

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

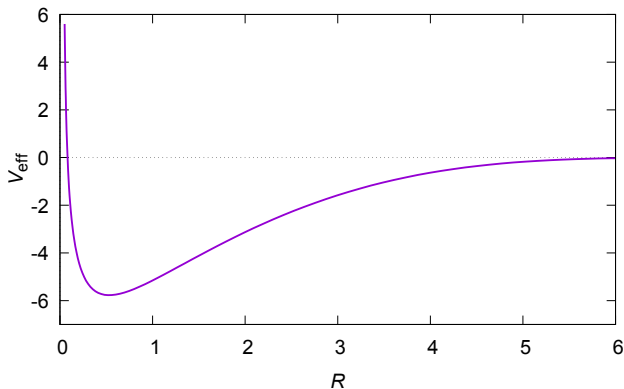
Potential energy curve/surface:

- **Vibrational (infrared) spectroscopy**

Orbital energy diagram:

- **Photoelectron spectroscopy**
- Electronic absorption (UV/visible) spectroscopy
- Fluorescence spectroscopy

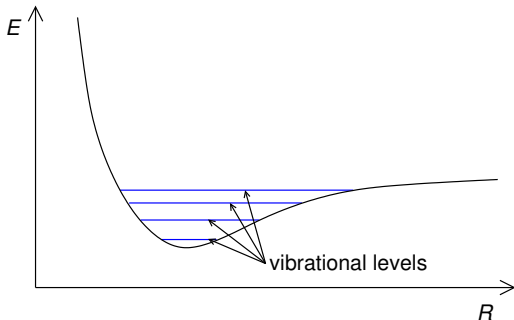
The effective potential



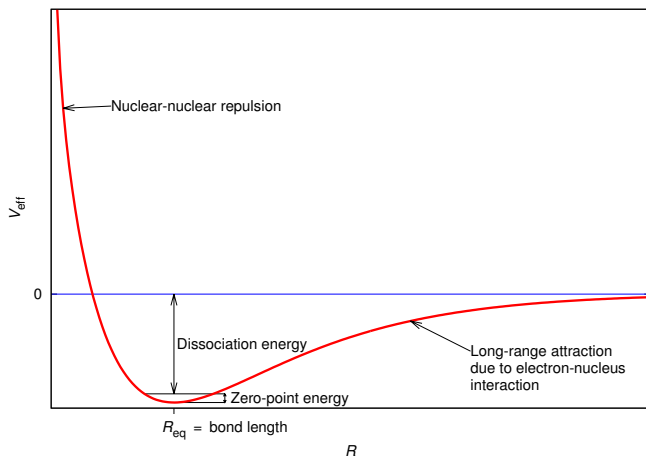
- The shape of the effective potential implies that a molecule below its dissociation energy vibrates, i.e. a diatomic molecule behaves like two balls connected by a spring.

Quantization of vibrational energy

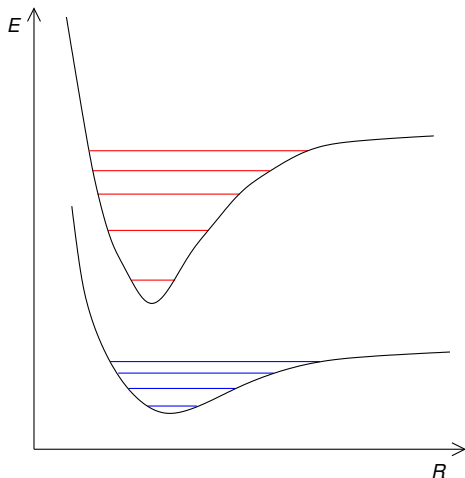
- Vibrational energy is **quantized**, i.e. only certain vibrational energies are allowed:



The effective potential: interpretation



Vibrational levels

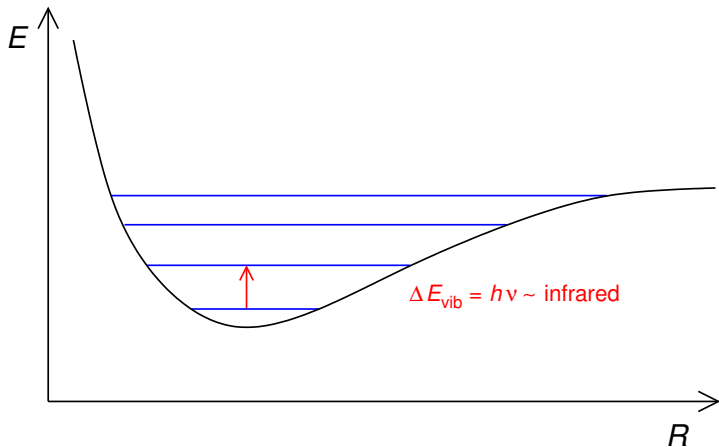


Stronger bond \longleftrightarrow narrower potential well \longleftrightarrow larger vibrational spacing

Infrared (vibrational) spectroscopy

- **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



Summary of IR spectroscopy

- IR spectroscopy gives us information about the strength of a chemical bond:
Stronger bond \longleftrightarrow 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.

Units in spectroscopy

- The energy of a photon is given by

$$E = h\nu = \frac{hc}{\lambda}$$

SI units of E :

Units of ν :

Units of λ :

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

$$1 \text{ eV} = 1.602\,176\,634 \times 10^{-19} \text{ J}$$

Units in spectroscopy

Wavenumbers

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

$$E = hc\tilde{\nu}$$

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

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

Photoelectron spectroscopy

- 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

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

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.

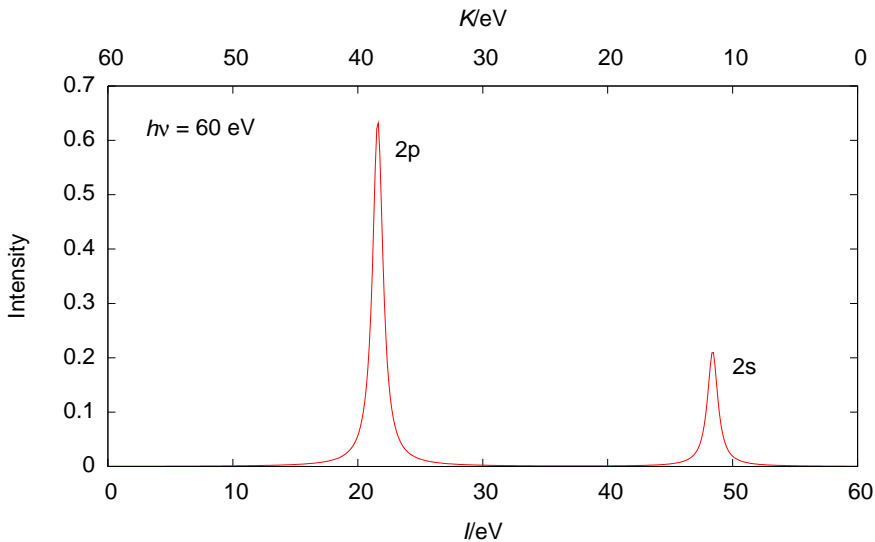
- The ionization energy of an electron in a particular orbital is the negative of its orbital energy (ε_i).
- We measure K and calculate the orbital energy of **occupied orbitals**:

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

Photoelectron spectroscopy (continued)

- Removing a **valence** electron typically requires a photon in the **ultraviolet** range.
- Removing a **core** electron typically requires an **x-ray** photon.

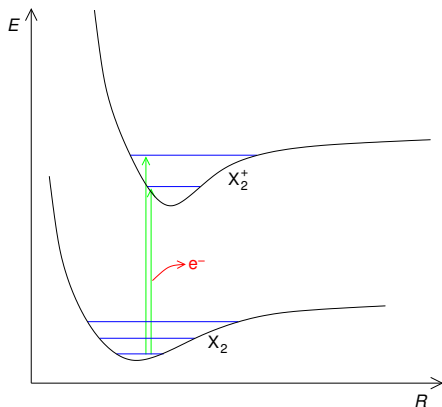
Example: Photoelectron spectrum of Ne



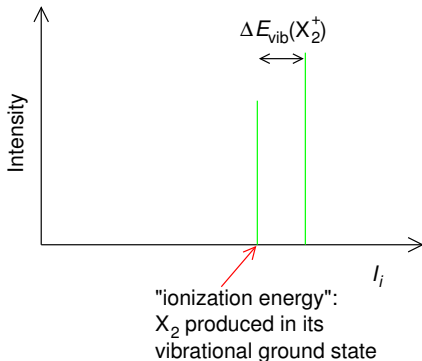
Orbital energy level diagram? Rotate clockwise!

A complication

- For **molecules**, the ion formed also has vibrational levels.
- As a result, the photoelectron spectrum typically has vibrational substructure:



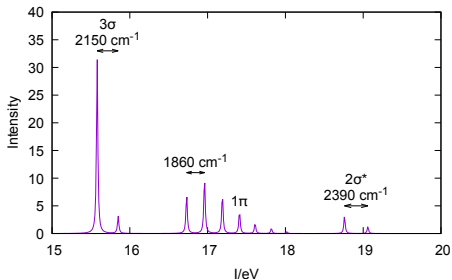
- Instead of one ionization energy, the photoelectron spectrum gives us a band of several lines corresponding to the ionization of an electron from a particular orbital.



- 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 1π 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. . .

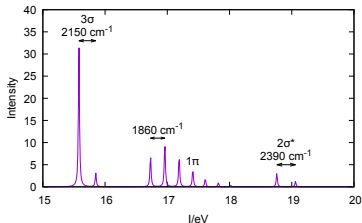
Example: UV photoelectron spectrum of N₂



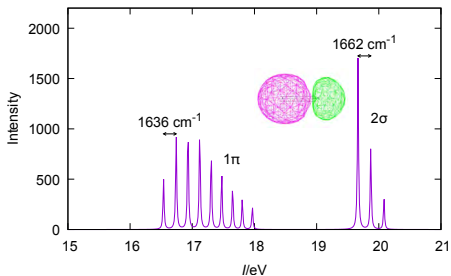
Note: The vibrational “frequency” of N₂ is 2358 cm⁻¹.

Additional hints for interpreting photoelectron spectra

- Orbitals that are strongly bonding/antibonding will produce a number of lines.
(See the 1π 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.



Example: UV photoelectron spectrum of CO



Note: The vibrational frequency of CO is 2170 cm⁻¹.