Photoelectron Spectroscopy

- Empirically determine a.o. energies for use in M.O. theory
  
  Verify predictions of M.O. theory by measuring a.o. energies.

Physical Principle

Lennard-Jones/Morse potential to describe energy of bond (or collection of bonds) distortion(s).

\[ V_L = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \]

- \( \varepsilon \) = depth of potential well
- \( \sigma \) = \( r \) for which \( V_L = 0 \).
- \( r \) = bond length, nuclear coordinates, etc.

\[ M + h\nu \rightarrow M^+ + e^- \]

\[ h\nu = IE_n + \frac{1}{2} m v_e^2 \]

For a given \( e \)-configuration, approximate by harmonic/parabolic potential.

\[ V_n = \left( n + \frac{1}{2} \right) \hbar \omega \]

\[ \omega = \frac{1}{2\hbar} \sqrt{\frac{k}{m}} \]

* In actually, shape of potential well is not perfectly symmetric, has anharmonicity.

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

\[ E_0 = \left( 1 + \frac{1}{2} \right) \hbar \omega \]

+ higher terms.
Three possibilities in PES (as far as we are concerned)

1) No change in bond order (upon ionization) (\(e^-\) taken from non-bonding m.o.)
   
   Adiabatic transition: no change in nuclear coordinates, observe \(n\rightarrow n'\) transition.
   
   \(\text{Quantum vibrational probabilities.}\)
   
   \(\text{PES spectrum}\)

2) Increasing bond order (upon ionization) (\(e^-\) taken from anti-bonding m.o.).
   
   Vertical transition: because electrons are very fast (faster than nuclei, as per the Born-Oppenheimer approximation), transitions are straight up, no change in \(r\), or nuclear coordinates.
   
   \(\text{Several peaks, primary peak } \neq \text{IE. Shape of multiplet determined by shape of potential wells, shift in } r, \text{ others.}\)
   
   \(\text{PES spectrum}\)

3) Decreasing bond order (upon ionization) (\(e^-\) taken from bonding m.o.).
   
   as above, only vertical transitions observed, giving multiplet of peaks.
   
   For most cases, particularly harmonic potentials, cannot readily distinguish between multiplets from bonding vs. anti-bonding m.o.'s. Very detailed modeling, taking into account anharmonicity could help, but beyond the scope of this course.
(4.) Special case for paramagnetic molecules, i.e. unpaired e.

For O₂:

\[
\begin{align*}
\frac{1}{1\pi^*} & \quad \text{unpaired e.} \\
1\pi_u & \\
1\pi_g & \\
2\sigma_g & \\
1\nu & \\
10\nu^* & \\
10\nu & \\
10\pi & \\
\end{align*}
\]

→ para magnetic, unpaired e.

Ideal, perfectly resolved spectrum.

electron spin-spin coupling splits the PES multiplet, for all e⁻ (in theory).
Molecular Orbital Theory

- Mix atomic orbitals from different atoms (compare to VBT, same atom) to get bonding (stabilized) and antibonding (destabilized) orbitals.

\[ \text{build up of } e^- \text{ density between} \]
\[ \text{node, depletion of } e^- \text{ density between nuclei.} \]
\( \text{(add symmetry matched orbitals)} \)

- Can also combine m.o.'s w/ each other. (for more complicated molecules coming next week).

- Energies and spatial distribution of resulting m.o.'s predict chemical properties, (i.e. reactivity, magnetism, spectra, etc.).

Orbital Interaction Diagram

1) Plot energy level of a.o.'s (or fragment m.o.'s).
   - From PES (directly for a.o.'s)
   - From CTO (indirectly for fragment m.o.'s).

2) Determine which orbitals will m.i.p.
   - Energies \( \leq 15 \text{eV} \)
   - Same symmetry.

3) Determine magnitude of interaction:
   - Overlap (shape of orbital, nuclear distance)
   - Energy difference

4) Plot MOs and draw resulting orbital shapes.
   - For every orbital pair, get one bonding and one antibonding m.o.

5) Fill in \( \psi \) electrons (Aufbau principle).
Generally: Energy matching

Strong covalent bond  polar-covalent  ionic, non-bonding

Overlap

Maximum  Small  Medium  Small

* delta bond (d-d overlap) smallest.

See slides for depiction of possible bonding combinations.
Example: $NF, \, NF^+, \, NF^-$

1) $2s(N) = -25.6 \, ev \quad 2s(F) = -40.2 \, ev$
   $2p(N) = -18.2 \, ev \quad 2p(F) = -18.6 \, ev$

2) $\bigcirc \bigcirc \bigcirc \bigcirc \bigcirc$
   $S-S(\odot) \quad P-P(\odot)$
   $x^2$
   $P-P(\odot)$
   $\odot \odot \odot$ $\odot \odot \odot$
   all energies within $\pm 15 \, ev$ from each other. $S-S, \, P-P$ and $SP$ mixing.

3) $F$ $n$ $NF$

First consider
no mixing of $S-P$.

Then mix $S-P$ m.o.'s.
Bond orders: \( \text{NF}^+ : \frac{5}{2} \)  
\( \text{NF} : \frac{3}{2} \)  
\( \text{NF}^- : \frac{1}{2} \)  
\( \frac{8 \text{ bonding } \pi - 3 \text{ anti-bonding } \pi}{2} \)  
\( \bar{I} \)  
\( \text{filled } 1\pi^g + 1\sigma^* \)  
\( \text{gives net B.O. } = 0 \).

Para magnetism? All exhibit paramagnetism (unpaired \( \pi^- \)).

Is splits each peak in the paramagnetic PES, except for \( 1\sigma^g \).

In NF, NF\(^+\), \( 1\pi_g^* \) will split in NF\(^-\).

\[ \begin{array}{c}
1\pi_g^* \\
2\sigma_g \\
1\pi_m \\
1\sigma^* \\
1\pi_g \\
1\sigma^* \\
\end{array} \]

\[ \begin{array}{c}
\text{slightly bonding} \\
(\text{non-bonding}) \\
\text{slightly anti-bonding} \\
(\text{non-bonding}) \\
\end{array} \]