NOTES AND INSIGHTS

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XPS insights: Asymmetric peak shapes in XPS

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The misinterpretation of peak asymmetry as higher oxidation states in x-ray photoelectron spectroscopy (XPS) is regretfully all too common. This *XPS Insight* note introduces the theory of peak asymmetry in x-ray photoelectron spectra and such asymmetry is discussed for a range of different classes of materials to afford analysts a more informed view of their spectra.

KEYWORDS
asymmetry, fitting, peak, XPS

1 | INTRODUCTION

In a recent analysis of XPS data submitted over a 6-month window to three high-quality journals, it was found that a significant proportion of the published XPS spectra had flaws that contributed to misinterpretation and potentially erroneous conclusions; this was particularly evident in the use of photoelectron peaks from metallic materials.[1] From the authors own ad hoc analysis of published data, a significant degree of error comes from the authors using simple bell-shaped curves for the analysis of metal states, when a peak shape with asymmetry to the higher binding energy side is more appropriate. In this *XPS Insight*, the theory of peak asymmetry is addressed together with examples which it is hoped will improve analysis.

In terms of peak analysis, following suitable subtraction of the inelastic electron background,[2,3] the resulting peak for a single well-defined state can be modelled by a Gaussian-Lorentzian/Voigt function (either product or sum), which is symmetrical.[4] The peak width is a convolution of spectrometer related phenomena, including the X-ray source width, the detector pass energy (resolution) and physical phenomena such as core-hole lifetime broadening. However, electronic excitations occurring after the initial photoemission event can distort this profile leading to asymmetry, which are discussed in the following sections. It is noted the practicalities of line-shape selection, especially those requiring asymmetric tail functions such as Doniach-Sunjic and asymmetric Lorentzian line-shapes,[4,5] and fitting will not be addressed in this paper; instead, readers are asked to familiarise themselves with previous studies[6–8] and the references therein.

2 | WHY DOES PEAK ASYMMETRY OCCUR?

Asymmetry in XP spectra may arise from effects such as (i) overlap of several signals arising from different chemical states or satellite structure of the element, (ii) excitation of vibrational modes during photoemission, which is especially seen in hydrocarbon materials,[9–12] and (iii) multi-electron excitations and electron–hole pair creation in metallic valence bands.[13,14]

In simple terms, peak asymmetry in metals,[15,16] arises due to a series of unfilled one-electron levels (the conduction band), which can accept electrons that have undergone shake-up type processes following ejection of the initial core electron. Instead of discrete features observed for shake-up peaks (such as the well-known Cu (II) satellite structure[16]), a tail to the higher binding energy side of the main peak is evident, giving the peak asymmetry, whilst in the case of a metal oxide, these energy levels are not available, and hence, a more symmetric form is observed, as illustrated in Figure 1 for the Mo(3d) core-level for metallic Mo and MoO_3.
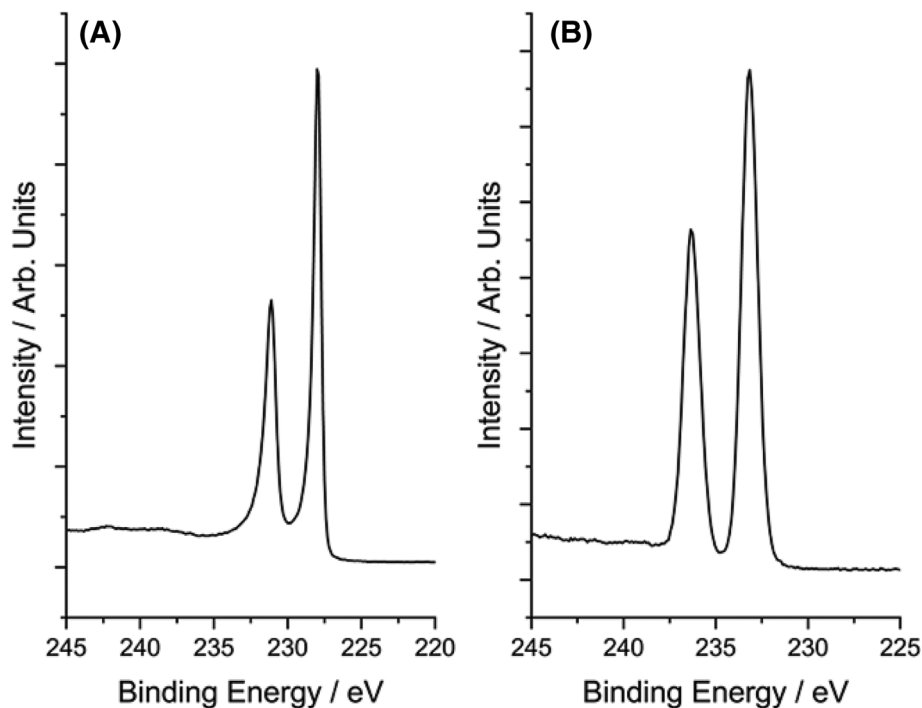
FIGURE 1 Mo(3d) core-level spectra for (A) Mo foil and (B) MoO$_3$. The asymmetry in the metal is clear, whereas the oxide peaks are more symmetrical.
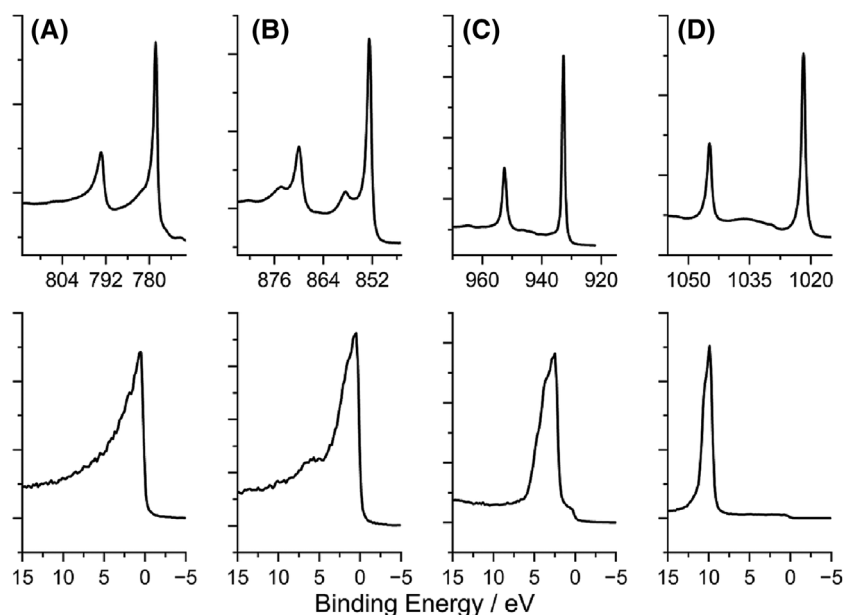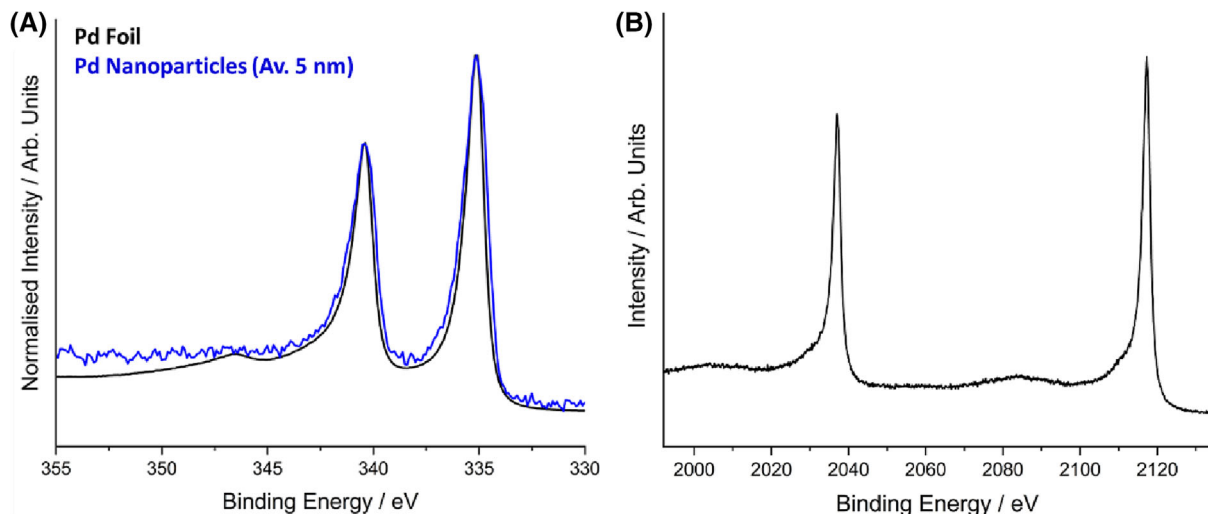

FIGURE 2 Main 2p core-level photoemission spectra (upper) and valence band spectra measured by XPS (lower) for (A) cobalt, (B) nickel, (C) copper and (D) zinc illustrating the change in core-level asymmetry as the density of states (DOS) at the Fermi level changes.

Given our discussion on the multi-electron excitations, it is logical to assume the asymmetry will be influenced by the density of states (DOS) at the Fermi level. Indeed, if we consider the first-row transition metals from scandium to copper, then as we fill the d-band, we move from asymmetric peaks to more Voigt-like shape as shown in Figure 2 for cobalt to copper, and zinc is also included as a full-shell material for reference. A similar trend is observed for the second and third row transition metals, with Rh-Pd-Ag and Ir-Pt-Au showing a similar loss of symmetry as we move along the row.[14] Similar correlations can be made in x-ray absorption spectroscopy (XAS) where the whiteline for the L$_3$ adsorption edge for 4d (Mo to Ag) and 5d metals (Re to Au) exhibit a decrease in intensity due to

the fewer available unfilled d states for electronic transitions form 2p states.[17,18]

Notwithstanding binding energy shifts that are possible based on the cluster shape, size and substrate interaction,[19,20] or changes due to alloying,[21] the degree of asymmetry of core-levels for nanoparticulate metals can also vary as a function of cluster size as has been discussed by Wertheim[20] and Cheung[22] amongst others. A simple example of Pd nanoparticles compared to bulk Pd foil recorded under identical conditions is given in Figure 3A. Again, this change in asymmetry is a response of the valence electrons to the core-hole.

Appreciation of such peak asymmetry is even more warranted given the recent explosion of lab based high energy XPS (HAXPES)

FIGURE 3 Highlighting core-level asymmetry for (A) Pd metal (black) compared to Pd nanoparticles of 5 nm average size (blue) recorded under identical conditions, and (B) the deeper Pt(3d) core-level photoemission peaks from sputtered Pt foil measured at SPring-8 using an excitation energy of 7938.96 eV (spectrum adapted from the Materials Data Repository, DOI: 10.48505/nims.3275 and used under a creative commons license).

FIGURE 4 Ir(4f) and O(1s) core-levels for anhydrous IrO_2. The asymmetry arises due to screened states, the unscreened (dark grey) and screened (light grey) states for the O(1s) level are shown (adapted from Freakley et al.[23]).
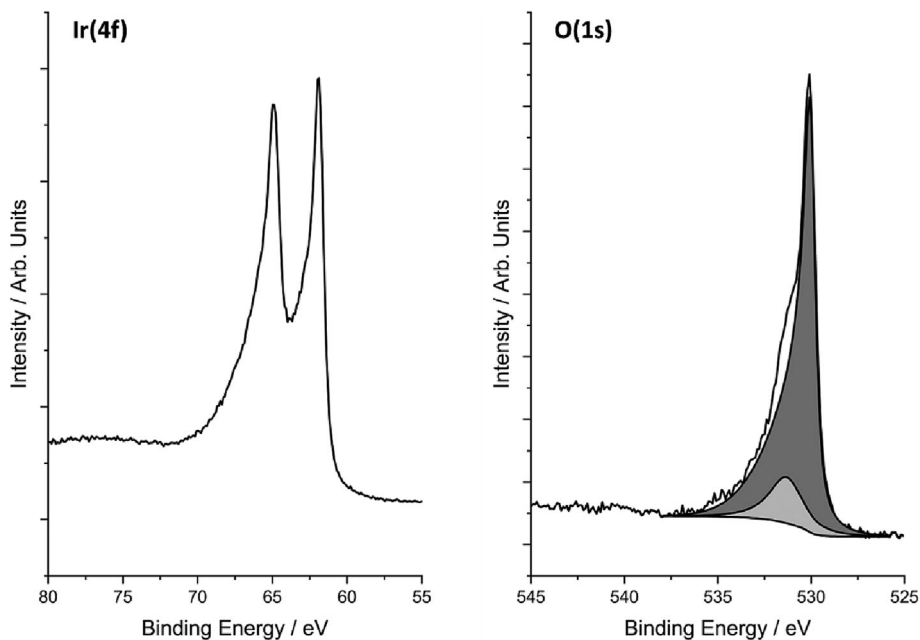
sources, where deeper core-levels such as Pt(3d) lines shown in Figure 3B, will also exhibit different degrees of asymmetry, which should be appreciated rather than erroneously assign as a second oxidation state or similar.

3 | ASYMMETRY IN OTHER MATERIALS

Despite transition metal oxides typically being insulating, some oxides are conductors and hence exhibit asymmetric peaks; such oxides include RuO_2,[15] IrO_2,[23] OsO_2,[24] MoO_2[25] and PbO_2.[26] In some of these materials, for example, IrO_2, it is not just the metallic core-levels

that are asymmetric; the O(1s) core-level also exhibits asymmetry caused by screening effects (see Figure 4 for the Ir(4f) and O(1s) core-levels of anhydrous IrO_2). Comparing the core levels of anhydrous and hydrated IrO_2,[23] then it is evident that a lack of appreciation of these factors can lead to misinterpretation of chemical states. Therefore, comparison with well-defined reference samples may be warranted, and if doubt exists, systematic changes to line shapes can to be elucidated through controlled heating or ion beam modification of the sample.[27,28]

Peak asymmetry also exists for graphitic carbon materials,[6,29] which may seem counter intuitive based on our discussion of metals, due to the absence of a high DOS near the Fermi edge needed for the

same final state effects observed in metals. Nevertheless, the asymmetry can still be explained on the basis of the core hole formation. These holes are screened by electron relaxation, resulting in excitation of valence band electrons to unoccupied states in the conduction band, resulting in a loss of energy of the ejected photoelectrons leading to asymmetry, which has been suggested to be independent of interactions between carbon layers.[30,31]

HOPG is perhaps the most ubiquitous reference for a graphitic carbon[29,32] consisting of a well-ordered carbon network, with delocalisation of electrons arising for overlap of the 2p orbitals. Should there be a perturbation in this network, such as defects or curvature such as in nanotubes, the delocalisation of the electrons will be affected,[33] and consequently, screening of the charge located at these defect sites must be screened, hence changing the asymmetry of the peak. It is not until there is a sufficient density of defects that the spectra will change due to defect and disordered carbon peaks.[34]

With the discussion on graphitic carbon, it is worthy to reiterate at the juncture the vibrational structure, which can be observed in hydrocarbon and polymer species.[9–12] Whilst vibrational excitation is observed in ultraviolet photoelectron spectroscopy (UPS) experiments, caused by changes in in bond lengths through removal of bonding valence electrons, it is not typically considered in XPS measurements. However, as shown by Beamson et al.,[9] asymmetry arises from C-H vibrations comparable to that observed in gas phase CH_4. Such asymmetry has been observed in ethyl trifluoroacetate, classically called 'the ESCA molecule', where developments in resolution at synchrotrons has allowed asymmetry to be observed due to the different molecular conformations.[12]

It is not just polymers or adsorbed hydrocarbons that exhibit asymmetry. For example, Tillborg et al. elegantly showed the variation of the O(1s) core-level asymmetry varied as a function of substrate, caused by adsorbate-substrate 2p-3d hybrid states.[35] More recently Acres et al. have shown asymmetry for adsorbed oxygen and sulfur on an Fe(110) single crystal surface concluding similar hybridisation of adsorbate and substrate orbitals.[36]

4 | SUMMARY

Generally peak asymmetry is one of the largest causes of data misinterpretation in XPS analysis. This *XPS Insight* has sought to illustrate the importance of understanding the causes of and appreciating changes in peak asymmetry in photoemission experiments. Discussion of peak fitting parameters, line shape selection and so-forth are beyond the scope of this paper and it is hoped that readers will seek out the appropriate references, of which some have already been given within this paper. Furthermore, it is anticipated that use this paper, together with other insight notes published in this journal, will help to stop the proliferation of poor data analysis.

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