Sum frequency generation vibrational spectroscopy (SFG-VS) for complex molecular surfaces and interfaces: spectral lineshape measurement and analysis plus some controversial issues

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Abstract

Sum-frequency generation vibrational spectroscopy (SFG-VS) was first developed in the 1980s and it has been proven a uniquely sensitive and surface/interface selective spectroscopic probe for characterization of the structure, conformation and dynamics of molecular surfaces and interfaces. In recent years, there have been many progresses in the development of methodology and instrumentation in the SFG-VS toolbox that has significantly broadened the application to complex molecular surfaces and interfaces. In this review, after presenting a unified view on the theory and methodology focusing on the SFG-VS spectral lineshape, as well as the new opportunities in SFG-VS applications with such developments, some of the controversial issues that have been puzzling the community are discussed. The aim of this review is to present to the researchers and students interested in molecular surfaces and interfacial sciences up-to-date perspectives complementary to the existing textbooks and reviews on SFG-VS.

Keywords

Sum-frequency generation vibrational spectroscopy; Surface selectivity; Surface nonlinear spectroscopy; Surfaces and interfaces; Molecular orientation; Dipole contribution; Phase-resolved SFG-VS; Chiral SFG-VS; Vibrational spectral lineshape; Bloch dynamics model.

1. Introduction

Surfaces and interfaces are the entity in between the two different phases of matter. They are ubiquitous in nature and man-made world, and they control and influence all the heterogeneous chemical and biological processes. Even though characterization and understanding of the structural properties and interactions of molecular surfaces and interfaces are in need for many scientifically and technologically important fields, since the surfaces and interfaces are only molecularly thin, and the molecular structure and conformation are usually significantly different from those in the isotropic bulk due to the asymmetric forces the molecules experience on the surfaces or at the interfaces, surfaces and interfaces

have been the most elusive subjects to be studied and understood at the molecular level [1]. Particularly, our understanding of the buried interfaces, such as the liquid/solid interface [2], has been even more limited. It is not an exaggeration to view surfaces and interfaces as among the last frontiers of our scientific endeavors towards the understanding of the physical and biological world. Venturing into such territories, unique tools, such as sum-frequency generation vibrational spectroscopy (SFG-VS), that can selectively make non-invasive and in-situ measurement on the surfaces and the interfaces, are required (Fig. 1).

Over the more than three decades since the inception of the surface SFG-VS in the early 1980s [3-5], there have been many review articles and a most recent monograph by the founder of the field [6] on the fundamentals theory [7-16], methods and technical developments [17-31], specific applications to various systems [32-55], and progresses reports [56-62] of SFG-VS on the studies of the structure and dynamics of various surfaces and interfaces. Instead of repeating what has been covered in the literature, this review aims to focus on the recent progresses and understandings that need to be summarized for the reference of the researchers and students, who are interested in the nonlinear vibrational spectroscopy of complex molecular surfaces and interfaces, by focusing on the new developments on the accurate measurement and analysis of SFG-VS spectral lineshape that is crucial for the applications to complex molecular surfaces and interfaces.

Figure 1 Broad applications of SFG-VS as a characterization tool for molecular level structure and dynamics information of molecular surfaces and interfaces in various fields of fundamental and applied studies. Molecular level characterization and understanding are the foundation for understand and control of surface and interfacial structures and properties that have been crucial and useful for many field of studies and applications.

SFG-VS is the coherent second-order nonlinear optical process where a signal at the frequency of the sum ($\omega = \omega_1 + \omega_2$) of a visible photon (ω_1) and an infrared (IR) photon (ω_2) is generated from the simultaneous interaction of the two photons with a nonlinear optical medium (Fig. 2a) [63]. When the two photons are with the same frequency and come from the same light beam, the process is called second harmonic generation (SHG). SFG-VS, as well as SHG, is intrinsically surface/interface selective because the symmetry requirements for the second order nonlinear optical processes dictate that the SFG-VS signal from the surface of an isotropic medium or the interface between two isotropic media is dominated by the surface or interfacial dipolar contributions [12]. The SFG and SHG processes are intrinsically weak, and even with intense IR and visible laser beams the resulted SFG signal is small. Typically with 10^{12} IR and visible photons, respectively, the SFG signal is only around the 10 photon level. However, since the SFG frequency is different from the frequencies of the intense IR and visible light, the SFG-VS process is essentially background free. With the development of the laser and sensitive photon detection technologies, SFG-VS spectra of the surface or interface with sub-monolayer coverage can be routinely achieved [5, 64-66]. By tuning the visible or IR frequencies, SFG-VS can be

used to probe the electronic and the vibrational spectra, respectively [67] (Fig. 2b), and to provide chemically specific information of the molecular surfaces or interfaces. From the signal intensity, and its frequency, polarization and time dependences, SFG-VS can be used to obtain quantitative information about the molecular (group) number density, molecular (group) orientation and conformation, molecular vibrational and electronic spectroscopy, and kinetics and dynamics of chemical changes and relaxations, etc. of molecular surfaces and interfaces.[31]. Therefore, SFG-VS is a unique spectroscopic tool for interrogating the structural and dynamic information of molecular surfaces and interfaces, and it has been applied to almost all kinds of molecular surfaces and interfaces that the visible and infrared lights can access [58, 68].

In the past three decades, SFG-VS has been proven a versatile spectroscopic technique for it is non-invasive or non-destructive, and it can be designed to make in-situ measurement. SFG-VS has been applied to almost all type of molecular surfaces and interfaces, including vapor/liquid, vapor/solid, liquid/liquid, liquid/solid and solid/solid, as well as nanoparticle surfaces and interfaces [44, 58, 69-71]. These include not only the exposed surfaces, i.e. vapor/liquid, vapor/solid, but also the buried interfaces, i.e. liquid/liquid, liquid/solid and solid/solid interfaces, which are usually inaccessible by many other non-optical surface characterization techniques. In recent years, spectroscopic imaging with SFG-VS has also made great advances [72, 73], adding new dimensions to the SFG-VS tool repertoires.

Figure 2 Illustration of the SFG-VS. (a) Showing the infrared (IR) and visible (Vis) beams incident in the same plane in a co-propagating geometry, with the SFG signal, the visible beam and the IR beam in the *ssp* polarization combination. The polarization of the optical field is defined as p polarization when the optical field vector is within the incident plane, and it is s polarization when the optical field is perpendicular to the incident plane. (b) Various types of SFG processes that can be used to study ground state vibrational spectra and electronic spectra of molecular surfaces and interfaces. Type a is called the IR-SFG-VS, the most common single resonance SFG-VS with only the IR frequency in resonance with the ground state vibrational transition of the molecule of interest; Type b is called the IR-Vis double resonance SFG-VS (IR-Vis SFG-VS), where the IR frequency is in resonance with the ground state and the visible is in resonance with the electronic resonance of the molecule; Type c is called the Vis-IR double resonance SFG-VS (Vis-IR DR-SFG-VS); and the Type d is the Vis-Vis SFG-VS.

Despite many developments on instrumentation and methodology on quantitative measurement and interpretation of the SFG data [13, 17, 18, 21, 29, 31, 64, 65], as well as many successes in applying SFG-VS to all different kind of surfaces and interfaces [62], the main limitations for its application to different complex molecular surfaces and interfaces have been the still limited abilities to make accurate and reliable measurement and to make quantitative analysis and interpretation of the SFG spectral data. Particularly, they are limited by the spectral resolution in the SFG-VS measurement [31, 65] that is required to obtain detailed spectral lineshape for dynamics and interactions for complex molecular surfaces and interfaces. Typically, many vibrational spectral features are $5\text{-}10\text{ cm}^{-1}$ broad and there are overlapping peaks in the SFG spectra due to similar vibrational groups under different chemical environment or with specific interactions. The commonly used picosecond scanning system with resolution of $\sim 6\text{ cm}^{-1}$ or the broadband SFG-VS systems with resolution of $\sim 15\text{ cm}^{-1}$ is far less ideal in accurate measurement of the spectral lineshape and to obtain detailed spectral information (Fig. 3). Even though the nanosecond scanning SFG-VS can achieve sub-wavenumber spectral resolution [74], but to obtain a spectral with such resolution by scanning is time-consuming, and the spectra quality is subject to the laser energy fluctuations and the stability of the laser pulse properties over time [65]. The recently developed sub-wavenumber high-resolution broadband SFG-VS (HR-BB-SFG-VS) with resolution as high as $\sim 0.6\text{ cm}^{-1}$ has shown to be an effective alternative to achieve high enough spectral resolution and obtain accurate lineshape for spectral analysis, and it has revealed many unprecedented

details of the molecular structure and interactions of molecular surfaces and interfaces [13, 31, 66, 75-79]. Particularly, spectral lineshape analysis in SFG-VS in the frequency domain has usually been neglected since the lower resolution measurement usually does not provide accurate enough data to allow such analysis. Therefore, these developments with broadband sub- 1cm^{-1} resolution SFG-VS have opened up new directions in using SFG-VS spectral lineshape to understand detailed structure and dynamics of complex molecular surfaces and interfaces. Here, the word complex refers to the two aspects of the structure, conformation and interaction of the intrinsically inhomogeneous surfaces or interfaces, that can be revealed with the new tool, i.e. the complex behaviors of the simple molecules, and the complex properties of the even more complex molecules, such as lipids, peptides and proteins, DNAs, as well other polymeric and biological macromolecules.

Figure 3 Typical SFG-VS spectral and time resolution using different laser systems. The most recent development is the sub wavenumber high-resolution broadband SFG-VS (HR-BB-SFG-VS) with which spectral resolution of $\sim 0.6\text{ cm}^{-1}$ has been achieved [13, 66], in comparison to the typical 6 cm^{-1} resolution with the picosecond scanning SFG-VS, and about typically $\sim 15\text{ cm}^{-1}$ resolution with the conventional broadband SFG-VS (BB-SFG-VS) [65]. Achieving ultimate spectral and time resolution is crucial in advancing SFG-VS studies on complex molecular surfaces and interfaces.

The key to achieve understanding of the complexities of the molecular surfaces and interfaces using SFG-VS, is to have a unified view on the SFG-VS as the quantitative probe to reveal the detailed structure and interactions of the complex molecular surfaces and interfaces. Previous quantitative SFG-VS studies have focused on the polarization dependence that can provide symmetry properties of the

vibrational transition of molecular groups for spectral assignment [21, 80-84], and for molecular orientation analysis [17, 31, 82, 85, 86]. Polarization dependence in SFG-VS was also used to study chiral structures and interfaces at molecular and biological surfaces and interfaces [27, 30, 31, 87-90]. Phase resolved SFG-VS was also used to study molecular orientational structures and interactions at liquid surfaces, particularly at the air/water interfaces [29, 52, 91-94]. There have been several well-cited review articles covering these aspects in SFG-VS [17, 21, 29-31] to be referred to, and these aspects are not repeated in this review.

Here in this review the unified view on SFG-VS will focus on the relationship between SFG-VS with other vibrational spectroscopy techniques such as IR absorption, Raman spectroscopy, and 2D-IR and 2D-SFG spectroscopy etc., and on the SFG-VS spectral lineshape unifying the frequency-domain and time-domain SFG-VS, as well as unifying the intensity and the phase-resolved SFG-VS. These shall provide a novel perspective on the understanding of SFG-VS not only as a unique spectroscopic tool for surface and interface studies, but also as the vibrational spectroscopy that interrogates the dynamics and interactions of molecules on surfaces and at interfaces. In addition, discussions on several controversial issues that often puzzle researchers and students in the field will follow. The overall aim here is to provide a complementary reference to the existing literature in order to help advance the quantitative studies on complex molecular surfaces and interfaces and to enable broad applications in materials, energy, industrial, environmental, and biological researches (Fig. 1).

2. Unified view on the SFG-VS spectral lineshape

Unlike in the two-dimensional infrared (2D-IR) studies, where spectral lineshape in both the frequency- and time- domains has been extensively discussed and investigated [95-98], the investigation on the spectral lineshape in the surface IR spectroscopy [99-101] has been limited, and in SFG-VS it has been particularly scarce. In SFG-VS it has only been gaining steam recently [13, 26, 31, 76, 78, 102-110].

The vibrational spectral lineshape contains the details of the microscopic dynamics, intermolecular couplings and time dependent behavior of the solvation that influences the energy of the vibrational transitions [98, 111, 112]. Therefore, it is essential to discuss the lineshape aspects in SFG-VS with the advances of the sub-wavenumber HR-BB-SFG-VS. Understanding of the SFG-VS spectral lineshape shall also put the more complicated 2D-SFG-VS studies on a solid base [28].

2.1 SFG-VS as a two-dimensional nonlinear spectroscopy

SFG-VS is already a two-dimensional nonlinear spectroscopy.

As shown in the Fig. 2b, the normal SFG-VS process is the product of an IR transition (with the transition dipole of $\frac{\partial \mu_k}{\partial Q_q} = \mu'_k$) associated with an anti-Stokes Raman process (with the Raman polarizability tensor of $\frac{\partial \alpha_{ij}}{\partial Q_q} = \alpha'_{ij}$) back to the same initial state [9, 113-115], whose tensorial molecular polarizability is,

$$\beta_{q,ijk}^{(2)} \propto \alpha'_{ij} \mu'_k \quad (1)$$

Here q denotes the q th vibrational mode, Q_q is the normal coordinate of the q th mode, and the indexes i, j, k each denotes one of the Descartes coordinates in the molecular frame. In comparison, in the 2D-IR processes, there are four IR transitions involved and as a third-order nonlinear process, one has [97],

$$\beta_{ijkl}^{(3)} \propto \mu'_i \mu'_j \mu'_k \mu'_l \quad (2)$$

Here the vibrational modes are not specified because these transitions do not need to belong to the same vibrational mode. When this happens, $\beta_{ijkl}^{(3)}$ measures the coupling between the different modes involved in the process. In 2D-SFG, one has [28],

$$\beta_{ijklm}^{(4)} \propto \alpha'_{ij} \mu'_k \mu'_l \mu'_m \quad (3)$$

Here the Raman tensor indexes can be ij , jk , kl or lm , and the indexes for the IR transition dipoles change accordingly.

One can now immediately see that SFG-VS (second order process) and 2D-SFG-VS (fourth order process) contain information of both the vibrational states and electronic states (through the Raman), while the IR (first order process) and 2D-IR (third order process) spectroscopy contain information of only the vibrational states in the ground states. Nevertheless, for the third order process, one can also have the so-called two-dimensional vibronic-electronic (or electronic-vibrational) spectroscopy (2D-VE or 2D-EV spectroscopy) [116], with,

$$\beta_{ijkl}^{(3)} \propto \alpha'_{ij} \mu'_k \mu'_l \quad (4)$$

In such a way, the third order spectroscopy can also probe both the vibrational and electronic states. These different spectroscopy techniques can be classified into three types: the IR only type, i.e. IR and 2D-IR, which probe only the vibrations in the electronic ground states; the Raman type, i.e. Raman spectroscopy; and the IR-Raman mixed type, i.e. SFG, 2D-SFG, 2D-VE and 2D-EV. With the Raman and IR-Raman mixed type, both the vibrational (in the ground or electronic excited states) and electronic states can be probed depending on whether there is electronic resonance. Just like the case for the 2D-VE and 2D-EV, there is also the IR-Vis Double Resonance SFG-VS (IV-DR-SFG-VS, or VE-DR-SFG-VS) and Vis-IR DR-SFG-VS (VI-DR-SFG-VS or EV-DR-SFG-VS) [117-119]. There is also another difference between these spectroscopic techniques, i.e. all the SFG-VS and 2D-SFG-VS techniques are surface/interface selective, an intrinsic property of all the even order (second and fourth order) processes, while all the others odd order (first and third order) processes are not surface/interface selective.

SFG-VS has usually been treated as a one-dimensional spectroscopy [28, 107]. This is true in the sense that either IR-Vis-DR-SFG or Vis-IR-DR-SFG are one dimensional for the vibrational and the electronic transitions, respectively. However, when one uses the DR-SFG to investigate the vibronic coupling, the DR-SFG is indeed a 2D spectroscopic technique [117]. Even though IR-IR-DR-SFG (or VV-DR-SFG)

process would be unlikely detectable due to the difficulty of detecting weak signal in the IR frequency, Vis-Vis DR-SFG-VS (or EE-DR-SFG) has been used to study electronic spectroscopy of molecules on surfaces or at interfaces [120-123]. It is therefore important to realize that SFG itself is a two-dimensional spectroscopic technique with surface/interface selectivity. While the other techniques usually called 2D are in the third or fourth order, such as the 2D-IR, 2D-VE, 2D-EV, 2D-ES, or 2D-SFG, are actually high-dimensional spectroscopy [110, 124, 125] in their degenerated 2D special cases. Most importantly, the 2D aspects of the IR-Vis, Vis-IR and Vis-Vis DR-SFG that can be used to study the vibrational-electronic (ground state vibration), electronic-vibrational (electronic vibration), and electronic-electronic couplings have yet to be explored and utilized in studying molecular systems on surfaces and at interfaces, such as optoelectronic thin films, etc. [126].

The complete descriptions of the polarizability tensors and their connections to the macroscopic measurement in experiment in the frequency- and time-domain for the second, third and fourth order nonlinear processes are often complicated and require efforts beyond the scope of this review. Nevertheless, through above discussions, one can see several aspects of SFG as a 2D nonlinear spectroscopy in addition to its surface/interface selectivity.

Firstly, SFG-VS contains information of both the IR vibrational transition and its coupling to the anti-Stokes Raman process. It is not a 1-D spectroscopy. Its treatment is therefore much more complicated than the IR or 2D-IR spectroscopy that involves the vibrations only in the electronic ground states. This contributes partially to the difficulty in calculating the SFG-VS spectra because not only to calculate the Raman tensors accurately is intrinsically difficult, but also the orientation structure and orientational distribution of the molecular surface has to be reliably calculated. Therefore, the computed SFG spectra are usually not as good as in agreement with the SFG experimental spectra, in comparison to the cases with the IR or 2D-IR spectra. In comparison, empirical treatment of the SFG signal assisted with the

molecular group symmetry and the Raman depolarization data has been more reliable in analyzing the SFG-VS data [21, 80, 81, 127-130].

Secondly, the application of DR-SFG-VS in exploring the vibrational-electronic coupling of molecules on surfaces and at interfaces shall find many important applications. Both the intramolecular and intermolecular vibrational-electronic couplings are expected to have strong dependence on the molecular orientations. Energy and charge transfer are directional and controlled by the detailed steric chemistry and interactions. Therefore, SFG-VS and SFG-ES have many advantages in obtaining information on the directional interactions and steric chemistry of molecules. In addition, comparing to the third order 2D-VE or 2D-EV spectroscopy whose molecular responses are described by the fourth rank tensors (Eq. 4), the molecular tensors for DR-SFG-VS are only third rank (Eq. 1), making the latter easier and more accurate to be experimentally determined and to be theoretically calculated.

Thirdly, one of the most important aspects of the multidimensional spectroscopy is its ability to measure the spectral lineshape through either frequency-domain or time-domain measurement, particularly the dynamic aspect of the spectral lineshape [95-97]. Such issues have not been a major subject of research in SFG-VS until very recently [104, 131]. In these SFG-VS studies, usually only the Bloch dynamics model is considered. The Bloch dynamics model relies on the assumption that the time scales of the homogeneous and the inhomogeneous broadening in the spectral lineshape can be strictly separated, i.e. the dynamic spectral diffusion is insignificant and can be neglected [95-97]. Otherwise, the more complicated Kubo lineshape model would take over [95-97, 111]. Even though in general in room temperature liquid phase, the Bloch dynamics usually fails to represent the vibrational dynamics of the system [98, 132-134], it has been known that at low temperature in the condensed phase, where molecular thermal motion are limited, the dynamic spectral diffusion is insignificant. Therefore, in such cases the Bloch assumption can give a reasonable description of the vibrational dynamics [112, 135, 136]. Molecules in the monolayer at the surfaces are usually packed and ordered with limited

orientational fluctuation and disorder [31, 76, 137]. Polarization SFG-VS measurement have shown that even the water molecules at the top-layer of the air/water interface is well-ordered [83, 138]. Recent HR-BB-SFG-VS also showed that for DMSO (dimethyl sulfoxide) at the air/DMSO interface, the two methyl groups of the DMSO molecule assumed different orientations, suggesting the structure fluctuation of the DMSO molecules at the interface is much slower than commonly expected [66, 75]. Direct experimental measurement using ultrafast 2D vibrational echoes also showed that the spectral diffusion is indeed much slower and much more insignificant in the molecular monolayer in comparison to that in the bulk liquid [133, 134]. Therefore, in the treatment of the surface vibrational spectral lineshape, the Bloch dynamics is usually a reasonable approximation of the surface vibrational dynamics, particularly for well packed molecular monolayers [61, 100, 101, 139]. Thus, the vibrational spectral lineshape based on Bloch dynamics model will be explicitly discussed along with the development of the HR-BB-SFG-VS in this review. However, spectral diffusion might be significant for interfacial species, particularly water species at aqueous interfaces [140, 141], and the explorations of the higher order SFG-VS spectroscopy, such as 2D-SFG-VS, are important and shall bring in new details of the surface spectral lineshape and dynamics of the surface interactions [26, 28, 107, 137, 142].

In short, in addition to understanding and utilizing the uniqueness of the surface/interface selectivity of SFG-VS, it is also useful and helpful to put SFG-VS in the context of a unified view with other vibrational spectroscopies. In such a way, concepts, techniques and methodologies developed in other multidimensional nonlinear spectroscopy can be borrowed and utilized to advance SFG-VS studies, as it has been making exciting advances in recent years [26, 28, 107, 137].

2.2 Unified treatment of frequency- and time- domain SFG-VS

Vibrational spectral lineshape analysis on the spectral frequencies, frequency shifts, linewidth and lineshape changes, degeneracy and frequency splitting, etc. is powerful tool for understanding molecular

dynamics and interactions in the condensed phases and surfaces. In order to understand the dynamic information from frequency-domain spectral measurement, a unified treatment of frequency-domain and time-domain lineshapes of SFG-VS is necessary. In principle of all spectroscopy, the time-domain and the frequency domain response function are equivalent to each other and are connected through a time-frequency Fourier transformation. Here we only discuss the case for single resonance IR-Vis SFG-VS, the cases for DR-SFG-VS can be extended accordingly with additional considerations of the double-resonance processes.

For SFG-VS, the SFG emitting field in the time domain is proportional to the time-dependent SFG polarization $P^{(2)}(t; \tau)$ [13, 26, 103, 106],

$$P^{(2)}(t; \tau) = \int_0^\infty dt_2 \int_0^\infty \chi^{(2)}(t_2, t_1; \tau) E_{vis}(t - t_2) E_{IR}(t - t_2 - t_1) dt_1 \quad (5)$$

Here $\chi^{(2)}(t)$ is the time-dependent SFG response function of the molecular surface/interface, $E_{vis}(t)$ and $E_{IR}(t)$ are the local electric fields of the visible and IR laser lights interacting with the molecular system. $P^{(2)}(t)$ depends parametrically on τ , the time delay between the arrival of the IR and VIS pulses. t_1 and t_2 are the integral variables of the IR and visible light-matter interaction time, respectively.

Upon the excitation by the IR pulse in the SFG-VS process, the molecular system starts a slower vibrational coherence evolution of all the molecular vibrational states being excited, and the Raman process as the result of the interaction with the visible light is instantaneous [13, 26]. Thus,

$$P^{(2)}(t; \tau) = E_{vis}(t; \tau) \left[\chi^{(2)}(t) \otimes E_{IR}(t) \right] \quad (6)$$

in which $\otimes$ is the convolution operator. One can see below, the instantaneous response of the molecular system to the action of the visible light makes the frequency-domain measurement much more advantageous. As the Fourier transformation of the time-domain polarization $P^{(2)}(t; \tau)$, the frequency domain SFG polarization $\tilde{P}^{(2)}(\omega_{SF}; \tau)$ is,

$$\tilde{P}^{(2)}(\omega_{SF}; \tau) = \tilde{E}_{vis}(\omega_{vis}; \tau) \otimes \left[\chi^{(2)}(\omega_{SF}) \tilde{E}_{IR}(\omega_{IR}) \right] \quad (7)$$

Here $\omega_{SF} = \omega_{vis} + \omega_{IR}$ is the sum-frequency of the visible and IR frequencies, $\tilde{E}_{vis}(\omega_{vis}; \tau)$ and $\tilde{E}_{IR}(\omega_{IR})$ are the corresponding visible and IR optical field in the frequency domain representation, respectively. The tilde symbol ‘~’ indicates that the field is a function of frequency, and τ is the parameter representing the time delay between the visible and the IR fields. Using the Fourier transform convolution theorem, the convolution in the time-domain becomes a direct product in the frequency domain, and *vice versa*.

Most importantly, in the frequency-domain, the IR field no longer convolutes with the response function $\chi^{(2)}(\omega_{SF})$. Consequently, if $\tilde{E}_{vis}(\omega_{vis}; \tau) = E_{vis}(\omega_{vis}; \tau) \delta(\omega)$, i.e. if the visible light is narrow in frequency, one has

$$\tilde{E}_{vis}(\omega_{vis}; \tau) \otimes \left[\chi^{(2)}(\omega_{SF}) \tilde{E}_{IR}(\omega_{IR}) \right] = \chi^{(2)}(\omega_{SF}) E_{vis}(\omega_{vis}, \tau) \tilde{E}_{IR}(\omega_{IR}) \quad (8.1)$$

or,

$$\begin{aligned} I_{SFG}(\omega_{SF}; \tau) &\propto \left| \tilde{P}^{(2)}(\omega_{SF}; \tau) \right|^2 \\ &= \left| \tilde{E}_{vis}(\omega_{vis}; \tau) \otimes \left[\chi^{(2)}(\omega_{SF}) \tilde{E}_{IR}(\omega_{IR}) \right] \right|^2 \\ &= \left| \chi^{(2)}(\omega_{SF}) \right|^2 \left| E_{vis}(\omega_{vis}; \tau) \tilde{E}_{IR}(\omega_{IR}) \right|^2 \\ &= \left| \chi^{(2)}(\omega_{SF}) \right|^2 I(\omega_{vis}) \tilde{I}(\omega_{IR}) \end{aligned} \quad (8.2)$$

Here the parameter τ can be dropped since the visible pulse so narrow in frequency is so broad in time that the overall functional form no longer depends on the delay between the visible and IR pulses. Eq. 8.2 means that if the IR laser pulse is broad and its frequency intensity profile $\tilde{I}(\omega_{IR})$ can be accurately known, from the measured SFG intensity $I_{SFG}(\omega_{SF}; \tau)$, the intensity of the response function $\left| \chi^{(2)}(\omega_{SF}) \right|^2$ in the frequency-domain can be accurately determined. This is the whole physical basis for the high-resolution broadband SFG-VS (HR-BB-SFG-VS) that has been achieved recently [13, 66, 76]. On the other hand, if $\tilde{E}_{vis}(\omega_{vis}; \tau) = E_{vis}(\omega_{vis}; \tau) \delta(\omega)$ is not satisfied, i.e. the fixed visible frequency is not narrow

enough, then the convolution operator ($\otimes$) in Eq. 7 cannot become a simple product as in the Eq. 8.1. This suggests that the accurate measurement of the response function $\left| \chi^{(2)}(\omega_{SF}) \right|^2$ in the frequency-domain cannot be achieved directly under such condition.

However, if both the visible and the IR pulse have finite widths, and the IR frequency needs to be scanned to obtain the SFG-VS spectrum. Then the scanning SFG-VS spectra is [143],

$$I_{SFG}(\omega_{SF}; \tau) \propto \left| \sum_{\omega_{IR, start}}^{\omega_{IR, end}} \tilde{E}_{vis}(\omega_{vis}; \tau) \otimes \left[\chi^{(2)}(\omega_{vis} + \omega_{IR}) \tilde{E}_{IR}(\omega_{IR}) \right] \right|^2 \quad (9)$$

$$= \left| \tilde{E}_{vis}(\omega_{vis}; \tau) \otimes \left[\chi^{(2)}(\omega_{vis} + \omega_{IR}) \otimes \tilde{E}_{IR}(\omega_{IR}) \right] \right|^2$$

Here in obtaining Eq. 9, one assumes that the laser profile of each scanning IR frequency is identical. Eq. 9 suggests that the measured SFG-VS spectra are double convolution function with both the visible and the IR laser pulse profiles in the scanning SFG-VS.

The above discussion is general and not limited to specific spectral lineshape model. The discussion below is limited to the Bloch dynamics model of the vibrational spectral lineshape as the reason mentioned in Section 2.1.

The vibrational coherence of the intrinsic time-domain response function $\chi^{(2)}(t)$ can be well approximated by its linear and quadratic terms in the solution to the optical Bloch equations [13, 26, 95, 97]. One has,

$$\chi^{(2)}(t) = |A_{NR}| e^{i\omega_{NR}t} \delta(t) - i\theta(t) \sum_q A_q e^{-i\omega_q t} e^{-t/T_{2q}} e^{-\Delta\omega_q^2 t^2 / 2} \quad (10.1)$$

Here, ω_q is the resonance frequency of the q th mode in angular frequency unit, T_{2q} is the homogeneous broadening parameter (linear coherence term) and $\Delta\omega_q$ is the inhomogeneous dephasing (quadratic coherence term) parameter for the q th mode. To connect to the commonly used spectroscopic values, one has $\omega_q = 2\pi c \tilde{\nu}_q$ and $\Delta\omega_q = 2\pi c \delta \tilde{\nu}_q$, where $\tilde{\nu}_q$ is the q th vibrational mode frequency in

wavenumbers and c the speed of light in cm s^{-1} . A_{NR} and ψ_{NR} are the amplitude and phase of the non-resonant term. $\delta(t)$ is the δ -function at the zero IR excitation time, and $\theta(t)$ is the step Heaviside function introduced by the causality of the IR interaction.

Accordingly, the frequency domain response function $\chi^{(2)}(\omega_{SF})$ is the Fourier transformation of $\chi^{(2)}(t)$, as

$$\begin{aligned}\chi^{(2)}(\omega_{IR}) &= |A_{NR}| e^{i\psi_{NR}} + \sum_q \frac{A_q}{\omega_q - \omega_{IR} - i\Gamma_q} \otimes e^{-\frac{\omega_{IR}^2}{2\Delta\omega_q^2}} \\ &= |A_{NR}| e^{i\psi_{NR}} + \sum_q \int_0^\infty \frac{A_q}{\omega_q - \omega' - i\Gamma_q} e^{-\frac{(\omega_{IR} - \omega')^2}{2\Delta\omega_q^2}} d\omega'\end{aligned}\quad (10.2)$$

Here, the variable ω_{SF} is replace by ω_{IR} because as the visible frequency ω_{vis} in SFG-VS is usually fixed, the change of ω_{SF} is the same as the change of ω_{IR} . The lineshape in eq. 10.2 is called the Voigt lineshape, which is the result of convolution with a Lorentzian lineshape, i.e. the homogeneous lineshape from the linear coherence term, and a Gaussian lineshape, i.e. the inhomogeneous lineshape from the quadratic coherence term.

Thus, Eqs. 10.1 and 10.2 are the unified descriptions of the SFG response in the time- and frequency-domains, respectively. Since the molecular parameters in Equations 10.1 and 10.2 are identical, accurate determination of either the $\chi^{(2)}(\omega_{SF})$ or the $\chi^{(2)}(t)$ provides completely the same information of the molecular system. As discussed above, $\chi^{(2)}(\omega_{SF})$ or $|\chi^{(2)}(\omega_{SF})|^2$ can be accurately obtained from the frequency-domain SFG-VS experiment as long as the visible pulse is spectrally narrow.

Therefore, the unified treatment of the frequency-domain and time-domain SFG-VS provided the theoretical foundation for the high-resolution broadband SFG-VS (HR-BB-SFG-VS) that has been achieved for the first time in 2011 [66].

2.3 Sub-1 cm⁻¹ high-resolution broadband SFG-VS (HR-BB-SFG-VS)

In 2011, a sub-wavenumber resolution high-resolution broadband SFG-VS (HR-BB-SFG-VS) spectrometer was constructed by synchronization of an 90 ps visible laser pulse at 800nm with a FWHM (full width at half maximum) about 0.25cm⁻¹ width and a sub 100 femtosecond (fs) broadband infrared (IR) pulse with a typical FWHM about 270cm⁻¹. Using a 750mm spectrograph and detected with a EM-CCD, the spectral resolution of 0.6 cm⁻¹ was achieved [66].

HR-BB-SFG-VS operates on the same broadband mode as the conventional BB-SFG-VS [64] except that its visible (near IR at ~800nm) pulse is much longer in time and much narrower in bandwidth. The 90 ps visible pulse used in this HR-BB-SFG-VS is not only narrow in frequency, it is a 1000 time longer in time than the sub 100fs IR pulse. Therefore, it can usually cover the whole vibrational coherence of the molecular system initiated by the short IR pulse. When there are closely overlapping peaks, the vibrational coherence can be as long as several tenth of picosecond. It is the vibrational coherence of the molecular the visible pulse is probing, not the short IR pulse that initiates the coherence [13]. While in the conventional BB-SFG-VS, the visible (near IR at ~800nm) pulse is usually 1- 4 ps, it is usually not long enough to cover the whole molecular vibrational coherence created by the short IR pulse, causing distortions in the final spectra and lower resolution.

With spectral resolution as small as 0.6 cm⁻¹, the instrument broadening of the SFG vibrational spectra is small. For example, for a peak with FWHM of 5 cm⁻¹, the instrumental broadening is about 0.08 cm⁻¹; for a peak with FWHM of 10 cm⁻¹, the instrumental broadening is merely 0.04 cm⁻¹ [31]. These values are way below the experimental uncertainty, and it has minimum distortion on the spectral lineshape. In contrast, with a spectral resolution of 6cm⁻¹ which is the typical spectral resolution of the picosecond scanning system in literature [17, 80], the 5cm⁻¹ peak will be broadened by 4.1 cm⁻¹, and a 10cm⁻¹ peak will be broadened by 2.9 cm⁻¹ [31]. While with a spectral resolution of 15cm⁻¹, typical resolution for the

conventional BB-SFG-VS system, the 5 cm^{-1} peak will be broadened by 12.9 cm^{-1} , and a 10 cm^{-1} peak will be broadened by 11.0 cm^{-1} [31].

It is necessary to know how to quantitatively evaluate the experimental lineshape deviation from the intrinsic spectral lineshape by the instrumentation function. Eq. 11 gives the simple formula with an accuracy of 0.02% on the spectral width and it can be used to evaluate the measured Voigt linewidth ($\text{FWHM} = \Delta\nu_V$) from a peak with a typical Lorentzian lineshape ($\text{FWHM} = \Delta\nu_L = 2\Gamma_q$) measured by a laser pulse with a typical instrumental response function of a Gaussian spectral profile ($\text{FWHM} = \Delta\nu_I$) [13, 144].

$$\Delta\nu_V = 0.5346\Delta\nu_L + \sqrt{0.2166(\Delta\nu_L)^2 + (\Delta\nu_I)^2} \quad (11)$$

For BB-SFG-VS, the instrumental width $\Delta\nu_I$ is determined only by the measured visible linewidth $\Delta\nu_{vis}$. However, for scanning SFG, it is easy to derive from Eq. 9 that $(\Delta\nu_I)^2 = (\Delta\nu_{vis})^2 + (\Delta\nu_{IR})^2$ [77, 109]. If the intrinsic spectral lineshape also has a Gaussian component with FWHM of $\Delta\nu_G$, then the term $(\Delta\nu_I)^2$ in Eq. 11 should be replaced by $(\Delta\nu_G)^2 + (\Delta\nu_I)^2$.

Figure 4 Comparison of C-H region ssp polarization combination spectra of the air/DMSO (Dimethyl sulfoxide) interface with HR-BB-SFG-VS (spectral resolution 0.6 cm^{-1}) (red), and with the conventional BB-SFG-VS (spectral resolution 14.7 cm^{-1}) (Blue). The experimental visible incident angle is 65° and the IR incident angle is 55° . The FWHM of the strongest 2920 cm^{-1} peak is 8.6 cm^{-1} with the HR-BB-SFG-VS, and its FWHM is 22 cm^{-1} with the conventional BB-SFG-VS. The instrumental broadenings are consistent with Eq. 11.

Figure 4 presents the comparison of the SFG-VS spectra of the air/DMSO (dimethyl sulfoxide) interface in the 2800-3050 cm^{-1} region. The strongest peak at 2920 cm^{-1} belongs to the CH_3 symmetric stretching vibrational modes. With HR-BB-SFG-VS (0.6 cm^{-1} spectral resolution), the FWHM of this peak is 8.6 cm^{-1} ; while with conventional BB-SFG-VS (14.7 cm^{-1} spectral resolution), the FWHM is about 22 cm^{-1} . Calculation using $\Delta\nu_L = 8.6 \text{ cm}^{-1}$ and $\Delta\nu_I = 14.7 \text{ cm}^{-1}$ gives $\Delta\nu_V = 20 \text{ cm}^{-1}$, which is in good agreement with the measured FWHM value of 22 cm^{-1} . One can also notice that the spectrum with the conventional BB-SFG-VS is much broader than the HR-BB-SFG-VS spectra, and its lineshape is also with much higher noise.

With the sub-1 cm^{-1} HR-BB-SFG-VS, the 2920 cm^{-1} peak of the air/DMSO interface turned out to be not a much narrower single peak, but consists of two peaks closely overlapping with each other [66]. This surprising secret was revealed by measuring both the ssp and ppp polarization combination spectra under two sets of experimental configurations, i.e. Configuration I with the visible incident angle at 65° and IR incident angle at 55°, and Configuration II with visible angle at 45° and IR angle at 55° (Fig. 5). In Configuration I (Fig. 5a), the FWHM of the 2920 cm^{-1} peak of the ssp spectrum is almost twice of the FWHM of the ppp spectra, suggesting existence of at least two peaks separated by about 2.8 cm^{-1} from each other underneath this 2920 cm^{-1} peak; while in Configuration II, the FWHM is almost identical for the ssp and ppp spectra. All the intensity changes in the ssp and ppp spectra under the two configurations can be quantitatively understand with the picture that the two methyl groups of each DMSO molecule are with different tilt angles at the interface, and the difference in their local interactions resulted in spectral splitting, and different spectral phases in the ppp polarization. The ppp spectral peak is narrower in configuration I because the two spectral peaks happened to be with opposite phases, resulted in a weaker and narrower peak through destructive interference. While under Configuration II, the two peaks in the ppp polarization are in phase, and through constructive

interference the peak is not only stronger, but is also as broad as that of the ssp spectra under the two configurations.

This HR-BB-SFG-VS study on air/DMSO interface benchmarked the importance of almost all the elements that have ever been discussed in SFG-VS measurement and data analysis in the literature: spectral resolution, polarization dependence, visible incident angle dependence, spectral phase, spectral interference, molecular orientation, inhomogeneity and asymmetry at the molecular interface, etc. It also provided an explicit example for the complex behaviors of simple molecules at interface. One has to realize that the spectral phase that is associated to the molecular orientation is a unique property for the second order nonlinear spectroscopy, as the susceptibility tensor elements are pseudo scalars [63, 145]. Therefore, such spectral resolving power is unique to the SFG-VS and other even order nonlinear spectroscopy, and they should find future applications in resolving overlapping spectral peaks. In such applications the accuracy in the spectral lineshape measurement is essential as such spectral interference due to spectral phase can only be revealed by capturing the detailed differences in the SFG-VS spectral lineshape under different measurement conditions.

The fact that the narrow spectral feature contains two closely overlapping peaks distinctive from each other is crucially important in understand the dynamics of the DMSO molecule at the air/DMSO liquid interface. It implies that the spectral diffusion dynamics of the DMSO vibrations is long and can be neglected. Such dynamics at the liquid interface is significantly different from that of the DMSO in the bulk DMSO aqueous solution mixtures, where solvent fluctuation and dynamics spectral diffusion dynamics is much faster and no such closely overlapping of the distinctive spectral peaks is expected [146, 147]. This also implies that the spectral resolution and the additional spectral resolving ability of the HR-BB-SFG-VS are essential in understand the inhomogeneities and the dynamics of the molecular surfaces/interfaces. Such inhomogeneities are unique to the molecular surface/interface as it is intrinsically anisotropic, while the bulk liquid is usually isotropic. The interpretation of the structure and

dynamics of the molecular surface/interface can only be reliably based on the knowledge of whether the apparent peak is one peak or the result of separate peaks closely overlapping with each other due to such surface/interface inhomogeneities [26, 134]. Therefore, additional cautions need to be taken in comparing the structure and dynamics of the molecular surface/interface with that of the molecular liquid.

The spectral resolving power of the sub-1 cm^{-1} HR-BB-SFG-VS was further demonstrated with several other benchmark systems of complex molecules and many overlapping spectral peaks. For cholesterol at the air/water interface, twelve peaks were unambiguously resolved in the C-H stretching vibration region using the sub-1 cm^{-1} HR-BB-SFG-VS, and the peak position and width parameters were used to successfully predict the time dependent SFG-VS spectra with conventional BB-SFG-VS [13]. This work also quantitatively confirmed the unified treatment of SFG-VS in the frequency and time domains as described above. For α -pinene, one of the most abundant monoterpene hydrocarbon molecules emitted by trees in the forest and one of the major source of secondary organic aerosols (SOA), ten spectral peaks were resolved from its HR-BB-SFG-VS spectra on solid substrate surfaces [77]. For limonene, an isomer of α -pinene, also an important SOA source, the achiral and chiral spectra of the chiral liquid surfaces for the two limonene enantiomers were quantitatively measured and analyzed. The results helped to develop the concept and experimental methodology to study intrinsic chirality and prochirality of chiral molecules on surfaces. It was also found that the two limonene enantiomers are actually not mirror image to each other on the liquid surfaces [90].

Figure 5 HR-BB-SFG-VS resolves two closely overlapping peaks in the 2920 cm^{-1} peak of the air/DMSO interface. Even though this peak looks like a single peak, the narrower and weaker spectral lineshape in the ppp polarization under Configuration I unambiguously suggests it is the result of two peaks with opposite spectral phases. Fig. from Ref. [66].

These studies not only validated the unified treatment described above, but also demonstrated how the HR-BB-SFG-VS can take the SFG-VS quantitative measurement and analysis to a new level. All these progresses have demonstrated that the sub-1 cm^{-1} HR-BB-SFG-VS is ready for applications to studying complex structures and interactions of the molecular surfaces and interfaces.

2.4 Spectral lineshape in intensity and phase-resolved SFG-VS

With the unified treatment of SFG-VS lineshape in both the frequency- and time-domains and the development of the sub-1 cm^{-1} HR-BB-SFG-VS, one not only can obtain SFG-VS spectra with accurate lineshape, but also can make detailed lineshape analysis to understand much more on the molecular dynamics and interactions of the molecular surfaces and interfaces. These studies also reveal novel understanding and applications of the SFG-VS spectral lineshape.

Figure 6 Left panel: HR-BB-SFG-VS spectra of the -CN group of the 4-n-octyl-4'-cyanobiphenyl (8CB) Langmuir monolayer at the air/water interface, and lineshape analysis with Eq. 10.2 in capturing the Lorentzian and Gaussian lineshape parameters. Right panel: Time dependent FID-SFG measurement on the same vibration and the lineshape analysis with Eq. 10.1. The quantitative agreement between the two analyses is the first direct demonstration of the equivalency of the frequency-domain and time-domain lineshape as discussed in Section 2.1. Both figures are from Ref. [76].

The marked advantage of the sub-1 cm^{-1} HR-BB-SFG-VS-VS in obtaining SFG-VS spectra with accurate lineshape for coherent vibrational dynamics was demonstrated with the measurement of the stretching vibration of the -CN group of the 4-n-octyl-4'-cyanobiphenyl (8CB) Langmuir monolayer at the air/water interface [76]. In this study, the homogeneous and inhomogeneous broadening parameters of the -CN group peak at $\omega_0 = 2234.00 \pm 0.01 \text{ cm}^{-1}$, i.e. $\Gamma_0 = 2.35 \pm 0.18 \text{ cm}^{-1}$ and $\Delta\omega = 3.45 \pm 0.09 \text{ cm}^{-1}$, respectively, were accurately determined from the HR-BB-SFG-VS spectra in the frequency domain, and these results were also quantitatively in agreement with the results of the free-induction decay (FID) SFG measurement in the time-domain, i.e. $\Gamma_0 = 2.1 \pm 0.2 \text{ cm}^{-1}$ and $\Delta\omega = 3.36 \pm 0.14 \text{ cm}^{-1}$, respectively. The frequency-domain measurement was not only able to accurately determine the spectral peak position that the time-domain FID-SFG measurement does not

have, experimentally it was also much easier to make the HR-BB-SFG-VS spectral measurement than doing the FID. This work was the first example that quantitatively demonstrated the equivalency of the frequency-domain and time-domain measurements in SFG-VS.

Further investigation on the SFG-VS spectral lineshape using the stretching vibration of the -CN group of the 4-n-octyl-4'-cyanobiphenyl (8CB) molecule as the benchmark system reveals unique connections between the spectral lineshape of the intensity and phase resolved SFG-VS [78]. It has been known that the phase-resolved SFG-VS measures the imaginary component of the SFG susceptibility of the molecular surface/interface, and it is advantageous in directly obtaining the unambiguous absolute spectral phase information that is present in the SFG field and is usually lost in the SFG intensity [29]. It has been known that for the air/water interface, the phase-resolved SFG-VS and the intensity SFG-VS does not always give consistent information [29, 148-152]. Those controversies will be discussed in Section 3.3 below. Nevertheless, the understanding of the connections and differences between the spectral lineshape of the phase-resolved and intensity SFG-VS is a fundamental issue.

According to Eq. 10.2, the spectral lineshape function for a single vibrational peak of the imaginary spectrum (phase-resolved) is,

$$\begin{aligned}\text{Im } R^{(2)}(\omega_{IR}) &= \text{Im} \left(\frac{A_q}{(\omega_q - \omega_{IR}) - i\Gamma_q} \otimes e^{-\frac{\omega_{IR}^2}{2\Delta\omega_q^2}} \right) \\ &= \frac{A_q \cdot \Gamma_q}{(\omega_q - \omega_{IR})^2 + \Gamma_q^2} \otimes e^{-\frac{\omega_{IR}^2}{2\Delta\omega_q^2}}\end{aligned}\tag{12.1}$$

and the lineshape function for the intensity spectrum is,

$$\begin{aligned}|R^{(2)}(\omega_{IR})|^2 &= \left| \frac{A_q}{(\omega_q - \omega_{IR}) - i\Gamma_q} \otimes e^{-\frac{\omega_{IR}^2}{2\Delta\omega_q^2}} \right|^2 \\ &= |\text{Im } R^{(2)}(\omega_{IR})|^2 + |\text{Re } R^{(2)}(\omega_{IR})|^2\end{aligned}\tag{12.2}$$

It is known that if $\Delta\omega_q = 0$, i.e. there is no inhomogeneous broadening in the spectral lineshape, both the $\text{Im} R^{(2)}(\omega_{IR})$ and $|R^{(2)}(\omega_{IR})|^2$ lineshapes are pure Lorentzian, and they have the same normalized form with the expression of $1/(1+(\omega_q - \omega_{IR})^2/\Gamma_q^2)$. The phase-resolved and the intensity spectral lineshape are identical. However, when $\Delta\omega_q \neq 0$, the normalized $|R^{(2)}(\omega_{IR})|^2$ lineshape is always broader than that of the $\text{Im} R^{(2)}(\omega_{IR})$. In this case, the lineshape for $\text{Im} R^{(2)}(\omega_{IR})$ is the standard Voigt lineshape function (Eq. 12.1), while the lineshape for the $|R^{(2)}(\omega_{IR})|^2$ is the square modulus of the complex Voigt lineshape function (Eq. 12.2). It turned out that the difference of the FWHM between the two lineshapes can be quantitatively evaluated by using the following dimensionless parameters, i.e. $d = \frac{\Delta\nu_{1/2}^L - \Delta\nu_{1/2}^G}{\Delta\nu_{1/2}^L + \Delta\nu_{1/2}^G}$,

denoting the relative contribution of the Lorentzian and Gaussian FWHM in the lineshape, and

$R_V = \frac{\Delta\nu_{1/2}^{V^{Im}} - \Delta\nu_{1/2}^{V^{Im}}}{\Delta\nu_{1/2}^{V^{Im}}}$, denoting the relative differences of the FWHM of the intensity lineshape function

$|R^{(2)}(\omega_{IR})|^2$ from that of the phase resolved lineshape function $\text{Im} R^{(2)}(\omega_{IR})$ [78]. The R vs. d plot is in Fig. 7 [78]. Also in Fig. 7 are the HR-BB-SFG-VS measurements on the imaginary and intensity spectra of the stretching vibration of the -CN group of the 4-n-octyl-4'-cyanobiphenyl (8CB) Langmuir-Blodgett monolayer on z-cut α -quartz crystal surface.

Fitting the spectra gives $\omega_0 = 2238.00 \pm 0.02 \text{ cm}^{-1}$ with the homogeneous FWHM of $\Delta\nu_{1/2}^L = 2\Gamma_0 = 10.6 \pm 0.1 \text{ cm}^{-1}$ and the inhomogeneous FWHM of $\Delta\nu_{1/2}^G = 2.35482\Delta\omega_0 = 12.8 \pm 0.1 \text{ cm}^{-1}$, making the dimensionless parameter $d = 0.094 \pm 0.002$. The measured FWHM values for the imaginary and intensity spectra are $\Delta\nu_{1/2}^{V^{Im}} = 19.2 \pm 0.2 \text{ cm}^{-1}$ and $\Delta\nu_{1/2}^{V^{Im}} = 21.6 \pm 0.4 \text{ cm}^{-1}$, respectively, making $R_V = 0.125 \pm 0.003$. According to the R vs. d plot in Fig. 7, when $d = 0.094$, one has $R_V \sim 0.11$. Therefore, the experimental measurement on the homogeneous and inhomogeneous parameters, as well

as the differences between the FWHM values of the imaginary and intensity spectra agree with each other quite well [78].

Figure 7. Left panel: Calculated FWHM difference parameter R between the normalized imaginary and intensity Voigt lineshapes as a function of the normalized Lorentzian and Gaussian FWHM parameter d . When the imaginary lineshape is pure Lorentzian $d = 1$, and when $d = -1$ the imaginary lineshape is pure Gaussian, which in general does not exist in the real spectra. Right panel: Comparison of the imaginary spectral lineshape and the intensity spectral lineshape of the stretching vibration of the -CN group of the 4-n-octyl-4'-cyanobiphenyl (8CB) Langmuir-Blodgett monolayer on z-cut α -quartz crystal surface. Figures are from Ref. [78].

There are several things that can be learned from the R vs. d plot in Fig. 7.

Firstly, when there is no inhomogeneous broadening, i.e. $d = 1$, the intensity and phase-resolved imaginary spectra are all with the same Lorentzian lineshape.

Secondly, when there is homogeneous broadening, i.e. $-1 < d < 1$, the intensity spectral lineshape is always broader than the imaginary spectra. When the Lorentzian and Gaussian widths are comparable, the intensity spectral lineshape is about 10% broader than that of the imaginary spectrum. When Gaussian width is dominant, the intensity spectral lineshape can be 20% broader.

Thirdly, the discontinuity point at $d = -1$ suggests that there is no such thing as pure Gaussian lineshape, no matter how dominant the Gaussian contribution is to the overall lineshape. However, one cannot tell this from the imaginary spectral lineshape, as the $\text{Im} R^{(2)}(\omega_{IR})$ function (Eq. 12.1) is indeed indistinguishable from the Gaussian function when the Gaussian contribution is dominant. While the

$|R^{(2)}(\omega_{IR})|^2$ function (Eq. 12.2) always deviates significantly from the Gaussian function as long as there is a tiny trace of Lorentzian contribution and the convolution shall make the $|R^{(2)}(\omega_{IR})|^2$ lineshape significantly broader than that of the $\text{Im } R^{(2)}(\omega_{IR})$ lineshape. This suggests that the SFG-VS intensity spectrum does contain additional information to the imaginary spectrum [78]. This last point has been overlooked before, as the lineshape of the intensity SFG-VS spectrum was essentially not quite a subject of study in the past.

The lineshape properties for the imaginary and intensity SFG-VS from the single peak are all relevant to surfaces and interfaces with more complex SFG-VS spectra. One can notice the significant difference in the spectral width between the imaginary and intensity spectra of the air/water interface in the literature [29]. These are evidences for the significant contribution from inhomogeneous broadening, giving away the secret of the coherent vibrational dynamics of the water molecules at the interface. Through the unified treatment of the spectral lineshape in SFG-VS and the accurate measurements on benchmark systems using the HR-BB-SFG-VS, we have already learned so much on the detailed structure and dynamics of the molecular surfaces and interfaces. These have provided insightful theoretical and experimental tools for pushing forward the applications of SFG-VS studies on complex molecular surfaces and interfaces. SFG-VS is a label-free vibrational spectroscopy. Therefore, every vibrational mode is a unique probe. By interrogating the detailed spectral lineshape of all the vibrational modes on complex molecular surfaces and interfaces, their structure and interactions at the molecular level will be revealed. In addition, the ability to accurately measure and obtain the different homogeneous and inhomogeneous lineshape parameters for the $-\text{CN}$ vibrations on different surfaces provided opportunities of using the $-\text{CN}$ vibration as vibrational probes to study the detailed structure, interactions and couplings on various solid surfaces, oxides, oxide films, minerals and metal surfaces [153] [78]. The above discussion on the difference between the FWHM of the imaginary and the

intensity spectra was based only on the Bloch dynamic model, and should not be limited to it. As long as there is inhomogeneous contribution to the lineshape, such difference is present. It is therefore a general issue in discussing the lineshape and width of the SFG-VS spectra and need to be explored.

3. Some controversial or interesting issues in SFG-VS

Advancement of SFG-VS cannot go very far with many standing controversies or difficult issues in the SFG-VS studies not properly addressed, understood or resolved. Some of the issues are intrinsic to the method, and some of the issues are expected to be addressed with improved experiments and computational methods. With the development of the unified treatment of the SFG-VS spectral lineshape and the ability of making accurate measurement on the SFG-VS spectral lineshape, as well as other advances in SFG-VS, one might expect some of these issues will be resolved or clarified. Here some of the controversial or puzzling issues in SFG-VS are briefly reviewed.

3.1 Surface and bulk contributions in SFG-VS

SFG-VS can only be surface specific when the bulk contribution to the signal is negligible. How much contribution is to the total SHG or SFG-VS signal from the multipolar responses of the centrosymmetric bulk other than the dipolar contribution of the surface/interface has been a long-standing issue in SHG and SFG-VS studies [12, 154-161]. A systematic theoretical treatment of the dipolar and quadrupolar contribution to the surface SFG-VS can be found in the recent monograph on SFG-VS by Shen [6]. Accordingly, the total effective susceptibility of the surface of a centrosymmetric medium is [6, 161],

$$\chi_{S,eff}^{(2)} = \chi_{SS}^{(2)} - \frac{\chi_{BB}^{(2)}(\vec{k}_1, \vec{k}_2)}{i\Delta k} \quad (13.1)$$

with

$$\chi_{SS}^{(2)} = \chi_S^{(2)} - \hat{z} \cdot \vec{\chi}_q^{(2)} = \chi_{Sd}^{(2)} + \langle \hat{z} \cdot \vec{\chi}_{qa}^{(2)} \rangle_{\text{int}} - \hat{z} \cdot \vec{\chi}_q^{(2)} \quad (13.2)$$

$$\chi_{BB}^{(2)}(\vec{k}_1, \vec{k}_2) = -i(\vec{k}_1 + \vec{k}_2) \cdot \vec{\chi}_q^{(2)} + i\vec{k}_1 \cdot \vec{\chi}_{q1}^{(2)} + i\vec{k}_2 \cdot \vec{\chi}_{q2}^{(2)} \quad (13.3)$$

and

$$\Delta k = k_{1z} + k_{2z} \pm |k_z| \quad (13.4)$$

Here $\chi_{ss}^{(2)}$ includes the interfacial electric dipole (ED) term $\chi_{sd}^{(2)}$, the electric quadrupole (EQ) term $\langle \hat{z} \cdot \vec{\chi}_{qa}^{(2)} \rangle_{\text{int}}$ from the field variation in the interfacial layer, and the bulk EQ term $\hat{z} \cdot \vec{\chi}_q^{(2)}$. $\chi_{BB}^{(2)}$ is the additional bulk EQ term, whose contribution to the total $\chi_{s,\text{eff}}^{(2)}$ depends on the phase mismatching wave vector Δk , in which the plus sign denotes the case of surface reflection and the minus sign corresponds to the case of transmission. This formulation allows the separation of the tensor elements of $\chi_{ss}^{(2)}$ and $\chi_{BB}^{(2)}$ from reflection and transmission SFG-VS measurements. From Eq. 13.1 and 13.4, one can see that the $\left| \frac{\chi_{BB}^{(2)}(\vec{k}_1, \vec{k}_2)}{i\Delta k} \right|$ term is many times smaller for the reflection SFG-VS than that of the transmission SFG-VS. Therefore, this term is usually small or negligible in the reflection SFG-VS, particularly when the interface dipoles are relatively well oriented close to the interface normal. However, the surface ED, surface EQ and bulk EQ terms in the Eq. 13.2 cannot be directly separated from the SFG-VS measurement.

In one of the recent studies by Shen et al., C-H stretching SFG-VS spectra in both the reflection and the transmission geometries of the nonpolar benzene liquid surface was carefully measured and compared [161]. What was found was that the $\left| \frac{\chi_{BB}^{(2)}(\vec{k}_1, \vec{k}_2)}{i\Delta k} \right|$ term in the reflection geometry is negligibly small in both ssp and sps polarizations. However, even though the $\hat{z} \cdot \vec{\chi}_q^{(2)}$ term is negligible in the ssp spectrum, it appeared to be significant in the sps spectrum. Also found was that the $\langle \hat{z} \cdot \vec{\chi}_{qa}^{(2)} \rangle_{\text{int}}$ term is insignificant in comparison to the surface ED term $\chi_{sd}^{(2)}$. This was concluded by comparing ssp spectra of the air/benzene, silica/benzene and silica/OTS/benzene interfaces, which are significantly different from each other.

The above studies have set an upper limit for the EQ contributions to the overall SFG-VS response. One has to keep an open mind on the definitiveness of these measurements which might have overestimated the EQ contributions, as they are quite difficult and subject to experimental errors. Nevertheless, so far the theoretical formulation is solid, and it is generally known that for most of the surfaces or interfaces there are indeed strong ordering and the SFG-VS signal in the reflection geometry is dominated by the ED term. For these surfaces, the surface specificity of SFG-VS is ensured and ED approximation can be readily applied. Often times the vibrational spectra of the surface molecules are significantly different from those in the bulk phase. For these cases, the bulk contribution is not a problem at all.

Careful lineshape analysis with HR-BB-SFG-VS data might also improve our understandings of the surface versus bulk contribution problem for liquid surface and interfaces. One can recall the case for the air/DMSO interface studies discussed in Section 2.3, where the two CH_3 groups in the same DMSO molecule at the air/water interface are with different stretching vibrational frequencies due to their different local interactions at the interface. Even the same molecules in the bulk and interfaces are under significantly different environment, and the differences in their respective vibrational spectra can be picked up in the SFG-VS spectral lineshape with HR-BB-SFG-VS.

There have been theoretical calculations predicting significant quadrupole contributions to surface susceptibilities for liquid benzene and water surfaces [162, 163]. For the water bending mode at the air/water interface, calculation indicates that the bulk quadrupole contributions are 8.7 times of that for the surface dipole contribution [163]. In spirit, these results seem to be in drastic disagreement with the studies by Shen et al. as described above [161]. It is known that there are ambiguities in the surface nonlinear susceptibility calculations [160], particularly the calculated quadrupole contributions are known to be coordinate-dependent. Therefore, the magnitude of the calculated quadrupole contributions in the literature is better not being taken for granted without careful examination. Before these contradictions are carefully resolved, it seems that the bulk quadrupole contribution problem will remain

to be a controversial issue for a period of time in the interpretation of the SFG-VS data of the liquid surfaces and interfaces. Luckily, for most of the SFG-VS applications with practical purposes, it is generally irrelevant.

3.2 Surface $\chi^{(2)}$ and bulk $\chi^{(3)}$ contribution to SFG-VS

In comparison to the bulk quadrupole contribution to the surface SHG and SFG-VS signal of liquid interfaces, the bulk $\chi^{(3)}$ contribution is an important or even more relevant topic as many of the surfaces or interfaces are charged in nature. Moreover, according to current understandings [23], the $\chi^{(3)}$ contributions are usually much more prominent than the quadrupole contributions as observed in SHG or SFG-VS experiments.

For charged surface or interfaces, the electric field created by the surface/interfacial charges may break the centrosymmetry of the adjacent liquid or solid medium, and this additional asymmetry extending into the bulk phase subsequently contributes to the overall SHG or SFG signal through the so-called electric field induced SHG or SFG (EFISHG or EFISFG) mechanism. The overall response is therefore not a pure surface term. EFISHG in the bulk liquid has long been studied and was known due to the induced polarization by the third order $\chi^{(3)}$ mechanism by the static zero frequency field [164, 165]. Eisenthal *et al.* first studied EFISHG at the air/water interface and concluded that it is surface potential dependent [166, 167]. Accordingly, the total SHG or SFG signal from the charged interface and the adjacent polarized bulk is [166, 167],

$$\begin{aligned}
 \chi_{total}^{(2)} &= \chi_S^{(2)} + \chi_{EFI}^{(2)} \\
 &= \chi_S^{(2)} + \int_0^\infty \chi_B^{(3)} E_z(z) dz \\
 &= \chi_S^{(2)} + \chi_B^{(3)} \Phi(0)
 \end{aligned} \tag{14.1}$$

with

$$\chi_B^{(3)} = N_B \left(\langle \alpha_{ijk}^{(3)} \rangle + \frac{\langle \alpha_{ijk}^{(2)} \cdot \mu_m \rangle}{bkT} \right) \quad (14.2)$$

Here $\chi_s^{(2)}$ represents the surface $\chi^{(2)}$ contributions, and the $\chi_B^{(3)}$ represents the bulk $\chi^{(3)}$ contributions through the surface electric field $E_z(z)$, with $\Phi(0)$ as the potential at the surface/interface. $\langle \alpha_{ijk}^{(3)} \rangle$ is the ensemble averaged third order molecular polarizability, $\langle \alpha_{ijk}^{(2)} \cdot \mu_m \rangle$ is the ensemble averaged produce of the second order molecular polarizability $\alpha_{ijk}^{(2)}$ and the molecular dipole μ_m , b is the constant determined by the particular susceptibility element under consideration, k is the Boltzmann constant and T is the temperature. The $\frac{\langle \alpha_{ijk}^{(2)} \cdot \mu_m \rangle}{bkT}$ term represents the field induced alignment of the dipole due to the interaction with the static electric field and its randomization due to thermal fluctuation. However, this term does not depend on the absolute orientation of the molecular orientation as both the $\alpha_{ijk}^{(2)}$ and μ_m terms change signs as the molecular dipole flips direction. This $\chi^{(3)}$ mechanism in surface SHG of the charged surfaces/interfaces have been applied to measure the surface/interfacial potentials, ion adsorption on to liquid solid interfaces and surface/interface acid-base equilibriums [23, 166-169].

Among the two charged interfaces studied to establish the $\chi^{(3)}$ mechanism, the first one was the charged Langmuir monolayers on the air/water interface [167], and the other was the negatively charged silica/water interface under different bulk solution pHs [166]. For the charged Langmuir monolayers, the surface non-resonant SHG signal changes with the sign of the surface charge, the surface charge density, and the bulk electrolyte concentration. For the silica/water interface, the SHG signal increases tremendously as the interface got charged as bulk pH increases, the SHG signal follows similar trend with the bulk electrolyte concentration as that of the case with the charged Langmuir monolayer on the air/water interface. Even though these results firmly established the surface charge induced SHG

phenomenon and has been successfully used to measure and calculate surface charge density and surface potentials, there are still fundamental questions remain to be addressed.

One question is what are the relative contributions of the $\langle \alpha_{ijk}^{(3)} \rangle$ and $\frac{\langle \alpha_{ijk}^{(2)} \cdot \mu_m \rangle}{bkT}$ terms in Eq. 14.2.

According to the SHG temperature dependent measurement of the $\chi^{(3)}$ contribution from the silica/water interface [166], the contributions of the two terms are comparable. However, quite few SHG/SFG studies on the charged surfaces or interfaces simply ignored the contribution from the $\langle \alpha_{ijk}^{(3)} \rangle$ term [45, 92, 170, 171]. Another question is regarding the fact that the magnitude of the $\chi^{(3)}$ in the non-resonant SHG measurement from the charged silica/water are more than an order stronger than that of the charged Langmuir monolayer on the air/water interface [166, 167]. Since the $\chi^{(3)}$ contributions are both from the polarized water molecules in the bulk, the charge density on fully charged silica/water interface and the fully charged Langmuir monolayer on the air/water interfaces are not likely to result in such big differences in the SHG signal in these two cases. Recently, there have been several studies regarding the $\chi^{(3)}$ mechanism of the SHG/SFG from charged surfaces and interfaces [172, 173]. There are also reports showing significant discrepancies when the SHG and SFG-VS data from the same silica/water interface are compared [174]. The discrepancies between the SHG and SFG-VS measurements of the silica/water interface may be understood by the fact that since the SHG measurement is non-resonant, the surface potential dependence has contributions from both the polarized water bulk and the polarized silica bulk [175]. While in the SFG-VS measurement, only the O-H frequencies of the water species are measured, and there is no contribution from the silica bulk, which does not have response in the O-H frequency region, as in the non-resonant SHG measurement. By including the polarized silica bulk contribution, one can also understand why the non-resonant SHG measurement from the charged silica/water are more than an order stronger than that of the charged Langmuir monolayer on the air/water interface [166, 167]. Here, the potential dependent polarized silica

bulk contribution must be dominant. However, there are more recent progresses on the understanding of the $\chi^{(3)}$ mechanism.

According to Gonella et al. [172], one important thing missing in the formulation in the Eq. 14 is that the integration into the bulk has to include the phase matching factor $e^{-i\Delta k_z z}$, with $1/\Delta k_z$ as the coherent length of the SHG or SFG process. One has,

$$\begin{aligned}\chi_{EFI}^{(2)} &= \int_0^\infty \chi^{(3)} E_{dc}(z) e^{-i\Delta k_z z} dz \\ &= \int_0^\infty -\chi^{(3)} \frac{d\Phi(z)}{dz} e^{-i\Delta k_z z} dz\end{aligned}\tag{15.1}$$

with $E_{dc}(z) = -d\Phi(z)/dz$, i.e. the surface field is the gradient of the surface potential function. A good approximation is that $\Phi(z) = \Phi(0)e^{-kz}$ with $1/k$ as the Debye screening length factor of the surface potential. Then, following the treatment by Gonella *et al.* [172], one has,

$$\begin{aligned}\chi_{EFI}^{(2)} &= \int_0^\infty -\chi^{(3)} \frac{d\Phi(z)}{dz} e^{-i\Delta k_z z} dz \\ &= -\chi^{(3)} \Phi(z) e^{-i\Delta k_z z} \Big|_0^\infty + \chi^{(3)} \int_0^\infty \Phi(z) (-i\Delta k_z) e^{-i\Delta k_z z} dz \\ &= \chi^{(3)} \Phi(0) - i\Delta k_z \chi^{(3)} \int_0^\infty \Phi(0) e^{-kz} e^{-i\Delta k_z z} dz \\ &= \chi^{(3)} \Phi(0) + \frac{-i\Delta k_z}{k + i\Delta k_z} \chi^{(3)} \Phi(0) \\ &= \frac{k}{k + i\Delta k_z} \chi^{(3)} \Phi(0)\end{aligned}\tag{15.2}$$

i.e.

$$\begin{aligned}\chi_{total}^{(2)} &= \chi_s^{(2)} + [\chi_1^{(3)} - i\chi_2^{(3)}] \Phi(0) \\ &= \chi_s^{(2)} + \chi_B^{(3)} \Phi(0)\end{aligned}\tag{15.3}$$

with,

$$\chi_1^{(3)} = \frac{k^2}{k^2 + (\Delta k_z)^2} \chi^{(3)} \quad (15.4)$$

$$\chi_2^{(3)} = \frac{k \Delta k_z}{k^2 + (\Delta k_z)^2} \chi^{(3)} \quad (15.5)$$

The physical picture one can get from the Eqs. 15 is that because the real surface electrostatic field (potential) and complex phase matching factor are both z (depth) dependent, the total $\chi^{(3)}$ term is $\chi_B^{(3)} = \chi_1^{(3)} - i\chi_2^{(3)}$. When $k \ll \Delta k_z$, i.e. the Debye length is big (very low electrolyte concentration), the term is essentially imaginary and small, with $\chi_1^{(3)} \sim 0$ and $\chi_2^{(3)} \sim (k / \Delta k_z) \chi^{(3)}$; When $k \gg \Delta k_z$, i.e. the Debye length is big (very low electrolyte concentration), the real term is dominant, with $\chi_1^{(3)} \sim \chi^{(3)}$ and $\chi_2^{(3)} \sim (\Delta k_z / k) \chi^{(3)}$; When $k \sim \Delta k_z$, i.e. the Debye length and phase matching coherent length are comparable, the real and imaginary terms are comparable and $\chi_B^{(3)} = \chi_1^{(3)} - i\chi_2^{(3)}$ is with complex value. Recently, with the above formulation, Gonella et al. discussed the relationship between the measured SHG/SFG signal with different Debye (charge screening) lengths for the cases of reflection, transmission and scattering SHG/SFG [172]. However, the aspect of complex nature of the $\chi_B^{(3)} = \chi_1^{(3)} - i\chi_2^{(3)}$ and its implications need to be further discussed.

Here, the existence of the imaginary term $-i\chi_2^{(3)}\Phi(0)$ originated from the bulk $\chi^{(3)}$ contributions is interesting and important. This latter term has not been considered in the $\chi^{(3)}$ mechanism of SHG and SFG from charged surfaces or interfaces before, but it was recently experimentally determined by the non-resonant SHG measurement on the water/z-cut quartz interface with electrolyte solutions under different pH values [173]. Because the z-cut quartz interface is dominated by the bulk term that is also 90° out of phase from the surface terms, one has,

$$\begin{aligned}
\left| \chi_{total}^{(2)} \right|^2 &= \left| \chi_s^{(2)} + [\chi_1^{(3)} - i\chi_2^{(3)}]\Phi(0) + i\chi_{Quartz}^{(2)} \right|^2 \\
&= \left| \chi_s^{(2)} + \chi_1^{(3)}\Phi(0) \right|^2 + \left| \chi_{Quartz}^{(2)} - \chi_2^{(3)}\Phi(0) \right|^2
\end{aligned} \tag{16.1}$$

Since the $\chi_{Quartz}^{(2)}$ term is much larger than the $\chi_s^{(2)}$, the $\chi_{B,Re}^{(3)}\Phi(0)$ and the $\chi_{B,Im}^{(3)}\Phi(0)$ terms, one has,

$$\begin{aligned}
\left| \chi_{total}^{(2)} \right|^2 &\approx \left| \chi_{Quartz}^{(2)} - \chi_2^{(3)}\Phi(0) \right|^2 \\
&\approx \left| \chi_{Quartz}^{(2)} \right|^2 - 2\chi_{Quartz}^{(2)} \cdot \chi_2^{(3)}\Phi(0)
\end{aligned} \tag{16.2}$$

As the $\chi_{Quartz}^{(2)}$ term changes sign by rotating around its z-axis, one can directly observe constructive and destructive interferences between the $\Phi(0)$ dependence (by changing bulk pH) of the $-\chi_2^{(3)}\Phi(0)$ and the $\chi_{Quartz}^{(2)}$ term. If the complex $-i\chi_2^{(3)}\Phi(0)$ term does not exist, there should have been no such interference with the quartz bulk signal. Such observation is a direct validation of the new formulation for the bulk $\chi^{(3)}$ mechanism [173]. One can also see how the new formulation can be used to understand the previous results of the water/charged monolayer and the water/silica interfaces in the literature, where dramatic increase of the SHG signal was observed [166, 167]. One has,

$$\begin{aligned}
\left| \chi_{total}^{(2)} \right|^2 &= \left| \chi_s^{(2)} + [\chi_1^{(3)} - i\chi_2^{(3)}]\Phi(0) \right|^2 \\
&= \left| \chi_s^{(2)} + \chi_1^{(3)}\Phi(0) \right|^2 + \left| \chi_2^{(3)}\Phi(0) \right|^2
\end{aligned} \tag{16.3}$$

with

$$\left| \chi_{total}^{(2)} \right|^2 \approx \left| \chi_s^{(2)} \right|^2 + 2\chi_s^{(2)} \cdot \chi_1^{(3)}\Phi(0) \tag{16.4}$$

when $\chi_s^{(2)}$ is much larger than the $\chi_1^{(3)}\Phi(0)$ and $\chi_2^{(3)}\Phi(0)$. And with

$$\begin{aligned}
\left| \chi_{total}^{(2)} \right|^2 &\approx 2\chi_s^{(2)} \cdot \chi_1^{(3)}\Phi(0) + \left| \chi_1^{(3)}\Phi(0) \right|^2 + \left| \chi_2^{(3)}\Phi(0) \right|^2 \\
&= 2\chi_s^{(2)} \cdot \chi_1^{(3)}\Phi(0) + \left| \chi^{(3)}\Phi(0) \right|^2
\end{aligned} \tag{16.5}$$

when $\chi_s^{(2)}$ is much smaller than the $\chi_1^{(3)}\Phi(0)$ and $\chi_2^{(3)}\Phi(0)$ terms. Eq. 16.4 represents the case for the water/charges monolayer case, where the $|\chi_2^{(3)}\Phi(0)|^2$ term is insignificant to the overall SHG signal, and the overall SHG signal is linearly dependent on the overall surface potential and changes sign when the charge of the monolayer is flipped [166]. In comparison, Eq. 16.5 represents the case for the water/silica interface SHG measurement, where the $2\chi_s^{(2)}\cdot\chi_1^{(3)}\Phi(0)$ and the $|\chi^{(3)}\Phi(0)|^2$ terms are significantly larger than the $|\chi_s^{(2)}|^2$ term starting from the low pH, as the main $\chi^{(3)}$ contribution is from the polarized silica bulk phase rather than the polarized water bulk phase. Therefore, the overall SHG increases monotonically and much more significantly as the pH of the solution increases [167]. Therefore, the quantitative interpretation of the water/silica interface SHG data needs to be revised accordingly. Nevertheless, it is clear that using the non-resonant SHG, it is impossible to catch the existence of the $-i\chi_2^{(3)}\Phi(0)$ term, because it does not interfere with any other terms and only add to the overall SHG intensity. More importantly, this new formulation of the $\chi^{(3)}$ mechanism also suggests a new perspective on the SFG-VS data of the charges surface/interface. In the non-resonant SHG studies, all the $\chi_s^{(2)}$, $\chi_1^{(3)}\Phi(0)$ and $\chi_2^{(3)}\Phi(0)$ terms in the Eq. 15.3 are in real values. However, in the resonant SFG-VS or SHG, considering the fact that each of the $\chi_s^{(2)}$, $\chi_1^{(3)}$ and $\chi_2^{(3)}$ term is complex, containing its own real dispersive term and imaginary absorptive term, one has,

$$\begin{aligned}
\chi_{total}^{(2)} &= \chi_s^{(2)} + [\chi_1^{(3)} - i\chi_2^{(3)}]\Phi(0) \\
&= [\chi_{s,Re}^{(2)} + \chi_{1,Re}^{(3)}\Phi(0) + \chi_{2,Im}^{(3)}\Phi(0)] + i[\chi_{s,Im}^{(2)} + \chi_{1,Im}^{(3)}\Phi(0) - \chi_{2,Re}^{(3)}\Phi(0)] \\
&= \chi_{total,Re}^{(2)} + i\chi_{total,Im}^{(2)}
\end{aligned} \tag{17}$$

Therefore, Eq. 17 suggests that the imaginary term $\chi_{total,Im}^{(2)} = \chi_{s,Im}^{(2)} + \chi_{1,Im}^{(3)}\Phi(0) - \chi_{2,Re}^{(3)}\Phi(0)$ is no longer a collection of ‘pure’ imaginary (absorptive) terms, as it also contains the real (dispersion) term of the bulk $\chi_2^{(3)}$ term, i.e. $\chi_{2,Re}^{(3)}\Phi(0)$. The mixing of the absorptive and dispersive terms in the imaginary term

in Eq. 17 suggests that unless the $\chi_2^{(3)}$ term in the $\chi_B^{(3)}$ is negligible, the interpretation of the phase-resolved imaginary SFG-VS spectra on the charged surface/interfaces can be much more complicated. And strikingly, in such cases the assumption that the imaginary SFG-VS spectrum contains only the absorptive terms is no longer valid [29].

In summary, the $\chi^{(3)}$ mechanism in the surface SHG and SFG-VS contains both a real term and the imaginary term, which are 90° out of phase from each other. When both of the two terms are themselves complex due to the resonance, the absorptive and dispersive terms of these terms are mixed in the phase resolved real and imaginary spectra, making it much more complicated for the analysis and interpretation of the SFG-VS data of the charged surfaces/interfaces. There have been still many puzzles regarding the $\chi^{(3)}$ mechanism. With more experimental data from combined SHG and SFG studies, these issues are expected to be carefully examined and addressed.

3.3 Accuracy of phase reference in phase-resolved SFG-VS

Normal SFG-VS measures the $|\chi_{S,eff}^{(2)}|^2$ instead of the $\chi_{S,eff}^{(2)}$, with the latter contains absolute phase information. The knowledge of the phase information of the $\chi_{S,eff}^{(2)}$ is important because the relative and absolute phase of different spectral features in $\chi_{S,eff}^{(2)}$ can be directly related to the relative and absolute orientations of the corresponding molecular groups [29]. Particularly, as the imaginary part of the $\chi_{S,eff}^{(2)}$ usually contains only absorptive terms that change signs with the up or down orientation of the corresponding vibrational transition dipoles, such orientational information can be unambiguously obtained from the phase-resolved imaginary spectra [29]. Phase-resolved SFG-VS have found many applications particularly in measuring the broad hydrogen-bonded O-H stretching vibrational spectra at various aqueous interfaces, and those results have helped to identify unique spectral features in those spectra [47, 91-93, 170, 171, 176]. There have been many developments in measuring phase-resolved

spectra of the much narrower spectral features in the C-H stretching vibration region and protein amide band region, etc. [79, 177-180]. However, as discussed in Section 3.2, when there are non-negligible bulk contributions, such as the $\chi^{(3)}$ mechanism from charges surfaces/interfaces, the notion that the imaginary SFG-VS spectrum contains only the absorptive term of the susceptibility can no longer be taken for granted, and the interpretation of the SFG-VS imaginary spectra based only on this notion needs to be cautioned and carefully examined [29], particularly for charged aqueous surfaces/interfaces [92, 181] and aqueous surfaces/interfaces of accumulated ions [93, 182]. Before getting into these complications, one of the benchmark discoveries of the phase-resolved SFG-VS, i.e. the lower frequency spectral feature below 3200 cm^{-1} of the neat air/water interface in the imaginary SFG-VS spectrum, has recently been found to be most likely an experimental artifact due to the errors in the calibration of the phase reference standard [91, 149-152]. Therefore, some discussion on the accuracy of the phase reference in SFG-VS measurement is pertinent in helping to set a straight record.

It has been known that by fitting the SFG-VS intensity spectrum, i.e. $\left|\chi_{S,eff}^{(2)}\right|^2$, the relative phases of the overlapping spectral features can be obtained as long as the data is good enough and the knowledge of the lineshape and broadening parameters can be understood. However, the quality of the $\left|\chi_{S,eff}^{(2)}\right|^2$ data and the knowledge on the specific spectral lineshape are not always attainable, particularly, the SFG-VS spectra of the hydrogen bonded O-H stretching modes at the aqueous interfaces has complex lineshape and are with multiple overlapping spectral features that have only been qualitatively identified [45, 83, 183]. Therefore, there have always been questions on the reliability of the spectral fitting in obtaining the correct relative spectral phase in SFG-VS [45, 184], and the direct measurement of the phase-resolved imaginary SFG-VS spectra has become an attractive and broadly accepted idea and practice in the field [29, 91, 92, 176]. Specifically, the lower frequency spectral feature below 3200 cm^{-1} of the neat air/water interface was identified in the imaginary SFG-VS spectrum [29, 91, 92, 176]. However, this feature cannot be identified in the intensity spectra [83, 183]. This disagreement between the phase-

resolved and intensity SFG-VS was widely held as the evidence that the phase-resolved SFG-VS is advantageous over the intensity SFG-VS.

Such consistency or rather the inconsistency issues between the phase-resolved and intensity SFG-VS spectra of the air/water interface was carefully examined five years ago [148, 185]. Those results and analysis suggested that the inconsistency might be related to the phase reference standard used in the phase-resolved SFG-VS measurement. The lineshapes of the intensity SFG-VS spectra of the air/water interface was shown to be quantitatively reliable and overlapping with each other quite well from the data collected in different laboratories in the world. They all agree quantitatively with the ‘standard’ intensity spectra measured by Wei et al. first published in 2001 [148, 186]. Based on previous SHG phase measurement results [148, 187], which discovered that the absolute phases of various non-resonant liquid surfaces are consistent with the phase of the air/water interface, while there was significant phase shift (about 25°) from that of the air/water interface and that of the z-cut quartz crystal surface, which have been used as the standard phase reference in SHG and SFG-VS phase measurement [91, 114, 176, 188-191]. Such inconsistency between all the non-resonant liquid surfaces and the quartz crystal surface was attributed to the different degrees of interferences between the SFG-VS signal generated from the non-resonant liquid surfaces with the quartz crystal phase reference, and the interference between the SFG-VS signal generated from the quartz crystal standard with the same quartz crystal phase reference. It was further suggested that in order to make improvement of the phase measurement in the phase-resolved SFG-VS of the air/water interface and to resolve the inconsistency between the phase-resolved and intensity spectra of the air/water interface, non-resonant liquid surfaces are recommended to be the phase standard for comparison [148].

In 2015, the idea of using the non-resonant liquid surfaces as phase references for the air/water interface phase-resolved spectra was independently demonstrated by two groups using the broadband SFG-VS and picosecond scanning SFG-VS, respectively [123, 149]. The conclusions of both works were that the

peak below 3200cm^{-1} of the air/water interface in the phase-resolved SFG-VS spectra, which has been controversial and has puzzled theoreticians for almost a decade [152], essentially disappeared after the phase corrections using the non-resonant liquid surfaces, i.e. the air/D₂O and the air/C₉F₂₀ liquid surfaces [149, 150]. This result of the disappearance of the lower frequency peak was also confirmed by the recent phase-resolved SFG-VS measurement using multiple nonlinear crystal phase references, including BiBO, BBO and z-cut quartz crystals [151], even though there are still some remained inconsistencies on whether the non-resonant air/D₂O surface or the quartz crystal surface is the more accurate phase reference standard [151, 192, 193]. These development nevertheless suggest that the intensity and phase-resolved SFG-VS are more consistent with each other, and the main issue is to ensure the accuracy of the data and the reliability of the experiment measurement.

For qualitatively resolving the main spectral features, either the non-resonant liquid surfaces or the nonlinear crystal surfaces are good and reliable as the phase reference. However, in order to obtain accurate lineshape and to resolve relatively smaller features or obtain relative phases of overlapping peaks, not only the spectral phase needs to be accurate, but also the measured spectral lineshape needs to be accurate and reproducible. Therefore, a high-resolution phase-resolved SFG-VS measurement is desirable, since as discussed and demonstrated in the Section 2, HR-BB-SFG-VS are ideal in obtain intrinsic spectral lineshape in SFG-VS. However, it is not likely the currently implemented scheme for broadband phase-resolved SFG-VS [92, 150] can be applied to the HR-BB-SFG-VS for HR phase measurement. The current phase-resolved BB-SFG-VS depends on the measurements on the interference fringes and the shift of fringes by the phase reference standard to determine the spectral phase. In order to resolve the phase of a spectral peak, it is required to have enough number of well-resolved fringes within the range of each spectral peak. For a relatively narrower peak, it is not likely that several interference fringes can be accurately measured to phase resolve the peak while achieving high resolution. Time domain heterodyne measurement can also be used to achieve phase-resolved SFG-

VS spectra (Laaser, 2011 #247}. However, FT-SFG-VS and time-domain heterodyne phase-resolved SFG-VS studies showed that the spectral resolution is limited to about 6.7cm^{-1} [26, 106], and this is unlikely to be significantly improved.

Direct phase reference measurement [176] has shown that accurate relative phase information can be readily obtained by the HR-BB-SFG-VS [79]. The direct phase reference method, also called the internal heterodyne phase-resolved (IHPR) method, work by directly measurement of the interference between the adsorbed molecular layer or LB monolayer film on the z-cut α -quartz surface. The imaginary spectra of the adsorbed molecular layer can be obtained using the simple relationship as the followings.

$$\begin{aligned} I \propto \left| \chi_{S,eff}^{(2)} \right|^2 &= \left| \chi_{S,Re}^{(2)} + i\chi_{S,Im}^{(2)} + i\chi_{Quartz}^{(2)} \right|^2 \\ &= \left| \chi_{Quartz}^{(2)} \right|^2 + 2\chi_{Quartz}^{(2)} \cdot \chi_{S,Im}^{(2)} + \left| \chi_S^{(2)} \right|^2 \end{aligned} \quad (18.1)$$

The key idea in the Eq. 18.1 is that the bulk quartz crystal term $\chi_{Quartz}^{(2)}$ is always 90° out of phase from that of the surface layer adsorbed on it [78, 79]. Due to its D_3 symmetry, the azimuthal rotation angle (ϕ) dependence of the SFG response from the z-cut α -quartz crystal follows either the function of $\cos 3\phi$ or $\sin 3\phi$, depending on the specific polarization combination in the SFG-VS measurement [79, 194, 195]. This means that when rotate the z-cut α -quartz crystal around its z-axis by 180° or 60° , the $\chi_{Quartz}^{(2)}$ term changes sign but is still with the same absolute value [79, 195, 196]. For the rotationally isotropic adsorbed molecular layer or LB monolayer on the quartz surface, one has,

$$\begin{aligned} I_{\phi_0} &= \left| \chi_{Quartz,\phi_0}^{(2)} \right|^2 + 2\chi_{Quartz,\phi_0}^{(2)} \cdot \chi_{S,Im}^{(2)} + \left| \chi_S^{(2)} \right|^2 \\ I_{\phi_0+180^\circ} &= \left| \chi_{Quartz,\phi_0}^{(2)} \right|^2 - 2\chi_{Quartz,\phi_0}^{(2)} \cdot \chi_{S,Im}^{(2)} + \left| \chi_S^{(2)} \right|^2 \end{aligned} \quad (18.2)$$

When all the signal is normalized to the $\left| \chi_{Quartz,\phi_0}^{(2)} \right|^2$, i.e quartz signal with $\phi = 0^\circ$, one has,

$$\begin{aligned}\chi_{S,\text{Im}}^{(2)} &= \pm \frac{I_{\phi_0} - I_{\phi_0+180^\circ}}{4} \\ |\chi_S^{(2)}|^2 &= \frac{I_{\phi_0} + I_{\phi_0+180^\circ}}{2} - 1\end{aligned}\tag{18.3}$$

In such a way both the imaginary ($\chi_{S,\text{Im}}^{(2)}$) and the intensity ($|\chi_S^{(2)}|^2$) spectra of the adsorbed molecular layer or LB monolayer on the quartz crystal surface can be measured with intensity SFG-VS measurement through direct interference with the quartz crystal surface [78, 79]. The data in Fig. 7 were measured with the IHPR method using the HR-BB-SFG-VS [78]. The beauty of this method is that the measurement is the just the same as the SFG-VS intensity measurement in everybody's SFG-VS laboratory, and it can work with any type of SFG-VS spectrometer. The interference between the adsorbed molecular layer and the α -quartz crystal is direct and free from additional phase shift, making the α -quartz crystal an accurate phase reference. The limitation of the IHPR method is of course that it can only measure molecules on the quartz crystal surface. However, because of its simplicity and effectiveness for making HR-BB-SFG-VS phase-resolved spectra, it is a useful tool for the poor men to understand and test the spectral phase relationship of various complex molecules, and to validate the accuracy and effectiveness of HR-BB-SFG-VS intensity spectral measurement and spectral fitting in obtaining the spectral phase information of complex molecular surfaces and interfaces [78, 79].

As long as the absolute phase of one or more than one spectral peaks can be determined or reliably referred, the absolute phase of each peak for most of the molecular systems under study can be reliably determined through fitting of HR-BB-SFG-VS spectra [13, 79]. This recent development not only provided validation of the accuracy of the HR-BB-SFG-VS in spectral lineshape measurement, but also provided an important tool for retrieving the much needed spectral phase information for complex molecular surfaces and interfaces where many spectral peaks closely overlapping with each other.

In addition, lineshape retrieving techniques such as the maximum entropy method (MEM) were employed to help resolving relative phase between overlapping spectral features in intensity spectrum

[184, 197, 198]. These techniques work much better when the spectral lineshape is accurately measured and overlapping peaks can be effectively resolved. Therefore, there are multiple methods that can be used to determine and confirm the phase measurement results. However, as discussed in the sections above, more of the efforts for understanding and interpretation of the phase-resolved and intensity SFG-VS data are on what lineshape functions are needed, and how to determine and resolve the surface and bulk contributions to the measured SFG spectra. Particularly, understanding and quantitatively analyzing the aqueous interface SFG-VS spectra with bulk contributions is one of the toughest problems and there can be more controversies and puzzles lay ahead in these studies. The concepts and issues discussed here are nevertheless useful guides for these endeavors.

In short summary, phase-resolved measurement in SFG-VS aims to provide more information in addition to the intensity measurement, and it has been more and more adopted by laboratories over the world in the past few years. In the process of applying the phase-resolved SFG-VS to complex molecular surfaces and interfaces, it is important to remember that the end of the means is to obtain reliable and accurate information about the spectral phase, and to make physically sound interpretation on molecular spectral, structure and interactions. The discussions in the above sections on the contributions to the SFG-VS signal and the review on the factors in phase reference standards are expected to be useful towards these purposes.

3.4 Surface Selectivity of Chiral SFG-VS

The biological world is intrinsically full of chiral molecules, macromolecules and chiral structures. One of the most unique and useful aspects of SFG-VS that can find applications in the biological science and technology is its ability to probe the chiral structures, interactions and transformations during the reactions. Second order nonlinear optical spectroscopy is one ideal probe for chirality, which is uniquely three dimensional, because the susceptibility tensors describing the second order nonlinear process is with the third rank [6, 63, 199, 200]. Recently, there have been tremendous advances in chiral SFG-VS

as probes of biological interfaces [30, 54]. However, as it has been known that a chiral liquid also generates SFG-VS signal [199, 200], the surface selectivity of chiral SFG-VS has often been questioned [20].

Chiral SFG-VS from the bulk chiral liquids was found to be much weaker than initially reported in the 1960s [22, 201-204], partly because measurements aimed for obtaining pure chiral elements can often be contaminated by signals from achiral sources. The surface chiral SFG signal without enhancement from electronic resonance was also initially considered to be too weak to be observed [20, 205]. Thus, early reports claiming observation of surface chiral SFG were often questioned and debated [20, 206, 207].

Recent studies have shown that surface chiral SFG is not only allowed, but also comparable to the surface achiral SFG signal at the chiral liquid surface [30, 208]. Chiral SFG is also surface-selective because the almost perfect cancellation between the different chiral tensors in the isotropic ensemble average in the isotropic chiral liquid does not happen on the surface or at the interface where molecules are intrinsically without centrosymmetry as they are always partially aligned due to the asymmetric forces across the surface or interface [30, 208, 209].

One recent experiment with the HR-BB-SFG-VS clearly showed that the chiral and achiral SFG-VS spectra of the R-(+)-limonene and S-(-)-limonene liquid surfaces [90] are both significantly different from the chiral spectra in the limonene bulk liquid [210]. This study not only provided a clear demonstration of the surface-selectivity of the chiral SFG-VS, but also presented a detailed analysis of the intrinsic chirality and orientational (prochiral) chirality contributions in the observed SFG signal [90]. The relative phases of each spectral peaks from the R-(+)-limonene and S-(-)-limonene liquid surfaces can be obtained by fitting the HR-BB-SFG-VS [90]. These results are consistent with the direct phase-resolved measurement [207] and are with much better spectral accuracy and better resolved peaks. There have been techniques based on the interference between the chiral and achiral terms for chiral SFG-VS measurement of chirality on molecular surfaces and interfaces, such as the PMP polarization

method [31, 90, 210, 211], and the twin polarization angle (TPA) method [87], etc. Recently, Petersen et al. developed a robust self-referencing method for chiral SFG-VS measurement [212]. Like the discussion above, careful examination to separate the surface and bulk contributions to the chiral SFG-VS is the first step for interpretation and analysis of the chiral SFG-VS data from the chiral liquid surface/interface. When the liquid phase itself is not chiral or can only generate insignificant amount of chiral SFG-VS signal, then the chiral signal can only come from the intrinsic chiral and prochiral contributions from the molecular surface/interface [9, 90, 208, 213].

The application of chiral and achiral SFG-VS in studying proteins, DNA, lipids and sugars, the chiral molecules and macromolecules as the building blocks of life has only been at its beginning [30, 60, 206, 211]. There are also important aspects of chiral recognition and chiral selective reactions in organic chemistry and catalysis that can be studied with chiral and achiral SFG-VS. As molecular chirality and prochirality on surfaces and interfaces can be effectively probed with SFG-VS [27, 90], there will be many advances in this direction in the foreseeable future.

3.5 Beyond the polarization selection rules and SFG-VS spectral assignment

It has been over ten years since the first development of the polarization selection rules for SFG-VS spectral assignment [21, 80, 81, 128, 214]. However, the application of these rules or the idea of these rules in spectral assignment and analysis still need to be more adopted in helping the applications of SFG-VS for complex surfaces and interfaces.

From the beginning of SFG-VS, studies have been predominantly on the C-H stretching vibrations congesting in the $2800\text{--}3100\text{cm}^{-1}$ frequency range [80, 81]. Before the development of the polarization selection rules in SFG-VS, assignment of the spectral peaks in this region relied on previous IR and Raman studies in the gas and condensed phase, along with DFT calculations. However, due to the many combination bands and Fermi resonance bands of the CH_2 and CH_3 vibrations, the assignment in the IR

and Raman studies were confusing even for some relatively simple molecules, such as ethylene glycol, ethanol, etc. [21, 80, 81, 214]. The polarization selection rules of SFG-VS are based on the fact that the polarization dependences of the intensity of the vibrational spectral peaks in different SFG-VS polarization combinations are determined by the basic symmetry of the particular vibrational transition and the molecular group orientations on the molecular surfaces. The rule of thumb of the polarization selection rules is that peaks belong to different symmetries often do not have their most strong intensity in the same polarization. This have worked effectively in resolving many confusions in the C-H vibrations in the IR and Raman spectral assignment by using the SFG-VS data [21, 80, 81, 214, 215]. In addition to the polarization selection rules, isotope editing in SFG-VS, as in traditional IR and Raman studies, can also help greatly in spectral analysis and assignment [214, 216]. However, isotope editing is usually expensive and not always attainable for complex molecules, and it often lead to additional complications due to the changes of the coupling between the vibrational modes, which can be a particular problem in the C-H region vibrational spectra which are usually congested with Fermi-resonance and combinational bands. Of course, the so-called polarization selection rules are not just a set of simple rules. Ultimately, they are the application of the more fundamental spectral transition symmetry analysis and the polarization analysis in SFG-VS, and one can always go back to work out the detail polarization dependent properties of particular vibrational mode under particular experimental geometry conditions. It has been known that on metal surfaces and semiconductor surfaces near the band gap, usually spectra in ppp polarization dominant and there is also strong interference with the SFG-VS contribution from the substrate [217, 218], so that the SFG-VS polarization selection rules derived from the non-resonant dielectric surfaces or interfaces cannot be directly applied [21, 80, 81]. To help these studies, one can always measure the polarization dependent SFG-VS spectra of same molecule on a dielectric surface and apply the polarization selection rules, and then use the knowledge of the assignment of spectral peaks to help understand the SFG-VS spectral on metal and semiconductor

surfaces or interfaces, as well as test the polarization and relative intensity dependences of different peaks in the spectral on these surfaces or interfaces through simulation using known dielectric constants of those substrates.

One of the most interesting findings with the polarization selection rules for dielectric surfaces or interfaces is that the asymmetric mode of alkyl CH_2 are usually around $2890\text{-}2900\text{ cm}^{-1}$ and stronger in the ppp polarization than the ssp polarization. However, in most of the textbooks and spectral databases, this asymmetric mode was often assigned to the peaks around $2920\text{-}2940\text{ cm}^{-1}$, which usually belong to the Fermi resonance band of the symmetric CH_2 stretching vibrations, which are stronger in the ssp polarization than in the ppp polarization [21, 81]. Another example is that the strong peaks in the ssp polarization around $2945\text{-}2960\text{ cm}^{-1}$ were often assigned to the CH_3 asymmetric stretching mode, which often should be one of the Fermi resonance pairs of the CH_3 symmetric stretching mode which is strong in the ssp polarization and weak in the ppp polarization [80]. Unfortunately, even as of today, many researchers in IR, Raman and SFG-VS studies have not utilized the knowledge based on symmetry and polarization dependence and are still using some of the questionable assignments in the literature or popular databases in explaining their vibrational spectral data. The correct approach should always be to check the symmetry of the transition by using the Raman depolarization ratio or the SFG-VS polarization dependence.

Fig. 8 is a good example to illustrate why IR and Raman spectra in the condensed phase are usually incapable of help spectral assignment in SFG-VS. Moreover, it suggests that it actually should be the other way around, i.e. SFG-VS can be used to help the assignment and analysis of the IR and Raman spectra. One can see that the HR-BB-SFG-VS spectra (lower panel) of the cholesterol molecules on the air/water interface exhibit well separated and resolved spectral features. Fitting of this SFG-VS spectrum gave 12 well-resolved peaks with accurately determined spectral parameters, such as peak positions, peak width and the relative spectral phase [13]. In comparison, even though all the peaks that can be

identified in the SFG-VS do have their corresponding peaks in the IR and Raman spectra (upper panel) with similar spectral resolution, those spectral features in the IR and Raman spectra are all congested and significantly broadened. One can also see that it would be difficult to obtain the Raman depolarization ration for the individual peaks in the over-crowded and congested Raman spectra.

Figure 8. Comparison of 0.6 cm^{-1} HR-BB-SFG-VS spectra of a cholesterol monolayer (surface density $35\text{ \AA}^2$ per molecule) on the air/water interface with the bulk stimulated Raman loss (SRL) (parallel polarization) and IR absorption spectra of solution of 100mM cholesterol in CCl_4 . The resolution of IR absorption spectra is 0.6 cm^{-1} , and the resolution of SRL spectra is 1.5 cm^{-1} . Figure is from Ref. [13].

In this respect, SFG-VS can go beyond just being the vibrational spectroscopy of the molecular surfaces and interfaces, and it can also be employed as an effective tool to study the vibrational spectroscopy of molecules by using SFG-VS measurement on the surfaces and interfaces. This shall make SFG-VS as spectroscopy for surfaces and interfaces studies into to use surfaces and interfaces as the tool for spectroscopy studies. In SFG-Vs studies, there are also two tasks that one has to understand and correctly assign the spectra and then to use this assignment to make analyses of structure, orientation and interactions of molecular surfaces and interfaces. With all the detailed information of the spectral

lineshape and phase-resolved measurement from HR-BB-SFG-VS as described above, SFG-VS can be broadly applied to make detailed studies on the molecular vibrational spectroscopy [13]. The preliminary study below is a good example to show what kind of spectral details can be resolved with the HR-BB-SFG-VS intensity and phase resolved measurement.

Figure 9. HR-BB-SFG-VS as vibrational spectroscopy. (a) Structures of cholesterol, 7-keto cholesterol, and epoxy cholesterol; (b) Comparison of the HR-BB-SFG-VS spectra of cholesterol, 7-keto cholesterol, and epoxy cholesterol Langmuir monolayers on the air/water interfaces in the ssp and ppp polarization combinations. There are clear differences in the ssp and ppp polarization spectra for the three molecules; (c) HR-BB-SFG-VS phase-resolved imaginary spectra in ssp and ppp polarization configurations of the three molecules. The phase-resolved spectra are obtained using the internal-heterodyne phase-resolved (IHPR) method and measured on the z-cut α -quartz crystal surface as described in Refs [79] and [78]. In all the measurement, the surface densities of the molecules are at $35\text{\AA}^2$ per molecules.

In Figure 9, the intensity and phase-resolved HR-BB-SFG-VS spectra of cholesterol, 7-keto cholesterol and epoxy cholesterol are measured on glass and quartz surfaces [13, 79]. The dramatically different spectral lineshapes for the three molecules in different polarizations can provide detailed spectral information to make assignments of the spectral features on each spectrum to the corresponding

molecular vibrational modes. Detailed assignment is beyond the scope of the review here. However, one can immediately see the dramatic changes in the 7-keto cholesterol and epoxy cholesterol spectra just due to a single substitution on the cholesterol molecule. Such sensitivity to the molecular structure changes is unprecedented for the vibrational spectra in the C-H region. This is what is required for making detailed spectral assignment and structure analysis.

For complex spectra like these in Fig. 9, assignment of the SFG-VS cannot rely on the knowledge from the studies on the IR and Raman spectra of the same molecule in the bulk solution phase or other bulk phase. And the understanding from the HR-BB-SFG-VS studies can actually help to understand the IR and Raman spectra of these molecules in different condensed phases. Thus, the SFG-VS polarization dependence and polarization analysis are expected to play more important roles in vibrational spectroscopy studies in general [215] [214].

One can go beyond the promise of SFG-VS as the unique spectroscopic tools for surface and interface studies towards making SFG-VS into an important and unique tool for using surfaces and interfaces as the loci to study broader problems regarding complex molecular structure and interactions. As SFG-VS is sensitive enough to make measurement at the sub-monolayer level, tiny amount of the precious molecules are needed in the SFG-VS measurement. It is relatively easy to introduce adsorbed layers or monolayer films of the molecules or molecular complexes of interest onto the air/water interfaces, solid substrate surfaces, such as the silica, CaF_2 and other mineral surfaces for HR-BB-SFG-VS intensity measurement, and also onto the nonlinear crystal surfaces, such as the α -quartz crystal surface, for phase-resolved HR-BB-SFG-VS measurement. The SFG-VS data with accurate spectral lineshape in multiple polarizations shall allow detailed quantitative analysis of the molecular structure, conformation as well as interactions of the molecules of interest. For these studies, the accurate spectral lineshape from HR-BB-SFG-VS intensity and phase measurement are essential tools, and the concepts and methodology for polarization measurement and analysis are necessary methodology to understand such

data. These shall further expand the applications of SFG-VS as a powerful spectroscopic analytical tools for broad applications.

4. Conclusions and future directions

This review focused on the SFG-VS spectral lineshape and some controversial issues in SFG-VS that are likely be crucial for the application of quantitative SFG-VS to the study of complex molecular surfaces and interfaces. SFG-VS is a unique in-situ spectroscopic tool for molecular surface and interface studies. Its applications to broad surface and interfacial problems rely on its ability to make quantitative measurement and quantitative analysis of the SFG-VS data.

The SFG-VS spectral lineshape theory as described in this review provided a coherent view on developing HR-BB-SFG-VS and on its application to obtain accurate spectral lineshape of complex molecular surfaces and interfaces. Particularly, SFG-VS was discussed in the context with other linear and nonlinear vibrational spectroscopy techniques; the unified treatment on the frequency-domain and time-domain SFG-VS was discussed as the foundation for the development of the HR-BB-SFG-VS; also discussed was the connections between the spectral lineshapes of the intensity and phase-resolved SFG-VS. These discussions provided the framework and included some benchmark examples for the future applications of the HR-BB-SFG-VS as the effective tool for quantitative measurement and analysis of SFG-VS spectra of complex molecular surfaces and interfaces.

Also reviewed and discussed are some of the issues that are often controversial or puzzling in the SFG-VS studies for complex molecular surfaces and interfaces, including the surface dipole and bulk quadrupole contributions to the SFG-VS signal, a new formulation of the $\chi^{(3)}$ mechanism of the charged interfaces, as well as its consequences in understanding and interpretation of the intensity and phase-resolved SFG-VS spectra, the phase reference standard in phase-resolved SFG-VS measurement, and

how to go beyond SFG-VS as the spectroscopy for surface and interface studies towards using SFG-VS of molecules on surfaces and at interfaces for spectroscopy and molecular structure studies.

The issues in polarization dependence and polarization analysis for spectral assignments and orientational analysis in SFG-VS hold the keys for SFG-VS applications. These subjects have been covered comprehensively in previous reviews elsewhere [21, 31]. It seems that quite many researchers have been avoiding making measurement and analysis in the ppp polarization, except for metal or some semiconductor surfaces, because the ppp polarization is usually the results a combination of different susceptibility tensor elements [31], or making polarization measurements at different visible incident angles. In fact, precisely because the ppp polarization is not a single element measurement, it is highly sensitive to molecular orientational structure changes and sensitive to the change of the visible incident angle, as the visible beam probes directly the Raman tensor of the second order polarizability or susceptibilities. Numerous examples have shown that multiple polarization measurements and particularly with the comparison of the ppp polarization measurements have provided some of the most interesting and crucial information about the spectral interference, spectral assignment and orientational analysis [21, 80-84, 128, 129, 138]. For example, a recent study have shown unambiguously that the free O-H group of the top-layer water molecules at the air/water interface undergone re-orientation around the hydrogen bond formed by the other O-H group of the same top-layer water molecule as the NaF concentration increases [138]. Only by having the ppp polarization data such sensitive molecular structure changes and the motion of the top-layer water molecules can be revealed.

The concepts and examples reviewed here can be readily extended to studies on different surface and interface problems. As SFG-VS has become increasingly popular among researchers, a clear understanding of the capabilities and limitations of the technique as discussed in this review is necessary.

For the purpose of quantitative measurement and analysis with SFG-VS, constantly return to several of the references are necessary and helpful [6, 10, 13, 17, 21, 30, 31]. Nevertheless, the content covered in

this review is unique and includes some of the most up-to-date developments and understandings in SFG-VS as viewed by the author himself. These developments have opened opportunities for many new applications of the SFG-VS for complex molecular surface and interface studies.

The future direction of the field is on one hand to further develop the concepts and tools that can make more sensitive and quantitative measurement of SFG-VS spectra, intensity or phase-resolved, and on the other hand to make applications of available quantitative tools to a broad range of surface and interface problems in chemistry of materials, energy, environmental and biological systems.

Finally, there will be many new SFG-VS studies employing the IR-Vis DR-SFG-VS, Vis-IR DR-SFG-VS and Vis-Vis DR-SFG-VS on intramolecular, intermolecular and molecule-surface vibronic and electronic couplings, electron and proton transfer processes of complex molecules on surfaces and interfaces [121-123, 126, 219]. Some concepts and methodology discussed in this review can be extended to those studies. As more and more researchers familiar with the multi-dimensional vibrational spectroscopy joining the effort, 2D-SFG-VS as well as 3D-SFG-VS have already been employed for specific problems on molecular surfaces and interfaces [28, 61, 107, 110, 220]. However, the principles and status of research in these directions are beyond the scope of this review, and should be provided by experts working on them.

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