

Water Interaction with Iron Oxides

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Abstract: We present a mechanistic study on the interaction of water with a well-defined model $\text{Fe}_3\text{O}_4(111)$ surface that was investigated by a combination of direct calorimetric measurements of adsorption energies, infrared vibrational spectroscopy, and calculations based on density functional theory (DFT). We show that the adsorption energy of water (101 kJ mol^{-1}) is considerably higher than all previously reported values obtained by indirect desorption-based methods. By employing ^{18}O -labeled water molecules and an Fe_3O_4 substrate, we proved that the generally accepted simple model of water dissociation to form two individual OH groups per water molecule is not correct. DFT calculations suggest formation of a dimer, which consists of one water molecule dissociated into two OH groups and another non-dissociated water molecule creating a thermodynamically very stable dimer-like complex.

Materials based on iron oxides are of crucial importance for many technological and environmental applications.^[1] Under natural humid conditions, they are exposed to water, which strongly affects their structure and reactivity in surface chemical processes.^[2] Despite of the vast importance of the water/iron oxide(s) interaction, the atomistic-level understanding of this system is rather limited, mostly due to the fact that it has been commonly addressed by methods, such as for example, temperature programmed desorption (TPD) or photoelectron spectroscopy (PES), which are based on assumptions in order to extract information on adsorption energies and molecular speciation. Interaction of water with different types of oxides was previously investigated at the atomistic level on model surfaces of TiO_2 ,^[3] ZnO ,^[4] Fe_3O_4 ,^[5] Fe_2O_3 ,^[6] RuO_2 ,^[7] and some others. Despite the large amount of available data, mainly obtained by imaging techniques, the reliable spectroscopic identification of surface species formed

on these oxides is rare and relates mostly to very high water coverages;^[4b,8] nearly no spectroscopic information is present on the initial stages of water interaction with oxides.

Particularly for magnetite (Fe_3O_4), there is a limited knowledge on the nature of the surface species formed upon water adsorption and dissociation. Even though infrared vibrational spectroscopy of adsorbed water on well-defined model Fe_3O_4 surfaces provides some evidences for the formation of hydroxy groups, the spectra are rather complex^[5c] and not fully understood. Specifically, it is not clear if the simplest model which suggests the formation of two individual hydroxy groups upon dissociation of one water molecule^[3b,5c]—usually discussed in the literature—is valid.

Previous TPD studies suggest a very low binding energy of water on Fe_3O_4 (ca. 65 kJ mol^{-1}),^[2a,5c,9] that is, close to adsorption energies typical of molecular adsorption on chemically inert surfaces (50 kJ mol^{-1}). This observation cannot be rationalized on the common chemical grounds as water is known to dissociate on Fe_3O_4 and form hydroxy groups, as clearly evidenced by the corresponding spectroscopic signatures.^[5c,10] This apparent contradiction arises most likely from the limited applicability of TPD to complex dissociative processes and from the need for a kinetic modeling of the desorption process. A strategy to overcome these limitations is the direct calorimetric measurement of adsorption energies under isothermal conditions.^[11]

Here, we report the first direct calorimetric measurement of the water interaction strength with a well-defined model $\text{Fe}_3\text{O}_4(111)$ surface grown on $\text{Pt}(111)$ under ultrahigh vacuum (UHV) conditions. So far $\text{Fe}_3\text{O}_4(111)$ has been studied to a lesser extent compared to the (100) surface, but the (111) orientation^[12] is the natural growth facet making it more relevant for applications under ambient conditions. We apply a recently developed UHV single-crystal adsorption calorimeter^[11b] (SCAC) based on molecular beam techniques to directly measure water adsorption and dissociation energies as a very detailed function of surface coverage. Complementary, we employ infrared reflection absorption spectroscopy (IRAS) in combination with molecular beam techniques to identify the nature of the surface species formed upon water adsorption and to find detailed correlations between the structures of the adsorbates and the energies of their formation. We show that the water dissociation energy on $\text{Fe}_3\text{O}_4(111)$ is considerably higher than previously reported, based on indirect desorption methods. By employing IRAS on isotopically labeled water and Fe_3O_4 , we experimentally prove that the generally accepted simple model of water dissociation to form two individual OH groups is not valid. Previous computational studies on water adsorption at the

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201506439>.

$\text{Fe}_3\text{O}_4(111)$ surface^[5a,13] could not provide a definite atomistic picture of this process. Combining experimental findings with calculations based on density functional theory (DFT), we show that surface OH groups formed upon water dissociation establish a very stable complex with molecular water. Conversely, formation of two individual spatially separated OH groups could be unambiguously ruled out. Calculated spectroscopic vibrational signatures as well as the formation energy of the corresponding OH–water complex agree with experimental observations.

Figure 1a shows the differential adsorption energy of water measured at 120 K at three different surfaces—metallic

results in water ice formation at high coverage, the initial adsorption energy at higher temperatures reaches $101 \pm 2 \text{ kJ mol}^{-1}$ and no multilayer ice is formed, in agreement with previous observations.^[9] An increase of the initial binding energy from 87 kJ mol^{-1} at 120 K to 101 kJ mol^{-1} at temperatures above 180 K is most likely related to a kinetic hindrance of water dissociation at 120 K. Since the initial adsorption energy remains constant for all temperatures above 180 K, this value can be considered as the true thermodynamic value that is not affected by slow kinetics of water dissociation. Qualitatively, the coverage dependence of the water adsorption energy remains similar to 120 K,

however, saturation is reached at lower absolute water coverage (see Table S3.1 in the Supporting Information). After reaching saturation, the adsorption system runs into a dynamic adsorption–desorption equilibrium (indicated as solid lines at the end of each adsorption curve), in which adsorption during the molecular beam pulse is compensated by desorption between two pulses. Water adsorption energies previously measured by TPD are 30–35 kJ mol^{-1} lower than the value of

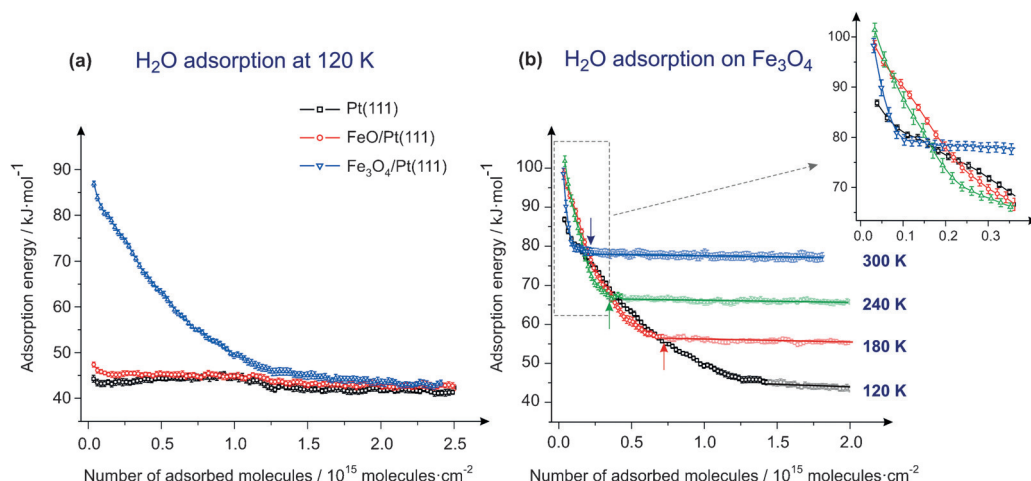


Figure 1. a) Differential adsorption energy measured at 120 K plotted as a function of the number of adsorbed H₂O molecules for Pt(111), FeO(111)/Pt(111), and Fe₃O₄(111)/Pt(111). b) Differential adsorption energy of H₂O on Fe₃O₄(111)/Pt(111) as a function of the number of adsorbed H₂O molecules measured at different temperatures.

Pt(111) and two thin iron oxide layers FeO/Pt(111) and Fe₃O₄(111)/Pt(111)—as a function of the number of adsorbed water molecules. The energy measurement was combined with a sticking coefficient measurement using the King–Wells method,^[14] allowing for a quantitative determination of the absolute number of adsorbed water molecules. On the first two surfaces, the initial adsorption energy amounts to about 47 kJ mol^{-1} and remains nearly constant while water is accumulated and finally forms water ice. Low adsorption energies measured on these surfaces are indicative of a molecular adsorption process. In contrast, the initial adsorption energy of water on the Fe₃O₄/Pt(111) surface reaches 87 kJ mol^{-1} , pointing to a strong chemical interaction, that is, dissociation. The adsorption energy strongly decreases with increasing water coverage, which might be due to interatomic repulsion of neighboring adsorbates and/or increasing competition for the electrons of the Fe₃O₄ substrate to participate in the bonding. The measured energy levels off after adsorption of about 1.25×10^{15} water molecules per square centimeter.

The differential adsorption energies of water interacting with the Fe₃O₄ substrate at four different surface temperatures (120, 180, 240, and 300 K) are shown in Figure 1b. While water adsorption at 120 K starts from 87 kJ mol^{-1} and

101 kJ mol^{-1} obtained in the present study,^[2a,15] which we attribute to the kinetic nature of the TPD experiment and the often crude assumptions for pre-exponentials.

To obtain more insight into the atomistic details of water adsorption and dissociation on magnetite surfaces, we monitored the formation of different surface species by IRAS in a temperature range between 120 and 500 K. Figure 2a shows the IR spectra obtained after water adsorption on Fe₃O₄(111) at 300 K. The uppermost trace was recorded for D₂O molecules adsorbed on regular Fe₃O₄(111). This spectrum exhibits two distinct vibrational bands at 2720 and 2695 cm^{-1} , which were also observed for all other investigated temperatures at lowest water coverage. At 300 K, there are no coverage-dependent changes of the spectra, except of the absolute intensity of the bands. At lower temperatures new vibrational features appear with increasing coverage. In a previous study, vibrational bands in a similar frequency range were observed at low water coverage and were assigned to two individual hydroxy groups.^[5c] It was suggested that one of the OD groups binds to an iron atom, while D binds to a surface oxygen to form a second type of an OD group. To verify or falsify this assignment, we prepared an isotopically labeled Fe₃¹⁸O₄(111) film and recorded IR spectra of D₂O. The expected shift of the vibrational band at 2695 cm^{-1}

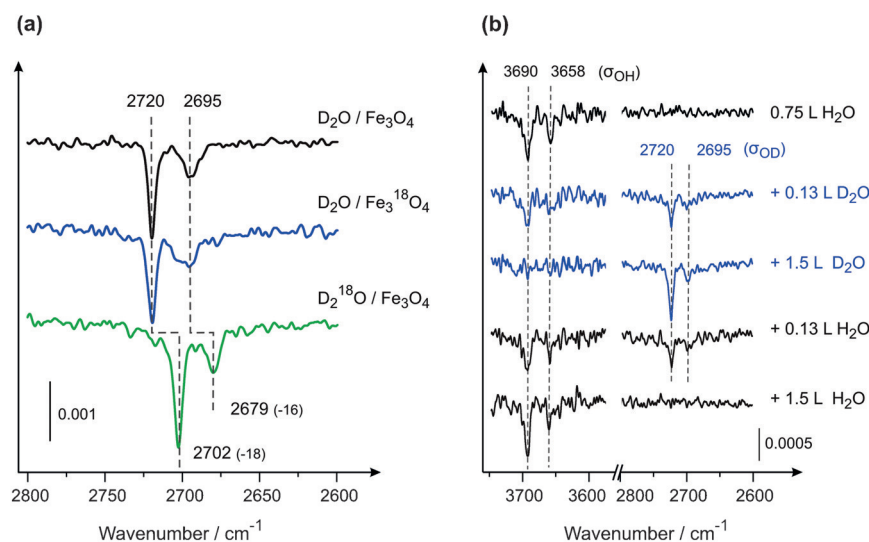


Figure 2. a) IRAS spectra obtained at 300 K on $\text{Fe}_3\text{O}_4(111)$ surfaces saturated with water for normal and isotopically labeled water and Fe_3O_4 . b) IRAS spectra obtained at 300 K on $\text{Fe}_3\text{O}_4(111)$ surfaces in an isotope-exchange experiment.

(previously assigned to an OD group involving lattice oxygen) was not observed (blue spectrum in Figure 2a). In contrast, when double isotopically labeled water (D_2^{18}O) was adsorbed on regular Fe_3O_4 , both vibrational peaks shifted to lower frequencies by 16 and 18 cm^{-1} , correspondingly (green spectrum in Figure 2a). These observations clearly prove that the low-frequency vibrational band (2695 cm^{-1}) does not originate from D adsorption on the surface oxygen as previously assumed. Instead, both OD vibrations involve an O-atom originating from gas-phase dosed water. This observation provides clear experimental evidence, that these vibrational features cannot be explained in a simple way by two individual OD groups created upon dissociation of a single water molecule and that the previously discussed model is incorrect.

The series of spectra shown in Figure 2b demonstrates that adsorption of the surface species is fully reversible. The surface was saturated first with H_2O (uppermost spectrum) and subsequently was exposed to D_2O via a second molecular beam. After about 1.5 L (1 L = 10^{-6} Torr) D_2O exposure, full replacement of H_2O -related species (3690 and 3658 cm^{-1}) by the D_2O -related species (2720 and 2695 cm^{-1}) was detected (blue spectra in Figure 2b). Vice versa, by exposing the D_2O -covered surface to an H_2O molecular beam, a complete exchange of D_2O -related species by H_2O -related species was observed. Importantly, the intensity of both vibrational bands was decreasing (increasing) simultaneously with the same characteristic time constant, that is, there was no pronouncedly faster vanishing of one of the bands as compared to the other. These observations—alongside with results of the isotopic labeling experiments—indicate that the observed surface species are very likely coupled rather than fully spatially separated on the surface as in the latter case exchange kinetics with different characteristic time constants are to be expected.

To obtain detailed atomistic insight into the interaction of water with the magnetite surface, we accomplished a DFT study using the PBE+U approach. Figure 3 shows the optimized structures of one and two water molecules adsorbed on the octahedrally ($\text{Fe}_{\text{oct}2}$, Figure 3a and b) and tetrahedrally ($\text{Fe}_{\text{tet}1}$, Figure 3c and d) terminated $\text{Fe}_3\text{O}_4(111)$ surfaces as well as the respective adsorption enthalpies. According to our data and previously published studies on the stabilities of bulk terminated $\text{Fe}_3\text{O}_4(111)$ surfaces, the $\text{Fe}_{\text{oct}2}$ and $\text{Fe}_{\text{tet}1}$ terminations are 1) comparably stable in surface energy, and 2) they are the most stable ones for a broad range of oxygen chemical potentials.^[16] Vibrational frequencies computed for all experimentally investigated isotopically labeled configura-

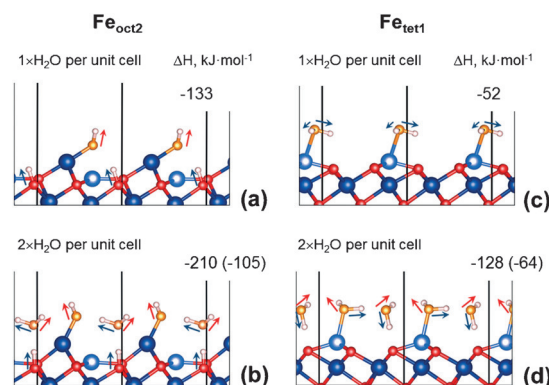


Figure 3. Calculated PBE+U adsorption structures of one and two water molecules on the a,b) $\text{Fe}_{\text{oct}2}$ - and c,d) $\text{Fe}_{\text{tet}1}$ -terminated $\text{Fe}_3\text{O}_4(111)$ surface. The reaction enthalpy at 0 K in kJ mol^{-1} is given in the upper right of individual graphs. For dimer formation, the reaction enthalpy per molecule is given in parentheses. Octahedrally coordinated Fe atoms are dark blue, tetrahedrally coordinated Fe atoms light blue, lattice oxygen is red, oxygen in water is orange, and hydrogen is white.

tions of either water or the iron oxide surface are summarized in Table 1.

Adsorption of a single D_2O molecule on the $\text{Fe}_{\text{oct}2}$ terminated surface, which corresponds to a coverage of $3.2 \times 10^{14} \text{ cm}^{-2}$, results in water dissociation and formation of two individual OD groups with the corresponding formation enthalpy of -133 kJ mol^{-1} (Figure 3a). While the calculated frequency of the OD group coordinated to the Fe cation (2754 cm^{-1}) agrees well with the experimentally observed range 2720–2695 cm^{-1} ; the frequency of an OD vibration involving a 3-fold coordinated surface oxygen atom - indicated in the literature as “bridging OH”^[3b]—was found to be considerably lower (2439 cm^{-1}). Experimentally, no vibra-

Table 1: Computed^[a] vibrational frequencies in cm^{-1} compared with experiment. Shifts induced upon ^{18}O labeling of either water or Fe_3O_4 are given in parenthesis. Terminal, bridging, and hydrogen-bonded OH groups are labeled with t, b, and h, in square brackets, respectively.

	Experiment	$\text{H}_2\text{O}/\text{Fe-oct2}$	$(\text{H}_2\text{O})_2/\text{Fe-oct2}$	$\text{H}_2\text{O}/\text{Fe-tet1}$	$(\text{H}_2\text{O})_2/\text{Fe-tet1}$
$(\text{D}_2\text{O})_n/\text{Fe}_3\text{O}_4$	2720	2754 [t]	2740 [t]	2687	2707 [t]
	2695	2439 [b]	2710 [t]	2569	2692 [t]
			2270 [b]		1832 [h]
			2020 [h]		1638 [h]
$(\text{D}_2\text{O})_n/\text{Fe}_3^{18}\text{O}_4$	2720	2754 (0)	2740 (0)	2687	2707 (0)
	2695	2423	2710 (0)	2569	2692 (0)
			2255		1832
			2020		1638
$(\text{D}_2^{18}\text{O})_n/\text{Fe}_3\text{O}_4$	2702 (−18)	2737 (−17)	2723 (−17)	2667	2690 (−17)
	2679 (−16)	2439	2692 (−18)	2558	2675 (−17)
			2270		1818
			2006		1625

[a] Harmonic scaled frequencies obtained using the PBE + U approach with $U = 3.8$ eV and a scaling factor of 0.9935 (see the Supporting Information).

tional band was observed for such a low frequency range. In addition, calculated frequency shifts for the various isotopically labeled structures do not agree with observed values.

In contrast to the Fe_{oct2} terminated surface, water adsorbs non-dissociatively on the Fe_{tet1} terminated surface with the corresponding formation enthalpy of -52 kJ mol^{-1} (Figure 3c). Computed vibrational frequencies (2687 and 2569 cm^{-1}) and isotopic shifts of this molecular water adsorbate are in strong disagreement with experimentally measured IR spectra.

As a result for the adsorption of a single water molecule on both investigated terminations, neither calculated adsorption enthalpies nor vibrational frequencies nor frequency shifts upon isotopic labeling were found to match the experimentally measured values. This observation agrees well with the above discussed experimental IR data, implying that both observed vibrational peaks involve an oxygen atom from gaseous water molecules and proving that the formation of two individual hydroxy groups is inconsistent with the experiment. Thus, based on both theoretical and experimental results, formation of two individual and spatially separated OD groups out of a single water molecule can be safely ruled out.

Next, we examined the formation of a possible dimer-like structure upon adsorption of two water molecules per unit cell (corresponding to formal water coverage 6.4×10^{14} cm^{-2}) for both surface terminations. On the Fe_{oct2} terminated surface, the first water molecule undergoes dissociation and forms two individual OD groups. According to the calculations, the second water molecule does not dissociate and forms a complex with the hydroxy groups instead. Figure 3b shows the optimized, most stable structure of this dimer complex, in which two hydrogen bonds are created. The adsorption enthalpy of this dimer is -210 kJ mol^{-1} , or -105 kJ mol^{-1} per water molecule, which is very close to the measured value of 101 kJ mol^{-1} . This dimer complex involves stretching modes of the terminal OH (OD) groups (red arrows in Figure 3b) as well as modes assigned to H-bonded hydroxy groups or water species (blue arrows). The two calculated frequencies of the terminal OD vibrations (2740 and

2710 cm^{-1} , see Table 1) as well as the difference between these vibrational frequencies ($\Delta\nu_{\text{theor}} = 30$ cm^{-1}) are in very good agreement with the experimental data (2720 and 2695 cm^{-1} , $\Delta\nu_{\text{exp}} = 25$ cm^{-1}). The vibrational frequencies related to the H-bonded normal modes of this complex are 2270 and 2020 cm^{-1} . For this particular range, no vibrations were experimentally observed, most likely due to band broadening caused by H bonding^[17] and due to the metal surface selection rule.^[18]

The latter explanation can be corroborated by a normal mode analysis, which shows that the surface OD group and the D atom of the

intact water molecule (blue arrows in Figure 3b) couple to a single vibrational mode with a pronounced parallel component to the metallic magnetite surface. Therefore, they cannot be compared with the experiment. The computed shifts upon isotopic labeling are also in agreement with the observations. Labeling of the Fe_3O_4 surface with ^{18}O did not result in any frequency shift of the terminal OD groups, while labeling of the water with ^{18}O shifts both terminal OD peaks by 17 and 18 cm^{-1} . In total, the computationally characterized dimer complex consisting of one dissociated and one intact water molecule in the Fe_{oct2} terminated $\text{Fe}_3\text{O}_4(111)$ surface was found to match all experimental observations.

On the Fe_{tet1} -terminated surface both water molecules adsorb molecularly. Two non-dissociated molecules form a complex with an adsorption enthalpy of -64 kJ mol^{-1} per water molecule (see Figure 3d), which is about two thirds of the measured value (101 kJ mol^{-1}). The two highest frequencies computed for this dimer— 2707 and 2692 cm^{-1} —lie close to the experimentally observed values (2695 and 2720 cm^{-1}). However, the remaining frequencies are predicted to be within 1630 – 1830 cm^{-1} , where no bands were observed. While the vibrational frequencies and their shifts upon isotopic labeling of the water dimer on the Fe_{tet1} -terminated surface are in relatively good agreement with experimental observations, its calculated formation enthalpy markedly disagrees with the measured energies (for additional discussion of adsorption energies and stability see the Supporting Information). Overall, the calculated properties of only one structure—the hydroxy–water complex adsorbed on the Fe_{oct2} -terminated $\text{Fe}_3\text{O}_4(111)$ —are fully consistent with all available experimental observations.

Previously, formation of long-range ordered dimer-like superstructures of water was reported for ZnO, in which half of the water molecules on the fully covered on ZnO(10-10) surface self-dissociate resulting in a well-defined (2×1) superlattice.^[4a] Spectroscopically, two vibrational peaks and a shoulder were observed for this structure, which were assigned to two individual OH groups and molecular water. However, no isotopic labeling of water and ZnO were performed in this study that would make possible the

unambiguous assignment of these peaks to water and lattice oxygen-related species. It remained also unclear if the dimer-like structures could be formed at low water coverages or their stabilization by H bonding in the long-range superlattice is required. Other vibrational studies carried out on TiO_2 ^[3e,8] and Fe_3O_4 ^[5c] suggest dissociation of a water molecule to two individual OH groups.

In summary, the interaction of water with a well-defined model $\text{Fe}_3\text{O}_4(111)$ surface was investigated for the first time using highly accurate direct calorimetric measurements under UHV conditions. Complementary, spectroscopic identification of the surface species was performed by IRAS. We showed that the adsorption energy of water on $\text{Fe}_3\text{O}_4(111)$ is considerably higher than all previously reported values obtained by indirect desorption-based methods. By employing isotopically labeled water and Fe_3O_4 substrate, we experimentally proved that the generally accepted simple model of water dissociation to form two individual OH groups per water molecule is not correct. DFT calculations suggest formation of a dimer, which consists of one water molecule dissociated into two OH groups and another non-dissociated water molecule creating a thermodynamically very stable dimer-like complex. Calculated vibrational frequencies, their shift upon selective isotopic labeling of either water or the substrate with ^{18}O as well as the formation energy of an OH–water complex on the $\text{Fe}_{\text{oct}2}$ -terminated $\text{Fe}_3\text{O}_4(111)$ surface are in agreement with corresponding experimental data. Less agreement was found for water adsorption on the $\text{Fe}_{\text{tet}1}$ -terminated surface.

Acknowledgements

This work has been supported by Deutsche Forschungsgemeinschaft within the Sonderforschungsbereich SFB 1109 and by grants for computing time at the high-performance computer center HLRN (North-German Supercomputing Alliance in Berlin and Hannover). Financial support by the Verband der Chemischen Industrie (VCI) is gratefully acknowledged.

Keywords: calorimetry · density functional calculations · infrared spectroscopy · surface science · water adsorption

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 13942–13946
Angew. Chem. **2015**, *127*, 14148–14152

- [1] R. M. Cornell, U. Schwertmann, *The Iron Oxides*, Wiley-VCH, Weinheim, **2004**, pp. 1–7.
- [2] a) W. Weiss, W. Ranke, *Prog. Surf. Sci.* **2002**, *70*, 1–151; b) C. Lemire, R. Meyer, V. E. Henrich, S. Shaikhutdinov, H. J. Freund, *Surf. Sci.* **2004**, *572*, 103–114.
- [3] a) U. Diebold, *Surf. Sci. Rep.* **2003**, *48*, 53–229; b) M. A. Henderson, *Surf. Sci. Rep.* **2002**, *46*, 1–308; c) I. M. Brookes,

- C. A. Muryn, G. Thornton, *Phys. Rev. Lett.* **2001**, *87*, 266103; d) C. Di Valentin, A. Tilocca, A. Selloni, T. J. Beck, A. Klust, M. Batzill, Y. Losovyj, U. Diebold, *J. Am. Chem. Soc.* **2005**, *127*, 9895–9903; e) G. A. Kimmel, M. Baer, N. G. Petrik, J. Vande-Vondele, R. Rousseau, C. J. Mundy, *J. Phys. Chem. Lett.* **2012**, *3*, 778–784.
- [4] a) B. Meyer, D. Marx, O. Dulub, U. Diebold, M. Kunat, D. Langenberg, C. Wöll, *Angew. Chem. Int. Ed.* **2004**, *43*, 6641–6645; *Angew. Chem.* **2004**, *116*, 6809–6814; b) H. Noei, H. Qiu, Y. Wang, E. Löffler, C. Wöll, M. Muhler, *Phys. Chem. Chem. Phys.* **2008**, *10*, 7092–7097.
- [5] a) K. T. Rim, D. Eom, S.-W. Chan, M. Flytzani-Stephanopoulos, G. W. Flynn, X.-D. Wen, E. R. Batista, *J. Am. Chem. Soc.* **2012**, *134*, 18979–18985; b) T. Kendelewicz, P. Liu, C. S. Doyle, G. E. Brown, Jr., E. J. Nelson, S. A. Chambers, *Surf. Sci.* **2000**, *453*, 32–46; c) U. Leist, W. Ranke, K. Al-Shamery, *Phys. Chem. Chem. Phys.* **2003**, *5*, 2435–2441.
- [6] S. Yamamoto, T. Kendelewicz, J. T. Newberg, G. Ketteler, D. E. Starr, E. R. Mysak, K. J. Andersson, H. Ogasawara, H. Bluhm, M. Salmeron, G. E. Brown, Jr., A. Nilsson, *J. Phys. Chem. C* **2010**, *114*, 2256–2266.
- [7] R. Mu, D. C. Cantu, X. Lin, V.-A. Glezakou, Z. Wang, I. Lyubnitsky, R. Rousseau, Z. Dohnalek, *J. Phys. Chem. Lett.* **2014**, *5*, 3445–3450.
- [8] M. A. Henderson, *Surf. Sci.* **1996**, *355*, 151–166.
- [9] Y. Joseph, W. Ranke, W. Weiss, *J. Phys. Chem. B* **2000**, *104*, 3224–3236.
- [10] a) Y. Joseph, C. Kuhrs, W. Ranke, M. Ritter, W. Weiss, *Chem. Phys. Lett.* **1999**, *314*, 195–202; b) T. Kendelewicz, P. Liu, C. S. Doyle, G. E. Brown, E. J. Nelson, S. A. Chambers, *Surf. Sci.* **2000**, *453*, 32–46; c) R. S. Cutting, C. A. Muryn, D. J. Vaughan, G. Thornton, *Surf. Sci.* **2008**, *602*, 1155–1165.
- [11] a) H. M. Ajo, H. Ihm, D. E. Moilanen, C. T. Campbell, *Rev. Sci. Instrum.* **2004**, *75*, 4471–4480; b) J.-H. Fischer-Wolfarth, J. Hartmann, J. A. Farmer, J. M. Flores-Camacho, C. T. Campbell, S. Schauermaier, H.-J. Freund, *Rev. Sci. Instrum.* **2011**, *82*, 024102.
- [12] a) A. R. Lennie, N. G. Condon, F. M. Leibsle, P. W. Murray, G. Thornton, D. J. Vaughan, *Phys. Rev. B* **1996**, *53*, 10244–10253; b) J. Ahdjoudj, C. Martinsky, C. Minot, M. A. Van Hove, G. A. Somorjai, *Surf. Sci.* **1999**, *443*, 133–153.
- [13] a) M. E. Grillo, M. W. Finnis, W. Ranke, *Phys. Rev. B* **2008**, *77*, 075407; b) C. Zhou, Q. Zhang, L. Chen, B. Han, G. Ni, J. Wu, D. Garg, H. Cheng, *J. Phys. Chem. C* **2010**, *114*, 21405–21410.
- [14] D. A. King, M. G. Wells, *Proc. R. Soc. London Ser. A* **1974**, *339*, 245–269.
- [15] Y. Joseph, C. Kuhrs, W. Ranke, W. Weiss, *Surf. Sci.* **1999**, *433*, 114–118.
- [16] a) L. Zhu, K. L. Yao, Z. L. Liu, *Phys. Rev. B* **2006**, *74*, 035409; b) X. Yu, C.-F. Huo, Y.-W. Li, J. Wang, H. Jiao, *Surf. Sci.* **2012**, *606*, 872–879; c) A. Kiejna, T. Ossowski, T. Pabisiak, *Phys. Rev. B* **2012**, *85*, 125414.
- [17] C. M. Huggins, G. C. Pimentel, *J. Phys. Chem.* **1956**, *60*, 1615–1619.
- [18] F. M. Hoffmann, *Surf. Sci. Rep.* **1983**, *3*, 107–192.

Received: July 13, 2015

Revised: August 14, 2015

Published online: October 12, 2015