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Review

Variable energy photoelectron spectroscopy: electronic structure and electronic relaxation

Edward I. Solomon*, Lipika Basumallick, Peng Chen, Pierre Kennepohl

Department of Chemistry, Stanford University, Stanford, CA 94305, USA

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* Corresponding author. Tel.: +1-650-723-4694; fax: +1-650-725-0259.
E-mail address: edward.solomon@stanford.edu (E.I. Solomon).

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Abstract

Use of variable photon energy with polarization available from synchrotron radiation has revolutionized the use of photoelectron spectroscopy (PES) in the study of transition metal complexes. The intensity dependence of PES peaks allows their definite assignment, a quantitation of the covalent mixing of the metal and ligand valence orbitals over the entire valence band, and an experimental determination of electronic relaxation. The last effect is the change in electronic structure with ionization, which is found to be large for transition metal complexes. Variable energy PES (VEPES) provides a powerful method to study bonding and its change with ionization and this provides fundamental insight into redox processes in inorganic and bioinorganic chemistry.

Keywords: Photoelectron spectroscopy; Variable photon energy; Electronic structure; Electronic relaxation

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1. Introduction

Modern photoelectron spectroscopy (PES) has been recognized for over three decades as a powerful spectroscopic method to elucidate the character of both inner-shell (core) and outer-shell (valence) electrons in molecular species. The photoelectric effect was discovered in 1887 by Heinrich R. Hertz, who showed that ultraviolet light changes the voltage at which various metal electrodes spark. Then, in 1905 Albert Einstein, building on Max Plank's concept that light is quantized explained the photoelectric effect. It was postulated that the energy required for ejection of a photoelectron was directly related to the binding energy of that electron (i.e. by conservation of energy). The spectroscopic utility of this phenomenon was only developed much later (in the 1960s), when it was noted that a photoelectron spectrum could be generated by using high-energy photons and accurately measuring the kinetic energy of the photo generated electrons. The energy and intensity of the peaks in the kinetic energy spectrum provide direct information on the electronic structure of the species being studied.

The kinetic energy of the photoelectron (E_k) is directly related to its initial state binding energy (E_b) through the Einstein expression of the law of conservation of energy as given in Eq. (1.1).

$$E_\mathrm{k} = h\upsilon - E_\mathrm{b} \tag{1.1}$$

This basic relationship directly relates the energy of peaks observed in a photoelectron kinetic energy spectrum with the binding energy of electrons in the initial molecule and thus provides a theoretical frame to correlate the PES spectrum with the molecular energy levels. The intensity of the peaks is determined from the electric dipole transition moment that connects the initial and final states (including the ejected photoelectron) and the incident photon ($\langle\Psi_f|r|\Psi_i\rangle^2$). Conventional high intensity sources used for PES (i.e. ultra high vacuum discharge tubes and X-ray anodes) provide discrete incident photon energies at high resolution but cannot be used to probe the photon energy dependence of PES spectra. These sources are therefore limited in their ability to extract detailed information from the photoionization cross-section (vide supra) of PES spectra. By contrast, synchrotron radiation sources are completely tunable over a large range of photon energies and surpass the intensity of conventional laboratory VUV and X-ray sources. Synchrotron-based PES thus give significant benefits by enabling variable photon energy experiments, which can allow unambiguous assignment of the photoionization spectra.

When the electron is ionized there can be a large change in electron repulsion in the resultant ion. Its remaining electron density then redistributes to compensate for the hole produced. This is electronic relaxation. The change in wave function of the relaxed final states relative to the initial state leads to intensity in more than one final state. This gives rise to satellite structure in the spectrum, which can then be used as a direct probe of the change in electronic structure upon ionization.

This review first provides a description of the experimental setup for synchrotron-based PES experiments (Section 2) as well as the methodological basis for detailed analysis of core and valence PES spectra for transition metal complexes (Section 3). The evaluation of electronic structure through PES is described (Section 4) with special emphasis on electronic relaxation, a phenomenon that plays a significant role in defining the redox properties of transition metal complexes. Recent applications from the literature are chosen (Section 5) to illustrate the power of synchrotron-based PES in elucidating the electronic structure of systems of interest in inorganic and bioinorganic chemistry. From this, it should become clear to the reader that synchrotron-based photoelectron spectroscopy can be a powerful probe of electronic structure and its change with ionization, and thus provides a unique perspective in defining and understanding the physical properties and reactivity of important systems in inorganic and bioinorganic chemistry.

2. Experiment and instrumentation

As described above, the photoelectric effect is key in photoelectron spectroscopy and the PES experiment involves the measurement of the kinetic energy of the electron ejected due to incident radiation. The ionization energy, intensity as a function of photon energy and angular distribution of the emitted electrons are evaluated to obtain insight into the electronic structure of molecules.