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Adsorption of formic acid on rutile TiO₂ (110) revisited: An Infrared Reflection-Absorption Spectroscopy and Density Functional Theory study

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Abstract

Formic acid (HCOOH) adsorption on rutile TiO₂ (110) has been studied by s- and p-polarized infrared reflection-absorption spectroscopy (IRRAS) and spin-polarized density functional theory together with Hubbard U contributions (DFT+U) calculations. To compare with IRRAS spectra, the results from the DFT+U calculations were used to simulate IR spectra by employing a three-layer model, where the adsorbate layer was modelled using Lorentz oscillators with calculated dielectric constants. To account for the experimental observations, four possible formate adsorption geometries were calculated, describing both the perfect (110) surface, and surfaces with defects; either O vacancies or hydroxyls. The binding energy was found to be $E_{bind} = -1.84$ eV for the bridging bidentate formate species, which bonds with its two O atoms to two neighbouring Ti_{5c} atoms in the Ti trough along the [001] direction. The

two species which bind to an O vacancy site were found to have similar binding energies (-1.85 eV and -1.87 eV). Formate adsorbed to one Ti_{5c} and a protonated, two-fold coordinated O_{2c} in the bridging oxygen row (or equivalent, a hydroxylated O vacancy), was found to have the weakest binding energy of the four possible adsorption geometries ($E_{\text{bind}} = -1.31$ eV). The majority species seen in IRRAS was confirmed to be the bridging bidentate formate species with associated symmetric and asymmetric frequencies of the $\nu(\text{OCO})$ modes measured to be at 1359 cm^{-1} and 1534 cm^{-1} , respectively. The in-plane $\delta(\text{C-H})$ wagging mode of this species couples to both the tangential and the normal component of the incident p-polarized light, which results in absorption and emission bands at 1374 cm^{-1} and 1388 cm^{-1} . IRRAS spectra measured on surfaces prepared to be either reduced, stoichiometric, or to contain surplus O adatoms, were found to be very similar. By comparisons with computed spectra, it is concluded that formate binds to in-plane Ti_{5c} atoms rather than to O vacancy sites. The results emphasize the importance of protonation and reactive surface hydroxyls – even under UHV conditions – as reactive sites in e.g. catalytic applications.

I. Introduction

Titanium dioxide (TiO_2) has been the subject of numerous studies in the past few decades, which partly has been driven by its catalytic properties, with applications in e.g. photocatalysis^{1, 2} and low temperature oxidation catalysis.³ Fundamental surface science studies have hitherto mainly been performed on the rutile TiO_2 (110) surface.⁴ This is the thermodynamically preferred rutile facet and can readily be obtained as single crystals in large dimension (of the order of 1 cm^2) to allow for a wide variety of experimental investigations.

Recent scanning tunnelling microscopy (STM) studies have shown how the outermost surface of rutile TiO_2 (110) can be made either reduced (large percent of O vacancies), stoichiometric (minimum of O vacancies) or oxidized (O adatoms adsorbed on the surface) by

altering the surface preparation procedures.⁴⁻⁷ Most ultra-high vacuum (UHV) studies so far have been conducted on reduced TiO₂ surfaces simply because of the sputtering-annealing procedures involved in the sample preparation.⁴ This is commonly believed to give rise to O vacancies in the rutile TiO₂ (110) surface, where two-fold coordinated bridging O (O_{2c}) surface atoms are missing. In a recent STM study it was shown that these bridging O vacancies rapidly become hydroxylated to form OH defects even at good UHV conditions. For example, a typical reduced surface, with 5% ML bridging O vacancies, became hydroxylated within a few minutes at a base pressure of approximately 2×10^{-10} Torr.⁶

Formate adsorption on TiO₂ has been studied extensively.⁸⁻²¹ Previous studies of adsorption of formic acid (HCOOH) on rutile TiO₂ (110) surfaces have shown that upon adsorption it dissociates into a formate ion (HCOO⁻) and a proton (H⁺), which bind to low-coordinated Ti and O surface atoms, respectively.^{22, 23} The adsorption structure of small molecules, such as HCOOH, can be studied favourably by infrared spectroscopy, and in particular infrared reflection-absorption spectroscopy (IRRAS) has been employed to study e.g. NO, CO and H₂O adsorbed on TiO₂ (110).²⁴⁻²⁶ However, the only infrared study of HCOOH adsorption on single crystal TiO₂ (110) we are aware of is the study by Hayden et al.²² Based on the azimuthal dependence of p-polarized IRRAS measurements they showed that two differently coordinated formate species existed on the (110) surface. The majority species, denoted “A”, was attributed to bridging bidentate formate bonded to two five-fold coordinated Ti_{5c} atoms in the troughs, with the molecular O-C-O axis oriented along [001] direction, whereas a minority species, denoted “B”, was attributed to formate adsorbed with the molecular axis aligned in the $[\bar{1}\bar{1}0]$ direction, with one oxygen atom sitting in an oxygen vacancy, and with the other O atom bonded to a Ti_{5c} atom. The coverage of these two species were estimated to be 0.4 and 0.2 monolayer, respectively. Comparisons with other experimental studies, such as scanning tunnelling microscopy (STM), photoelectron

diffraction (PhD), and low energy electron diffraction (LEED),^{13, 27, 28} reveal, however, that the concentration of the minority species may be very low. In light of the fast hydroxylation of the surface at pressures in the 10^{-10} mbar range^{6, 7} it may therefore be anticipated that the formate ion could interact with OH defects rather than O vacancies.

Here we present a combined study employing s- and p-polarized IRRAS measurements and density functional theory with Hubbard U (DFT+U) calculations to explore the adsorbate structure and vibrational properties of HCOOH adsorbed on rutile TiO₂ (110) surfaces prepared to mimic a stoichiometric, reduced and oxidized surface, respectively. Our results show that the observed IR spectra are consistent with two main formate structures; one agreeing with the main species (“A”) proposed by Hayden et al.,²² and a second due to a formate ion forming a hydrogen bond to an OH group identified as a protonated bridging O atom – regardless of surface preparation. Our results support the conclusions from the STM study of oxygen vacancies on rutile TiO₂ by Wendt et al.,⁶ i.e. that O vacancy sites rapidly become hydroxylated, which is qualitatively also supported in the STM study by Cui et. al.²⁹, and therefore necessitates a reinterpretation of the formate adsorption structure on TiO₂ (110), and the role of O vacancies for the surface reactivity of TiO₂ in general.^{14, 15}

II. Experimental

IRRAS measurements were performed in an UHV chamber connected to a vacuum-pumped FTIR spectrometer (Bruker IFS 66v/S, Ettlingen, Germany). The spectrometer was coupled to the UHV vacuum chamber through a vacuum-pumped beam path connected to the spectrometer pump. A KRS-5 wire grid polarizer (Specac, Orpington, UK) mounted between the focusing optics and the KBr window connected to the UHV chamber was used to select polarization of the IR light. A narrow band liquid nitrogen cooled HgCdTe detector (Infrared Associates, Stuart, FL, USA) was mounted on the opposite side of the UHV chamber at 170

degrees with respect to the incident IR beam. IRRAS measurements were performed at a grazing incident angle of 85° . Each spectrum was averaged over 1024 scans with 4 cm^{-1} resolution (~ 7 min per spectrum). Background spectra were collected on freshly prepared surfaces immediately before formic acid dosing.

The UHV vacuum chamber was pumped by a turbo molecular pump (Varian, Palo Alto, CA, USA) and a Ti sublimation pump (Eurovac, Stockholm, Sweden) giving a base pressure of 2×10^{-10} mbar. A $20 \times 20\text{ mm}^2$ rutile TiO_2 (110) single crystal (PI-KEM Ltd., Tamworth, UK) was mounted on a sample holder that allowed for sample movement in x, y, z, θ and ϕ -direction (Omniax Translator, Vacuum Generators Inc., Hastings, UK). Heating of the sample was achieved by an on-board resistive heater. Cooling was made with copper braids connected to the sample holder and a liquid nitrogen reservoir.

The samples were cleaned by repeated cycles of sputtering of Ar ions at 1 keV and an ion current of $1\text{ }\mu\text{A}$ on the sample at 323 K for 10 min. Depending on the desired surface condition ('reduced', 'stoichiometric' or 'oxidized'), different preparation procedures adapted from the literature was employed.⁴⁻⁶ To create a reduced surface (r- $\text{TiO}_2(110)$), the sample was annealed at 973 K in vacuum for 20 min. For the stoichiometric (s- $\text{TiO}_2(110)$) and oxidized surfaces (o- $\text{TiO}_2(110)$), the samples were annealed at 973 K for 10 min at 1×10^{-6} mbar O_2 , and subsequently 10 min in UHV. This cycle was repeated four times before each IRRAS measurement. The low-energy electron diffraction (LEED) pattern of the surface was regularly measured (model BDL800, OCI Vacuum Microengineering, London, Canada) to ensure that sharp spots due to the typical 1×1 surface structure were observed. After the LEED measurements, the samples were flashed to 600 K to obtain surfaces as hydroxyl-free as possible. In the case of the o- $\text{TiO}_2(110)$ surface, the sample was subsequently cooled to 140 K, followed by 2 Langmuir (L) of O_2 dosing, and brief annealing of the sample to 273 K. Employing different surface preparations is expected to result in different concentrations of O

vacancies on the surface. However, as the experiments show, no large difference between HCOOH adsorption on the r-TiO₂ and s-TiO₂ surface is observed. As we argue here, and as reported by Wendt *et al.*⁶, this is due to hydroxylation of O vacancies during sample preparation.

Exposure of formic acid (HCOOH puriss, Fluka, Schnelldorf, Germany) was achieved with a directed gas doser placed in front of the sample, which sprayed the gas through a 1 μ m pinhole. The gas doser was mounted on a linear translator on the UHV chamber, and connected to a reservoir of formic acid, which could be evacuated by a mechanical pump. Prior to dosing, the formic acid was subjected to several freeze-thaw cycles. Formic acid dosing was performed for 60 s, followed by 60 s evacuation of the directed gas doser before the IRRAS measurement started. This gas dose corresponds to saturation coverage of formate ($\theta = 0.5$ for species A, see Section III.B and Fig. 1 for definition of species A), as deduced from IRRAS measurements as a function of dosing time.

III. Calculations

A. Methods

Spin-polarized DFT+U calculations were performed within the Vienna ab initio simulation package (VASP),³⁰⁻³³ using periodic boundary conditions and a plane wave basis-set for stoichiometric and reduced TiO₂ (110) surfaces, with and without adsorbed HCOOH. For the reduced TiO₂ system, the Hubbard U parameter is often considered as an affordable way to capture the polaronic nature of the extra electrons in the reduced system.³⁴ Combined with the gradient generalized approximations (GGA) exchange-correlation functional in the version of Perdew, Burke and Ernzerhof (PBE),³⁵ the DFT+U method implementation of Dudarev *et al.*³⁶ was used. The value $U=4.2$ eV was applied; this value has been widely used for TiO₂ related system with oxygen vacancies.^{37, 38} The core-valence electrons interaction

was described by the projector augmented-wave (PAW) method,³⁹ and an energy cut-off of 500 eV for the basis-set expansion was used. One k-point (Γ) only, and a Γ -centred $2\times 2\times 1$ k-points grid, sampled with the Monkhorst-Pack method,⁴⁰ were used for structure relaxation and static energy calculations, respectively. The structures were relaxed until the residual force on each atom was $< 0.02 \text{ eV } \text{\AA}^{-1}$, and the total energy calculations were converged to $< 10^{-5} \text{ eV}$ per supercell. The dipole correction was adopted in the surface normal direction.⁴¹ We also calculated the transition energy barriers of some configurations transformation and estimated the reaction rates, by employing the Climbing-Image Nudged Elastic Band (CI-NEB) method⁴²⁻⁴⁴ as implemented in VASP. We used five images, and the force convergence criterion here was $0.1 \text{ eV } \text{\AA}^{-1}$.

B. Structural models

First, the geometry of bulk rutile TiO_2 was relaxed, giving the lattice parameters $a = 4.68 \text{ \AA}$, $c = 3.03 \text{ \AA}$, and the internal parameter $u = 0.3051$. The corresponding experimental values are $a = 4.5937$, $c = 2.9587$, $u = 0.3048$.⁴⁵ Then, for all the TiO_2 (110) surface structures a slab model was constructed consisting of a (4×2) supercell in the xy plane, and four O-Ti-O trilayers perpendicular to the z -direction $[110]$. The lattice vectors in the xy plane along the crystallographic $[001]$ and $[1\bar{1}0]$ directions were always fixed at 12.12 and 13.24 $\text{\AA}$, respectively, based on the optimized bulk structure. To prevent the interaction between virtually repeated images in the surface normal direction, the vacuum layers between the images was set to be at least 15 $\text{\AA}$ for all surface systems studied. Geometry relaxation was performed with the bottom O-Ti-O trilayer of the slab frozen, but all other atoms were free to move. The *stoichiometric* TiO_2 (110) surface is characterized by the two-fold coordinated O atoms (O_{2c}) forming ridge rows along the $[001]$ direction, and the in-plane five-fold coordinated Ti atoms (Ti_{5c}) forming troughs between the O-ridges. The thickness of the optimized clean stoichiometric TiO_2 (110) slab is 12.53 $\text{\AA}$. The *reduced* surface system was

modelled by removing an O_{2c} atom in the O-ridge row in the (4×2) supercell, thereby creating an O vacancy (O_{vac}). This structure was then reoptimized.

Here and for all systems with adsorbates, the HCOOH was adsorbed on one side of the stoichiometric or reduced surface slab, in the dissociated form, i.e. a $HCOO^-$ and a proton. Based on previous reports,^{6, 22} as well as our own IRRAS results presented below, different configurations of formate ion adsorption were considered and are schematically shown in Fig. 1. The proton always binds to the O_{2c} atom in the ridge to form surface hydroxyls. To follow the notation introduced by Hayden et al.,²² the bridging bidentate configuration for the $HCOO^-$ ion, with the two O-atoms on formate bonded to two neighbouring Ti_{5c} atoms in the Ti trough, is denoted species A. The bridging bidentate configuration with formate bonded to a Ti_{5c} atom in the trough and the second filling an O_{vac} site is denoted species B. Moreover, we introduce a monodentate configuration (species C), where the formate ion occupies an O_{vac} site and forms a hydrogen bond with an H atom bound to O_{2c} , as well as a monodentate configuration (species D) where the formate ion is bound to one Ti_{5c} atom and accepts a hydrogen bond from a protonated O_{2c} atom.¹¹ Species A and D do not involve O_{vac} sites and may thus be seen on the stoichiometric, oxidized and reduced surfaces (with not too many O_{vac} sites), while species B and C need O_{vac} sites, and are only expected to exist on a reduced surface – if at all.

Fig. 1. Schematic picture of possible formate (HCOO^-) structures on TiO_2 (110) surface, denoted species A, B, C and D. The B and C species bind to an oxygen vacancy, A and D do not. The crystal orientation and the directions of electromagnetic vectors as defined in the text are shown. The orientation of the incident IR beam with respect to the x -axis and projected onto the xy -plane is denoted by azimuthal angle ϕ , where $\phi = 0^\circ$ is defined to be in the $[1\bar{1}0]$ direction, and $\phi = 90^\circ$ in the $[001]$ direction.

C. Simulation of IRRAS spectra

1. Vibrational frequencies and polarizability tensors

First we performed DFT+U calculations for the systems described in section III.B to calculate the properties that will be used for the spectra model in the following section III.C.2. The harmonic vibrational frequencies and the normal mode eigenvectors of the adsorbate on

the rigid optimized TiO₂ surface were calculated using the finite difference method. Moreover, the Born effective charge tensor of each atom, which is the partial derivative of the macroscopic polarization with respect to atomic displacement at zero external electric field, was calculated by using the density functional perturbation theory (DFPT) inherent in the VASP program.^{46, 47} Local field effects, including both the Hartree potential and the exchange correlation potential, were considered.

The vibrational polarizability, α , was calculated following the formalism of Pedersen *et al.*⁴⁸ and Karhánek *et al.*⁴⁹ Thus the Born effective charge tensor $\mathbf{Z}$ was projected to an arbitrary direction $\hat{e}$ of the eigenvector of each normal mode $|\nu\rangle$, to obtain the charge vector of this selected normal mode,

$$Z_{e,\nu} = \hat{e} \cdot \mathbf{Z} |\nu\rangle, \quad (1)$$

where $\hat{e}$ is the unit direction vector in x , y , or z direction. The vibrational polarizability tensor of this normal mode then becomes

$$\alpha_{\nu,ij} = Z_{i,\nu} \omega_{\nu}^{-2} Z_{\nu,j}^T. \quad (2)$$

Here the subscript i, j represent the directions (x , y , or z), $\omega_{\nu} = 2\pi c\tilde{\nu}$ is the angular frequency of the normal mode, c is the speed of light, and $\tilde{\nu}$ is the wavenumber of the mode.

2. Three-layer model for IRRAS spectra simulation

The IRRAS spectra were simulated using a three-layer model assuming that the system is consisting of a vacuum layer, an adsorbate layer, and a semiconductor substrate layer. The vacuum and substrate layer are simply represented by dielectric constants, and the adsorbate

layer is represented as Lorentz oscillators,^{50, 51} in which polarizabilities are calculated from our atomic models as described above. The light is incident from the vacuum medium. Within this model the reflectance spectrum $\Delta R/R_0$ for the different components of the electromagnetic vector can be calculated according to eqns. 3 – 5, where $\Delta R=R_0-R_a$, and R_0 and R_a are the reflectivity without and with the adsorbate layer respectively, viz.

$$\left. \frac{\Delta R}{R_0} \right|_{E_{t,s}} = 2\pi\tilde{\nu} \frac{4\sqrt{\varepsilon_v} \cos \theta}{\varepsilon_v - \varepsilon_s} 4\pi N_s \text{Im}(\alpha_{t,s}), \quad (3)$$

$$\left. \frac{\Delta R}{R_0} \right|_{E_{t,p}} = 2\pi\tilde{\nu} \frac{4\sqrt{\varepsilon_v} \cos \theta \left(\frac{\varepsilon_v}{\varepsilon_s} \sin^2 \theta - 1 \right)}{(\varepsilon_v - \varepsilon_s) \left(\frac{\varepsilon_v + \varepsilon_s}{\varepsilon_s} \sin^2 \theta - 1 \right)} 4\pi N_s \text{Im}(\alpha_{t,p}), \quad (4)$$

$$\left. \frac{\Delta R}{R_0} \right|_{E_{n,p}} = 2\pi\tilde{\nu} \frac{4\varepsilon_v \varepsilon_s \sqrt{\varepsilon_v} \cos \theta \sin^2 \theta}{(\varepsilon_v - \varepsilon_s) \left(\frac{\varepsilon_v + \varepsilon_s}{\varepsilon_s} \sin^2 \theta - 1 \right)} \frac{4\pi N_s \text{Im}(\alpha_{n,p})}{|\varepsilon_a|^2}, \quad (5)$$

$$\left. \frac{R_a}{R_0} \right|_{E_s} = 1 - \left. \frac{\Delta R}{R_0} \right|_{E_{t,s}}, \quad (6)$$

$$\left. \frac{R_a}{R_0} \right|_{E_p} = 1 - \left. \frac{\Delta R}{R_0} \right|_{E_p} = 1 - \left(\left. \frac{\Delta R}{R_0} \right|_{E_{n,p}} + \left. \frac{\Delta R}{R_0} \right|_{E_{t,p}} \right). \quad (7)$$

here $E_{t,s}$ denotes an s-polarized E -field, which is always perpendicular to the incident plane and tangential to the substrate surface plane, E_p denotes the p-polarized E -field of light, which always is in the incident plane, thus $E_{t,p}$, and $E_{n,p}$ denote the components of a p-polarized E -field, being tangential and normal to the substrate surface, respectively. And $\tilde{\nu}$ is the wavenumber (cm^{-1}), θ is the angle of incidence (85° in our experiments), ε_s , ε_a and $\varepsilon_v=1$ are

the dielectric functions for the substrate, adsorbate and vacuum respectively, N_s is the number of adsorbate molecule per surface unit cell, and α is the polarizability of the adsorbate.

Implicit in this model is that the adsorbate polarizability can be anisotropic, but with principal components being along the x -, y - (or in-plane) and z -(or out-of-plane) directions (i.e. the dielectric tensor and polarizability tensor describing the adsorbate layer are diagonal). If the molecule is oriented so that the principal axes not corresponds to the in-plane or out-of-plane directions of the crystal, the contribution to s - and p -polarized light will be a combination of the projections of the contributions from the molecule principal axes on the x , y and z directions. When we apply the three-layer model to our experimental condition, a general result is that s -polarized light only gives rise to *emission* bands ($E_{t,s}$, $\Delta R/R_0 < 0$ or $R_a/R_0 > 1$, eqn. 3), while p -polarized light can gives rise to both *absorption* (in-plane, $E_{t,p}$, $\Delta R/R_0 > 0$ or $R_a/R_0 < 1$, eqn. 4) and *emission* bands (out-of-plane, $E_{n,p}$, $\Delta R/R_0 < 0$ or $R_a/R_0 > 1$, eqn. 5) depending on the direction of the E -vector, see Fig. 1. The total reflection spectra in IRRAS measurements with p -polarized light can therefore consist of either absorption or emission bands when the components are added (eqn. 7).

TiO₂ is a wide bandgap semiconductor, so ϵ_s is real in the infrared spectral range, and $\epsilon_s = n_s^2$. For a stoichiometric surface, we use $n_s = 2.4$, and for the reduced surface, $n_s = 1.9$ is used.^{52, 53} The wavenumber-dependent polarizability is calculated by summation of the electronic (α_e) and the vibrational (α_v) parts of all the normal modes, expressed as Lorentz oscillators, as follows:

$$\alpha(\tilde{\nu}) = \alpha_e(\tilde{\nu}) + \alpha_v(\tilde{\nu}) = \alpha_e + \sum_v \frac{\alpha_v \tilde{\nu}_v^2}{\tilde{\nu}_v^2 - \tilde{\nu}^2 - i\Gamma_v \tilde{\nu}}. \quad (8)$$

In eqns. 3 – 5, $\text{Im}(\alpha)$ for each component is only related to the diagonal component of the vibrational part, and it can be calculated if the line width, Γ_v , is known. We assume a uniform line width with a reasonable value ($\Gamma_v = 5 \text{ cm}^{-1}$), since the focus here is on the IR peak positions and their relative amplitude. Finally, ε_a , which is needed in eqn. 5 is also related to the electronic and vibrational parts of the polarizability, α_e and α_v , as follows:

$$\varepsilon(\tilde{\nu}) = 1 + 4\pi \frac{N_s}{d} \alpha(\tilde{\nu}) = 1 + 4\pi \frac{N_s}{d} \alpha_e + 4\pi \frac{N_s}{d} \alpha_v(\tilde{\nu}). \quad (9)$$

Note that in eqn. 5, only the z component of ε_a is needed.

In eqn. 9, the variable d can be expressed as $d = 4\pi N_s / C N_s^{3/2}$,⁵⁰ with the constant $C \approx 9.03$, since our surface model is close to a square cell.⁵⁴ From literature it can be found that α_e for formic acid and methyl formate is 3.32 and 5.05 Å³, respectively,⁵⁵ and it is assumed that α_e for the adsorbed formate are close to these values. We find that with values in this magnitude, α_e contributes very little to ε_a and can therefore be ignored. Thus eqn. 9 reduces to

$$\varepsilon(\tilde{\nu}) \approx 1 + 4\pi \frac{N_s}{d} \alpha_v(\tilde{\nu}). \quad (10)$$

From the above equations, the IRRAS spectrum for each adsorbate structure (A, B, C, and D) was calculated. From these spectra, the experimental spectra were then simulated by varying the concentration ratio of possible configurations of adsorbate species. It is also worth noting that, the perpendicular component ($E_{n,p}$) of the IRRAS spectra may be sometimes shifted in frequency relative to the parallel components ($E_{t,s}$ and $E_{t,p}$), a phenomenon which can be understood from the three-layer model: due to the frequency dependence of ε_a in eqn. 5.

V. Results

A. Polarization, angle and substrate dependence on IRRAS measurements

Before we go into IRRAS measurements, it is necessary to first consider the polarization, incident angle, and substrate dependence of the infrared reflection from the surface. According to eqn. 4 and 5, the sign of $\Delta R/R_0$, i.e. the adsorbate-induced change in reflectivity, for $E_{t,p}$ and $E_{n,p}$ may change if the angle of incidence, θ , or the refractive index of substrate, n_s , change. In our setup with $\theta=85^\circ$, $\Delta R/R_0$ for $E_{t,p}$ and $E_{n,p}$ can only change sign when the substrate refractive index is unphysically large $n_s > 11.43$ (the refractive index n_s is expected to be approximately 1.9 and 2.4 for reduced and stoichiometric TiO_2 surfaces, respectively^{52, 53}). This also implies that the critical angle of incidence for $\Delta R/R_0$ to change sign is $\theta = 62^\circ$ and $\theta = 67^\circ$, respectively, for these values of n_s , i.e. much smaller than the grazing angle used here. Thus in our experimental setup, $\Delta R/R_0$ for $E_{t,p}$ and $E_{n,p}$ is not expected to change sign due to changes of n_s regardless of surface preparation.

However, it is also important to note that a change in n_s (and thereby ϵ_s) will scale differently for $\Delta R/R_0$ for $E_{t,p}$ and $E_{n,p}$ (eqns. 4 and 5) and thus may affect the sign of $\Delta R/R_0$ for E_p (eqn. 7). This can easily be seen by using a simplified three-layer model. As before, vacuum is the incident medium and TiO_2 the non-absorbing substrate, but the adsorbate layer is in this simplified case described by a homogenous layer with an effective refractive index instead of Lorentz oscillators with calculated ϵ_a (by means of eqn. 10). With this simplification the reflectance spectrum for different light polarizations, angles of incidence and refractive indexes can readily be expressed analytically (Fig. 2).⁵⁶ This approach has e.g. been utilized by Xu et al. to qualitatively interpret IRRAS spectra for NO adsorbed on rutile TiO_2 (110).²⁴

Using reasonable values of the refractive index of formic acid,⁵⁷ it is evident from Fig. 2 that $\Delta R/R_0$ for E_p may change sign as a function of n_s by varying n_a only slightly. The corresponding results using the refractive index as obtained from the DFT+U calculations are shown in the inset of Fig. 2. We find that the optical properties of the adsorbate layer will dictate whether or not a change of sign for a particular vibrational mode with p-polarized light is to be seen on a reduced and fully stoichiometric TiO_2 substrate. In the measured reflectance spectra, for the different surface preparations, no change of sign is seen (vide infra), indicating that n_a is sufficiently small to prevent a change of sign of the IRRAS signal as n_s changes (going from a reduced to a stoichiometric surface).

Fig. 2. Calculations of the relative change of the reflectivity, R_a/R_0 , at a frequency $\tilde{\nu} = 1540 \text{ cm}^{-1}$ for s- and p-polarized light as a function of refractive index of the substrate, n_s , for two different values of the refractive index of an absorbing adsorbate layer, n_a . The adsorbate

later thickness was set to 1 nm in the calculations. The calculations were based on the results in Ref. ^{24, 56}. The inset shows the results using the refractive index $n_a = 1.56 + 0.63i$ for the $\nu_a(\text{OCO}) = 1503 \text{ cm}^{-1}$ bond frequency obtained from the DFT+U calculations.

B. Experimental IRRAS spectra on r-TiO₂(110) surface

Fig. 3a shows the measured IRRAS spectra of formate adsorbed on the r-TiO₂(110) surface using p-polarized light. An absorption band at 1534 cm^{-1} and an emission band at 1359 cm^{-1} can be seen for IR light incident in the [001] direction ($\phi = 90^\circ$). In addition, a weak emission band is present at 1388 cm^{-1} . In the $[1\bar{1}0]$ direction ($\phi = 0^\circ$) the reflectance spectrum looks different. A broad and weak absorption band is here seen in the 1575 cm^{-1} region, consisting of two absorption bands at ~ 1562 and $\sim 1582 \text{ cm}^{-1}$, and no absorption band at 1534 cm^{-1} . A distinct emission band appears at 1388 cm^{-1} , whereas the position and intensity of the emission band at $\sim 1360 \text{ cm}^{-1}$ remains approximately unchanged compared with the situation for the [001] direction.

Fig. 3. Experimental IRRAS spectra of formate adsorbed on r-TiO₂(110) with p-polarized (a) and s-polarized (b) light measured at $T = 273$ K for two different crystal orientations. Simulated IRRAS spectra with p-polarized (c, e) and s-polarized (d, f) light assuming the surface is covered by a mixture of species A and species B (c and d), or species A and species D (e and f). The value used for the ratio of the A and B coverages, or the A and D coverages, is 0.485:0.03 in both cases.

In Fig. 3b, the corresponding IRRAS spectra of HCOO/r-TiO₂(110) obtained with s-polarized light are shown. For $\phi = 0^\circ$, emission bands appear at 1534 cm⁻¹ and 1374 cm⁻¹. An additional weak emission band at ~ 1582 cm⁻¹ is also observed. For $\phi = 90^\circ$, an additional absorption band around 1262 cm⁻¹ (not marked) can be discerned. This absorption peak is not consistent with the models used in the present study (in particular, $R_a/R_0 < 1$, i.e. $\Delta R/R_0 > 0$, cannot be explained by the models employed here for s-polarized light, see section III.C). We believe that this absorption band is likely due to variations in the background caused by build up of contaminants in the optical path in the UHV chamber as the strength of this band appears randomly on different samples and increases over time.

C. Simulated IRRAS spectra

In this section, we show results of simulated IRRAS spectra using the procedure outlined in section III.C. First we will present calculated spectra for (HCOO⁻+H⁺)/TiO₂ for each of the species, A, B, C and D, and then we will present calculated spectra for mixture of adsorbed species and compare with the experimental spectra.

The simulated p- and s-polarized IRRAS spectra for the four dissociated configurations on the stoichiometric surface (for A and D), and on the partially reduced surface (for B and C), are shown in Fig. 4. It can be seen that the calculated IRRAS spectrum of species A exhibits the main features observed in the experimental spectra (Figs. 3a and 3b), although at slightly lower frequencies. The calculated spectra of species B and species D are similar to each other, but with a larger separation of the symmetric and asymmetric $\nu(\text{OCO})$ modes for species B than species D. Compared with the possible symmetric $\nu_s(\text{OCO})$ peak identified in the IRRAS experiments, the position of the calculated symmetric $\nu_s(\text{OCO})$ peak is shifted to a lower

wavenumber for species D and even lower for species B. The assignment and origin of the peaks and dips in the experimental spectra will be discussed in detail in section VI.B.

Fig. 4. Simulated p-polarized (left panel), and s-polarized (right panel) IRRAS spectra of species A (a, b), species B (c, d), species C (e, f), and species D (g, h) for $\phi = 0^\circ$ and $\phi = 90^\circ$.

In Figs. 3c-3f the corresponding simulated spectra are shown for a surface covered with a mixture of A and B, or A and D species. We find that the best agreement with the experimental spectra is obtained if the surface coverage of species A was adjusted to $\theta = 0.485$ with the B or D species occupying the remaining sites, i.e. $\theta = 0.03$ (since they occupy only one Ti_{5c} site each, see Fig. 1), for a surface fully covered by formic acid.

D. Comparison of experimental IRRAS spectra on r-, s-, and o-TiO₂(110) surfaces

Experimental IRRAS spectra of formic acid adsorbed on oxidized, stoichiometric and reduced TiO₂ (110) surfaces are shown in Fig. 5 and Fig. 6 for $\phi = 0^\circ$ and $\phi = 90^\circ$, respectively. With p-polarized light the spectra appear almost identical for the three different surface preparations, with emission peaks at 1361 and $\sim 1388 \text{ cm}^{-1}$ and absorption bands at 1374, 1534, ~ 1562 and $\sim 1582 \text{ cm}^{-1}$. For s-polarized light all three surface preparations exhibit two strong emission peaks at 1374 and 1534 cm^{-1} and a weak emission peak at $\sim 1582 \text{ cm}^{-1}$. For $\phi = 90^\circ$ no clear emission bands are seen, and mainly background noise in the measurement is evident.

Fig. 5. Experimental IRRAS spectra of formic acid adsorbed on oxidized, stoichiometric and reduced TiO_2 (110) with p-polarized (a) and s-polarized (b) light with $\phi = 0^\circ$. Formic acid was adsorbed at $T = 273$ K.

Fig. 6. Experimental IRRAS spectra of formic acid adsorbed on oxidized, stoichiometric and reduced TiO_2 (110) with p-polarized (a) and s-polarized (b) light with $\phi = 90^\circ$. Formic acid was adsorbed at $T = 273$ K.

E. Energy calculations of adsorbed species

The binding energies obtained from the DFT+U calculations for the different formate configurations depicted in Fig. 1 were calculated from eqn. 11, viz.

$$E_{bind} = E_{tot}(\text{HCOOH+slab}) - E_{tot}(\text{HCOOH}) - E_{tot}(\text{slab}). \quad (11)$$

When all these systems were geometry optimized. The calculated binding energies of the geometry optimized structures are shown in Table I. As mentioned in section III.B, a stoichiometric surface slab model was used for species A and D. For species B and C, a reduced surface with a surface O_{vac} in the (4×2) supercell was used. The binding energies are also affected by the precise location of the detached H atom formed in the HCOOH adsorption process ($\text{HCOOH} \rightarrow \text{HCOO} + \text{H}$). According to our calculations, the energy varies by about 0.3 eV depending on the hydrogen position. For instance, for species B, we find that when the dissociated H atom is far away from the formate ion, i.e. not on the same bridging oxygen row as the O vacancy, the binding energy is lowered from -1.85 to -2.16 eV (a situation which may be difficult to realize experimentally). In contrast, for species C and D, the H atom is by construction always near so that the formate ion can form a hydrogen bond with the adsorbed H atom. Overall the binding energies of species B and C, which both requires oxygen vacancies, are close to the species A, while species D is the least stable species ($E_{bind} = -1.31$ eV) of the investigated adsorbate structures according to our calculations.

To investigate the kinetic barrier for transformation of species D to species A, the CI-NEB method was employed. The calculated transition energy barrier from species D to species A on stoichiometric surface by rotating the formate ion with the O-Ti bond is found to be 0.38eV. The corresponding reaction rate constant resulting from this barrier at 273 K will be discussed later. We have here assumed that the H atoms are near the formate ion. For comparison, the binding energies for species A and D on a partially reduced surface (a missing bridge oxygen atom in the supercell) were also calculated, the binding energies here

are around -1.75 and -1.23 eV respectively, thus these species are less stable on the reduced surface.

Table I. Calculated binding energy, E_{bind} , for different configurations of formate adsorbed on the TiO_2 (110) surface with the H located nearby. Species B and C correspond to surfaces with one O vacancy in the supercell. See Fig. 1 for adsorption geometry.

	Species A	Species B	Species C	Species D
$E_{bind}(\text{eV})$	-1.84	-1.85	-1.87	-1.31

VI. Discussion

A. Coupling between incident light and adsorbate structure

Fig. 1 depicts schematically the proposed formate structures on the TiO_2 (110) surface. The p-polarized light has two components of the electric vector (E -vector): one normal ($E_{n,p}$) and one tangential ($E_{t,p}$) component, which both lie in the plane of incidence of the light. In contrast, s-polarized light has only one tangential component ($E_{t,s}$), which is perpendicular to the plane of incidence of the light. These E -vectors couple differently to the vibrational modes of the formate species depending on the incident azimuthal angle (ϕ) of the light.

It is evident that for species A, the asymmetric $\nu_a(\text{OCO})$ mode only couples to $E_{t,p}$ when $\phi = 90^\circ$.²² For $\phi = 0^\circ$ the $\nu_a(\text{OCO})$ mode of A is silent under p-polarized light. Conversely, the symmetric $\nu_s(\text{OCO})$ mode due to species A couples to $E_{n,p}$ independently of ϕ . This is due to the C_{2v} symmetry of species A. The in-plane $\delta(\text{CH})$ mode of species A is associated with a small variation of the dipole moment in the surface normal direction [110], while the variation is very large in the [001] direction. This mode is thus predicted to couple weakly to $E_{n,p}$ for all ϕ , to appear as an absorption band (coupled to $E_{t,p}$) in the IRRAS spectra for p-polarized light

with $\phi = 90^\circ$ (eqn. 4), and as an emission band in the IRRAS spectra with $\phi = 0^\circ$ of s-polarized light (eqn. 3). The corresponding simulated spectra are shown in Figs. 4a and 4b. The weaker signal of the $\delta(\text{CH})$ mode than for $\nu(\text{OCO})$ modes is due to its smaller polarizability.

Since species B binds to an O_{vac} site, it is aligned with the molecular plane perpendicular to the [001] direction and the orientation of the molecule is slightly tilted with respect to the surface normal and therefore the C_{2v} symmetry is broken, and reduced to C_s symmetry. Thus the dipole moment for the $\nu_s(\text{OCO})$ mode is aligned slightly tilted from the surface normal, and it should therefore couple to $E_{n,p}$ for all ϕ . The $\nu_s(\text{OCO})$ mode should thus also couple to both the $E_{t,p}$ component of p-polarized light at $\phi = 0^\circ$, and $E_{t,s}$ of s-polarized light at $\phi = 90^\circ$. Similarly, $\nu_a(\text{OCO})$ and in-plane $\delta(\text{CH})$ should in principle also couple to both the $E_{n,p}$ and $E_{t,p}$ components of the E_p -field as well as $E_{t,s}$. These characteristics are shown in the simulated spectra in Figs. 4c and 4d.

As for species C, the formate ion orients also in [001] direction like species A. But the strong asymmetric geometry makes the symmetric and asymmetric $\nu(\text{OCO})$ vibrations more close to the vibrations of C-O single bond and C=O double bond. It thus gives largest symmetric and asymmetric (OCO) frequency separation between these species. The C-O single bond occupying the O_{vac} site is almost perpendicular to the surface, the $E_{n,p}$ light couples to it independent of ϕ . The $E_{n,p}$ also couples to the C=O vibration at any ϕ , while $E_{t,p}$ couples to it at $\phi = 90^\circ$, and $E_{t,s}$ couples to it at $\phi = 0^\circ$. The simulated spectra (Figs. 4e and 4f) are far away from the characteristic bands found in the experimental spectra, and the existence of species C on the TiO_2 (110) surface may thus be excluded.

Species D has the same orientation as species B, and by the same arguments, the symmetric and asymmetric (OCO), and in-plane $\delta(\text{CH})$ vibrations couple to $E_{n,p}$ at any ϕ , and couple to $E_{t,p}$ at $\phi = 0^\circ$, and to $E_{t,s}$ at $\phi = 90^\circ$. The simulated spectra of D thus show similar

characteristics as species B (Figs. 4c, 4d, and 4g, 4h). Properties of species B and D will be discussed further in the following section.

B. Assignment of vibrational modes and surface species

1. Experimental and calculated vibrational frequencies and vibrational mode assignments

The experimental measured vibrational frequencies and the possible mode assignments, together with the theoretical calculated vibrational frequencies of each species are presented in Table II. The calculated frequencies are generally lower than the experimental ones.

Table II. Vibrational frequencies and mode assignments of formate adsorbed on TiO₂ (110). Both the measured experimental values and the calculated values for species A, B, C and D are given. All values are given in units of cm⁻¹. The possible polarization direction for each species are also indicated in parenthesis in x-, y-, or z-direction after wavenumbers following the scheme of Fig. 1.

Experimental	Calculated				Mode assignment
	Species A	Species B	Species C	Species D	
1359	1344 (z)	1258 (x,z)	1203 (y,z)	1303 (x,z)	$\nu_s(\text{OCO})$
1374	1359 (y,z)	1364 (x,z)	1348 (y,z)	1352 (x,z)	$\delta(\text{C-H})$ ($E_{t,p}$)
1388					($E_{n,p}$)
1534	1503 (y)		1656 (y,z)		$\nu_a(\text{OCO})$
1562		1562 (x,z)		1536 (x,z)	$\nu_a(\text{OCO})$

2. Assignment of IR bands at 1359 and 1534 cm⁻¹

The results presented in Fig. 3a for p-polarized light and in Fig. 3b for s-polarized light can be explained by our theoretical calculations. The bands at 1534 cm⁻¹ and 1359 cm⁻¹ at $\phi = 90^\circ$ (Fig. 3a) correspond to the $\nu_a(\text{OCO})$ and $\nu_s(\text{OCO})$ mode for species A, which appears at 1503 cm⁻¹ and 1344 cm⁻¹ in the calculated spectra of species A (Fig. 4a). Furthermore,

according to eqn. 3 and eqn. 6, s-polarized light only gives rise to emission bands, and the $E_{t,s}$ -vector should couple with the $\nu_a(\text{OCO})$ mode in species A (1503 cm^{-1}) only when $\phi = 0^\circ$, (Fig. 4b). This agrees well with the experimental results, where the $\nu_a(\text{OCO})$ mode in species A (1534 cm^{-1}) for s-polarized light incident is only seen in the $[1\bar{1}0]$ direction ($\phi = 0^\circ$, Fig. 3b). The very good agreement between of the calculated spectra of species A and the measured IRRAS spectra shows that the majority species on the surface is species A.

3. Assignment of IR bands at 1374 and 1388 cm^{-1}

The emission band at 1374 cm^{-1} in Fig. 3b, which is seen for s-polarized light at $\phi = 0^\circ$, can be attributed to the $\delta(\text{C-H})$ in-plane wagging for species A in agreement with the simulations, where it is seen as a weak peak at 1359 cm^{-1} (Fig. 4b). Rotating the crystal to $\phi = 90^\circ$ quenches the 1374 cm^{-1} band completely. Further support for the assignment of this band can be found by a closer examination of the IRRAS spectra for p-polarized light which also reveals a dip around 1374 cm^{-1} in the measurement (Fig. 3a), and at 1359 cm^{-1} for the simulation (Fig. 4a). For p-polarized light this dip is only seen for $\phi = 90^\circ$ and thus correlates well with coupling of $E_{t,p}$ with the in-plane $\delta(\text{C-H})$ mode in species A.

Considering just the coupling to the surface, the perpendicular component of a vibration mode will be shifted to higher wavenumbers compared to components aligned parallel to the surface.²² Thus the weak emission band at 1388 cm^{-1} seen for p-polarized light (see Fig. 3a) may be assigned to $\delta(\text{C-H})$ in species A coupled to $E_{n,p}$. The lower intensity for $\phi = 90^\circ$ compared to $\phi = 0^\circ$ in Fig. 3a is explained by the overlap with the same vibrational mode coupled to $E_{t,p}$, which gives rise to the absorption peak at 1374 cm^{-1} and hence suppresses the 1388 cm^{-1} emission band. The band at 1388 cm^{-1} is not seen in the simulated spectra. We attributed this to the model, which is unable to resolve the shift between the perpendicular and parallel components of the vibrational mode. The term ε_a in eqn. 5, which is frequency

dependent, may give rise to the shift of the $\Delta R/R_0$ for $E_{t,p}$ and $E_{n,p}$ components in the model. However, with the parameter setup used here, the shift is negligible in our simulations, and hence it is not resolved.

4. Assignment of experimental signals at 1562 and 1582 cm⁻¹

Inspection of the broad absorption band in the 1560 – 1590 cm⁻¹ region for $\phi = 0^\circ$ of p-polarized light (Fig. 3a) reveals that the band consists of two weak absorption peaks, one at ~1582 cm⁻¹ and one at ~1562 cm⁻¹. The mode at ~1582 cm⁻¹ is attributed to hydrogen bonded formate ions (outer-sphere complexes) present on the surface, guided by previous reports.^{16, 50} The band at ~1562 cm⁻¹ is due to the $\nu_a(\text{OCO})$ mode of the minority species. Within the three-layer model, coupling to the $E_{n,p}$ component yields only $\Delta R/R_0 < 0$ ($R_a/R_0 > 1$, emission bands), see eqn. 5. Geometrical considerations exclude that it is due to species A. Therefore coupling of $E_{t,p}$ to species perpendicular to A must be included to account for the absorption band seen at ~1562 cm⁻¹ with p-polarized light for $\phi = 0^\circ$ (Fig. 3a).

The geometry with a tilted molecular axis with respect to the surface normal for these minority species (Fig. 1) implies that the $\nu_a(\text{OCO})$ modes should couple to both $E_{n,p}$ and $E_{t,p}$ components of the incident E -field for p-polarized light. No emission bands due to the $E_{n,p}$ components is however seen in Fig 3a. This may be due to the weak coupling to the $E_{n,p}$ component and the low coverage of the minority species, seen as the weak signal of the $\nu_a(\text{OCO})$ mode coupled to the $E_{t,p}$ component. The calculated frequencies for the $\nu_a(\text{OCO})$ mode for the different configurations show that species B (1562 cm⁻¹) and D (1536 cm⁻¹) have an absorption band in this region, whereas species C (1656 cm⁻¹) has a transmission band at much higher wavenumbers (Figs. 4c, 4e and 4g). Thus the band at 1562 cm⁻¹ in Fig. 3a is due to the $\nu_a(\text{OCO})$ mode of either species B or species D.

Since species B occupies an O_{vac} site and if we assign the 1562 cm^{-1} absorption band to $\nu_a(\text{OCO})$ mode of species B, one would expect it to be more prominent on the r-TiO₂ surface than on the s-TiO₂ or o-TiO₂ surfaces. This is, however, not observed in our experiments, where we see no clear and systematic differences in the IRRAS spectra for different surface preparations (Figs. 5 and 6).

Based on the DFT+U calculations, the weighted simulated spectra consisting of either A and B species, or A and D species, show very similar spectral characteristics (Figs. 3c-3f). The existence of species D does, however, not require O_{vac} sites, so it could for that reason be expected to exist on all the three surfaces. The assignment of the 1562 cm^{-1} band to the $\nu_a(\text{OCO})$ mode of species D is thus more consistent with the experimental results (Fig. 5). However, the binding energy for species D is much higher than the other species (Table I), and it is reasonable to assume that species D will transform into species A if there are unoccupied neighbouring Ti_{5c} sites available. However, as the DFT+U calculations show, the energy barrier for a transition from species D to species A is $E_a = 0.38\text{ eV}$. Applying the Arrhenius equation $k = A \exp(-E_a / k_B T)$ with $T = 273\text{ K}$ and assuming a pre-exponential factor $A = 10^{13}\text{ s}^{-1}$, gives $k = 0.96 \times 10^6\text{ s}^{-1}$. Since the surface coverage is of the order $10^{14}\text{ molecules cm}^{-2}$, this corresponds to a conversion rate $<0.004\%$ of the full surface coverage per hour (about 0.1% of the estimated coverage of species D per hour). Formate molecules bonded as D species are thus kinetically hindered to transform into A species under our experimental conditions, and will remain as D species in the duration of the complete measurement times employed here (and most likely also in the experiments reported by Hayden et al.²²). The intensity of the 1562 cm^{-1} band is weak regardless of surface preparation, and shows that concentration of species D is very small (estimated to be $\theta = 0.03$ in the simulations, about three times lower than the maximum O_{vac} coverage ($\theta \approx 0.1$) on r-TiO₂ reported in previous studies⁶). Due to the weak signal in the measurements with s-polarized

light (Fig. 3b), no unambiguous identification of this emission band with $E_{t,s}$ can be made, although we can infer that it should couple to $E_{t,s}$ for species B, or species D when $\phi = 90^\circ$ (Fig. 4d and Fig. 4h). The absence of any mode for $\phi = 90^\circ$ with s-polarized light (Fig. 3b and Fig. 6b) further confirms that the concentration of B or D species must be small compared to the majority species A.

We therefore re-interpret the weak band appearing around 1562 cm^{-1} in p-polarized light $\phi = 0^\circ$ IRRAS spectra (Fig. 3a and Fig. 5) as being due to species D on s-TiO₂ and o-TiO₂ surfaces, i.e. a formate ion adsorbed in a monodentate fashion on one Ti_{5c} ion and forming a hydrogen bond with an OH defect on the surface with the molecular plane oriented perpendicular to the [001] direction (Fig. 1). By the same reasoning we predict that the D species will disappear at elevated temperatures, and the surface chemistry is dominated by reactions with Ti_{5c} sites.

C. Hydroxylation of O vacancies

For r-TiO₂ surface, the existence of species B cannot be excluded, since the coverage of the minority species is low and prevents unambiguous detection of the complementary modes in the $1200\text{ to }1300\text{ cm}^{-1}$ region. The presence of O_{vac} sites on reduced TiO₂ have been observed with STM by different research groups.⁷ These STM experiments are generally performed with a base pressure in the 10^{-11} mbar range, whereas in the present study the base pressure is in the 10^{-10} mbar range. A surface with oxygen vacancies corresponding to 5% of a monolayer will have the O_{vac} sites fully hydroxylated within a few minutes at pressures of about 2×10^{-10} Torr due to the near unity sticking coefficient of water according to Wendt et al.⁶ With the time scale of our experiments, which includes the time needed to cool down the sample to 273 K, and the time needed to acquire a background spectrum measurement (~ 7 min.), we expect the oxygen vacancies to be fully hydroxylated when formic acid is adsorbed

on the surface. Furthermore, the introduction of formic acid from a liquid reservoir will introduce additional water to the system both via the liquid formic acid reservoir that is kept at higher pressures, and via desorption from the chamber walls when the formic acid is dosed. This will further accelerate the hydroxylation of the sample. Although the measurement time was shorter in the study by Hayden and Newton (3.5 min.),²² it is reasonable to assume that their surface also is fully hydroxylated considering the dosing of formic acid, and the time needed to cool down the sample to 300 K after annealing, and employing a UHV chamber with a base pressure of 4×10^{-10} Torr.⁵⁸ In general, the rapid healing of oxygen vacancies would favour adsorbate structures similar to species D (i.e. species interacting with protonated O_{2c} atoms) also for other adsorption systems on the well-studied r-TiO₂(110) surface, and therefore necessitates a re-interpretation of reported surface reactions of TiO₂ (110). In Fig. 5 it can be seen that the absorption band at 1582 cm^{-1} is largest on the r-TiO₂ surface. As discussed above, this band is attributed to the asymmetric mode in hydrogen bonded formate ions. The fact that the intensity of this band is strong for the r-TiO₂ surface compared to the other surfaces implies that there are more OH groups, i.e. hydroxylated oxygen vacancies, on this surface. This is in line with the surface preparation method employed for the r-TiO₂ surface, which, by the reasoning here, produces more oxygen vacancies which rapidly becomes hydroxylated. This can thus be seen as an indirect confirmation of the rapid healing of oxygen vacancies by OH groups at high UHV pressures seen in STM studies.⁶ It is thus important to be aware of the experimental conditions (surface preparation time, partial pressure of water in the chamber, gas dosing conditions, etc.) if adsorption and photo-reactions of adsorbates on surface with O_{vac} sites are to be studied.

VII. Conclusions

IRRAS measurements were conducted for formic acid adsorption on differently prepared rutile TiO_2 (110) surfaces with s- and p-polarized light incident in two different azimuthal crystal directions ($[001]$ and $[1\bar{1}0]$). This was paired with extensive DFT+U calculations employing four different bonding structures of the formate ion coordinated to the TiO_2 surface, denoted species A, B, C and D. The DFT+U calculations show that the binding energy of the two formate bonding configurations, which require an O vacancy site (species B and C) is similar to that of the bridging bidentate configuration, where the formate O atoms bind to two neighbouring Ti_{5c} atoms (species A). The least stable of the computed configurations is a formate bonded to one Ti_{5c} atom and to a protonated O_{2c} atom. The DFT+U calculations show, however, that the energy barrier for transition from species D to species A is relative high at 273 K, 0.38 eV. This implies that that formate molecules adsorbed in the D configuration are kinetically hindered to transform into species A during the experiments.

From the DFT+U calculations, simulated IRRAS spectra were constructed for both p- and s-polarized light for each of the different configurations. From these combined results it can be inferred that two different species exist on the surface. The most abundant is species A, in agreement with previous studies. This species has its asymmetric and symmetric $\nu(\text{OCO})$ vibrations at 1534 and 1359 cm^{-1} , respectively. The in-plane $\delta(\text{C-H})$ wagging mode is observed at 1374 cm^{-1} for both s-polarized and p-polarized light. The second species seen in the experimental IRRAS spectra is characterized by an asymmetric $\nu(\text{OCO})$ stretching mode, which appear as a weak band at $\sim 1562\text{ cm}^{-1}$, and is assigned to formate coordinated to a proton sitting on an O_{2c} atom, i.e. a hydroxylated O vacancy site (species D). This assignment is based on IRRAS results obtained on surfaces prepared with different concentrations of O vacancies (reduced, stoichiometric and oxidized TiO_2 (110)), which show similar spectra regardless of surface preparation. We explain this by rapid hydroxylation of O vacancy sites

during sample preparation, even under UHV conditions, in good agreement with recent STM results. Our results suggest that low-coordinated Ti_{5c} sites, and protonated low-coordinate surface O_{2c} atoms are important for the reactivity of TiO_2 (110), and should, in addition to O_{vac} sites be considered in modelling of surface reactions on TiO_2 (110). These results necessitate a re-interpretation of active sites and the role of O vacancies for the reactivity of TiO_2 in many technical applications. From an applied viewpoint we argue that the protonated surfaces are more realistic model systems when the surface temperature is not high enough to desorb all water.

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(110) surface

Light direction
 $\phi=0^\circ$

B

Light direction
 $\phi=90^\circ$

A

D

C

a)

Expt: r-, s-, o-TiO₂, p-pol, $\phi=0^\circ$

b)

Expt: r-, s-, o-TiO₂, s-pol, $\phi=0^\circ$

a)

Expt: r-, s-, o-TiO₂, p-pol, $\phi=90^\circ$

b)

Expt: r-, s-, o-TiO₂, s-pol, $\phi=90^\circ$