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Core Level Photoemission Line Shape Selection:

Atomic Adsorbates on Iron

(Short Title: XPS Line Shapes)

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Abstract

Robust fitting of core level photoemission spectra is often central to reliable interpretation of X-ray photoelectron spectroscopy (XPS) data. One key element is employment of the correct line shape function for each spectral component. In this study, we consider this topic, focusing on XPS data from atomic adsorbates, namely O and S, on Fe(110). The potential of employing density functional theory (DFT) for generating adsorbate projected electronic density of states (PDOS) to support line shape selection is explored. O 1s core level XPS spectra, acquired from various ordered overlayers of chemisorbed O, all display an equivalent asymmetric line shape. Previous work suggests that this asymmetry is a result of finite O PDOS in the vicinity of the Fermi level, allowing O 1s photoexcitation to induce a weighted continuum of final states through electron-hole pair excitation. This origin is corroborated by O DFT-PDOS generated for an optimised 5 layer Fe(110)(2x2)-O slab. Adsorbate DFT-PDOS were also computed for Fe(110)($\sqrt{2} \times \sqrt{2}$)-S. As, similar to adsorbed O, there is a significant continuous distribution of states about the Fermi level, it is proposed that the S 2p XPS core levels should also have asymmetric profiles. S 2p XPS data acquired from Fe(110)($\sqrt{2} \times \sqrt{2}$)-S, and their subsequent fitting, verify this prediction, suggesting that DFT-PDOS could aid line shape selection.

Keywords: XPS, line shape, asymmetry, atomic adsorbate, *ab initio* modelling. Fe(110), oxygen, sulfur.

1. Introduction

The binding energy (BE) and intensity of core level X-ray photoelectron spectroscopy (XPS) features acquired from solids can provide great insight into surface chemical composition [1]. With the exception of very simple systems, such features invariably comprise an envelope of components, resulting from the presence of different states that give rise to distinctive BEs. Given this scenario, as discussed in a recent perspective article by Sherwood [2], reliable interpretation of these data relies upon fitting the core level XPS signal with appropriate line shape functions to describe each component, in tandem with a function to account for the secondary electron background. Concerning the former, symmetric Gaussian-Lorentzian (G-L) functions are commonly employed, although the well-known asymmetric Doniach-Sunjić (D-S) function is adopted for certain systems, e.g. metallic substrates [3]. Clearly, line shape function selection will influence the outcome of fitting, and so can impact upon data interpretation. Nevertheless, this choice is widely undertaken without explicit justification. Here, we address this issue, focussing on the potential utility of *ab initio* electronic structure calculations to aid XPS core level line shape selection through a study of atomic adsorbates on Fe(110).

In the early 1990s, Tillborg *et al.* published an elegant study of the O 1s XPS line shape for ordered overlayers of atomic oxygen on Ni(100) and Cu(100) [4]. They demonstrated that the asymmetry of this core level peak can vary significantly with substrate, as a result of changes in the location of the adsorbate/substrate hybrid (2p – 3d) states relative to the Fermi level. Given this insight, one may have expected that all subsequent studies of analogous systems would have at least considered the impact of varying the core level line shape on XPS fitting. Such an approach, however, does not appear to have been consistently adopted, with effort to validate line shape selection being variable, e.g. Refs. 5-16. For instance, on low Miller index silver surfaces, an O 1s XPS feature (BE ~ 503.3 eV) ascribed to atomic oxygen was fitted

with an asymmetric D-S line shape function in earlier work [6], but a symmetric G-L function has been adopted latterly [12].

Motivated by a desire to improve the rigour of XPS core level line shape selection, a possible approach is presented in this study. More specifically, projected electronic density of states (PDOS) plots generated with density functional theory (DFT) calculations (i.e. DFT-PDOS) are employed to support line shape function selection. O 1s core level XPS spectra from various ordered structures of atomic O on Fe(110), formed through dissociative adsorption of either O₂, H₂O, or CO₂, are presented. All display an equivalent asymmetric line shape, which is consistent with the significant DFT-PDOS in the vicinity of the Fermi level (E_F) for O on Fe(110). Furthermore, we predict and verify a comparable S 2p XPS profile for chemisorbed atomic S on the same substrate.

2. Methodology

XPS data were acquired with a SPECS instrument, which is capable of measurements at both ultra-high vacuum (UHV) and near ambient pressure (not utilised here). Monochromated Al K α X-rays ($h\nu = 1486.6$ eV, $\Delta h\nu \sim 0.16$ eV) were employed as the photon source. Emitted photoelectrons were collected using a 150 mm hemispherical energy analyser (Phoibos 150, SPECS). Data were acquired at an analyser pass energy of 60 eV for wide energy scan overview spectra, and 30 eV for short higher energy resolution spectra of single core levels. A photoelectron emission angle (θ_E) of 0° (emission along the surface normal) was used for all measurements. The BE scale was calibrated through setting E_F to BE = 0 eV.

In situ preparation of the Fe(110) sample involved repeated cycles of Ar⁺ bombardment whilst annealing at ~ 790 K. This procedure resulted in a clean and well-ordered (1x1) surface, as determined from XPS and low energy electron diffraction (LEED), respectively. Once prepared, this surface was exposed to either O₂ (BOC, 99.999%),

CO₂ (BOC, 99.999%), H₂O vapour (purified with freeze-pump-thaw cycles), or H₂S (CK gas, 99.5%) by back filling of the UHV chamber; an *in situ* mass spectrometer was used to check gas/vapour purity.

All *ab initio* optimisations of atomic structure and subsequent calculations of DFT-PDOS were carried out using the CRYSTAL17 program, based on the expansion of the crystalline orbitals as a linear combination of a local basis set consisting of atom centred Gaussian orbitals [17,18]. A spin polarised solution to the Kohn-Sham equations was sought in the unrestricted open shell formalism. High quality all electron triple valence basis sets with polarisation were used, which had been developed in previous studies [19-21]. Employing the typical Hehre notation these were: an 8-64111d41G basis set for iron atoms and an 8-411d11G basis set for oxygen atoms, with the exponents of the latter being fixed to those validated in studies of CaCO₃ [22]. A 73211-5111d1G basis set, developed by Peintinger *et al.* [23], was employed for sulfur atoms. The details of these basis sets are provided in Supplementary Information.

Furthermore, electron exchange and correlation are approximated using the PBE exchange-correlation functional. Reciprocal space was sampled with a shrinking factor of 8 following the Pack-Monkhorst method and 16 for the “Gilat net” [24-26]. This grid converges the integrated charge density to an accuracy of about 10⁻⁷ electrons per unit cell. The coulomb and exchange series are summed directly, and truncated using overlap criteria with thresholds of 10⁻⁸, 10⁻⁸, 10⁻⁸, 10⁻⁸, and 10⁻¹⁶.

The Fe bulk geometry was optimized in the cubic Im-3m (229) space group, resulting in the lattice parameter $a = 2.814 \text{ \AA}$, and a magnetic moment of 2.15 μ_B . Fe(110)(2x2)-O and Fe(110) $\begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}$ -S surfaces were cut from the bulk structure with a thickness of 5 atomic layers. For oxygen adsorption, O atoms were adsorbed on the three-fold-hollow site. For sulphur adsorption, S atoms were adsorbed on the 4-fold-hollow site. These configurations reflected the most energetically most favourable adsorption site for each

adsorbate. The surface geometry optimization was carried out while the cell parameters were fixed.

3. Results and Discussion

Figure 1 shows overview XPS spectra acquired from four ordered phases formed on Fe(110), following exposure to either H₂O, O₂, or CO₂. Core level features are labelled. In addition, details of exposure (in mbar.s), substrate temperature (in K), and the resulting surface unit cells (matrix notation) are provided. All of the spectra appear analogous, except for some variation in O 1s intensity. Notably, there is no significant C 1s core level signal, including following exposure to CO₂. Given that molecular CO₂ adsorption should lead to a clearly visible C 1s feature [27], its absence suggests that CO₂ adsorbs dissociatively, with the carbon desorbing as CO.

Higher resolution Fe 2p and O 1s core level XPS spectra, corresponding to the overviews in Figure 1, are displayed in Figure 2. Focussing initially upon the Fe 2p data (Figure 2 (a)), it is evident that they are all highly similar. Indeed, superimposition of these spectra (see inset) indicates that, within experimental uncertainty, they are identical. Furthermore, the spectral profile and the BE maxima of the spin-orbit split doublet, Fe 2p_{3/2} at BE = 706.7 eV and Fe 2p_{1/2} at BE = 719.8 eV, are consistent with metallic Fe (Fe⁰) [28], i.e. the exposures to either H₂O, O₂, or CO₂ have not given rise to cationic Fe. This result suggests that any surface bound species have simply undergone chemisorption, rather than forming a discrete surface phase, e.g. an iron oxide or hydroxide.

Turning to the O 1s core level XPS spectra in Figure 2 (b), they are also essentially indistinguishable, as demonstrated most strikingly in the inset. Moreover, they exhibit a single maximum (BE = 529.7 eV) and an asymmetric profile. One possible interpretation of this shape is that the O 1s signal comprises multiple components due to various adsorbed states. Alternatively, following Tillborg *et al.* [4], it may be that

there is only a single component, arising from chemisorbed O, which is asymmetric as a result of the presence of O 2p - Fe 3d hybrid states in the vicinity of the Fermi level. Given that the O 1s line shape is independent of the chemistry of the dosed species (O₂, CO₂, or H₂O), the latter explanation is more plausible, as it is unlikely that the spectral profile would be invariant in the former scenario.

To support the above interpretation, DFT-PDOS ($-2 \text{ eV} \leq E_F \leq 2 \text{ eV}$) from an optimised 5 layer Fe(110)(2x2)-O slab are presented in Figure 3. As expected for a metal, the DFT-PDOS for the Fe atoms, labelled Fe1, Fe2 and Fe3, display a continuum around the Fermi level. More notably, the DFT-PDOS for adsorbed O are analogous (i.e. there is no band gap at the Fermi level), with the O/Fe1 DFT-PDOS ratio being ~ 0.3 at E_F . This distribution is a result of significant mixing of the O and Fe states, primarily 2p and 3d, at the Fermi level. Hence, the O 1s DFT-PDOS are consistent with the suggestion that the most likely origin of the asymmetric O 1s profiles in Figure 2 is a result of O 2p - Fe 3d hybridisation. Analogous to metallic core levels, this electronic coupling leads to the O 1s photoexcitation inducing a weighted continuum of final states through electron-hole pair generation, and so a spectral profile displaying a tail to higher BE [3,4].

To confirm that the O 1s spectra in Figure 2 (b) can be described with a single asymmetric peak, the CasaXPS software [29] has been employed for data fitting. A so-called Lorentzian based asymmetric (LF) line shape, which is convoluted with a Gaussian function, was selected to model the peak [30]. This function has four adjustable parameters, which were iteratively optimised, to define the line shape, i.e. $LF(\alpha, \beta, w, m)$. α and β describe the spread of the tail to higher and lower BE relative to the maximum of the Lorentzian function, respectively, with asymmetry being achieved through using different values of α and β ; w is a damping parameter to limit the range over which the asymmetry extends; m specifies the width of the Gaussian used to convolute the Lorentzian function. A Shirley-type function was employed to

describe the secondary electron background [29,31]; other background functions were also explored, but resulting fits were always less optimal.

The best fit, using the approach outlined above, is shown for the bottommost O 1s spectrum (i.e. H₂O: 1×10^{-5} mbar.s at 373 K) in Figure 2(b). Evidently, there is good agreement between the experimental spectrum and the sum of the LF line shape (LF(0.7, 1.8, 75, 35)) and Shirley background functions, which is consistent with the O 1s XPS signal arising from a single surface species, chemisorbed O, displaying an asymmetric line shape. We note that Weissenrieder *et al.* [8] have fitted a higher energy resolution O 1s XPS spectrum acquired from a (2x2) overlayer of atomic O on Fe(110) with two asymmetric peaks ($\Delta BE = 0.4$ eV), concluding that there are two distinct O bonding environments. A similar two component fit is feasible for the data in Figure 2, but is not essential due to the somewhat lower energy resolution of the current measurements; the choice to fit with either one or two asymmetric peaks does not materially affect the primary message of this paper.

Given that the DFT-PDOS for O chemisorbed on Fe(110) is apparently consistent with an O 1s asymmetric core level line shape, it is pertinent to predict and verify the line shape for another atomic adsorbate on Fe(110). To this end, we have studied the ordered $\left(\begin{smallmatrix} 2 & 1 \\ 1 & 2 \end{smallmatrix}\right)$ phase formed on Fe(110) through exposure to 1×10^{-4} mbar.s of H₂S at a substrate temperature of 473 K; previous work reports that this overlayer consists of chemisorbed atomic sulfur [32]. Figure 4 (a) shows the DFT-PDOS ($-2 \text{ eV} \leq E_F \leq 2 \text{ eV}$) from an optimised 5 layer Fe(110) $\left(\begin{smallmatrix} 2 & 1 \\ 1 & 2 \end{smallmatrix}\right)$ -S slab. Analogous to those plotted for the Fe(110)(2x2)-O slab (Figure 3), both Fe and S display a significant continuous distribution of states in the vicinity of the Fermi level; S/Fe1 DFT-PDOS ratio is ~ 0.3 at E_F . On this basis, it is proposed that the S 2p core level XPS profile will exhibit asymmetry.

Fe 2p and S 2p XPS spectra acquired from Fe(110) $\left(\begin{smallmatrix} 2 & 1 \\ 1 & 2 \end{smallmatrix}\right)$ -S are shown in Figures 4 (b) and (c), respectively. Again, the Fe 2p spectrum is consistent with that of metallic iron, and so is in accord with a chemisorbed S overlayer. The S 2p data exhibit two peaks, corresponding to the S 2p_{3/2} - S 2p_{1/2} spin-orbit split doublet. As predicted on the basis of DFT-PDOS, and illustrated in Figure 4 (b), the S 2p feature can be effectively fit with a doublet of asymmetric LF line shapes functions (LF(0.9, 1.8, 75, 35)) in tandem with a Shirley background; the 2p_{3/2} - 2p_{1/2} BE difference (1.2 eV) and intensity ratio (2:1) are as expected [33]. Hence, the experimental S 2p XPS core level line shape for Fe(110) $\left(\begin{smallmatrix} 2 & 1 \\ 1 & 2 \end{smallmatrix}\right)$ -S is consistent with the DFT-PDOS.

The above results suggest that applying *ab initio* modelling to generate adsorbate DFT-PDOS can facilitate line shape selection for XPS fitting. Such an approach would almost certainly improve the rigour of XPS analysis, in particular where there are multiple adsorbate states. For example, near ambient pressure (NAP) XPS data are often quite complex, such as those in Refs 11-16, with minority adsorbed species possibly driving surface processes, and so robust fitting is essential for reliable data interpretation, e.g. correct identification of reaction intermediates. Interestingly, a very recent review article concerned with NAP-XPS of catalyst surfaces discusses core level line shapes, appearing to suggest selection depends upon the photoexcited subshell [34].

Finally, it should be emphasised that the approach described here is not restricted to *surface science* type studies of atomic adsorbates on single crystal metallic surfaces. It could equally well be employed to aid analysis of XPS spectra acquired from more *applied* substrates, as well as molecular adsorbates (e.g. H₂O), and fragments thereof (e.g. OH). For example, it has been demonstrated with XPS that carbon-steel immersed in a strongly acidic solution in the presence of an organic corrosion inhibitor has an oxide-free termination, i.e. there is no surface iron oxide film present [35]. On this basis, the possibility of asymmetric adsorbate core level line shapes should be

considered. Moreover, even for oxide surfaces, DFT-PDOS could be computed for those displaying metallic character to direct core level line shape selection for both substrate and adsorbate features, such as the interface formed following exposure of LaFeO_3 to either O_2 or H_2O [36]. Clearly, for other oxide surfaces, where there are no states at the Fermi level, XPS core level asymmetry through adsorbate-substrate orbital hybridisation is not a concern.

4. Conclusions

In summary, we have examined the core level XPS spectra acquired from ordered overlayers of two atomic adsorbates, O and S, on Fe(110). Both the O 1s and the S 2p spectra display asymmetric line shapes. On the basis of earlier work [3,4], it is suggested that this profile is a result of their being finite adsorbate PDOS in the vicinity of the Fermi level, arising from hybridisation of adsorbate and substrate orbitals. DFT-PDOS, generated for both chemisorbed O and S, substantiate this supposition, demonstrating that undertaking such *ab initio* calculations has the potential to support XPS core level line shape selection.

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References

1. Ratner BD, Castner DG. Electron Spectroscopy for Chemical Analysis. In: Vickerman JC, ed. *Surface Analysis: The Principal Techniques*. Chichester: John Wiley & Sons; 1997. 43–98.
2. Sherwood PMA. The use and misuse of curve fitting in the analysis of core X-ray photoelectron spectroscopic data. *Surf Interface Anal* 2019;51:589-610.
3. Wertheim GK, Citrin PH. Fermi Surface Excitations in X-ray Photoemission Line Shapes from Metal. In: Cardona M, Ley L, eds. *Topics in Applied Physics, Volume 26, Photoemission in Solids I, General Principles*. Berlin, Heidelberg, New York: Springer-Verlag; 1978, 197-236.
4. Tillborg H, Nilsson A, Wiell T, Wassdahl N, Mårtensson N, Nordgren J. Electronic structure of atomic oxygen adsorbed on Ni(100) and Cu(100) studied by soft x-ray emission and photoelectron spectroscopy. *Phys Rev B* 1993;47:16464-16470.
5. Öfner H, Zaera F. Surface Defect Characterization in Oxygen-Dosed Nickel Surfaces and in NiO Thin Films by CO Adsorption-Desorption Experiments. *J Phys Chem B* 1997;101:9069-9076.
6. Rocca M, Savio L, Vattuone L, Burghaus U, Palomba V, Novelli N, Buatier de Mongeot F, Valbusa U, Gunnella R, Comelli G, Baraldi A, Lizzit S, Paolucci G, Phase transition of dissociatively adsorbed oxygen on Ag(001). *Phys Rev B* 2000;61:213-227.
7. Baraldi A, Lizzit S, Comelli G, Paolucci G. Oxygen adsorption and ordering on Ru(10 $\bar{1}$ 0). *Phys Rev B* 2001;63:115410-1-115410-7.
8. Weissenrieder J, Göthelid M, Månsson M, von Schenck H, Tjernberg O, Karlsson UO. Oxygen structures on Fe(110). *Surf Sci* 2003;527:163-172.
9. Kinne M, Fuhrmann T, Zhu JF, Whelan CM, Denecke R, Steinrück H-P. Kinetics of the CO oxidation reaction on Pt(111) studied by *in situ* high-resolution x-ray photoelectron spectroscopy. *J Chem Phys* 2004;120:7113-7122.

10. Bohao C, Yunsheng MA, Liangbing D, Lingshun XU, Zongfang WU, Qing Y, Weixin H. XPS and TPD study of NO interaction with Cu(111): Role of different oxygen species. *Chinese J Catal* 2013;34:964-972.
11. Jones TE, Rocha TCR, Knop-Gericke A, Stampfl C, Schlögl R, Piccinin S. Thermodynamic and spectroscopic properties of oxygen on silver under an oxygen atmosphere. *Phys Chem Chem Phys* 2015;17:9288-9312.
12. Heine C, Eren B, Lechner BAJ, Salmeron M. A study of the O/Ag(111) system with scanning tunneling microscopy and x-ray photoelectron spectroscopy at ambient pressures. *Surf Sci* 2016;652:51-57.
13. Eren B, Weatherup RS, Liakalos N, Somorjai GA, Salmeron M. Dissociative Carbon Dioxide Adsorption and Morphological Changes on Cu(100) and Cu(111) at Ambient Pressures. *J Am Chem Soc* 2016;138:8207-8211.
14. Yu Y, Koh YE, Lim H, Jeong B, Isegawa K, Kim D, Ueda J, Kondoh H, Mase K, Crumlin EJ, Ross Jr EJ, Gallet J-J, Bournel F, Mun BS. Chemical states of surface oxygen on Pt(110) surface revealed by ambient pressure XPS. *J Phys: Condens Matter* 2017;29: 464001.
15. Posada-Borbón A, Hagman B, Schaefer A, Zhang C, Shiplin M, Hellman A, Gustafson J, Grönbeck. Initial oxidation of Cu(100) studied by X-ray photoelectron spectroscopy and density functional theory calculations. *Surf Sci* 2018;675:64-69.
16. Yu Y, Kim D, Lim H, Kim G, Koh YE, Kim D, Ueda K, Hiwasa S, Mase K, Bournel F, Gallet J-J, Rochet F, Crumlin EJ, Ross Jr EJ, Kondoh H, Moh DY, Mun BS. Operando study of Pd(100) surface during CO oxidation using ambient pressure x-ray photoemission spectroscopy. *AIP Advances* 2019;9:015314 (2019).
17. Dovesi R, Erba A, Orlando R, Zicovich-Wilson CM, Civalleri B, Maschio L, Rérat M, Casassa S, Baima J, Salustro S, Kirtman B, Quantum-mechanical condensed matter simulations with CRYSTAL. *WIREs Comput Mol Sci* 2018;8:e1360.

18. Dovesi R, Saunders VR, Roetti C, Orlando R, Zicovich-Wilson CM, Pascale F, Civalleri B, Doll K, Harrison NM, Bush IJ, D'Arco P, Llunell M, Causà, Noël Y, Maschio L, Erba A, Rerat M, Casassa S. CRYSTAL17 User's Manual. Torino: University of Torino; 2017.
19. Muscat J, Wander A, Harrison NM. On the prediction of band gaps from hybrid functional theory. *Chem Phys Lett* 2001;342:397-401.
20. Wilson NC, Muscat J, Mkhonto D, Ngoepe PE, Harrison NM. Structure and properties of ilmenite from first principles. *Phys Rev B* 2005;71:075202.
21. MacKrodt WC, Harrison NM, Saunders VR, Allan NL, Towler MD, Aprá E, Dovesi R. Ab initio Hartree-Fock calculations of CaO, VO, MnO and NiO. *Phil Mag.* 1993;A68:653-666.
22. Valenzano L, Torres FJ, Doll K, Pascale F, Zicovich-Wilson CM, Dovesi R. *Ab Initio* Study of the Vibrational Spectrum and Related Properties of Crystalline Compounds; the Case of CaCO₃ Calcite. *Z Phys Chemie* 2006;220:893–912.
23. Peintinger MF, Vilela Oliveira D, Bredow T. Consistent Gaussian basis sets of double- and triple-zeta valence with polarization quality of the fifth period for solid-state calculations. *J Comput Chem* 2013;34:451-459.
24. Gilat G, Raubenheimer LJ, Accurate Numerical Method for Calculating Frequency-Distribution Functions in Solids. *Phys Rev* 1966;144:390–395.
25. Gilat G, Analysis of methods for calculating spectral properties in solids, *J Comput Phys* 1972;10:432–465.
26. Monkhorst HJ, Pack JD. Special points for Brillouin-zone integrations. *Phys Rev B* 1976;13:5188–5192.
27. Freund H-J, Roberts MW. Surface chemistry of carbon dioxide, *Surf Sci Rep* 1996;25:225-273.
28. Graat P, Somers MAJ. Quantitative Analysis of Overlapping XPS Peaks by Spectrum Reconstruction: Determination of the Thickness and Composition of Thin Iron Oxide Films. *Surf Interface Anal* 1998;26:773-782.
29. Casa Software Ltd., Teignmouth, Devon, UK. <<http://www.casaxps.com>>.

30. Fairley N. CasaXPS Manual 2.3.15 Spectroscopy rev. 1.2. UK: Casa Software Ltd; 2009. 55.
31. Shirley DA. High-resolution X-ray photoemission spectrum of the valence bands of gold, *Phys Rev B* 1972;5:4709–4714.
32. Weissenrieder J, Göthelid M, Le Lay G, Karlsson UO. Investigation of the surface phase diagram of Fe(110)-S. *Surf Sci* 2002;515:135-142.
33. Moulder JF, Stickle WF, Sobol PE, Bomben KD. Handbook of X-ray Photoelectron Spectroscopy. Perkin-Elmer, Physical Electronics Division; 1992.
34. Nguyen L, Tao FF, Tang Y, Dou J, Bao X-J. Understanding Catalyst Surfaces during Catalysis through Near Ambient Pressure X-ray Photoelectron Spectroscopy, *Chem Rev* 2019;119:6822-6905.
35. Morales-Gil P, Walczak MS, Cottis RA, Romero JM, Lindsay R. Corrosion inhibitor binding in an acidic medium: Interaction of 2-mercaptobenzimidazole with carbon-steel in hydrochloric acid. *Corros. Sci* 2014;85:109-114.
36. Stoerzinger KA, Comes R, Spurgeon SR, Thevuthasan S, Ihm K, Crumlin EJ, Chambers SA. Influence of LaFeO₃ Surface Termination on Water Reactivity. *J Phys Chem Lett* 2017;8:1038-1043.

Figure Captions

Figure 1 Overview XPS spectra ($h\nu = 1486.6$ eV, $\theta_E = 0^\circ$) acquired from four ordered phases formed on Fe(110) following exposure to either O₂, CO₂, or H₂O. Core level features are labelled and details of exposure (in mbar.s), substrate temperature (in K), and the resulting surface unit cells (matrix notation) are provided. Each spectrum has been normalised to have a maximum (minimum) intensity of 1 (0).

Figure 2 (a) Fe 2p and (b) O 1s XPS spectra ($h\nu = 1486.6$ eV, $\theta_E = 0^\circ$) acquired from four ordered phases formed on Fe(110) following exposure to either O₂, CO₂, or H₂O. Details of exposure (in mbar.s), substrate temperature (in K), and the resulting surface unit cells (matrix notation) are indicated. Each spectrum has been normalised to have a maximum (minimum) intensity of 1 (0). Insets (top left of each panel) show superimposition of spectra displayed in panel. Also shown is the best fit (blue markers) to the bottommost O 1s spectrum, using a LF line shape function (broken red lines) and a Shirley-type background function (broken grey line).

Figure 3 To the left, schematic plan and side views of Fe(110)(2x2)-O structure used to generate DFT-PDOS. The O atoms are located in their most energetically favourable adsorption sites, as determined from DFT modelling. Atom labels are employed to identify the source of plotted DFT-PDOS. To the right O, Fe1, Fe2, and Fe3 DFT-PDOS (-2 eV $\leq E_F \leq 2$ eV) from an optimised 5 layer Fe(110)(2x2)-O slab.

Figure 4 (a) To the left, schematic plan and side views of Fe(110) $\begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}$ -S structure used to generate DFT-PDOS. The S atoms are located in their most

energetically favourable adsorption sites, as determined from DFT modelling. Atom labels are employed to identify the source of plotted DFT-PDOS. To the right, S, Fe1, Fe2, and Fe3 DFT-PDOS ($-2 \text{ eV} \leq E_F \leq 2 \text{ eV}$) from an optimised 5 layer $\text{Fe}(110)\begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}$ -S. (b) Fe 2p and (c) S 2p XPS spectra ($h\nu = 1486.6 \text{ eV}$, $\theta_E = 0^\circ$) acquired from $\text{Fe}(110)\begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}$ -S. Each spectrum has been normalised to have a maximum (minimum) intensity of 1 (0). Also shown is the best fit (blue markers) to S 2p spectrum, using an appropriate combination of LF line shape functions (broken red lines) and a Shirley-type background function (broken grey line).

Figure 1

Figure 2

Figure 3

Figure 4