NOTES AND INSIGHTS OPEN ACCESS

XPS Insight Note: Coster-Kronig Broadening

Mark A. Isaacs^{1,2} Phillip R. Davies^{2,3} | Arthur Graf^{2,3} | David J. Morgan^{2,3} Robert Palgrave^{1,2}

¹Department of Chemistry, University College London, London, UK | ²HarwellXPS, Research Complex at Harwell, London, UK | ³School of Chemistry, Cardiff University, Cardiff, UK

Correspondence: Mark A. Isaacs (mark.isaacs@ucl.ac.uk)

Received: 10 March 2025 | Revised: 24 April 2025 | Accepted: 5 May 2025

Funding: This work was supported by Engineering and Physical Sciences Research Council (EP/Y023587/1, EP/Y023609/1, EP/Y023536/1, EP/Y023552/1 and EP/Y023544/1).

ABSTRACT

Inconsistent peak broadening of doublet peaks in X-ray photoelectron spectroscopy is commonly observed for many transition metals, lanthanides and actinides, which may complicate peak fitting—especially for newer practitioners. In this insight note, we discuss why this broadening occurs, what governs the degree of broadening and how analysts and spectroscopists can account for this in their modelling.

1 | Introduction

X-ray photoelectron spectroscopy (XPS) has become an invaluable tool for the analysis and understanding of a huge range of materials and is now fully established as a central technique in modern analytical chemistry [1–3]. The increasing popularity of XPS as a tool to study solid-state materials has been accompanied by an increase in its accessibility to researchers without specialist knowledge of the technique and its background. Inevitably, this has led to an increasing number of papers in which aspects of XPS data have been misunderstood and inaccurate conclusions drawn [4], which has been increasing since 2010 [5].

One fundamental aspect of XPS that sometimes leads to confusion is spin–orbit coupling, which arises from the interactions between different spin states $(+^{1}/_{2} \text{ and } -^{1}/_{2})$ with the angular momentum of the electronic orbital—resulting in two distinct orbital angular momentums (provided that the angular momentum quantum number is greater than zero) and a doublet of peaks. The two spin-orbit coupling derived peaks in most cases have an equivalent peak width [6], for reasons we detail herein. Some elements, however, particularly those of the first and second row transition metals, exhibit a disparity in their doublet widths where the higher binding energy peak appears broader than the lower binding energy emission. This phenomenon can be attributed to the so-called 'Coster–Kronig–Auger–Meitner processes' which must be accounted for if the analyst is to accurately model any curve fitting [7].

In this insight, note that we explore the phenomena occurring in this process and provide guidance for accounting for this in the data modelling of affected doublets.

1.1 | Line Broadening in XPS

There are a number of factors that affect the recorded peak width in XPS, though the fundamental determinant is the core-hole lifetime (τ), which dictates the 'natural linewidth' (Γ) of the photoemission peak [8]. The natural energy spectrum of an emitted

© 2025 The Author(s). Surface and Interface Analysis published by John Wiley & Sons Ltd.

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

photoelectron is best represented by a Lorentzian distribution, where I the intensity (I) at energy E is given by the following:

$$I(E) = I(E_0) \frac{\Gamma^2}{(E - E_0)^2 + \Gamma^2}$$
 (1 Lorentzian peak distribu-
tion function)

where E_0 is the peak centroid and the natural linewidth is given by the following:

$$\Gamma = \frac{\hbar}{\tau}$$
 (2 Natural linewidth relation-
ship with core-hole lifetime)

Other factors can influence the peak width of photoelectron emissions and tend to do so as a Gaussian function. Table 1 outlines the typical ways in which peak broadening may be observed.

The factors unrelated to lifetime broadening typically do not discriminate between spin states (e.g., instrument factors and crystallinity) or do so at a level far below any practical significance (e.g., vibrational/conformity broadening of different final states may have slightly different Franck–Condon broadening envelopes; however, these are subtle enough differences to have no practical impact on a resultant photoelectron spectrum. As such, these cannot explain the significant difference between the peak widths we see for selected doublets—so we must consider core-hole lifetimes only.

1.2 | Spin-Orbit Coupling

Before we consider the Coster–Kronig process, we will provide a short background to spin–orbit coupling in order to ensure that this resource contains a complete understanding of the names process for newer spectroscopists. This is not intended to be an exhaustive overview, and for a more detailed work through of spin–orbit coupling, we recommend consulting the JVST practical guide series [19, 20] or reading one of the many textbooks on the subject [21]. We will assume familiarity with the basic electronic quantum numbers of n,

 l, m_l and m_s . Equation (3) is an approximation derived from Sommerfeld's calculations, while a more complete expression can be found elsewhere [22]. According this relationship, the separation between the peaks is expected to increase with the atomic number [23]. This relationship was later refined by Condon and Shortley in a fully quantum mechanical approach, which modifies the Sommerfield approach with specific quantum mechanical terms [24]. We show only the original Sommerfield equation here for simplicity.

$$\Delta E = \frac{Z^4}{n^3 \left(l + \frac{1}{2}\right)(l+1)}$$
 (3 Doublet energy separation (ΔE) for
a spin-orbit coupled doublet, where
 $Z =$ atomic number)

Electron spin states that $(\pm \frac{1}{2})$ can couple with the angular momentum of the orbital (m_l) to result in a pair of states of slightly higher and slightly lower energy of total angular momentum (J), where

$$J = |m_l + m_s|$$
 (4 Total angular momentum)

The nomenclature of these spin states is derived from the total angular momentum; for example, a 2p orbital has an orbital angular momentum of 2, and so the two values for *J* are therefore $3/_2$ and $1/_2$. Finally, the degeneracy of these states can be determined through comparing the ratios of 2(J+1), given the expected peak area intensities of the resultant doublets in XPS. It should also be noted that when discussing Auger–Meitner processes, we tend to use traditional X-ray notation (Table 2) to refer to the relevant energy states (Table 1).

1.3 | Coster-Kronig Processes

In the conventional Auger–Meitner process (Figure 1a), a photoelectron core-hole is created by the initial incoming radiation, which results in the atom reconfiguring to a lower energy state through the relaxation of an electron from a higher orbital to fill the newly created core-hole. In order to relax to a lower energy

Broadening factor	Description	Lineshape of broadening	Ref.
Lifetime broadening	Broadening due to natural linewidth (Equation (2))	Lorentzian	[8]
Vibrational/Franck–Condon broadening	Broadening due to differences in the nuclear geometry between initial and final state	Gaussian	[9–12]
Phonon broadening	Excitation of phonons following core-hole formation	Gaussian	[13]
Crystallinity	Poorly crystalline or amorphous materials tend to produce broader peaks	Gaussian	[14]
Temperature	Broadening due to temperature induced vibration	Gaussian	[15]
Molecular conformity	Different conformers exhibit different nuclear dynamics—not distinct enough to produce multiple peaks but enough to contribute to overall peak breadth	Gaussian	[16]
Instrument factors	For example, X-ray source linewidth and instrument performance factors	Gaussian	[17, 18]

TABLE 1 | Factors affecting peak broadening in XPS.

TABLE 2 | X-ray notation nomenclature.

Orbital	X-ray notation		
1s	K	1	
2s	L	1	
2p 1/2	L	2	
2p 3/2	L	3	
3s	М	1	
3p 1/2	М	2	
3p 3/2	М	3	
3d 3/2	М	4	
3d 5/2	М	5	
4f 5/2	Ν	6	
4f 7/2	Ν	7	

state, this electron must release energy (in the form of X-rays) which in turn may then trigger a second photoelectron emission resulting in a double core-hole system [25].

The Coster–Kronig transition (Figure 1b) [7] has a distinct difference in that the relaxing electron does not originate in a higher energy orbital but from the same orbital, emitting an Auger–Meitner electron from the valence shell [26]. There also exists the possibility to undergo a 'Super Coster–Kronig' transition, whereby the photoelectron core-hole, the relaxing electron and the final Auger–Meitner emitted electron are all from within the same orbital—though these are less commonly observed, since there are fewer orbitals capable of undergoing this process [27].

The relevant outcome from this process is that the lifetime of the lower energy core-hole will be shorter than its higher state counterpart. In the example in Figure 1, this would result in a decreased lifetime for the L_2 state as it is quickly filled by the



FIGURE 1 | (a) Typical Auger-Meitner electron emission process and (b) Coster-Kronig transition Auger-Meitner electron emission process.

decaying L₃ state after formation—resulting in the release of the Coster–Kronig Auger–Meitner electron.

In a simplistic model, ignoring relaxation and screening effects, in order to emit an Auger–Meitner electron, we must have enough energy to overcome the ionisation energy of the electron in question. For conventional Auger–Meitner emissions, this is relatively trivial, since the difference between the original core-hole and the decaying electron tends to be quite large. For example, for a Ni 2p $(L_{2,3})$ core-hole, the hole is filled by a 3d $(M_{4,5})$ valence electron—with an energy difference of around 850 eV. Such high-energy radiation is therefore capable of ejecting a large number of photoelectrons—with the predominant emission occurring with a kinetic energy of around 845 eV $(L_3M_{4,5}M_{4,5})$ [28], the result of the photoexcitation of valence electrons (Figure 2).

By contrast, the determining factor of the Coster–Kronig Auger–Meitner electron for the Ni 2p core-hole will be the doublet separation between the L_3 and L_2 states—since the process in question is an Ni $L_3L_2M_{4,5}$ Auger–Meitner emission. The doublet separation of the Ni 2p L_3 and L_2 states (Equation (3)) is 17.3 eV, and hence, the kinetic energy of the Coster–Kronig Auger–Meitner electron will



FIGURE 2 | Ni metal Auger-Meitner peaks in an XPS survey spectrum.



FIGURE 3 | Electronic levels of (a) Ni and (b) Mo.

be very low (Figure 3a) and is unlikely to be observed due to the high background in this region of the spectrum.

Given this energy gap is the source of the exciting energy for the subsequent photoemission process, if we have a scenario where the doublet separation is quite small (e.g., molybdenum, Figure 3b) then for the cases of localised electron energy states (e.g., nonmetals), this energy may be insufficient to overcome the binding energy of the final Auger-Meitner electron [29], and therefore, this Coster-Kronig process is forbidden [30]. In Figure 4a, we report the measured full-width at half maximum (FWHM) for a titanium metal and oxide sample (doublet separation energy > ionisation potential for both system) and (Figure 4b) a MoTe chalcogenide and MoO₂ oxide (doublet separation energy > ionisation potential for chalcogenide, doublet separation energy < ionisation potential for oxide), which highlights the forbidden process once the ionisation potentially exceeds the doublet separation of the initial core-hole orbital. The valence regions of the MoTe and MoO₂ are presented in Figure 4c, with the summary of the energetics involved in Figure 4d. From this figure, we can see that the only case where our valence band maximum (VBM) energy > our doublet separation, the peak widths are equivalent.

The degree of broadening, dependent on the rate of the Coster– Kronig transitions, is influenced by the kinetic energy of the emitted electron (higher kinetic energies=higher rate) [31], number of electrons capable of participating in the Coster– Kronig process [32] and screening effects [33].

1.4 | Data Fitting

The degree of broadening for specific orbitals can be found in literature [30, 32], and these broadenings can be used within modelling functions by adding a fixed value on to the measured FWHM of the higher energy (unbroadened) peak—though there are often other factors affecting the recorded spectrum such as plasmons or satellites [34–37], and as such, it might prove easier





FIGURE 4 | (a) Ti 2i regions for titanium metal and titanium (IV) oxide, (b) Mo 3d regions for MoTe and molybdenum (VI) oxide, (c) valence band XPS regions for MoTe and molybdenum (VI) oxide and (d) energies of doublet separation, measured VBM and FWHM for high and low spins, spin-orbit couplet doublet peaks for titanium metal, titanium (IV) oxide, MoTe and molybdenum (VI) oxide.

to model standard reference data before incorporating the developed peak models into your unknown dataset.

2 | Summary

Doublet peaks in XPS arise due to spin–orbit coupling interactions, and in cases where both spin states have the same core-hole lifetime, these peaks should have equivalent peak widths. A number of cases, however, result in systems where the different spin states have inequivalent core-hole lifetimes due to a so-called Coster– Kronig Auger–Meitner transition involving a core-hole and decaying electron from the same orbital. We have provided a bullet point summary of this process below for simple consideration.

- XPS peak width is related to the lifetime of the core-hole that results from **photoionisation**
- Orbitals with orbital angular momenta **higher than zero** (p, d, f) produce doublet peaks due to interaction with the different **electron spin states**
- E₁ at a lower binding energy
- E_2 at a higher binding energy

- Secondary decay processes involving both electrons of the doublet pair may occur in which E_2 is photoexcited, and E_1 relaxes to fill the newly created core-hole
- Since the binding energy of $E_2 > E_1$, this process can only occur in one direction, E_2 does not have enough energy to fill an E_1 core-hole
- This gives our E_2 state an additional decay pathway unavailable to E_1 , and thus, a shorter lifetime for the resultant core-hole
- The shorter lifetime of this higher binding energy electron results in a broader linewidth and ultimately the disparity in peak widths associated with certain elements such as Ti, Ru, and others.

We hope that this insight note has given the readers some context behind the commonly observed broadening phenomenon in doublet peaks in XPS.

Author Contributions

Mark A. Isaacs: conceptualization. Mark A. Isaacs: data curation: Mark A. Isaacs: formal analysis: Phillip R. Davies, David J. Morgan and Robert Palgrave: funding acquisition. Mark A. Isaacs, David J. Morgan and Arthur Graf: visualisation. Mark A. Isaacs: writing – original draft preparation. Mark A. Isaacs, Arthur Graf, David J. Morgan, Phillip R. Davies, Robert Palgrave: writing – review and editing.

Acknowledgments

Some of the work included herein has been generated through the authors' provision of the EPSRC National Facility for Photoelectron Spectroscopy (HarwellXPS) (*"HarwellXPS"*, *EP/Y023587/1*, *EP/Y023609/1*, *EP/Y023536/1*, *EP/Y023552/1* and *EP/Y023544/1*)'.

We would like to thank the reviewers of this article for their thoughtful and helpful contributions towards improving this work.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

1. D. R. Baer, J. F. Watts, A. Herrera-Gomez, and K. J. Gaskell, "Evolving Efforts to Maintain and Improve XPS Analysis Quality in an Era of Increasingly Diverse Uses and Users," *Surface and Interface Analysis* 55 (2023): 480–488.

2. A. Roberts and C. Moffitt, "Trends in XPS Instrumentation for Industrial Surface Analysis and Materials Characterisation," *Journal of Electron Spectroscopy and Related Phenomena* 231 (2019): 68–74.

3. C. Brundle, G. Conti, and P. Mack, "XPS and Angle Resolved XPS, in the Semiconductor Industry: Characterization and Metrology Control of Ultra-Thin Films," *Journal of Electron Spectroscopy and Related Phenomena* 178 (2010): 433–448.

4. G. H. Major, T. G. Avval, B. Moeini, et al., "Assessment of the Frequency and Nature of Erroneous X-Ray Photoelectron Spectroscopy Analyses in the Scientific Literature," *Journal of Vacuum Science & Technology A* 38 (2020): 38.

5. B. M. Clark, G. H. Major, J. W. Pinder, et al., "Following the Propagation of Erroneous X-Ray Photoelectron Spectroscopy Peak fitting Through the Literature. A Genealogical Approach," *Journal of Vacuum Science & Technology A* 42 (2024): 063213, https://doi.org/10.1116/6. 0004093.

6. G. H. Major, V. Fernandez, N. Fairley, E. F. Smith, and M. R. Linford, "Guide to XPS Data Analysis: Applying Appropriate Constraints to Synthetic Peaks in XPS Peak Fitting," *Journal of Vacuum Science & Technology A* 40 (2022): 063201.

7. D. Coster and R. D. L. Kronig, "New Type of Auger Effect and Its Influence on the X-Ray Spectrum," *Physica* 2 (1935): 13–24.

8. J. C. Fuggle and S. F. Alvarado, "Core-Level Lifetimes as Determined by X-Ray Photoelectron Spectroscopy Measurements," *Physical Review A* 22 (1980): 1615–1624.

9. P. S. Bagus and C. J. Nelin, *Rare Earth Elements and Actinides: Progress in Computational Science Applications*, vol. 1388, ch. 9 (American Chemical Society, 2021): 181–206.

10. G. Beamson, D. T. Clark, J. Kendrick, and D. Briggs, "Observation of Vibrational Asymmetry in the High Resolution Monochromatized XPS of Hydrocarbon Polymers," *Journal of Electron Spectroscopy and Related Phenomena* 57 (1991): 79–90.

11. U. Gelius, "Recent Progress in ESCA Studies of Gases," *Journal of Electron Spectroscopy and Related Phenomena* 5 (1974): 985–1057.

12. K. Siegbahn, "Electron Spectroscopy - An Outlook," Journal of Electron Spectroscopy and Related Phenomena 5 (1974): 3–97.

13. P. H. Citrin, P. Eisenberger, and D. R. Hamann, "Phonon Broadening of X-Ray Photoemission Linewidths," *Physical Review Letters* 33 (1974): 965–969.

14. G. Beamson, D. T. Clark, N. W. Hayes, and D. S.-L. Law, "Effect of Crystallinity on the XPS Spectrum of Poly(Ethylene Terephthalate)," *Surface Science Spectra* 3 (1994): 357–365.

15. P. Unsworth, J. Evans, P. Weightman, A. Takahashi, J. Matthew, and Q. Herd, "Temperature Dependence of the Phonon Broadening of the Si 2pXPS Line," *Physical Review B* 54 (1996): 286–290.

16. O. Travnikova, K. J. Børve, M. Patanen, et al., "The ESCA Molecule—Historical Remarks and New Results," *Journal of Electron Spectroscopy and Related Phenomena* 185 (2012): 191–197.

17. D. Ketenoglu, "A General Overview and Comparative Interpretation on Element-Specific X-Ray Spectroscopy Techniques: XPS, XAS, and XRS," *X-Ray Spectrometry* 51 (2022): 422–443.

18. J. F. Watts, "X-ray Photoelectron Spectroscopy," *Surface Science Techniques* 45 (1994): 5–23.

19. G. H. Major, N. Fairley, P. Sherwood, et al., "Practical Guide for Curve Fitting in X-Ray Photoelectron Spectroscopy," *Journal of Vacuum Science & Technology A* 38 (2020): 061203.

20. G. Greczynski and L. Hultman, "A Step-by-Step Guide to Perform X-Ray Photoelectron Spectroscopy," *Journal of Applied Physics* 132 (2022): 011101.

21. F. De Groot and A. Kotani, *Core Level Spectroscopy of Solids* (CRC Press, 2008).

22. H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer Science & Business Media, 2013).

23. A. Barrie, I. Drummond, and Q. Herd, "Correlation of Calculated and Measured 2p Spin–Orbit Splitting by Electron Spectroscopy Using Monochromatic X-Radiation," *Journal of Electron Spectroscopy and Related Phenomena* 5 (1974): 217–225.

24. E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, 1935).

25. T. A. Carlson and M. O. Krause, "Experimental Evidence for Double Electron Emission in an Auger Process," *Physical Review Letters* 14 (1965): 390–392.

26. E. McGuire, "Auger and Coster–Kronig Transitions," *Atomic Inner-Shell Processes* 1 (1975): 293–330.

27. R. Bruhn, B. Sonntag, and H. Wolff, "3p-Excitation of Atomic Mn; Experimental Evidence for the Super Coster–Kronig Decay," *Physics Letters A* 69 (1978): 9–11.

28. M. C. Biesinger, L. W. M. Lau, A. R. Gerson, and R. S. C. Smart, "The Role of the Auger Parameter in XPS Studies of Nickel Metal, Halides and Oxides," *Physical Chemistry Chemical Physics* 14 (2012): 2434–2442.

29. M. H. Chen, B. Crasemann, K.-N. Huang, M. Aoyagi, and H. Mark, "Theoretical L-Shell Coster–Kronig Energies $11 \le Z \le 103$," *Atomic Data and Nuclear Data Tables* 19 (1977): 97–151.

30. N. Mårtensson and R. Nyholm, "Electron Spectroscopic Determinations of M and N Core-Hole Lifetimes for the Elements Nb—Te (Z=41–52)," *Physical Review B* 24 (1981): 7121–7134.

31. L. I. Yin, I. Adler, M. H. Chen, and B. Crasemann, "Width of Atomic L2 and L3 Vacancy States near Z=30," *Physical Review A* 7 (1973): 897–903.

32. R. Nyholm, N. Martensson, A. Lebugle, and U. Axelsson, "Auger and Coster–Kronig Broadening Effects in the 2p and 3p Photoelectron Spectra From the Metals 22Ti-30Zn," *Journal of Physics F: Metal Physics* 11 (1981): 1727–1733.

33. E. J. Callan, "Sensitivity of L1, L2, 3M4, 5 Coster–Kronig Transition Rates to Variations in Energy Levels and Screening Parameters," *Reviews of Modern Physics* 35 (1963): 524–527.

34. D. J. Morgan, "Resolving Ruthenium: XPS Studies of Common Ruthenium Materials," *Surface and Interface Analysis* 47 (2015): 1072–1079.

35. M. C. Biesinger, "Advanced Analysis of Copper X-ray Photoelectron Spectra," *Surface and Interface Analysis* 49 (2017): 1325–1334.

36. A. P. Grosvenor, M. C. Biesinger, R. S. C. Smart, and N. S. McIntyre, "New Interpretations of XPS Spectra of Nickel Metal and Oxides," *Surface Science* 600 (2006): 1771–1779.

37. M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. Lau, A. R. Gerson, and R. S. C. Smart, "Resolving Surface Chemical States in XPS Analysis of First Row Transition Metals, Oxides and Hydroxides: Cr, Mn, Fe, Co and Ni," *Applied Surface Science* 257 (2011): 2717–2730.