cold fusion
These 2 MOs have same energy in BENZENE.

Why is this orbital lower in Pyrazine?

Homo

Homo-1 “non-bonding”

Homo-2

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Why is this orbital lower in Pyrazine?
molecule in terms of a simple Born-Oppenheimer state function which assumes the separability of the electronic and nuclear motions (12)

\[ \psi(q,Q) = \psi_e(q,Q)\psi_v(Q) \]  

(1)

The vibrational state function, \( \psi_v \), depends only upon nuclear coordinates, \( Q \), whereas the electronic state function, \( \psi_e \), depends on electronic coordinates, \( q \), and parametrically on the nuclear coordinates. The independence of the electronic and nuclear motions implies that the electronic energy, \( E_e \), and the vibrational energy, \( E_v \), will simply add to give the total energy of a particular vibronic state

\[ E = E_e + E_v \]  

(2)

Each of the \( 3N - 6 \) vibrations in a polyatomic molecule may be described in terms of displacements along normal coordinates of the molecule. It is found that for a single vibrational mode, each atom in the molecule
Born-Oppenheimer wave functions for the ground ($\psi''$) and excited ($\psi'$) states

$$P \propto \left[ \int_{-\infty}^{\infty} \psi_e'(q,\bar{Q}) \hat{M}(q) \psi_e''(q,\bar{Q}) \, dq \int_{-\infty}^{\infty} \psi_{v_m'}(Q) \psi''_{v_n''}(Q) \, dQ \right]^2$$

(9)

where $\hat{M}(q)$ is the transition moment operator. The first integral, called the electronic transition moment integral, is evaluated at the average value of the nuclear coordinates, $\bar{Q}$, and determines the transition probability between electronic states $\psi_e'$ and $\psi_e''$. The second integral is called the Franck-Condon overlap integral and determines the probability that the transition will be allowed for a given electronic state. Therefore, the overall probability of the transition is given by the square of the integral of the product of the electronic wave functions and the transition moment operator.
“Vibronic” transitions from absorbing photon

0 Kelvin

Possible Transitions

Vibrational wave functions

No bond length change

Large bond length change

Two actual cases

Relative intensities of vibrations are determined by the square of the overlap integral. The overlap is shown visually.
Figure 4. Vibronic spectra of pyrazine: (a) vapor, (b) in cyclohexane, and (c) in methanol.
λ is the "spring energy" (in units of cm) caused by the sudden change in potential due to electronic transition.

More precisely $\frac{f_{0\rightarrow v'}}{f_{0\rightarrow v'-1}} = \frac{\lambda'}{\lambda'} = \frac{(V'-1)!}{\lambda'!}$

So ratio of $0\rightarrow 1$ to $0\rightarrow 0 = \lambda$

and $f_{0\rightarrow v'} = f_{0\rightarrow v1}$ for $v' = \lambda$

Page 8 (last) same as p.6 of old notes #4
Figure 1. Vibronic transitions and schematic bands. The $1'' \leftarrow 0''$ infrared transition is shown for comparison.
<table>
<thead>
<tr>
<th>Type</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>Pure electronic transition</td>
<td>Progression in one vibrational frequency characteristic of excited electronic state. Found to high energy side of ((0' \leftarrow 0'')).</td>
</tr>
<tr>
<td>Combination band. Simultaneous excitation of two vibrational modes, each independently.</td>
<td>Hot band progression in ground state vibrational frequency of the (j)th mode. Found to low energy side of ((0' \leftarrow 0'')).</td>
</tr>
<tr>
<td>Difference band. Transition within a vibrationally excited molecule in which there is no change in (v). Separation from ((0' \leftarrow 0'')) band depends on ((\tilde{v}' - \tilde{v}'')). See eqn. (7).</td>
<td>Progessions in an excited state frequency in combination with another excited state vibration arising from a ground state molecule having one vibration excited by one quantum.</td>
</tr>
</tbody>
</table>

**Example Image**: Vibronic transitions and schematic bands. The \(1'' \leftarrow 0''\) transition is shown for comparison.
Normal Modes of Vibration
moves in a definite phase relationship to every other atom, and that this complex motion is described by a single frequency (13). Three of the modes active in the lowest electronic transition of pyrazine are shown below with their vibrational frequencies in the ground ($\tilde{v}''$) and excited ($\tilde{v}'$) electronic states (14, 15).

![Pyrazine molecule diagrams](image)

really?

$\tilde{v}'' = 596 \text{ cm}^{-1}$  \hspace{1cm} $\tilde{v}'' = 1230 \text{ cm}^{-1}$  \hspace{1cm} $\tilde{v}'' = 919 \text{ cm}^{-1}$

CC in plane  \hspace{1cm} CH in plane  \hspace{1cm} CH out of plane

The vibrational energy states for each of these complicated modes are found to be nearly equally spaced, and so may be described by the same simple one-dimensional harmonic oscillator expression that is used for diatomic molecules (11). Hence for the $n$th vibrational mode

$$E_{vn} = \left(v_n + \frac{1}{2}\right) \hbar \nu_n$$

where $v_n = 0, 1, 2, 3, \ldots$