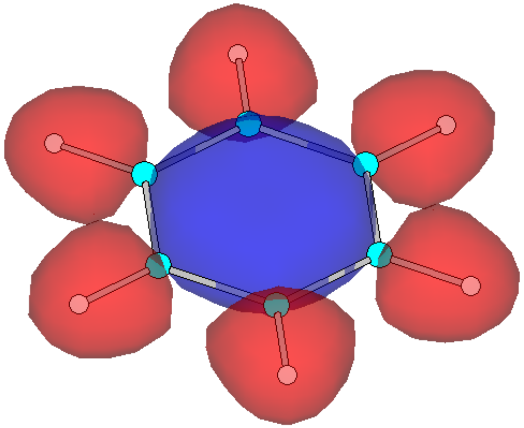
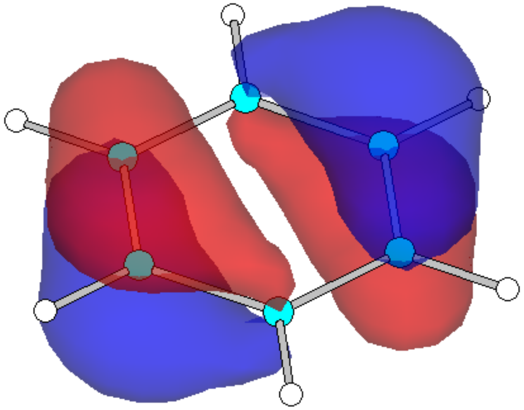
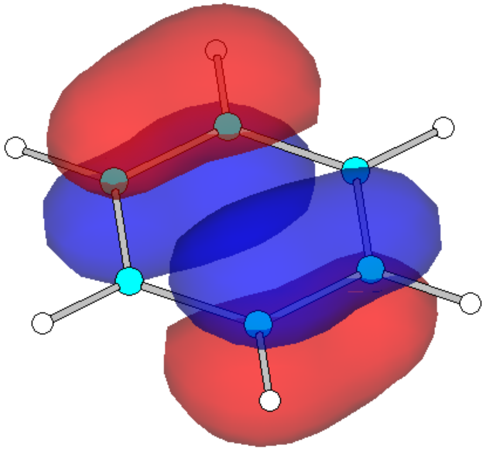




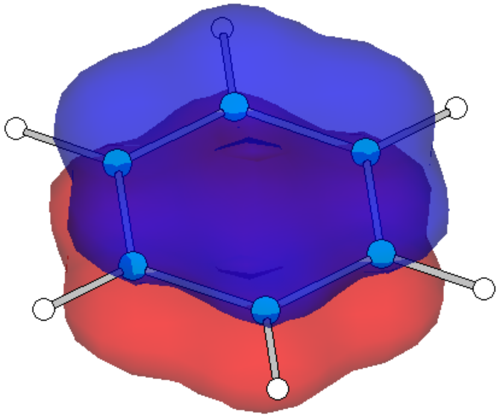
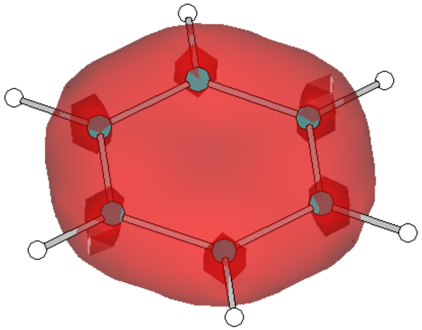
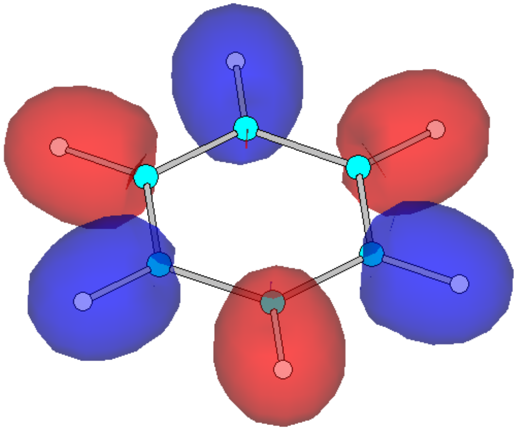
CHEMISTRY 2000

Topic #1: Bonding – What Holds Atoms Together?

Fall 2020

Dr. Susan Findlay

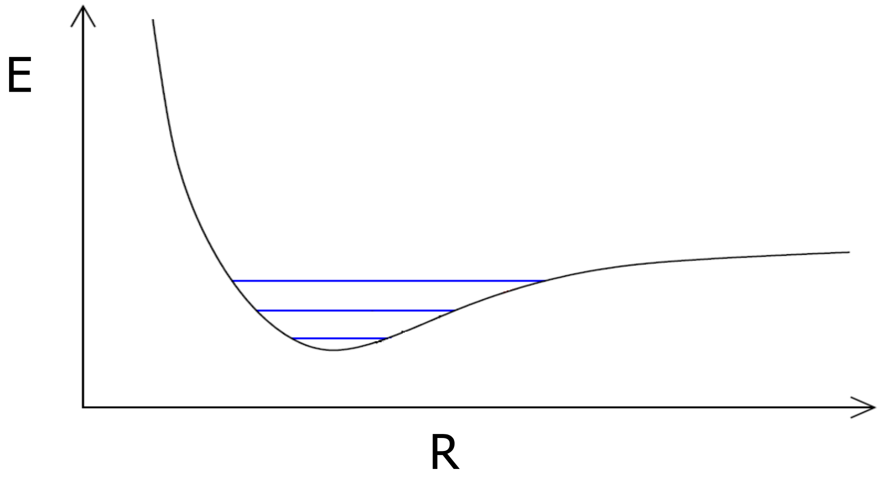
See Exercise 3.3

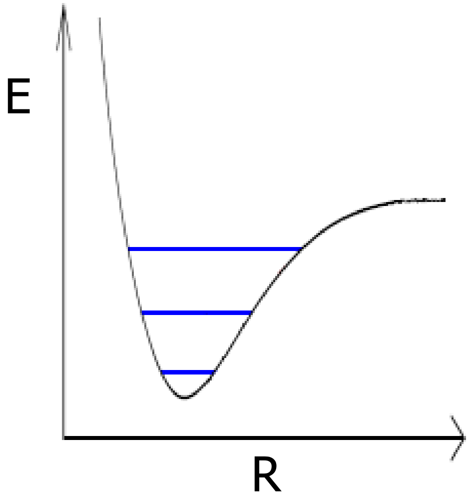
Experimental Evidence for MO Predictions

- Every possible electron configuration for a molecule gives a different potential energy curve. Why is this?

- The shape of a particular potential energy curve dictates the spacing between the different vibrational energy levels for the molecule. Compare a potential energy diagram for with a shallow well to one with a sharp well:



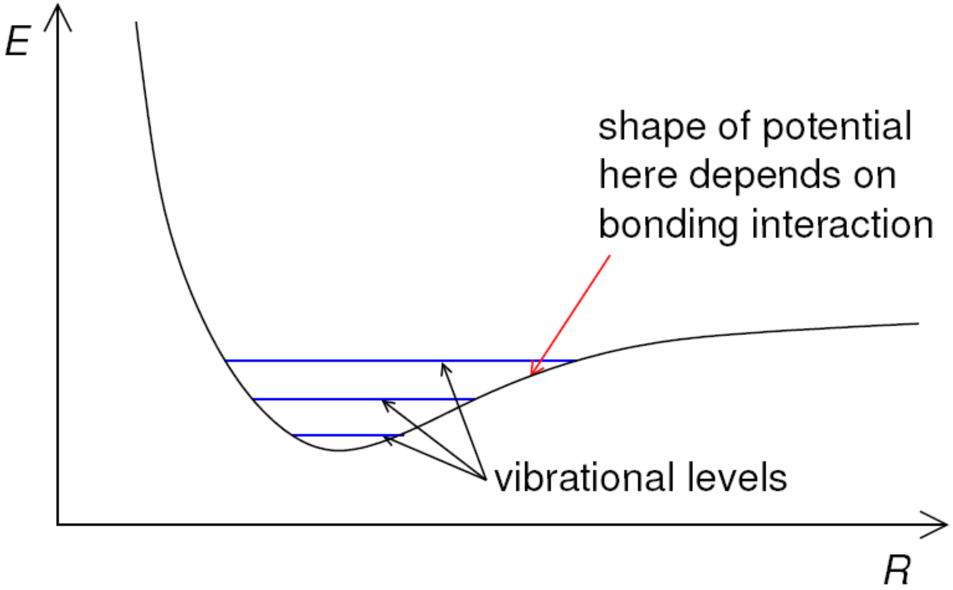
vs.



Which diagram corresponds to a more rigid bond?

Experimental Evidence for MO Predictions (IR)

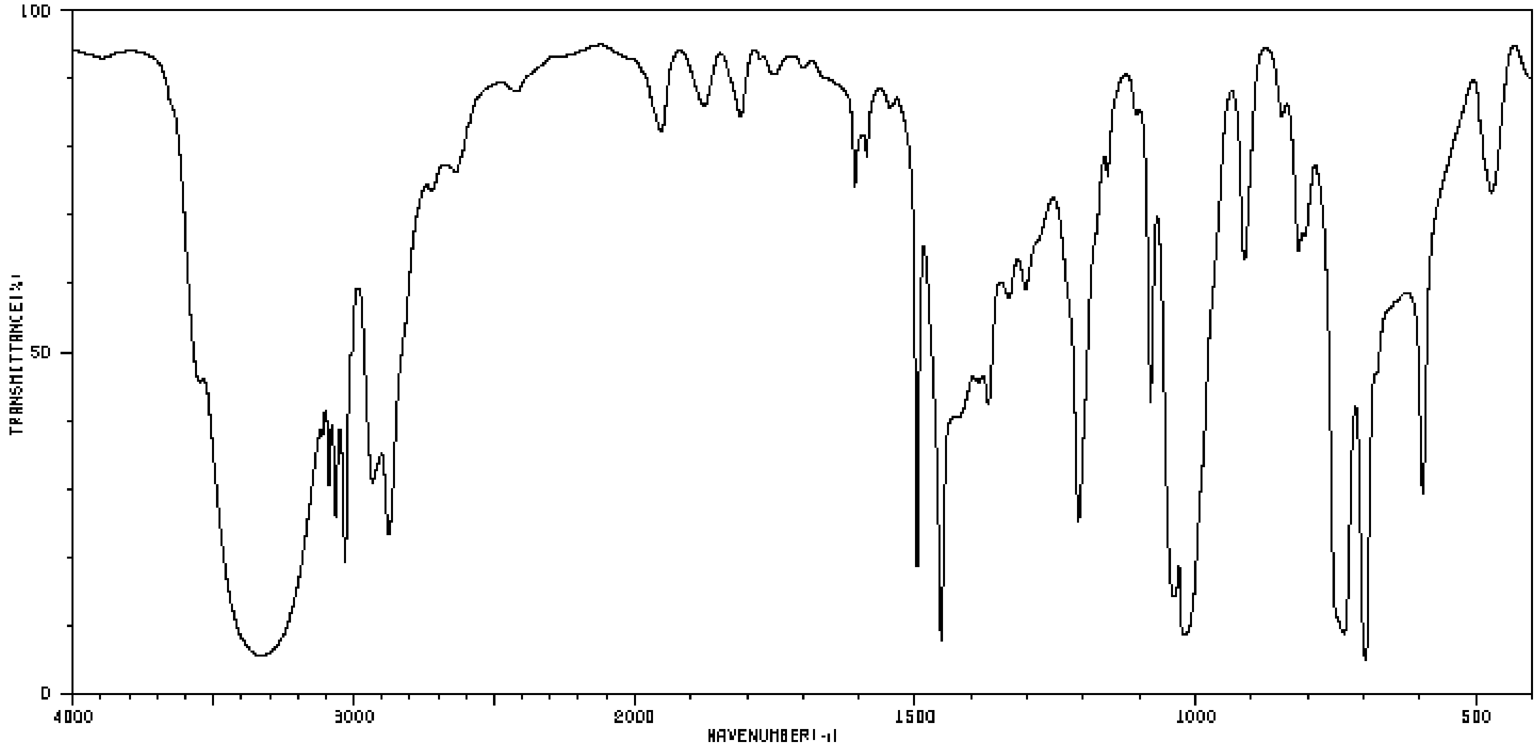
- We can study the shape of a potential energy diagram using vibrational spectroscopy in which photons of infrared light are absorbed by the molecule, exciting it from one vibrational state to another. This is also known as infrared spectroscopy, or IR.



- In practical terms, IR is used to identify the strength and rigidity of bonds. e.g. It readily discriminates between C-O and H-O bonds or between C-O and C=O bonds.

Experimental Evidence for MO Predictions (IR)

- The IR spectrum for a common alcohol looks like this:



3326	6	1962	79	1497	18	1080	41	806	64
3088	29	1876	84	1454	7	1039	13	736	8
3065	24	1811	81	1370	41	1018	8	698	4
3031	18	1607	72	1332	66	913	60	696	27
2932	29	1593	79	1303	57	846	81	473	70
2875	22	1587	77	1209	23	817	62		
2419	84	1644	81	1167	72	812	64		

Experimental Evidence for MO Predictions (IR)

- It’s important to recognize that molecules will only absorb infrared radiation if doing so changes the dipole moment of the molecule.

- For diatomic molecules, this means that only polar ones will be **IR active**. Exciting the molecule to a higher vibrational energy level slightly changes the average bond length – which also slightly changes the bond’s dipole moment (since it depends on both electronegativity difference and bond length).

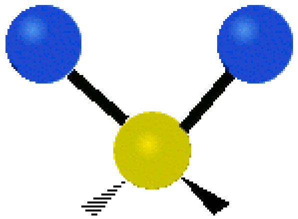
- Most polyatomic molecules are IR active since most of them have at least one vibrational mode that changes the dipole moment of the overall molecule. It’s important to note that these vibrational modes don’t just involve vibration of a single bond – but, rather, of the molecule as a whole.

Experimental Evidence for MO Predictions (IR)

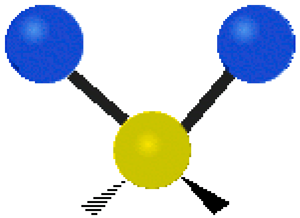
- We can count the number of unique vibrational modes (aka **normal modes**) for a polyatomic molecule using the following logic:
  - Every atom may move along the x, y or z axis. So, if there are N atoms in a molecule, to account for every possible motion, you'd have $3N$ modes in total (3 directions times N atoms).
  - Some of those motions aren't vibrations. e.g. If everything moves along the x axis, the whole molecule just moves along the x axis. So, subtract 3 (one for each axis). Now, we're at $3N - 3$.
  - Some of those motions are rotations not vibrations. For linear molecules, two of the motions are rotations. For nonlinear molecules, three of the motions are rotations. So, now we have:
    - $3N - 5$ normal modes for linear molecules
    - $3N - 6$ normal modes for nonlinear molecules

Experimental Evidence for MO Predictions (IR)

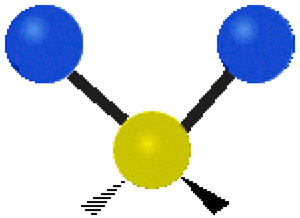
- What might these normal modes look like?



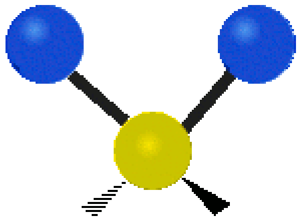
symmetric stretch



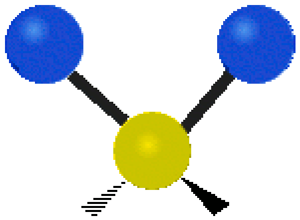
scissor



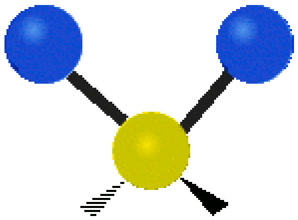
wag



asymmetric stretch



rock



twist

Experimental Evidence for MO Predictions (IR)

- The five gases below are the most prevalent in our atmosphere (highest to lowest abundance – except that water varies). Which do you expect to be IR active?

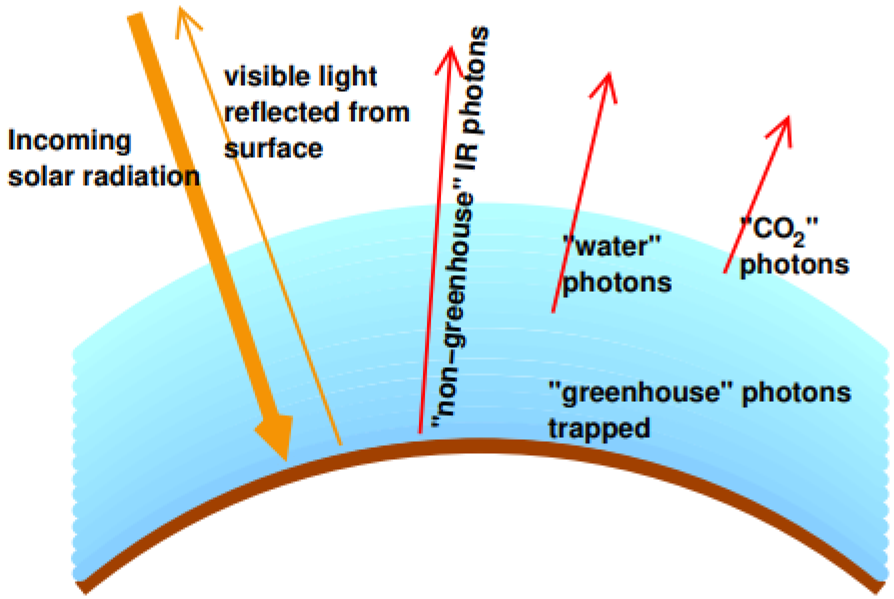
$$N_2 \qquad O_2 \qquad \mathrm{Ar} \qquad CO_2 \qquad H_2O$$

- Why did I pick atmospheric gases for this question?
  - Gases that absorb infrared radiation are called **greenhouse gases**!
  - CO_2 isn't the only greenhouse gas – but its concentration has been rapidly rising. So, it's the one we worry the most about.
  - Greenhouse gases play an important role in temperature regulation of the planet:
    - If there were NO greenhouse gases, Earth would be very cold.
    - As concentration of any greenhouse gas increases, Earth's temperature increases. Different greenhouse gases increase the temperature at different rates.
    - Temperature increase varies with geography (as do its effects)

Experimental Evidence for MO Predictions (IR)

- How do greenhouse gases warm the planet?
  - Light from the sun passes through the Earth’s atmosphere (which is especially transparent to light in the visible range of the spectrum).
  - About 30% of that light is simply reflected back into space.
    (Not evenly; the snowy/ice poles reflect more than other areas.)
  - The Earth absorbs the rest of that light energy.
  - The Earth radiates energy mostly as infrared “blackbody radiation”.
  - If that infrared radiation doesn’t encounter anything that absorbs it along its path from the surface, it leaves the planet and keeps traveling through space.
  - If the infrared radiation encounters a greenhouse gas, the gas absorbs that energy, raising its energy. As gas particles bump into each other, they transmit energy to one another. So, the increased vibrational energy can thus get converted to kinetic energy.
  - As you may recall from CHEM 1000, temperature of a gas is directly proportional to its kinetic energy. So, increasing the kinetic energy of atmospheric gases raises the temperature of the atmosphere.

Experimental Evidence for MO Predictions (IR)



- The following links lead to some interactive tools relating to infrared radiation, greenhouse gases and climate developed by the King’s Centre for Visualization in Science:
  - http://www.kcvs.ca/details.html?key=climateModel
  - http://www.kcvs.ca/details.html?key=irWindows

Experimental Evidence for MO Predictions (IR)

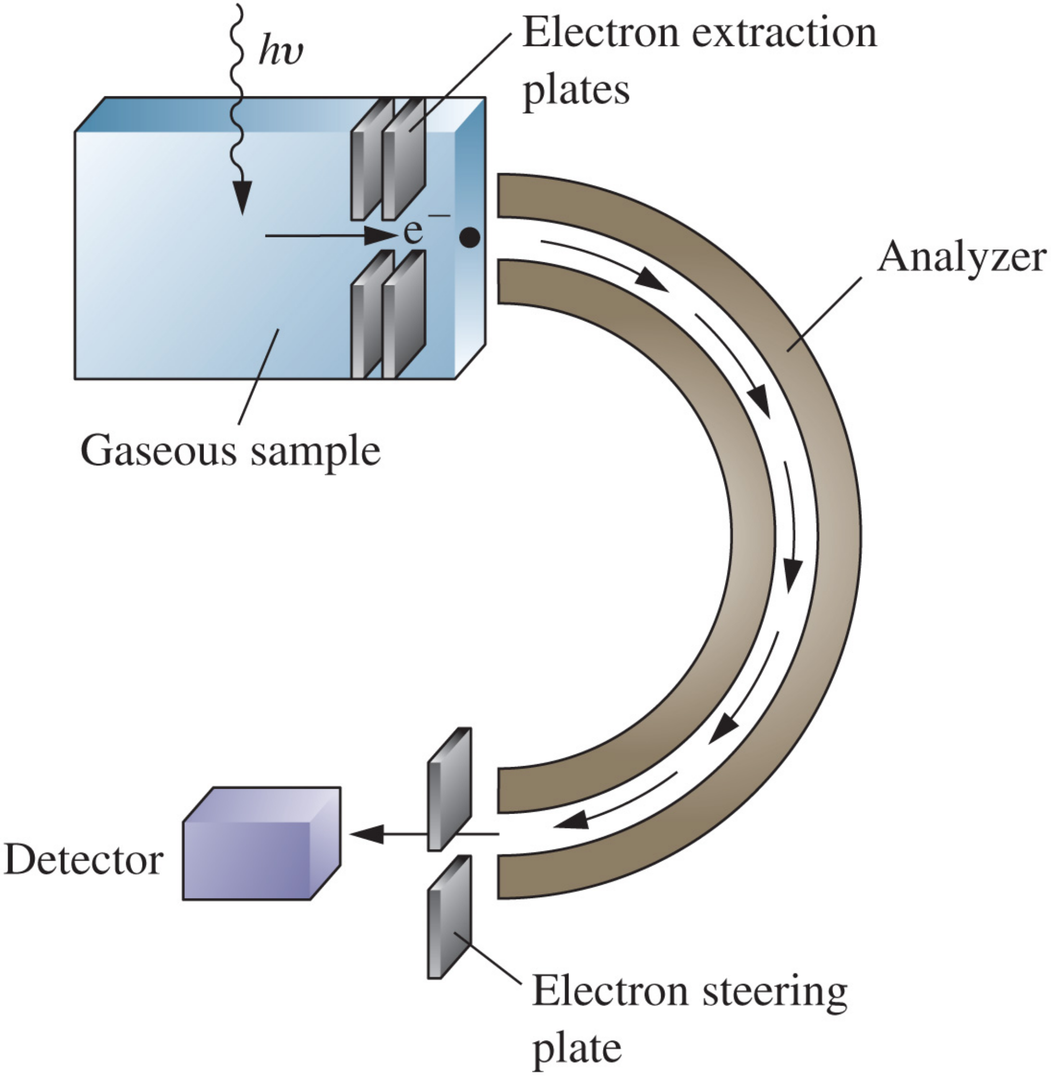
- A few “cold hard facts” about greenhouse gas levels
  - Atmospheric concentration of CO_2 measured at the Mauna Loa observatory was 316 ppm in 1959 and 411 ppm in 2019. Over those 60 years, it rose by 30%
  - In the early 1960s, the concentration was rising by about 0.6 ppm per year. It’s currently rising by about 2.6 ppm per year.
  - When the average global temperature rises, more water evaporates and the atmospheric concentration of water (also a greenhouse gas) rises too. So, rising CO_2 levels cause rising water vapour levels.
  - If the planet warms enough to melt permafrost, CH_4 is released from it. CH_4 is an even more powerful greenhouse gas than CO_2.

Experimental Evidence for MO Predictions (PES)

- Another form of spectroscopy can be used to corroborate the orbital occupancies predicted by MO theory – **photoelectron spectroscopy** (PES).
- In CHEM 1000, we talked about the **photoelectric effect**. The principles behind photoelectron spectroscopy are the same as those behind the photoelectric effect:
- The figure on the following page shows the instrument used for photoelectron spectroscopy. The page after that shows one of the simplest possible spectra (that of neon).

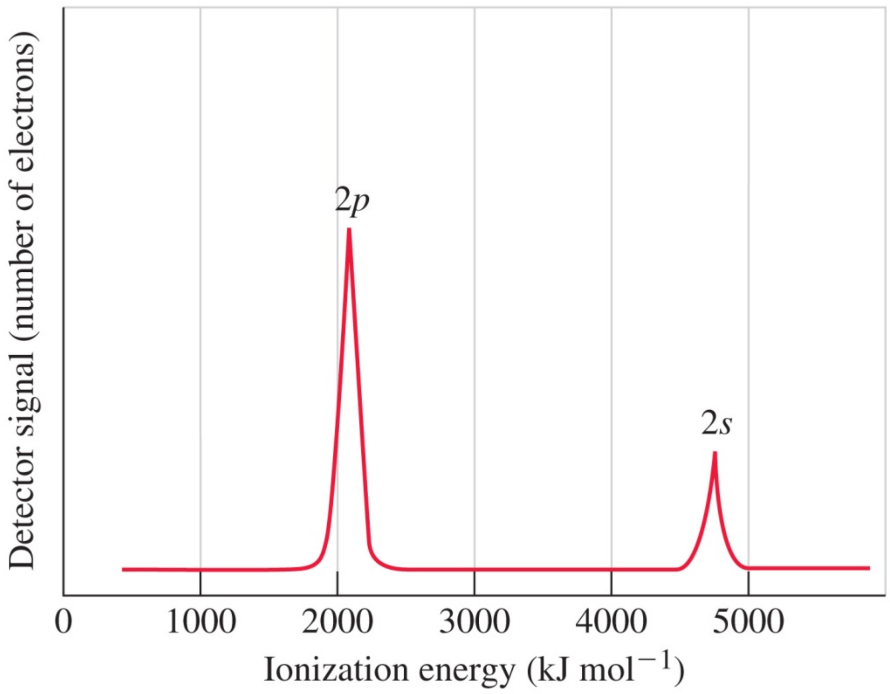
Experimental Evidence for MO Predictions (PES)

- A spectrometer is the instrument used for photoelectron spectroscopy.
- Since the energies being measured typically correspond to the energy of ultraviolet light, this is also called a UPES (ultraviolet photoelectron spectroscopy) spectrometer.



Experimental Evidence for MO Predictions (PES)

- The spectrum below is the result of performing photoelectron spectroscopy on a sample of neon gas (Ne):



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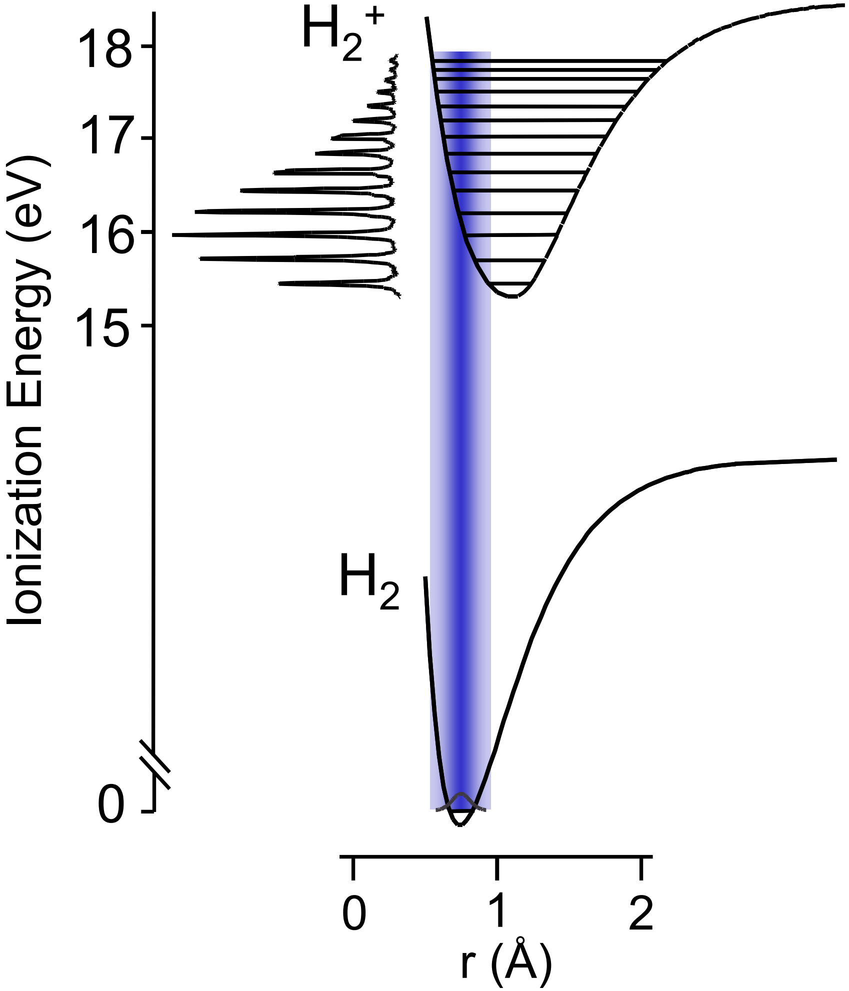
- This particular spectrum is very simple, showing only one line for each orbital, because a single atom of neon has no visible vibrations. Why not?

Experimental Evidence for MO Predictions (PES)

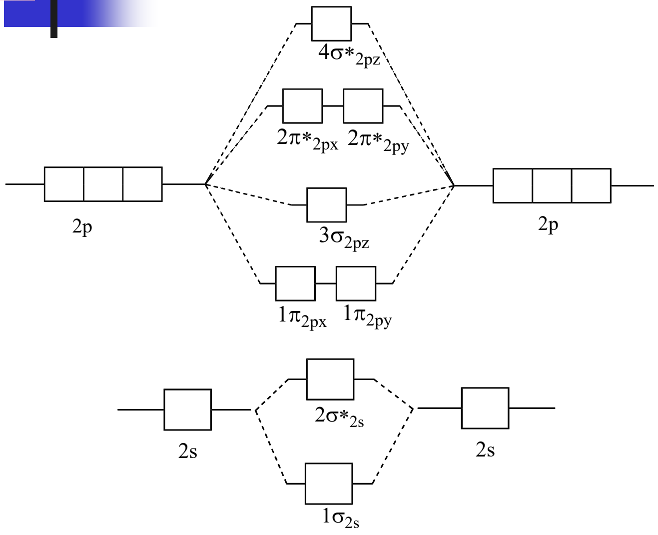
- The spectrum at the right (shown sideways) is more complex because there are vibrational energy levels in H_2.
- If there were no vibrational energy levels, this would give the energy of an orbital directly (as it did for neon).
- In practice, we must account for the different vibrational energy levels in the cation produced. The photoelectron spectrum will have a band of many lines, each corresponding to the energy difference between a vibrational level of the initial molecule and a vibrational level of the cation:

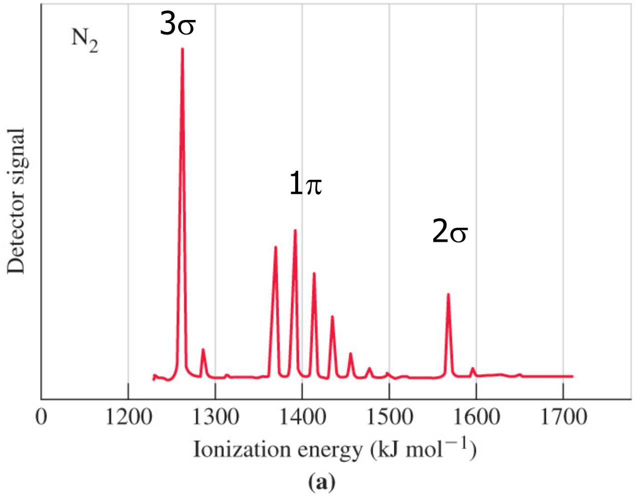


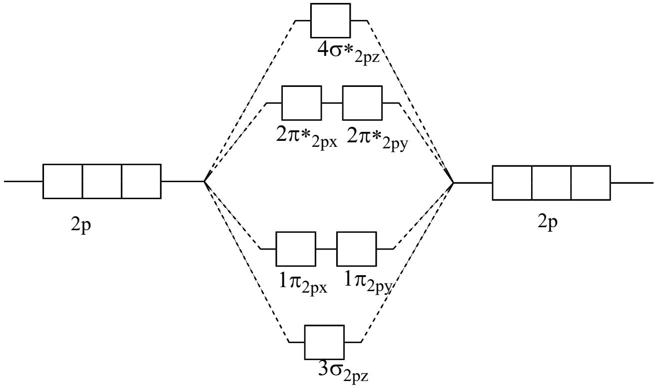
Experimental Evidence for MO Predictions (PES)

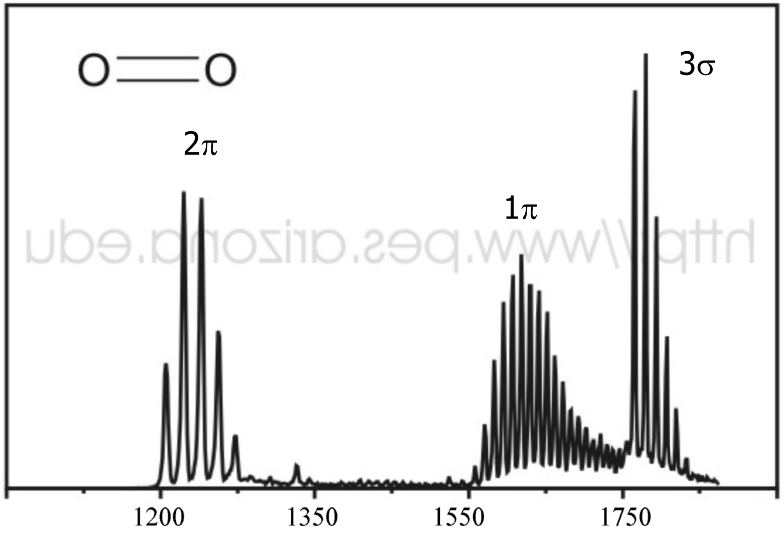
- This allows us to indirectly obtain a vibrational spectrum for the cation produced. Comparison of the two vibrational spectra tells us if/how the bond was affected:
  - If a nonbonding electron is removed, the shape of the potential energy diagram for the molecule changes little.
  - If a bonding electron is removed, the shape of the potential energy diagram changes drastically – indicating weakening of the bond.
  - If an antibonding electron is removed, the shape of the potential energy diagram again changes drastically – this time, indicating strengthening of the bond.
- Thus, photoelectron spectroscopy allows us to measure energies of orbitals – as well as confirming behaviour predicted by MO.

Experimental Evidence for MO Predictions (PES)

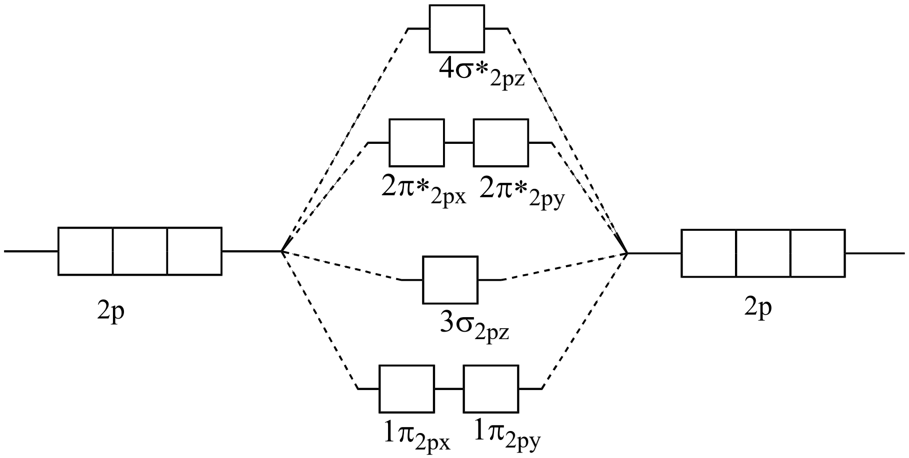


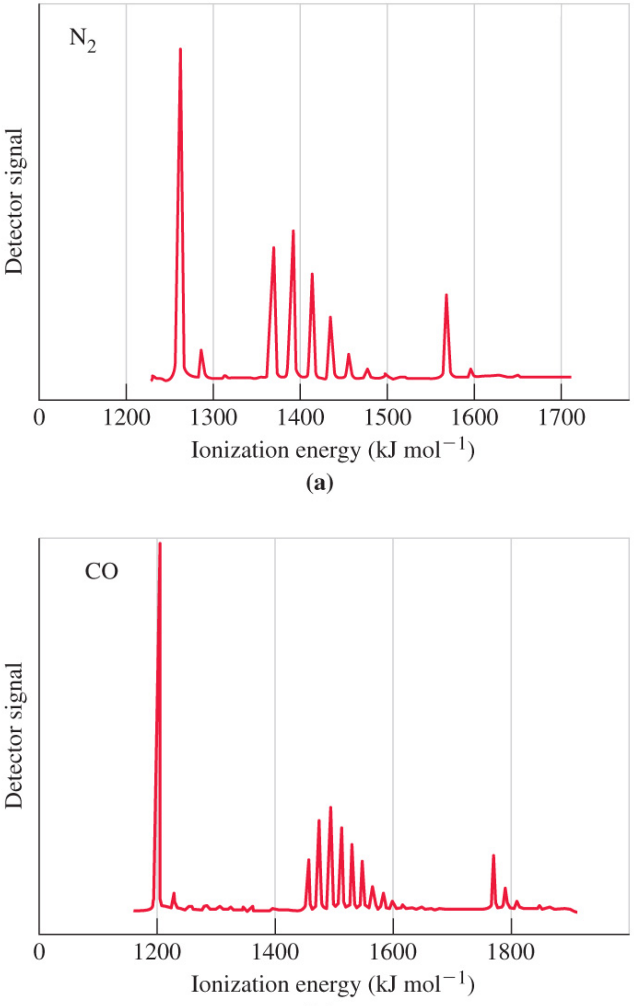






Experimental Evidence for MO Predictions (PES)





(b)