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Coherent Vibrational Dynamics and High-resolution Nonlinear Spectroscopy: A Comparison with the Air/DMSO Liquid Interface†

Luis Velarde‡, Zhou Lu§, Hong-fei Wang∗

William R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, 902 Battelle Boulevard, P. O. Box 999, Richland, WA 99352, USA

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We present a comparative study on the C−H stretching vibrations at air/DMSO (dimethyl sulfoxide) interface with both the free-induction decay (FID) coherent vibrational dynamics and the sub-wavenumber high resolution sum-frequency generation vibrational spectroscopy measurements. In principle the frequency-domain and time-domain spectroscopic measurements should generate identical information for a given molecular system. However, when the molecular systems are with several coupled or overlapping vibrational modes, obtaining detailed spectroscopic and coherent dynamics information is not as straightforward and rather difficult from either the time-domain or the frequency domain measurements. For the case of air/DMSO interface that is with moderately complex vibrational spectra, we show that the frequency-domain measurement with sub-wavenumber high-resolution sum-frequency generation vibrational spectroscopy is probably more advantageous than the time-domain measurement in obtaining quantitative understanding of the structure and coherent dynamics of the molecular interface.

Key words: Sum-frequency generation vibrational spectroscopy (SFG-VS), High-resolution broadband SFG-VS, Free-induction decay, Dimethyl sulfoxide, Air/DMSO interface

I. INTRODUCTION

Molecular vibrational spectra and dynamics are sensitive to small differences in molecular structure and conformation, influenced by the interactions with the surrounding chemical environment, as vibrational frequencies are the characteristics of the quantum-mechanical degrees of freedom of the molecular nuclear motions. In the past four decades and recent two decades in particular, with the development of ultrafast laser technologies, experimental methodology and theory on molecular vibration, studies on vibrational spectra in the frequency-domain and dynamics in the time-domain, the two complementary approaches to investigate the molecular vibrations, have provided tremendous detailed understanding on the structure, conformation and dynamic interactions within and between molecules and their chemical surroundings [1−4]. Ultrafast vibrational spectroscopic techniques, either the straightforward infrared (IR) and Raman spectroscopy, or the more complicated nonlinear spectroscopy, that can probe various combinations of the molecular vibrational and electronic processes, have formed the indispensable toolbox for molecular science studies in achieving detailed understandings, fundamental or practical, of a broad range of material and biological molecular systems [4, 5]. Ideally, the dynamical response in the time-domain and the spectroscopic response in the frequency-domain of a molecule, in principle, contain the identical information about the same molecular system [1−3]. The typical spectral linewidth of molecular vibrations in the condensed phase at ambient temperature is in the order of a few to a few tens of wavenumbers, depending on the conformation and interaction dynamics of the vibrational motions. Such linewidth corresponds to a time-domain dynamics in a few hundreds of femtoseconds (fs) to a few tens of picoseconds (ps). In practice, either the time-domain or the frequency-domain approaches, or both, can be chosen for a particular molecular system one would like to study, depending on how the information on its vibrational spectral lineshape and dynamics can be experimentally obtained and theoretically treated.

Sum-frequency generation vibrational spectroscopy (SFG-VS), since its inception in the 1980s [6, 7], has proven to be an effective methodology for detailed investigation of surface and interfacial molecular struc-
ture and dynamics [8−15]. SFG-VS is a vibrationally-enhanced three-wave mixing process that combines a IR laser pulse and a visible pulse simultaneously in time and space onto a molecular surface or interface to generate a signal at the frequency of the sum of the IR and the visible frequencies. The symmetry selection rule of such second-order nonlinear optical response dictates its surface selectivity, since generation of light at the sum-frequency is electric-dipole forbidden in centro-symmetric bulk media. Since the centro-symmetry is by definition broken at the interface, where the molecules are naturally aligned and the atoms are naturally polarized, SFG-VS is intrinsically interface selective [16, 17]. This interfacial specificity combined with sub-monolayer sensitivity has made SFG-VS an unrivaled tool for the in situ investigation of liquid surfaces and interfaces without the otherwise overwhelming contributions from the bulk, in comparison to other non-interface selective spectroscopy techniques [9, 13, 18, 19].

SFG-VS is not only a spectroscopic tool that can be used to probe the molecular interface. With SFG-VS, one can study molecules and their interactions and reactivities using the interface as the unique medium. When the interface is not strongly interacting with the molecules, which is true for most soft interfaces, the role of the interface is to provide an somewhat controllable asymmetric environment that can naturally anchor and align the molecules of interest. Thus, the orientation and conformation dependent interactions and reactivities can be studied and evaluated. Such studies may handily contribute to the understanding of steric effects in chemical reactivity. Using SFG, orientation and conformation of molecules and molecular groups at the interface can be effectively characterized [10, 11, 20−22]. It has been shown that molecules at interfaces have unique polarization selection rules. These polarization selection rules can be used to unambiguously understand the symmetry of vibrational transitions and help to make correct assignments on vibrational modes [11, 23−25]. SFG-VS is also the simplest form of nonlinear spectroscopy that contains information both from the vibrational dipole and Raman transitions [16, 17]. Therefore, there is a better chance to make quantitative measurement and to have quantitative understanding of the SFG-VS process that can provide unique and detailed information on molecular structure, conformation and interactions. For example, SFG-VS is known to be sensitive to chiral structures of proteins and macromolecules in solution and at interfaces [26, 27] SFG-VS is also a unique technique to probe chemistry at buried interfaces [28, 29]. Therefore, understanding the advantages and the limitations of the SFG-VS techniques is important and imperative for applications to complex molecular interfaces in material, environmental and biological studies.

In principle, the frequency-domain and time-domain SFG-VS measurements should generate identical information for a given molecular system. However, limited by the accuracy and signal noise ratio (SNR) in the frequency-domain and the time-domain SFG-VS lineshape measurement, the quantitative connections between the SFG spectral lineshape parameters and the coherent vibrational dynamics constants have not been well examined based on an explicit framework until recently [30, 31]. Developments in such directions became possible with the sub-wavenumber high-resolution broadband SFG-VS (HR-BB-SFG-VS) recently developed in our laboratory. The spectral resolution as high as 0.6 cm$^{-1}$ of this HR-BB-SFG-VS was achieved by synchronization of a ∼40 fs mid-IR laser and a ∼100 ps visible laser [32]. With such resolution and significantly improved SNR, HR-BB-SFG-VS was shown to have additional spectral resolving power because of the unique polarization and spectroscopic phase relationship of the even-order nonlinear optical processes [32]. More recently, it is also shown both experimentally and theoretically that HR-BB-SFG-VS is an effective way to obtain nearly intrinsic spectral lineshape for molecular surface and interface studies [30, 31]. One example demonstrated that the homogeneous and inhomogeneous spectral lineshape parameters obtained from the HR-BB-SFG-VS spectra are identical to the homogeneous and inhomogeneous dynamics parameters obtained from the free-induction decay (FID) SFG vibrational coherent dynamics measurement of simple model molecular system with a single vibrational peak [30]. And another example demonstrated that with the unified theoretical treatment on the frequency-domain and time-domain SFG, the SFG spectral lineshape parameters, such as the oscillator strength, the peak position and the width, accurately obtained from the HR-BB-SFG-VS measurement can quantitatively predict the time-dependent spectroscopic behavior of a complicated model molecular system with as many as twelve interfering peaks [31]. These studies have not only provided a unified treatment on the frequency-domain and the time-domain SFG-VS but also made possible direct comparison of the frequency-domain and the time-domain SFG-VS data for detailed structural and dynamics information of the molecular surfaces and interfaces.

In this work, we present such a direct comparison of the FID-SFG dynamics data and HR-BB-SFG-VS spectral data of the C−H stretching vibrational modes at air/dimethyl sulfoxide (DMSO) interface. Even though the air/DMSO interface SFG spectra are only moderately complex, data analysis becomes less straightforward and rather difficult for both the time-domain and the frequency domain measurements. Nevertheless, we show that for molecular interfaces with closely overlapping peaks, the frequency-domain measurement with sub-wavenumber HR-BB-SFG-VS is advantageous in obtaining detail understanding on the structure and coherent dynamics of the molecular interface. It further suggests that high spectral resolution and good
data quality is not only a new possibility, but also a necessity, for studies on molecular surfaces and interfaces, where inhomogeneity is the norm rather than an exception.

II. THEORETICAL BACKGROUND

Based on a time-dependent perturbative approach widely used in describing linear and nonlinear spectroscopy [2, 3, 33], a unified treatment on the time domain and frequency domain SFG was described in Refs.[30, 31]. Here we present the parts that are most relevant to this work, and add additional necessary discussions.

In the time-domain SFG-VS using sub 100 fs ultrafast IR and visible laser pulses, the second order polarization \(P^{(2)}(t; \tau)\) at time \(t\) that produces the time dependent SFG response is described as

\[
P^{(2)}(t; \tau) = E_{VIS}(t; \tau)[R^{(2)}(t) \otimes E_{IR}(t)]
\]  

(1)

here \(\otimes\) is the convolution operator, denoting that a vibrational coherence of the molecular system is prepared by the IR pulse. \(R^{(2)}(t)\) is the second order time-domain response function that interacts first with the IR optical laser field \(E_{IR}(t)\) (the IR pump) and then the visible optical laser field \(E_{VIS}(t; \tau)\) (the up-converting SFG probe). The parameter \(\tau\) is the relative delay between the arrival of the probing visible pulse against the pumping IR pulse that initiates the vibrational coherence of the molecular system.

\(R^{(2)}(t)\) is the intrinsic molecular SFG response that contains all the molecular information the SFG process probes, including the frequency and time dependence, as well as polarization and symmetry dependence that dictates the surface selectivity. \(R^{(2)}(t)\) is a solution to the optical Bloch equations and is well-approximated by [2, 3, 34]:

\[
R^{(2)}(t) = |A_{NR}| e^{i\psi_{NR}} \delta(t) - i \theta(t) \sum_q A_q e^{-i\omega_q t} e^{-t/T_{2q}} e^{-\Delta\omega_q^2 t^2} 
\]  

(2)

In this equation, the resonant frequency \(\omega_q\) and the inhomogeneous dephasing parameter \(\Delta\omega_q^2\) are with the angular frequency units. The relationships to the commonly used spectroscopic values are \(\omega_q = 2\pi c \nu_q\) and \(\Delta\omega_q = 2\pi c \delta\nu_q\) with \(\nu_q\) being the \(q\)th vibrational frequency in wavenumbers (cm\(^{-1}\)) and \(c\) as the speed of light in cm/s. The first term in Eq.(2) is the non-resonant contribution (\(A_{NR}\)) since it dephases so much faster than the resonant vibrational response, it can be approximated with a \(\delta\)-function in time, resulting a constant background in the frequency space. Its phase is described with the \(\psi_{NR}\) parameter. For liquids and dielectrics that are not in resonance electronically with the visible or SF frequencies, the typical value is \(\psi_{NR} = 0\) or \(\pi\), i.e. the non-resonant term is real. \(\theta(t)\) is the Heaviside function describing the causality of the event, i.e. the starting point of the dynamics initiated by the excitation with the very short IR pulse at time zero, for the vibrationally resonant part of the response [35]. The \(e^{-t/T_{2q}}\) (Lorentzian) and \(e^{-\Delta\omega_q^2 t^2}/2\) (Gaussian) terms describe the homogeneous and inhomogeneous decay of the vibrational coherence in this model [2, 3].

The overall homogeneous and inhomogeneous dephasing processes described by Eq.(2) is called the FID coherent dynamics. FID dynamics measurement can provide information on the overall homogeneous and inhomogeneous dynamics parameters. However, in order to decompose the homogeneous dynamics into the individual components from different homogeneous dynamic processes, additional experiments with SFG photon echo for pure dephasing dynamics and pump-probe measurements for population relaxation lifetimes and re-orientational dynamics are needed [36]. As discussed in the literature on ultrafast vibrational coherence [37], the overall coherence time of homogeneous broadening \(T_{2q}\) is dictated by three sources of contributions. They are the thermal randomization rate of the vibrational coherence, so-called pure dephasing time \(T_{2q}\), the rate of population relaxation, so-called vibrational lifetime \(T_{1q}\), and the re-orientational relaxation times \(T_{Rq}\). The overall homogeneous broadening has a Lorentzian line shape, and the individual contributions to the homogeneous line width are \(1/T_{2q} = 1/(2T_{1q} + 1/(2T_{Rq}) + 1/(3T_{Rq})\).

Heterogeneous distribution of vibrational frequencies in the molecular system can introduce inhomogeneous broadening of the spectra due to the loss of coherence between oscillators with different frequencies. This heterogeneous distribution of vibrational frequencies is usually described with the Gaussian width parameter \(\Delta\omega_q^2\).

Since \(E_{SFG}(t) \propto P^{(2)}(t)\), SFG-FID intensity as a function of \(\tau\) can be obtained from:

\[
I_{SFG-FID}(\tau) \propto \int_{-\infty}^{\infty} |P^{(2)}(t; \tau)|^2 \, dt
\]  

(3)

Here, a closer look of the expression in Eq.(2) can help to understand the time behavior of the time-domain vibrational coherence of \(R^{(2)}(t)\). In Eq.(2), there are three time-dependent terms, namely \(e^{-i\omega_q t}, e^{-t/T_{2q}}\) and \(e^{-\Delta\omega_q^2 t^2}/2\). Since vibrational frequency \(\omega_q\)'s understudy are usually in the 1000 cm\(^{-1}\) to 3000 cm\(^{-1}\) range, corresponding to time period about 0.033 ps to 0.011 ps, the term \(e^{-i\omega_q t}\) in Eq.(2) is not only complex but also oscillates at a fast time scale than one can usually measure even with sub-100 fs time resolution experiment. Usually, the ultrafast IR or visible pulses used in the time-domain measurement as in Eq.(1) are \(\sim\)100 fs. This means that the IR and visible pulses are usually much longer in time than the oscillation period of the \(e^{-i\omega_q t}\) term. Thus, the time-domain measurement is an average of many \(e^{-i\omega_q t}\) oscillations. In
the SFG-FID intensity measurement, the parameter \( \omega_q \) can not be directly determined from the time-domain SFG intensity measurement as the phase in the \( e^{-i\omega \tau} \) term is lost. Direct phase stabilized and phase-resolved measurement of the \( E_{\text{SFG}}(t) \) is required for such information \[34\]. The \( e^{-i(\omega_{q1}-\omega_{q2})t} \) and the \( e^{-\Delta \omega \tau^2/2} \) terms do not oscillate but only decay with time. Usually these two terms decay in the sub-picosecond or a few picosecond time scale. Thus, they are the measurable quantities in typical time-domain ultrafast dynamics experiment. However, the total vibrational coherence with multiple vibrational modes is more complex. The long time coherence between coherently excited modes \( q_1 \) and \( q_2 \) is determined by the term \( e^{-i(\omega_{q1}-\omega_{q2})t} \) in the cross term when SFG-FID is measured. When \( \omega_{q1}-\omega_{q2} \) is in the range of 60 cm\(^{-1} \), typical in many molecular systems, a beating oscillation with a period of 0.55 ps would appear on top of the \( R^{(2)}(t) \). When \( \omega_{q1}-\omega_{q2} = 10 \) cm\(^{-1} \), the oscillation period is as long as 3.33 ps. For \( \omega_{q1}-\omega_{q2} = 2 \) cm\(^{-1} \), the oscillation period is 16.7 ps. Since the \( e^{-i(\omega_{q1}-\omega_{q2})t} \) and the \( e^{-\Delta \omega \tau^2/2} \) terms usually decay within a few picoseconds, it would be difficult or nearly impossible to measure the much longer period oscillations in \( R^{(2)}(t) \) in order to determine accurately the beating oscillation period much longer than the decay time. Thus, closely overlapping vibrational modes with \( \omega_{q1} - \omega_{q2} \) equals to a few wavenumbers can hardly be revealed and determined in the FID data. Usually, spectral resolution from time-domain measurement is limited to about 6 – 7 cm\(^{-1} \) \[34, 38\]. The above discussion is true for SFG-VS, and is also true for all other vibrational spectroscopy.

In the frequency-domain SFG measurement, \( E_{\text{SFG}}(t) \) is Fourier-analyzed by a dispersive spectrograph and the frequency response can be detected with sensitive photon-counting CCD camera. From \( \tilde{E}_{\text{SFG}}(\omega) \times \tilde{P}^{(2)}(\omega) \), one has:

\[
\tilde{E}_{\text{SFG}}(\omega_{\text{SF}}) \times \tilde{P}^{(2)}(\omega_{\text{SF}}; \tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i \omega t} P^{(2)}(t) dt = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i \omega t} E_{\text{VIS}}(t; \tau) |R^{(2)}(t) \otimes E_{\text{IR}}(t)| dt
\]

\[= E_{\text{VIS}}(\omega_{\text{VIS}}; \tau) \otimes [\hat{R}^{(2)}(\omega_{\text{SF}}) \tilde{E}_{\text{IR}}(\omega_{\text{IR}})] \]  

(4)

here \( \omega_{\text{SF}} = \omega_{\text{VIS}} + \omega_{\text{IR}} \) is the sum frequency of the visible and IR frequencies. Using the Fourier-transform convolution theorem, the convolution in the time-domain becomes product in the frequency-domain, and product in the time-domain becomes convolution in the frequency-domain. Therefore, the frequency domain polarization \( \tilde{P}^{(2)}(\omega_{\text{SF}}; \tau) \) is the result of the frequency domain second order response function interacting with the frequency domain IR filed \( \tilde{E}_{\text{IR}}(\omega_{\text{IR}}) \) and the visible field \( \tilde{E}_{\text{VIS}}(\omega_{\text{VIS}}; \tau) \) delayed by the time constant \( \tau \). The intensity of the SFG response is:

\[
I_{\text{SFG}}(\omega_{\text{SF}}) \propto |\tilde{E}_{\text{SFG}}(\omega_{\text{SF}})|^2
\]

(5)

It is clear that \( \tilde{E}_{\text{SFG}}(\omega_{\text{SF}}) \) and \( E_{\text{SFG}}(t) \) are directly related by Fourier transformation, while \( I_{\text{SFG}}(\omega_{\text{SF}}) \) and \( I_{\text{SFG,FID}}(\tau) \) are not.

Now one has,

\[
\tilde{R}^{(2)}(\omega_{\text{IR}}) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i \omega t} \tilde{R}^{(2)}(t) dt = A_{\text{NR}} e^{i \psi_{\text{NR}}} + \sum_q \frac{A_q}{(\omega_q - \omega_{\text{IR}}) - i \Gamma_q} e^{-\frac{\omega_q^2}{4 \Gamma_q}}
\]

\[= A_{\text{NR}} e^{i \psi_{\text{NR}}} + \sum_q \int_{-\infty}^{\infty} A_q \left( \frac{1}{\omega_q - \omega_{\text{IR}}} - i \Gamma_q \right) e^{-\frac{(\omega_{\text{IR}} - \omega_q)^2}{4 \Gamma_q}} d\omega' \]  

(6)

with \( \Gamma_q = T_{2q}^{-1} \) as the half-width at half-maximum (HWHM) of the lorentzian lineshape. When \( \Gamma_q \) is with the unit of cm\(^{-1} \) and \( c \) is with the unit of cm/s, one has \( T_{2q} = 1/(2 \pi c \Gamma_q) \) with the unit of s (second). Here the \( \omega_{\text{IR}} \) is used instead of \( \omega_{\text{SF}} \) in the \( R^{(2)}(\omega_{\text{IR}}) \) because in any given SFG experiment \( \omega_{\text{VIS}} \) is uniformly fixed frequency. Therefore, \( R^{(2)}(\omega_{\text{SF}}) \) can be reduced to a function of \( \omega_{\text{IR}} \), i.e., the SFG vibrational spectrum of the molecular interface. But this spectrum is not the same as the IR spectrum or as the Raman spectrum as the response function and polarization selection rules associated to this response function are different. The important fact is that the Eqs. (2), (4), and (6) directly connected the SFG spectra and FID dynamics to each other with the same homogeneous and inhomogeneous widths and coherent lifetime parameters. Once one set of the parameters is determined from experiment, either through time- or frequency-domain measurements, the other set of parameters are also known. In other words, these basic equations unify the time-domain and frequency-domain description of the SFG process from molecular interface.

It is to be noted that the denominator term in Eq.(6) is \([\omega_q - \omega_{\text{IR}}] \) instead of \([i \omega_{\text{IR}} - \omega_q + i \Gamma_q] \) conventionally used in previous SFG literature \[10, 11, 31\]. This new convention is the direct result of the Fourier transformation between the time domain equation as Eq.(2) and the frequency-domain equation as Eq.(6). The consequence of this new convention in comparison to the previous convention is that the relative sign of the \( \chi_{\text{NR}} \) and the \( A_q \) terms in the data fitting need to be changed to the opposite sign accordingly in comparison to the fitting with the previous used convention. For example, the signs of the \( \chi_{\text{NR}} \) values in Table I are changed to the opposite from those \( \chi_{\text{NR}} \) values in the literature, and the signs of all other fitting parameters remain to be the same \[32\].

As discussed and demonstrated in Refs. \[30, 31\], accurate measurement of the \( R^{(2)}(\omega_{\text{SF}}) \) can be achieved by using a visible probe pulse that is significantly longer than the vibrational coherence as described by the time-dependent behavior of the time-domain SFG response.
function $R^2(t)$ as discussed above. In practice, with a ∼90 ps visible probe pulse, a spectral resolution about 0.6 cm−1 can be routinely achieved [30–32].

To summarize, in the frequency-domain HR-BB-SFG-VS measurement, the intrinsic linewidth function $R^2(\omega_\text{IR})$ (phase-resolved or field-resolved SFG) or $|R^2(\omega_\text{IR})|^2$ (intensity SFG) as described in Eq.(6) can be experimentally obtained with straightforward spectral normalization [30, 31]. In the time-domain SFG-FID measurement, the intrinsic what is directly measured is the $E_{\text{VIS}}(t; \tau)[R^2(t)E_{\text{IR}}(t)]$ (phase-resolved SFG-FID) or $E_{\text{VIS}}(t; \tau)[R^2(t)E_{\text{IR}}(t)]^2$ (intensity SFG-FID). The intrinsic time-dependent lineshape function $R^2(t)$ or $|R^2(t)|^2$ can only be obtained after deconvoluting the data with accurately measured temporal profiles of the IR and visible pulses. Accordingly, it is reasonable to believe that HR-BB-SFG-VS can be more advantageous than the SFG-FID in obtaining detailed structural and dynamics information of molecular interfaces, especially for complex interfaces. This shall be shown and discussed with the case of air/DMSO interface below.

### III. EXPERIMENTS

The details on the experimental setup for sub-wavelength HR-BB-SFG-VS and FID-SFG intensity measurement were described in Refs.[30, 32].

To make HR-BB-SFG-VS possible, one needs to generate well synchronized sub 100 fs IR pulses and ∼100 ps 800 nm pulses. The sub 100 fs IR pulses provide broad IR spectral coverage and the ∼100 ps 800 nm pulse provides the sub-wavelength spectral resolution. This is achieved by electronically synchronization two sets of Ti:Sapphire oscillators/amplifiers at 1 kHz repetition rate running at 40 fs and ∼100 ps pulses at the fundamental (∼800 nm), respectively. Such system was constructed with lasers from Coherent, Inc. and is capable of generating synchronized 800 nm pulses with >3.5 W at ∼90 ps and >7.5 W at ∼40 fs, respectively. The overall timing jitter between the laser pulses from the two amplifiers is estimated to be <250 fs [30, 32].

To generate the IR pulse for SFG measurement, about 3.75 mJ of the 40 fs output is used to pump an OPERA Solo optical parametric amplifier (OPA) equipped with a AgGaS2 difference frequency generation (DFG) stage (Coherent, Inc.). The OPA/DFG unit is capable of providing >35 µJ/pulse of IR light at 4.5 µm. The IR beam was delivered to the sample with an angle about βIR=55°±1° with respect to the surface normal.

In the HR-BB-SFG-VS experiment, about half of the fundamental output generated by the ps amplifier (∼90 ps as measured by cross-correlation) was further attenuated by a variable neutral density filter to ∼60 µJ/pulse and used as the source of VIS radiation. The incident angle of the VIS beam (800 nm) is βVIS=45°±1° and βVIS=65°±1° with respect to the surface normal.

In the time-domain SFG-FID experiment, ∼40 fs VIS pulses are obtained from the 800 nm fundamental of the fs amplifier and split before the OPA/DFG unit. The beam is collimated and delivered to the sample with a pulse energy of 15–20 µJ. The 800 nm visible beam was delivered to the sample with an incident angle about βVIS=45°±1° with respect to the surface normal. The delay between the ∼40 fs 800 nm pulse and the IR pulse is controlled with a delay line equipped with a precision motorized linear stage (Newport, ILS250HA) before merging into the path traced by the ps VIS beam.
described above (the later used only on the frequency-domain experiments by means of a flip mirror in the up position).

The SFG beam produced in either case was collimated by an achromatic lens and isolated from the VIS and IR beams by the combination of an optical iris, an 800 nm notch filter, and a 785 nm shortpass filter (Semrock Inc.). The SFG signal is polarization selected and imaged onto the spectrometer slit (typically open to <100 μm) of a 750 mm spectrograph (Andor Shamrock). The SFG signal is dispersed by a 1200 lines/mm grating and recorded by a thermoelectrically cooled (−80 °C) Electron-Multiplied CCD camera (Andor Newton 971P, back-illuminated) containing a 1600×400, 16 μm2, pixel array.

For the frequency-domain experiments a 2-min exposure for the ssp polarization combination and a 15-min exposure for the ppp and sps polarization was usually used, and three background subtracted spectra were arithmetically averaged. A background reading was obtained for each spectrum by delaying the ps VIS and fs IR pulses by >1 ns. The spectra were normalized with the SFG profile from the top surface of a thick Z-cut α-quartz crystal.

For the FID measurements, a 90-s acquisition time per data point was used with a scanning step of 33 fs. For each point, the entire region detected by the CCD was later integrated, normalized over the laser IR spectral profile, and plotted as a function of the time-delay between the two incoming pulses as described elsewhere [39, 40].

Neat dimethyl sulfoxide (Sigma-Aldrich 99.9+%) was used as received and ~8 mL were poured onto a teflon Petry dish which was carefully cleaned with a Nochronix (Godax Laboratories, Inc) and sulfuric acid mixture, rinsed with 18 MΩ-cm water (Millipore Corp.), and followed by 12 min of UV/ozone cleaning. All experiments were performed with a freshly poured sample. All experiments were performed at room temperature 22±2 °C.

IV. RESULTS AND DISCUSSION

First let us examine on how HR-BB-SFG-VS works with C−H stretching vibrational modes of the air/water interface [32, 41, 42].

Figure 1 presents the ssp and ppp polarization combination spectra of the air/DMSO interface in the C−H stretching region in two different experimental configurations (configuration I: \(\beta_{\text{VIS}}=65^\circ\) and \(\beta_{\text{IR}}=55^\circ\), and configuration II: \(\beta_{\text{VIS}}=45^\circ\) and \(\beta_{\text{IR}}=55^\circ\)). These data were previously reported in different forms [32]. On all four spectra, there are two apparent peaks, one slightly below 2920 cm\(^{-1}\) and another slightly below 3000 cm\(^{-1}\). The striking discovery in the previous study with the HR-BB-SFG-VS is that even though the peak around 2920 cm\(^{-1}\) is sharp and narrow, the spectral FWHM (full width at half maximum) is significantly different for the ~2920 cm\(^{-1}\) peak on the two ppp spectra in the two configurations. While the visible incident angles differ by about 20° for the two SFG experimental configurations, the FWHM of the ~2920 cm\(^{-1}\) peak on the two ppp spectra changed from 4.7 cm\(^{-1}\) (\(\beta_{\text{VIS}}=65^\circ\)) to 8.4 cm\(^{-1}\) (\(\beta_{\text{VIS}}=45^\circ\)). In comparison, the FWHM of the ~2920 cm\(^{-1}\) peak on the ssp spectra with both experimental configurations are 8.8 cm\(^{-1}\). It was purely lucky to accidently observe such line width differences in the ppp spectra under particular experimental configuration before the simple physical picture behind it was figured out [32].

It has been known that the ppp spectra lineshape can change significantly with different visible incident angles in the SFG experiment, due to the interference effects of the four different susceptibility elements contributing differently under different incident angles to the ppp spectra [22, 43, 44]. Such spectral interference originated from the SFG spectroscopic phase that is directly related to the molecular orientation at the interface is unique phenomenon for the even-order coherent nonlinear spectroscopy. Such interference effects result in additional spectral resolving power to the SFG-VS, also to other coherent even-order nonlinear spec-
homogeneous broadening effect is insignificant for the

discussed below with the SFG-FID data) [31].

The FWHM of the air/DMSO interface for two sets of incident angles (65° and 45° with βIR = 55°) in the ssp, ppp, and sps polarization combinations. Global fitting of these spectra provided accurate lineshape parameters, as listed in Table I, that cannot be obtained by fitting single spectrum [32]. Even though the ppp intensity in configuration I is near 2920 cm⁻¹ is more than an order of magnitude smaller than that of ssp, its excellent SNR (that can be clearly seen in Fig.1) is the crucial and anchoring point for additional resolving power in determination of the two overlapping peaks with a splitting as small as 2.78 cm⁻¹ [32].

Therefore, the change of the FWHM of the ~2920 cm⁻¹ peak in the ppp spectra under different visible incident angles indicates that there are more than one peak contributing to the ~2920 cm⁻¹ peak. Observation of such evident change of the spectral width in the SFG-VS measurement is the direct result of the sub-wavenumber spectral resolution and the excellent signal to noise ration (SNR) made possible with the HR-BB-SFG-VS [32].

With above facts and physical picture firmly established [32], it is straightforward to make global fit on all the HR-BB-SFG-VS spectra in different polarizations and under different experimental configurations, as in Fig.2, to obtain accurate spectral parameters, such as peak position, width, and oscillator strength, etc. Table I lists all such parameters from global fit of the six spectra in Fig.2 using Eq.(7) directly derived from Eqs. (6) and (5).

$$I_{HR\text{-SFG}}(\omega_{NR}) \propto |A| e^{i\psi_{NR}} + \sum_q \frac{A_q}{(\omega_q - \omega_{NR}) - i\Gamma_q}$$

Here, the convolution with the inhomogeneous broadening term $$\sum_q \frac{A_q}{(\omega_q - \omega_{NR}) - i\Gamma_q}$$ in Eq.(6) is dropped since the inhomogeneous broadening effect is insignificant for the C–H stretching at the air/DMSO interface (to be further discussed below with the SFG-FID data) [31].

As one can see from Table I, the two peaks contributing to the ~2920 cm⁻¹ peak closely overlap with each other, with one peak at 2916.88±0.07 cm⁻¹ and another at 2919.66±0.06 cm⁻¹. The splitting is only 2.78±0.07 cm⁻¹, less than 50% of the FWHM of each of the two interfering peaks, whose FWHMs are 7.22±0.06 and 5.86±0.09 cm⁻¹, respectively. No wonder by looking at each spectrum separately one would not be able to tell that the ~2920 cm⁻¹ peak can have two distinctive peaks overlapping with each other. Moreover, we can show below that it is also nearly impossible to identify such splitting by simply fitting each individual spectrum with high-resolution, if no difference in the FWHM of the same peak is observed in spectrum with different polarization or under different experimental configuration.

Figure 3 shows the global fitting results of the ssp and ppp spectra in configuration II (65° and 55°) with two apparent peaks near ~2920 and 3000 cm⁻¹. The fitting results are listed in Table II. The ppp data and fittings are plotted both against the left axis and the right axis. Because the widths in the ssp and ppp spectra are nearly identical in this configuration, even for the spectra with excellent SNR, it is impossible to obtain stable fitting with more peaks. The fitting with two peaks can be considered very good by conventional standard. However, one can see that the left sides of the waist of both the ssp and ppp curves are not ideal fit to the data with excellent SNR.

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The separation of the is that somewhere above the air/DMSO separation and is about twice narrower. Therefore, the rule-of-thumb closest two are separated by 8.9 cm. The separation is calculated using $T_2q=1/(2\pi c\Gamma_\chi)$. 

TABLE II Parameters from global fitting of the ssp and ppp spectra in configuration II ($\beta_{11S}=45^\circ$ and $\beta_{1R}=55^\circ$) with two apparent peaks near $\sim2920$ and $\sim3000$ cm$^{-1}$. The fitting curves are shown in Fig.3. The $T_2q$ value is calculated using $T_2q=1/(2\pi c\Gamma_\chi)$.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>$A_1^a$</th>
<th>$A_2^a$</th>
<th>$\chi_{NH}^a$</th>
<th>$\omega_1^b$</th>
<th>$\Gamma_1^b$</th>
<th>$\omega_2^b$</th>
<th>$\Gamma_2^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ssp II</td>
<td>$+3.64\pm0.01$</td>
<td>$-0.95\pm0.00$</td>
<td>$0.083\pm0.001$</td>
<td>$2918.37\pm0.02$ cm$^{-1}$</td>
<td>$4.21\pm0.02$ cm$^{-1}$</td>
<td>$2995.4\pm1.4$ cm$^{-1}$</td>
<td>$12.2\pm1.6$ cm$^{-1}$</td>
</tr>
<tr>
<td>ppp II</td>
<td>$+1.44\pm0.01$</td>
<td>$-1.32\pm0.15$</td>
<td>$0.003\pm0.003$</td>
<td>$2920\pm0.01$ cm$^{-1}$</td>
<td>$2995.4\pm1.4$ cm$^{-1}$</td>
<td>$12.2\pm1.6$ cm$^{-1}$</td>
<td>$0.43\pm0.06$ ps</td>
</tr>
</tbody>
</table>

a: $\omega_1=2918.37\pm0.02$ cm$^{-1}$, $\Gamma_1=4.21\pm0.02$ cm$^{-1}$ ($T_{21}=1.260\pm0.006$ ps). 
b: $\omega_2=2995.4\pm1.4$ cm$^{-1}$, $\Gamma_2=12.2\pm1.6$ cm$^{-1}$, $T_{22}=0.43\pm0.06$ ps. 

The non-resonant background is kept real in the fitting.

With above understandings on the advantages and limitations in the SFG frequency domain measurement and data interpretation, now one can take a closer examination of the time-domain data and interpretations. Figure 4 presents the SFG-FID measurement in the ssp polarization combination under experimental configuration II in the C–H stretching vibration region. The IR pulse in the SFG-FID measurement is more than 300 cm$^{-1}$ broad and it is enough to simultaneously excite all the vibrational modes as in Fig.2. Oscillation with a period around 400 fs can be clearly identified from the FID data. As demonstrated previously [30, 31], the sub-wavenumber HR-BB-SFG-VS spectra can provide nearly intrinsic spectral lineshape of the SFG response of the molecular interface, and the spectral lineshape parameters from fitting the HR-BB-SFG-VS spectra can be used to quantitatively predict or reproduce the SFG-FID or delay-dependent broadband SFG spectra through simulations using Eqs.(2), (1), and (6), as long as the laser temporal profile can be independently measured from cross-correlation experiment between the visible and the IR pulses. In Fig.4, the solid curve is the simulation using the ssp II parameters in Table I. One can see that as expected the simulation result reproduced the SFG-FID data quantitatively in both the intensity scale plot and the log intensity scale plot.

In Fig.4, the FID data with log intensity scale in the lower panel appear to have small oscillation on top of a straight line. Therefore, the FID decay is dominated by the linear decay. The absence of quadratic decay term suggests insignificant contribution from the inhomogeneous broadening term in Eq.(2). As mentioned above, the fitting parameters in the Table I were obtained using Eq.(7) that is without the inhomogeneous broadening term as in Eq.(6). The fact that the parameters thus obtained can quantitatively reproduce the SFG-FID data, also indicates that inhomogeneous broadening in these C–H vibrational modes is indeed negligible. As shown in Refs.[30, 31], if there is significant inhomogeneous character in these vibrational motions, it would have been revealed from the HR-BB-SFG-VS spectra and the SFG-FID data.

It is important to note that the simulated curves in Fig.4 are not the square of the intrinsic time-domain lineshape $R(t)$ as in Eq.(2). Instead, it is the square of the lineshape convoluted with the laser profile in the experiment as described with Eq.(1) plus a contribution proportional to the coherent spike with the shape of the cross-correlation peak centered at $\tau=0$ [46, 47].

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FIG. 4 ssp polarization combination SFG-FID data in configuration II ($\beta_{\text{VIS}}=45^\circ$ and $\beta_{\text{IR}}=55^\circ$) and simulation using Eq.(2) with the spectral lineshape parameters (ssp II) as listed in Table I and the measured cross-correlation profile. The upper panel is the normal intensity plot, and in the lower panel the intensity is in log scale. The nearly quantitative agreement between the FID data and simulation results indicates that the spectral lineshape parameters from the HR-BB-SFG-VS can accurately capture the coherent vibrational dynamics.

48]. Unlike the HR-BB-SFG-VS that provides nearly intrinsic lineshape measurement of the SFG frequency-domain response function $R(2)(\omega_{\text{IR}})$ or $|R(2)(\omega_{\text{IR}})|^2$, the SFG-FID lineshape in the time-domain is not intrinsic time-domain response function $R(2)(t)$ or $|R(2)(t)|^2$. This fact suggests that the interpretation and fitting of the SFG-FID data can be much more complicated than processing and interpreting the HR-BB-SFG-VS data. As discussed in Section II, since in actual SFG-FID measurement the FID signal intensity usually dies out quickly as the time delay between the pump and the probe pulses moves to a few picosecond, even without the laser pulse convolution that results in reduction of the information content of the FID measurement, the spectral resolution can be achieved using ultrafast laser pulses and is still limited to about 6–7 cm$^{-1}$ [34, 38]. From the SFG-FID data as in Fig.4, it is not feasible that detailed spectral lineshape parameters the same as listed in Table I can be obtained. Simultaneous fitting of SFG-FID data in different polarization combinations and under different experimental configurations may help to improve the situation [40, 49]. However, it is not expected to significantly improve the spectral resolving ability that is limited by the not long enough delay time in the data.

Figure 5 illustrates comparison of the SFG-FID data with the intrinsic time-domain FID, i.e. $|R(2s)(t)|^2$, calculated with the data in Table I (with parameters from global fit using five peaks) and in Table II (with parameters from global fit using only two peaks) according to Eq.(2). The oscillation amplitudes on both simulated intrinsic time-domain FID curves are bigger (with deeper oscillation) than the actual SFG-FID data. As discussed above, the actual SFG-FID data are the result of the intrinsic FID convoluted with the visible and IR laser pulses with finite width. Convolution with visible and IR pulses is equivalent to average, or to smooth, the time dependent intrinsic SFG-FID curve using the pulse width window. Therefore, the reduced oscillation amplitude is the result of the smoothing effect of this convolution. Apparently, the intrinsic FID curve simulated with the five-peak fit parameters reproduces the experimental SFG-FID oscillation peak positions (as illustrated with vertical dashed lines) much more accurately than the curve simulated with the two-peak fit parameters. This unambiguously indicates that the global fit with five peaks are quantitatively more reliable than the fit with two peaks. The position of these peak positions are also telling interesting stories. On the curve of the five-peak simulation, the peak positions are 0.16, 0.59, 0.94, and 1.36 ps, respectively. The separations between neighboring peak positions are 0.43, 0.35, and 0.42 ps, respectively. These separations faithfully capture the peak positions on the experimental SFG-FID data. Such uneven separations is the indication of interference with more than two vibrational modes.

In comparison, the peak positions on the two-peak simulation curve are 0.18, 0.60, 1.03, and 1.44 ps, respectively. The separations between neighboring peaks are 0.42, 0.43, and 0.41 ps, respectively. These separations are almost identical to each other within the
measurement error of 0.02 ps i.e. 20 fs. Such an even separation about 0.42 ps is the results of interference between two peaks separated by about 80 cm⁻¹, matching the separation of 77.0 cm⁻¹ of the two peaks listed in Table II. If there is a third peak, the separation will become uneven. Therefore, even though the SFG-FID data cannot be fitted to generate accurate lineshape parameters as that from the HR-BB-SFG-VS spectra fitting, it still can unambiguously exclude the possibility that the spectrum is from the contribution of only two vibrational modes. On the other hand, the five-peak simulation matches the SFG-FID data quantitatively, suggesting the parameters from the five-peak fit are truthful representation of the actual coherent vibrational dynamics.

Another interesting and important observation is that the positions of the first peak (the highest peak) on both the five-peak simulation and two-peak simulation FID curves shift away from the time zero ($\tau=0$), the point where the pump and probe pulses completely coincide with each other. This position is 0.16 ps on the five-peak simulation curve, and 0.18 ps on the two-peak simulation curve. The delayed maximum (peak position of the first beat) on the intrinsic FID curve, according to further simulations with different parameters, is the result of the interference between separated peaks with opposite signs. In Table I and Table II, it is clear that the signs of the $\sim2920$ cm⁻¹ peaks are opposite to the signs of the $\sim3000$ cm⁻¹ peaks. At $\tau=0$, because the signs of these two groups of modes are opposite to each other, their amplitudes cancel each other and this cancellation results in a reduced total amplitude. As the delay time moves away from the time zero, the two groups of modes evolving with different speeds would finally become in phase with each other after about 0.17 ps. Consequently, the first maximum appears at a delayed time away from the time zero. The interference between these two groups of modes separated by about 80 cm⁻¹ would correspond to an oscillation period around 0.42 ps. This is the main oscillation period as discussed above.

In comparison, on the SFG-FID data, the first maximum is at $\tau=0$, and there is a small bump identifiable around 0.17 ps. This position coincides with the delayed maximum on the simulated FID curves. The $\tau=0$ peak on the SFG-FID data, is simply the contribution from the coherent spike at $\tau=0$ [46-48]. The coherent spike (or coherent artifact) is known to be significantly minimized when the visible pulse duration is much longer than that of the short femtosecond IR pulse [48]. This is why in the HR-BB-SFG-VS measurement using a $\sim90$ ps, the coherent artifact at $\tau=0$ is significantly suppressed; while in the SFG-FID experiment, where the IR and the visible pulse durations are well matched, the coherent spike is with maximum contribution to the SFG-FID measurement at $\tau=0$. On the other hand, if the two peaks or the two groups of the peaks interference with each other are having the same signs, the first maximum in the SFG-FID would not have such a delayed maximum. Then the first maximum would add on top of the coherent spike at $\tau=0$. Together, these signatures in the SFG-FID data can be used to qualitatively understand and to confirm the phase relationship between the beating peaks.

V. CONCLUSION

In this work, using the moderately complex air/DMSO interface as the model system, we reported a detailed comparison of the advantages and limitations of the frequency-domain and time-domain SFG measurement and analysis.

In order to resolve closely overlapping peaks such as in the HR-BB-SFG-VS from the air/DMSO interface, SFG spectra with high enough resolution and good enough SNR in multiple polarization combinations and experimental configurations, showing clearly identifiable differences in the spectral lineshape, are necessary. The parameters from analysis of HR-BB-SFG-VS data obtained under such condition can then be used to quantitatively simulate and predict the coherent vibrational dynamics of the same molecular interface. The closely overlapping peaks as small as less than 3 cm⁻¹ in the C–H stretching vibration region spectra of the air/DMSO interface were quantitatively identified from multiple HR-BB-SFG-VS spectra [32]. Such fine splitting is further confirmed with the SFG-FID data.

SFG-FID data from complex molecular interfaces can be useful in confirming the results from analysis of good HR-BB-SFG-VS data and in excluding the results from analysis of inadequate SFG-VS data. Particularly, delayed maximum in the SFG-FID data is the result of the interference between different groups of vibrational modes with opposite signs. It is a unique feature one can immediately recognize in the SFG-FID measurement. Such data can be used for determination of the relative phases of different groups of vibrational modes in the SFG response from complex molecular interfaces. Such phase information can be very useful in understanding orientation and conformation at complex molecular interface.

HR-BB-SFG-VS has been shown to be able to provide measurement on the intrinsic spectral lineshape of SFG response. It is also shown that due to intrinsic limitations on how far the delay between the visible and IR pulses can go in the measurement, SFGFID measurement is not likely to be able to provide intrinsic lineshape at the same level of accuracy as from the sub-wavenumber spectral resolution measurement in the frequency-domain. It is therefore fair to conclude that in comparison to the SFG-FID, HR-BB-SFG-VS data with good SNR appear to be more advantageous in terms of obtaining quantitative parameters to characterize the structure and dynamics of the complex molecular interface.
However, such distinction between the frequency-domain and time-domain approaches does not suggest that results from the HR-BB-SFG-VS analysis are always reliable. For example, the data and fit to the SSP and PPP HR-BB-SFG-VS spectra in the $\beta_{HS}=45^\circ$ and $\beta_{HR}=55^\circ$ configuration appeared to be satisfactory. However, it cannot capture the details in the coherent dynamics data from SFG-FID measurement. This is a cautionary example for understanding the limitations in the SFG-VS studies in particular, and in vibrational spectroscopy studies in general.

Nevertheless, detailed understandings on the advantages and limitations in SFG-VS studies shall lead to better and more applications of various SFG-VS techniques in molecular interfaces studies.

VI. ACKNOWLEDGMENTS

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