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Supplementary Information for "Auto-dissociation of atmospheric water on TiO_2: insights from sum-frequency spectroscopy of Ti-O vibrations"

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1. Basic principle of sum-frequency vibrational spectroscopy

The basic principle of SFG is described elsewhere.[1-4] Briefly, when the IR frequency (ω_{IR}) is near vibrational resonances, the SF signal (S_{SF}) generated by the incident beams is:

$$S_{SF} \propto \left|\chi_{eff}^{(2)}\right|^2 = |\chi_{NR} + \chi_R|^2 = \left|\chi_{NR} + \sum_q \frac{A_q}{\omega_{IR} - \omega_q + i\Gamma_q}\right|^2 \qquad \text{(S1)}$$

where χ_{NR} and χ_R are the non-resonance and resonance contributions, with A_q, ω_q, and Γ_q being the amplitude, frequency, and damping coefficient (half width at half maximum) of the q_{th} resonance mode, respectively. With inhomogeneous broadening considered, the SF output of Equation (S1) becomes:

$$S_{SF} \propto \left|\chi_{NR} + \sum_q \int_{-\infty}^{\infty} \frac{A_q}{\omega_{IR} - \omega' + i\Gamma_q} \frac{1}{\sqrt{2\pi}\Gamma_q} exp\left(-\frac{(\omega' - \omega_q)^2}{2\Gamma_q^2}\right) d\omega'\right|^2 \qquad \text{(S2)}$$

2. The local field intensity at interfaces

In our previous study, the nonlinear matrix formalism has been used to calculate the local field strength successfully.[5] Briefly, the boundary conditions with the presence of an interfacial polarization sheet $P_S(\omega)$ could be written as:

$$\Delta E_x = \sigma_z = -\frac{4\pi}{\epsilon'} i k_x P_{sz},$$

$$\Delta E_y = 0,$$

$$\Delta H_x = \sigma_y = -\frac{4\pi}{c} i\omega P_{sy},$$

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where ϵ' is the effective dielectric constant of the interfacial layer, the lab coordinates (x, y, z) are set with z parallel to the surface normal and $x - z$ is the beam incident plane. σ is the discontinuity in the electromagnetic field caused by $P_S(\omega)$. We define $\sigma_E = 0$, $\sigma_H = \sigma_y$ for S-polarized (TE wave) and $\sigma_E = \sigma_z$, $\sigma_H = \sigma_x$ for P-polarized (TM wave). For our system with 3 layers, the matrix formalism of the TiO$_2$/air (labeled as I) interface could be written as:

$$\begin{bmatrix} E_{I,1} \\ H_{I,1} \end{bmatrix} = M_2 \begin{bmatrix} E_{II,2} \\ H_{II,2} \end{bmatrix},$$

$$\begin{bmatrix} E_{II,2} + \sigma_{II,E} \\ H_{II,2} + \sigma_{II,H} \end{bmatrix} = M_3 \begin{bmatrix} E_{III,4} \\ H_{III,4} \end{bmatrix},$$

where the I, II, III are indices of interface and 1, 2, 3, 4 are indices of media. M_i is the characteristic matrix of the i^{th} medium:

$$M_i = \begin{bmatrix} cos\delta_i & -\frac{isin\delta_i}{n_{i,eff}} \\ -in_{i,eff}sin\delta_i & cos\delta_i \end{bmatrix},$$

$$n_{i,eff} = \begin{cases} n_i \cos\delta_i & \text{(TE wave)} \\ \frac{n_i}{\cos\theta_i} & \text{(TM wave)}' \end{cases}$$

where n_i is the refractive index and θ_i is the beam refraction angle in the i_{th} medium, and $\delta_i = n_i d_i \cos\theta_i d_i$ is the wave propagation phase through the i_{th} section of the medium with thickness d_i. The square of the calculated local field changes with the thickness of the film, as shown in Figure 1b. Through calculation, the optimal film thickness is about 85nm, and the film thickness of a few tens to a hundred nanometers has been widely used in research.[6-8] We also calculated the variation of the local field in the range of 800~1200cm^{-1} when the film thickness is 85nm, as shown in Figure S4.

3. Raman and XRD experiments

Raman spectra were measured by a confocal microscope, with a 532 nm diode pumped solid state laser as excitation and the laser power is 100mW. The excitation light was focused on the sample by a 50 x/0.55 NA objective lens (Nikon-CFI, LU Plan ELWD WD 10.1 mm). The Raman signal was detected by the same spectrograph and CCD camera with the SFG.

The TiO_2 film sample was analyzed using X-ray reflectometry (XRR) (D8 A25 Discover, Bruker) with CuKα radiation (0.15418 nm) as the X-ray source. The film thickness was calculated to be approximately 90 nm using the Bragg formula. The XRD spectra of crystal phase and film thickness are shown in Figure 1d and Figure S1, respectively.

4. Estimation of the coverage of TiOH groups

By assuming a one-to-one conversion between methoxy and TiOH groups, the amount of methoxy corresponds to the amount of the TiOH loss, and we estimated the coverage of the TiOH groups. First, we estimated the coverage of methanol on the thin film samples by comparing the fitted SF amplitudes of methanol CH resonances to those adsorbed on single crystalline anatase (101) surface, which we studied in Ref. 3. Since all C-H spectra were normalized to the quartz reference, the fitted amplitudes were directly comparable. The ratio between the methanol CH amplitudes on the thin film samples and those on the anatase (101) surface ranged from 0.88~1.19, so we concluded that on average the two surfaces are of the same methanol coverage. Based on Ref. [9], the saturated coverage of methanol is 1.5 monolayers on anatase (101) (ML, one monolayer is defined as one molecule per surface Ti adsorption site). Next, based on the fitting results in Table S1, at the highest methanol coverage, methoxy's amplitude is about 21.5% of that of methanol. Assuming the two molecules have the same hyperpolarizability, then the highest coverage of methoxy is about 0.32 ML. Meanwhile, the corresponding TiOH amplitude is about 29.3% lower than its initial value (Table S2). By assuming a one-to-one conversion, the initial coverage of TiOH groups is then about 0.725 ML, which means that the coverage of the dissociated OH is 72.5% in the ambient atmosphere.

Table S1 Fitting parameters of methanol spectrum at the maximum coverage

Time	ω_q (cm^{-1})	A (arb. u.)	2Γ (cm^{-1})
2 min	2843±2	-0.29±0.07	16±0.8
	2866±1	1.33±0.09	20±1.1
	2922±2	-0.04±0.01	8±1.3
	2974±0	1.45±0.11	18±0.6
	2996±5	0.52±0.19	34±7.2
	$\chi_{NR}^{(2)} = (0.12 \pm 0) + i(-0.06 \pm 0)$		
3 min	2842±2	-0.28±0.07	17±0.8
	2866±1	1.33±0.10	20±1.2
	2920±1	-0.06±0.01	11±1.4
	2973±0	1.38±0.10	18±0.5
	2995±5	0.44±0.18	34±7.3
	$\chi_{NR}^{(2)} = (0.12 \pm 0) + i(-0.07 \pm 0)$		

Table S2 Fitting parameters for SF spectra in the Ti-O vibrational region

Time (min)	ω_1 (cm^{-1})	A_1 (arb. u.)	$2\Gamma_1$ (cm^{-1})	ω_2 (cm^{-1})	A_2 (arb. u.)	$2\Gamma_2$ (cm^{-1})
0	1017±3.7	0.076±0.00	109±3	1062±0.3	0.08±0.00	62±1.4
1	989±0.3	0.062±0.00	94±1	1072±0.1	0.06±0.00	50±0.4
2	990±0.2	0.057±0.00	86±1	1072±0.1	0.06±0.00	51±0.3
3	992±0.3	0.056±0.00	80±1	1072±0.1	0.061±0.00	51±0.4
4	991±0.3	0.053±0.00	80±1	1070±0.1	0.062±0.00	51±0.3
5	991±0.3	0.052±0.00	80±1	1070±0.1	0.063±0.00	52±0.3
6	991±0.4	0.053±0.00	78±1	1070±0.1	0.066±0.00	53±0.4
7	990±0.3	0.052±0.00	76±1	1069±0.1	0.068±0.00	54±0.3
8	990±0.3	0.055±0.00	81±1	1068±0.1	0.072±0.00	56±0.3
9	991±0.3	0.056±0.00	84±2	1067±0.1	0.075±0.00	57±0.3
10	993±0.6	0.059±0.00	96±2	1065±0.1	0.079±0.00	58±0.3
11	992±0.4	0.060±0.00	96	1064±0.1	0.084±0.00	60±0.2
12	993±1.0	0.059±0.00	92±3	1063±0.2	0.088±0.00	62±0.4
13	1000±1.4	0.064±0.00	97±3	1063±0.2	0.089±0.00	62±0.5
14	1004±2.9	0.067±0.00	106±4	1061±0.3	0.091±0.00	63±0.8
15	1007±4.6	0.069±0.00	108±6	1060±0.3	0.091±0.00	63±1.3
16	1009±5.5	0.073±0.00	109±7	1061±0.4	0.091±0.00	63±1.7
17	1005±4.2	0.073±0.00	109±6	1060±0.3	0.092±0.00	63±1.3
18	1008±4.7	0.074±0.00	108±6	1060±0.4	0.092±0.00	64±1.5
19	1008±5.0	0.074±0.00	109±6	1060±0.4	0.092±0.00	64±1.6
20	1012±4.9	0.077±0.00	108±5	1061±0.4	0.089±0.00	62±1.7

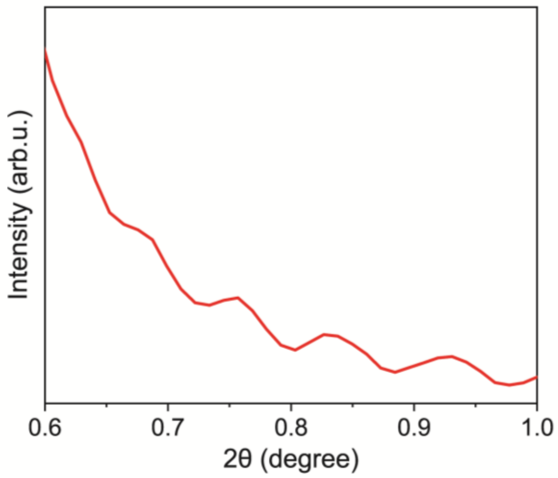

Figure S1. XRR spectrum of TiO_2 film.

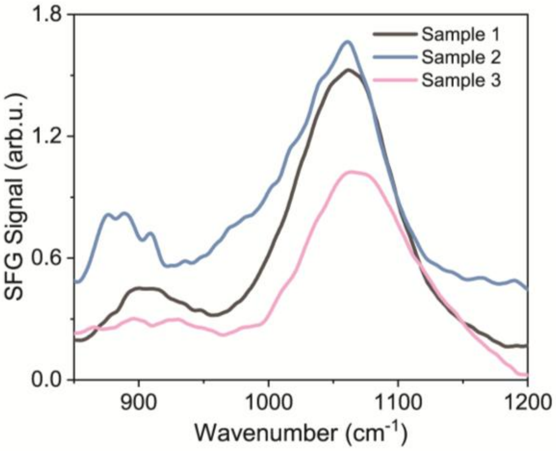

Figure S2. SFG Spectra from different TiO_2 film samples in the Ti-O vibrational frequency range.

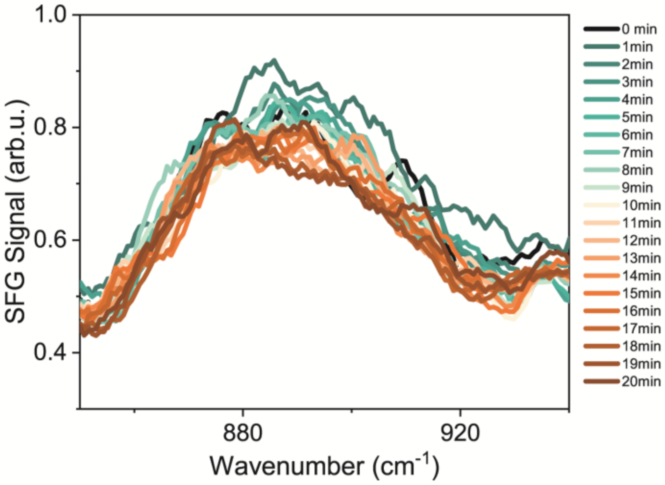

Figure S3. The SFG spectra of low-frequency mode near ~900 cm^{-1} upon the methanol adsorption/desorption.

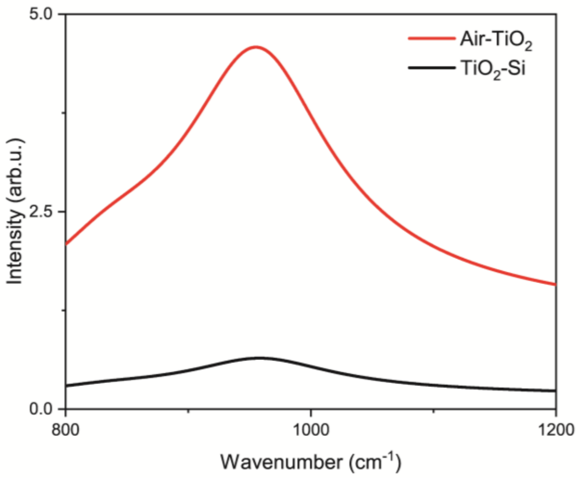

Figure S4. The calculated total local field intensity in the range of 800~1200cm^{-1} at 85 nm thickness.

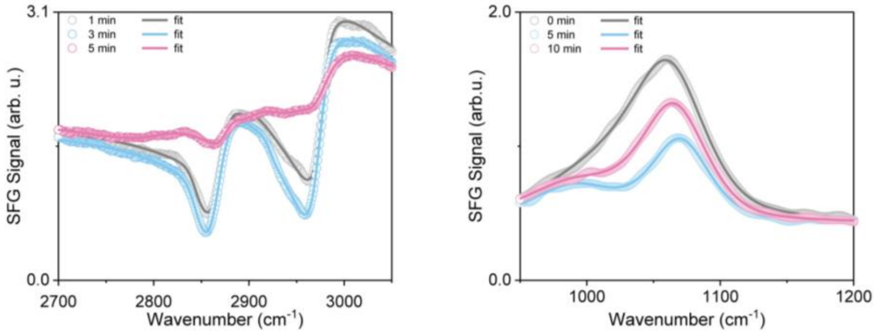

Fig. S5. Typical fits for spectra in Fig. 3a and 3c of the main text.

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