)} \\
u \times u \times u &= u \text{ (forbidden)}
\end{align*}
\]
Term symbols for linear molecules

\[ M_L = \sum_i m_{li} \]

\[ \Lambda = |M_L| \]

\[ \Lambda = 0, 1, 2, 3, \ldots \]

\[ 2S+1 \Lambda^{(+/-)}_{\Omega,(g/u)} \]

\[ \Sigma, \pi, \Delta, \phi \ldots \]
A, B, C… are excited states with the same spin quantum number as the ground state.

a, b, c… are excited states with different spin quantum numbers from the ground state.

X is the ground state
Collision between $\text{O} \ (^{3}\text{P})$ and $\text{H} \ (^{2}\text{S})$ controlled by laser pulses.

Electronic spectroscopy

Electrons are moved between orbitals (and not ionized).

Example: Nitrogen (molecular gas)

\[ N_2 : (1\sigma_g^+)^2 (1\sigma_u^+)^2 (2\sigma_g^+)^2 (2\sigma_u^+)^2 (1\pi_u)^4 (3\sigma_g^+)^2 (1\pi_g)^0 \]

A photon with wavelength 145 nm causes the following excitation:

\[ 3\sigma_g^+ \rightarrow 1\pi_g \]
Electronic spectroscopy

Example: Oxygen (molecular gas)

\[ O_2 : (1\sigma_g^+)^2 (1\sigma_u^+)^2 (2\sigma_g^+)^2 (2\sigma_u^+)^2 (3\sigma_g^+)^2 (1\pi_u)^4 (1\pi_g)^2 \]

A photon with a given energy causes an excitation giving rise to three electronic states:

\[ 3\Sigma_g^- \quad 1\Delta_g \quad 1\Sigma_g^+ \]

Different transitions are observed where the electrons are distributed in \(1\pi_g\) differently, but the overall electron configuration is the same.

The whole electron cloud changes its state – use the total electronic wavefunction.
Electronic spectroscopy

Transitions occur between vibronic states.

\[ \varepsilon = 1, \nu = 2 \]

\[ |1,2\rangle \]

\[ \psi \]

\[ \varepsilon = 0, \nu = 5 \]

\[ |0,5\rangle \]

Each state has a wavefunction.
Franck-Condon principle: because the nuclei are so much more massive than the electrons, electronic transitions take place much faster than the nuclei can respond.

Vertical lines represent transitions.
Franck-Condon principle

The Photochemistry Portal
photochemistry.wordpress.com
Franck-Condon principle

Not all vibrational states are equally likely.

Transition intensity

The relative intensity of a vibronic transition depends on the relative horizontal placement of states.

\[ \mu_{fi} = \langle f | \hat{\mu} | i \rangle \]

\[ \mu = -e \sum_i \vec{r}_i + e \sum_i Z_i \vec{R}_i \]

- **Electrons**
- **Nuclei**

**Franck-Condon factor**

\[ S \left( \nu_f, \nu_i \right)^2 \]

- **Transition intensity** \( \propto |\mu_{fi}|^2 \)
- **S** is the overlap integral between vibrational states.

\[ \langle \nu_f | \nu_i \rangle \text{ or } \int \psi_{\nu_f}^* \psi_{\nu_i} d\tau \]

- **S** = 1 \( \Rightarrow \) complete overlap
- **S** = 0 \( \Rightarrow \) no overlap

- Vectors are distances from the center of charge.
Franck-Condon principle

\[
\mu_{fi} = \langle \varepsilon_f \nu_f | -e \sum_i \vec{r}_i + e \sum Z_i \vec{R}_i | \varepsilon_i \nu_i \rangle
\]

\[
= -e \sum_i \langle \varepsilon_f | \vec{r}_i | \varepsilon_i \rangle \langle \nu_f | \nu_i \rangle + e \sum Z_i \langle \varepsilon_f | \varepsilon_i \rangle \langle \nu_f | \vec{R}_i | \nu_i \rangle
\]

overlap integral \quad = 0 \quad \text{(orthogonality)}

Electronic transition moment: \( \mu_e(R) = \langle \nu_f | \hat{\mu}_e | \nu_i \rangle \)

The overall transition moment is given by \( \overline{\mu}_e(R) \)

over the vibrational wavefunctions in the upper and lower states.
Franck-Condon factors

\[ \mu_{fi} = \int \mu_e(R) \psi^*_f \psi_i dR \]

Assuming the R-dependence of \( \mu_e \) is small,

\[ = \bar{\mu}_e(R) \int \psi^*_f \psi_i dR = \bar{\mu}_e(R) \langle \nu_f | \nu_i \rangle \]

the relative intensity of a transition is the square of the vibrational overlap integral

\[ \left| \int \psi^*_f \psi_i dR \right|^2 = \left| \langle \nu_f | \nu_i \rangle \right|^2 \]

This is the Franck-Condon factor \( q_{fi} \)
Vanishing integrals redux

Selection rules depend on a transition dipole, e.g.,

$$\mu_{fi} = \int \psi^* \hat{\mu} \psi d\tau$$

To find if integrals of this form vanish by symmetry:

1. Find the symmetry species of each function.
2. Multiply them and reduce the representation if necessary.
3. If the resulting representation does not contain $A_1$, there is no overlap.

Remember, $A_1$ is invariant to all transformations.
Vanishing integrals redux

Can x-polarized radiation induce a transition between a 3dz² orbital and a 3dxy orbital in a C$_{2v}$ molecule?

transition dipole: \[ \mu_x = \int (3dz^2) x (3dxy) \, d\tau \]

\[ I = \int f_1 f_2 f_3 \, d\tau \]

\[
\begin{array}{cccccc}
C_{2v} & E & C_2 & \sigma_v & \sigma_{v'} & \\
f_3 \ (3dxy) & 1 & 1 & -1 & -1 & A_2 \\
f_2 \ (x) & 1 & -1 & 1 & -1 & B_1 \\
f_1 \ (3dz^2) & 1 & 1 & 1 & 1 & A_1 \\
f_1 f_2 f_3 & 1 & -1 & -1 & 1 & B_2 \\
\end{array}
\]

no A_1, no overlap
Transition dipole

A transition is allowed if the integral for the transition dipole is nonzero.

\[ \mu_{fi} = \int \psi^* \hat{\mu} \psi \, d\tau \quad \text{or} \quad \mu_{fi} = \langle f | \hat{\mu} | i \rangle \]

Consider components of the dipole moment operator separately:

\[ \hat{\mu}_x, \hat{\mu}_y, \hat{\mu}_z \]

all have \( u \) symmetry

\[ \Sigma \leftrightarrow \Sigma \quad \text{transitions are related to} \quad \hat{\mu}_z \quad (+ \text{symmetry}) \]

+ to - \quad (+)(+)(-) \quad = 0 \quad \text{(forbidden)}

+ to + \quad (+)(+)(+) \quad \neq 0 \quad \text{(allowed)}
Weakly allowed transitions

Forbidden transitions can be weakly allowed if a vibration breaks the symmetry.

Fig. 5 $e_g$ and $t_{2g}$ molecular orbitals of Fe(OH$_2$)$_6^{2+}$
Weakly allowed transitions

Electronic excited state

Electronic ground state

No vibronic coupling

With vibronic coupling

Fig. 4 Pure electronic transition and the electronic transition couples with the vibrational transition
Sum rule

\[ \sum_{v''} q_{v',v''} = \sum_{v''} |\langle v' | v'' \rangle|^2 = \sum_{v''} \langle v' | v'' \rangle \langle v'' | v' \rangle \]

\[ \sum_{v''} |\langle k | k \rangle| = 1 \quad \sum_{v''} q_{v',v''} = \sum_{v''} \langle v' | v' \rangle = 1 \]

closure relation

Eigenfunctions form a complete set – we can represent any function as a linear combination of them.
\( I_2 \) energy levels

\( \nu = \text{vibrational quantum number} \)

\( \tilde{\nu} = \text{vibrational frequency} \)

\( D_0 = \text{dissociation energy} \)

\( D_e = \text{equilibrium dissociation energy} \)

\( T'_e = \text{electronic energy} \)

\( \tilde{x}_e' = \text{anharmonicity constant} \)

\( (\nu' = b) \text{ convergence limit} \)
$I_2$ spectrum

$I_2$ Laser Induced Fluorescence

Laser Line

Emission Wavelength [Angstroms]
I$_2$ spectrum
I$_2$ spectrum - analysis

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

Birge-Sponer plot
I₂ spectrum - analysis

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

D_{e} = 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'}