Electronic transitions in molecules

Atomic vs molecular spectroscopy

Atoms:

\[ \begin{align*}
A & \quad \uparrow 3 \\
2 & \quad \uparrow \\
1 &
\end{align*} \]

Molecules:

\[ \begin{align*}
\text{vibronic levels}
\end{align*} \]

Franck-Condon progression

Molecules in condensed phase:

\[ \begin{align*}
\text{continuous spectrum of states}
\end{align*} \]
Vibrations of a diatomic molecule

\[ \theta = N_2 \]

\( r_e \) \text{ equilibrium bond length}

\( q \) \text{ bond elongation}

Harmonic potential: \( V(q) = \frac{1}{2} k q^2 \)

Hamiltonian: \( H(q, \dot{q}) = \frac{m_1 q^2}{2} + \frac{1}{2} k q^2 \)

Quantum harmonic oscillator:

\[ V(q) \]

\[ E_n = \hbar \omega (n + \frac{1}{2}) \]

\( \omega = \sqrt{\frac{k}{m}} \)

Zero-point energy

Selection rules for dipolar transitions

\[ \langle n_1 | \vec{\mu} | n_2 \rangle \neq 0 \]

\( \Delta n = n_2 - n_1 = \pm 1 \). Vibrational excitation and cooling can happen only by one step up or down.
The anharmonic oscillator

Stretching the molecular bond eventually leads to dissociation, the potential must be **anharmonic**

$$V(q)$$

$u=0 \rightarrow u=1$ is the fundamental transition

$u=0 \rightarrow u=2$ is the first overtone

The vibrational spacing decreases with increasing $u$ for the anharmonic potential

**Common approximation**: Morse potential

$$V(q) = D_e \left( 1 - e^{-\beta q} \right)^2$$

$q < 0$  \hspace{0.5cm} $V(q) \approx D_e e^{2\beta q}$ — exponential repulsion

$q > 0$, $q \gg 1$  \hspace{0.5cm} $V(q) \approx D_e (1 - 2e^{-\beta q})$
Energy levels of the Morse potential

\[ E_n = \hbar \omega (n + \frac{1}{2}) - \hbar \omega x e \left( n + \frac{1}{2} \right)^2 \]

\[ E_{n+1} - E_n = \hbar \omega - 2 \hbar \omega x e (n + 1) \]

spacings between energy levels linearly decreasing with increasing \( n \)

The population of the vibrational states

\[ \frac{N_2}{N_1} = e^{-\frac{\Delta E}{kT}} \]

For harmonic oscillator:

\[ \frac{N_n}{N_0} = \frac{e^{-(n+\frac{1}{2}) \frac{\hbar \omega}{kT}}}{e^{-\frac{1}{2} \frac{\hbar \omega}{kT}}} = e^{-\frac{n}{2} \frac{\hbar \omega}{kT}} \]

\[ kT \approx 200 \text{ cm}^{-1} \approx \frac{1}{40} \text{ eV at } T \approx 300 \text{ K} \]

\[ \frac{N_1}{N_0} \]

\[ H_2 \quad 4159 \quad 2.2 \times 10^{-3} \]

\[ I_2 \quad 213 \quad 0.36 \]
Electronic transitions

Q: How to decide which transition will have a non-zero intensity?
A: One needs to formulate molecular selection rules.

Molecular wave function:

\[ \psi = \psi_V \psi_e \psi_s \]

- Vibrational wave function, often taken from harmonic approximation
- Electronic wave function
- Spin wave function

Born-Oppenheimer approximation

"a" x "s"
\[ \psi_e \times \psi_s \rightarrow \text{antisymmetric} \]

"s" x "a"
(Pauli exclusion principle)
Selection rules for electronic transitions

Let's consider a diatomic molecule going from the electronically ground state \( \text{A-B} \) to an electronically excited state \( \text{A-B}^* \). This transition can potentially change spin(s) and vibrational \((n)\) states: \( (n,\, s) \rightarrow (n^*,\, s^*) \)

The selection rule for this transition is determined by whether the transition dipole is non-zero or zero.

\[
M = \langle \Psi_{e^*} \Psi_{s^*} \Psi_{v^*} | \vec{\mu} | \Psi_{e} \Psi_{s} \Psi_{v} \rangle
\]

Dipole moment operator:

\[
\vec{\mu} = -e \sum_i \vec{r}_i + e \sum_j Z_j \vec{R}_j = \vec{\mu}_e + \vec{\mu}_n
\]

sum over electrons \quad \text{sum over electronic nuclei}
Transition dipole:

\[ \tilde{M} = \langle \psi_e | \psi_s \psi_u | (\vec{\mu}_e + \vec{\mu}_u) | \psi_e \psi_s \psi_u \rangle \]

\[ = \langle \psi_e | \psi_e \psi_u \rangle + \langle \psi_e | \psi_u \psi_e \rangle \]

\[ = \langle \psi_e | \psi_e \psi_u \rangle \langle \psi_u | \psi_e \psi_s \rangle < \psi_s | 1 \psi_s > \]

\[ + \langle \psi_e | \psi_e \psi_u \rangle \langle \psi_u | \psi_u \psi_s \rangle < \psi_s | 1 \psi_s > \]

One can always orthogonolize the electronic wave functions to make \( \langle \psi_e | \psi_e \rangle = 0 \)

\[ \tilde{M} = \langle \psi_e | \psi_e \psi_u \rangle \langle \psi_u | \psi_e \psi_s \rangle < \psi_s | 1 \psi_s > \]

orital selection rules

Franck-Condon spin selection factor rule

Approximations:

- Born-Oppenheimer approximation

- Neglect of spin-orbit coupling (terms of 3\textit{L} in the Hamiltonian)

Selection rules are not rigorous
Selection Rules:

A transition is spin-allowed if the spin multiplicities of the two states are identical, \( \Delta S = 0 \).

This is the strongest selection rule, spin-forbidden transitions result in lowest intensities in the electronic spectra.

Q: Are there any selection rules for the Franck-Condon factor?

**Scenario 1**

\[
\begin{align*}
A - B & \rightarrow A - B^* \\
\text{ground} & \quad \text{excited}
\end{align*}
\]

Assume that \( \text{re} = \text{re}^* \), the bond length is not affected by excitation.

\[
-E_0 + V^*(q) = V(q) = \frac{kq^2}{2}
\]

Since the potential energies for harmonic vibrations are shifted by a constant, the wave functions of vibrations are identical.

\[
\langle \psi_{v^*} | \psi_v \rangle = \delta_{v^*v}
\]
If $\hbar w \gg kT$, only ground vibrational state is occupied and one will observe only $0 \to 0$ transition.

**Scenario 2.**

\[
\begin{align*}
A & \quad B \\
\overline{r_e} & \rightarrow \\
A & \quad B^* \\
\overline{r_e^*}
\end{align*}
\]

$\overline{r_e} \neq \overline{r_e^*}$

The common situation is $\overline{r_e^*} - \overline{r_e} \approx 0.1 - 0.3 \text{ Å}$

Since harmonic oscillators are displaced,

\[
\langle \psi_{u'} | \psi_u \rangle \neq 0 \text{ for any } u^*, u
\]
**Franck-Condon principle**

**Q:** Can we say anything about the Franck-Condon factor $\langle \psi_u | \psi_v \rangle$?

**A:** 

An electron transition is so fast ($\approx 10^{-15}$ s) compared to the nuclear motion ($\approx 10^{-13}$ s) that the nuclei do not change their positions and momenta during the transition.

- The momentum is small at $q \approx 0$
- The momentum is still small at 1
- Transition to B involves change in momentum (2)
- Transition to C is forbidden by classical mechanics
Franck-Condon principle (consequence):

Vertical transition to a state closest to the turning point has the highest probability.

Turning point, $k = 0$

highest probability, highest intensity in the spectrum

Franck-Condon factor for harmonic vibrations

$$|<\psi_{v}\Psi_{0}|^2 = \frac{S^{v*}}{(v^*)!} e^{-S} \quad \text{Huang & Rhys, 1950}$$

$S = \frac{\lambda v}{\hbar w v}$ \quad \text{Huang-Rhys factor}

$\lambda v \quad \text{vibrational reorganization energy}$
\[ \lambda v = \frac{1}{2} k (\Delta q)^2 = \frac{1}{2} k (\Delta r_e)^2 \]  

harmonic potential energy to extend the bond length by \( \Delta r_e \)

\[ V(q) \]

\[ V^*(q) \]

absorption

emission

vertical transition

\[ \delta E_0 \]

\[ \lambda v \]

\[ \Delta q = \Delta r_e \]

In Franck-Condon approximation:

absorption energy: \( h\omega_{abs} = \Delta E_0 + \lambda v \)

emission energy: \( h\omega_{em} = \Delta E_0 - \lambda v \)

\[ h(\omega_{abs} - \omega_{em}) = h\Delta \omega_{st} = 2\lambda v \]

Stokes shift

\[ h\Delta \omega_{st} = 2\lambda v \]  

energy dissipated to heat in absorption/emission cycle