Hydrogen Donors in Anatase TiO₂

Eduard V. Lavrov,* Igor Chaplygin, Frank Herklotz, and Vladlen V. Melnikov

Two hydrogen-related donors in anatase TiO₂—interstitial hydrogen (Hᵢ) and hydrogen substituting for oxygen (Hₒ)—are addressed by means of ab initio density functional theory and vibrational mode spectroscopy. First-principles calculations and infrared (IR) absorption measurements reveal that Hᵢ forms an O—H bond lying in the basal plane of the crystal characterized by a stretch local vibrational mode (LVM) with a frequency of 3412 cm⁻¹. According to the calculations, the vibrational spectrum of the threefold-coordinated hydrogen in Hₒ includes two stretch LVMs with the frequencies of 1014 and 1294 cm⁻¹. The theoretically predicted modes occur within the strong two-phonon absorption band of TiO₂, so the conclusions of theory cannot be verified by conventional IR absorption spectroscopy. In accordance with experimental findings, Hᵢ is shown to be unstable at room temperature, whereby formation of interstitial H₂ should be a preferential sink for hydrogen in defect-free anatase. It is also found that of H₂, Hᵢ, and Hₒ, the latter is the most energetically favorable defect, which may account for the “hidden” hydrogen unavailable for the standard spectroscopic techniques.

1. Introduction

Titanium dioxide or titania (TiO₂) has attracted a great deal of attention since the discovery of photocatalytic splitting of water under ultraviolet light exposure. TiO₂ in nature occurs as rutile, anatase, or brookite, of which only rutile is a stable polymorph of bulk titania. Contribution of the surface free energy causes a reversal in the relative stabilities of the three polymorphs for nanosized particles of TiO₂; rutile is stable at sizes above 35 nm, brookite at sizes between 11 and 35 nm, and anatase at sizes below 11 nm. Bulk anatase substrates are currently not available except those prepared from natural crystals, which suffer from a high amount of impurities, defects, and crystal imperfections. Moreover, depending on the experimental conditions, anatase transforms into the equilibrium rutile phase in the temperature range from 550 to 1000 °C. The lack of good quality synthetic bulk anatase single crystals seriously hinders the progress in understanding its electrical and optical properties, which is prerequisite for efficient applications of titania because it is this polymorph that shows the best performance in energy-related applications and optoelectronics. Hydrogen is a common impurity in oxides—of which titania by no means is an exception—with a strong impact on their electrical and optical properties. In wide-bandgap metal oxides, hydrogen preferentially binds to oxygen and acts either as an amphoteric defect or as a shallow donor.

Another hydrogen-related donor in anatase suggested by theory is formed when interstitial hydrogen becomes trapped by the oxygen vacancy (Vₒ) with the binding energy of 1.12 eV. The defect can be regarded as a substitutional H impurity at the original O site (Hₒ), similar to the hydrogen multicenter bond found in ZnO.

During the past few years, hydrogen-related defects in natural anatase TiO₂ were also addressed by infrared (IR) absorption spectroscopy. As-received material always reveals a number of absorption peaks in the spectral range 3200–3500 cm⁻¹ due to the stretch local vibrational modes (LVMs) of the hydroxyl groups, all of which are aligned perpendicular to the c-axis of the crystal. It was shown that hydrogenation of anatase from the gas ambient at temperatures above 450 °C results in the appearance of two IR absorption lines at 3412 and 3417 cm⁻¹ originating from the same defect labeled H—I that occurs in the neutral and the positive charge state, respectively. Thermal stability, temperature dependences, and correlation with the free electrons in the conduction band are in favor of the Hᵢ donor as the likely origin of H—I. Here, we report the results of a follow-up combined first-principles calculations and vibrational mode spectroscopy study of hydrogen-related donors in anatase TiO₂. The microscopic structure of Hᵢ and Hₒ, diffusion of hydrogen, as well as the nature of “hidden” hydrogen species unavailable for the standard spectroscopic methods are discussed.

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/pssb.202100171.

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DOI: 10.1002/pssb.202100171
2. Experimental Section

2.1. Computational Details

To estimate the local structure and vibrational properties of the hydrogen-related defects in anatase TiO$_2$, first-principle calculations were carried out within the framework of the density functional theory (DFT) using the projector-augmented wave (PAW) method\cite{24} and the PBEsol exchange-correlation energy functional,\cite{22} as implemented in Quantum ESPRESSO codes.\cite{23–25}

The conventional tetragonal unit cell of anatase TiO$_2$ is shown in Figure 1. Under the chosen level of theory, the calculated lattice constants of bulk anatase TiO$_2$, \(a = 3.774 \text{Å} \) and \(c = 9.588 \text{Å} \), were in good agreement with the corresponding experimental values of 3.784 and 9.544 Å.\cite{26} The lengths of Ti–O bonds oriented along the \(c\)-axis and lying in the basal plane were found to be 1.987 and 1.931 Å, respectively; the Ti–O–Ti basal bond angle (e.g., Ti–O$_2$–Ti in Figure 1) was 155.5°. The corresponding experimental values were 1.979, 1.932 Å, and 156.3°.

To construct the defect model, a \(3a \times 3a \times c\) tetragonal supercell with periodic boundary conditions comprising 36 formula units was used. One or two hydrogen atoms were added, an oxygen vacancy was created by removing an appropriate atom. All atomic positions were fully relaxed. Uniaxial stress along the \([100]\) direction was modeled by varying of the lattice constants.

A series of high-precision structure optimizations and subsequent calculations were conducted using the \(3 \times 3 \times 3\) grid of \(k\)-points. The energy cutoffs were set to 140 and 576 Ry for the plane wave basis set and the fine fast-Fourier transform (FFT) grid, respectively. The phonon modes at the \(\Gamma\) point were calculated using the density-functional perturbation theory.\cite{27} In doing so, all possible displacements of H atoms were taken into account. In the case of interstitial hydrogen \(H_i\), the displacement of the oxygen atom to which it was bound was considered as well.

![Figure 1. Conventional tetragonal unit cell of anatase TiO$_2$. Oxygen atoms labeled O1, O2, O3, and O4 stand for closely spaced equivalent sites where an interstitial hydrogen is considered to be bound.](https://www.advancedsciencenews.com)

Migration barriers for the interstitial hydrogen diffusion were calculated under basic assumptions of the transition-state theory. Saddle points of interest were searched by probing the full-dimensional ab initio potential energy surface, that is, all atomic positions in the supercell were varied.

2.2. Experimental Procedure

Anatase TiO$_2$ samples used in the present study were (100)- and (001)-oriented natural single crystals provided by SurfaceNet GmbH. The dimensions of the samples were around \(5 \times 5 \times 1 \text{ mm}^3\). Incorporation of hydrogen and/or deuterium was achieved via anneal for 1 h in H$_2$, D$_2$, or H$_2$ + D$_2$ ambient (pressure 0.5 bar at room temperature) at temperatures in the range of 450–600 °C in sealed quartz ampules. This process was terminated by quenching the sample to room temperature in water.

IR absorption spectra were obtained in the temperature range of 7–300 K with a Bomem DA3.01 Fourier-transform spectrometer equipped with a globar light source, a KBr beam splitter, and a liquid nitrogen-cooled InSb detector. The sample was cooled down in the cryostat equipped with ZnSe windows. The spectral resolution was 0.25–1 cm$^{-1}$. Polarized light was produced by a wire-grid polarizer on a KR5-S substrate.

To study the thermal stability of hydrogen-related defects, IR absorbance spectra were recorded at \(T \leq 10 \text{ K}\) after each step in a series of isochronal heat treatments (annealings) at temperatures in the range 100–450 °C. The annealings were conducted in a furnace purged with air and with a duration for each treatment of 30 min. Uniaxial stress measurements with stress directed along the \([100]\) crystallographic axis of the sample were carried out with a home-built stress rig. The stress was supplied via a push rod by a pneumatic cylinder. More details about the Fourier-transform infrared (FTIR) setup and the uniaxial stress rig can be found in other studies.\cite{17,18,28}

The Raman measurements were carried out in a 90° scattering geometry using the frequency-doubled 532 nm line of a Nd:YVO$_4$ laser with a power of 0.5 W for excitation in the temperature range 50–300 K. The scattered light was analyzed using a single-grating monochromator and a liquid nitrogen-cooled Si charge-coupled device (CCD) detector array. The spectral resolution was 3.5 cm$^{-1}$.

Ohmic contacts for photoconductivity measurements with an area of about \(2 \times 1 \text{ mm}^2\) were generated by scratching a mixture of an In–Ga alloy onto the sample surface. Contacts were located on the illuminated face of the samples.

3. Calculations

3.1. Interstitial Hydrogen

We first consider interstitial hydrogen in a defect-free anatase. Figure 2 shows the relaxed atomic configuration of \(H_i\) projected onto the \(c\)- and \(a\)-plane of the anatase lattice. The O–H bond with an approximate length of 0.9913 Å is formed almost parallel to the \([100]\) direction. The bound oxygen atom noticeably shifts out of its regular position.
The calculated LVMs of H$_i$ and its deuterium counterpart are shown in Table 1. Note that for deuterium one wag mode occurs within the phonon spectrum of anatase.

The response of the stretch mode to the stress applied parallel to the a-axis was investigated for $\sigma < 0.4$ GPa. The frequency shift was found to be practically independent of the orientation of the O–H bond relative to the stress direction. In both cases, the shift rate was found to be $A_i \approx A_c \approx -3$ cm$^{-1}$ GPa$^{-1}$. Surprisingly, the calculated energy difference for the defects with the O–H bond oriented parallel and perpendicular to the stress direction appears to be less than 1 meV (which is within the calculation error) even for the largest modeled value of stress, $\sigma \approx 0.4$ GPa.

We also investigated diffusion of the interstitial hydrogen. Four elementary diffusion steps of the interstitial hydrogen were considered. We studied transitions of a H atom between two equivalent equilibrium O–H positions with the shortest reaction pathways. Oxygen atoms to which the interstitial hydrogen considered to be bound are shown in Figure 1. It should be noted that due to reflection symmetry there are two equivalent H$_i$ positions for every oxygen atom (with almost opposite directions of the O–H bond).

We find that the transitions within the basal plane O1 → O2 and O1 → O3 are the easiest ones with the energy barriers of 0.33 and 0.41 eV, respectively. We observe that the hydrogen atom remains trapped inside the void of the elementary cell during the transitions. An elementary diffusion step in the direction perpendicular to the c-axis of the crystal is the transition between the symmetric positions of the O–H bond with hydrogen remaining bound to the same oxygen atom. This transition (O1 → O1) was found to have a barrier of 0.50 eV. The diffusion step along the c-axis (O2 → O4) turned out to have a barrier of 1.56 eV. The values of the barriers are shown in Table 2.

3.2. Hydrogen Molecule

The next possible defect formed by hydrogen in the defect-free anatase is an interstitial molecule. The determined equilibrium atomic configuration is shown in Figure 2c. We find that the H$_2$ molecule lies in the [100] plane between two chains of oxygen atoms at an angle of about $50^\circ$ relative to the c-axis. The H–H bond length is about 0.7375 Å, which is shorter than that of free H$_2$ molecule which equals 0.7414 Å.[29] In accordance with the bond stiffening, the vibrational frequency of H$_2$ in the harmonic approximation was found to be 4382.9 cm$^{-1}$, which is significantly higher than those of hydrogen molecules occurring in other semiconductors.[30–36]

Our calculations also reveal that formation of H$_2$ is energetically favorable as compared with two separated uncharged H, though the energy gain amounts only to marginal 0.2 eV. At the same time, it should be noted that the coupling mechanism of two H$_i$ leading to the formation of H$_2$ is not a straightforward process. The energy gain of 0.2 eV stands for equilibrium configurations in the ideal crystal at zero temperature. According to our findings, even two neutral H$_i$ donors repel and have to overcome a barrier of about 1 eV to form the molecule. Altogether, this indicates that the formation of H$_2$ is an unlikely process.

3.3. Hydrogen Trapped by Oxygen Vacancy

Finally, we consider hydrogen trapped by the oxygen vacancy. The optimized atomic configuration of H$_O$ is shown in Figure 2d. The local symmetry of the defect is C$_{5v}$. The distances between threefold-coordinated hydrogen and the neighboring titanium atoms—one “parallel” and two “perpendicular” to the c-axis—are 2.0846 and 2.0140 Å, respectively.

Calculated bend and two stretch vibrational modes of H$_O$ are at 647.8 (B$_1$), 1014 (A$_1$, along the c-axis), and 1294.3 (B$_3$) cm$^{-1}$, respectively. The relative low frequencies of the stretch modes result from the “softening” of the Ti–H bonds.

| Table 2. Calculated barrier heights ($\Delta E$) of the hydrogen motion in anatase TiO$_2$ (see Figure 1) |
|---|---|---|
| Transition path | Direction | $\Delta E$ [eV] |
| O1 → O2 | $\perp c$ | 0.33 |
| O1 → O3 | $\perp c$ | 0.41 |
| O1 → O1 | $\perp c$ | 0.50 |
| O2 → O4 | $||c$ | 1.56 |

and 0.41 eV, respectively. We observe that the hydrogen atom remains trapped inside the void of the elementary cell during the transitions. An elementary diffusion step in the direction perpendicular to the c-axis of the crystal is the transition between the symmetric positions of the O–H bond with hydrogen remaining bound to the same oxygen atom. This transition (O1 → O1) was found to have a barrier of 0.50 eV. The diffusion step along the c-axis (O2 → O4) turned out to have a barrier of 1.56 eV. The values of the barriers are shown in Table 2.

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compared with the free titanium hydride. For example, the Ti–H bond in titane (TiH₂) has a length of 1.710 Å, whereas the bend, symmetric, and asymmetric stretch modes have frequencies of 496, 1436, and 1483 cm⁻¹, respectively.⁴⁶

4. Experimental Results

4.1. 3412 and 3417 cm⁻¹ Lines

Figure 3 shows IR absorption spectra taken at 16 and 40 K for a c-plane-cut natural anatase TiO₂ sample after thermal treatment in D₂ gas at 450 °C. The lines at 3412 and 3417 cm⁻¹ were previously associated with a hydrogen-related defect labeled H–I, which comprises a single O–H bond aligned perpendicular to the c-axis of the crystal.¹⁸ The 3412 cm⁻¹ line was associated with the neutral charge state (H–I⁰) of the defect whereas the one at 3417 cm⁻¹ was assigned to the positive charge state (H–I⁺) of the same complex. The peaks at 2527 and 2531 cm⁻¹ are deuterium counterparts of the two hydrogen modes shifted downward in frequency by a factor of \( \sqrt{\mu_H/\mu_D} \), where \( \mu_H \) and \( \mu_D \) are reduced masses of the \( ^{16}\text{O–H} \) and \( ^{16}\text{O–D} \) units, respectively.

The presence of hydrogen-related modes in the IR absorption spectra of natural anatase is explained by the relative low temperature at which the deuteriation has to take place. As anatase is a metastable phase of titania, precautions must be taken to avoid its transformation into the stable rutile phase. Because of this, the temperature of the treatment should not exceed 600 °C. As mentioned in the Introduction, the H–I defect was previously associated with an interstitial hydrogen, which in anatase is expected to act as a shallow donor.²⁸ The spectra shown in Figure 3 are in line with this assignment. As the temperature rises, the donor becomes ionized, which eventually results in disappearance of the spectroscopic signals corresponding to the neutral charge state.

Calculated frequencies of the stretch modes of H₁⁰ and D₁⁰ shown in Table 1 match those observed experimentally, which we take as a further support of our model of H–I as an interstitial hydrogen. The wag modes of interstitial hydrogen are expected to occur in the spectroscopic region unavailable for the conventional IR absorption spectroscopy due to the dominant two-phonon lattice absorption, which is typical for the hydrogen-related complexes occurring in metal oxides.²⁹,₃⁰

The 3412 and 3417 cm⁻¹ signals as a function of annealing temperature. Importantly, the thermal stability of the defect depends on its isotope composition. As follows from the figure, the H–I defect anneals out at 300 °C, whereas the D–I signal is gone from the spectra only at temperatures above 350 °C. Such a behavior is not uncommon. Intermittent hydrogen in ZnO anneals out via diffusion process, ending up with a trapping at other defects or via formation of interstitial H₂.³⁵,₄₃ The different thermal stability of H₁ and D₁ in ZnO is explained by the lower mobility of the heavier isotope. Under a reasonable assumption that a similar situation should also take place in anatase, the results shown in Figure 4 are also in line with the H₁ model of the H–I complex.¹⁸

The anisotropy of the anatase lattice (see Figure 1) implies anisotropy of hydrogen diffusion. Our calculations predict that the diffusion barriers \( \Delta E \) (see Table 2) in the basal plane and along the c-axis are 0.50 and 1.56 eV, respectively. Such a difference implies that the ratio of the corresponding diffusion constants, \( D \propto \exp(-\Delta E/kT) \), at 300 °C is around \( D_1/D_2 \approx 5 \times 10^{-10} \).

Experimentally, insight into an elementary diffusion step of hydrogen can be gained by the stress-induced dichroism of the corresponding IR absorption lines.²⁹,₃⁸,₄₂–₄⁵ In particular, this technique was successfully used to determine the activation barrier of hydrogen diffusion in In₂O₃⁴⁶ and rutile TiO₂.⁴⁷,₄₈ In regard to anatase, the method should work as follows.

Hydroxyl group formed by interstitial hydrogen (see Figure 2) has four equivalent orientations. Uniaxial stress applied
along the [100] crystallographic direction should lift the orientational degeneracy between the O–H bonds aligned perpendicular and parallel to the stress direction. Subsequent annealing under the stress at elevated temperature would result in the preferential alignment of the hydroxyl groups in accordance with Boltzmann’s distribution. The observed thermalization process should enable the determination of the activation energy of hydrogen diffusion in the basal plane of anatase.

Figure 5 shows the effect of uniaxial stress along the [100] axis on the H–I defect. Notably, the stress response turned out to depend on its charge state. The 3412 cm⁻¹ line does not split with the stress. For both orientations of the O–H bond relative to the stress, the IR absorption line shifts as \( \Delta \lambda = \Delta \lambda_1 \approx -1 \text{ cm}^{-1} \text{ GPa}^{-1} \). The stress response of the 3417 cm⁻¹ line, in contrast, does depend on the orientation of the O–H bond. The bond aligned perpendicular to the stress “red” shifts its LVM frequency with the rate of \( \Delta \lambda_1 \approx -2 \text{ cm}^{-1} \text{ GPa}^{-1} \), whereas the one aligned parallel to the stress changes only marginally as \( \Delta \lambda_1 \approx 0.3 \text{ cm}^{-1} \text{ GPa}^{-1} \). We note that the mean value of shift \( \Delta = (\Delta \lambda_1 + \Delta \lambda_2)/2 \) remains independent of the charge state.

The absence of the splitting of the 3412 cm⁻¹ line agrees with the conclusions of theory (see Section 3), predicting that independent of the relative orientation of the O–H bond and the stress direction, the stretch LVM of H\(_2\) will experience a “red” shift with a rate of \(-3 \text{ cm}^{-1} \text{ GPa}^{-1}\). At the same time, it implies that the stress-induced dichroism does not allow us to determine the energy barrier separating equivalent orientations of hydrogen in the c-plane of the crystal.

In contrast, the different response of the 3417 cm⁻¹ line to the stress applied perpendicular and parallel to the O–H bond seems to enable determination of the energy barrier of the hydrogen motion. Yet no alignment of the defect was detected up to 250 K. This might imply that either the barrier separating equivalent hydrogen sites exceeds 0.9 eV or that their stress-induced energy difference is too small to be detected experimentally. Taking into account the results of our calculations (see Table 2), together with the known energy barriers determined experimentally for hydrogen-related defects in other oxides\(^{[28, 45–47]}\) and, more importantly, for two dominant complexes occurring in natural anatase characterized by IR absorption lines at 3373 and 3389 cm⁻¹ (see ref. [19]), we believe that the latter explanation is more unlikely.

The absence of the alignment of the 3412 cm⁻¹ mode (in view of the marginal energy difference between differently oriented states of the neutral state of the defect) offers however an alternative explanation. The shallow donor nature of the H–I defect suggests that its neutral and positive charge states occur in the dynamical rather than statical equilibrium. This may prevent the stress-induced alignment of the 3417 cm⁻¹ mode due to the continuous exchange of an electron between the defect and the conduction band.

### 4.2. Hidden Hydrogen

Our previous results strongly indicate that hydroxyl groups resulting in the vibrational modes in the region around 3300–3450 cm⁻¹ cannot account for all hydrogen occurring in anatase titania.\(^{[17–20]}\) There must be additional hydrogen which is invisible for the conventional FTIR absorption and/or electrical characterization methods. Two candidates—interstitial H\(_2\) and H\(_2\)O—are usually considered by theory and detected experimentally in other metal oxides. Both defects play a significant role in ZnO though the detection methods are different in each case. The hydrogen molecule is electrically and IR inactive but is observed by Raman scattering.\(^{[15, 49]}\) Fourfold-coordinated hydrogen substituting for oxygen in ZnO was discovered by means of photocurrent spectroscopy, whereby vibrational modes of H\(_2\)O manifest themselves as Fano resonances in the broad photocurrent spectrum arising from direct transitions of electrons bound to the shallow donors to the conduction band.\(^{[16, 50]}\)
Our calculations (see Section 3) reveal that H₂ is a plausible candidate for the role of a “hidden” species. The energy gain compared with isolated H₂ constitutes noticeable 0.1 eV per atom. The calculated vibrational mode frequency of H₂ in harmonic approximation is found to be 4383 cm⁻¹, which is very close to that of the free molecule which equals 4411 cm⁻¹. We would expect therefore that the experimental frequency of H₂ in anatase is slightly below 4155 cm⁻¹.

Figure 6 shows an exemplary Raman scattering spectrum taken for an anatase sample hydrogenated at 450 °C for 18 h. The line at 3373 cm⁻¹, typical for natural crystals,[17,19,20] dominates the spectrum. Like all hydroxyl groups found in anatase it is aligned perpendicular to the c-axis of the crystal. Another, much weaker feature next to the dominant line can be also spotted. The arrows in the figure show positions of interstitial H₂ signals observed in Si,[51] GaAs,[30] and ZnO,[15]—the only semiconductors where the interstitial hydrogen molecule has been detected.

The Raman spectrum presented in Figure 6 shows that even though molecular hydrogen is energetically favorable in a defect-free anatase, it cannot account for the hidden species in the natural material. A straightforward explanation is the presence of more efficient traps which must occur in large amount in natural TiO₂. A similar situation happens in hydrothermally grown ZnO, where the dominant trap for hydrogen is Li substituting for Zn, forming a Li···H—O complex.[3,54]

H₂O is another candidate for the role of an “invisible” species. Our calculations predict that the energy gain compared with H₂ constitutes a significant 0.7 eV. In contrast, the two stretch vibrational modes calculated in the harmonic approximation occur at 1014 and 1294 cm⁻¹, that is, in the spectroscopic region where the two-phonon and/or free carrier absorption dominates. This difficulty in ZnO has been overcome by means of photoconducting detection of LVMs.

Photoconductivity spectra taken by us on natural anatase titania did not reveal any signals which could be associated with the LVMs of H₂O. For this reason the question about the nature of hidden hydrogen in anatase TiO₂ remains open. Synthetic bulk crystals are necessary to unveil the nature of “hidden” hydrogen in anatase titania.

5. Conclusion

A combined first-principles theory and vibrational mode spectroscopy study of hydrogen-related donors in anatase titania is presented. Interstitial hydrogen is found to form a hydroxyl group lying in the basal plane of the crystal, which is characterized by a stretch LVM with a frequency of 3412 cm⁻¹. According to our calculations, hydrogen is mobile already at room temperature, whereby formation of interstitial H₂ molecule should be a preferential sink for hydrogen in defect-free anatase. The calculated LVMs of hydrogen trapped at the oxygen vacancy are predicted to be at 1014 and 1294 cm⁻¹. The conclusions of theory cannot be readily verified by the conventional IR absorption spectroscopy due to the overlapping with the strong two-phonon absorption of TiO₂.

Acknowledgements

This work was funded by the Deutsche Forschungsgemeinschaft (grant nos. LA 1397/13 and LA1397/17). V.V.M. acknowledges the support from the Ministry of Education and Science of the Russian Federation. The authors are grateful to the Centre for Information Services and High Performance Computing TU Dresden and the Cyberia Supercomputer Center of Tomsk State University for providing the facilities for high-throughput calculations.

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

titania, anatase, hydrogen, donors, local vibrational modes, first-principles calculations

Received: April 22, 2021
Revised: June 15, 2021
Published online: July 14, 2021

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