

UV-PHOTOELECTRON SPECTROSCOPY

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Photoelectron spectroscopy is an extension of the photoelectric effect – Einstein's famous experiment, which allowed him to observe the emission of electrons when certain elements were bombarded with high energy radiation.

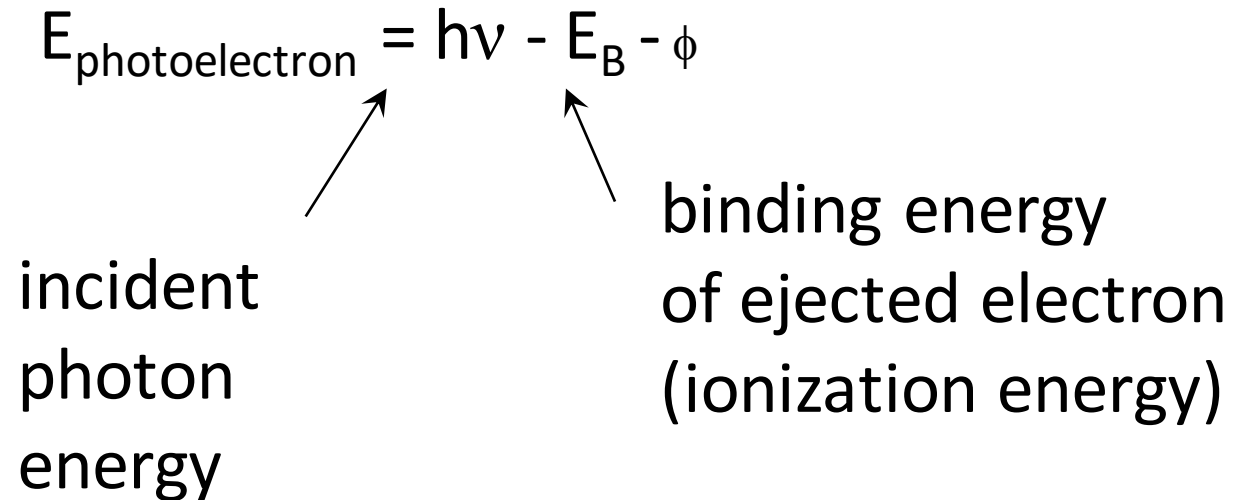
This experiment confirmed the particulate nature of radiation, the existence of photons. He also found that different alkali metals have different work functions, the minimum energy required to remove an electron from the outermost shell. The principle of photoelectron spectroscopy is based on the same.

K.E. of ejected electron is characteristic of the element :

$$E_{\text{photoelectron}} = h\nu - E_{\text{B}} - \phi$$

incident photon energy

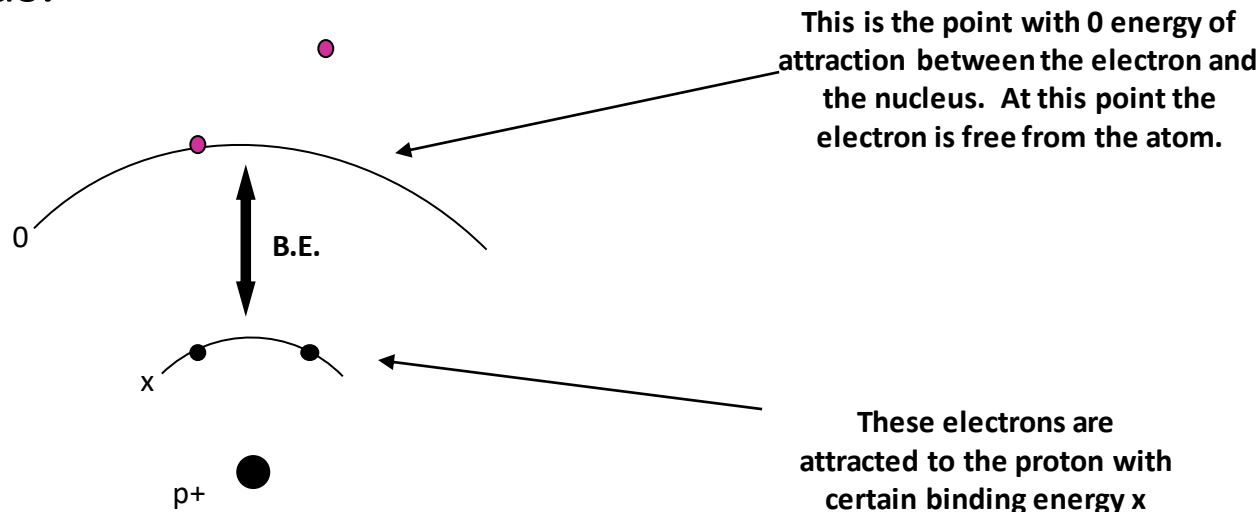
binding energy of ejected electron (ionization energy)

The diagram shows the equation $E_{\text{photoelectron}} = h\nu - E_{\text{B}} - \phi$. Below the equation, the text "incident photon energy" is positioned under $h\nu$, and "binding energy of ejected electron (ionization energy)" is positioned under E_{B} . Two arrows originate from these labels: one points from "incident photon energy" to $h\nu$, and the other points from "binding energy of ejected electron (ionization energy)" to E_{B} .

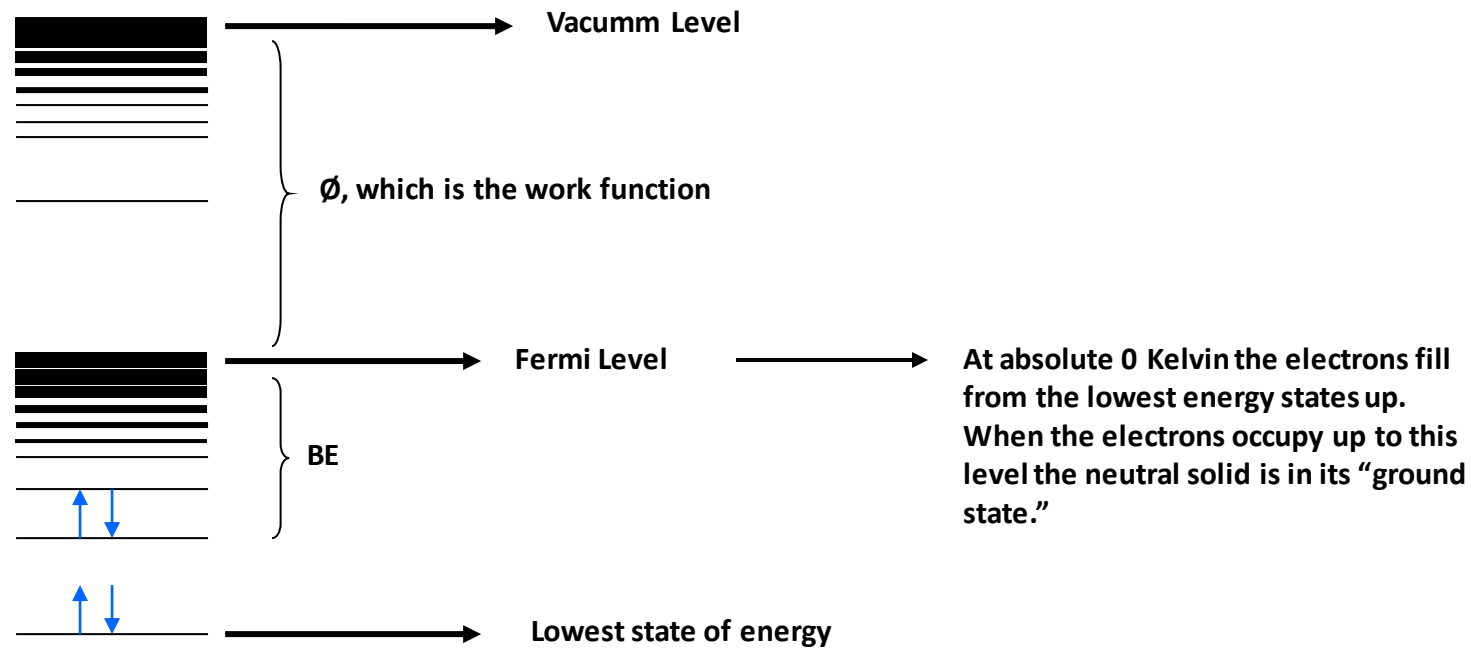
- Can detect elements above Li
- Requires very good spectrometer for H, He

Binding Energy

The Binding Energy (BE) is characteristic of the core electrons for each element. The BE is determined by the attraction of the electrons to the nucleus. If an electron with energy x is pulled away from the nucleus, the attraction between the electron and the nucleus decreases and the BE decreases. Eventually, there will be a point when the electron will be free of the nucleus.



Energy Levels



Photoelectron spectroscopy (PES) utilizes photo-ionization and analysis of the kinetic energy distribution of the emitted photoelectrons to study the composition and electronic state of the surface region of a sample.

X-ray Photoelectron Spectroscopy (XPS) uses soft x-rays (with a photon energy of 200-2000 eV) to examine electrons in core-levels.

Ultraviolet Photoelectron Spectroscopy (UPS) using vacuum UV radiation (with a photon energy of 10-45 eV) to examine electrons in valence levels.

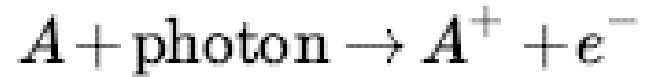
Both photoelectron spectroscopy is based upon a single photon in/electron out process. The energy of a photon of all types of electromagnetic radiation is given by the Planck–Einstein relation:

$$E = h\nu$$

where h is Planck constant and ν is the frequency (Hz) of the radiation.

UPS is a powerful technique to exam molecular electron structure since we are interested in the molecular orbitals from polyatomic molecules (especially the valence orbitals).

Photoelectron spectroscopy uses monochromatic sources of radiation (i.e. photons of fixed energy). In UPS the photon interacts with valence levels of the molecule or solid, leading to ionization by removal of one of these valence electrons.



The kinetic energy distribution of the emitted photoelectrons (i.e. the number of emitted photoelectrons as a function of their kinetic energy) can be measured using any appropriate electron energy analyzer and a photoelectron spectrum can thus be recorded. The process of photoionization can be considered in several ways. One way is to look at the overall process for a species A:

Conservation of energy then requires that (after using Equation):

$$E(A) + h\nu = E(A^+) + E(e^-)$$

Since the free electron's energy is present solely as kinetic energy (KE) (i.e., there is no internal energy in a free electron)

$$E(e^{-}) = KE$$

Equation can then be rearranged to give the following expression for the KE of the photoelectron:

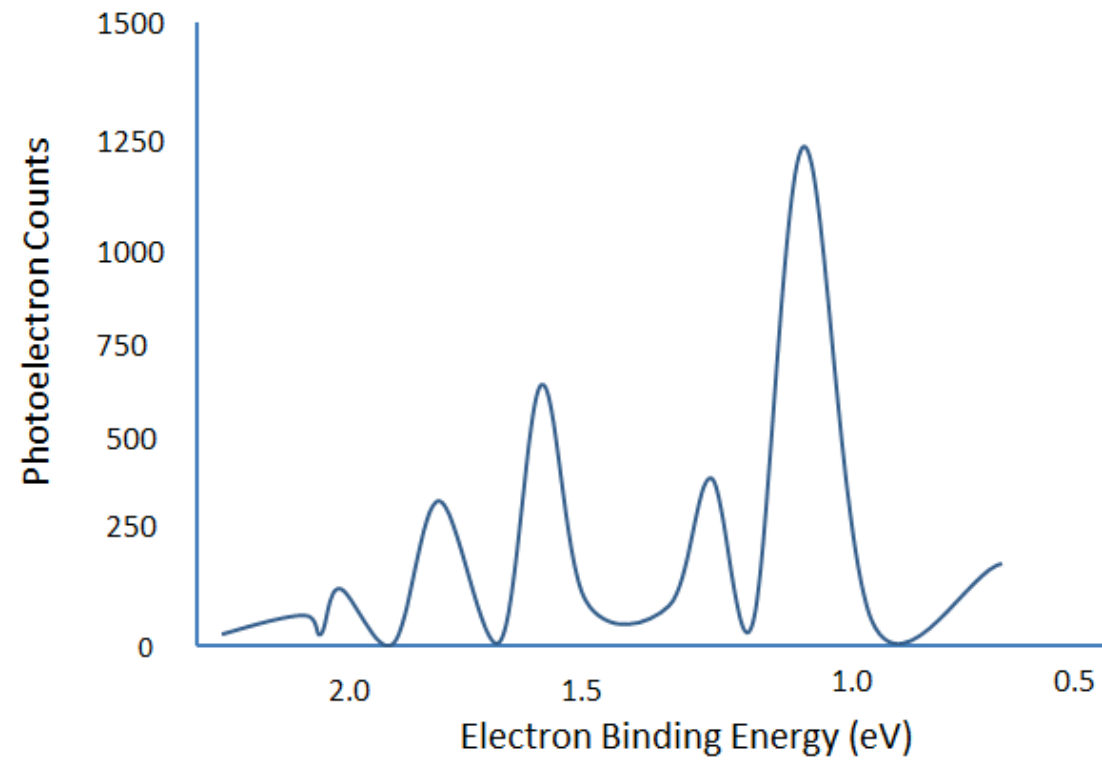
$$KE = h\nu - [E(A^{+}) - E(A)]$$

The final term in brackets represents the difference in energy between the ionized and neutral species and is generally called the vertical ionization energy (IE) of the ejected electron; this then leads to the following commonly quoted equations:

$$KE = h\nu - IE$$

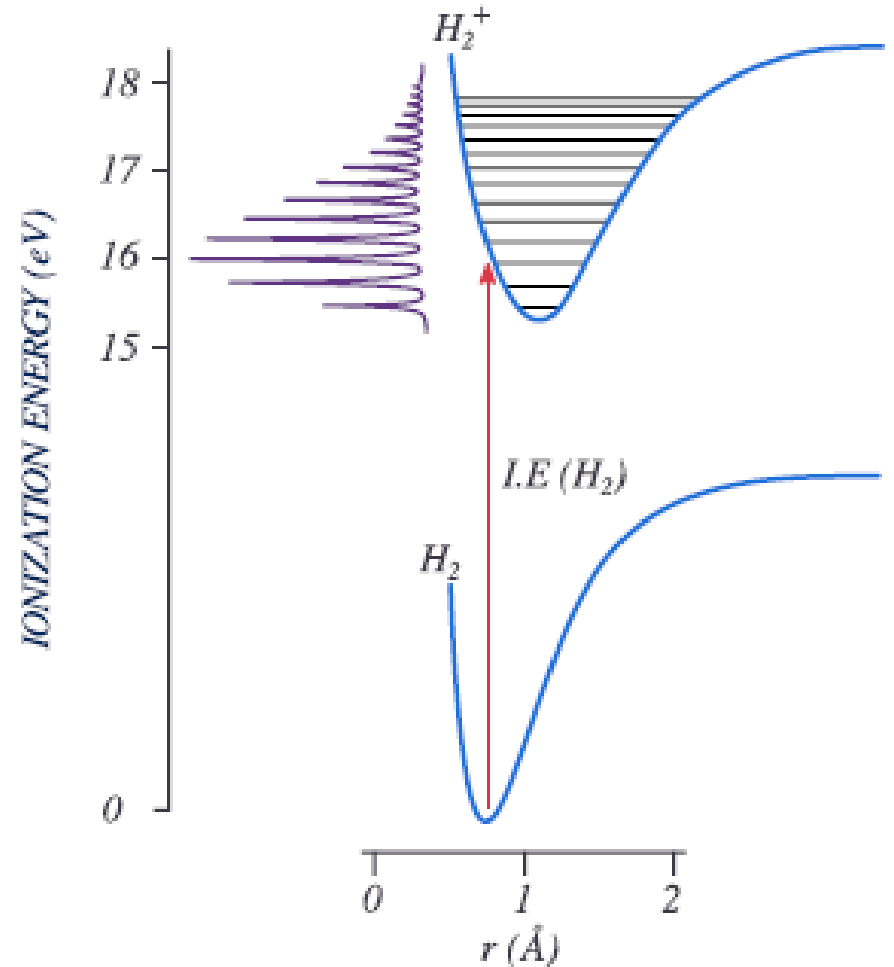
or

$$IE = h\nu - KE$$



The vertical 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.



At a 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.

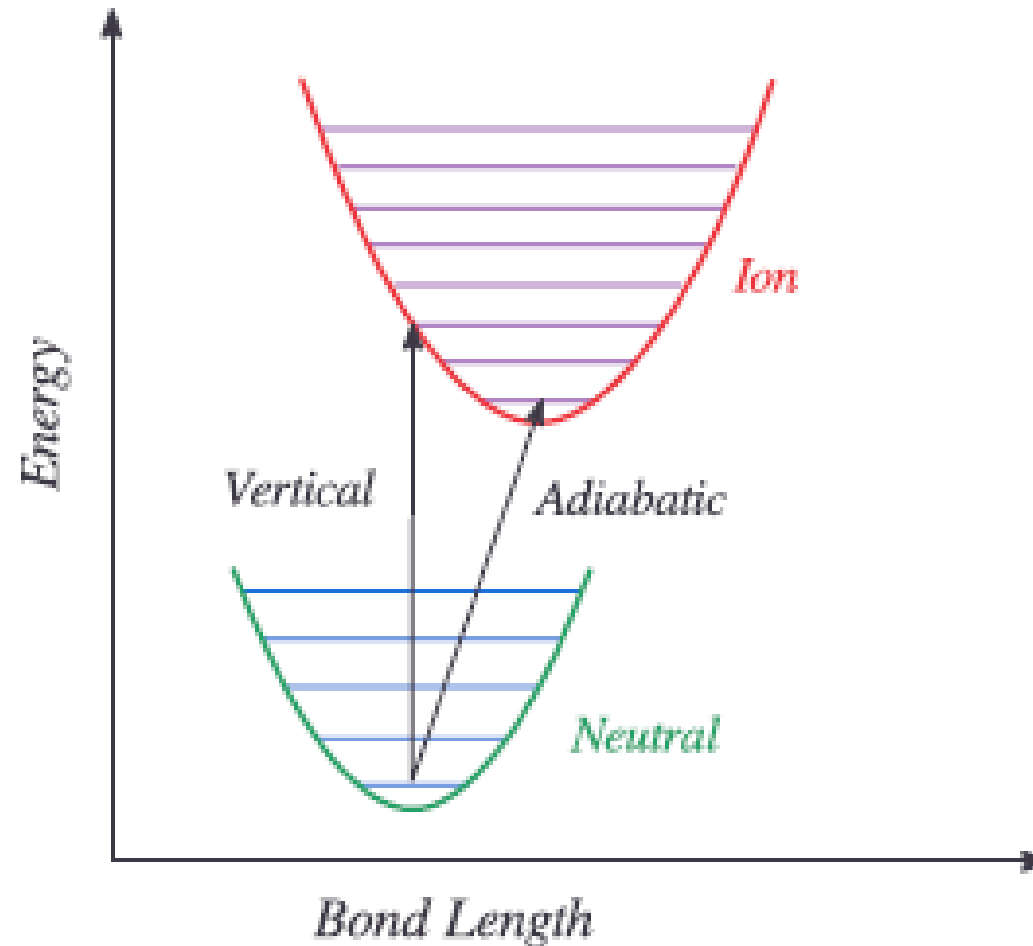
The energies and other characteristic features of the ionization bands observed in photoelectron spectroscopy provide some of the molecular orbitals detailed and specific quantitative information regarding the electronic structure and bonding in molecules.

Ionization is explicitly defined in terms of transitions between the ground state of a molecule and ion states as shown in Equation and as illustrated in the 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.

The He-I radiation has sufficient energy (21.2 eV) to cause emission of only the valence electrons. There is another helium emission He-II at 40.8 eV, and photoelectron spectroscopy studied using helium lamps with this emission falls in the domain of ultraviolet photoelectron spectroscopy (UPS).



Difference between vertical and adiabatic ionization energies for a simple harmonic oscillator system.

Several different ionization energies can be defined, depending on the degree of vibrational excitation of the cations. In general, the following two types of ionization energies are considered:
Adiabatic ionization energy corresponds to the ionization energy associated with this transition



Adiabatic ionization energy that is, the minimum energy required to eject an electron from a molecule in its ground vibrational state and transform it into a cation in the lowest vibrational level of an electronic state x of the cation.



Vertical ionization energy corresponds to the ionization energy associated with this transition where, the value n of the vibrational quantum number v' corresponds to the vibrational level whose wavefunction gives the largest overlap with the $v'' = 0$ wavefunction. This is the most probable transition and usually corresponds to the vertical transition where the internuclear separations of the ionic state are similar to those of the ground state.

The geometry of an ion may be different from the neutral molecule. The measured ionization energy in a PES experiment can refer to the vertical ionization energy, in which case the ion is in the same geometry as the neutral, or to the adiabatic ionization energy, in which case the ion is in its lowest energy, relaxed geometry (mostly the former though).

For a diatomic the only geometry change possible is the bond length. The figure shows an ion with a slightly longer bond length than the neutral. The harmonic potential energy surfaces are shown in green (neutral) and red (ion) with vibrational energy levels. The vertical ionization energy is **always greater** than the adiabatic ionization energy.

The *ionization energy* (also called *adiabatic ionization energy*) is the lowest energy required to effect the removal of an electron from a molecule or atom, and corresponds to the transition from the lowest electronic, vibrational and rotational level of the isolated molecule to the lowest electronic, vibrational and rotational level of the isolated ion.

The *binding energy* (also called *vertical ionization energy*) is the energy change corresponding to an ionization reaction leading to formation of the ion in a configuration which is the same as that of the equilibrium geometry of the ground state neutral molecule.

The *work function* is the minimum energy needed to remove an electron from a (bulk) solid to a point in the vacuum.

Koopmans' theorem

The third aspect of photoelectron spectroscopy is Koopmans' theorem which bridges the gap between experiment and theory. The energy of an electron and the ionized atom is taken as zero when they are at infinite distance from each other and there is no interaction between the two. As they are brought together, the mutual attraction lowers the potential energy. Thus, the energy of a bound electron in an orbital is always negative. In order to remove this electron against the attraction of the positively charged ion, an energy equal to the orbital energy has to be supplied so that the two move apart and the total energy becomes zero.

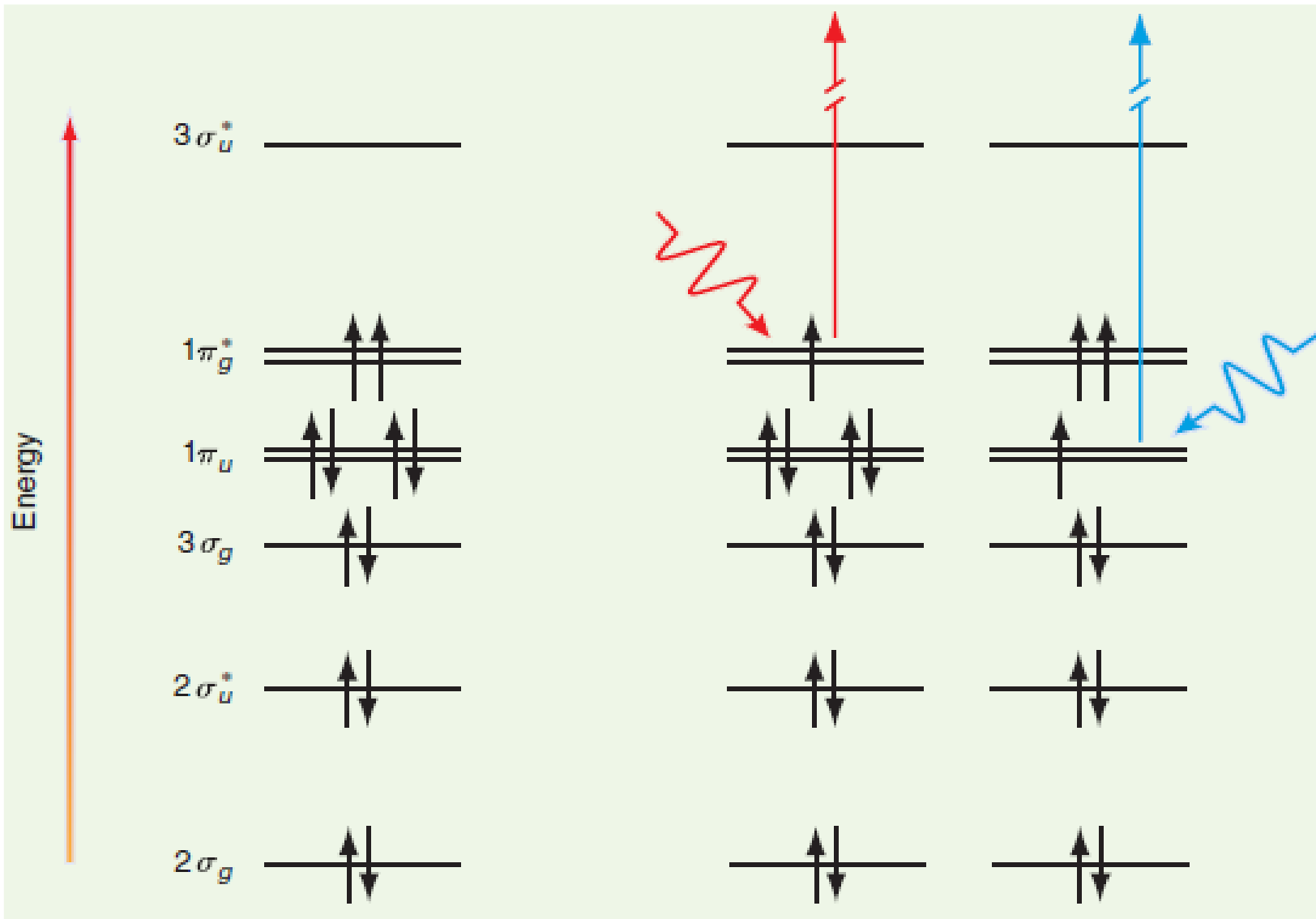
Of all the possible forms of electronic spectroscopy, UV photoelectron spectroscopy comes closest to the goal of directly identifying the orbital energy level from which an electronic transition originates.

What is the principle of this spectroscopy?

In the photoelectric effect, an incident photon of sufficiently high energy ejects an electron from one of the filled valence orbitals of the molecule, creating a positive ion as shown in Figure, using O₂ as an example. The kinetic energy of the ejected electron is related to the total energy required to form the positive ion via photoionization,

$$E_{kinetic} = h\nu - \left[E_f + \left(n_f + \frac{1}{2} \right) h\nu_{vibration} \right]$$

where E_f is the energy of the cation, which is formed by the removal of the electron, in its ground state. Equation takes vibrational excitation of the cation into account, which by conservation of energy leads to a lower kinetic energy for the photoejected electron. Because, in general, either the initial or final state is a radical, a delocalized MO model must be used to describe UV photoelectron spectroscopy.



The ground-state molecular orbital diagram of O₂ is shown on the left. An incident UV photon can eject an electron from one of the occupied MOs, generating an O²⁺ ion and an unbound electron whose kinetic energy can be measured as shown for two different MOs in the center and right of the figure. Electrons ejected from different MOs will differ in their kinetic energy.

The measured value of $E_{kinetic}$ can be used to obtain the energy of the orbital $\varepsilon_{orbital}$ from which the electron originated. The energy of the cation, E_f , which can be determined directly from a photoelectron spectrum, is equal to $\varepsilon_{orbital}$ if the following assumptions are valid:

- ❑ The nuclear positions are unchanged in the transition (Born–Oppenheimer approximation).
- ❑ The orbitals for the atom and ion are the same (**frozen orbital approximation**). This assumes that the electron distribution is unchanged in the ion, even though the ion has one fewer electron.
- ❑ The total electron correlation energy in the molecule and ion are the same.

The association of E_f with $\varepsilon_{orbital}$ for the neutral molecule under these assumptions is known as Koopmans' theorem.

In comparing spectra obtained for a large number of molecules with high-level numerical calculations, the measured and calculated orbital energies are often found to differ by approximately 1 to 3 eV. The difference results primarily from the last two assumptions not being entirely satisfied.

UV photoelectron spectrum of gas-phase H₂O. Three groups of peaks are seen. The structure within each group results from vibrational excitation of the cation formed in the photoionization process.

