Electronic transitions.

Configuration of electronic states in molecules:

Ground state configuration and electronic excitations:

Pot. Energy profiles of the ground state configuration and excited states:

Selection rules for electronic transitions:

\[ g \leftrightarrow u, \quad g \leftrightarrow g, \quad u \leftrightarrow u; \]
\[ \Delta J = 0, \pm 1 \text{ but } J = 0 \leftrightarrow J = 0 \text{ and for } \Omega = 0 \rightarrow \Omega = 0, \quad \Delta J \neq 0 \]
\[ \Delta A = 0, \pm 1; \quad \Delta \Omega = 0, \pm 1; \]
\[ \Delta S = 0; \quad \Delta \Sigma = 0 \text{ (for weak spin–orbit coupling)} \]
\[ \Sigma^+ \leftrightarrow \Sigma^+, \quad \Sigma^- \leftrightarrow \Sigma^-, \quad \Sigma^+ \leftrightarrow \Sigma^- \].

Fig. 9.23. Some potential curves of the Li₂ molecule up to the ionization limit, including some doubly excited states (black dashed curves).
Vibronic transitions

- Each electronic level has a stack of vibrational levels associated with it - depending on the shape of the potential energy curve, there may be a large series of vibrational energy levels (deep minimum), very few vibrational levels (shallow minimum), or no vibrational levels (no minimum).

- Vibronic: transitions between two different vibrational states in two electronic states.

- Transition may involve also change in rotational state – rotovibronic transitions

- Progression: Set of all vibronic transitions from or into one same vibronic state.

- There are no selection rules for rotovibronic transitions. So, every vibronic state can be final/initial state. The intensity depend on their wave-function matching: The Franck-Condon principle

- Absorption spectrum of benzene (arising predominantly from $\pi-\pi^*$ transitions from C=C bonds). Typically only a broad peak is observed. Under certain circumstances, the vibrational structure can be resolved
Rotovibrational transitions in electronic spectra.

- Selection rules for transitions between rotovibronic states:
  \[ \Delta v = \pm 1, \pm 2, \pm 3, \ldots \]
  \[ \Delta J = \pm 1 \]
  \[ \Delta J = 0; \text{ now allowed if } \Delta \Lambda = \pm 1 \]

- Besides P and R branches, now Q branches are also observable.
- Constants B and D may differ a lot in each electronic state. Generally, if \( R^* > R_e \) (the normal case) the constants are smaller in the excited state \( \Rightarrow \) red shift of the branches.

![Red shift and Blue shift diagrams](image)

- Why is it interesting?
  - Knowledge on rotational and centrifugal constants
  - Knowledge on excited state Pot. Energy surfaces
  - Does the molecule compress or stretch on excited states?
  - Rotational information of non-polar molecules.
Vibronic transitions and the Franck-Condon principle

- The nuclear conformation is rearranged after an electronic transition occurs, and not during the excitation process itself.
- If excited state Potential Energy curve differs from ground state (i.e. equilibrium atomic positions differ) then after electronic excitation, nuclei remain in same position $R_e$, but now in a vibrationally excited state.
- The wave function overlap vibronic states (combined electronic and vibrational wave functions) dictates the transition probability. This is the Franck-Condon factor:

$$\text{FCF}(v_i, v_k) = \left| \int \psi_{\text{vib}}^{v_i}(R) \cdot \psi_{\text{vib}}^{v_k}(R) dR \right|^2$$

- The maximum transition probability occur for two vibrational states connected through **vertical transitions**.
- In the excited state a vertical transition implies that the vibrational state excited upon electronic excitation is that for which the ground state equilibrium position $R_e$ is at its classical turning point (in a classical way of thinking), or where the wave function amplitude near it has its maximum (in a quantum way of thinking).

- No change in $E_{\text{POT}}$
- Final electronic state leaves nuclei in vibrational excitation
- The larger the change in molecular conformation, the intensity of vibronic peaks become more pronounced