5.3.1.4: Photoelectron Spectroscopy

A photoelectron spectrum can show the relative energies of occupied molecular orbitals by ionization. The *ionization energy* is a direct measure of the energy required to just remove the electron concerned from its initial level to the vacuum level (free electron). Photoelectron spectroscopy measures the relative energies of the ground and excited positive ion states that are obtained by removal of single electrons from the neutral molecule.

$$A + \text{photon} \rightarrow A^{+} + e^{-}$$

The information obtained from photoelectron spectroscopy is typically discussed in terms of the electronic structure and bonding in the ground states of neutral molecules, with ionization of electrons occurring from bonding molecular orbitals, lone pairs, antibonding molecular orbitals, or atomic cores. These descriptions reflect the relationship of ionization energies to the molecular orbital model of electronic structure.

Ionization energies are directly related to the energies of molecular orbitals (by Koopmans' theorem).

Example: Photoelectron spectrum of dihydrogen

The molecular orbital description of dihydrogen involves two $1s$ atomic orbitals generating two molecular orbitals: a bonding σ_g and an antibonding σ_u^*. The two electrons occupy the σ_g bonding orbital, leaving the molecule with a bond order of one (Figure $5.3.1.4.1$). The PES spectrum of dihydrogen (Figure $5.3.1.4.1$) has a single band that corresponds to the ionization of one electron from the σ_g. The multiple peaks are due to electrons ejecting from a range of stimulated vibrational energy levels. When extensive vibrational structure is resolved in a PES molecular orbital, then the removal of an electron from that molecular orbital induces a significant change in the bonding (in this case an increase in the bond length due to decrease in bond order).

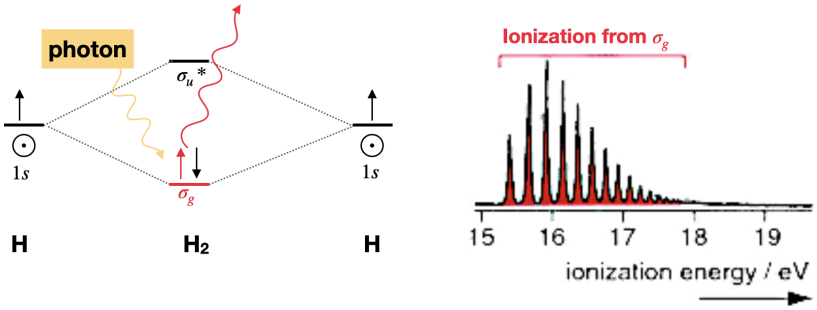

Figure $5.3.1.4.1$: The molecular orbital diagram and photoelectron spectrum of dihydrogen. (CC-BY-NC-SA; Libretexts)

Example: Photoelectron spectrum of dinitrogen

Diatomic nitrogen is more complex than hydrogen since multiple molecular orbitals are occupied. Five molecular orbitals are occupied; two of them are degenerate. Three bands in the photoelectron spectrum correspond to ionization of an electron in $\sigma_g(2p)$, $\pi_u(2p)$ and $\sigma_u^*(2s)$ molecular orbitals. Ionization of the fourth type of orbital, $\sigma_g(2s)$, does not appear in Figure $5.3.1.4.2$because it is either off scale or because the incident light $h\nu$ used did not have sufficient energy to ionize electrons in that deeply stabilized molecular orbital. Note that extensive vibrational structure for the $\pi_u(2p)$ band indicates that the removal of an electron from this molecular orbital causes a significant change in the bonding.

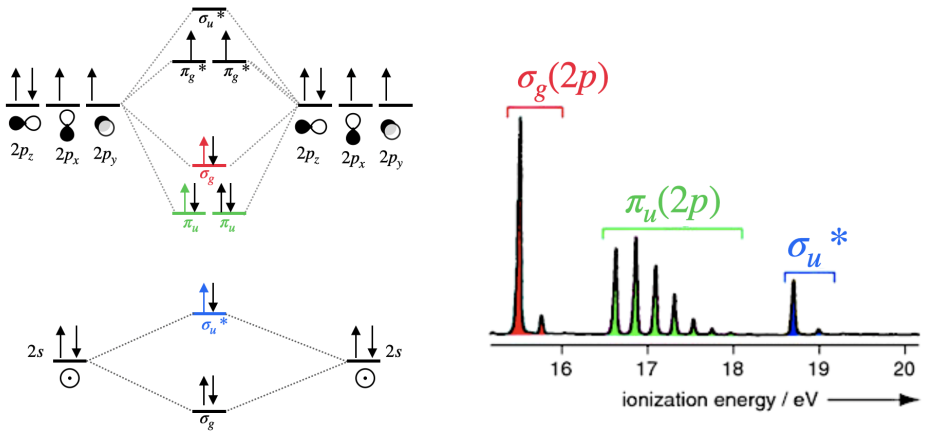

Figure 5.3.1.4.2 : The molecular orbital diagram and photoelectron spectrum of dinitrogen. (CC-BY-NC-SA; Libretexts)

From the photoelectron spectrum of dinitrogen, we can see that the electrons in the $\sigma_g(2p)$ orbital can be ionized using less energy than required to ionize electrons in the $\pi_u(2p)$ orbital. This is evidence for $\sigma_g(2p)$ existing at a higher energy than the $\pi_u(2p)$ orbitals.
