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Communication

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Why Can't We See Hydrogen in X-ray Photoelectron Spectroscopy?

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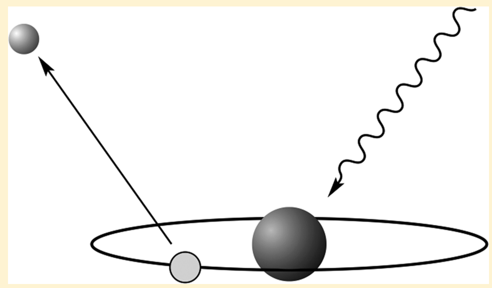
ABSTRACT: Literature describing X-ray photoelectron spectroscopy (XPS) generally assumes that the reader will understand why the method cannot detect hydrogen atoms. On the other hand, students struggle finding the answer even after extensive literature search and reading.



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At the beginning of the semester, I posted a bonus question in my spectroscopy class: "Why can't we see hydrogen in X-ray photoelectron spectroscopy (XPS)?" My students taking this special topic class unsuccessfully searched the literature for the answer and at the end of the semester gave up. In general, books[1] discussing XPS often state that hydrogen cannot be seen in XPS, with no explanation given. This question stimulated students to think and read, which was my goal, and their failure to answer it inspired me to write this communication. I found that the difficulty originates from misunderstanding of the effect on which the XPS method is based: the photoelectric effect. A common misunderstanding is that above the so-called cutoff frequency, any further increase in frequency of light will not change the number of generated photoelectrons and will only increase their kinetic energy. Generally, students are neither familiar with ionization cross sections nor with the Fermi golden rule and transition probabilities. The best place for chemistry students to be exposed to this question would be in physical chemistry class when studying photoelectric effect and photoelectron spectroscopy. The question could be incorporated within the homework assignment and students may be given some hints. For example, the question could be asked as "What is the physical meaning of cross sections and why can't we see hydrogen in XPS".

PHOTOELECTRON SPECTROSCOPY

In photoelectron (PE) spectroscopy, the kinetic energy of ejected electrons is measured in the spectrometer and spectra are displayed as intensity (electron yield) versus binding energy. PE spectroscopy is excellent tool is studying densities of states and band structures. XPS, in particular, is one of the most common analytical instruments used for elemental composition analysis of solid surfaces and is essential tool in many surface chemistry laboratories.[2,3] X-ray photons have energies suited for ejecting inner-shell (core) electrons. In an XPS experiment, the sample, kept under vacuum, is typically exposed to photons having energy, $\hbar\omega$, high enough to eject inner-shell electrons from the surface atoms. The process can be represented as

$$A + \hbar\omega \rightarrow A^{+} + e^{-}$$

where A is an atom, A^+ is a positively charged ion, and e^- is the photoelectron. The kinetic energy, E_{kin}, of the photoelectron can be expressed as

$$E_{kin} = \hbar\omega - E_b - W$$

where E_b is the binding energy of the electron, and W is the work function, with the kinetic and binding energies referenced to the Fermi level of the sample.

IONIZATION CROSS SECTIONS

The more complete description of the photoelectric effect would be to point out that even if the frequency of incoming photon is larger than the cutoff frequency, the photoionization occurs with certain probability. Generally, different orbitals with different symmetries have different probabilities of ionization, that is, different ionization cross sections. For example, for a given element, photoionization cross section, σ, of a $2s_{1/2}$ orbital differs from that of a $3s_{1/2}$ orbital, $\sigma(np_{1/2})$ differs from $\sigma(np_{3/2})$, whereas $\sigma(nd_{3/2})$ differs from $\sigma(nd_{5/2})$ and so on. Also, it should be specified, at least as a footnote, that the photoionization cross sections of atomic orbitals depend on photon energies. Photoelectric cross sections for the $K\alpha$ lines of magnesium (1254 eV) and of aluminum (1487 eV) for various elements (including hydrogen) have been reported by Scofield.[4] The total photoionization cross section of hydrogen, using 1254 eV photons, expressed in units of the carbon 1s cross section, $\sigma_C(1s)$ = 22,200 barns, is 0.0002. This means that hydrogen has 5000 times smaller cross section than the carbon 1s orbital.

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HYDROGEN ELECTRON

Hydrogen has no core electrons and, therefore, core−electron XPS is impossible. The H 1s electrons are valence electrons and as such participate in chemical bonding. Any signal from hydrogen would overlap with signals from excitation of valence electrons from other surface atoms. Namely, photoionization cross sections for valence electrons are also small and their binding energies significantly change with chemical environment. Also, the valence orbitals often appear in the spectra as broad bands. It is generally not possible to distinguish between H 1s valence electrons and valence electrons of other elements. Therefore, H 1s valence electrons are not useful in elemental identification using XPS method.

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Notes

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