Why can't we observe hydrogen & helium in XPS analysis?

It is a question we are often asked by those new to the field of X-ray Photoelectron Spectroscopy (XPS) and typically one that many students of all abilities find hard to explain. Whilst this may be answered with a simple statement, we should first reacquaint ourselves with some background which we discuss below.

Photoelectron spectroscopy & photoionization cross-sections

If we think about the photoemission process, we are causing the ejection of electrons from different core-levels according to equation (1).

$$M + h\upsilon \rightarrow M^{+} + e^{-} \tag{1}$$

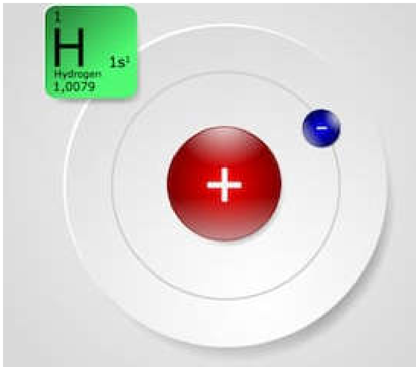
Where M and M^{+} are the ground and photo-ionized states of a molecule respectively, e^{-} is the ejected photoelectron and $h\upsilon$ the incoming photon energy. The kinetic energy (E_k) of this electron is related to the orbital binding energy (E_b) as in equation (2).

$$E_k = h\upsilon - E_b \tag{2}$$

Each orbital from which electrons are ejected will have different probabilities for photoionization which, in turn, are defined by photoionization cross-sections. These difference in probabilities arise due to different orbital symmetries (recall that *s*, *p*, *d* and *f* orbitals all have different shapes) and closeness to the nucleus. Clearly, the energy of the impinging photon will also have an influence on the ionization probability of electrons from a given orbital, so depending on our photon source, we will have different line intensities.

Photoelectric cross sections for the Kα lines of aluminium (1486.6 eV) and magnesium (1253.6 eV) for a large number of elements, including hydrogen have been tabulated by Scofield[1]. Using Scofield's values the cross section for hydrogen is 0.0002, and relative to C(1s) with a value of 1.0 the sensitivity of XPS to hydrogen is 5000 times lower.

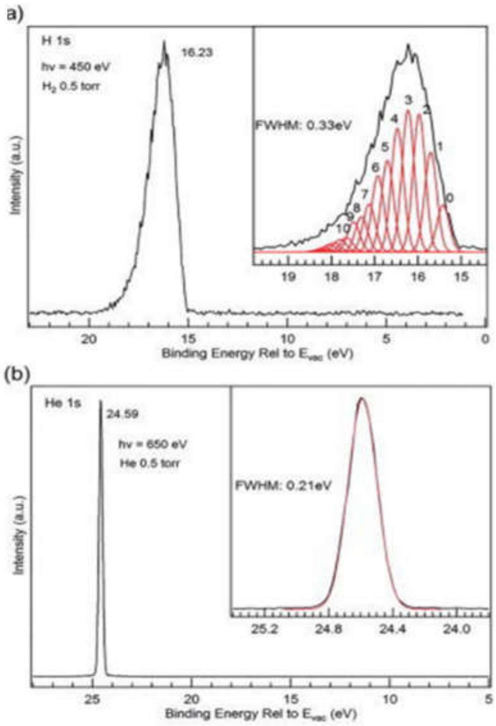
The hydrogen electron



Let us consider the hydrogen atom as shown to the right. From a physical point of view hydrogen has **no** core-electrons. So performing core-level spectroscopy (i.e. XPS) is impossible.

For the H(1s) orbital, the electrons are valence electrons which therefore take part in chemical bonding. Consequently, any potential signal arising from hydrogen would overlap with other excited valence electrons within the species under study. Similar arguments hold for helium.

Measuring the impossible?



Under specific conditions, namely ambient pressures (AP) and using high intensity photon sources (synchrotrons), the x-ray photoelectron spectra of hydrogen and helium may actually be measured, such as that show on the right and recorded at the National Synchrotron Light Source II[2].

The figure shows the AP-XPS spectra of (a) H 1σg and (b) He 1s, recorded under 0.5 torr of H_2 (hν = 450 eV) and He (hν = 650 eV). The insets in (a) and (b) show the detailed features of the H 1σg and He 1s peaks, where in the case of helium gas, the spectrum shows a symmetric peak from its only orbital, whilst for hydrogen gas molecules, an asymmetric peak is observed, relating to the different possible vibrational modes of the final state.

References

[1] J. H. Scofield, *J. Electron Spectrosc. Relat. Phenom*. 8 (1976) 129

[2] J-Q Zhong, M. Wang, W. H. Hoffmann, M. A. van Spronsen, D. Lu, J. A. Boscoboinik; *Appl. Phys. Lett.* 112 (2018) 091602