Supporting Information

Adatom Bonding Sites in a Nickel-Fe$_3$O$_4$(001) Single-Atom Model Catalyst and O$_2$ Reactivity Unveiled by Surface Action Spectroscopy with Infrared Free-Electron Laser Light

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Supporting Information

Table of Contents

Experimental details
Computational methods
Computation of simulated SAS spectra
Table S1-S4
Figure S1-S10
References

Supplementary Movies
Movie S1-3
**Experimental details**

The experiments were performed in a two-chamber system\(^1\)-\(^3\). One chamber is equipped with sample cleaning facilities, LEED/AES (SPECS), a sample manipulator with a helium flow cryostat, and a quadrupole mass spectrometer (EXTREL) for surface action spectroscopy (SAS) and temperature programed desorption (TPD). The base pressure is below $3 \times 10^{-10}$ mbar. Infrared radiation from the free electron laser of the Fritz-Haber institute enters the chamber through a diamond window. The other chamber is equipped with a scanning tunneling microscope (STM, SPECS EVT 250). Here, the base pressure is below $2 \times 10^{-10}$ mbar. All STM images were obtained in constant current mode at room temperature.

Fe\(_3\)O\(_4\) (001) thin-films were prepared on Pt(001) according to a published recipe \(^4\). At first, a Fe-buffer layer with a thickness of 3-4 nm was deposited onto clean Pt(001) at 300K. Following this, 4-6 nm Fe was deposited in $5 \times 10^{-6}$ mbar O\(_2\). Finally, an Fe\(_3\)O\(_4\) (001) oxide film was obtained by oxidation at ~920 K in $2 \times 10^{-6}$ mbar O\(_2\) for 3 min. The thickness of the Fe\(_3\)O\(_4\) (001) film depends somewhat on the degree of oxidation of the buffer layer, but a number in the range of 8 - 12 nm may be considered as a lower limit for the thickness.

Ni and Au were deposited with electron beam evaporators (Focus, EFM3) using a 2mm diameter Ni rod as source for Ni and a gold-filled tungsten crucible for gold deposition. Before deposition, the evaporators were degassed for 1 hour. During deposition, the Fe\(_3\)O\(_4\) (001) covered Pt(001) substrate was kept at 300K. The deposition rate was calibrated with a quartz crystal microbalance (QCM). Here, 1 monolayer (ML) coverage is defined as one adatom per Fe\(_3\)O\(_4\) (001) ($\sqrt{2} \times \sqrt{2})R45$ surface unit cell, which corresponds to $1.42 \times 10^{-14}$ atoms/cm\(^2\).

**Computational methods**

Spin-polarized first-principles calculations including dipole corrections were carried out using density functional theory (DFT) with generalized gradient approximation (GGA) of Perdew-
Burke-Ernzerhof (PBE) implemented in the Vienna Ab-Initio Simulation Package (VASP)\textsuperscript{[5,6]}. The valence electronic states were expanded on the basis of plane waves with the core-valence interaction represented using the projector augmented plane wave (PAW) approach\textsuperscript{[7]} and a cutoff of 550 eV. For Fe and Ni on-site Coulomb correlation effects, effective Hubbard-type $U$ parameters ($U_{\text{eff}} = 3.61$ eV) were added as in previous work\textsuperscript{[8]}. A $\Gamma$-centered $k$-mesh of $5 \times 5 \times 5$ was used for bulk calculations, adjusted to $2 \times 2 \times 1$ for (001) surface calculations. Convergence is achieved when the forces acting on ions become smaller than 0.01 eV/Å.

The calculations are based on the SCV reconstructed (\sqrt{2}×\sqrt{2})R45° model of the Fe$_3$O$_4$(001) surface in which the atomic coordinates are from experimental LEED-IV fitting \textsuperscript{[8]}. Two slabs are considered for DFT simulation of Fe$_3$O$_4$(001) vibrational spectra: an asymmetric slab with 12 layers (Fe$_{35}$O$_{48}$) and a symmetric slab with 11 layers (Fe$_{33}$O$_{48}$) (see Fig. S1). If not specified otherwise, the DFT simulated spectra shown are based on Fe$_{35}$O$_{48}$.

All slabs are separated by at least 18 Å in the direction normal to the surface. The vibrational frequencies and modes were calculated from finite differences with atomic displacements of $\pm 0.015$ Å. During the calculation, the symmetry of the surface slab was considered and only symmetry-restricted displacements are considered (i.e., IBRION=6). The adsorption of oxygen molecules on the Fe$_3$O$_4$(001) surface was investigated on a symmetric slab (Figure S1 b) by DFT with the van der Waals correction (Grimme D3)\textsuperscript{[9–11]}. The topmost six planes are allowed to relax during the structure relaxation.

The adsorption energy is calculated based on the following equation 1:

$$\Delta E = E_{\text{slab-adsorbate}} - E_{\text{adsorbate}} - E_{\text{slab}}$$

where, $E_{\text{slab-adsorbate}}$, $E_{\text{adsorbate}}$, and $E_{\text{slab}}$ are the total energy of the whole system, the isolated adsorbed species, and the slab.

Raw data of the DFT calculations in this study is available from the NOMAD repository (http://nomad-repository.eu) via the DOI https://dx.doi.org/10.17172/NOMAD/2022.03.31-3.
Computation of simulated SAS spectra

The computed infrared spectra $S(x)$ are sums of Lorentzians $L(x, \Delta_i, I_i, E_i)$:

$$S(x) = \sum_{i=0}^{N} L(x, \Delta_i, I_i, E_i)$$

with $N$ being the number of vibrational modes, $x$ the photon energy, $\Delta_i$ the FWHM of mode $i$ peak, $E_i$ the energy of mode $i$, and $I_i$ the Lorentzian peak maximum. $I_i$ was set to a value proportional to the infrared absorption cross section of mode $i$. All $\Delta_i$ were set to 6 cm$^{-1}$, which is the approximate energetic width of the infrared radiation delivered by the FEL.

In the harmonic approximation the infrared absorption cross section is proportional to the squared derivative of the dipole moment with respect to the vibrational motion at the equilibrium positions$^{[12]}$. We have approximated the derivative by the change of the dipole moment, $\Delta \mu_i$, when the atoms move along the normal coordinate of mode $i$ with the length of the movement vector normalized to one:

$$\Delta \mu_i = \mu(R_0 + \Delta R_i) - \mu(R_0)$$

$$I_i = |\Delta \mu_i|^2$$

$\mu(R_0)$ is the dipole moment of the ionic arrangement with the ions at their equilibrium positions $R_0$ and $\mu(R_0 + \Delta R_i)$ is the dipole moment with the ions at displaced positions with $\Delta R_i$ being the normal coordinate of the vibrational mode $i$ normalized to one. For the computation of the dipole moment we assumed that the ions are points with charges $q_k$. For such an arrangement the dipole moment may be computed as

$$\mu(R) = \sum_{k=0}^{M} R_k q_k$$

Therefore:

$$\Delta \mu_i = \sum_{k=0}^{M} (\Delta R_i)_k q_k$$
Here $M$ is the number of atoms and $R_k$ is the position of ion $k$. The charges $q_k$ were approximated by the nominal charges: +2 for Fe$_{tet}$, +3 for Fe$_{oct}$ and -2 for the oxygen atoms. The normal coordinates were computed with VASP using the finite displacement approach. Only the components perpendicular to the surface plane (z-direction) were considered since for a thin film on a metallic substrate the so-called metal surface selection rule$^{[13]}$ prevents that x and y components contribute to the excitation. This is related to the screening of the ionic charges by the substrate electrons, which cancels the horizontal components of the dipole moment$^{[13]}$.

According to present understanding$^{[3,14,15]}$, messenger desorption is governed by vibrational coupling between the excited surface vibration and the messenger-surface bond. One aspect of this coupling is that it is most sensitive to atomic oscillations at the surface, but only weakly to sub-surface oscillations, which gives SAS its surface sensitivity. To simulate this effect to some extent, we have included a layer-depth dependent weighting of the oscillation amplitudes. All the oscillation amplitude in x,y and z directions can contribute to the desorption of the messenger.

In the following discussion $C(k)$ is the weighting factor for atom $k$. All atoms in a layer with the thickness $T$ contribute with a weight of $C(k)=1$. $T$ is chosen by the user. Here, we set $T=2$ Å which guarantees that the weighting factor of the two topmost layers is 1. Atoms below $T$ have a lower weight:

$$C(k) = \exp (-H \times (D(k) - T))$$

$D(k)$ is the depth of atom $k$ below the surface, and $H$ is a user-selectable value, which was set to $2 \times 10^{10}$ m$^{-1}$ in the present calculation. These weights are used to compute a factor $F_i$, which may be seen as an effective oscillation amplitude experienced by a messenger atom/molecule at the surface, with sub-surface atoms having a reduced contribution:
\[ F_i = \sum_{k=0}^{M} C(k) \times |dz(i, k)| \]

\( dz(i, k) \) is the oscillation amplitude of atom \( k \) along \( z \) for the vibrational mode \( i \).

Finally, the factor \( F_i \) is used to compute the peak intensity \( P_i \) (for every vibrational mode \( i \)):

\[ P_i = \exp(\alpha \times F_i) \times I_i \]

The exponential term was introduced to simulate that messenger desorption has an activation energy which must be overcome by the energy transferred by vibrational coupling to the messenger-surface bond. \( \alpha = 2 \) was used in the present calculation.
Table S1: Energies and intensities of Fe$_3$O$_4$(001) vibrational surface modes according to SAS spectra and DFT simulations. In the last column the atoms with the largest vibrational amplitude for the given mode are listed.

| Energy SAS / cm$^{-1}$ | SAS – peak Intensity | DFT simulated Energy / cm$^{-1}$ | DFT - peak intensity* | Oxygen atom(s) with the largest oscillation amplitude** | Label*** |
|------------------------|-----------------------|---------------------------------|------------------------|--------------------------------------------------------|----------|
| 427                    | Very strong           | 428.5                           | 1059.0                 | O$_u$, O$_z$                                           | 62 f     |
|                        |                       | 432.4                           | 659.6                  | O$_u$                                                 | 60 f     |
| 527                    | Strong                | 519.1                           | 700.9                  | O$_z$                                                 | 40 f     |
|                        |                       | 534.4                           | 134.5                  | O$_z$                                                 | 33 f     |
| 393                    | medium                | 389.3                           | 489                    | O$_i$                                                 | 75 f     |
|                        | medium                | 380.8                           | 288.4                  | O$_i$                                                 | 81 f     |
| 497                    | weak                  | 493.1                           | 140.3                  | O$_z$                                                 | 48 f     |
| 620                    | Very weak             | 614.0                           | 138.9                  | O in 3$^{rd}$ layer                                   | 18 f     |
| 660                    | Very weak             | 664.8                           | 114.3                  | O$_u$, O$_i$                                          | 7 f      |
|                        |                       | 660.4                           | 88.9                   | O in 3$^{rd}$ layer                                   | 9 f      |
|                        |                       | 683.6                           | 213.3                  | O$_u$, O$_i$                                          | 5 f      |
| 746                    | Weak                  | 720.3                           | 167.2                  | O in 3$^{rd}$ layer                                   | 1 f      |

*For details of the calculation of the peak intensities see the section “Computation of simulated SAS spectra”.

** The notation is the same as in Figure S6. Some animations illustrating the vibrational modes are included in the supplementary movies.

*** The labels refer to the “eigenvectors and eigenvalues of the dynamical matrix” tables in the VASP output file. We have uploaded the tables in the file “DFT Calculated Vibration Modes of Fe$_3$O$_4$(001) surface. txt” as part of the supplementary material. For details of the table format see [16].
Table S2: Ni adsorption energies for different geometries computed with DFT. Structural models may be found in Figure S6.

| Binding geometry | Adsorption energy per Ni atom (eV) |
|------------------|-----------------------------------|
| Ni$_{ad}$-O$_z$  | -3.14                             |
| Ni$_{ad}$-O$_i$  | -2.94                             |
| Ni$_{ad}$-O$_u$  | -2.07                             |
| Ni$_{sub}$(S-2)  | -3.25                             |
Table S3: O$_2$ adsorption energies and O-O bond lengths computed with DFT for different O$_2$ geometries on Fe$_3$O$_4$(111) with a single Ni adatom per surface unit cell and Ni in a sub-surface position (third layer below the surface), respectively.

| Ni position | O-O bond length (Å) | Adsorption energy (eV) | O-O vibrational frequencies (cm$^{-1}$) | Adsorption site | Structure model |
|-------------|---------------------|------------------------|-----------------------------------------|----------------|----------------|
| adatom      | 1.34                | -0.97                  | 1100.3                                  | Ni             | Fig. 4d        |
| adatom      | 1.33                | -0.87                  | 1063.8                                  | Ni             | Fig. 4f        |
| adatom      | 1.33                | -0.80                  | 1174.5                                  | Ni-Fe          | Fig. 4e        |
| adatom      | 1.31                | -0.47                  | NA                                      | Fe             | NA             |
| adatom      | Dissociated         | -0.93                  | NA                                      | Ni-Fe          | Fig. S9d       |
| sub-surface | 1.30                | -0.38                  | NA                                      | Fe             | NA             |
| sub-surface with O$_{\nu}$ | 1.46                | -1.56                  | 854                                     | Fe             | Fig. S10       |
Table S4: Bader Charge analysis\textsuperscript{[17]} for Ni-Fe\textsubscript{3}O\textsubscript{4}(001) before and after O\textsubscript{2} adsorption. We list the computed bond lengths \(d(O-O)\) and Bader charges (\(Q\)) for Ni and O\textsubscript{2}. The structure model of superoxide with \(d(O-O)\) of 1.34 Å (first data row) is shown in Fig. S3d.

| Surface model          | Ni Charge before O\textsubscript{2} adsorption | Ni Charge after O\textsubscript{2} adsorption | \(\Delta Q\)(Ni) | \(Q\)(O\textsubscript{2}) | \(d(O-O)\) (Å) |
|------------------------|-----------------------------------------------|-----------------------------------------------|------------------|----------------|-----------------|
| Ni\textsubscript{ad}-Fe\textsubscript{3}O\textsubscript{4}(001) | +0.71                                        | +0.99                                         | +0.28            | -0.51          | 1.34            |
| Ni\textsubscript{sub}-Fe\textsubscript{3}O\textsubscript{4}(001) | +1.25                                        | +1.28                                         | +0.03            | -0.47          | 1.30            |
| Ni\textsubscript{sub}-Fe\textsubscript{3}O\textsubscript{4}(001)-O\textsubscript{v} | +1.16                                        | +1.28                                         | +0.12            | -1.12          | 1.46            |
Figure S1: Side views of two slabs used for DFT slab calculations of Fe₃O₄(001). a) asymmetric slab with 12 layers (Fe₃₅O₄₈); b) symmetric slab with 11 layers (Fe₃₃O₄₈). Color codes: Fe: golden; Oxygen atoms: red.

Figure S2: Comparison of results for Fe₃₃O₄₈ and Fe₃₅O₄₈ slabs. SAS spectrum of pristine Fe₃O₄(001) compared to two DFT simulated surface vibrational spectra based on the structure models shown in Figure S1.

Comparison of results for Fe₃₃O₄₈ and Fe₃₅O₄₈ slabs show that the predicted intensities and wavenumbers can deviate (by up to 10 wavenumbers) for different structural models. This highlights the sensitivity of the SAS spectra to subtle changes in surface structure and the need for accurate surface models for DFT calculations. Ball-stick models of both slabs are shown in Figure S1, and Figure S2 show the simulated vibrational spectra and compare them with an experimental SAS spectrum.
Figure S3: STM images of Ni single atoms deposited on Fe$_3$O$_4$(001) at 300K. a.) 0.7 ML; b) 1.0 ML; c) 1.3 ML. The yellow squares in c) mark the presence of brighter protrusions which indicate a partial occupation of second layer positions. Scanning parameters (bias voltage, tunneling current): a) +1.2 V, 0.07 nA; b) +1.0 V, 0.06 nA; c) +1.2 V, 0.25 nA.

Figure S4: Series of SAS spectra of Fe$_3$O$_4$(001) with different Ni coverages. The deposition temperature was 300 K.
Figure. S5: SAS spectrum of a pristine Fe$_3$O$_4$(001) surface and the same surface after deposition of 0.2 ML Au at 300 K.

Figure. S6: Top (upper panels) and side (bottom panels) views of ball-sticks models of Ni atoms at different positions on/in Fe$_3$O$_4$(001). The dashed open circles indicate the position of the subsurface cation vacancies. Color codes: Fe$_{\text{oct}}$: blue; Fe$_{\text{tet}}$: purple; O$_z$ atoms: pink; Other lattice oxygen atoms: red; Ni adatom: green.
Figure S7: SAS spectra of 1 ML Ni on Fe$_3$O$_4$(001) after deposition (300 K) and after annealing at different temperatures from 300 K to 830 K.
Figure S8: LEED patterns of pristine Fe$_3$O$_4$(001) and Ni on Fe$_3$O$_4$(100) (different coverages and temperatures). The electron energy was 95 eV.
Figure S9: a) Three subsequently recorded TPD runs of oxygen on 0.2 ML Ni on Fe$_3$O$_4$(001).

b) TPD traces (masses 32, 34, and 36) of $^{18}$O$_2$ on 0.3 ML Ni on Fe$_3^{16}$O$_4$(001).

c) and d) Structural models for superoxide and dissociated O$_2$ on Fe$_3$O$_4$(001) with a single Ni atom per unit cell coordinated to two O$_2$ surface anions. Dissociated oxygen atoms in d) have a higher energy ($\Delta E=1.73$ eV) than the superoxide in c), which shows that the dissociation is energetically unfavorable. Color codes: Fe$_{oct}$: blue; Fe$_{tet}$: purple; O$_2$ atoms: pink; Other lattice oxygen atoms: red; Ni adatom: green; adsorbed O$_2$ molecule and dissociated oxygen atoms: orange.
Figure S10: Structural model and adsorption energy ($E_a$) for peroxide on Fe$_3$O$_4$(001) with a single sub-surface Ni atom and a surface oxygen vacancy. Color codes: Fe$^{\text{oct}}$: blue; Fe$^{\text{tet}}$: purple; O$_2$ molecules: orange; Other lattice oxygen atoms: red; Ni adatom: green.

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**Movie S1.** DFT simulated vibrational animation for 389 cm\(^{-1}\) mode. The yellow arrows indicate the displacement amplitude of atoms in this vibrational mode according to the DFT simulation. The displacement amplitude shown have been multiplied by a factor of 5. Color codes: O: red; Fe: orange.

**Movie S2.** DFT simulated vibrational animation for 427 cm\(^{-1}\) mode. The yellow arrows indicate the displacement amplitude of atoms in this vibrational mode according to the DFT simulation. The displacement amplitude shown have been multiplied by a factor of 5. Color codes: O: red; Fe: orange.

**Movie S3.** DFT simulated vibrational animation for 519 cm\(^{-1}\) mode. The yellow arrows indicate the displacement amplitude of atoms in this vibrational mode according to the DFT simulation. The displacement amplitude shown have been multiplied by a factor of 5. Color codes: O: red; Fe: orange.