Chemistry 2000 Lecture 4:
Molecular spectroscopy of diatomic molecules

Marc R. Roussel

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

$V_{\text{eff}}$ vs $R$

$R_{\text{eq}}$ = bond length
Vibrational levels

Stronger bond $\leftrightarrow$ narrower potential well
$\leftrightarrow$ larger vibrational spacing
We are going to need to be able to decide what is a “large” and what is a “small” gap in energy.

$k_B T$ gives us this yardstick.

$k_B$ is Boltzmann’s constant.

$k_B = \frac{R}{N_A} = 1.3806504 \times 10^{-23} \text{ J/K}$

$T$ is the absolute temperature.

$k_B T$ is a measure of the average thermal energy of particles in a material.

Near room temperature, $k_B T \approx 4 \times 10^{-21} \text{ J}$. 
Suppose we have two energy levels separated by $\Delta \epsilon$.

If $\Delta \epsilon \gg k_B T$, then only the lower energy level will be populated because the average energy of the system isn’t enough to let the system access the higher level.

Otherwise, there will be some molecules in the higher energy level, moreso the smaller $\Delta \epsilon$ is compared to $k_B T$. 
Typical relationship of vibrational and rotational spacing to $k_B T$

- **Ground vibrational state, no rotation**
- **1st excited vibrational state, no rotation**
- **Rotational levels**
Under some circumstances (to be discussed later), molecules can absorb a photon and be excited from (usually) the ground vibrational state to (usually) the first excited vibrational state.

Vibrational energy spacings correspond to the infrared region of the electromagnetic spectrum.
In the gas phase, we get a combination of rotational and vibrational excitation, so we get bond length information as well.

Example: Gas-phase IR spectrum of HCl:

Note: \( \tilde{\nu} \) is the wavenumber, i.e. the inverse of the wavelength, so it’s proportional to the photon energy and to its frequency.
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: This notation 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

\[ h\nu = 60 \text{ eV} \]

2s, 2p

MO 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.

\[ \Delta E_{\text{vib}}(X_2^+) \]

"ionization energy": \( X_2 \) produced in its vibrational ground state

• 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 \( \text{N}_2 \)

Note: The vibrational “frequency” of \( \text{N}_2 \) is 2358 cm\(^{-1}\).
Example: UV photoelectron spectrum of CO

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