http://www.chem.arizona.edu/facilities/pes/facility/PES_description.htm

What is Photoelectron Spectroscopy?

Photoelectron spectroscopy is based on Einstein's photoelectric effect [1]. A photon can ionize an electron from a molecule if the photon has an energy greater than the energy holding the electron in the molecule. Any photon energy in excess of that needed for ionization is carried by the outgoing electron in the form of kinetic energy.

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The kinetic energy of the ejected (photo)electron is measured in the photoelectron spectrometer. As shown in equation (1), the difference between the photon energy (*h*n), which is known, and the electron kinetic energy (K.E.), which is measured, is the ionization energy (I.E.).

$$\mathrm{I.E.} = E(h\nu) - \mathrm{K.E.}(e^-) \tag{1}$$

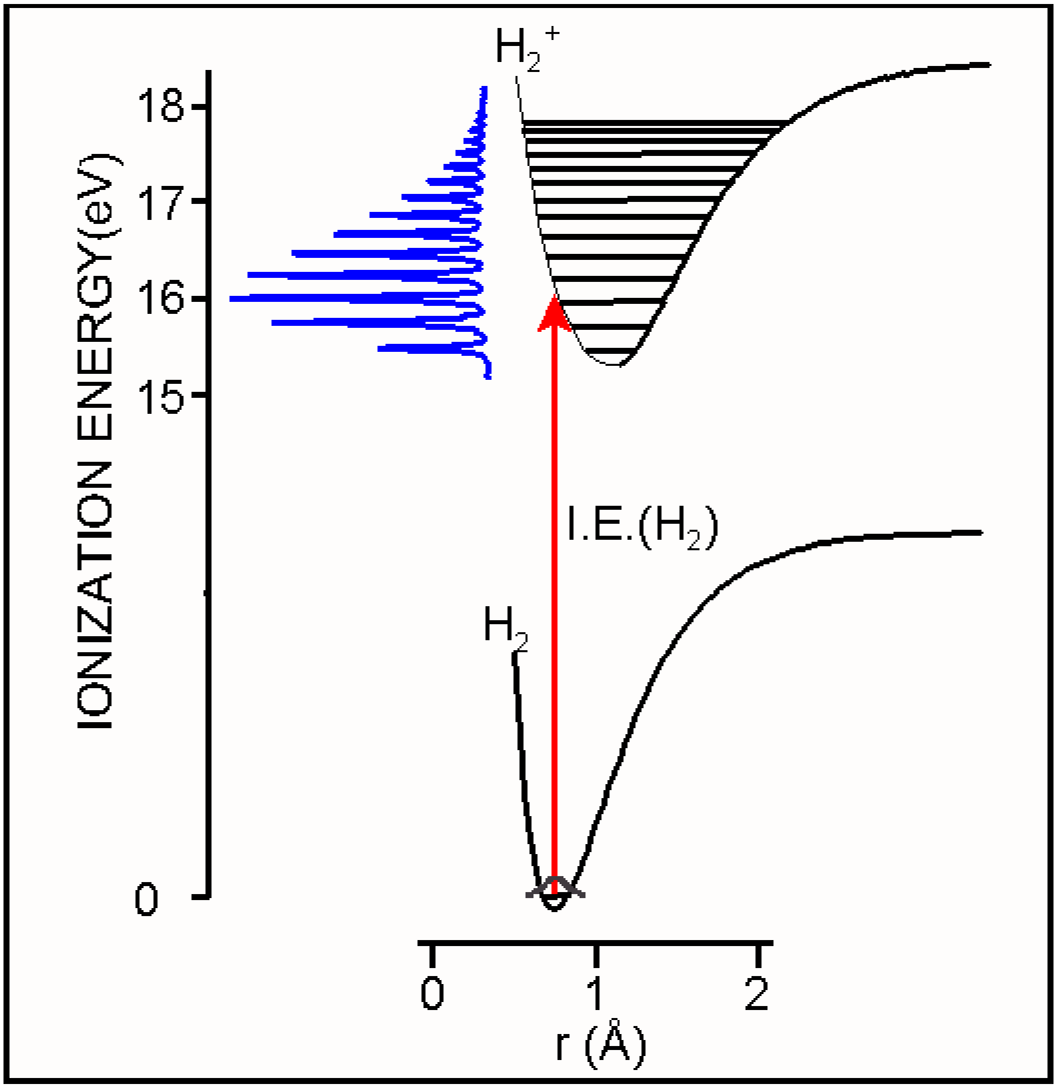
For a neutral molecule in the gas phase, the photon ionizes the molecule (M) and leaves the molecule in a positively charged ion state (M_i^+) according to equation (2).

$$M + \mathrm{photon}(h\nu) \rightarrow M_i^+ + e^- \tag{2}$$

Rearranging equation (2) and considering the energy components of the process as in equation (3) shows that a measure of the ionization energy is also a measure of the difference in energy between the positive ion state M_i^+ and the initial state of the molecule M.

$$E(M_i^+) - E(M) = E(h\nu) - \mathrm{K.E.}(e^-) = \mathrm{I.E.} \tag{3}$$

Thus 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.

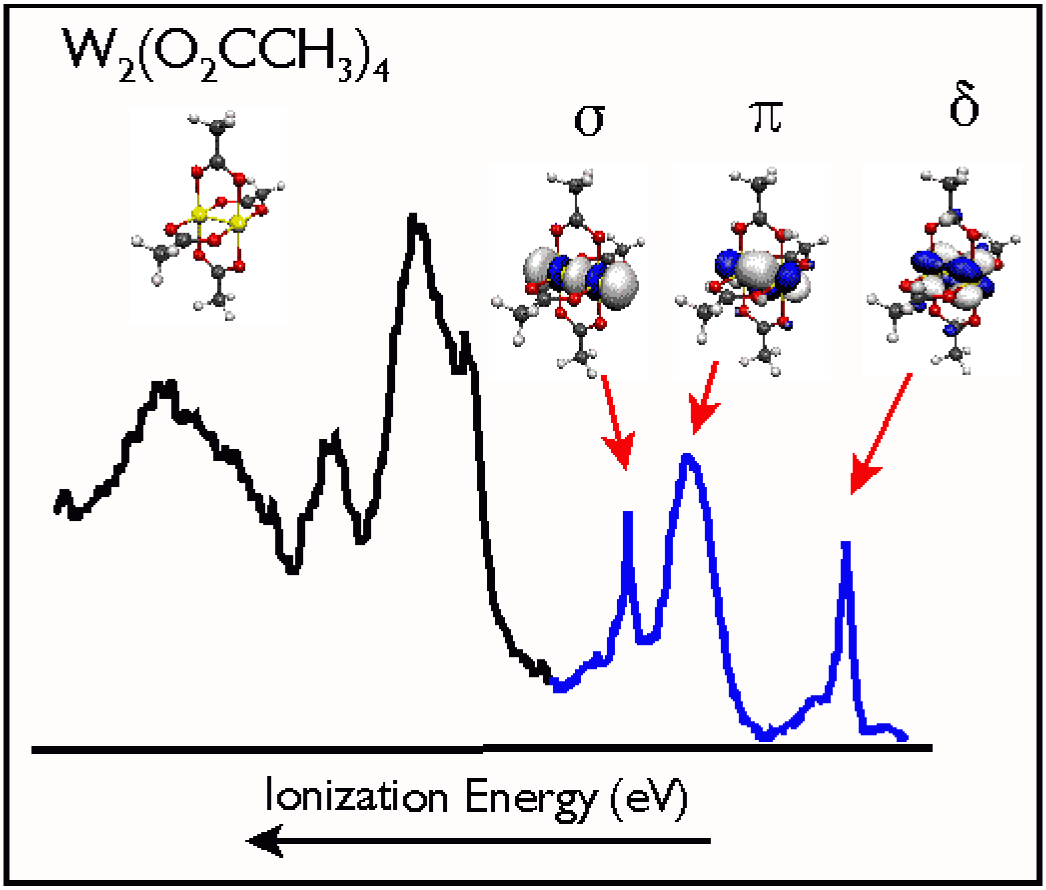


At the most fundamental level ionization energies are well-defined thermodynamic quantities related to the heats of protonation, oxidation/reduction chemistry, and ionic and covalent bond energies. Ionization energies are closely related to the concepts of electronegativity, electron-richness, and the general reactivity of molecules. The energies and other characteristic features of the ionization bands observed in photoelectron spectroscopy provide some of the most detailed and specific quantitative information regarding the electronic structure and bonding in molecules. Photoelectron spectroscopy has served as a particularly important basis for the bonding models used to describe organic, inorganic, and organometallic molecules because the energetics of ion formation from the neutral ground state are directly related to orbital electron configurations, oxidation states, charge distributions, and covalency.

The Orbital Model of Ionization

Ionization is explicitly defined in terms of transitions between the ground state of a molecule and ion states as shown in equation (2) and as illustrated in the above figure. Nonetheless, 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 [2], which states that the negative of the eigenvalue of an occupied orbital from a Hartree-Fock calculation is equal to the vertical ionization energy to the ion state formed by removal of an electron from that orbital, provided the distributions of the remaining electrons do not change. There are many limitations to Koopmans' theorem, but in a first order approximation each ionization of a molecule can be considered as removal of an electron from an individual orbital. The ionization energies can then be considered as measures of orbital stabilities, and shifts can be interpreted in terms of orbital stabilizations or destabilizations due to electron distributions and bonding. Koopmans' theorem is implicated whenever an orbital picture is involved, but is not necessary when the focus is on the total electronic states of the positive ions.



The direct ionization transition is not restricted by any symmetry selection rules because the ejected electron can carry any necessary angular momentum to make the process electric dipole allowed. Therefore, ionization to any excited positive ion state obtained by removal of a single electron and within range of the photon energy can be observed. That is, ionizations can be observed that correspond to removal of electrons from any of the occupied orbitals. Photons with energies in the keV (X-ray) range are able to ionize down to the core electrons of atoms and molecules. Core ionizations of molecules are associated with the individual atoms present and fall in characteristic energy ranges related to the specific elements. The exact ionization energy of a core level is influenced by the charge potential around the atom and is useful for distinguishing between atoms in different chemical environments.

Information Content in Photoelectron Spectroscopy

While the energy information that is contained in a photoelectron spectrum is surely the most important information, further insight into the electronic structure of molecules is contained in other information within the spectrum. This information includes:

Ionization Band Shape: Removal of an electron changes the electronic structure and bonding in the molecule and results in a shift of the equilibrium internuclear separations. If the geometry changes are sufficiently great, the most probable (vertical) transitions from the neutral ground state are to excited vibrational levels of the final ion state. When these vibrational levels are resolved, the change in vibrational spacing from the initial state to the final state gives a measure of the change in vibrational frequencies and force constants associated with the excitation, and the intensity pattern of the transitions to the excited vibrational levels (the Franck-Condon factors) gives a measure of the change in equilibrium bond distances.

Ionization Intensity: The probability of ionization is dependent upon the energy of the ionizing photon, the atomic character of the orbitals ionized, the angle at which photoelectrons are collected, and the polarized nature of the photons. These probabilities of photoionization are understood in terms of photoionization cross-sections. The dependence of photoionization cross-sections upon the energy of the ionization photon and the character of the molecular orbital has been particularly useful in the assignments of the spectra of multi-atomic molecules. The general trends that have been observed for photoionization behavior often lead to a clear and convenient differentiation between ionization from metal-based and ligand-based orbitals in the photoelectron spectra of inorganic and organometallic molecules.

References

1. Einstein, A. "On a Heuristic Point of View Concerning the Production and Transformation of Light." *Ann. Phys.* **1905**, *17*, 549.

2. Koopmans, T. "Ordering of Wave Functions and Eigenvalues to the Individual Electrons of an Atom." *Physica* **1933**, *1*, 104.