The expression of the transition dipole moment implies that each of its 3 terms has to be non-zero. These conditions are at the basis of selection rules for light absorption.

\[ m_{1\rightarrow 0} = \langle \psi_1 \bar{R} \psi_0 \rangle = \langle \phi_1 \bar{R} \phi_0 \rangle \cdot \langle S_1 \mid S_0 \rangle \cdot \langle \eta_1 \mid \eta_0 \rangle \neq 0 \]

**Symmetry-forbidden transitions**

\( \langle \phi_1 \bar{R} \phi_0 \rangle \neq 0 \) means the symmetry of occupied orbitals must be conserved during the transition.

Example: formaldehyde

The nuclear frame of the molecule belongs to the point group \( C_{2v} \), whose symmetry elements include identity \( I \), a 2-fold rotation axis \( C_2 \) and two planes of symmetry \( \sigma(xy) \) and \( \sigma'(yz) \) crossing along the \( C_2 \) axis.

**Born-Oppenheimer approximation:**
Nuclei do not move during the transition. Only electrons configuration is affected. Point group, thus, remains unchanged.

The \( C_{2v} \) character table

<table>
<thead>
<tr>
<th>( C_{2v} )</th>
<th>( l )</th>
<th>( C_2 )</th>
<th>( \sigma_{e}(xy) )</th>
<th>( \sigma_{g}(yz) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>( B_1 )</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>( B_2 )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

The \( \pi \) orbital is antisymmetric with respect to rotation about \( C_2 \) axis, to reflection in the \( \sigma'(yz) \) plane, but is symmetric with respect to reflection in the \( \sigma(xy) \) vertical plane. It has therefore the symmetry properties of the \( b_1 \) species (small cases are used conventionally for orbitals).

Same considerations show that the \( \pi^* \) antibonding orbital also transforms as \( b_1 \), while the \( n \) nonbonding orbital has the symmetry properties of \( b_2 \) species.

\[ \pi \rightarrow b_1 \]
\[ n \rightarrow b_2 \]
\[ \pi^* \rightarrow b_1 \]
Electronic structure

<table>
<thead>
<tr>
<th>State</th>
<th>Symmetry properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>ground state $\pi^2 n^2 \pi^0$</td>
<td>$\pi$ $b_1$</td>
</tr>
<tr>
<td>$n-\pi^<em>$ excited state $\pi^2 n^1 \pi^</em>$</td>
<td>$n$ $b_2$</td>
</tr>
<tr>
<td>$\pi-\pi^<em>$ excited state $\pi^1 n^2 \pi^</em>$</td>
<td>$\pi^*$ $b_1$</td>
</tr>
</tbody>
</table>

Considering the irreducible representation for each electron, global symmetries of the three different states are:

- **ground state**: $b_1 \times b_1 \times n^1 = a_1$
- **$n-\pi^*$ excited state**: $b_2 \times b_2 \times b_1 = a_2$
- **$\pi-\pi^*$ excited state**: $b_1 \times n^2 \times b_1 = a_1$

The nuclear frame of benzene belongs to the point group $D_{6h}$.
Symmetry elements include in particular a third order rotation axis, perpendicular to the ring plane.

Among $\pi$ and $\pi^*$ orbitals, only $\pi_1$ and $\pi_6^*$ are symmetric with respect to the $C_3$ rotation axis.

HOMO-LUMO transitions $\pi_2-\pi_4^*$ or $\pi_3-\pi_5^*$, for instance, are thus symmetry-forbidden and are characterized by a rather weak $\epsilon$ value ($\sim 200 \text{ mol}^{-1} \text{ cm}^{-1}$). The first symmetry-allowed transition of benzene is then $\pi_1-\pi_6^*$, which would take place at a much higher energy.
**Case of transition metal complexes**

The Laporte rule is a spectroscopic selection rule named after Otto Laporte (1902-1971). It is relevant in particular to the electronic spectroscopy of transition metals. Laporte's rule states that electronic transitions conserving either symmetry or anti-symmetry with respect to an inversion center \( g \rightarrow g \) (gerade) or \( u \rightarrow u \) (ungerade) are forbidden.

In other words, if a molecule has a center of symmetry, transitions within a given set of \( p \) or \( d \) orbitals (i.e. those which only involve a redistribution of electrons within a given subshell) are forbidden.

\[
\begin{align*}
  p & \not\rightarrow p \\
  d & \not\rightarrow d
\end{align*}
\]

**Vibronic coupling**

If the Born-Oppenheimer assumption is not verified, electronic and nuclear movements are coupled. This vibronic coupling can be treated as a perturbation of the Hamiltonian of the excited state:

\[
\hat{H} = \hat{H}^0 + \hat{H}'
\]

perturbation term

This yields a new expression of the transition dipole moment:

\[
m_{i\rightarrow0} = \langle \psi_i^0, \hat{R}, \psi_0^0 \rangle = \langle \psi_i^0, \hat{R}, \psi_0^0 \rangle + \sum_i a_i \langle \psi_i^0, \hat{R}, \psi_i^0 \rangle
\]

where:

\[
a_i = \frac{\langle \psi_i^0, \hat{H}', \psi_i^0 \rangle}{E_i^0 - E_i^0}
\]

In such conditions, a formally symmetry-forbidden transition, with \( \langle \psi_i^0, \hat{R}, \psi_0^0 \rangle = 0 \), can still yield a significant \( m_{i\rightarrow0} \) value, provided a coupling exists between the excited state wave function \( \psi_i^0 \) and that of another state \( \psi_i^0 \) and the energy difference \( E_i^0 - E_i^0 \) is small enough.

In this case, one says that the forbidden \( 1 \leftarrow 0 \) transition "borrows" some intensity from the \( i \leftarrow 0 \) transition.
Vibronic coupling in \(n \rightarrow \pi^*\) transitions

In the example of formaldehyde, the \(n-\pi^*\) transition was found to be symmetry-forbidden (p.32). Hence, \(\langle \psi_i^0 | R | \psi_0^0 \rangle = 0\).

The condition for the transition dipole moment to be non-zero is therefore:

\[
m_{1-0} = \sum_{i} a_i \langle \psi_i^0 | R | \psi_i^0 \rangle \neq 0
\]

Here, the role of the \(\psi_i^0\) state is played by the \(\sigma^*\) molecular orbital. Bending of the molecule out of the \(yz\) plane during a vibration causes the vibronic coupling between \(\pi^*\) and \(\sigma^*\) orbitals, whose respective \(b_l\) and \(a_l\) symmetries are compatible.

Although both \(n-\pi^*\) and \(n-\sigma^*\) transitions are symmetry forbidden, this \(\pi^*,\sigma^*\) coupling allows the \(n-\pi^*\) transition to "borrow" some intensity, typically yielding an oscillating strength \(f_{\pi^*,n} = 2 \cdot 10^{-4}\).

---

**Frank-Condon principle**

Electronic transitions take place typically on time frames of \(10^{-16} - 10^{-15}\) s (0.1-1 fs). Nuclei, however, move much slower, within the 10-1000 fs timescale and can be considered as immobile during an electronic transition.

The probability of a transition depends on the nuclear wave-functions overlap integral squared.

\[
f_{1,0} \propto m_{10}^2 \propto \langle \eta_1 | \eta_0 \rangle^2
\]

\(\langle \eta_1 | \eta_0 \rangle^2\) Frank-Condon factor

The intensity of a "vertical" transition thus depends upon the overlap of vibrational wave-functions.
Spin-forbidden transitions

Electron has an intrinsic angular momentum, independent of its orbit angular momentum. The intrinsic angular momentum quantum number is called the electron spin. Its value can be either $s = +\frac{1}{2}$ or $s = -\frac{1}{2}$. A molecule containing $i$ electrons is then characterized by a total spin $S = \sum_i s_i$.

The spin multiplicity $M$ is the number of possible orientations, calculated as $M = 2S + 1$, of the spin angular momentum corresponding to a given $S$ value.

Spin conservation rule (Wigner rule)

$$M_{i \to 0} \propto \langle S_i | S_0 \rangle \neq 0$$

Both radiative and non-radiative transitions between terms of the same spin multiplicity $M$ are allowed, while transitions between terms of different multiplicity are spin-forbidden.

Physically, this corresponds to a magnetic momentum conservation rule (no magnetic momentum is carried by a photon).
Spin-orbit coupling

Interaction of the intrinsic angular momentum of an electron with the magnetic field $\vec{B}$ induced by the movement of other electrons on large atomic orbits (heavy atoms) as well as delocalized electrons on aromatic rings can cause spin degeneracy.

Partial allowance of a formally spin-forbidden transition can then result from this spin-orbit coupling. The oscillating strength remains, however, extremely weak, with typically $f = 2 \cdot 10^{-7}$. 