Quantitative structure determination of adsorbed formate and surface hydroxyls on Fe$_3$O$_4$(001)

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§1 Normal incidence X-ray standing waves (NIXSW)

The NIXSW technique$^1$ exploits the creation of an X-ray standing wave (XSW) by the interference between the incident and reflected photon beams when the Bragg condition is satisfied for a crystal. The XSW extends into and out of the bulk of the crystal and has a periodicity equal to the real space distance, $d_{hkl}$, that corresponds to the interplanar spacing between the Bragg diffraction planes$^2$ of the selected reflection. By using dynamical diffraction theory to determine the amplitude of the XSW, it can be found that scanning the incident photon energy across the Bragg condition causes the phase of the XSW relative to the Bragg diffraction planes to change by $\pi$.$^3$ As such, while scanning the incident photon energy, the X-ray intensity experienced by a selected emitter, and thus the X-ray absorption yield or photoelectron yield from a selected emitter, will be characteristic of the emitter’s location relative to the Bragg diffraction planes of the reflection. These photoelectron yield profiles can be modelled and fitted using dynamical diffraction theory$^1$:

$$I = 1 + R \frac{(1+Q)}{(1-Q)} + 2f^{hkl}\sqrt{R}\frac{[1+Q]}{[1-Q]^{1/2}}\cos(\varphi - 2\pi P^{hkl}).$$

(1)

Both $R$ and $\varphi$ (the reflectivity and phase of the standing wave respectively) can be calculated from the known bulk structure and the measured reflection intensity. $Q$ takes into account the angular dependence of the photoemission intensity and is calculated from tabulated values of the photoemission dipole and higher order asymmetry parameters. Thus, this model equation yields two fitting parameters; the coherent fraction, $f^{hkl}$, and the coherent position, $P^{hkl}$.$^1$ The latter parameter can be interpreted as the position the emitter takes between the Bragg diffraction planes of the
chosen reflection, taking values in the range 0-1 representing the fractional height of the emitter between the Bragg diffraction planes. The former can be loosely interpreted as an order parameter of the emitter around this position in the direction of the reflection, taking values between 0-1 with 1 representing complete order and 0 representing complete disorder.

The application of Fourier analysis to the NIXSW technique allows for the imaging of the real space locations of the selected emitters projected into the primitive unit cell of the substrate in a model free manner (as opposed to the trial and error methodology for the analysis of both SXRD and PhD). With such an analysis, the fitting parameters \( f^{hkl} \) and \( P^{hkl} \) can more formally be described as the magnitude and phase of the \( H^\text{th} \) order Fourier component, \( F_{H} \), of the structure factor for the selected emitter, \( F \). In turn, by measuring the photoelectron yield from a number of symmetrically inequivalent reflections, the real space atomic density, \( \rho(xyz) \), of the selected emitter can be determined as such:

\[
\rho(xyz) \propto \sum f^{hkl} \cos \left( 2\pi \left( P^{hkl} - [hx + ky + lz] \right) \right).
\]

The (004), (044), (113), (1̅13), (131) and (311) reflections were measured which, after taking into account the symmetry of the inverse spinel \( \text{Fe}_3\text{O}_4 \), provides 17 reflections or sets of Fourier components for equation 1.

### §2 Energy scanned photoelectron diffraction (PhD)

PhD\(^5\) exploits the inference of the directly emitted photoelectron wave-field from the core-level of a selected surface emitter with that of the same wave-field backscattered from neighbouring atoms. By scanning the incident photon energy and thus the wavelength of the photoelectron, the directly emitted and backscattered components of the wave-field will come into and out of phase with one and other, producing core-level intensity modulations as a function of photoelectron kinetic energy that are indicative of the local structure of the emitter. PhD spectra were measured for the O 1s core-level region. As with the SXPS and NIXSW measurements, each feature in the O 1s XP spectra were fitted with Voigt functions. To model the variations in intensity due to Auger decay spectra and other secondary electron features in the kinetic energy background, a background template was created by also measuring an extended tail section at higher binding energies than the core-level at each photon energy. The resulting modulations in photoemission intensity from each of the O 1s core-level peaks, \( I(E) \), were then used to define a stiff spline, \( I_0(E) \), representing the non-diffractive variations in photoelectron intensity (e.g. varying cross-section). The PhD spectra, \( \chi_{\text{exp}} \), were then calculated by:

\[
\chi_{\text{exp}} = \frac{I(E) - I_0(E)}{I_0(E)}.
\]

Multiple scattering of the backscattered photoelectrons renders it impossible to directly retrieve quantitative structural information from the modulations in \( \chi_{\text{exp}} \). As such, a trial an error approach is utilised by calculating, using multiple scattering theory, the spectra for a given structure, \( \chi_{\text{theory}} \), comparing that to the experimentally determined \( \chi_{\text{exp}} \) and iterating this process until reasonable agreement between the two is reached. Thus, the technique, like SXRD (but unlike NIXSW), is model dependent. Calculations of \( \chi_{\text{theory}} \) were undertaken using codes developed by Fritzsche.\(^6-8\)

The level of agreement between the calculated and measured spectra for each optimisation iteration was quantified using a reliability factor (R factor):\(^9\)

\[
R_{\text{factor}} = \frac{\sum (\chi_{\text{exp}} - \chi_{\text{theory}})^2}{\sum \chi_{\text{exp}} + \chi_{\text{theory}}},
\]
An R factor of 0 corresponds to perfect agreement, a value of 1 corresponds to uncorrelated data and a value of 2 corresponds to anti-correlated data. Whilst the lowest achievable R factors are normally found in the range 0.2-0.4, the best achievable R factor is heavily dependent on the quality of the data and the complexity of the system under study. Optimisation of the test structures was undertaken using a particle swarm optimisation (PSO) global search algorithm.\textsuperscript{10} In order to calculate the associated uncertainties in the determined structural parameters, a variance in R factor (var(R\text{min})) was determined as described by Booth et. al.\textsuperscript{11}. Using this variance, the uncertainty in a variable was calculated by varying that parameter until the R factor exceeded the sum of the minimum found R factor and this variance. By this method, the difference between the value of the parameter when it exceeds the variance and at the minimum found R factor is defined as that parameter’s uncertainty at one standard deviation.

The optimisation calculations were performed by considering the carboxylate O atoms (O\textsubscript{HCOO}) and hydroxyl O atoms (O\textsubscript{OH}) data to consist of a single \(\chi\)\textsubscript{exp} dataset. Two distinct bidentate sites were considered for the formate molecule: with the carbon coincident in the [110] direction with either the 1\textsuperscript{st} subsurface Fe\textsubscript{tet} (tet) or an Fe\textsubscript{tet} interstitial site (int) (see Figure 1 in the main article). A bulk terminated substrate was utilised for all calculations present in the main article. For this substrate there are two distinct sites for the O\textsubscript{OH} atom: tet and int (see Figure 1 in the main article). Other substrate terminations, i.e. the SCV reconstruction and a one vacancy substrate, are considered and discussed here in the ESI §7,8. Relaxation of the substrate atoms and a comparison between the substrates are outlined below in §9.

Thus, four different combinations of O\textsubscript{HCOO} and O\textsubscript{OH} site were considered. For each of the O\textsubscript{HCOO} and O\textsubscript{OH} species, data from 9 different photoelectron emission geometries were considered in the structural optimisations. Specifically: 5 beams measured in the [110] crystallographic direction and 4 measured in the [100] crystallographic direction. Note that, PhD is generally insensitive to intramolecular distances in organic molecules due to the weak scattering by low mass atoms and scattering from atoms that lie between the emitter and the detector. Therefore, although the carboxylate carbon atom was present in the modelling, the PhD measurements were insensitive to its position. Hydrogen atoms were not included in the calculation as its scattering cross-section is negligible.
§3 Synchrotron X-ray photoelectron spectroscopy

Figure S1 – Shown are the O 1s soft X-ray photoelectron spectroscopy (SXPS) spectra for the as prepared clean Fe₃O₄(001) surface and the surface after exposure to 10 L of formic acid. A peak fit of the spectrum for the 10 L formic acid dose is given in the main article.

§4 NIXSW measurements from (044), (113), (1̅13), (311) and (311) reflections

Figure S2 – (044), (113), (1̅13), (311) and (311) absorption profiles and reflections for the O_HCOO species.
Figure S3 - (044), (113), (I13), (311) and (311) absorption profiles and reflections for the OOH species.
Table S1 – The resulting coherent fractions, $f_{hkl}$, and position, $p_{hkl}$, from fitting the (044), (113), (1̅13), (311) and (3̅11) measurements for the O$_{HCOO}$, O$_{OH}$ and C$_{exp}$ (experiment) species. Also given are the theoretical $f_{004}$ and $p_{004}$ for a carbon atom in the tet, C$_{tet}$, and int, C$_{int}$, positions. The values in brackets are the uncertainty in the last significant figure.

|   | O$_{HCOO}$ | O$_{OH}$ | C$_{exp}$ | C$_{tet}$ | C$_{int}$ |
|---|------------|----------|-----------|-----------|-----------|
| $f^{044}$ | 0.59(3)    | 0.62(4)  | 0.76(8)   | 1         | 1         |
| $p^{044}$ | 0.97(1)    | 0.98(2)  | 0.75(4)   | 0.75      | 0.75      |
| $f^{113}$ | 0.34(4)    | 0.09(1)  | 0.39(7)   | 0.70      | 0.70      |
| $p^{113}$ | 0.89(3)    | 0.97(2)  | 0.05(4)   | 0.21      | 0.96      |
| $f^{1̅13}$ | 0.32(4)    | 0.10(2)  | 0.32(8)   | 0.70      | 0.70      |
| $p^{1̅13}$ | 0.63(3)    | 0.68(2)  | 0.80(5)   | 0.96      | 0.71      |
| $f^{311}$ | 0.11(4)    | 0.17(2)  | 0.52(7)   | 0.70      | 0.70      |
| $p^{311}$ | 0.80(5)    | 0.88(2)  | 0.88(4)   | 0.82      | 0.07      |
| $f^{3̅11}$ | 0.05(4)    | 0.12(2)  | 0.48(7)   | 0.70      | 0.70      |
| $p^{3̅11}$ | 0.52(8)    | 0.63(2)  | 0.63(4)   | 0.57      | 0.82      |

§5 Fitting of carbon real space unit cell densities

To determine the percentage occupation of the two possible bidentate adsorption sites on the Fe$_3$O$_4$(001) surface for the formate molecule, mixtures theoretical unit cell densities of the C$_{HCOO}$ atom in the tet and int sites were fitted to the measured real space density for the C$_{HCOO}$ species. The theoretical unit cell densities for the tet and int sites were determined by first calculating their corresponding $f_{hkl}$ and $p_{hkl}$ values. For such calculations, the C$_{HCOO}$ atom was placed at the experimentally determined (004) height above the Fe$_3$O$_4$(001) surface and all possible positions within the unit cell were determined by taking into account the complete symmetry of the Fe$_3$O$_4$(001) unit cell. The resulting coherent fractions were reduced by 0.1 to take into account inherent atomic vibrations that were not modelled directly during the calculation. The complete set of $f_{hkl}$ and $p_{hkl}$ for the two theoretical positions and for the measured C$_{HCOO}$ species are shown in Table S1. The theoretical unit cell densities were then calculated in the exact same manner as was done for the experimental real space imaging which is described in detail in the main article.

The resulting theoretical density map, at the experimentally determined (004) adsorption height, are shown for the tet (Figure S5c) and int (Figure S5d). The measured density map for C$_{HCOO}$ is shown in Figure S5a, and the resulting best fit with a combination of 63 ± 5% tet and 37 ± 5% int site occupancy is shown in Figure S5b, again taken at the measured (004) height above the surface. For the fitting, all unit cell densities were normalised to their maximum values. Errors in the percentage occupations were determined by undertaking the same fittings of the unit cell densities but with all the experimental $f_{hkl}$ and $p_{hkl}$ errors either added or subtracted from their experimentally fitted $f_{hkl}$ and $p_{hkl}$ values.
Figure S4 – Given are a) the measured $C_{\text{HCOO}}$ real space imaging (as shown in the main article) and b) the fitted real space image comprised of $68 \pm 5\%$ $C_{\text{HCOO}}$ in the tet site and $32 \pm 5\%$ $C_{\text{HCOO}}$ in the int site. Given in c) and d) are the corresponding real space images for the tet and int site respectively. Note: for the fitting, the complete unit cell of the measured $C_{\text{HCOO}}$ density and the calculated tet and int site densities were used. The images shown here were taken at the corresponding (004) height for the $C_{\text{HCOO}}$ species as determined by the NIXSW measurements.

§ 6 Real space imaging

Figure S5 – The real space imaging taken at the corresponding (004) NIXSW heights for the a) $O_{\text{HCOO}}$ and b) $O_{\text{OH}}$ species. For comparison in c) is given the topmost octahedrally and tetrahedrally coordinated layers of the Fe$_3$O$_4$(001) surface.
§7 Other surface terminations - Introduction

In addition to the bulk terminated surface, two other substrate terminations were investigated; an SCV reconstructed surface and a reconstructed surface comprising of no Fe\textsubscript{tet} interstitial and one subsurface Fe\textsubscript{oct} cation vacancy (see Figure S6) which will be termed the one vacancy structure. With the SCV and one vacancy terminations there are three possible unique sites for the O\textsubscript{OH} atom: tet, int\textsubscript{α} and int\textsubscript{β} (see Figure S6). Note that on a bulk terminated surface, the int\textsubscript{α} and int\textsubscript{β} site are identical due to the lack of subsurface vacancies and the lack of the interstitial Fe\textsubscript{tet}. Thus, six different combinations of O\textsubscript{HCOO} and O\textsubscript{OH} site were considered.

Figure S6 - Schematic a is of the topmost octahedral and tetrahedral layers of the Fe\textsubscript{3}O\textsubscript{4}(001) surface. The light blue boxes mark the surface Fe\textsubscript{oct} cations that the O\textsubscript{HCOO} bond to while in the tet site and the larger, purple boxes are for those of the int site. The three O\textsubscript{OH} sites used in the optimisations (tet, int\textsubscript{α} and int\textsubscript{β}) across all substrate structures are marked by the black dotted circles. Note: the O\textsubscript{OH} int\textsubscript{α} and int\textsubscript{β} sites are equivalent for the bulk substrate structure. Schematic b) depicts the next set of octahedral and tetrahedral layers. The orange circles demark the two subsurface cation vacancies of the SCV structure. For the one vacancy structure, only the “1\textsuperscript{st} V\textsubscript{oct}” is a vacancy.

§8 Other surface terminations – Results

The results of fitting of the PhD data for the SCV and one vacancy structure are provided in Table S2 along with the bulk substrate data from the main article. Out of all four structures optimised, only two other structures fall within the variance of this best fit bulk structure; an SCV and a one vacancy terminated surface both with the formate and O\textsubscript{OH} atom in equivalent positions to the best fit bulk structure. All structures with the formate in the int position, the O\textsubscript{OH} at the tet or with the O\textsubscript{OH} above a subsurface Fe\textsubscript{oct} cation vacancy, had R-factors higher than the variance of the best fit bulk structure. While there is an SCV and one-vacancy
structure within the variance of the best fit bulk structure, the bulk structure is a better fit to
the experimental data and agrees with the results of Arndt et al.\textsuperscript{12}

Table S2 - R factors and variances of all 16 optimised structures. The top row structure, a
bulk substrate with the formate in the \textit{tet} position and the \textit{O\textsubscript{OH}} atom in the \textit{int} position
above a subsurface Fe\textsubscript{oct} cation, is the structure that best fits the experimental PhD
modulations with the lowest R factor (= 0.22). Highlighted in bold are the only other
structures whose R-factor is within the variance.

| Substrate      | HCOO position | \textit{O\textsubscript{OH}} position | R factor | variance |
|----------------|---------------|--------------------------------------|----------|----------|
| Bulk           | \textit{tet}  | \textit{int}                          | 0.22     | 0.02     |
|                | \textit{tet}  | \textit{tet}                          | 0.32     | 0.03     |
|                | \textit{int} | \textit{int}                          | 0.30     | 0.03     |
|                | \textit{tet} | \textit{tet}                          | 0.36     | 0.03     |
| SCV            | \textit{tet}  | \textit{int\textsubscript{a}}         | 0.24     | 0.02     |
|                | \textit{tet} | \textit{int\textsubscript{b}}         | 0.34     | 0.03     |
|                | \textit{tet} | \textit{tet}                          | 0.32     | 0.03     |
|                | \textit{int} | \textit{int\textsubscript{a}}         | 0.26     | 0.03     |
|                | \textit{tet} | \textit{int\textsubscript{b}}         | 0.34     | 0.03     |
|                | \textit{tet} | \textit{tet}                          | 0.34     | 0.03     |
| One vacancy    | \textit{tet} | \textit{int\textsubscript{a}}         | 0.24     | 0.02     |
|                | \textit{tet} | \textit{int\textsubscript{b}}         | 0.33     | 0.03     |
|                | \textit{tet} | \textit{tet}                          | 0.35     | 0.03     |
|                | \textit{int} | \textit{int\textsubscript{a}}         | 0.29     | 0.03     |
|                | \textit{int} | \textit{int\textsubscript{b}}         | 0.30     | 0.03     |
|                | \textit{tet} | \textit{tet}                          | 0.35     | 0.03     |

Table S3 gives the optimised vertical relaxation parameters for the first three tetrahedrally
and octahedrally coordinated layers of the substrate with all values given as changes from
bulk positions as well as the lateral relaxation of the \textit{O\textsubscript{OH}} atom in the \textit{y} direction. The ‘bulk’
height for the \textit{O\textsubscript{OH}} atom is coincident with the surface Fe\textsubscript{oct} atoms. Note, the larger variance
of the parameters for the SCV and one vacancy structures can be attributed to those
structures having slightly larger R-factors. The general directions of the relaxations from bulk
positions for all three substrate structures are very similar. All substrate layers are found to
relax outwards with respect to the idealised bulk-like termination. Generally however, all
substrate atoms are found to have moved to more bulklike positions when compared to the
LEED-IV determined structure of the SCV reconstruction,\textsuperscript{13} corroborating the results of the
SXRD study by Arndt et. al.\textsuperscript{12} The \textit{O\textsubscript{OH}} atom is found to relax inwards towards the Fe\textsubscript{int} site
along the \textit{y} direction (the crystallographic [110] direction).
Table S3 – Given are the vertical changes from bulk positions for the first three substrate octahedral and tetrahedral layers as well as the lateral y relaxation (in the crystallographic [110] direction) for the O$_{OH}$ atom. Also given are the uncertainties for each parameter.

|                | Bulk                          | SCV                          | One vacancy                    |
|----------------|-------------------------------|------------------------------|--------------------------------|
|                | Δ from bulk (Å) + -           | Δ from bulk (Å) + -           | Δ from bulk (Å) + -            |
| O$_{OH}$ - y   | 0.17 0.2 0.07                 | 0.2 0.2 0.03                 | 0.23                           |
| O$_{OH}$ - z   | -0.2 0.1 0.1                  | 0.0 0.2 0.08                 | 0.03                           |
| 1$^\text{st}$ oct layer O - z | 0.1 0.2 0.2                   | 0.1 0.2 0.1                  | 0.03                           |
| 1$^\text{st}$ oct layer Fe - z | 0.1 0.1 0.1                   | 0.1 0.2 0.07                 | 0.08                           |
| 1$^\text{st}$ tet layer - z | 0.5 0.1 0.1                   | 0.1 0.2 0.07                 | 0.08                           |
| 2$^\text{nd}$ oct layer - z | 0.1 0.1 0.1                   | 0.1 0.2 0.07                 | 0.15                           |
| 2$^\text{nd}$ tet layer - z | 0.2 0.1 0.1                   | 0.2 0.1 0.04                 | -0.003                         |
| 3$^\text{rd}$ oct layer - z | 0.2 n/a n/a                   | 0.2 n/a n/a                  | 0.2                            |
| 3$^\text{rd}$ tet layer - z | 0.08 n/a n/a                  | 0.1 n/a n/a                  | 0.15                           |

§9 Substrate relaxations

The first three octahedrally coordinated and tetrahedrally coordinated layers of each optimised substrate could relax independently of each other vertically. Only atoms in the top octahedral and tetrahedral layers were allowed to relax in either the x (crystallographic [1 $\overline{1}$ 0]) or y (crystallographic [1 1 0]) directions, symmetrically about the interstitial site defined as the centre of the unit cell. All surface oxygens not bound to the 1$^\text{st}$ layer Fe$_{tet}$ atoms were only allowed to relax in the y direction, with positive relaxations being in towards the closest interstitial site. The four oxygens bound to the 1$^\text{st}$ layer Fe$_{tet}$ atoms and the four surface Fe$_{oct}$ cations were allowed to relax in both the x and y directions, with both the positive y and x relaxations being in towards the central interstitial site. The two Fe cations in the 1$^\text{st}$ Fe$_{tet}$ layer were relaxed in the x direction only. A schematic showing the positive relaxations of each atom in the top layer is given in the Figure S7. Additionally, five vibrational amplitudes for the Fe$_{tet}$, Fe$_{oct}$, O$_{bulk}$, O$_{OH}$ and O$_{HCOO}$ atoms were optimised as well as the inner potential of the substrate. The additional Fe$_{tet}$ interstitial atom present in the SCV structure was allowed to relax only vertically. In total, 27 parameters for the bulk and one vacancy structures and 28 parameters for the SCV structures were optimised.
Figure S7 – Shown are the relaxations of the top octahedral and tetrahedral layer atoms in the positive x and y directions. These relaxations were used for all three substrate structures. The additional interstitial Fe_{tet} atom in the SCV structure was only allowed to relax in the vertical direction (out of the plane of the page).

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