

Active Species in Photocatalytic Reactions of Methanol on TiO₂(110) Identified by Surface Sum Frequency Generation Vibrational Spectroscopy

Xingxing Peng,^{†,‡} Ruidan Zhang,^{†,‡} Ran-ran Feng,^{†,§} An-an Liu,[†] Chuanyao Zhou,^{‡,||} Qing Guo,^{‡,||} Xueming Yang,^{‡,||} Ying Jiang,[†] and Zefeng Ren^{*,†,‡,||}

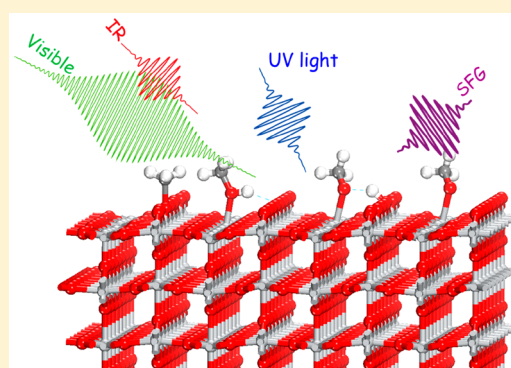
[†]International Center for Quantum Materials (ICQM) and School of Physics, Peking University, 5 Yiheyuan Road, Beijing 100871, P. R. China

[‡]State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, Liaoning, P. R. China

[§]Key Laboratory of Microgravity (National Microgravity Laboratory), Beijing Key Laboratory of Engineered Construction and Mechanobiology, Institute of Mechanics, Chinese Academy of Sciences, 15 Beisihuanxi Road, Beijing 100190, China

^{||}Department of Chemistry, Southern University of Science and Technology, 1088 Xueyuan Road, Shenzhen 518055, Guangdong, P. R. China

ABSTRACT: The photocatalytic reactivity of one monolayer of methanol on TiO₂(110) was measured with the surface sum frequency generation vibrational spectroscopy in the C–H stretching range, which shows high photon energy dependence. The photocatalytic reactivity was systematically investigated for different active species on TiO₂(110), dissociative adsorbed methanol at five-coordinated Ti sites (Ti_{5c}), methoxy without adsorbed methanol at Ti_{5c} sites, and methoxy O_b sites. The results show that the methoxy at Ti_{5c} sites has much higher photocatalytic reactivity than that of dissociative adsorbed methanol at Ti_{5c} sites, and the methoxy at O_b sites might be inactive. This work demonstrates that methoxy at Ti_{5c} sites is the most active species on TiO₂(110) and suggests that effectively removing surface OH could enhance the photodegradation of surface organics.



1. INTRODUCTION

Titanium dioxide, TiO₂, has attracted remarkable interest in both scientific and industrial fields since Fujishima and Honda's report of photochemistry on TiO₂.¹ TiO₂ is considered as a promising material applying in photocatalytic splitting of water, photodegradation of environmental pollutants, surface superwetting, and so on.^{2–8} Methanol, as the simplest alcohol, is often used in model studies for photocatalytic mechanism on TiO₂ for understanding chemistry and photochemistry on oxide surfaces.^{9–16} In photocatalysis, methanol can act as a hole scavenger to promote the reaction activity to produce hydrogen from water.^{17–21}

In the past decade, many experimental and theoretical studies have been carried out on the structure and photochemistry of methanol on the rutile TiO₂(110), a prototypical model.^{13–15,22–28} Alcohol molecules adsorb primarily on bridge-bonded oxygen (O_b) vacancy site and spontaneously dissociates to form the alkoxy and the hydroxyl (OH_b) groups on O_b sites.^{4,6,12} The desorption of molecular hydrogen was observed at high coverage of OH_b on the TiO₂(110) surface, which competes with the recombination of OH_b to form water.²⁹ Temperature-programmed desorption spectroscopy was successfully used to investigate the photocatalytic reaction

mechanism in detail, which provides a clear picture of how methanol is stepwisely photooxidized on TiO₂(110).^{22,24–27} In the last years, we employed sum frequency generation vibrational spectroscopy (SFG-VS) to systematically study adsorption structures and photocatalytic reactions of methanol on TiO₂(110) in the C–H stretching range. We have resolved the methanol adsorption structure on five-coordinated Ti sites (Ti_{5c}) on TiO₂(110),^{30,31} ceasing the debate whether the methanol can dissociate on Ti_{5c} sites.^{9–15,17,28,32–38} We have assigned the symmetric stretching, Fermi resonance, and antisymmetric stretching of the dissociative and molecular adsorbed methanol on Ti_{5c} sites and the methoxy on O_b sites by changing the methanol coverage and ultraviolet (UV) irradiation.³¹ The coverage-dependent adsorption structure of methanol on TiO₂(110) was also observed.³⁰ With UV irradiation on the methanol/TiO₂(110) sample, we successfully determined all stepwise photocatalytic products, formaldehyde and methyl formate, from vibrational spectra in C–H

Received: April 26, 2019

Revised: May 8, 2019

Published: May 13, 2019

stretching range.³⁹ In addition, temperature-dependent photocatalytic reactivity on this system was also measured.³⁹

In our last work, we did not resolve the antisymmetric stretching of CH₂ from formaldehyde and the symmetric stretching of CH₃ from molecular adsorbed methanol on Ti_{5c} sites due to their occasional overlap. To avoid this interference, only methoxy on Ti_{5c} sites without methanol was prepared by coadsorption of oxygen. Its vibrational spectrum was acquired and assigned, and its photocatalytic reactivity was measured. We also used SFG-VS to measure the photocatalytic reactivity of the dissociative adsorbed methanol on Ti_{5c} sites, methoxy without methanol on Ti_{5c} sites, and methoxy on O_b sites with UV light, 400 and 267 nm. Their photocatalytic reactivities were compared. Our results further deepen our understanding of this important photochemical reaction of methanol on TiO₂(110).

2. EXPERIMENTAL DETAILS

All SFG measurements were performed in a homemade high pressure/ultrahigh vacuum (UHV) chamber that was described before.⁴⁰ A commercial rutile TiO₂(110) single crystal (Princeton Scientific) was mounted at 45° with crystal orientation [001] relative to the plane of light incidence for simple data processing.³¹ The sample was prepared by cycles of 500 eV Ar⁺ ion sputtering and vacuum annealing at 850 K. Methanol (99.95% purity) was purified by cycles of freeze–pump–thaw cycles before experiments. One monolayer methanol was prepared by overdosing methanol on TiO₂(110) at 120 K and subsequent flashing at 216 K.⁹

The optical system of SFG-VS has been described in detail before.³⁰ A femtosecond regenerative amplifier (800 nm center wavelength, 35 fs pulse width, 5 W, 1 kHz, Spitfire Ace, Spectra-Physics) pumps an optical parametric amplifier (TOPAS-C, Light Conversion) with 3 W power. It then pumps a noncollinear difference frequency generator (NDFG1, Light Conversion) to deliver a tunable infrared (IR, 2.6–9 μm) with a sliver gallium disulfide (AgGaS₂) crystal. The central wavelength used in this work was about 3.4 μm with about 300 cm⁻¹ full-width at half-maximum (fwhm) bandwidth. The IR was measured as 20 mW before the CaF₂ window on the UHV chamber in our experiments. The spectrally narrowed visible (VIS, normally 4.5 cm⁻¹ fwhm, 7.5 mW) was obtained by using a pulse shaper (1800 l/mm pulse compression grating, Spectrogon; cylindrical lens with 200 mm focal length) from 1 W of 800 nm light. The residual 1 W of 800 nm light was used to generate second and third harmonic UV light at 400 and 267 nm without pulse width optimization. The IR and VIS pulses were temporally and spatially overlapped on the surface, and the reflected broadband SFG signal was collected by a spectrometer, including a monochromator (Acton SP-2556, Princeton Instrument) and an electron-multiplying CCD (Princeton Instrument). The incidence angles of SFG, VIS, and IR were 47.9°, 45°, and 57°, respectively. Both polarizations of IR and VIS were tuned by true zero-order half-wave plates, and the SFG signal polarization was selected by the combination of an achromatic half-wave plate and a Glan polarizer. The acquired SFG spectra were normalized to the nonresonance SFG signal of ppp (referring to p-polarized SF output, p-polarized visible input, and p-polarized IR input, respectively) polarization combination on the bare TiO₂(110) surface obtained by flashing the sample to 700 K in UHV.

3. RESULTS AND DISCUSSIONS

3.1. Photon Energy Dependence of Photocatalytic Reactivity of Methanol on TiO₂(110). Photon energy dependence of photocatalytic reaction of methanol on TiO₂(110) has been thoroughly studied before by comparing the reactivity under 355 and 266 nm irradiation.⁴¹ Here, we carried out the in situ studies with SFG-VS with UV irradiation. Figure 1 shows the SFG vibrational spectra with

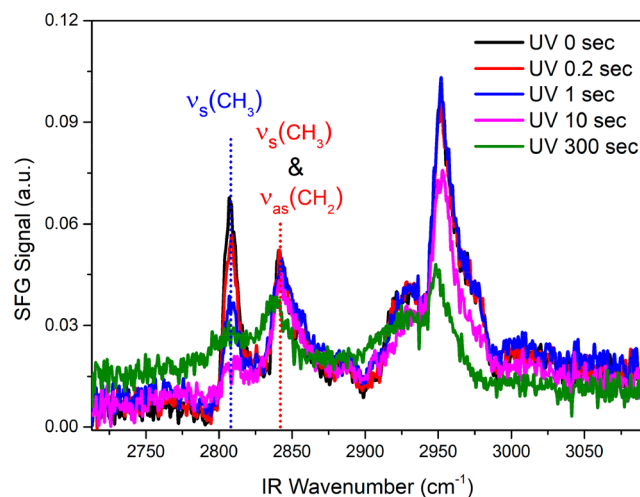
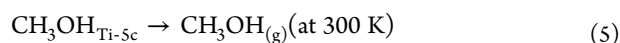
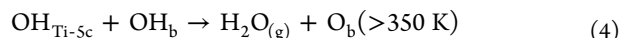
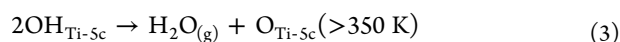
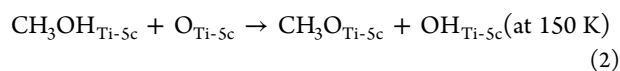
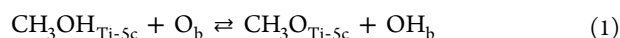


Figure 1. SFG vibrational spectra with ssp polarization combination of methanol with one monolayer coverage on TiO₂(110) before and after variant UV irradiation times at 267 nm (0.75 mW, diameter 1.5 mm). The substrate was kept at 120 K when the substrate was irradiated by UV and the SFG spectra were taken. Vertical dashed lines indicate the resonant frequencies of dissociative adsorbed methanol (blue) and molecular adsorbed methanol (red) on Ti_{5c} sites.

ssp polarization combination of one monolayer (ML) methanol on the TiO₂(110) surface before and after different 267 nm UV irradiation (0.75 mW, diameter 1.5 mm) durations. The substrate was kept at 120 K during UV irradiation and the SFG spectra acquisition. The spectra without UV irradiation show complicated features, which we have systematically assigned as symmetric stretching ($\nu_s(\text{CH}_3)$), Fermi resonance ($\nu_F(\text{CH}_3)$), and antisymmetric stretching ($\nu_{as}(\text{CH}_3)$) from both dissociative adsorbed methanol (methoxy, CH₃O-Ti_{5c}) and molecular adsorbed methanol (CH₃OH-Ti_{5c}) at Ti_{5c} sites. After only 0.2 s of 267 nm UV irradiation, the methoxy peak (indicated by blue dashed line) decreases obviously in Figure 1. After 1 s irradiation, this peak dramatically drops, whereas the feature for methanol (indicated by red dashed line) turns a little broader. As mentioned before,³⁹ we assigned this feature to the occasional overlapping from the symmetric stretching of CH₃ from methanol and the antisymmetric stretching of CH₂ from the photocatalytic reaction product formaldehyde. We will provide the unambiguous evidence for the spectral assignment with methoxy at Ti_{5c} sites below. Comparing with recent published work on the same system under 400 nm UV irradiation (Figure 1a in ref 39), we can find the similar trend with 267 nm. The difference is the photocatalytic reactivity under 267 nm is much higher than that under 400 nm. This photon energy dependence is consistent with the previous report.⁴¹

3.2. Photocatalytic Activity of Methoxy at Ti_{5c} Sites on $\text{TiO}_2(110)$. To simplify the spectral assignment and exclude the interference from the overlapping of methoxy and methanol at Ti_{5c} sites, we prepared the $\text{TiO}_2(110)$ surface only with methoxy adsorbed at Ti_{5c} sites. We followed the reported procedure to prepare the surface.^{9,22} Several Langmuir O_2 was dosed on the surface at 150 K; then the surface was flashed to 300 K. This procedure repaired the O_v and prepared the adsorbed $\text{O}_{5c-\text{Ti}}$ atom at Ti_{5c} sites.⁴² A sequential overdosing of methanol was done at 150 K, followed by flashing the sample to 400 K to remove water (by OH recombination) and molecularly adsorbed methanol. Co-adsorbed oxygen enhances methoxy formation by promoting $\text{CH}_3\text{O}-\text{H}$ bond cleavage according to reactions 2–4.⁹



where (g) denotes desorbed gaseous species, and the subscript Ti_{5c} denotes the species adsorbs at Ti_{5c} sites. Reaction 1 shows the adsorbing equilibrium between the molecular adsorbed methanol ($\text{CH}_3\text{OH}-\text{Ti}_{5c}$) and the dissociative adsorbed methanol (methoxy, $\text{CH}_3\text{O}-\text{Ti}_{5c}$) at Ti_{5c} sites. The coverage of methoxy was not checked in our experiment, and 20% of the first layer methanol coverage on the clean surface was suggested.²²

Figure 2A shows the SFG vibrational spectra with ppp polarization combination of methoxy at Ti_{5c} sites on $\text{TiO}_2(110)$ before and after variant UV irradiation times at 400 nm (4 mW, diameter 1.5 mm). The substrate was kept at 100 K during the UV irradiation and spectra acquisition. Due to the low coverage of methoxy, we only obtained the ppp-SFG with good signal-to-noise because the large nonresonance from ppp-SFG enhanced signals by the interference between the nonresonance and resonances. After only 2 s of 400 nm irradiation, the intensity of the feature at 2818 cm^{-1} , which is assigned to symmetric stretching of CH_3 , $\nu_s(\text{CH}_3)$, decreases more than half, the feature at 2848 cm^{-1} turns obvious, and the nonresonance increases. In addition, a weak feature at around 3010 cm^{-1} can be distinguished. After longer UV irradiation durations, $\nu_s(\text{CH}_3)$ continued to decrease, and the features at 2848 and 3010 cm^{-1} become larger. Comparing with the one monolayer methanol/ $\text{TiO}_2(110)$ result in Figure 1a in ref 39, the photocatalytic reactivity of methoxy at Ti_{5c} sites is extremely high. Note that the low coverage has higher photodissociation efficiency.⁴³ Taking into account the relation between the reactivity and the coverage, we can still get the conclusion. This agrees with the previous result with low-intensity UV light.²²

For spectral assignments, Figure 2B provides the fitting result for the spectra before UV irradiation, and Table 1 shows the fitting parameters. Vertical blue dashed lines indicate the resonant frequencies for the symmetric stretching (ν_s), two Fermi resonances (ν_{F1} , ν_{F2}), and two antisymmetric stretchings (ν_{as1} , ν_{as2}) of CH_3 from methoxy at Ti_{5c} sites. The resonance

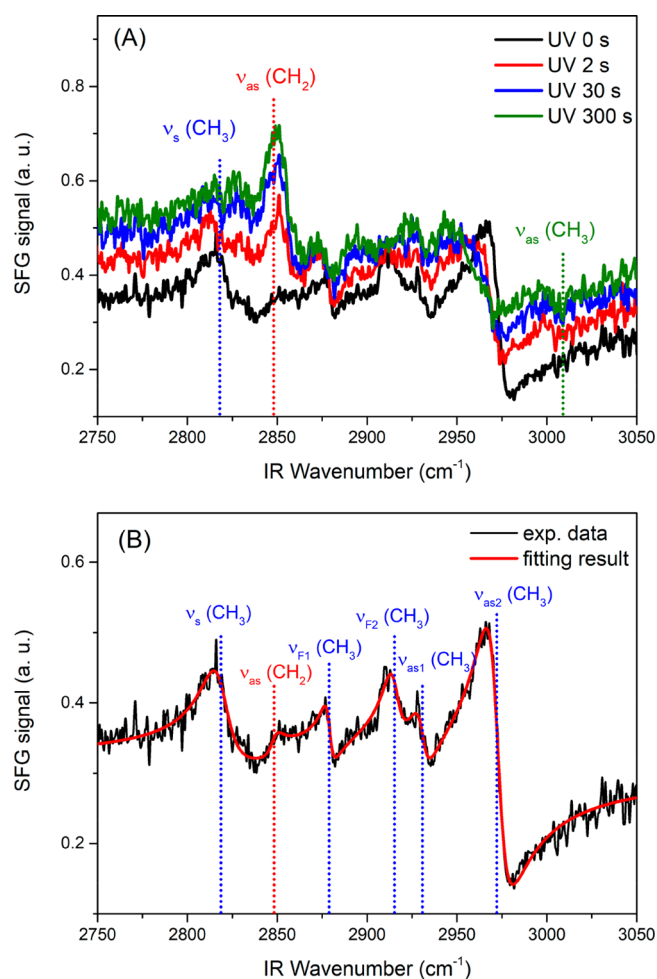


Figure 2. (A) SFG vibrational spectra with ppp polarization combination of methoxy at Ti_{5c} sites on $\text{TiO}_2(110)$ before and after variant UV irradiation times at 400 nm (4 mW, diameter 1.5 mm). The substrate was kept at 100 K when the substrate was irradiated by UV and the SFG spectra were taken. Vertical dashed lines indicate the resonant frequencies of the methoxy (blue), formaldehyde (red), and methyl formate (olive) at Ti_{5c} sites. (B) The fitting result of the SFG vibrational spectrum of methoxy at Ti_{5c} sites without UV irradiation. Vertical dashed lines indicate the resonant frequencies of methoxy (blue) and formaldehyde (red) at Ti_{5c} sites.

frequencies from methoxy at Ti_{5c} sites are consistent with our previous assignments for methanol on $\text{TiO}_2(110)$.^{30,31}

To get good fitting, one resonance at 2848 cm^{-1} must be included. The methanol can be photooxidized to formaldehyde and methyl formate in a stepwise process, which has been thoroughly studied,^{24–27} and methoxy at Ti_{5c} sites shows much higher photocatalytic reactivity to generate formaldehyde. Further, without interference from the molecular adsorbed methanol at the Ti_{5c} sites, this resonance is unambiguously assigned to the antisymmetric stretching from CH_2 of the photocatalytic reaction product, CH_2O . This assignment is contradicted with the high resolution electron energy loss spectroscopy.⁴⁴ The symmetric stretching of CH_2 at around 2770 cm^{-1} is too weak to distinguish because the ppp SFG is not as sensitive to the symmetric stretching mode as the antisymmetric stretching mode.⁴⁵ However, the photocatalytic reaction is normally only activated by UV light, not by IR or 800 nm light. The reduced $\text{TiO}_2(110)$ sample is normally blue color, which originates from the electronic transitions (or

Table 1. Spectral Assignment and the Fitting Results of the SFG Vibrational Spectrum from CH₃ of Methoxy at Ti_{5c} Sites on TiO₂(110) without UV Irradiation in the C–H Stretching Range^a

ν_s	$\nu_s(\text{CH}_2)$	ν_{Fermi1}	ν_{Fermi2}	ν_{as1}	ν_{as2}	A_{NR}
A_1	A_2	A_3	A_4	A_5	A_6	
1.03 ± 0.09	0.11 ± 0.05	0.20 ± 0.03	0.43 ± 0.09	0.32 ± 0.08	2.50 ± 0.06	0.56 ± 0.00
φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	
2.42 ± 0.08	0.74 ± 0.46	3.00 ± 0.17	2.55 ± 0.19	3.18 ± 0.24	3.28 ± 0.03	
ω_1 (cm ⁻¹)	ω_2 (cm ⁻¹)	ω_3 (cm ⁻¹)	ω_4 (cm ⁻¹)	ω_5 (cm ⁻¹)	ω_6 (cm ⁻¹)	
2818.6 ± 0.8	2848.3 ± 2.2	2878.9 ± 0.6	2915.3 ± 0.9	2930.8 ± 1.0	2972.2 ± 0.2	
Γ_1 (cm ⁻¹)	Γ_2 (cm ⁻¹)	Γ_3 (cm ⁻¹)	Γ_4 (cm ⁻¹)	Γ_5 (cm ⁻¹)	Γ_6 (cm ⁻¹)	
9.8 ± 0.8	4.6 ± 2.3	3.1 ± 0.6	5.6 ± 1.0	4.7 ± 1.0	7.4 ± 0.2	

^aOnly the second resonance is from the CH₂ of the photocatalytic reaction product CH₂O. Fitting errors are shown with 95% confidence level. A_q , φ_q , ω_q and Γ_q are the resonant amplitude, phase, frequency, and damping constant (half-width at half-maximum) of the q th mode, respectively.

photoabsorption) of the Ti³⁺-induced states in the band gap.⁴⁶ Further studies show that the localized excitation of Ti³⁺ ions via 3d → 3d transitions from the gap state to the lowest empty resonant state increases the photoabsorption and extends the absorbance to the visible region.^{45,47} In addition, judging from the extremely high photocatalytic reactivity of methoxy at Ti_{5c} sites from Figure 2A; hence, the weak signal from CH₂O could be attributed to the weak photoexcitation by 800 nm or multiphoton excitation of IR and consequent photocatalytic reactions from methoxy.

Methyl formate from the photocatalytic reaction of methoxy at Ti_{5c} sites was observed. The resonance at around 3010 cm⁻¹ is attributed to the antisymmetric stretching from CH₃ of the photocatalytic reaction product, methyl formate.³⁹ This resonance frequency is red-shifted by about 30 cm⁻¹ comparing with our previous results on one monolayer methanol on TiO₂(110).³⁹ Due to low signal-to-noise and too many possible resonance features, we cannot get reliable fitting for the data after UV irradiation. The features at 2922 and 2945 cm⁻¹ could be from the resonances of symmetric stretching from CH and symmetric stretching from CH₃ of methyl formate. These two features are also red-shifted by about 20 cm⁻¹ comparing with spectral assignments in the literature.^{39,48–50} This could be due to the low coverage and the less repulsion from OH_b. There are detailed discussions about the reaction mechanism about the formation of methyl formate through hemiacetal (reaction of CH₃OH or CH₃O with CH₂O) process or formyl radical (HCO) intermediate process.²⁵ To form methyl formate, the reactants in the cross coupling reaction must be close with each other. If HCO was formed, it would be in conjunction with O_b atoms to form formate. And it is difficult to diffuse and close to methoxy and form methyl formate at 100 K at such low coverage. While the formaldehyde can diffuse easily and is close to methoxy because formaldehyde has a much lower adsorption energy from the TPD measurement, it could also be more diffusive due to local phonon excitation.³⁹ After 300 s of UV irradiation (olive curve) in Figure 2A, the feature for $\nu_s(\text{CH}_2)$ is still larger than that after 30 s of UV irradiation. This suggests that the further photooxidation from formaldehyde, CH₂O, to the formyl group, CHO, without the cross-coupling reaction is difficult.

3.3. Photocatalytic Activity of Methoxy at O_b Sites on TiO₂(110). Methoxy species can be at both O_b and Ti_{5c} sites on TiO₂(110). The O_b vacancy site is the most active site in thermal chemistry.⁴ Alcohol molecules, once adsorbing at the O_b vacancy site, spontaneously dissociate to form the alkoxy and OH_b groups.^{4,6,12} The methoxy species at O_b sites are very

stable. They will not leave the TiO₂ surface until the substrate temperature goes up to 400 K.^{9,51} A high concentration of O_b vacancies on the surface was generated by 500 eV Ar ion sputtering of the surface with 2 μA for 3 min at 300 K.⁴⁴ A subsequent flashing at 500 K was used to reduce the surface roughness. Methanol was overdosed on TiO₂(110), and the substrate was flashed to 400 K to desorb all methanol and some H₂O (by OH_b combination). Only CH₃O_b and some OH_b were left on the surface. The coverage of CH₃O_b produced by this method was not quantitatively determined and must be still very low.

The photocatalytic reactivity of methoxy at O_b sites has not been measured but could be expected very low. Here, 267 nm was used because the photon energy dependence shows that the photocatalytic reactivity with 267 nm is much higher than that with 400 nm. However, a previous result shows that 267 nm UV light higher than 50 $\mu\text{J}/\text{cm}^2$ can induce O_b vacancies on TiO₂(110),⁵² so we used low UV intensity (0.3 mW, diameter 1.5 mm, that is $\sim 13 \mu\text{J}/\text{cm}^2$; the same way to generate UV light in the literature⁵²) to reduce this effect in our experiment. Figure 3 shows the SFG vibrational spectra with ssp polarization combination of methoxy at O_b sites on TiO₂(110) before and after variant UV irradiation times. Two

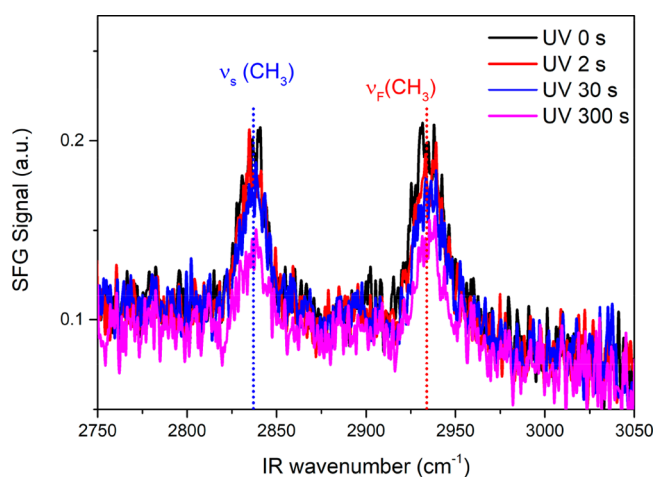


Figure 3. SFG vibrational spectra with ssp polarization combination of methoxy at O_b sites on TiO₂(110) before and after variant UV irradiation times at 267 nm (0.3 mW, diameter 1.5 mm). The substrate was kept at 100 K when the substrate was irradiated by UV and the SFG spectra were taken. Vertical dashed lines indicate the resonant frequencies of symmetric stretching (blue) and Fermi resonance (red) of CH₃.

resonant features can be clearly resolved. The resonance at about 2937 cm^{-1} is assigned to the symmetric stretching of CH_3 , and the other resonance at about 2935 cm^{-1} is the Fermi resonance. The antisymmetric stretching resonance was not resolved due to the low signal. The nonresonance in Figure 3 is smaller than that in Figure 7 in our previous report.³¹ The difference for preparing the sample is the sample was flashed at 500 K after Ar ion sputtering, while the sample was not flashed in our previous result. The relation between the nonresonance and the surface structure needs further studies. Judging from the spectra after UV irradiation, the photocatalytic reactivity of methoxy at O_b sites must be very low. Comparing with Figure 1 for one monolayer methanol/ $\text{TiO}_2(110)$, the reactivity for methoxy at O_b sites might be 3 orders lower. Due to very high adsorption energy of methoxy at O_b sites, it might be completely inactive with 267 nm light. UV light of 267 nm could induce desorption of the surface O_b ,⁵² so it is possible that here the depletion of the CH_3 resonance features could be attributed to the direct desorption of CH_3 radical induced by 267 nm light.

4. CONCLUSION

In summary, the surface SFG-VS in the C–H stretching range was used to measure the photocatalytic reactivity of one monolayer methanol on $\text{TiO}_2(110)$ with 400 and 267 nm UV light. High photon energy dependence shows that the photocatalytic reactivity of 267 nm is much higher than that of 400 nm. The photocatalytic reactivity was systematically investigated for different active species, dissociative adsorbed methanol at Ti_{5c} sites and methoxy at Ti_{5c} and O_b sites. The methoxy at Ti_{5c} sites has much higher photocatalytic reactivity than that of dissociative adsorbed methanol at Ti_{5c} sites. While the methoxy at O_b sites might be inert even under 267 nm UV light. Our results demonstrate that methoxy at Ti_{5c} sites is the most active species on $\text{TiO}_2(110)$ and suggests that effectively removing surface OH could enhance the photodegradation of surface organics. This work further deepens our understanding of the photocatalytic reaction of methanol/ $\text{TiO}_2(110)$ system. Our series of work in the last years provide systematic vibrational spectral assignments in the C–H stretching range for all species, molecular adsorbed methanol at Ti_{5c} sites, dissociative adsorbed methanol at Ti_{5c} sites, methoxy at Ti_{5c} sites, methoxy at O_b sites, and photocatalytic products, formaldehyde and methyl formate on $\text{TiO}_2(110)$. These provide detailed vibrational spectroscopy information for future time-resolved experiments on TiO_2 surfaces in our group.

AUTHOR INFORMATION

Corresponding Author

*Email: zfren@dicp.ac.cn.

ORCID

Chuanyao Zhou: 0000-0002-3252-2992

Qing Guo: 0000-0003-0265-1184

Zefeng Ren: 0000-0002-5263-9346

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Science and Technology of China (grant no. 2018YFA0208700 and 2016YFA0200602), Chinese Academy of Sciences (grant no.

XDB17000000), National Natural Science Foundation of China (grant no. 91645125 and 21688102), and the Youth Innovation Promotion Association of CAS under grant no. 2017224.

REFERENCES

- (1) Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, *238*, 37–38.
- (2) Linsebigler, A. L.; Lu, G. Q.; Yates, J. T. Photocatalysis on TiO_2 Surfaces: Principles, Mechanisms, and Selected Results. *Chem. Rev.* **1995**, *95*, 735–758.
- (3) Thompson, T. L.; Yates, J. T. Surface Science Studies of the Photoactivation of TiO_2 -New Photochemical Processes. *Chem. Rev.* **2006**, *106*, 4428–4453.
- (4) Dohnálek, Z.; Lyubinetsky, I.; Rousseau, R. Thermally-driven Processes on Rutile $\text{TiO}_2(110)$ - (1×1) : A Direct View at the Atomic Scale. *Prog. Surf. Sci.* **2010**, *85*, 161–205.
- (5) Chen, H.; Nanayakkara, C. E.; Grassian, V. H. Titanium Dioxide Photocatalysis in Atmospheric Chemistry. *Chem. Rev.* **2012**, *112*, 5919–5948.
- (6) Henderson, M. A.; Lyubinetsky, I. Molecular-Level Insights into Photocatalysis from Scanning Probe Microscopy Studies on $\text{TiO}_2(110)$. *Chem. Rev.* **2013**, *113*, 4428–4455.
- (7) Guo, Q.; Zhou, C.; Ma, Z.; Ren, Z.; Fan, H.; Yang, X. Elementary photocatalytic chemistry on TiO_2 surfaces. *Chem. Soc. Rev.* **2016**, *45*, 3701–3730.
- (8) Guo, Q.; Zhou, C.; Ma, Z.; Ren, Z.; Fan, H.; Yang, X. Elementary Chemical Reactions in Surface Photocatalysis. *Annu. Rev. Phys. Chem.* **2018**, *69*, 451–472.
- (9) Henderson, M. A.; Otero-Tapia, S.; Castro, M. F. The Chemistry of Methanol on the $\text{TiO}_2(110)$ Surface: the Influence of Vacancies and Coadsorbed Species. *Faraday Discuss.* **1999**, *114*, 313–329.
- (10) Farfan-Arribas, E.; Madix, R. J. Role of Defects in the Adsorption of Aliphatic Alcohols on the $\text{TiO}_2(110)$ Surface. *J. Phys. Chem. B* **2002**, *106*, 10680–10692.
- (11) Farfan-Arribas, E.; Madix, R. J. Different binding sites for methanol dehydrogenation and deoxygenation on stoichiometric and defective $\text{TiO}_2(110)$ surfaces. *Surf. Sci.* **2003**, *544*, 241–260.
- (12) Zhang, Z. R.; Bondarchuk, O.; White, J. M.; Kay, B. D.; Dohnálek, Z. Imaging Adsorbate O–H Bond Cleavage: Methanol on $\text{TiO}_2(110)$. *J. Am. Chem. Soc.* **2006**, *128*, 4198–4199.
- (13) Sanchez de Armas, R.; Oviedo, J.; San Miguel, M. A.; Sanz, J. F. Methanol adsorption and dissociation on $\text{TiO}_2(110)$ from first principles calculations. *J. Phys. Chem. C* **2007**, *111*, 10023–10028.
- (14) Zhao, J.; Yang, J.; Petek, H. Theoretical study of the molecular and electronic structure of methanol on a $\text{TiO}_2(110)$ surface. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2009**, *80*, 235416.
- (15) Zhou, C.; et al. Site-specific Photocatalytic Splitting of Methanol on $\text{TiO}_2(110)$. *Chem. Sci.* **2010**, *1*, 575–580.
- (16) Sánchez, V. M.; Cojulan, J. A.; Scherlis, D. A. Dissociation Free Energy Profiles for Water and Methanol on TiO_2 Surfaces. *J. Phys. Chem. C* **2010**, *114*, 11522–11526.
- (17) Bates, S. P.; Gillan, M. J.; Kresse, G. Adsorption of Methanol on $\text{TiO}_2(110)$: A First-Principles Investigation. *J. Phys. Chem. B* **1998**, *102*, 2017–2026.
- (18) Kawai, T.; Sakata, T. Photocatalytic Hydrogen-production from Liquid Methanol and Water. *J. Chem. Soc., Chem. Commun.* **1980**, 694–695.
- (19) Kawai, M.; Naito, S.; Tamaru, K.; Kawai, T. The Mechanism of Photocatalytic Hydrogen-production from Gaseous Methanol and Water-IR spectroscopic Approach. *Chem. Phys. Lett.* **1983**, *98*, 377–380.
- (20) Harada, H.; Ueda, T. Photocatalytic Activity of Ultra-fine Rutile in Methanol Water Solution and Dependence of Activity on Particle-size. *Chem. Phys. Lett.* **1984**, *106*, 229–231.
- (21) Saeed Al-Mazroai, L.; Bowker, M.; Davies, P.; Dickinson, A.; Greaves, J.; James, D.; Millard, L. The Photocatalytic Reforming of Methanol. *Catal. Today* **2007**, *122*, 46–50.

- (22) Shen, M.; Henderson, M. A. Identification of the Active Species in Photochemical Hole Scavenging Reactions of Methanol on TiO₂. *J. Phys. Chem. Lett.* **2011**, *2*, 2707–2710.
- (23) Shen, M.; Acharya, D. P.; Dohnálek, Z.; Henderson, M. A. Importance of Diffusion in Methanol Photochemistry on TiO₂(110). *J. Phys. Chem. C* **2012**, *116*, 25465–25469.
- (24) Guo, Q.; Xu, C.; Ren, Z.; Yang, W.; Ma, Z.; Dai, D.; Fan, H.; Minton, T. K.; Yang, X. Stepwise Photocatalytic Dissociation of Methanol and Water on TiO₂(110). *J. Am. Chem. Soc.* **2012**, *134*, 13366–13373.
- (25) Guo, Q.; Xu, C.; Yang, W.; Ren, Z.; Ma, Z.; Dai, D.; Minton, T. K.; Yang, X. Methyl Formate Production on TiO₂(110), Initiated by Methanol Photocatalysis at 400 nm. *J. Phys. Chem. C* **2013**, *117*, 5293–5300.
- (26) Yuan, Q.; Wu, Z.; Jin, Y.; Xu, L.; Xiong, F.; Ma, Y.; Huang, W. Photocatalytic Cross-Coupling of Methanol and Formaldehyde on a Rutile TiO₂(110) Surface. *J. Am. Chem. Soc.* **2013**, *135*, 5212–5219.
- (27) Phillips, K. R.; Jensen, S. C.; Baron, M.; Li, S.-C.; Friend, C. M. Sequential Photo-oxidation of Methanol to Methyl Formate on TiO₂(110). *J. Am. Chem. Soc.* **2013**, *135*, 574–577.
- (28) Li, Z.; Smith, R. S.; Kay, B. D.; Dohnálek, Z. Determination of Absolute Coverages for Small Aliphatic Alcohols on TiO₂(110). *J. Phys. Chem. C* **2011**, *115*, 22534–22539.
- (29) Xu, C.; Yang, W.; Guo, Q.; Dai, D.; Chen, M.; Yang, X. Molecular Hydrogen Formation from Photocatalysis of Methanol on TiO₂(110). *J. Am. Chem. Soc.* **2013**, *135*, 10206–10209.
- (30) Liu, S.; Liu, A.-a.; Wen, B.; Zhang, R.; Zhou, C.; Liu, L.-M.; Ren, Z. Coverage Dependence of Methanol Dissociation on TiO₂(110). *J. Phys. Chem. Lett.* **2015**, *6*, 3327–3334.
- (31) Liu, A.-a.; Liu, S.; Zhang, R.; Ren, Z. Spectral Identification of Methanol on TiO₂(110) Surfaces with Sum Frequency Generation in the C–H Stretching Region. *J. Phys. Chem. C* **2015**, *119*, 23486–23494.
- (32) Henderson, M. A.; Otero-Tapia, S.; Castro, M. E. Electron-induced decomposition of methanol on the vacuum-annealed surface of TiO₂(110). *Surf. Sci.* **1998**, *412–413*, 252–272.
- (33) Bates, S. P.; Kresse, G.; Gillan, M. J. The Adsorption and Dissociation of ROH Molecules on TiO₂(110). *Surf. Sci.* **1998**, *409*, 336–349.
- (34) Wang, L.-Q.; Ferris, K. F.; Winokur, J. P.; Shultz, A. N.; Baer, D. R.; Engelhard, M. H. Interactions of Methanol with Stoichiometric and Defective TiO₂(110) and (100) Surfaces. *J. Vac. Sci. Technol., A* **1998**, *16*, 3034–3040.
- (35) Wong, G. S.; Kragten, D. D.; Vohs, J. M. The Oxidation of Methanol to Formaldehyde on TiO₂(110)-Supported Vanadia Films. *J. Phys. Chem. B* **2001**, *105*, 1366–1373.
- (36) Onda, K.; Li, B.; Zhao, J.; Petek, H. The Electronic Structure of Methanol Covered TiO₂(110) Surfaces. *Surf. Sci.* **2005**, *593*, 32–37.
- (37) Oviedo, J.; Sánchez-de-Armas, R.; San Miguel, M. A.; Sanz, J. F. Methanol and Water Dissociation on TiO₂(110): The Role of Surface Oxygen. *J. Phys. Chem. C* **2008**, *112*, 17737–17740.
- (38) Martinez, U.; Vilhelmsen, L. B.; Kristoffersen, H. H.; Stausholm-Møller, J.; Hammer, B. Steps on Rutile TiO₂: Active Sites for Water and Methanol Dissociation. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2011**, *84*, 205434.
- (39) Zhang, R. In Situ Studies on Temperature-Dependent Photocatalytic Reactions of Methanol on TiO₂(110). *J. Phys. Chem. C* **2019**, *123*, 11101–11108.
- (40) Liu, S.; Liu, A.-a.; Zhang, R.; Ren, Z. Compact Ultrahigh Vacuum/High-pressure System for Broadband Infrared Sum Frequency Generation Vibrational Spectroscopy Studies. *Rev. Sci. Instrum.* **2016**, *87*, 044101.
- (41) Xu, C.; Yang, W.; Ren, Z.; Dai, D.; Guo, Q.; Minton, T. K.; Yang, X. Strong Photon Energy Dependence of the Photocatalytic Dissociation Rate of Methanol on TiO₂(110). *J. Am. Chem. Soc.* **2013**, *135*, 19039–19045.
- (42) Lira, E.; Hansen, J. O.; Huo, P.; Bechstein, R.; Galliker, P.; Laegsgaard, E.; Hammer, B.; Wendt, S.; Besenbacher, F. Dissociative and Molecular Oxygen Chemisorption Channels on Reduced Rutile TiO₂(110): An STM and TPD Study. *Surf. Sci.* **2010**, *604*, 1945–1960.
- (43) Yang, W. S.; Geng, Z. H.; Guo, Q.; Dai, D. X.; Yang, X. M. Effect of Multilayer Methanol and Water in Methanol Photochemistry on TiO₂. *J. Phys. Chem. C* **2017**, *121*, 17244–17250.
- (44) Qiu, H.; Idriss, H.; Wang, Y.; Wöll, C. Carbon–Carbon Bond Formation on Model Titanium Oxide Surfaces: Identification of Surface Reaction Intermediates by High-Resolution Electron Energy Loss Spectroscopy. *J. Phys. Chem. C* **2008**, *112*, 9828–9834.
- (45) Wang, Z.; et al. Localized Excitation of Ti³⁺ Ions in the Photoabsorption and Photocatalytic Activity of Reduced Rutile TiO₂. *J. Am. Chem. Soc.* **2015**, *137*, 9146–9152.
- (46) Diebold, U. The Surface Science of Titanium Dioxide. *Surf. Sci. Rep.* **2003**, *48*, 53–229.
- (47) Mao, X.; Lang, X.; Wang, Z.; Hao, Q.; Wen, B.; Ren, Z.; Dai, D.; Zhou, C.; Liu, L.-M.; Yang, X. Band-Gap States of TiO₂(110): Major Contribution from Surface Defects. *J. Phys. Chem. Lett.* **2013**, *4*, 3839–3844.
- (48) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies Consolidated Vol. I*; National Bureau of Standards, 1972.
- (49) Millar, G. J.; Rochester, C. H.; Waugh, K. C. Infrared study of methyl formate and formaldehyde adsorption on reduced and oxidised silica-supported copper catalysts. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2785–2793.
- (50) Chuang, C. C.; Wu, W. C.; Huang, M. C.; Huang, I. C.; Lin, J. L. FTIR study of adsorption and reactions of methyl formate on powdered TiO₂. *J. Catal.* **1999**, *185*, 423–434.
- (51) Hao, Q.; Zhiqiang Wang; Wang, T.; Ren, Z.; Zhou, C.; Yang, X. Role of Pt Loading in the Photocatalytic Chemistry of Methanol on Rutile TiO₂(110). *ACS Catal.* **2019**, *9*, 286–294.
- (52) Xu, C.; Yang, W.; Guo, Q.; Dai, D.; Chen, M.; Yang, X. Suppression of Photoinduced BBO Defects Generation on TiO₂(110) by Water. *Chin. J. Chem. Phys.* **2013**, *26*, 646–650.