Electronic Spectroscopy

The Morse Curve is often used to represent the potential energy surface of an electronic state of a molecule. Strictly speaking, this can only be applied to a diatomic molecule, but it is a useful approximation for more complex systems.

![Morse Curve Diagram]

Franck-Condon Principle. Electronic transitions are vertical, i.e. nuclear positions are unchanged during the time (~10^{-15} s) of an electronic transition..

The electronic ground state has vibrational states, \( v_0, v_1, v_2, \ldots \). The excited state has vibrational states \( v_0', v_1', v_2', \ldots \).
There are no restrictions on change of vibrational state accompanying an electronic transition.

The most probable internuclear distance for a given vibrational state is given by the square of the vibrational wave-function. For $v_0$ the most probable internuclear distance is $r_e$. For higher vibrational states the most probable internuclear distances are the extrema of the vibration.

For some electronic transitions the values of $r_e$ and $r_e'$ may be different and most intense transition could be from $v_0$ to higher vibrational states of the electronic excited state, see Figure.

Illustration of Franck-Condon transitions for cases where $r_e$ for the excited state is the same (a) or different (b). Probability distributions for vibrational states are shown.
As for vibrational spectroscopy there are selection rules for electronic transitions that are determined by symmetry. These can be deduced from the transition moment integral

\[ \langle \psi_{gd} M \psi_{ex} \rangle \]

where \( M \) is the dipole operator and the \( \psi \)'s are the appropriate molecular wave-functions.

The majority of organic molecules have fully occupied or fully unoccupied molecular orbitals. They are diamagnetic and the ground state wave-function is \( A_1 \) (or the appropriate symbol for the totally symmetric representation of the molecule’s point group.) Excitation of an electron from an occupied to an unoccupied orbital can be loosely described in terms such as

\[
\begin{align*}
  n &\rightarrow \pi^* \\
n &\rightarrow \sigma^* \\
\pi &\rightarrow \pi^* \\
\sigma &\rightarrow \sigma^*
\end{align*}
\]

The energy separation between \( \sigma \) and \( \sigma^* \) orbitals is generally so large as to place such transitions in the far UV region, and these are not easily observed.
In general the energy separation between the molecular *orbitals* is not the same as the energy separation between the molecular *states*, because of different electron-electron repulsions between full and partially-full orbitals.

[Diagram of orbital occupancies and energy states]
Consider the molecular orbitals of the simple carbonyl group in formaldehyde. There are the bonding and anti-bonding $\sigma$ and $\pi$ orbitals and two kinds of non-bonding electron pairs on the oxygen ($p_x$ and $p_y$ -like orbitals — molecule is assumed to lie in yz-plane).

In $C_{2v}$ we can show that these mo’s transform as the following representations

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_{(xz)}$</th>
<th>$\sigma'_{(yz)}$</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>

$n(p_y)$ .... $B_2$
$n(p_x)$ .... $A_1$
$\sigma$ ....... $A_1$
$\sigma^*$ ...... $A_1$
$\pi$ ....... $B_1$
$\pi^*$ ...... $B_1$

Convention : lower case letters for orbitals, capital letters for states.
Ground state *configuration* for formaldehyde

\[ a_1^2b_1^2a_1^2b_2^2b_1^0a_1^0 \] (corresponds to a state of \( A_1 \) symmetry)

After an \( n \rightarrow \pi^* \) transition, the excited state *configuration* is

\[ a_1^2b_1^2a_1^2b_2^1b_1^1a_1^0 \]

The symmetry of the excited state is determined by taking the direct product of the representations of the two half-filled orbitals,

i.e. \( B_2 \times B_1 = A_2 \)

Transition is represented as \( ^1A_2 \leftarrow ^1A_1 \)

[Note convention indicating spin multiplicity and of placing the excited state first.]

Since \( A_2 \) does not transform as \( x, y, \) or \( z \) in \( C_{2v} \), this transition is not dipole-allowed

The \( \pi \rightarrow \pi^* \) transition corresponds to state of \( B_1 \times B_1 = A_1 \) symmetry, and *is* dipole-allowed.
The UV spectrum of formaldehyde shows a weak band (\( \varepsilon = 100 \)) at 270 nm and a very intense band at 185 nm. These are currently attributed to the \( n \to \pi^* \) and \( \pi \to \pi^* \) transitions respectively.

Other evidence in favor of this assignment

\( n \to \pi^* \) transitions undergo a blue shift in polar or H-bonding solvents. Two factors – ground state is lowered by favorable solvation of polar group \( C^\delta+O^\delta- \). Excited state is elevated because the solvent molecules cannot orient fast enough to accommodate \( C^\delta-O^\delta+ \).

\( n \to \pi^* \) bands may disappear upon protonation
Bands also undergo blue shifts when electron donating group is attached to the CO chromophore,

cf MeC(O)H < MeC(O)OMe < MeC(O)NMe\(_2\)