Surface Action Spectroscopy: A Review and a Perspective on a New Technique to Study Vibrations at Surfaces

Y. Liu,[a] Z. Wu,[a, b] H. Kuhlenbeck,[a] and H.-J. Freund*[a]

Abstract: A new vibrational spectroscopy method aimed at the investigation of solid surfaces in ultrahigh vacuum, called "Surface Action Spectroscopy (SAS)", is described and the first results are reviewed. This technique is based on ideas and experiments performed in the gas phase. A surface is exposed to a messenger species at low temperature. This messenger species is desorbed via absorption of tunable infrared light from a free-electron laser and the desorption rate of the messenger species is recorded via mass spectrometry. It is shown that the technique is extremely surface sensitive and we discuss the basic mechanisms of the technique. We show a feasibility study on a $V_2O_3(0001)$ surface, where we know the surface structure. We then proceed to the example of iron oxide films to study the surface structure in parallel with calculations of the surface phonons, which allow us to confirm the surface structure of $Fe_3O_4(111)$ to be Fe_{tet} terminated. It also provides evidence for the so-called biphase structure. To conclude, we discuss possibilities to apply the technique to interesting questions in model and real catalysis, since the technique may provide interesting information independent of long-range order of the sample.

Keywords: Surface Structure, Surface Action Spectroscopy, Vibrational Properties, Oxide Surfaces

1. Introduction

Vibrational spectroscopy is a very important source of information in almost all fields of natural sciences. We restrict ourselves here to vibrational studies of molecules, small particles, and surfaces of solid materials.[1] Vibrational spectroscopy provides information on structure and structural changes upon modification of the system. Infrared absorption spectroscopy is a standard tool used for molecules in solution. For infrared absorption in the gas phase, one has to deal with the given sample density. In fundamental gas phase studies involving molecular beams the density is often so low that simple absorption measurements, even when sophisticated laser-based techniques are involved, are bound to fail. This situation has changed with the advent of IR photodissociation spectroscopy[2–10] in combination with messenger tagging.[11–13] At surfaces infrared reflection absorption spectroscopy (IRAS) is often employed to measure spectra of adsorbed molecules with concentrations well below a single monolayer.[14,15] However, surface-related signals are weak compared to bulk- and spectrometer-related contributions, so that one bases the analysis on so-called difference spectra, where a reference spectrum, for example of the clean surface, is divided by the sample spectrum. This leads to features in the spectra, that are not necessarily associated with the adsorbed molecules per se, and need to be identified separately.[16] Also, depending on the nature of the surface studied, particular selection rules apply. In general, an infrared band to be observed needs a non-vanishing dynamic dipole moment (first derivative of the dipole moment with respect to the movement of the atoms).

[a] Y. Liu,+ Z. Wu,+ H. Kuhlenbeck, H.-J. Freund
Fritz-Haber Institute of the Max-Planck Society, Berlin, Germany
E-mail: freund@fhi-berlin.mpg.de
[b] Z. Wu+
present address Material Physics, School of Engineering Sciences, KTH Royal Institute of Technology, Stockholm, Sweden
[+] Both authors contributed equally to this work.

At a metal surface a further restriction applies-the dynamic dipole moment must have a non-vanishing component along the surface normal because the metal electrons screen dipole moment variations parallel to the surface.[17] This is called the metal surface selection rule. There is another variation of infrared spectroscopy at surfaces called Surface Enhanced Infrared Absorption (SEIRA), where on rough metal surfaces the IR bands are enhanced by the presence of plasmons.[18,19] Non-linear laser based spectroscopy, i.e. Sum-Frequency Generation (SFG) has also been used to study surface vibrations. Here, the selection rules are different from IR spectroscopy, as they depend on the second order non-linear

optical susceptibility. Raman spectroscopy is another option to perform vibrational spectroscopy. Here the change in polarizability is essential. It is frequently applied in the investigation of powder heterogeneous catalysts, but less often in surface science due to sensitivity issues.[1] On the other hand, Electron Energy Loss Spectroscopy (EELS) is suitable for surface studies if low-energy electrons are employed.[20] Resolution is an issue-not more than 1–2 meV are commonly achieved in real-life studies. Also, there are classes of materials, such as oxides, where the substrate's very intense so-called Fuchs-Kliewer excitations[21] overshadow less intense transitions, which makes their identification difficult. However, EELS has a peculiar

Yun Liu received a B. E. degree in chemical engineering and technology from the Huazhong University of Science and Technology in 2011. He did his Ph.D. study under the supervision of Prof. Xinhe Bao and Prof. Fan Yang at the Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences (2011-2017). From 2017, he worked as a postdoc funded by Alexander von Humboldt Fellowship first in the Chemical Physics department headed by Prof. H.-J. Freund and later in the Interface Science Department headed by Prof. B. Roldán Cuenya at the Fritz Haber Institute in Berlin, Germany. His research is in the area of model catalysis using several surface science techniques including Surface Action spectroscopy and Scanning Tunneling Microscopy.

Zongfang Wu received her Ph. D in 2014 from the University of Science and Technology of China. She had worked as a postdoc at Fritz Haber Institute of the Max Planck Society under the supervision of Prof. Hans-Joachim Freund since 2015. She is now a postdoc working in the Department of Applied Physics at KTH Royal Institute of Technology. Her interests include surface science related to catalysis.

Helmut Kuhlenbeck majored in Physics at the University of Osnabrück, Germany. He received his PhD in 1988 for a study of adsorption on a single crystalline metal surfaces. Following this he moved to the University of Bochum studying topics related to oxide thin film model catalysis. In 1995 he habilitated on this topic. In 1996 he joined the Fritz-Haber-Institut in Berlin where he became a workgroup leader in the Chemical Physics department, focusing on the microscopy and spectroscopy of chemical processes on thin film oxides. Since 2019 he is working in the Interface Science Department of the Fritz-Haber-Institute on electro- and thermocatalytic model studies using crystalline thin film oxide samples.

Hans-Joachim Freund studied physics and chemistry at the University of Cologne where he received his Ph.D. in 1978 and his habilitation in 1983. Between 1979 and 1981, he worked in the Physics Department at the University of Pennsylvania as a postdoctoral fellow. In 1983, he became Associate Professor at Erlangen University and in 1987 Professor at Bochum University, and in 1995, he accepted a position as scientific member and director of the Department of Chemical Physics at the Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin. He serves as Honorary Professor of five universities. He received several national and international awards and is a member of several academies, scientific societies, and advisory boards of scientific journals.

property: two different excitations mechanisms with different selection rules. While in specular scattering dipole selection rules apply, similar to those active in infrared spectroscopy, under non- or off-specular conditions impact scattering dominates.[22]

This brief overview indicates that there are several tools to study vibrational properties, but it also shows that there is a need for development and there are difficulties that need to be overcome.

In gas phase studies a concept has been established, which is called "action spectroscopy". In molecular beam experiments the species to be analyzed with respect to vibrational properties is tagged with messengers.[23–29] Messengers are typically rare gas atoms or small molecules such as H_2 and isotopic variations. The composite is exposed to tunable laser light in the infrared spectral region, leading to the detachment of the messenger. The rate of the detachment of the messenger is measured via a mass spectrometer and plotted as a function of the photon energy. This plot, the "action spectrum" represents the vibrational properties of the system studied, as it reveals the "action" of the laser light towards a detachment of the messenger. A spectacular example for such a study is

documented in a paper[30] on the identification of the structure of an Au_7 cluster among 5 different possible isomers, whose vibrational spectra had been predicted using density functional calculations, and ranked with respect to stability. Figure 1 shows the structure of the isomers as well as the predicted vibrational spectra. At the bottom the "action spectrum" is documented, clearly indicating that Iso1 represents the likely structure of the Au_7 cluster. In this case Kr has been used as messenger.

Based on these ideas we have developed a strategy to use "action spectroscopy" to interrogate solid surfaces.[31–33] A schematic illustration of the experimental setup is shown in Figure 2.

A solid surface, for example, an oxide surface, is exposed to a messenger, for example, a rare gas, which adsorbs on the surface at low temperature. An infrared beam from a free-electron laser (in the present case the infrared free-electron laser of the Fritz Haber Institute, FHI-FEL) may desorb the messenger if the infrared light excites a surface vibration (either of the clean surface or of adsorbed molecules). The messenger desorption rate plotted as a function of the photon energy is
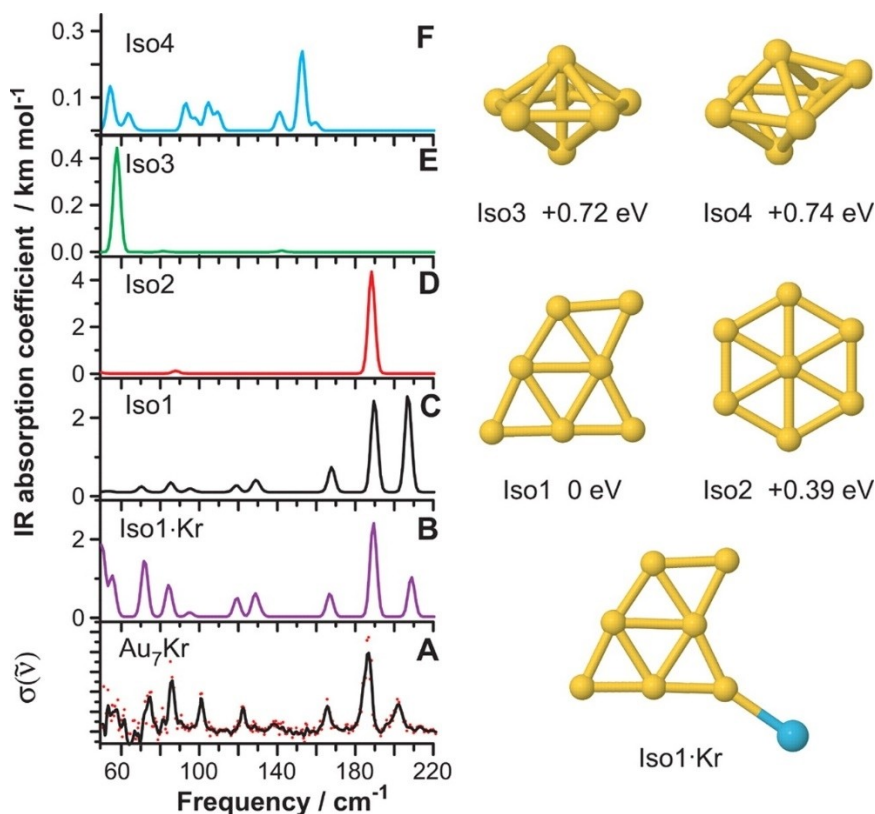

Figure 1. (A): FIR-MPD spectrum of Au_7 with a Krypton messenger attached. (C) to (F): calculated spectra (DFT) of 4 low-lying Au_7 isomers (Iso1 to Iso4). (B): computed spectrum of Iso1 with a Kr atom attached. From.[30] Reprinted with permission from AAAS.
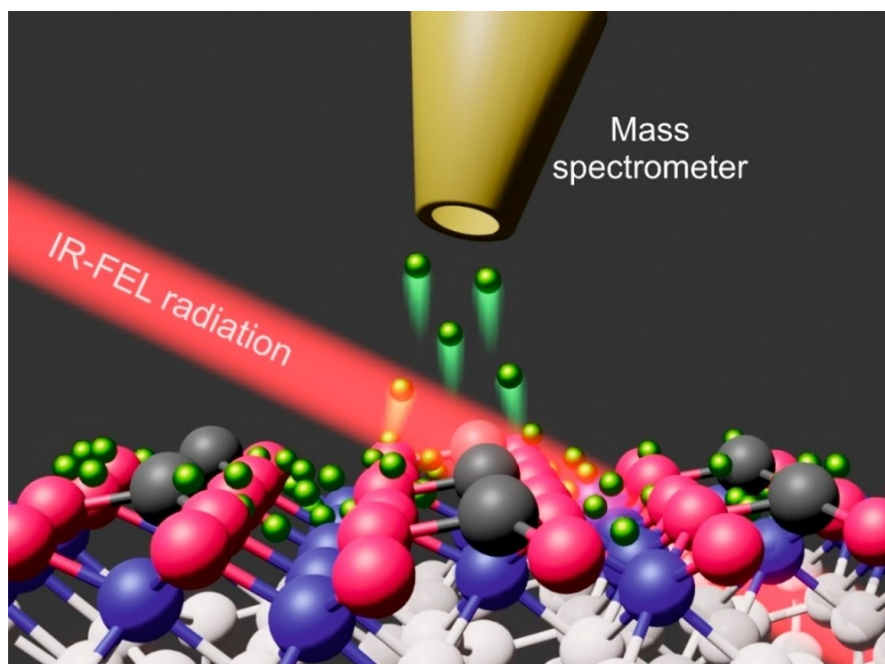
Figure 2. Schematic representation of a surface action spectroscopy experiment. Blue, red, gray, and white spheres represent substrate atoms, while the green spheres represent messenger species.[33] https://pubs.acs.org/doi/10.1021/jacs.9b13164 (further permissions related to the material excerpted should be directed to the ACS)(Ref.[33]).

the action spectrum, as mentioned above. This is schematically depicted in Figure 2.

This approach is not far-fetched as rare gas desorption via so-called DIET (desorption induced by electronic transitions) processes has been studied before using light or electrons. The most studied substrates were solid surfaces, in particular metal surfaces.[34,35] In DIET, desorption is based on electronic excitations and not on vibrational ones. Authors have also studied the effect of vibrational excitation of adsorbed molecules by pulsed infrared laser light.[36] They found only thermal desorption related to transient sample heating and alluded to the relevant role of energy dissipation into the metallic substrate. It has been shown in the literature that when DIET experiments are performed on dielectric substrates exhibiting a band gap, as opposed to a metal, the desorption cross sections increase considerably, due to different energy dissipation channels (see ref.[36] and references therein). This is one of the main reasons, why we have performed our specific experiments discussed below on dielectric thin films on single crystal metal substrates. For such samples, a significant part of the infrared beam power may be absorbed at vibrational resonance energies of the film and the sample may warm up to temperatures above the rare gas desorption temperature. The FHI free-electron laser reaches a time-averaged power in the range of 1 W,[37] which may warm up a cooled sample by a few Kelvin. This temperature rise will induce adsorbate

desorption if the sample temperature before laser illumination is not sufficiently low, allowing under laser illumination a temperature rise above the messenger desorption temperature. Vibrations of monolayer or sub-monolayer adsorbate films or microscopic vibrational surface states absorb at most a few percent of the infrared beam power (see for instance Refs.[38,39]). Consequently, the temperature rise will be much smaller and thermally induced desorption is unlikely. If desorption occurs, then most likely a non-thermal desorption channel is responsible for this. The two limiting cases of rare gas desorption will be discussed in the following:

1) Desorption in the **thermal channel** is induced by a temperature rise resulting from a high energy uptake. Vibrations with a high absorption cross section such as bulk polaritons are responsible for this. The energy is mostly absorbed in the bulk, and a transfer of energy to the surface is required as an intermediate step to induce desorption. For this reason, this channel may also be called **indirect channel**.

2) In the **direct coupling channel**, infrared light excites surface vibrations which directly couple to the adsorbed species. The energy dissipation channels guide sufficient energy into the bond of the messenger species to the surface, eventually breaking it. Both, the energy uptake rate and the time and position averaged sample temperature rise will be small. A weak coupling of the vibration to the bulk

(resulting in a high lifetime) should be beneficial since this reduces energy dissipation into the bulk.

It should be noted at this point that the term "action spectroscopy" is also used in connection with Inelastic Scanning Tunneling Microscopy.[40] Here the tunneling electrons of STM are used to excite vibrations of adsorbed molecules, which results in bond breaking or reactions in more general terms.[41]

The present paper reviews the experimental setup we have established, as well as the first experimental studies, so far published. Beyond this we will discuss possible future experiments and perspectives of the technique to study surfaces in general and catalyst surfaces in particular.

2. The Experiment

Figure 3 shows a schematic drawing of the experimental setup [Ref.29].

The sample holder with the sample is cooled by a liquid-helium cooled flow cryostat, and a quadrupole mass spectrometer (QMS) from Extrel (Extrel MAX 500 HT) is employed for detection of the desorbing messenger atoms/molecules. A low-temperature AFM/STM system is added to the setup to provide a possibility to characterize the sample. In the experiments, rare gas atoms (mainly neon or argon) as well as hydrogen molecules and their isotopic variations have been used as messenger atoms.

The QMS mounting is crucial for a proper operation of the instrument, as it is important to reduce the infrared radiation power reaching the sample from the surrounding (chamber walls, QMS housing, etc.). This is minimized by cooling the QMS housing with liquid nitrogen. As a side effect, this reduces the chamber pressure and the pressure in the QMS housing, which is essential as it minimizes the adsorption of rest gases at the cold sample surface. Further reduction of the infrared radiation power was achieved by blocking the direct view of the sample to the filament of the mass spectrometer with two cold metal sheets (see Figure 4).[31] Dosing of the messenger was carried out by filling the QMS housing with the rare gas, while the sample was positioned in front of the opening in the QMS housing. A computer-controlled piezo dosing valve was used to adjust the gas flow.

The sample surface is illuminated by the laser light at an angle of 83○ with respect to the surface normal through a cesium iodide window. The area on the surface illuminated by the beam had an extension on the surface of a few millimeters. A signal proportional to the infrared beam power is provided by a type K thermocouple coated with an infrared absorbing layer, as it is hit by the laser beam.

The characteristics of the FHI FEL are macro pulses (5–8 μs long pulse trains at 5 or 10 Hz repetition rate) consisting of some thousand short pulses ("micropulses") at a rate of 1 GHz. Each of them has a duration of a few picoseconds.[42] The energy per micropulse is ~10 μJ, corresponding to ~50–80 mJ per macro pulse. The spectral width of the radiation is
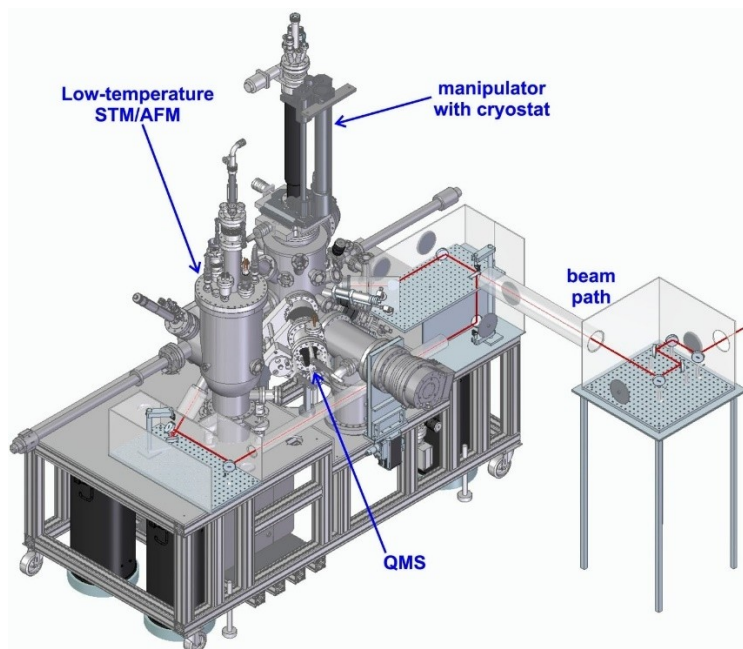

Figure 3. Experimental setup of the surface action spectroscopy experiment. Reprinted from,[31] with the permission of AIP Publishing.
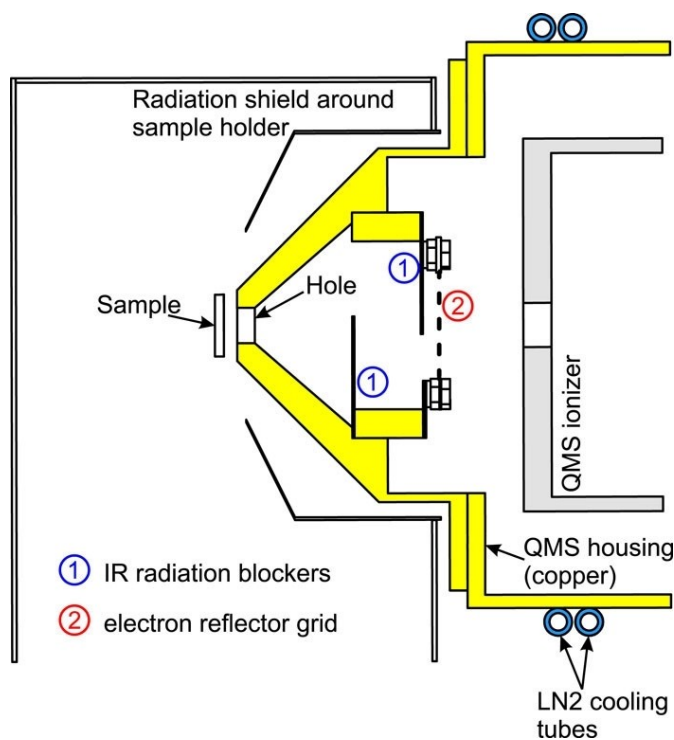
Figure 4. Schematic of the QMS housing seen from the side. Reprinted from,[31] with the permission of AIP Publishing.

about 0.5 % (full width at half maximum) of its central wavelength.[42]

The various thin oxide film systems described below have been prepared according to published recipes.[43–55] The metal was deposited with electron beam evaporators manufactured by Focus, Germany. The deposition rate of the evaporators was calibrated with a quartz microbalance before metal deposition onto the sample. After deposition the metal deposit has been oxidized and heated to elevated temperatures until LEED patterns indicated structural uniformity.

3. Systems Studied

Unraveling the structure-reactivity relationships in heterogeneous catalysis is vital for guiding the production of highly efficient heterogeneous catalytic materials, which involve significant industrial processes for energy and environment. Since the working catalysts are complex, and there are numerous factors influencing their structural and electronic properties which finally control their reactivity, it is a challenge to characterize the structure-reactivity relation of working catalysts at the atomic level. The model catalyst approach provides a pathway towards a better understanding by using simplified models for catalytic materials and systematically

increasing the complexity of those from simple to more complex.[56] Various levels of model catalysts have been developed starting from simple gas phase clusters towards systems containing deposited clusters on, for example, oxide single crystals or thin films. Through the interplay between experiment and theory, the hope is to understand those systems at the atomic level, and systematically build up an understanding of working catalysts (see Figure 5).

To reveal these fundamental phenomena on surface at the atomic level, it requires the development of specific, surface sensitive techniques. In this paper we restrict ourselves to the above-described surface action spectroscopy and its contributions towards a better understanding of complex surfaces.

To check whether the method is capable of detecting surface-located vibrations, a thin $V_2O_3(0001)$ film grown on an Au(111) substrate has been investigated. The $V_2O_3(0001)$ film is terminated with a layer of vanadyl (V=O) groups, only present at the surface but not in the bulk, as verified by an IV LEED and STM study.[57] The characteristic V=O stretching mode with an energy about 1040 cm$^{-[1]}$ as determined by IRAS and HREELS can be used to check the surface sensitivity of the surface action spectroscopy method.[58–60] The $V_2O_3(0001)$ film (around 10 nm thick) was prepared according to the recipe published in reference.[60] Neon atoms were used as messengers to determine the action spectra of clean and adsorbate covered $V_2O_3(0001)$/Au(111) surfaces. The data are shown in figure 6.

Curve c) in Figure 6 B represents the action spectrum of $V_2O_3(0001)$/Au(111) recorded with neon messenger atoms. The characteristic vibration of surface vanadyl groups is indeed detected at 1043 cm^{-1}. Apart from this characteristic vibration, there are vibrational states related to surface defects (mostly missing V=O groups) at 759 and 1008 cm^{-1}. They are commonly formed during heating of the film in UHV as verified by STM data.[60,61] A bulk-related feature is observed at 681 cm^{-1} which will be discussed later.[60,61] Next we look at the influence of adsorbates (Figure 6A). Curve c) represents the action spectrum of $V_2O_3(0001)$/Au(111) covered with a monolayer of methanol. The chemisorbed layer leads to vibrations at 1034 and 1134 cm^{-1} assigned to the C–O stretching and the C–H rocking modes, respectively,[62] while the vanadyl mode at 1043 cm^{-1} is quenched. Curve b) displays the action spectrum of $V_2O_3(0001)$/Au(111) covered with a half monolayer of iron deposited at 300 K. The surface vibrations of $V_2O_3(0001)$/Au(111) are completely quenched after iron deposition, while the vibration at 681 cm^{-1} is only slightly decreased in intensity. These data manifest that the surface action spectroscopy is a highly surface sensitive technique capable of detecting the surface vibrations as well as the vibrations of adsorbates.

The IRAS and HREELS spectra of a $V_2O_3(0001)$/Au(111) are shown in figure 6 B to illustrate how surface action
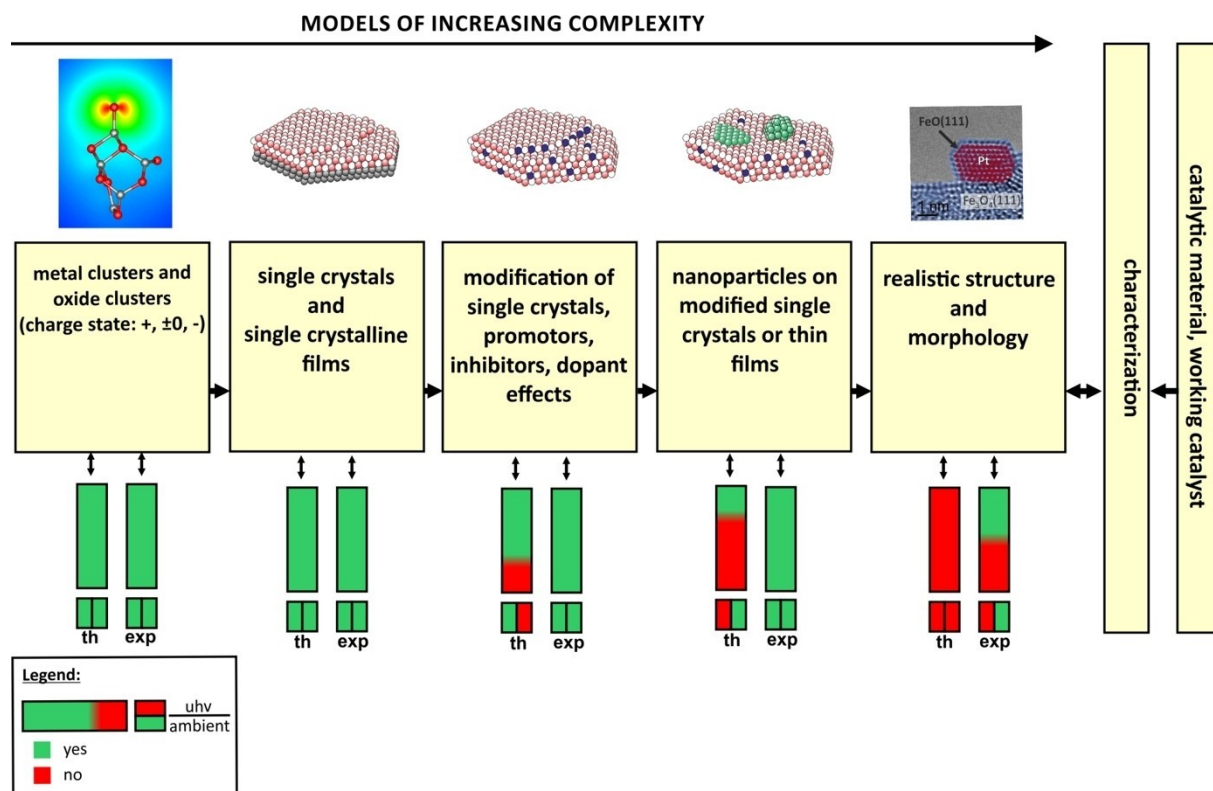
Figure 5. Pictorial representation of model systems with increasing complexity from left to right. Below each box the experimental and theoretical progress that has been made to achieve a proper representation/description is indicated: green: yes, achieved; red: no, not achieved. It is also indicated whether UHV and ambient condition studies have been performed. Reprinted by permission from Springer Nature: Catalysis Letters[56] with permission...Models in Catalysis, J. Sauer, H.-J. Freund, COPYRIGHT 2015.

spectroscopy compares to other vibrational spectroscopies. Curve a) displays the IRAS spectrum which was obtained via dividing the sample spectrum by a reference spectrum: the sample spectrum was taken from the $V_2O_3(0001)/Au(111)$ with a full coverage of vanadyl groups, while the reference spectrum was taken from a $V_2O_3(0001)/Au(111)$ film where the surface vanadyl groups were removed by electron bombardment.[63] This vanadyl free, reduced film is quite reactive and able to extract oxygen from CO_2 in the background to form isolated V=O groups on the surface, as we know from infrared spectroscopy.[64] The vibration of such isolated V=O groups has a lower energy than 1040 cm^{-1} due to the reduced dipole coupling between V=O groups,[64] leading to the peak at 1008 cm^{-1} in the action spectrum. Therefore, when the sample IRAS spectrum is divided by the reference spectrum, a negative peak shows up, related to the V=O vibration mode of isolated vanadyl groups at 1008 cm^{-1} as detected in the surface action spectroscopy. To properly detect surface-located vibrations using IRAS, one should carefully select a reference sample without vibrations at critical energies. The presence of spectral intensities at critical energies in the reference spectrum is a common, but rarely discussed

obstacle in IRAS. Surface action spectroscopy can overcome this problem (of course, only under UHV conditions), since it is a non-referenced spectroscopy. HREELS is also a reference free spectroscopy, but it contains large contributions from the bulk polaritons in oxide films or other samples of ionic materials.[20] As shown in figure 6 B, the bulk related states of $V_2O_3(0001)/Au(111)$ are much more obvious in HREELS than in IRAS and surface action spectroscopy, resulting in the broad and intense peak in the energy range between 600 and 700 cm^{-1} in HREELS (curve d). Besides, HREELS has a comparatively low resolution which is disclosed by the vanadyl peak which is much wider for HREELS than for IRAS and surface action spectroscopy.

We now move on to a discussion of the desorption mechanism relevant to the surface action spectroscopy method. The temperature of the sample is measured with a thermocouple spot-welded to the backside of the Au(111) single crystal. Curve e) in figure 6 B shows the change in temperature induced by the laser radiation. While in the energy range related to the V_2O_3 bulk states we see a considerable temperature increase,[60,61] no such temperature rise is observed in the energy range above 700 cm^{-1}, where the surface vibrations are
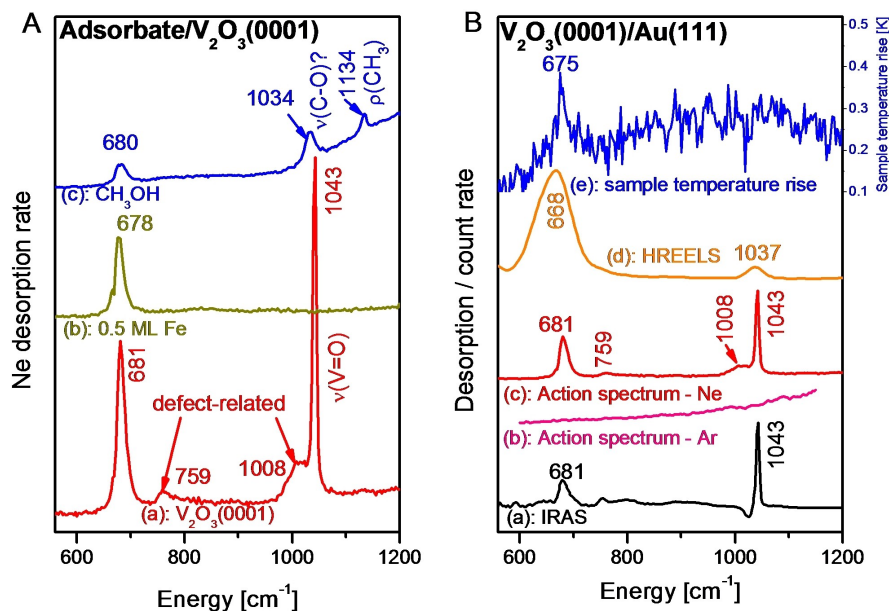
Figure 6. A) Surface action spectra with neon messengers of (a) vanadyl-terminated V₂O₃(0001)/Au(111), (b) 0.5 monolayer iron deposited at 300 K on V₂O₃(0001)/Au(111), (c) methanol on V₂O₃(0001)/Au(111) (dosage at 8 K followed by a short warm-up to 200 K to remove methanol above the first layer); B) Different spectra of V₂O₃(0001)/Au(111). Spectra (b) and (c) are surface action spectra measured with Ar and Ne messengers, respectively. Spectrum (e) shows the sample temperature increase for spectrum (c) relative to the temperature before infrared irradiation (blue scale on the right ordinate axis). Figure adapted with permission from Ref. 30. Copyright 2017 American Physical Society.

located. This indicates that there are two different channels for the desorption of messenger species: one is the thermal channel where the sample temperature is raised up due to the infrared light absorption by bulk-related states to result in the thermal desorption of messenger gas; the other one is the non-thermal channel without a detectable sample temperature rise. This was mentioned already above in this paper. How does the non-thermal channel work? According to the present interpretation, vibrational energy is transferred from the excited surface vibration to the surface-messenger bond via a direct vibrational coupling. The transferred energy should be sufficient to overcome the activation energy for desorption of messenger species from the sample. Curve b) in figure 6 B shows a surface action spectrum of the V₂O₃(0001) surface taken with argon, instead of neon, as a messenger species. Interestingly, the argon-based action spectrum shows no spectral features at all. The contrast between argon and neon may be understood as argon has a much higher activation energy for desorption from the surface than neon (660-960 cm⁻¹ vs. 80–300 cm⁻¹ according to the thorough thermal desorption study performed early on by Schlichting.[65,66]) The FEL micropulse has an energy of ~ 10 μJ with ~ 1 % being absorbed by the surface vanadyl groups according to the IRAS spectrum. The diameter of the infrared beam on the sample is around 3 mm and there is one vanadyl group per unit cell on the surface.[57] Therefore, we estimate that one vanadyl group

absorbs on average ~ 0.1 photons per micropulse. The time between two sequential micropulses (1 ns) is larger than the typical lifetime of a vibrational excitation, which renders it unlikely that excited states above the first excited state can be reached. Also, indications for non-linear optical processes were not found when the beam intensity was varied. Therefore, the process of infrared induced desorption in the case of vanadyl groups is probably a single photon process. If every absorbed photon would cause desorption, then all messenger gas atoms would have desorbed after one macro-pulse (containing thousands of micropulses). This is not the case, indicating that only a small fraction of the absorbed photons actually induces desorption. The same conclusion does apply to desorption generated by excitation of other surface-located vibrational levels. Since argon has much higher desorption energy, the fraction of photons leading to desorption will be too small to have the argon desorption detectable.

Based on the discussion of the desorption mechanism for surface action spectroscopy, we move to some considerations concerning the factors influencing the surface sensitivity of the method. We call this the selectivity rule of this method. After a surface mode has been excited, the vibrational energy will dilute into numerous channels. How much of this energy can be transferred to the desorption channels depends on the efficiency of channels transferring energy below the surface: the more efficient these channels are the less energy will be

available for desorption. Therefore, the more a surface vibration is decoupled from the bulk, the more energy may be transferred into the channels leading to messenger desorption, which will eventually increase the sensitivity of the detection of surface vibrations. In addition, the vibrational energy of the target vibration level should not be smaller than the activation energy for desorption of the chosen messenger gas from the sample surface. Thus, a careful choice of messenger gas is advised to improve the surface sensitivity of the surface action spectroscopy method. The lower the activation energy for desorption of the messenger species, the more sensitive the messenger will be. It also depends on the energy transfer paths provided by the messenger.

One way to proceed in this direction would be to compare messenger species with similar thermal desorption energies but different number of transfer paths.[66] The two candidates we studied were neon and a molecule, H_2. Shown in figure 7,
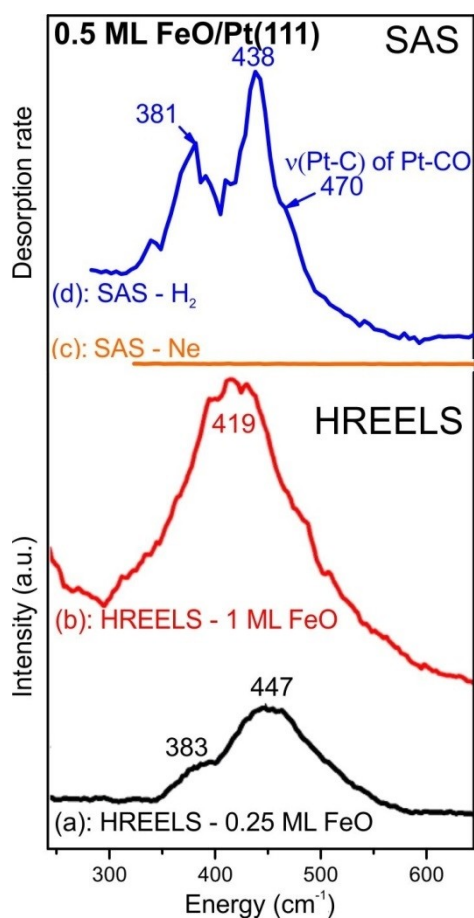

Figure 7. HREELS of 0.25 ML FeO nanoislands (a) and 1 ML FeO film (b) grown on Pt(111); Surface action spectra (SAS) of 0.5 ML FeO nanoislands on Pt(111) with Ne (c) and H_2 (d) as messenger gas; curve (a) and (b) are reproduced with permission from Ref.[67] Copyright 2010, American Chemical Society.

curve c) and d) are the action spectra of sub-monolayer FeO islands on Pt(111) measured with neon and H_2 as messenger gases; curves a) and b) are the HREELS spectra of nano-islands of FeO and a closed FeO film on Pt(111), taken from the reference.[67] HREELS shows that the Fe–O vibration and the interface vibration of FeO islands on Pt(111) have energies of 447 and 383 cm^{-1}, respectively.[67] In the surface action spectra, neon is blind to the vibrations of sub-monolayer FeO islands on Pt(111), whereas H_2 is able to respond to the surface vibrations of this system. Compared to HREELS, some detailed features are even better resolved in the surface action spectroscopy with H_2 as messenger gas. The data show that the sensitivity of H_2 is much higher than that of neon for the vibration levels of sub-monolayer FeO islands on Pt(111). A preliminary interpretation is that the enhanced sensitivity is due to the additional vibrational modes in the H_2-substrate system resulting from the additional atom. Some of these modes (possibly all except the H–H stretching mode) may be available for energy transfer to the H_2-substrate bond, resulting in an enhanced sensitivity. As a consequence, the surface sensitivity of the surface action spectroscopy method may be improved with a proper choice of the messenger species. With respect to hydrogen there is another option to vary the messenger properties by using isotopes, such HD and D_2. This has been briefly explored, and we will show below the results of a study on iron oxide films using HD. Helium has the smallest desorption energy among the gas atoms/molecules, hence the implementation of helium as messenger gas would be another beneficial choice.

Coming back to the iron oxide films, we show in Figure 8 the SAS spectra using HD as messenger of a number of iron oxide films in order to explore the applicability of SAS for surface structure determination.[33] The corresponding LEED patterns are shown on the right of Figure 8. The spectra vary considerably as we change the structure of the film, indicating that the SAS spectra represent fingerprints of the surface structure. The spectrum of the FeO(111)/Pt(111) system with its typical Moiré LEED pattern is plotted in Figure 8 c and shows similarities to the spectrum of the half monolayer film shown in Figure7 (above). Since the Moiré superlattice of the film leads to a strong variation of Fe–O bond lengths,[68–70] the phonon energies vary considerably, leading to a wide distribution of vibrational energies ranging from 380 to 450 cm^{-1} in the SAS spectrum (Figure 8 c). This broad feature bears similarities with 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).[71] A surface structure intensely discussed in the literature is that of Fe_3O_4(111). A thin film prepared on a Pt(111) substrate, with a LEED pattern as shown, leads to a SAS spectrum displayed in Figure 8 a. Its assignment will be discussed in the following. However, we note in passing, that the so-called biphase structure, where the
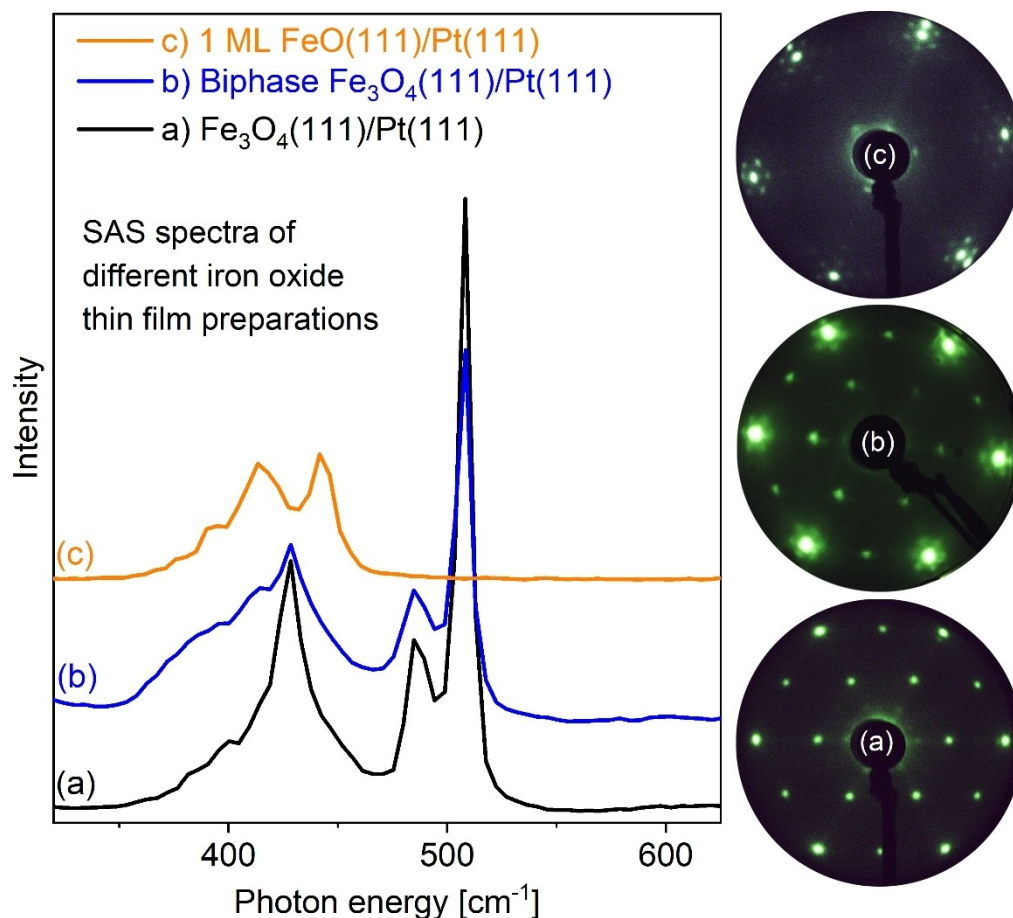
Figure 8. Surface action spectra obtained for different iron oxide films on Pt(111). LEED images for the samples are shown in the right panel [(a),(c): Eelectron = 66 eV; (b): Eelectron = 54 eV.

magnetite phase of Fe_3O_4 co-exists with a layer of FeO (the detailed structure is still under debate), and which is often encountered during the preparation procedure (LEED pattern is shown) displays a SAS spectrum as shown in Figure 8 b. The peak intensities are different and the features between 350 and 450 cm^{-1} are broader than those in the $Fe_3O_4(111)$ spectrum, but there are still considerable similarities. The larger width of the low energy features indicates, that, indeed, FeO like spectral features may contribute to the biphase spectrum.

In order to assign the $Fe_3O_4(111)$ spectral features, the phonon modes of the two commonly discussed surface terminations of $Fe_3O_4(111)$, one with Fe in tetrahedral sites and one with octahedral sites have been calculated[33] and they are compared with the experimental spectrum in Figure 8. Graphical illustrations of the three most intense Fe_{tet} surface vibrational modes are presented on the right of the figure. The comparison of vibrational energies with experiment reveals that the surface must be tetrahedrally

terminated. However, both calculations miss the peak at 485 cm^{-1}. It was shown in ref.,[33] that this peak is most likely related to a water contamination. The structure of the contaminated site is shown in Figure 9 together with its phonon spectrum, in direct comparison to the experimental spectrum. We refer to ref.[33] for a more detailed discussion.

4. Conclusion and Perspective

In summary, we have developed a novel method for the measurement of surface-located vibrations: surface action spectroscopy with messenger gas on the basis of ideas from gas phase studies. It is a non-referenced vibrational spectroscopy with a high surface sensitivity in particular with a proper choice of messenger gas. After a feasibility study on the $V_2O_3(0001)/Au(111)$ system and a detailed discussion of the desorption mechanisms, we have discussed SAS spectra of different iron oxide layers on Pt(111), with the goal of
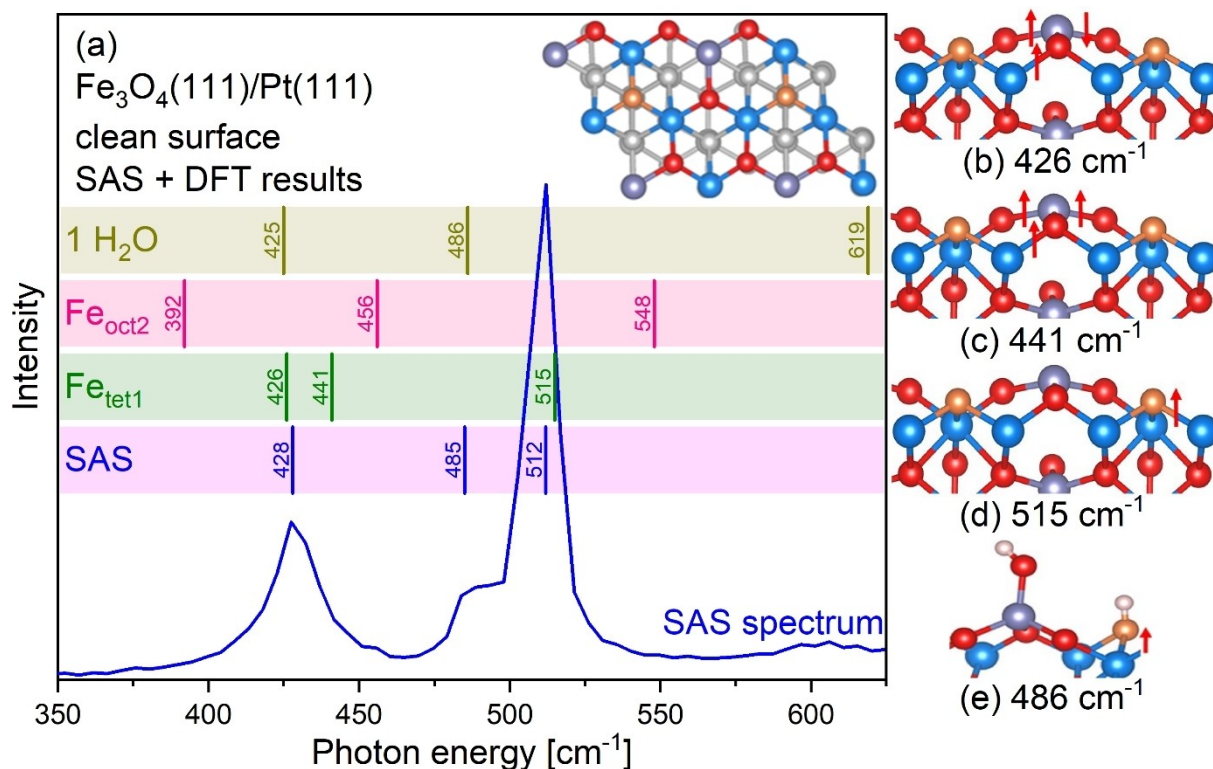
Figure 9. (a) Graphical comparison of computed vibrational energies with SAS peak energies for the Fe_{tet1} and Fe_{oct2} terminations of $Fe_3O_4(111)$ and for the Fe_{tet1} termination with one H_2O molecule adsorbed per unit cell. The blue curve is the experimental SAS spectrum. A model of Fe_{tet1} terminated clean $Fe_3O_4(111)$ (top view) is shown in the inset. (b),(c),(d): Graphical illustration of the three most intense Fe_{tet1} surface vibration modes (side view), and of the most intense vibration of Fe_{tet1} with a water adsorbate (e). Color code: Fe_{tet1} and Fe_{tet2}, violet balls; Fe_{oct1} and Fe_{oct2}, light blue balls; and orange and red balls represent two inequivalent surface oxygen atoms, denoted as O_b (orange), O_a (red), and H (in OH, light pink).

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 it was shown that Fe_3O_4 (111) is terminated with a Fe_{tet1} layer, which is contaminated with a small amount of dissociatively adsorbed H_2O under usual UHV conditions. In addition to this we were able to present spectroscopic evidence that biphase Fe_3O_4 (111) consists of regular $Fe_3O_4(111)$ coexisting with FeO(111), as also commonly discussed in the literature.

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 disordered systems suitable for full or partial structure determination as long as repeating structure elements are available, and comparison with calculations can be provided. To this point, one aspect of the surface action spectroscopy

that should be addressed is that it is possible to prepare messenger gas layers on inhomogeneous surfaces such that only areas with high adsorption energies are covered. By controlling the coverage of messenger gas or choosing the proper adsorption temperature of messenger gas, it is possible to populate surface sites such as clusters, defects, or interface sites in a selective way, thus the measured vibrational information would be exclusively from these selective-decorated sites. A schematic representation of such an approach is shown in Figure 10. Here, a surface is shown decorated with metal particles. If a proper temperature is chosen, one may succeed in only covering the supported metal particles with the messenger gas and via SAS record the vibrational spectra of such metal particles. Those may then be directly compared with the equivalent data from gas phase studies. Such studies are to be performed.
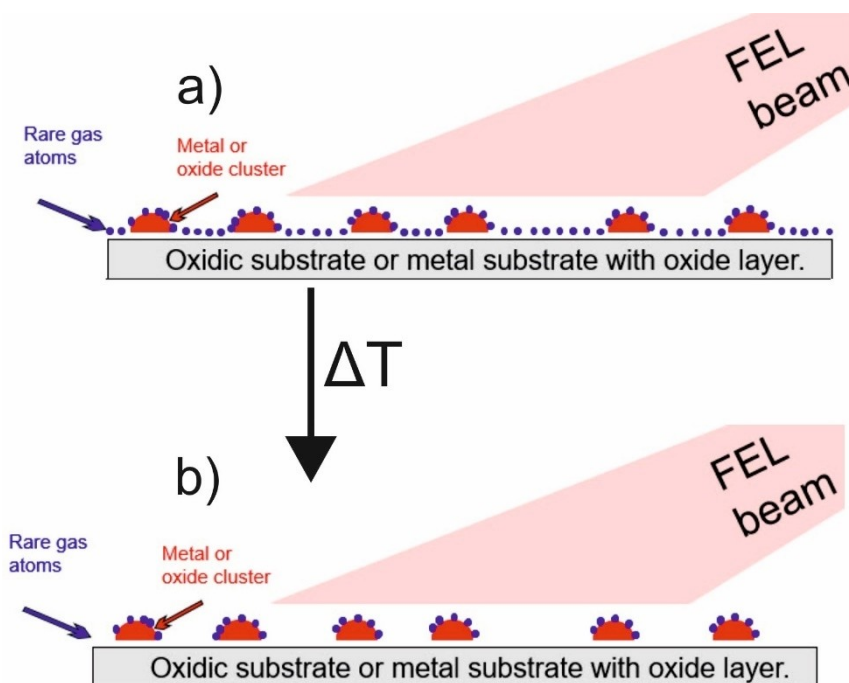
Figure 10. Schematic representation of messenger adsorption on oxide supported metal or oxide particles as an example for a structurally heterogeneous surface.

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