Chemistry 2000 Slide Set 4: Molecular spectroscopy of diatomic molecules

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Evidence for MO theory

How do we know that MO theory is correct?

Equilibrium bond lengths:
- X-ray or neutron diffraction for solids
- Rotational (microwave) or vibrational (infrared) spectroscopy for gases

Potential energy curve/surface:
- Vibrational (infrared) spectroscopy

Orbital energy diagram:
- Photoelectron spectroscopy
- Electronic absorption (UV/visible) spectroscopy
- Fluorescence spectroscopy
The shape of the effective potential implies that a molecule below its dissociation energy vibrates, i.e. a diatomic molecule behaves like two balls connected by a spring.
Vibrational energy is quantized, i.e. only certain vibrational energies are allowed:
The effective potential: interpretation

- Nuclear-nuclear repulsion
- Long-range attraction due to electron-nucleus interaction
- Zero-point energy
- Dissociation energy

$V_{\text{eff}} = \text{bond length}$

$R_{\text{eq}}$
Vibrational levels

Stronger bond $\leftrightarrow$ narrower potential well $\leftrightarrow$ larger vibrational spacing
Heteronuclear diatomics can absorb photons to undergo vibrational transitions. Homonuclear diatomics cannot make a vibrational transition by absorbing a single photon. (The basis for this rule will be seen later.)

At room temperature, almost all molecules are in the ground vibrational state.

By far the most likely process is the absorption of a photon to go from the ground state to the first excited vibrational state.

Vibrational energy spacings correspond to the infrared region of the electromagnetic spectrum.
Infrared (vibrational) spectroscopy

\[ \Delta E_{\text{vib}} = h\nu \sim \text{infrared} \]
IR spectroscopy gives us information about the strength of a chemical bond:
Stronger bond $\leftrightarrow$ higher-energy (shorter wavelength) IR absorption

The strength of the bond and spacing between vibrational levels are connected to the shape of the potential energy curve near the equilibrium bond length.
The energy of a photon is given by

\[ E = h\nu = \frac{hc}{\lambda} \]

SI units of \( E \):
- Units of \( \nu \):
- Units of \( \lambda \):

Photon energies are sometimes given in electron-volts (eV):

\[ 1\text{ eV} = 1.602176634 \times 10^{-19}\text{ J} \]
Units in spectroscopy

Wavenumbers

- If we define the wavenumber $\tilde{\nu} = 1/\lambda$,

$$E = h c \tilde{\nu}$$

- $\tilde{\nu}$ is often expressed in cm$^{-1}$.
- $\tilde{\nu}$ is often casually referred to as a frequency, to which wavenumber is proportional:

$$\nu = c \tilde{\nu}$$
How do we know that the orbital occupancies predicted by MO theory are correct?

Photoelectron spectroscopy is similar in principle to the analysis of the photoelectric effect.

An atom or molecule is ionized using a photon of energy $h\nu$.

The maximum kinetic energy of the ejected electron is then

$$K_{\text{max}} = h\nu - I_i$$

where $I_i$ is the ionization energy of an electron in orbital $i$.

Note: The notation for ionization energy differs from that used in Chem 1000.

The ionization energy of an electron in a particular orbital is the negative of its orbital energy ($\varepsilon_i$).

We measure $K$ and calculate the orbital energy of occupied orbitals:

$$-I_i = \varepsilon_i = K_{\text{max}} - h\nu$$
Removing a *valence* electron typically requires a photon in the *ultraviolet* range.

Removing a *core* electron typically requires an *x-ray* photon.
Example: Photoelectron spectrum of Ne

$h\nu = 60 \text{ eV}$

Orbital energy level diagram? Rotate clockwise!
A complication

- For **molecules**, the ion formed also has vibrational levels.
- As a result, the photoelectron spectrum typically has vibrational substructure:
Instead of one ionization energy, the photoelectron spectrum gives us a band of several lines corresponding to the ionization of an electron from a particular orbital.

The photoelectron spectrum thus allows us to recover the vibrational spectrum of the ion formed.
We compare the vibrational spectrum of the molecule to that of the ion.

The way in which the vibrational spectrum changed tells us how the potential energy curve changed, and thus how the bonding changed.

This can be correlated to the MO diagram:

- Removing an electron from an orbital not directly involved in bonding (e.g. the $1\pi$ orbital in HF) won't change the vibrational spectrum much.
- Removing an electron from a bonding orbital will lead to a weaker bond in the ion, thus to lower vibrational frequencies for the associated normal mode(s) than in the parent molecule.
- Removing an electron from an antibonding orbital...
Example: UV photoelectron spectrum of N$_2$

Note: The vibrational “frequency” of N$_2$ is 2358 cm$^{-1}$. 
Additional hints for interpreting photoelectron spectra

- Orbitals that are strongly bonding/antibonding will produce a number of lines. (See the $1\pi$ orbital in the photoelectron spectrum of N$_2$.)
- A strictly nonbonding orbital would produce exactly one line.
- Orbitals that are weakly bonding/antibonding tend to produce a small number of lines, often with the line at lower ionization energy being much more intense.

![Photoelectron spectrum diagram]
Example: UV photoelectron spectrum of CO

Note: The vibrational frequency of CO is $2170 \text{ cm}^{-1}$. 

\[ 1662 \text{ cm}^{-1} \quad 2\sigma \]

\[ 1636 \text{ cm}^{-1} \quad 1\pi \]