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COMMISSION ON MOLECULAR STRUCTURE  
AND SPECTROSCOPY

**NOMENCLATURE AND SPECTRAL  
PRESENTATION IN ELECTRON  
SPECTROSCOPY RESULTING FROM  
EXCITATION BY PHOTONS**

(RECOMMENDATIONS 1975)

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The Commission for Molecular Structure and Spectroscopy of IUPAC considers that it would be very valuable if agreement could be reached on nomenclature and conventions for spectral presentation in this rapidly developing and important field of spectroscopy. This type of spectroscopy involves the measurement of the kinetic energy of electrons emitted by chemical substances usually as a result of excitation by monochromatic X-rays (often termed ESCA—electron spectroscopy for chemical analysis) or ultraviolet radiation (often termed photoelectron spectroscopy). In many respects the two methods of excitation are complementary in their applications. In other cases, with which we shall not be concerned here, excitation of electron spectra can be by other processes such as electron bombardment.

AMBIGUITIES IN NOMENCLATURE

Examples of present ambiguities are as follows:

(a) The phrase "*photoelectron spectroscopy*"—commonly abbreviated to PES—is widely used to denote the analysis of the kinetic energies of electrons emitted after excitation by He I or He II photons in the UV region. But, logically, this description is equally applicable to the main features of spectra produced by X-ray photons (see later discussion).

(b) The phrase "*electron spectroscopy for chemical analysis*"—commonly abbreviated to ESCA—is widely used in connection with spectra produced by excitation with X-rays. But the spectra produced by ultraviolet irradiation also lead to applications to chemical analysis, particularly the identification of interatomic groupings within molecules.

It should be noted that other electron spectroscopic techniques, notably electron energy loss and Auger spectroscopy, also have important analytical uses.

A particular problem has arisen, leading to ungrammatical use of language, in connection with abbreviations which use "S" for "spectroscopy". For example, a phrase such as "NMR spectrometer"—meaning "nuclear magnetic resonance spectrometer"—is grammatically correct but, for example, the phrase "the ESCA spectrum" which literally means "the electron spectroscopy for chemical analysis spectrum" is incorrect. It is therefore recommended that as a general rule abbreviations or acronyms that incorporate S for "spectroscopy" or "spectra" should be discouraged. Exceptions are ESCA and PES

which, for historical reasons, have been widely adopted. It is recommended that these abbreviations be limited to their respective contexts and that in each case care should be taken to see that the acronym or abbreviation is not used in grammatically incorrect situations, such as for example, in the phrases "ESCA spectroscopy" or "PES spectrometer". It is also recommended that any abbreviations within electron spectroscopy should include the letter E standing for "electron".

The widely adopted description of spectra excited by UV photons, such as from He I or He II, as "photoelectron spectra" is recommended for general use. With this type of excitation of electrons from valence orbitals virtually all the electrons of which kinetic energies are measured derive from photoionization processes. Higher energy excitation, such as by X-ray photons, commonly leads to the production of electrons derived from Auger processes as well as from photoionization processes. Such complete and uninterpreted spectra are therefore logically described by the more general phrase "electron spectra". However, the more specific description "photoelectron spectra" may logically be applied to the appropriately identified features of such spectra. Under such circumstances, the spectra should be reported, as appropriate, in the fashion "the He I photoelectron spectrum" (spoken—the helium one photoelectron spectrum) or the "Al K<sub>α</sub> photoelectron spectrum" (spoken—the aluminium K alpha photoelectron spectrum). The use of the terms "photoemission spectroscopy" and "photoionization spectroscopy" in these contexts is to be discouraged.

THE ENERGY SCALE

Three designations of the energy scale—ionization energy, binding energy or electron kinetic energy—are in common usage in the presentation of diagrams of spectra derived from X-ray or UV excitation. The first two of these are alternative names for the same quantity but the electron kinetic energy, although linearly related to the others (it is the difference between the energy of the exciting photon and the ionization energy) increases in magnitude as the others decrease. Ionization potential (in volts) is also used as an alternative to ionization energy (in electron volts).

The general use of *ionization energy*,  $E_i$ , is recommended for the scale at the top of all spectral diagrams. It is also recommended that the experimentally measured parameter, electron kinetic energy, should be plotted along the bottom of the spectral diagram in the same units. The latter parameter is meaningful whether the electrons measured derive from photoionization or Auger processes. However, those spectral features derived from Auger processes, such as occur when using high energy excita-

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tion by X-rays, should be indicated clearly by asterisks because the ionization energy scale is not applicable to them.

The customary unit for  $E_i$  or electron kinetic energy per molecule is the electron volt, eV. Alternatively, where there is need to relate these energies to other quantities expressed in SI units, the unit recommended for the *molar ionization energy* is joule per mole,  $\text{J mol}^{-1}$ .

The direction of the ionization energy scale is not well defined in the literature. For X-ray excitation, ionization (binding) energy is usually plotted so as to increase from right to left. For ultraviolet He I or He II excitation the literature shows a limited preference for ionization increasing from left to right. For consistency between the two related fields it is recommended that the spectra be plotted with increasing electron kinetic energy to the right, i.e. increasing ionization energy to the left. This presentation is consistent with other branches of elec-

tronic spectroscopy where spectral features involving higher levels of molecular excitation are normally found to the left of the spectral diagram.

OTHER RECOMMENDATIONS FOR THE  
PRESENTATION AND PUBLICATION OF  
SPECTRAL DATA

(i) The primary ordinate scale of the normal differential curve should be given as  $(dI/dV)$ , i.e. ampere volt<sup>-1</sup>,  $\text{AV}^{-1}$ , or as (counts  $\text{s}^{-1}$ ).

(ii) Information about sweep rate (in  $\text{Vs}^{-1}$ ) and/or integration time (in s) should be given where appropriate.

(iii) A statement should be given of the method of calibration and the precision achieved.

(iv) Because different types of apparatus exhibit different sensitivity as a function of electron kinetic energy, relevant information should be given about the performance of the equipment used.