Title

Quantitative Orientation Analysis by Sum Frequency Generation in the Presence of Non-Resonant Signal;
Acetonitrile on Rutile TiO₂ (110)

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Abstract

Sum frequency generation (SFG) spectroscopic techniques are used to investigate the molecular orientation of adsorbed acetonitrile on rutile TiO_2 (110) at the solid-vapor interface. Generally, most molecular orientation analyses using SFG have been performed on dielectric substrates, to avoid the spectral interference between resonant and the non-resonant background signal. Although rutile crystal can be treated as a dielectric substrate, its electronic state contributes to the intensity and interferes with the resonant signal when the SFG frequency is close to its band gap energy. In addition, the rutile crystal is a uniaxial birefringent material and the (110) surface is anisotropic, which further complicates the spectral analysis. In this study, various SFG measurement techniques were applied and quantitative analytical methods were established to avoid misinterpretation of surface orientation. SFG vibrational spectra of acetonitrile on rutile TiO_2 (110) surface have been measured at distinct polarization combinations and compared to spectra obtained by the polarization mapping and null angle method. By varying the polarization combinations of SFG, the magnitude and shape of the spectra undergo substantial change, which originate from the interference between non-resonant signal from the rutile substrate and resonance signal from the adsorbed molecule. Theory, simulation, and analytical methods for obtaining quantitative orientation information in the presence of non-resonant signal of a molecule on an anisotropic semiconductor substrate are presented.

Keywords

Sum frequency generation, Rutile TiO_2 , Acetonitrile, Polarization mapping, Null angle analysis, non-resonant signal.

1. Introduction

Interfaces as common boundaries between two media play an important role in nature. Properties of interfaces such as chemical composition, structure and surface charge potential have been characterized using various techniques. For example, X-ray photoelectron spectroscopy (XPS) is a widely used technique to identify chemical composition at the near surface by measuring the kinetic energy of electrons emitted following X-ray irradiation.¹⁻⁴ Low energy electron diffraction (LEED), atomic force microscopy (AFM), and scanning tunneling microscopy (STM) provide a determination of crystalline structure and chemical potential of the surface.⁵⁻⁹ There is however an increasing demand for quantitative characterization of molecular orientation at interfaces. More specific molecular information can be obtained by means of spectroscopic techniques such as infrared reflection absorption spectroscopy (IRRAS) and sum frequency generation (SFG) vibrational spectroscopy that directly interact with surface molecules.¹⁰⁻¹⁶ Both techniques provide a useful tool for quantitative identification of molecular orientation and chemical functional groups of adsorbates at the interface, although linear spectroscopic techniques such as IRRAS lack surface specificity as they also interact with bulk phase molecules in the beam path. In contrast, SFG spectroscopy has become popular and widely used due to its unique characteristics as a second-order nonlinear process. Like other second-order nonlinear optical processes, a key advantage of SFG is that it is only generated in non-centrosymmetric crystals or at interfaces where inversion symmetry is broken. In addition, SFG is a coherent process, where the signals from ordered structures are amplified.

SFG has been applied to determine the orientation of various functional groups at the interface. The orientation of surface molecules is deduced from a series of SFG spectra obtained from several polarization configurations which provide access to the nonlinear susceptibility tensor elements. The key to this process is to determine the tilt angle of the vibrational dipole vector relative to the surface normal by calculating the ratio of the SFG resonant intensity measured at various polarization configurations.^{15,17-19} However, quantitative analysis in SFG is generally limited to dielectric substrate systems where non-resonant signal is negligible, since it prevents interference between the resonant signal and background signal arising from metal surface.²⁰ In addition, several factors such as poor optical constants and wide distribution of the molecular orientation limit access to ascertaining hyperpolarizability tensor elements of the probed molecules.²¹⁻²⁴ Another effective method of quantitative analysis is direct comparisons of the SFG intensities from the orthogonal set of the vibrational dipole vectors in one spectrum. This has proven to be effective for well-studied systems such as thiols on an isotropic gold substrate^{21,25,26}, but it requires careful assignment of each peak and the corresponding amplitude, as each vibrational mode will have a different nonlinear response as well as different dynamics influencing the intensity and band width of the peak. Moreover, their interpretation is ambiguous especially when there is a combination band or Fermi

resonance in the spectrum.^{27,28} For these reasons, the application of SFG on metal and semiconductor substrate has been limited to qualitative and intuitive analysis.

To overcome this limitation, theory, simulation, and analytical methods to interpret SFG spectra in the presence of a non-negligible non-resonant signal are established. SFG spectra measured with various methods have been analyzed in this work. As a model system, the orientation of acetonitrile molecule on TiO₂ (110) surface has been determined. TiO₂ is one of the most studied single crystalline systems in surface science due to its unique properties and wide range of usage in various fields such as medicine, catalysis, semiconductors, and solar energy conversion.²⁹⁻³³ Current studies on TiO₂ mainly focus on its application and fabrication. However, a lack of studies on the fundamental *in situ* properties at the interface lead to truncated output of further developments.

Second-order nonlinear spectroscopy is one of the most effective methods to study interfacial properties. The meta-stable TiO₂ crystal, anatase, is widely used in practical applications, while its stable form, rutile crystal has been studied for understanding its surface characteristics. The chemical property and structure of surface molecules on isotropic TiO₂ surface has been extensively studied using SFG technique by Shultz.³⁴⁻³⁸ With the single crystalline rutile, however, it has been a challenge to identify molecular interactions on the surface using spectroscopic techniques due to its crystal structure. Linear and non-linear optical fields are directional on the rutile crystals as it is a uniaxial birefringent semiconductor material. Although its tetragonal crystal symmetry prohibits the second-order nonlinear process from the bulk, all of the TiO₂ surfaces other than the one perpendicular to its optical axis are anisotropic as is the case with most crystalline surfaces. With these reasons, most research has been conducted by theoretical calculation³⁹⁻⁴¹, while several studies have successfully reported orientation of a molecule absorbed on single crystalline semiconductor; Hatch *et al.* studied surface orientation of acetonitrile on a ZrO₂ prism, finding a tilt angle of 19° at the solid/vapor and 22° at the solid/liquid interface.⁴² Recently, experimental results on covalent bond characteristics of CO₂ reduction catalysis on rutile TiO₂ surface have been reported with theoretical calculations.⁴³ Otherwise, most SFG studies are conducted on well-known metal and dielectric surfaces. By implementing an SFG analytical method developed in this paper to a model system, the possibility of extending the SFG field can be gauged. The goal of this work lies in developing and demonstrating a systematic quantitative analytical method for SFG to investigate molecular orientation on a semiconductor surface.

2. Theory

2.1. Background

Since details of basic SFG theory are well explained in other papers^{18,44-46}, a brief summary of the relevant equations is hereby presented. Within the electric dipole approximation, SFG is a second-order nonlinear process and its intensity, I_{SFG} , is directly proportional to the square of the second-order effective polarization, $P_{eff}^{(2)}$.^{20,47,48} It is induced by the nonlinear second-order effective susceptibility, $\chi_{eff}^{(2)}$, of the system in the presence of the two incident light fields (visible and IR).

$$I_{SFG} \propto |P_{eff}^{(2)} = \chi_{eff}^{(2)} E_{Vis} E_{IR}|^2 \quad (1)$$

where E_{Vis} and E_{IR} are the electric fields of visible and IR incident light, respectively. $\chi_{eff}^{(2)}$ is a third-rank tensor, which contains tensorial Fresnel factors at the interface and macroscopic second-order nonlinear susceptibility, $\chi_{ijk}^{(2)}$. Each element of macroscopic susceptibility is expressed as

$$\begin{aligned} \chi_{eff}^{(2)} &= [L_i \cdot e_i] \chi_{ijk}^{(2)} [L_j \cdot e_j] [L_k \cdot e_k] \\ i, j, k &= x, y, z \end{aligned} \quad (2)$$

Where, i , j , and k are laboratory coordinates of SFG, visible and IR, respectively. L_i is known as a diagonal tensor element of the nonlinear Fresnel coefficient for a SFG field originating from a monolayer at the interface between the two media. L_j and L_k are Fresnel coefficients of visible and IR incoming fields, respectively and e is the unit optical field vector. The Fresnel coefficients can be combined into a single coefficient for the monolayer, F_{ijk} . Thus, SFG intensity depends not only on the macroscopic susceptibilities but also on the magnitude of the local field at the interface as follows.⁴⁹

$$I_{SFG} \propto \left| \sum_i \sum_{j,k} F_{ijk} \chi_{ijk}^{(2)} E_{Vis} E_{IR} \right|^2 \quad (3)$$

Macroscopic susceptibility is expressed in two parts for describing the SFG process. χ_{NR} is a non-resonant susceptibility and is used for describing SFG intensity contribution from the substrate. $\chi_R^{(2)}$ is the second-order resonant susceptibility containing orientation information and second-order hyperpolarizability of the molecule on the surface. There are a total of 27 elements in the second-order resonant susceptibility tensor, $\chi_R^{(2)}$, but the actual independent elements are drastically reduced due to

symmetry considerations. In C_{2v} surface symmetry such as TiO_2 (110), there are 7 non-vanishing unique components as follows⁵⁰

$$\begin{aligned}
 &\chi_{xxz}^{(2)} \\
 &\chi_{yyz}^{(2)} \\
 &\chi_{zzz}^{(2)} \\
 &\chi_{xzx}^{(2)} = \chi_{zxx}^{(2)} \\
 &\chi_{yzy}^{(2)} = \chi_{zyy}^{(2)}
 \end{aligned} \tag{4}$$

Each of the 7 non-vanishing macroscopic susceptibility tensor elements is an orientational average of the second-order molecular hyperpolarizability. Similar to the susceptibility, the second-order hyperpolarizability tensor is also a third-rank tensor possessing 27 elements, and some of them vanish by molecular symmetry. As results, there are total 11 non-vanishing components, and 3 of them contribute to symmetric stretching vibration as follows

$$\begin{aligned}
 &\beta_{aac} = \beta_{bbc} \\
 &\beta_{ccc}
 \end{aligned} \tag{5}$$

The relation between macroscopic susceptibility and hyperpolarizability is made by Euler transformations between laboratory coordinates (x , y and z) and molecular coordinates (a , b and c). The diagram of the two coordinate systems and related angles used in this paper is illustrated in Supporting Information. The Euler transformation is achieved using three Euler angles, rotation, tilt, and twist angles. The rotation angle, ϕ , is formed by rotating molecular coordinates along the z -axis on the xy -plane of laboratory coordinate system. Tilt angle, θ , is a dihedral angle between xy - and ab -plane formed by tilting the molecular coordinates while the a -axis is in the xy -plane. Twist angle, ψ , is another rotation angle formed by rotating molecular coordinates along the c -axis. The relation between macroscopic susceptibility and hyperpolarizability is calculated as follows.^{18,45}

$$\begin{aligned}
\chi_{xxz}^{(2)} &= (\sin^2 \phi + R \cos^2 \phi) \cos \theta \beta_{ccc} - (\sin^2 \phi - R \sin^2 \phi) \cos^3 \theta \beta_{ccc} \\
\chi_{yyz}^{(2)} &= (\cos^2 \phi + R \sin^2 \phi) \cos \theta \beta_{ccc} - (\cos^2 \phi - R \cos^2 \phi) \cos^3 \theta \beta_{ccc} \\
\chi_{zzz}^{(2)} &= R \cos \theta \beta_{ccc} + (1 - R) \cos^3 \theta \beta_{ccc} \\
\chi_{xzx}^{(2)} &= (\sin^2 \phi - R \sin^2 \phi) \cos \theta \beta_{ccc} - (\sin^2 \phi - R \sin^2 \phi) \cos^3 \theta \beta_{ccc} \\
\chi_{zxx}^{(2)} &= (\sin^2 \phi - R \sin^2 \phi) \cos \theta \beta_{ccc} - (\sin^2 \phi - R \sin^2 \phi) \cos^3 \theta \beta_{ccc} \\
\chi_{yzy}^{(2)} &= (\cos^2 \phi - R \cos^2 \phi) \cos \theta \beta_{ccc} - (\cos^2 \phi - R \cos^2 \phi) \cos^3 \theta \beta_{ccc} \\
\chi_{zyy}^{(2)} &= (\cos^2 \phi - R \cos^2 \phi) \cos \theta \beta_{ccc} - (\cos^2 \phi - R \cos^2 \phi) \cos^3 \theta \beta_{ccc}
\end{aligned} \tag{6}$$

Here, R is the ratio of β_{aac} to β_{ccc} , which can be calculated from depolarization ratio of Raman scattering.^{51,52} It is noteworthy that the macroscopic susceptibility depends on the rotation angle, ϕ , as well as the tilt angle, θ , on the C_{2v} surface, while it is found that it does not depend on the twist angles, ψ . The dependence of the magnitude of macroscopic susceptibility on rotation angle is examined and simulated in the next section of this paper.

2.2. C_{2v} surface model

When the molecular coordinate system is matched with the laboratory coordinate system and the plane of incidence is set to the xz -plane, it is convenient to regroup the macroscopic susceptibility tensor elements according to the distinct polarization combination of three optical fields (SFG, visible, and IR). On the surface, the light can be expressed as a combination of two linear polarizations, s and p . The s -polarized and p -polarized lights have electric field vectors perpendicular and parallel to the plane of incidence, respectively. As a result, s -polarized light contains y -component and p -polarized light contains x - and z - components of the optical field. Thus, there are total eight possible unique combination of polarization in SFG measurement. The effective resonant susceptibility tensor elements related to the experimental polarization combination are as follows

$$\begin{aligned}
\chi_{eff,R,SSS}^{(2)} &= \chi_{eff,R,SPP}^{(2)} = \chi_{eff,R,PSP}^{(2)} = \chi_{eff,R,PPS}^{(2)} = 0 \\
\chi_{eff,R,SSP}^{(2)} &= F_{yyz} \chi_{yyz}^{(2)} \\
\chi_{eff,R,SPS}^{(2)} &= F_{yzy} \chi_{yzy}^{(2)} \\
\chi_{eff,R,PSS}^{(2)} &= F_{zyy} \chi_{zyy}^{(2)} \\
\chi_{eff,R,PPP}^{(2)} &= -F_{xxz} \chi_{xxz}^{(2)} - F_{xzx} \chi_{xzx}^{(2)} + F_{zxx} \chi_{zxx}^{(2)} + F_{zzz} \chi_{zzz}^{(2)}
\end{aligned} \tag{7}$$

As shown here, only 4 polarization combinations, ssp, sps, pss, and ppp, generate SFG signal on the C_{2v} surface. The negative sign of the Fresnel coefficients, F_{xxz} , and F_{xzx} indicates that the direction of the x-component optical vector in SFG field is opposite to that of the incident field.

Combining Equations (6) and (7), effective susceptibilities for each polarization combination can be expressed as a function of rotation, ϕ , and tilt, θ , Euler angles.

$$\begin{aligned}
 \chi_{eff,R,SSP}^{(2)} &= F_{yyz}((\cos^2 \phi + R \sin^2 \phi) \cos \theta - (\cos^2 \phi - R \cos^2 \phi) \cos^3 \theta) \beta_{ccc} \\
 \chi_{eff,R,SPS}^{(2)} &= F_{zyy}((\cos^2 \phi - R \cos^2 \phi) \cos \theta - (\cos^2 \phi - R \cos^2 \phi) \cos^3 \theta) \beta_{ccc} \\
 \chi_{eff,R,PSS}^{(2)} &= F_{zyy}((\cos^2 \phi - R \cos^2 \phi) \cos \theta - (\cos^2 \phi - R \cos^2 \phi) \cos^3 \theta) \beta_{ccc} \\
 \chi_{eff,R,PPP}^{(2)} &= -F_{xxz}((\sin^2 \phi + R \cos^2 \phi) \cos \theta - (\sin^2 \phi - R \sin^2 \phi) \cos^3 \theta) \beta_{ccc} \\
 &\quad - F_{xzx}((\sin^2 \phi - R \sin^2 \phi) \cos \theta - (\sin^2 \phi - R \sin^2 \phi) \cos^3 \theta) \beta_{ccc} \\
 &\quad + F_{zxx}((\sin^2 \phi - R \sin^2 \phi) \cos \theta - (\sin^2 \phi - R \sin^2 \phi) \cos^3 \theta) \beta_{ccc} \\
 &\quad + F_{zzz}(R \cos \theta + (1 - R) \cos^3 \theta) \beta_{ccc}
 \end{aligned} \tag{8}$$

Figure 1 illustrates the magnitude of each 4 effective susceptibility changes upon the averaged tilt angle, θ , with zero distribution (delta function distribution, $\Delta\theta = 0$) for methyl group (a) and nitrile group (b) of acetonitrile on the rutile TiO_2 (110) surface. The plot has been simulated at rotation angles, ϕ , of 0° , 45° , and 90° with R values of 2.3 and 0.48 for methyl and nitrile groups, respectively.⁵³⁻⁵⁶ The birefringence of TiO_2 (110) must be accounted for when calculating optical constants, so Figure 2 shows the orientation of the TiO_2 (110) crystal with respect to the laboratory coordinate system used in the theoretical simulation and SFG experiment. The optical axis of the crystal is set as the y-axis in laboratory coordinates which leads to p-polarized and s-polarized light to be oriented along the ordinary and extraordinary axes, respectively. Optical constants used for the SFG simulation are summarized in Supporting Information.

As noticed in Figure 1 (a), only ssp (dashed line) and ppp (solid line) have a dominant contribution to the resonant SFG intensity for symmetric stretching vibration of methyl group. In Equation (8), the magnitude of the effective susceptibility is given by the interference between the first term ($\cos \theta$) and second term ($\cos^3 \theta$). In the effective susceptibility of sps and pss, a substantial portion of magnitude of the first and second term in Equation (8) are balanced and cancel each other at the given rotation angle, ϕ . The destructive interference between the two terms leads to a reduced magnitude of the effective susceptibility in sps and pss polarization. In Figure 1 (b), on the other hand, the magnitude of ssp susceptibility for the nitrile group is calculated to be much smaller than that for the methyl group due to

its small R value. When acetonitrile is oriented close to the surface normal, SFG signal intensity is mainly observed in the ssp polarization for the CH₃ vibration and in the ppp polarization for CN vibration as shown in Figure 1 and 3.

The plot in Figure 1 also shows that the magnitude varies upon Euler rotation angle, ϕ . It is shown that the effective susceptibility for the CH₃ vibrational mode is more sensitive to rotation angle than the susceptibility for the CN vibration. As a vibrational dipole vector oriented close to surface normal (θ is small), the intensity becomes insensitive to the rotation angle of the molecule on the surface. With a vibrational dipole vector oriented far from surface normal (θ is large), the effective susceptibility of each polarization combination yields substantial changes in magnitude. However, the changes in the ratio of ssp to ppp become minimal. Figure 3 shows the SFG intensity ratio of ssp and ppp polarizations as a function of tilt angle for the CH₃ (a) and for the CN (b) symmetric stretching vibrations at each Euler rotation angle, ϕ . The plot shows that the intensity ratio is highly sensitive to the tilt angle while it is not sensitive to the rotation angles in both CH₃ and CN vibrations. Thus, one can estimate the average tilt angle, θ , of acetonitrile from the surface normal of rutile TiO₂ (110) by obtaining the SFG resonant signal intensity ratio of ssp and ppp polarization combinations using the orientational average curve (Red dotted plot, $\phi=45^\circ$) in Figure 3. Generally, all of the molecules on a surface do not have a unique orientational angle but show an orientational distribution. The convoluted orientation curve using Gaussian tilt distribution is presented in Supporting Information.

Figure 1. Magnitude of effective susceptibilities for methyl group (a) and nitrile group (b) symmetric stretching vibration as a function of the tilt angle θ , and rotation angle ϕ of acetonitrile on the rutile (110) surface. ssp (dashed line), sps (dash dot dotted line), pss (dash dotted line) and ppp (solid line) is simulated at different rotation angle ϕ . Black, red and green plots are at $\phi=0^\circ$, 45° and 90° , respectively.

Figure 2. Orientation of the TiO₂ (110) crystal with respect to the laboratory coordinate system and laser beam propagation geometry used in theoretical simulation and in SFG experiment.

Figure 3. Simulated SFG intensity ratio of ssp and ppp polarization combination as a function of tilt angle θ for methyl group (a) and nitrile group (b) symmetric stretching vibration at rotation angle $\phi=0^\circ$ (black, dashed line), 45° (red, dotted line) and 90° (green, dash dotted line).

2.3. Master equation

In order to obtain the SFG resonant signal intensity ratio of ssp and ppp polarization combinations, SFG vibrational spectra of the acetonitrile on rutile TiO₂ (110) have been measured by distinct polarization combination, polarization mapping, and null angle method. Each dataset from different measurements is treated using a master equation analytical consistency. When the SFG polarization angle is varied, while visible and IR are fixed at 45° and 0° from p-polarization, respectively, the effective susceptibility is expressed as

$$\begin{aligned}\chi_{eff,R}^{(2)} = & \sin \sigma \sin 45^\circ \cos 0^\circ \chi_{eff,R,SSP}^{(2)} \\ & + \sin \sigma \cos 45^\circ \cos 0^\circ \chi_{eff,R,SPP}^{(2)} \\ & + \cos \sigma \sin 45^\circ \cos 0^\circ \chi_{eff,R,PSP}^{(2)} \\ & + \cos \sigma \cos 45^\circ \cos 0^\circ \chi_{eff,R,PPP}^{(2)}\end{aligned}\quad (9)$$

where σ represents the polarizer angle of SFG from p-polarization. From the Equation (7), $\chi_{eff,R,SPP}^{(2)}$ and $\chi_{eff,R,PSP}^{(2)}$ are zero. Then Equation (9) is simplified as follows

$$\begin{aligned}\chi_{eff,R}^{(2)} &= \frac{1}{\sqrt{2}} (\gamma \sin \sigma + \cos \sigma) \chi_{eff,R,PPP}^{(2)} \\ \gamma &= \frac{\chi_{eff,R,SSP}^{(2)}}{\chi_{eff,R,PPP}^{(2)}}\end{aligned}\quad (10)$$

For spectral intensity in SFG measurement, the peak broadening due to time-dependent dephasing and vibrational damping of the surface molecule should be considered. The resonant part of susceptibility in an observed SFG spectrum can be simply described by a Lorentzian line shape to account for the broadening.

$$\chi_{eff,R}^{(2)} \propto \frac{A}{\omega_q - \omega_{IR} - i\Gamma}\quad (11)$$

A , ω_q , and Γ are the amplitude, resonant frequency, and damping constant of the vibration mode, respectively. The complete expression for the effective resonant susceptibility is made by combining Equation (10) and (11).

$$\chi_{eff,R}^{(2)} = \frac{1}{\sqrt{2}} \frac{A_{PPP} (\gamma \sin \sigma + \cos \sigma)}{\omega_q - \omega_{IR} - i\Gamma}\quad (12)$$

2.4. Non-resonant contribution

The rutile TiO_2 crystal possesses tetragonal symmetry, and all of the susceptibility tensor elements for second-order nonlinear processes in the bulk crystal vanish. However as a semiconductor, most of the second-order nonlinear response occurs through the coupling of nonlinear susceptibilities to its electronic state of the rutile TiO_2 (110) surface. The trap states from vicinal surface of rutile (1 $\bar{1}$ 1) can still contribute to the SFG intensity, even if the experiment has been conducted far from the band gap.^{57,58} The nonlinear response that is coupled to the electronic trap state due to discontinuity of symmetry at the defect site or step edge can occur in all of the polarization combinations as experimentally confirmed and represented in Figure 4. Thus, when the SFG polarization angle is varied, leaving visible and IR fixed at 45° and 0° from p-polarization, respectively, SFG non-resonant signals can be detected in four polarization combinations (ssp, psp, ppp, spp). Those susceptibilities from four polarization combinations are included in non-resonant effective susceptibility as follows

$$\chi_{\text{eff},NR}^{(2)} = \frac{1}{\sqrt{2}} \sin \sigma (\chi_{\text{eff},NR,SSP}^{(2)} + \chi_{\text{eff},NR,SPP}^{(2)}) + \frac{1}{\sqrt{2}} \cos \sigma (\chi_{\text{eff},NR,PSP}^{(2)} + \chi_{\text{eff},NR,PPP}^{(2)}) \quad (13)$$

Then, Equation (13) can be simplified as follows

$$\begin{aligned} \chi_{\text{eff},NR}^{(2)} &= (\gamma_n \sin \sigma + \cos \sigma) (\chi_{\text{eff},NR,PSP}^{(2)} + \chi_{\text{eff},NR,PPP}^{(2)}) \\ \gamma_n &= \frac{\chi_{\text{eff},NR,SSP}^{(2)} + \chi_{\text{eff},NR,SPP}^{(2)}}{\chi_{\text{eff},NR,PSP}^{(2)} + \chi_{\text{eff},NR,PPP}^{(2)}} \end{aligned} \quad (14)$$

Non-resonant effective susceptibility in each polarization combination contains its magnitude and phase. The magnitude varies depending on the polarization combinations of SFG, visible and IR beams. The phase relative to the incident beam, however, is identical with respect to the polarization combinations, because the surface electronic state coupled with nonlinear susceptibilities is the same. The magnitude, N , and phase, p , of each non-resonant susceptibility is expressed as follows

$$\chi_{\text{eff},NR}^{(2)} = N e^{ip} \quad (15)$$

Effective susceptibility tensor elements in Equation (14) are substituted by Equation (15),

$$\begin{aligned} \chi_{\text{eff},NR}^{(2)} &= \frac{1}{\sqrt{2}} (\gamma_n \sin \sigma + \cos \sigma) N e^{ip} \\ N &= N_{PSP} + N_{PPP} \end{aligned} \quad (16)$$

From the resonant part in Equation (12) and non-resonant part in Equation (16), the total spectral intensity is expressed as follows

$$I_{SFG}(\omega, \sigma) \propto \left| \frac{A_{PPP}(\gamma \sin \sigma + \cos \sigma)}{\omega_q - \omega_{IR} - i\Gamma} + (\gamma_n \sin \sigma + \cos \sigma) N e^{ip} \right|^2 + c \quad (17)$$

For the rutile TiO₂ (110) surface, it is necessary to add an additional term, c , to correct for background signal that might be due to nonlinear scattering⁵⁹ and multiphoton fluorescence.⁶⁰ Equation (17) can be expressed by the magnitude and phase term as follows

$$I_{SFG}(\omega, \sigma) \propto \left| \chi_{eff,R}^{(2)} \right|^2 + \left| \chi_{eff,NR}^{(2)} \right|^2 + 2 \left| \chi_{eff,R}^{(2)} \right| \left| \chi_{eff,NR}^{(2)} \right| \cos(\varepsilon - p) + c$$

$$\varepsilon = \arctan \left(\frac{\Gamma}{\omega_q - \omega_{IR}} \right) \quad (18)$$

Here, the first and second term represent magnitudes of the resonant and non-resonant susceptibility. The first term exhibits a symmetric Lorentzian line shape and its width is defined by the damping constant, Γ , while the second term is independent of IR wavenumber. The third term called the cross term is virtually negligible for dielectric substrates. In the presence of a substantial level of non-resonant intensity however, interference between resonant and non-resonant contributions develop the cross term. This interference plays several important roles in the SFG spectrum. Firstly, it amplifies the resonant signal even when $\left| \chi_{eff,R}^{(2)} \right| \ll \left| \chi_{eff,NR}^{(2)} \right|$, meaning that SFG becomes more intense on semiconductor and metal surfaces than on dielectrics. On the other hand, the cross term also changes the shape of the peak from the Lorentzian line shape, due to the interference between resonant and non-resonant signal. The mixing coefficients of resonant and non-resonant contribution to the interference and the shape of the peak vary with the SFG polarization angle, σ . When the coefficients of non-resonant contribution becomes null at a certain polarization angle, σ , interference does not occur and the shape of the peak remains symmetric. Thus, it is possible to separate each term by measuring SFG spectra at various polarization angles.

3. Experimental

3.1. Sample preparation

Preparation of a clean TiO₂ rutile (110) surface involves a series of sonication steps for 15 min each in acetone (Macron chemicals, ACS grade) and ethanol (Decon laboratory Inc., USP grade) to dissolve organic contamination. After one more sonication in milli-Q water (18.2 MΩ cm), the sample was placed in a quartz tube and annealed in a furnace at 550 °C for two hours. To remove possible surface metal contamination due to either the furnace or bulk impurities, samples were chemically cleaned in a concentrated aqua regia solution (HCl + HNO₃ in a ratio of 3:1) for 45 min and rinsed thoroughly in milli-Q water. Finally, the sample was dried under a gentle nitrogen stream. AFM and XPS were used to check surface flatness and contamination; flat, wide atomic terraces were observed via AFM and the surface chemical composition of the surface analyzed by XPS shows the cleaning procedure to be sufficient for this particular substrate. The relevant AFM and XPS data will be presented in a forthcoming publication. The surface will however have a thin layer of adventitious carbon. 30 min of UV irradiation (Xe arc lamp, 150W) shortly before introducing the target gas molecules was the most efficient way to remove the carbon layers.

Acetonitrile (Fisher, HPLC grade) is used as a target molecule to investigate molecular orientation on the TiO₂ (110) surface. A custom made Teflon sample cell with a CaF₂ wedge window serves as a sample chamber to isolate the vapor phase from the laboratory atmosphere, and spontaneous vaporization of acetonitrile from the internal cell reservoir creates a saturated gas environment by vapor pressure at room temperature *c.a.* 90 Torr. The UV treated TiO₂ (110) surface is transferred and exposed to saturated acetonitrile gas for 15 min before measuring SFG. Once the surface is cleaned and saturated with acetonitrile it is free from recontamination for a day. However, to check whether there are any changes during experimentation, a second set of spectra is then obtained in the reverse order and compared with the original data set.

3.2. Optical system

The fundamental 1064 nm from a Nd:YAG laser (PL2251A, Ekspla) is used to pump the optical parametric generator/amplifier (OPG/OPA, Laservision). The OPG/OPA generates tunable mid-IR between 2000 and 4000 cm⁻¹ with bandwidth of 8 cm⁻¹. The laser system including OPG/OPA is aligned on a daily basis to maintain the IR energy of ~150 μJ for CN and ~450 μJ for CH vibration frequency regions within of 5 % of standard deviation. The mid-IR beam generated from the OPG/OPA is passed through a germanium Brewster's angle polarizer and then fixed at a desired polarization using a half-wave

plate. The IR beam is loosely focused on the sample surface into a spot of roughly 1 mm in diameter. A visible second harmonic (532 nm) beam is generated from a portion of the fundamental beam and used at a fixed incidence for SFG measurements. A half-wave plate and a linear polarizer pair are used to attenuate the visible beam, and an additional half-wave plate controls the polarization of the visible beam. The pulse duration and repetition rate are 20 ps and 20 Hz respectively for both the tunable IR and fixed visible beam. The visible and IR pulse-trains are then overlapped spatially and temporally on the sample surface to generate the third SF beam. The angle of incidence at the sample surface was 60° for the IR and 50° for the visible beam with respect to the surface normal. The SFG signal generated from the sample is passed through a linear polarizer and filtered from the incident visible light by a short pass filter. The SFG polarization angle can be selected by changing the linear polarizer setting. The SFG signal is then passed through a quarter-wave plate to produce a circular polarization which compensates for the difference in reflectivity for s- and p-polarized light in the monochromator. For further separation from any unwanted stray light, a monochromator has been used as a filter, after which the purified SFG signal is collected by a photomultiplier tube and a gated integrator. A Labview program simultaneously collects the data from the integrator interface and controls the motor for tuning IR frequency at a rate of $1\text{ cm}^{-1}/\text{s}$ and while moving the monochromator grating with at a rate of $1\text{ nm}/50\text{ cm}^{-1}$ during the scan.

3.3. Reference signal

A secondary reference SFG signal is generated from potassium titanyl phosphate (KTP) powder to monitor the IR intensity fluctuation over the scan range due to OPG/OPA conversion efficiency and possible IR absorption by gas-phase acetonitrile in the sample cell. For collecting reference SFG, a gold coated silicon wafer is used instead of the rutile sample. The incident IR is passed through 1 mm of acetonitrile saturated cell atmosphere, is reflected off the gold surface, and is subsequently focused on to powdered KTP on sodium silicate glass. Then, a small portion of incident visible beam is sent to KTP powder and overlapped with the focused IR. The polarization insensitive reference SFG signal is then collected in transmittance configuration and used for correcting sample data. It was found that there is no noticeable IR absorption by acetonitrile vapor.

3.4. Distinct polarization combination

The SFG signal from acetonitrile on rutile TiO_2 (110) has been measured in eight of the possible polarization combinations. The polarization was set by using half-wave plates for the IR and visible beam and a linear polarizer for the SFG beam. Of the eight polarization combinations, the peak intensity ratio of ssp to ppp spectra was selected to determine the orientation analysis.

3.5. Polarization mapping

For polarization mapping, the IR and visible beams are fixed to 0° and 45° (counterclockwise along beam propagation) from p-polarization, respectively. The SFG signal is collected while varying the SFG linear polarizer from 0° to 90° in 15° increments with counterclockwise rotation along the beam propagation. The possible polarization combinations for these measurements are ssp and ppp for the resonant signal and ssp, spp, psp and ppp for non-resonant signal.

3.6. Null angle method

With the IR wavenumber fixed at the resonant frequency of acetonitrile C-H symmetric stretching, the SFG intensity is collected as a function of SFG polarization angle. Polarization of the incident beams for null angle analysis is the same as those for polarization mapping.

4. Result & Discussion

Acetonitrile generally exhibits two resonant peaks in the C-H stretching vibration region at 2945 cm^{-1} for symmetric and 3005 cm^{-1} for anti-symmetric stretching. SFG signals resulting from vibrational resonant intensity, phase effects and a non-resonant background vary depending on the orientation of the surface and the experimental configuration. The survey scan of all eight polarization combinations has been measured and shown in Figure 4. As predicted, the strong resonance of acetonitrile CH_3 symmetric stretching appears in ppp and ssp polarizations. The intensity of the anti-symmetric stretch peak is below the detection limit with a signal-to-noise ratio of ~ 8 in both ppp and ssp, which implies that the orientation of acetonitrile is close to the surface normal.

Figure 4 shows that the phase and intensity of the peak are different in each polarization combination because the resonant and non-resonant signals with different mixing coefficients interfere with each other. The ppp polarization spectrum clearly shows the amplification of resonant intensity through interference with the non-resonant background. Evidently, the interference yields asymmetric shape of the peak as explained in the theory section. The small shoulder appearing in ppp polarization is actually found to be an artifact due to a high noise level as has been confirmed by further measurements illustrated in Figure 6. As the IR wavenumber increases, the non-resonant intensity also increases slightly. This is possibly an effect of the increasing contribution of the nonlinear response from the substrate as the sum-frequency with higher IR wavenumbers approaches the band-gap edge of the rutile crystal.⁶¹ Since

the effect is far less significant than other changes, *i.e.* variation of phase and intensity, it has been treated as a constant in the analytical process.

The dependency of non-resonant intensity on the sample rotation angle has been measured and presented in Figure 5, to study the anisotropy of TiO_2 (110) surface. At 0° , the plane of incidence is perpendicular to the rutile crystal's optical axis. The angles in the plot indicate the angle between the rutile optical axis and plane of incidence. The black dotted line represents non-resonant SFG intensity from the bare rutile TiO_2 (110) surface measured in ppp polarization at 462 nm by mixing 532 nm visible and 2850 cm^{-1} (3509 nm) IR wavenumber, and is seen to exhibit two-fold symmetry due to anisotropic second-order nonlinear effective susceptibility of the TiO_2 (110) surface. The photon energy at 462 nm corresponds to 2.68 eV and it is matched to a shallow trap state formed on top edges and hillsides of step bunch along rutile TiO_2 ($1\bar{1}1$) and (001) observed by Takahashi *et al.*^{57,58} The non-resonant signal intensity shown in Figure 5 also exhibits an offset angle of $\sim 10^\circ$ (counterclockwise), which means that there are additional contributions to the non-resonant intensity other than the shallow trap electronic state of TiO_2 . When these additional contributions occur from other electronic states, the intensity changes typically show four-fold or higher symmetry with nodes due to the coupling of the states. Thus, it is predicted that these additional contributions originate from other nonlinear processes as mentioned above.

Figure 4. SFG spectrum from the CH vibration range survey scan of 8 possible polarization combinations of ppp (black square), pps (red circle), psp (green triangle), pss (blue down triangle), spp (cyan diamond), sps (magenta left triangle), ssp (yellow right triangle), and sss (dark yellow hexagon).

Figure 5. Non-resonant intensity as a function of the sample rotation angle. The intensity is measured at 2850 cm^{-1} of IR wavenumber from bare rutile (110) in ppp polarization.

4.1. Distinct polarization combination

For quantitative analysis, ssp and ppp spectra have been collected with improved signal to noise ratio (Figure 6) and fitted with the master equation (Equation (17)). The ppp and ssp polarization combination in Figure 6 correspond to $\sigma = 0^\circ$ and 90° , respectively. Also $\chi_{eff,NR,SP}^{(2)}$ and $\chi_{eff,NR,PP}^{(2)}$ vanish in distinct polarization measurements because the polarization of the visible beam is fixed to p or s polarization. Both ssp and ppp polarization spectra exhibit a resonant peak from the CH_3 symmetric stretching vibration at around 2950 cm^{-1} . In Figure 6, the resonant vibrational response in the SFG spectrum appears stronger in ppp than in ssp configuration. When there is sufficient level of non-resonant intensity, however, the overall spectral intensity is dominated by interference between the resonant and non-resonant parts. In addition, the shape of the peak in ppp polarization is asymmetric while it is close to symmetric in ssp polarization. This observation of the peak shape change is good evidence of the interference between resonant and non-resonant terms as posited in the theory section. For quantitative analysis, the fitting for ssp and ppp spectra has been performed by Mathematica 8.0 software with Equation (17). The fitting result plots of ssp (blue dot dashed line) and ppp (red solid line) polarizations are shown in Figure 6 and the resulting parameters have been summarized in Table 1. The ratio of $\chi_{eff,R,SSP}^{(2)}$ to $\chi_{eff,R,PP}^{(2)}$ is estimated to be 1.42 (± 0.074 , 95% confidence level) indicating that the actual resonant amplitude in ssp is 1.42 times greater than that in ppp polarization combination. It is inferred from a delta-distribution function orientation curve in Figure 3 that the average tilt orientation of acetonitrile is in the range of $\sim 33^\circ$ for $\phi = 0^\circ$ and $\sim 30^\circ$ for $\phi = 90^\circ$.

Figure 6. SFG spectrum in ppp (red square) and ssp (blue circle) polarization combination for acetonitrile on rutile (110) surface. Red and blue line shows the fitted plot of ppp and ssp spectrum. No constraints are used for fitting.

Table 1. Fitting result parameters for distinct polarization combination measurement. Initial and estimated values for the parameters in Equation (17) are listed. No constraints are used for fitting.

Parameter	Initial	Estimate	Error (95% Confidence level)
A_{ppp}	4	5.7	0.25
Υ	1.5	1.42	0.074
Γ	8	7.4	0.40
ω	2948	2948.3	0.39
N	0	1.795	0.0078
Υ_n	-0.4	-0.11	0.024
p	0	0.37	0.047
c	0.3	0.51	0.022
R^2		0.997485	

4.2. Polarization mapping

When more than one resonant species are present, SFG spectra become complicated due to the interference from different vibrational modes. Polarization mapping is a more sophisticated method to analyze SFG spectra and is proven to be useful in separating vibrational species from complicated spectra.^{19,62} Equally, it is the best method to justify the result from a distinct polarization analysis due to the interference between the resonant and non-resonant part. With the polarization of visible incident beam fixed at 45° from p-polarization, an SFG polarization map of CH₃ vibrational mode was obtained from 0° to 90° of SFG polarizations in 15° increments and as shown in Figure 7 (a). In the distinct polarization method, there are two other susceptibilities contributing to SFG because the visible incident light includes both s- and p-polarization components in polarization mapping. Thus, at $\sigma = 0^\circ$, the resonant and non-resonant part of the amplitude corresponds to $\chi_{eff,R,PPP}^{(2)}$ and $\chi_{eff,NR,PSP}^{(2)} + \chi_{eff,NR,PPP}^{(2)}$, respectively, whereas at $\sigma = 90^\circ$, the resonant and non-resonant part of the amplitude corresponds to $\chi_{eff,R,SSP}^{(2)}$ and $\chi_{eff,NR,SSP}^{(2)} + \chi_{eff,NR,SPP}^{(2)}$, respectively. The spectra obtained between $\sigma = 0^\circ$ and 90° contain a fraction of the two orthogonal polarization settings (0° and 90°). In Figure 7 (a), the spectral intensity and shape of the peak undergo gradual changes with varying σ (e.g. it is clear to see the shape of the peak become symmetric at $\sigma = 75^\circ$). Further analysis and simulation suggest that it is the null angle of the non-resonant SFG signal at $\sigma = 75^\circ$ (Figure 9).

The seven spectra in Figure 7 (a) were simultaneously fitted with a 2-dimensional model (Equation (17)) as a function of frequency and SFG polarization angle. Figure 7 (b) shows the polarization map reconstructed from the fitting. The initial parameters and fitting results are summarized in Table 2. Amplitude of the peak, A_{ppp} , is estimated to be 3.44. Compared with the fitting result of distinct polarization mapping, the value decreased due to the visible beam polarizer being fixed at 45° from p-polarization. The exact amplitude ratio of the two different methods is not half, since a higher intensity of the incident beam is used in polarization mapping for an adequate signal to noise ratio. As listed in Table 2, the amplitude ratio, γ , is estimated to be 1.55 (± 0.070 , 95% confidence level). Detailed error analysis with convoluted orientation function using Gaussian tilt distribution is presented in the Supporting Information. The orientation tilt angle deduced from the fitted value ranges from $\sim 32^\circ$ for $\phi = 0^\circ$ to $\sim 29^\circ$ for $\phi = 90^\circ$. The tilt angle calculated from the polarization mapping analysis agrees with the previous result from the distinct polarization method (Table 6). In addition, the width, Γ , peak position, ω , and the non-resonant phase, p , from both methods are comparable to each other, while the non-

resonant background response, N , and their ratio, γ_n , determined from the two methods, show different values. This is due to the two additional non-resonant susceptibilities ($\chi_{eff,NR,PSP}^{(2)}$ and $\chi_{eff,NR,SPP}^{(2)}$) contributing in the polarization mapping method as mentioned previously. Accordingly, the observation and the results from polarization mapping seem to support well the analysis carried out using the distinct polarization method.

Figure 7. SFG spectrum for polarization mapping. (a) SFG signals are collected by varying SFG polarizer angle σ , while IR and visible polarization angles are fixed at 0° and 45° from p-polarization respectively. (b) Reconstructed polarization map from fitting result. No constraints are used for fitting.

Table 2. Fitting result parameters for SFG polarization mapping for the methyl group measurement. Initial and estimated values for the parameters in Equation (17) are listed. No constraints are used for fitting. Detailed error analysis with convoluted orientation function using Gaussian tilt distribution is presented in the Supporting Information.

Parameter	Initial	Estimate	Error (95% Confidence level)
A_{ppp}	4	3.44	0.11
Υ	1.5	1.55	0.070
Γ	8	7.1	0.21
ω	2948	2947.3	0.19
N	0	0.995	0.0046
Υ_n	-0.4	-0.263	0.0073
p	0	0.43	0.031
c	0.3	0.374	0.0051
R^2		0.994082	

4.3. Null angle method

The null angle method is effective to analyze the orientation of molecules on dielectric surfaces when interference between multiple peaks is not present.^{15,63} In addition to distinct polarization and polarization mapping methods, the null angle method has been conducted at the resonant frequency of acetonitrile CH₃ stretching vibration by measuring the SFG intensity as a function of SFG polarization angle and the results are depicted in Figure 8. The black circle plots in Figure 8 (a) and (b) represent SFG intensity measured from the rutile TiO₂ (110) saturated with acetonitrile and the red square plot represents SFG intensity from the bare rutile TiO₂ (110) surface without acetonitrile. Due to the additional background signals mentioned in theory section (Equation (17)), the SFG intensity plot in Figure 8 does not show null angle but shows minima at 100° and 280° with acetonitrile and 75° and 255° without acetonitrile.

Figure 8 (a) and (b) show SFG intensity changes measured by the null angle method and its fitting result both with and without constraints, respectively. The parameters used for the fitting and the results with and without constraint are listed in Table 3 and Table 4, respectively. Although both fittings seem reasonable with R^2 of 0.983, the resultant values are quite different from each other. The estimated value of amplitude ratio, γ , from the constrained fitting is estimated to be 1.40 which is limited by the constraint boundary. Once the constraint is removed, the amplitude ratio, γ , is estimated to be 1. In addition, both fitting parameters estimated from constrained and un-constrained fitting exhibit a large standard error, indicating possible multiple minima during the fitting process. The tilt angle calculated from the null angle measurement is listed in Table 6. Due to the large standard error, it is not applicable to calculate the uncertainty of tilt angle.

Nevertheless, the average tilt angle ranged from ~34° ($\phi=0^\circ$) to ~30° ($\phi=90^\circ$) in the constrained fitting and ~39° ($\phi=0^\circ$) to ~37° ($\phi=90^\circ$) in the un-constrained fitting. Although the tilt angle calculated from the constrained fitting are in agreement with distinct polarization and polarization mapping methods, there is still a large range of error in the estimated value. In contrast, the resulting tilt angle from un-constrained model fitting exhibited a large deviation from the result of the previous analysis.

Figure 8. SFG intensity changes in null angle measurements of acetonitrile on the rutile (110) surface. Black circle and red square shows SFG intensity measured with acetonitrile and without acetonitrile. Black and red line shows the fitted plot of the null angle measurements with acetonitrile and without acetonitrile. (a) Fit with constraint. The constraint used for the fitting is listed in Table 3. (b) No constraints are used for fitting.

The null angle of resonant SFG signal can be obtained by simultaneously fitting the SFG intensity oscillation both with and without acetonitrile followed by deconvoluting non-resonant signal from the fitted model. At those null angles, the non-resonant signal only contributes to SFG intensity, therefore, the SFG intensity becomes the same with and without acetonitrile molecules.

The null angle from the resulting plot of constrained fitting (a) and un-constrained fitting (b) depicted in Figure 8 exhibit a small but noticeable difference. In the constrained fitting, the two SFG intensity plots measured with and without acetonitrile clearly exhibits the same intensity at the two pairs of SFG polarizer angle at 125° (305°) and 145° (325°), while the plots of the un-constrained fitting show the same intensity at only one pair of the SFG polarizer angle at 135° (315°). The two different fitting results are justified by simulated SFG plots.

Table 3. Fitting parameters for null angle measurement. Initial and estimated values for the parameters in Equation (17) are listed. Constraint for Υ is used for fitting.

Parameter	Initial	Estimate	Error (95% Confidence level)	Lower Limit	Upper Limit
A_{ppp}	4	3.96	9.32×10^6		
Υ	1.5	1.40	2.47	1.4	1.6
Γ	8	8.01	1.88×10^7		
c	0.3	1.23	0.19		
N	0	0.87	0.16		
Υ_n	-0.4	-0.35	0.20		
p	0	0.17	0.92		
R^2		0.983303			

Table 4. Fitting parameters for null angle measurement. Initial and estimated values for the parameters in Equation (17) are listed. No constraints are used for fitting. Detailed error analysis with convoluted orientation function using Gaussian tilt distribution is presented in Supporting Information.

Parameter	Initial	Estimate	Error (95% Confidence level)
A_{ppp}	4	5.67	1.07×10^7
Υ	1.5	1.00	2.83×10^6
Γ	8	8.92	1.11×10^7
C	0.3	1.23	0.19
N	0	0.86	0.16
Υ_n	-0.4	-0.35	0.18
P	0	0.00	1.56×10^6
R^2		0.98329	

Figure 9 (a) shows simulated null angle plots generated from the fitting results obtained from polarization mapping in the previous section. The black solid line in Figure 9 (a) corresponds to the magnitude of SFG intensity simulated at the acetonitrile resonance at 2947 cm^{-1} . The non-resonant intensity changes are simulated from Equation (17) by assuming there are no resonant species and are depicted by the red dashed line in Figure 9 (a). The additional term “c” in Equation (17) accounting for additional background signal is set to zero for the simulation purpose. Overall changes of SFG intensity in the simulation correspond well to the experimental results in Figure 9 and one can clearly see the two-fold oscillation of SFG signal intensity upon the polarizer angle changes in both resonant and non-resonant intensity. The plot shows that null angle for the non-resonant SFG appears at an SFG polarizer angle of 75° (255°). The resonant SFG plot (green dotted trace) deconvoluted from the non-resonant background is obtained by subtracting the magnitude of non-resonant part (red dashed plot) from the total SFG intensity (black solid line plot). It is interesting to note that the green dotted trace, which shows the difference between total SFG intensity and non-resonant contribution in Figure 9 (a), exhibits zero intensity at two pairs of different SFG polarizer angles, 110° (290°) and 147° (327°). SFG spectra at these three unique angles (75° , 110° and 147°) are generated and illustrated in Figure 9 (b). The black solid line represents the IR wavenumber domain SFG spectra at $\sigma=75^\circ$. The shape of the peak becomes symmetric at 75° because the non-resonant signal interfering with the resonant signal is null. This symmetric shape of the peak at $\sigma=75^\circ$ corresponds to the observations from polarization mapping. The red dashed line and green dotted line in Figure 9 (b) show simulated SFG spectra at 110° and 147° of SFG polarizer angle, respectively. As shown in the spectrum, the real null angle appears at 147° . The shape of the SFG spectrum at 110° is anti-symmetric and the center of the peak equals the same intensity as that of the non-resonant SFG. This virtual null angle at 110° is a result of coincidental interference of resonant and non-resonant components. The resonant, non-resonant, and cross term of the simulated SFG spectrum at 110° are separated using Equation (18) and illustrated in Figure 9 (c). While the resonant part shows a symmetric Lorentzian line shape, the cross term exhibits an asymmetric shape that is almost a dip. The overall shape of the spectrum is formed by combining these two parts and the non-resonant constant, and becomes anti-symmetric as shown by the black solid line in Figure 9 (c).

Figure 9. (a) Simulated SFG intensity as a function of SFG polarizer angle σ . The black solid line indicates the SFG intensity changes at resonant frequency (2947.3 cm^{-1}). The red dashed line shows the non-resonant part ($A_{ppp}=0$). The green dotted plot shows the intensity difference between total SFG intensity and non-resonant contribution. For the simulation, the estimated parameter values from polarization mapping fitting result are used. (b) Simulated SFG spectrum at SFG polarizer angle $\sigma=75^\circ$ (black solid line); $\sigma=110^\circ$ (red dashed line); $\sigma=147^\circ$ (green dotted line). (c) The resonant (red dashed line), non-resonant (green dotted line), cross term (blue dash dotted line), and SFG spectra (black solid line) simulated at $\sigma=110^\circ$.

In short, the null angle of the SFG non-resonant signal appeared as crossing points at $\sim 125^\circ$ and $\sim 145^\circ$ between the two null angle plots with and without acetonitrile. The actual null angle is identified at $\sim 145^\circ$ by the simulated null angle plot generated from the fitting results parameters obtained from polarization mapping. The first crossing point at $\sim 125^\circ$ is identified as a virtual null angle where the coincidental interference of resonant and non-resonant components forms an anti-symmetric spectral shape. Without this simulation based on previous fitting results, however, it is not clear to identify the two null angles from the experimental result plots of fitting in Figure 9 (b). Those results suggest that polarization null angle measurement alone is not an ideal method to deduce quantitative conclusions when there is non-resonant background interfering with resonant signal, and it should therefore be combined with other techniques for the pre-estimated value.

4.4. CN polarization mapping

For comparison with the methyl group, an SFG polarization map for the CN vibration is also measured and illustrated in Figure 10 (a). The SFG polarization mapping spectrum reveals a symmetric stretching resonance at around 2245 cm^{-1} . The shape and intensity of the CN vibration peak shows dramatic changes due to interference with the non-resonant component. The CN vibration resonance appears as a dip at 0° SFG polarization angle and its intensity gradually reduces showing null at 60° . The resonance gains intensity and reappears as a peak after 60° as the angle approaches 90° . The phase of the peak also changes from asymmetric at 0° to almost symmetric at 90° . In order to estimate tilt angle from the CN vibration and compare it with the result from the CH_3 vibration, the spectra were fitted and the polarization map has been reconstructed in Figure 10 (b). The initial fitting parameters, results and constraints used for defining peak position are summarized in Table 5. Detailed error analysis with convoluted orientation function using Gaussian tilt distribution is presented in Supporting Information. The fitting result shows an estimated amplitude ratio of $0.25 (\pm 0.20, 95\% \text{ confidence level})$, suggesting the average tilt orientation angle ranges from $\sim 28^\circ$ to $\sim 35^\circ$ as shown in Table 6.

Figure 10. SFG spectrum of the CN group for polarization mapping. (a) SFG signals are collected by varying SFG polarizer angle σ , while IR and visible beam polarization angles are fixed at 0° and 45° from p-polarization respectively. (b) Reconstructed polarization map from fitting result. No constraints are used for fitting.

Table 5. Fitting result for SFG polarization mapping of nitrile group measurement. Initial and estimated values for the parameters in Equation (17) are listed. No constraints are used for fitting. Detailed error analysis with convoluted orientation function using Gaussian tilt distribution is presented in Supporting Information.

Parameter	Initial	Estimate	Error (95% Confidence level)	Lower Limit	Upper Limit
A_{ppp}	2	1.5	0.19		
Υ	0.2	0.25	0.20		
Γ	8	4.7	0.66		
ω	2245	2246.0	0.63	2242	2246
N	0	-1.075	0.011		
Υ_n	-0.4	-0.286	0.015		
p	0	0.78	0.10		
c	0.3	0.402	0.010		
R^2		0.9926			

5. Conclusion

The delta-function distribution analysis for the tilt angle of acetonitrile on the TiO_2 (110) surface has been performed with the ratio of ssp and ppp effective susceptibilities obtained from fitting results of various SFG techniques. The resulting amplitude ratio parameters, γ , and the conclusive orientation tilt angle, θ , at 0° , 45° , and 90° of rotation angle, ϕ , of acetonitrile on the TiO_2 (110) surface as deduced from three different SFG techniques is summarized in Table 6.

The error ranges of the deduced tilt angle are fairly small in distinct polarization and polarization mapping method, while those are large in null angle method. Several factors contributing to the tilt angle error ranges are; (1) large fitting parameter error due to the experimental noise and insufficient number of data points, (2) inhomogeneity of surface molecules (orientation distribution) and substrate (terraces and defect sites), and (3) tilt angle sensitivity of the SFG geometry. It is generally accepted to assume that the orientation distribution of acetonitrile and the flatness of the TiO_2 (110) surface are the same in the three SFG measurement methods. As shown in Table 3, 4, and 6, however, the estimated parameter errors are large in the null angle method. The large range of estimated parameter errors in the null angle method yields the large uncertainty of deduced tilt angle. Controversially, the uncertainty of tilt angles (less than $\pm 1^\circ$) deduced from the distinct polarization and polarization mapping method are too small to consider them as an orientation distribution of acetonitrile, since even well-ordered monolayers such as self-assembled monolayers exhibit about 10° to 20° of tilt angle distribution.⁶⁴ In fact, the small uncertainty in the tilt angle obtained from distinct polarization and polarization mapping method is because the geometry of the SFG configuration leads to the loss of tilt angle sensitivity for the molecules perpendicular to the surface as shown in Figure 3 (a).

For the distinct polarization method, γ was predicted to be 1.42. Comparing γ^2 with the orientation curve in Figure 3, $\sim 33^\circ$, $\sim 32^\circ$, and $\sim 30^\circ$ tilt angles at 0° , 45° , and 90° rotation angles are deduced. This result obtained from the distinct polarization method shows good agreement with the tilt angles determined from polarization mapping, ranging from $\sim 32^\circ$ of tilt angle for $\phi=0^\circ$ and $\sim 29^\circ$ for $\phi=90^\circ$. The deduced deviation of tilt angle from fitting parameter error in both distinct polarization and polarization mapping analyses are fairly small. For null angle analysis, the orientation angles obtained from fitting with constraint and without constraint provide different results. When the constraint is used, the γ value is limited by the constraint and the tilt angle is estimated to be $\sim 34^\circ$, $\sim 32^\circ$, and $\sim 30^\circ$ at 0° , 45° , and 90° rotation angles, while the range of orientation angles calculated from fitting without constraint is far from these values (Table 6). The orientation of acetonitrile is also calculated from

polarization mapping of the CN group. The γ value of CN symmetric stretching vibration is estimated to be 0.25, corresponding to the average tilt angle of $\sim 28^\circ$, $\sim 31^\circ$, and $\sim 35^\circ$ at 0° , 45° , and 90° rotation angles.

From the simulation and experimental data analysis, it has been found that the SFG amplitude ratio factor, γ , for the methyl group alone, is not sensitive enough to deduce the rotation angle, ϕ . Even though SFG intensity ratio is insensitive to the rotation angle, it is possible to estimate the angle by comparing the methyl and nitrile groups. The tilt angles deduced from methyl and nitrile groups are close to each other at $\sim 30^\circ$ at a rotation angle of 45° (Table 6). The relationship of tilt angle and rotation angle is calculated using polarization mapping results for methyl and nitrile groups as presented in Figure 11. The two plots for the tilt angles estimated for the methyl and nitrile groups match at $\sim 30^\circ$ at a 45° rotation angle. Assuming it to be linear on the TiO_2 (110) surface, the average rotation angle of acetonitrile is predicted to be 45° or isotropic at room temperature. Even though this prediction is based on the average estimated fitting results and is inconclusive due to the large deviation in the CN orientation analysis, it is substantial to observe that the various analytical methods utilized with acetonitrile on TiO_2 (110) as a model system demonstrated in this paper, clearly shows a molecular orientation angle extracted from SFG spectra in the presence of a non-resonant background.

Figure 11. The relationship of tilt angle and rotation angle calculated using the polarization mapping results of the methyl (black solid line) and the nitrile (red dashed line) group.

Table 6. Tilt and rotation angle obtained from delta-distribution orientation analysis using the fitting parameters, Υ , for three different SFG techniques. Detailed error analysis with convoluted orientation function using Gaussian tilt distribution is presented in Supporting Information.

			Amp. Ratio	Int. ratio	Tilt angle (θ) at rotation angle (ϕ)		
			Υ	Υ^2	$\phi = 0^\circ$	$\phi = 45^\circ$	$\phi = 90^\circ$
CH ₃	Distinct polarization	Estimated	1.42	2.0	33.3°	31.7°	30.3°
		Pos. Error	+0.074	+0.2	-0.7°	-0.8°	-0.8°
		Neg. Error	-0.074	-0.2	+0.8°	+0.9°	+0.9°
	Polarization mapping	Estimated	1.55	2.4	31.9°	30.2°	28.8°
		Pos. Error	+0.070	+0.2	-0.6°	-0.6°	-0.6°
		Neg. Error	-0.070	-0.2	+0.7°	+0.7°	+0.7°
	Null angle (with constraint)	Estimated	1.40	1.96	33.5°	31.8°	30.4°
		Pos. Error	+2.47	+6.92	-10.0°	-10.0°	-9.98°
		Neg. Error	-2.47	-6.92	-	-	-
	Null angle (without constraint)	Estimated	1.00	1.0	39.1°	37.8°	36.7°
		Pos. Error	+2.83×10 ⁶	+5.66×10 ⁶	-	-	-
		Neg. Error	-2.83×10 ⁶	+5.66×10 ⁶	-	-	-
CN	Polarization mapping	Estimated	0.25	0.0625	27.6°	30.6°	34.7°
		Pos. Error	+0.20	+0.1	+17.6°	+17.3°	+16.4°
		Neg. Error	-0.20	-0.1	-27.6°	-30.6°	-34.7°

6. Summary

The theory and method are established to determine the orientation of adsorbate molecules on a semiconductor substrate and have been applied to deduce the orientation of acetonitrile on the TiO₂ (110) surface. SFG vibrational spectra have been measured in distinct polarization combination, polarization mapping, and null angle techniques. The series of data from each method is fitted using the master equation developed. From comparing the three methods, the result from distinct polarization combination and polarization mapping methods agree with each other, suggesting that the orientation of acetonitrile on the TiO₂ (110) possesses a tilt angle of ~30° while the rotation angle is predicted to be 45° or isotropic.

7. Acknowledgements

We gratefully thank the National Science Foundation (DMR-0856009) for providing generous support for this project. We also appreciate valuable discussions with Hongfei Wang (PNRL) and Tianquan Lian (Emory University).

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