Elucidating Surface Structure with Action Spectroscopy

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ABSTRACT: Surface Action Spectroscopy, a vibrational spectroscopy method developed in recent years at the Fritz Haber Institute is employed for structure determination of clean and H2O-dosed (111) magnetite surfaces. Surface structural information is revealed by using the microscopic surface vibrations as a fingerprint of the surface structure. Such vibrations involve just the topmost atomic layers, and therefore the structural information is truly surface related. Our results strongly support the view that regular Fe3O4(111)/Pt(111) is terminated by the so-called Fe tet1 termination, that the biphase termination of Fe3O4(111)/Pt(111) consists of FeO and Fe3O4(111) terminated areas, and we show that the method can differentiate between different water structures in H2O-derived adsorbate layers on Fe3O4(111)/Pt(111). With this, we conclude that the method is a capable new member in the set of techniques providing crucial information to elucidate surface structures. The method does not rely on translational symmetry and can therefore also be applied to systems which are not well ordered. Even an application to rough surfaces is possible.

INTRODUCTION

Structure—reactivity relationships are important descriptors for the catalytic activity of surfaces. The experimental determination of such a relationship requires reactivity studies but also an experimental determination of the surface structure on a microscopic scale. There is a number of surface-sensitive methods to reveal the atomic structure of surfaces; most of them may be classified either as scanning probe or as diffraction technique.

Vibrational methods are capable of providing useful information for elucidating surface structures, for instance via IRAS (Infrared Reflection Absorption Spectroscopy) with probe molecules. However, the latter information is somewhat indirect and a vibrational spectroscopy method providing direct access to surface properties would be desirable.

In recent years a new vibrational method, Surface Action Spectroscopy (SAS) as a tool to measure surface vibrational spectra, has been developed at the Fritz Haber Institute. This method is based on a concept that is now often applied in gas phase infrared spectroscopy if the sample’s density is extremely low and absorption measurements cannot be performed due to this. Molecules or clusters in a molecular beam are exposed to inert messenger species (for example rare gas atoms) which attach to them with a weak bond at low temperature. These messenger-decorated aggregates are then exposed to intense infrared radiation, often coming from a free electron laser (FEL). If the photon energy is suitable for excitation of one of the aggregate’s vibrational modes, then the energy absorbed from the infrared beam may break the bonds between the messengers and the aggregates (this is the “action” in the term “action spectroscopy”), such that a flow of messenger atoms may be detected with a mass spectrometer. Recording the messenger desorption rate as a function of the photon energy produces a vibrational spectrum. We have applied such a procedure to messengers adsorbed on surfaces and demonstrated its usefulness in surface vibrational spectroscopy.

Here we use this method to measure vibrational spectra of different iron oxide layers in the range of about 300 to 700 cm⁻¹, where a number of microscopic optical surface vibrations is situated. Such surface vibrations usually involve only a few surface layers of a sample and therefore the information contained in the vibrational spectra is truly surface-related. HREELS (high-resolution electron energy loss spectroscopy), HAS (helium atom scattering), and IRAS can also be used for such measurements, but there are issues. The spectral resolution of HREELS is only moderate. A commonly used type of spectrometer (Ibach design) has a resolution of 4 cm⁻¹ at best, with the real-life operation resolution being about 10 cm⁻¹ in favorite examples, but rather often significantly lower. Also, in HREELS intense Fuchs-Kliewer polariton losses and combination losses may hide part of the desired spectral information.
information. Off-specular measurement may partially alleviate this issue, but this leads to low intensities and may force consideration of surface phonon dispersion in the calculation of the vibrational spectrum. IRAS spectra are produced by dividing two spectra—the spectrum of the sample under investigation is divided by a reference spectrum, which would ideally be a spectrum of a sample with the same bulk absorption spectrum as the sample under investigation, but without surface absorption features since this would introduce spurious features into the IRAS spectrum. Such a reference sample does not usually exist, which severely limits the suitability of IRAS for the spectroscopy of surface vibrations. In the case of HAS, the energy is limited to below ~480 cm⁻¹, and the surfaces have to be very flat on a microscopic scale. SAS does not suffer from such issues; a spectrum can be measured in just a few minutes. The method does not rely on reflected intensities which has the consequence that it can also be applied to nonflat surfaces.

Common diffraction-based methods for structure determination at the atomic level are IV-LEED (intensity voltage low-energy electron diffraction) and GIXRD (grazing incidence X-ray diffraction), which are successfully used for surface structure determination since many years. In both cases well-ordered surfaces with well-defined diffraction spots are required. This is not the case for SAS since it is not based on diffraction, which is a relevant advantage with respect to the diffraction-based methods. Scanning probe techniques such as STM (scanning tunneling microscopy) and AFM (atomic force microscopy) are also suitable for surface structure determination, but they are not directly element sensitive and information about deeper layers is not revealed.

Iron oxides have been intensively studied for several decades since they are important compounds used in catalysis, magnetism, electrochemistry, and biomedical applications. The surface structure of magnetite (Fe₃O₄) (111) has been under discussion for a long time. Along (111), the Fe₃O₄ bulk lattice consists of six different planes denoted as Fetet₁, O₁, Fetet₂, O₂, Fetet₃, and Fetet₄. Two of these layers, Fetet₁ and Fetet₂, have been discussed as terminating layers of the (111) surface. Fetet layers in the bulk consist of a 1/4 ML of Fetet ions and Fetet bulk layers are made up of 1/4 ML of Fetet ions and 1/4 ML of Fetet ions. Models of the Fetet and Fetet terminations are shown in the Supporting Information, SI, Figure S1. The surface unit cells of these two terminations are identical, and therefore a LEED pattern-based differentiation between them is not possible. IV-LEED studies are in favor of the Fetet termination, even though surface inhomogeneities and defects somewhat hampered the studies. STM studies of Fe₃O₄(111) thin films on Pt(111) are mostly in favor of the Fetet termination, while studies of magnetite single crystal surfaces also find evidence of the Fetet termination under reducing preparation conditions. IRAS studies with a CO adsorbate led to mixed results, partially favoring the Fetet and partially the Fetet termination. We have used SAS to obtain surface vibrational spectra for different iron oxide thin films and present evidence that the biphase Fe₃O₄(111) does contain an FeO-type oxide at the surface. Via a comparison with vibrational spectra computed using density functional theory (DFT) for model surface terminations we show that Fe₃O₄(111) is terminated with Fetet, and that the method can differentiate between different water-derived species on Fe₃O₄(111). The DFT results confirm that most of the vibrational information stems from the outermost three atom layers, which means that the vibrational spectrum is a selective fingerprint of the surface structure.

**EXPERIMENTAL SECTION**

**Experimental Details.** The iron oxides thin films on a Pt(111) surface were prepared following published recipes: FeO(111) layers with a thickness of one O–Fe double layer were prepared by deposition of Fe at 300 K followed by annealing at 1000 K in 1 × 10⁻⁶ mbar of O₂. In the following we use the term ML such that 1 ML contains the same amount of iron as one complete FeO(111) layer on Pt(111). Fe₃O₄(111) and biphase Fe₂O₃(0001) films on Pt(111) were prepared in two steps: in the first step a 1–2 ML thick FeO(111) film was prepared on Pt(111). Following this, the Fe₃O₄(111) and biphase Fe₂O₃(0001) layers were prepared by several cycles of deposition of 10 ML of Fe at 300 K with subsequent oxidation. The oxidation was performed at 870–900 K in 1 × 10⁻⁶ mbar of O₂ for Fe₃O₄(111) and at 870 K in 3 × 10⁻⁵ mbar of O₂ for biphase Fe₂O₃(0001). For Fe₃O₄(111) cooling in UHV after oxidation was employed to avoid the growth of oxygen-rich steps on the surface. The biphase Fe₂O₃(111) studies were performed with reduced Fe₃O₄(111) samples—these were prepared by deposition of 1 Å of Fe at the SAS measurement temperature (5–10 K) followed by annealing at 800 K in UHV. Before each SAS measurement the samples were annealed at 800 K in UHV to remove contaminations.

The SAS experimental setup is schematically shown in Figure 1. A surface is decorated with weakly bound messengers (rare gas atoms or hydrogen molecules) at low temperature and exposed to an infrared beam, which comes from the free electron laser of the Fritz Haber Institute in the present case. Vibrations excited at the sample surface may lead to messenger desorption as an indicator of the vibrational excitation. Therefore, the messenger desorption rate as measured with a mass spectrometer represents a vibrational spectrum of the surface. Details of the experimental setup can be found in previous work. All SAS spectra shown here were obtained with a HD molecular messenger gas. The spectral resolution depends somewhat on the energy and was around 4 cm⁻¹ for the experiments discussed here.

**Computational Details.** The electronic and ionic structures were calculated using the projector-augmented-wave (PAW) method, which is implemented in the Vienna ab initio simulation package (VASP). Plane wave kinetic energies of up to 800 eV were employed. To describe exchange-correlation effects, the Perdew, Burke, and Ernzerhof (PBE) generalized-gradient approximation (GGA) with spin-polarization was used. For Fe 3d on-site Coulomb interactions, the outermost three atom layers, which means that the vibrational spectrum is a selective fingerprint of the surface structure.

**Figure 1.** Schematic sketch of the SAS setup. Blue, red, gray, and white balls are substrate atoms, and the small green balls are messengers.
correlation effects, an effective Hubbard-type U parameter of 3.8 eV was added as in previous work.22,34

We use PAW pseudopotentials released with VASP 5.2 to describe the electron–ion interaction. The pseudopotential for the Fe has 14 electrons (Fe pv: [Mg] 3p² 3d⁰ 4s⁴ as a ground state configuration) while there are 6 electrons ([He] 2s² 2p²) for O, and one valence electron for H. Electronic and ionic optimizations were performed using a break criterion of $10^{-5}$ eV, and a maximal atom force of 0.02 eV/Å was applied. For the self-consistent field (SCF) loops, the Gaussian smearing method with a width of 0.1 eV was employed.

Concerning the structures used in this work, the slab model includes 12 atomic layers to calculate Fe₃O₄(111) surfaces as reported before. For the Fe₃O₄(111)-(1 × 1) primitive cell, a Monkhorst–Pack k mesh of $5 \times 5 \times 1$ was employed. For the frequency calculation, central differences for the force derivative with atomic displacements of ±0.015 Å were used to calculate the (partial) Hessian matrix. The topmost three layers were free to move to get the energies of the surface vibrations. To test the convergence of the energy, utilization of four layers of clean Fe₃O₄(111) surface with Fe₄type termination was calculated. As a result of PBE+U, the lattice constant of Fe₃O₄ bulk is 8.508 Å, which slightly overestimates the experimental value of 8.396 Å, rendering computed vibrations softer. To compare with the observed surface vibrations, computed wavenumbers are scaled by a factor of 1.0655 (see SI Table S1). Regarding water adsorption structures, we use a Fe₃O₄(111)-(1 × 1) surface unit cell adsorbing a single OH, one, and two H₂O molecules.

# RESULTS AND DISCUSSION

We have studied a number of different iron oxide films (SAS spectra are shown in Figure 2) to explore the applicability of SAS for surface structure determination. It is clear from Figure 2 that SAS spectra of the microscopic surface vibrations are fingerprints of the surface structure, which means that we have access to the surface structure using such data.

One monolayer thick FeO(111) films on Pt(111) consist of a hexagonal Fe–O bilayer structure with oxygen termination.9,28 The characteristic Moiré pattern observed with LEED (see Figure 2) is due to the lattice mismatch between FeO(111) and Pt(111).9,25,28,35 Correspondingly, the STM images reveal a superlattice with long lattice vectors. The Fe–O bond length in the Moiré superlattice depends on the position above the Pt(111) substrate, 7¹–7³ leading to a wide distribution of vibrational energies ranging from 380 to 450 cm⁻¹ in the SAS spectrum (Figure 2c). This structured broad feature resembles a structure at about 20 cm⁻¹ lower energy in a surface phonon spectrum calculated by Spiridis et al. for 1 ML FeO(111) on Pt(111).38

Figure 2b shows that the spectrum of biphase Fe₃O₄(111) (produced by iron deposition as described in the Experimental Section) is slightly different from the spectrum of regular Fe₃O₄(111) (Figure 2a). The intense peak at above 500 cm⁻¹ is somewhat weaker and the feature at ~425 cm⁻¹ is wider, with part of the additional intensity reminding of the FeO(111) feature in a similar energy range (Figure 2c), indicating that a FeO(111)-type structure contributes to the spectrum in panel b. The corresponding LEED pattern exhibits Moiré spots (see Figure 2), and the STM image shows a well-defined Moiré structure on parts of the image area.9,16 (see SI Figure S2). A LEED pattern similar to that shown in Figure 2 for reduced Fe₃O₄(111) has been observed by Condon et al.39 who attributed it to a superlattice of Fe₃O₄(111) and Fe₁−xO(111) patches and invoked the term “biphase” for this structure. The conclusion that FeO-related structures show up at the surface after deposition of iron was also drawn by Spiridis et al.35 The spectral features in the SAS spectra of biphase Fe₃O₄(111) and FeO(111) in the range below ~470 cm⁻¹ (see Figure 2) are similar but not identical, which means that the extra intensity in the spectrum of biphase Fe₃O₄(111) is not due (at least not fully) to dewetting of the layer, which might expose FeO(111)/Pt(111), but also to something different such as an FeO(111)-type layer on Fe₃O₄(111), as also proposed by Spiridis et al.9,40 This conclusion is supported by indications of Moiré spots in the LEED image also around those Fe₃O₄(111) spots which are not near to the FeO(111)/Pt(111) spots. We note that even in Figure 2a, the spectrum of “regular” Fe₃O₄(111), weak indications of FeO(111) are visible in the left and right shoulders of the peak at ~425 cm⁻¹. Consequently, weak Moiré spots are visible in the LEED pattern. The spectrum of biphase Fe₃O₄(0001) will not be discussed in detail. It is just shown as another example that the SAS spectra are surface-specific.

It is clear from this discussion that the vibrational surface modes are characteristic for the arrangement of atoms at the surface. Therefore, it should be possible to use SAS spectra for the elucidation of the surface structure via comparison with computed vibrational data for model structures. This approach was tested for the spectrum of clean Fe₃O₄(111).

To this end we have computed surface vibrational energies for the Fe₄type and Fe₄type terminations of Fe₃O₄(111). The computed energies of the most intense modes are compared with the experimental data in Figure 3. We note that only the topmost three layers of the oxide were considered in the

![Figure 2](https://dx.doi.org/10.1021/jacs.9b13164)
The effect of a water adsorbate on the surface vibrational spectrum of Fe₃O₄(111) was investigated with SAS and DFT. Figure 4a compares an SAS spectrum of a surface after water dosage with a spectrum of a clean surface, and lists vibrational energies computed with DFT for Fe₃O₄(111) with different water-derived adsorbate layers. Recent studies of the H₂O–Fe₃O₄(111) interaction indicate that water in contact with the Fe₄tet terminated surface dissociates, giving rise to different structures depending on coverage. TPD (temperature-programmed desorption) data reveal a complex phase structure and LEED shows that the structures exhibit long-range ordering. The structures considered here (a hydroxyl group, a dissociated water molecule, and a dissociated water molecule plus a less affected water molecule coordinated via hydrogen bonds) are inspired by structures considered in those recent studies. They are sketched in Figure 4, panels (b–d), together with the energies of the modes which are correlated with the most intense one in the spectrum of the clean surface (at 512 cm⁻¹). It is clear that the peak at 485 cm⁻¹ in the “clean-surface” spectrum is best assigned to the Fe₄tet terminated clean Fe₃O₄(111) surface (at 512 cm⁻¹) with two water molecules per unit cell (dark yellow), and two water molecules per unit cell, one of them partially dissociated (magenta) on Fe₄tet terminated Fe₃O₄(111). (b), (c), (d): Sketches of the water-derived structures on Fe₄tet terminated Fe₃O₄(111) considered in the DFT calculations. The numbers refer to the energies of the most intense vibrations of the respective structures, which are all derived from the most intense vibration of the clean Fe₃O₄(111) surface at 512 cm⁻¹.
because the hydrogen atom is not coordinated to a surface atom with a high vibrational amplitude. This is different for the other structures where the energy shift is larger. Another effect of the water-derived adsorbate layer is a shift of the peak at 428 cm$^{-1}$ in the spectrum of the clean surface to a lower energy which may be attributed to the lower energies of the respective computed modes for the adsorbate covered surface. The wide feature between $\sim$565 and 612 cm$^{-1}$ in the experimental spectrum (Figure 4a(ii)) does probably consist of several vibrational transitions. One of them may be attributed to water dimers, water aggregates, adsorption on defects$^{41}$ or H$_2$O-related structures with a higher coverage.$^{45}$ Therefore, most of the features in the experimental spectrum may be attributed to the structures sketched in Figure 4, panels (b–d), which supports the assignments made in recent publications.$^{26,41}$

As we have shown, the spectrum of surface vibrational modes is a fingerprint of the surface structure and therefore computations may help to elucidate it. This does also apply to adsorbate structures. In the present case (water-derived adsorbates) the result is indirect since the observed bands are not directly adsorbate vibrations but modified substrate vibrations. This may also be seen as an advantage since the modification of these vibrations by the adsorbate is an indicator of the adsorbate’s effect on the substrate surface.

Atomic level structural information about a surface or an adsorbate/substrate complex is important for essentially all processes involving the interaction of molecules/atoms with surfaces such as heterogeneous catalysis, corrosion, sensing, wear, etc. A relevant aspect of the vibrational SAS approach is that translational symmetry is not required, which means that structure determination is possible also for surfaces without translational symmetry; ball and stick models of the Fe$_{tet}$ and Fe$_{oct}$ surfaces; STM images of FeO(111)/Pt(111), biphase Fe$_3$O$_4$(111), and regular Fe$_3$O$_4$(111); and graphical representations of the vibrational modes of OH, H$_2$O, and 2H$_2$O on Fe$_{tet}$ terminated Fe$_3$O$_4$(111) (PDF)

Conclusions

In conclusion, we have acquired SAS spectra of different iron oxide layers on Pt(111), and Fe$_3$O$_4$(111) covered with water-derived species, with the goal of elucidating the suitability of SAS for surface structural characterization with the help of computations. The surface modes are highly sensitive to the structural arrangement of the surface atoms, and therefore the surface vibrations represent a fingerprint of the surface structure. SAS may be used to reveal this information. In agreement with preceding publications we could show that Fe$_3$O$_4$(111) is terminated with an Fe$_{tet}$ layer, which is contaminated with a small amount of dissociatively adsorbed H$_2$O under usual UHV conditions. In addition to this we were able to present spectroscopic evidence that biphase Fe$_3$O$_4$(111) consists of regular Fe$_3$O$_4$(111) coexisting with FeO(111), as also commonly discussed in the literature. With the example of water on Fe$_3$O$_4$(111) we have shown that SAS may also be used to differentiate with high selectivity between different adsorbate structures. The two most relevant aspects of SAS are probably that it can be applied to rough surfaces and that it does not require the presence of long-range ordered structures, such as IV-LEED and GIXRD, which makes weakly ordered or even unordered systems suitable for full or partial surface structure determination as long as repeating structure elements are available.

Associated Content

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.9b13164.

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Notes

The authors declare no competing financial interest.
ACKNOWLEDGMENTS

Y.L. and Z.W. thank the Alexander von Humboldt Foundation (AvH) for supporting them with an AvH research grant. We thank the Deutsche Forschungsgemeinschaft for funds through the Collaborative Research Center (CRC) 1109 “Understanding of Metal Oxide/Water Systems at the Molecular Scale: Structural Evolution, Interfaces, and Dissolutions”. The Fonds der Chemischen Industrie is gratefully acknowledged for financial support. J.P. and X.L. acknowledge financial support by the Deutsche Forschungsgemeinschaft (DFG) within grant 426182295 and HPC resources provided by the Norddeutsche Verbund für Hoch- und Höchstleistungsrechnen (HLRN).

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