Infrared Absorption Study of a Dihydrogen Complex in Anatase TiO₂

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An infrared absorption study of natural anatase TiO₂ is performed. A complex with absorption lines at 3355.9 and 3357.3 cm⁻¹ is shown to consist of at least two equivalent hydrogen atoms, whereby these features are due to the stretch local vibrational modes of two O–H bonds located in the basal plane of the anatase crystal, forming an angle of approximately 90°. The complex is shown to be electrically active with a level in the upper part of the bandgap. The microscopic model of the defect is discussed.

1. Introduction

Since the discovery of the photocatalytic splitting of water on titanium dioxide (TiO₂) electrodes, this wide-bandgap semiconductor has become an object of both technological and fundamental interests.\[1\] TiO₂ or titania occurs in three crystalline modifications: rutile, anatase, and brookite of which anatase is the material of technological choice due to a longer carrier lifetime,\[2\] exciton diffusion length,\[3\] and higher electron mobility.\[4\] More importantly, anatase reveals photocatalytic activity which is an order of magnitude higher than that of rutile.\[5\] To manufacture efficient photocatalytic devices, TiO₂ should respond to visible light. However, due to the wide bandgap of 3.2 eV anatase can harvest only a small fraction of the solar energy. Engineering of “black” hydrogenated anatase with a narrow bandgap of 1.54 eV is a step forward toward manufacturing hydrogen cells of practical importance.\[7\]

Hydrogen is an omnipresent impurity in many solids and particularly in oxides which strongly affects the electronic and structural properties of these materials.\[8\] Interstitial hydrogen can act either as an amphoteric impurity, giving rise to deep gap levels with positive, neutral, and negative charge states, or it can form a shallow level at the conduction band edge and act as a donor.\[9–11\]

Theory predicts interstitial hydrogen in anatase to form a hydroxyl ion with the direction of the O–H bond pointing nearly along the a(h) axis.\[12\] The hydrogen impurity level is located above the conduction band minimum, implying that it acts as a shallow donor.\[13\] Hydrogen substituting for oxygen in the regular anatase lattice was also found to have a shallow donor level in the bandgap.\[13\]

However, numerous experimental studies on hydrogen in bulk rutile are reported,\[14–16\] in anatase, they deal mostly with nanosized material.\[17,18\] Recently, hydrogen-related defects in natural bulk crystals were probed by means of infrared (IR) absorption.\[19,20\] A group of lines was observed in as-received material and assigned to the stretch local vibrational modes (LVMs) of the hydroxyl groups, two of which at 3412 and 3417 cm⁻¹ were tentatively associated with different charge states of a hydrogen-related shallow donor.\[28\] More recently, a dominant hydrogen-related defect in natural anatase resulting in an LVM with a frequency of 3389 cm⁻¹ was probed by means of stress-induced dichroism.\[21\] It was shown that the energy barrier separating two adjacent equivalent in-plane sites of hydrogen equals 0.74 ± 0.02 eV.

Herein, we report the results of a follow-up IR absorption study of hydrogen-related complexes in anatase. Our investigation reveals that a defect responsible for IR absorption lines at 3355.9 and 3357.3 cm⁻¹ consists of two equivalent O–H bonds. We will show that this complex is electrically active with a level in the upper part of the bandgap.

2. Results

2.1. General Properties of the IR Lines

Figure 1 shows sections of IR absorption spectra obtained at 10 K for a c-plane cut natural anatase TiO₂ sample. The as-received material (spectrum a) reveals inter alia IR absorption lines at around 3358 cm⁻¹ marked by an asterisk. Earlier, they were shown to originate from stretch LVMs of some not yet identified hydrogen-related defect(s).\[19,20\] The treatment in H₂ at 450 °C (spectrum b) enhances their intensity and results in the appearance of additional peaks at 3355.9 and 3357.3 cm⁻¹ which are the topics of this study. In the following sections, strong evidences will be given that the defect responsible for these lines consists of two equivalent hydrogen atoms. We label it as XH₂.

Further annealing in air at 450 °C and subsequent treatment in D₂ at the same temperature (spectrum c) reduce the intensities of the hydrogen-related features and give rise to absorption...
lines at around 2490 cm\(^{-1}\). The frequency ratio between the two
groups of lines corresponds to the value expected for a
harmonic oscillator, consisting of a hydrogen bound to oxygen
\(\mu_D/\mu_H \approx 1.37\), where \(\mu_H\) and \(\mu_D\) are reduced masses of the
\(^{16}\text{O} \cdot \text{H}\) and \(^{16}\text{O} \cdot \text{D}\) units, respectively. Based on this we assign
the IR absorption lines shown in Figure 1 to stretch the LVMs of
hydrogen bound to oxygen.

Depending on the experimental conditions anatase transforms
into rutile after thermal treatment at temperatures above
600 °C.\(^{22}\) This prevented us from annealing our samples at ele-
vated temperatures and resulted in the presence of residual hydro-
gen after each step of thermal treatment and/or hydrogenation.

Importantly, the treatment with deuterium gives rise to an
additional line in the hydrogen-related part of the spectrum
marked by a star. This implies that the hydrogen-related
LVMs of the defect appearing as a result of hydrogenation are
affected by the nearby deuterium and should therefore include
more than one hydrogen atom.

Finally, the sample was annealed at 450 °C in air and treated in
a mixture of \(\text{H}_2\) and \(\text{D}_2\) at the same temperature (spectrum d). Such a treatment does not result in the appearance of new
features but rather in a redistribution of their relative intensities.

To gain a better insight into the vibrational mode frequencies
of all isotope configurations of \(\text{XH}_2\) the spectra shown in Figure 1 are “cross-subtracted”. First, the spectrum (a) of a virgin sample
was used as a reference to get undisturbed absorption lines due
to \(\text{XH}_2\) from spectrum (b). The result of this subtraction was fur-
ther used to generate the hydrogen-related part of the absorption
spectrum due to XHD. Such a step-wise procedure was repeated
until the “pure” spectra of \(\text{XH}_2\), \(\text{XD}_2\), and XHD were generated. The result is shown in Figure 2. Table 1 shows the LVM frequencies of all isotope configurations of \(\text{XH}_2\).

As shown in Figure 2 and Table 1, the XHD complex reveals
only two LVMs positioned nearly exactly in between those result-
ning from \(\text{XH}_2\) and \(\text{XD}_2\). This implies that within the accuracy of
our measurements XHD and XDH do not differ, which leads us
to the conclusion that both hydrogen atoms comprising the
defect occupy equivalent lattice sites.

2.2. Vibrational Hamiltonian

Based on these results, we can build the vibrational Hamiltonian
of \(\text{XH}_2\) and deduce microscopic parameters of the defect. We use
the valence force approximation and neglect the influence of

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**Figure 1.** Sections of IR absorption spectra obtained at 10 K for a c-plane cut natural anatase sample: a) virgin material; b) directly after thermal treatment in \(\text{H}_2\) gas at 450 °C; c) after annealing at 450 °C in air and subsequent treatment in \(\text{D}_2\) gas at 450 °C; and d) after annealing at 450 °C in air and subsequent treatment in \(\text{H}_2 + \text{D}_2\) gas at 450 °C. Spectra are vertically offset for clarity. A line marked by a star is due to the XHD complex (see text). Absorption lines marked by an asterisk are not related to the defect discussed here.

**Figure 2.** Sections of IR absorption spectra obtained as a result of “cross subtraction” between those shown in Figure 1. The spectra would correspond to pure \(\text{XH}_2\) (bottom), \(\text{XD}_2\) (mid), and XHD (top) complexes. Spectra are vertically offset for clarity.

**Table 1.** Frequencies of IR absorption lines and their full widths at half maximum (cm\(^{-1}\)) due to LVMs of different isotope configurations of \(\text{XH}_2\) versus those calculated from Equation (1). The “best-fit” parameters given in the lower part of the table.

| Isotope config. | \(\omega_{\text{exp}}\) | \(\Delta\omega\) | \(\omega_{\text{calc}}\) |
|-----------------|-----------------|---------------|-----------------|
| \(\text{XH}_2\)  | 3357.3          | 0.6           | 3357.3          |
|                 | 3335.9          | 0.5           | 3355.9          |
| \(\text{XD}_2\)  | 2490.6          | 0.3           | 2490.6          |
|                 | 2489.6          | 0.3           | 2489.5          |
| XHD            | 3356.6          | 1.1           | 3356.6          |
|                 | 2490.0          | 0.4           | 2490.1          |

\(D = 3.33 \text{ eV}\) \(a = 2.51 \text{ Å}^{-1}\) \(f = 18 \text{ meV Å}^{-2}\) \(\chi = 0.95\)

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bend modes. With a harmonic coupling term, f, the model Hamiltonian is
\[
\hat{H} = -\frac{\hbar^2}{2\mu_1} \frac{d^2}{dr_1^2} - \frac{\hbar^2}{2\mu_2} \frac{d^2}{dr_2^2} + V(r_1) + V(r_2) + f r_1 r_2
\]  (1)
where \(r_i\) are the O–H (O–D) bond extensions, \(V(\vec{r})\) is the potential energy, \(\mu_i^{-1} = M_i^{-1} + (x M_0)^{-1}\) are the reduced masses of the hydrogen isotopes bound to \(^{16}\)O, and \(x\) is the factor which accounts for the coupling to the lattice.

In the following consideration, we fit our results to the Morse potential
\[
V(r) = D(e^{-ar} - 1)^2
\]  (2)
which leads to the harmonic Hamiltonian
\[
\hat{H}_0 = -\frac{\hbar^2}{2\mu_1} \frac{d^2}{dr_1^2} - \frac{\hbar^2}{2\mu_2} \frac{d^2}{dr_2^2} + D\alpha^2 (r_1^2 + r_2^2) + f r_1 r_2
\]  (3)
and the cubic and quadratic contributions to the potential energy
\[
V_3 = -D\alpha^2 (r_1^2 + r_2^2), \quad V_4 = \frac{7}{12} D\alpha^4 (r_1^2 + r_2^2)^2
\]  (4)

The vibrational modes of the harmonic Hamiltonian (3) can be found from the secular equation
\[
||\mathbf{GF} - \omega^2 I|| = 0
\]  (5)
where \(I\) is 2×2 identity matrix, and
\[
\mathbf{G} = \begin{pmatrix} \mu_1^{-1} & 0 \\ 0 & \mu_2^{-1} \end{pmatrix}, \quad \mathbf{F} = \begin{pmatrix} 2D\alpha^2 & f \\ f & 2D\alpha^2 \end{pmatrix}
\]  (6)

To account for anharmonicity effects, the cubic and quadratic terms (4) were applied then to the well-known wave-functions of the harmonic oscillator.

Thus, we have four parameters \(D, a, x,\) and \(f\) to fit the six LVMs of XH₂, XD₂, and XHD complexes. The best fit values are shown in Table 1, together with the observed and calculated frequencies. As shown, the model represents a reasonably good fit of the experimental data within 0.1 cm⁻¹.

### 2.3. Microscopic Model

Figure 3 shows the likely orientations of the two O–H bonds comprising the XH₂ complex. Here, the O atoms are assumed to occupy the regular lattice sites, whereas the unidentified X species is positioned at the Ti site. We speculate that an impurity atom substituting for Ti or the Ti vacancy is a likely candidate for the unknown constituent of the XH₂ complex. The pairs of the O–H bonds with odd and even numbers (12, 23, 34, and 41) are possible combinations comprising the defect.

It follows from Equation (5) that for the XH₂ and XD₂ isotope configurations, the transition moment of the high-frequency mode is \(\mathbf{d}_+ = (d_+ + d_-)/\sqrt{2}\), whereas for the low-frequency one it equals \(\mathbf{d}_- = (d_+ - d_-)/\sqrt{2}\). In the case of XHD, the modes due to the O–H and O–D bonds are dynamically decoupled. For a given polarization \(\mathbf{E}\) of the incoming light (wave vector \(\mathbf{k} \perp \mathbf{E}\)), the intensity of an IR absorption line due to an LVM with the transition moment \(\mathbf{d}_\pm\) is obtained from

\[
I_\pm \sim \sum_{(ij)} |E(d_i \pm d_j)|^2
\]  (7)
where the sum is taken over all possible orientations of the transition moments in the anatase lattice.

The microscopic model of XH₂ shown in Figure 3 implies that both O–H bonds projected onto the c-plane are perpendicular to each other. It follows from here that for the measurement geometry with \(k \parallel c\) both the high- and the low-frequency modes should have equal intensities. The IR absorption spectra obtained for a c-plane cut sample (Figure 1 and 2) provide strong support to this conclusion.

Figure 4 shows a section of IR absorption spectra recorded at 10 K for a (100)-plane cut sample after treatment in D₂ gas at 450 °C. The strong dependence of the high-frequency component of the complex on the polarization can be understood on the basis of the microscopic model shown in Figure 3. As the nearby O–H bonds have opposite projections onto the c axis, the low-frequency mode with the transition moment \(\mathbf{d}_- \sim (d_+ - d_-)/\sqrt{2}\) should have an appreciable component along the axis, whereas the high-frequency one \(\mathbf{d}_+ \sim (d_+ + d_-)/\sqrt{2}\) is aligned perpendicular to it. The fact that the high-frequency mode does not disappear completely in spectra measured for polarization parallel to the axis we explain tentatively by structure imperfections of the natural anatase sample.

### 2.4. Thermal Stability

Figure 5 shows normalized intensities of the IR absorption lines due to the XH₂ and XD₂ complexes as a function of the annealing temperature. The results presented for XH₂ were obtained after hydrogenation of a virgin sample at 450 °C, whereas those for XD₂ after subsequent deuteration at the same temperature. Interestingly, XD₂ reveals a higher stability with respect to thermal treatment: the defect anneals out at around 325 °C, whereas XH₂ at 300 °C.
As already mentioned earlier, annealing in air at 450 °C always leaves residual hydrogen in titania, which implies that subsequent deuteration results in the appearance of all possible isotope configurations of the defect: $XH_2$, $XD_2$, and $XHD$. An analysis of the IR absorption spectra recorded on the deuterated sample has shown that not only $XD_2$ but all isotope configurations of the defect seem to anneal out at 325 °C. Because of this, we cannot exclude that the different stability of $XH_2$ and $XD_2$ (Figure 5) is an artifact not related to the differences in the two hydrogen isotopes. The mechanisms resulting in the disappearance of $XH_2$ from the spectra may involve a dissociation as well as trapping of other mobile defects, e.g., interstitial hydrogen. The latter process should strongly depend on the presence of other scattering centers whose nature and/or concentration obviously depend on the sample history.

### 2.5. Temperature Dependence

Figure 6 shows the intensity of the 3355.9 cm$^{-1}$ line for a $c$-plane cut sample as a function of temperature. The inset gives corresponding spectra recorded at 6, 30, and 40 K. Similar dependences were obtained for the IR absorption lines due to $XD_2$ and $XHD$. Independent of the isotope configuration all spectroscopic features of the defect disappear at temperatures above 60 K. At the same time, an IR absorption line at 3373 cm$^{-1}$ (not shown in the figure) becomes stronger, whereby the integrated intensity of the $XH_2$ and 3373 cm$^{-1}$ features remains constant. Similar results were recently reported for IR absorption lines at 3412 and 3417 cm$^{-1}$ tentatively assigned to LVMs of a hydrogen-related shallow donor in the neutral and the positive charge state, respectively,[20] From their intensity ratio as a function of temperature, the ionization energy was estimated to be about 20 meV.

A strong indication that the $XH_2$ complex also occurs in different charge states is supported by the results of measurements carried out without unintentional subbandgap illumination. Typically, IR absorption spectra are taken with a globar as a light source which provides light in the broad spectral range 100–7000 cm$^{-1}$. It turned out that the $XD_2$ and $XHD$ features become significantly stronger at the expense of the 3373 cm$^{-1}$ line if the spectra are recorded through a low-pass filter with a cutoff frequency of 3330 cm$^{-1}$.

The apparent anticorrelation between $XH_2$ and the 3373 cm$^{-1}$ line seems to suggest the same nature of the two IR absorption
features. At this stage, however, we cannot be sure that they are due to the different charge states of the same complex.

The most serious objection is the number of hydrogen atoms comprising the defects. Our findings unambiguously reveal that $\text{XH}_2$ consists of two equivalent $\text{O}–\text{H}$ bonds aligned nearly perpendicular to the $c$ axis. In contrast, isotope substitution experiments strongly suggest that a defect giving rise to the 3373 cm$^{-1}$ line includes a single $\text{O}–\text{H}$ bond lying in the basal plane of the crystal. In other words, the same origin of the two similarly different defects requires a rearrangement of $\text{O}–\text{H}$ bond in $\text{XH}_2$ parallel to $c$ upon changing its charge state. Such a situation is possible and was recently reported for a hydrogen-related defect in ZnO, resulting in a 3326 cm$^{-1}$ absorption line.$^{[26]}$ Alternatively, it is conceivable that the excited charge state consists of two opposite $\text{O}–\text{H}$ bonds (13 or 24 in the notation of Figure 3). In either case, the mode aligned along the $c$ axis should escape an observation in our measurement geometry. So far, however, the bulk of experimental data at our disposal can neither confirm nor rule out either of two models for the excited state of the $\text{XH}_2$ complex.

3. Discussion

The results of our study of natural anatase $\text{TiO}_2$ presented earlier reveal that there is a hydrogen-related defect which comprised two equivalent $\text{O}–\text{H}$ bonds lying practically in the basal plane of the crystal. IR absorption spectra taken with a low-pass filter to suppress a secondary subbandgap illumination as well as the temperature dependences of the absorption lines, however, do not exclude the possibility that the complex may include more $\text{O}–\text{H}$ units aligned parallel to the $c$ axis of the crystal. The notation $\text{XH}_2$ remains, therefore, tentative not only due to the unknown X constituent. Regardless of the number of hydrogen atoms, our results strongly suggest that $\text{XH}_2$ has a level in the upper part of the bandgap, where the transition from one into another charge state may occur either via the ionization process

$$\text{XH}_2^{(n)} \rightarrow \text{XH}_2^{(n+1)} + e^-$$

(8)

or trapping of an electron provided by another shallow donor

$$\text{XH}_2^{(n)} + e^- \rightarrow \text{XH}_2^{(n-1)}$$

(9)

where spectroscopic signals of $\text{XH}_2^{(n\pm1)}$ remain unveiled. The former process suggests a shallow donor behavior, whereas the latter a deeper acceptor state.

Hydrogen-related shallow donors discussed in the literature so far are interstitial species and hydrogen substituting for oxygen.$^{[12,13,20]}$ Obviously, none of them can be considered for the $\text{XH}_2$ complex.

The simplest hydrogen-related acceptor in anatase to consider is a Ti vacancy decorated by two hydrogen atoms $V_{\text{T}1}\text{H}_2$. Similar to other metal oxides, we expect $V_{\text{T}1}$ to act as an acceptor in $\text{TiO}_2$. As anatase always reveals n-type conductivity, $V_{\text{T}1}$ should naturally occur in the negative charge state and be an efficient trap for positively charged mobile interstitial hydrogen. Theoretically, $V_{\text{T}1}$ may host up to four hydrogen atoms, where only $V_{\text{T}1}\text{H}_4$ has assuming no level in the bandgap. These arguments are, of course, a speculation, which has to be verified by first-principles theory and further experiments on synthetic crystals of high purity.

It is known that natural anatase contains a significant amount of different transition metals, which may trap mobile interstitial hydrogen. We speculate therefore that a substitutional metal atom rather than $V_{\text{T}1}$ is the X constituent in the $\text{XH}_2$ complex. A similar defect in ZnO is Cu$_2$$\text{H}_2$. $^{[27,28]}$

Finally, we want to emphasize that not all hydrogen in anatase $\text{TiO}_2$ occurs in the form of $\text{O}–\text{H}$ bonds. The results of our annealing series indicate that there is a “hidden” species not seen in IR absorption. Heat treatment in air at 450 °C strongly reduces all IR absorption lines due to the $\text{O}–\text{H}$ bonds. However, subsequent annealing in air at the same temperature terminated by “quenching” to room temperature results in a reappearance of the $\text{O}–\text{H}$ LVMs in the spectra.

Obvious candidates to consider for the role of “hidden” species are hydrogen molecule and hydrogen bound to the O vacancy. The former is electrically inactive and invisible in IR absorption.$^{[29]}$ The latter is expected to have Ti–H LVMs with a frequency located in the spectral region of strong two-phonon absorption which practically excludes its detection by means of IR absorption spectroscopy. Other methods, i.e., photoconductive detection of LVMs, should be used in this case.$^{[30,31]}$ We also call for ab initio calculations to unveil the nature of hydrogen-related defects in anatase $\text{TiO}_2$.

4. Conclusions

An IR absorption study of natural anatase $\text{TiO}_2$ was performed. A complex with IR absorption lines at 3355.9 and 3357.3 cm$^{-1}$ is shown to consist of at least two equivalent hydrogen atoms, whereby these IR absorption lines are due to the stretch LVMs of two $\text{O}–\text{H}$ bonds located in the basal plane of the anatase crystal forming an angle of approximately 90°. The complex is shown to be electrically active with a level in the upper part of the bandgap.

5. Experimental Section

The samples used in this study were c- and (100)-plane cut natural single crystals provided by SurfaceNet GmbH. Hydrogen and/or deuterium were introduced via a thermal treatment in a closed quartz ampule filled with $\text{H}_2$, $\text{D}_2$, or $\text{H}_2 + \text{D}_2$ gas (pressure of 0.5 bar at room temperature). The treatments were conducted at 450–600 °C for 1 h and were terminated by quenching the ampules to room temperature in water.

IR absorption spectra were recorded with a Bomem DA3.01 Fourier transform spectrometer equipped with a globar light source, a KBr beamsplitter, and a liquid nitrogen-cooled InSb detector. The spectral resolution was 0.25–1.0 cm$^{-1}$.

The thermal stability of IR absorption lines was probed in a series of annealings in the temperature range 100–450 °C, which were conducted in air for 30 min and terminated by a cool down to room temperature within about 2 min.

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Conflict of Interest
The authors declare no conflict of interest.

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