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Andrew P. Carpenter and Joe E. Baio

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Andrew P. Carpenter[a)] and Joe E. Baio

AFFILIATIONS

School of Chemical, Biological, and Environmental Engineering, Oregon State University, Corvallis, Oregon 97331

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[a)]**Author to whom correspondence should be addressed:** carpeand@oregonstate.edu

ABSTRACT

Vibrational sum-frequency generation (VSFG) spectroscopy is a method capable of measuring chemical structure and dynamics within the interfacial region between two bulk phases. At the core of every experimental system is a laser source that influences the experimental capabilities of the VSFG spectrometer. In this article, we discuss the differences between VSFG spectrometers built with picosecond and broadband laser sources as it will impact everything from material costs, experimental build time, experimental capabilities, and more. A focus is placed on the accessibility of the two different SFG systems to newcomers in the SFG field and provides a resource for laboratories considering incorporating VSFG spectroscopy into their research programs. This Tutorial provides a model decision tree to aid newcomers when determining whether the picosecond or femtosecond laser system is sufficient for their research program and navigates through it for a few specific scenarios.

I. INTRODUCTION

Over the past four decades, vibrational sum-frequency generation (VSFG) spectroscopy has become an increasingly popular experimental choice to probe the chemical structure and dynamics present in a wide diversity of interfacial systems. VSFG possesses a surface specificity that makes it a powerful experimental probe of the physicochemical properties of interfaces. With the theory underlying the operation of VSFG having been firmly established,[1] it is anticipated that VSFG could approach the experimental accessibility of other vibrational spectroscopies (e.g., FTIR and Raman). As researchers turn to consider incorporating VSFG experimental capabilities into their research programs, there will be an array of choices that must be made. Of these decisions, none is more consequential than the choice of the pulsed laser source in the spectrometer design as it will impact everything from the spectrometer's experimental capabilities, start-up costs, data analysis, and more.

Pulsed laser sources at the heart of VSFG spectrometer systems can be broadly binned into two categories—narrowband and broadband. Within the VSFG community, the narrowband laser source is primarily referenced with respect to the temporal properties of the laser pulses. We address the time-frequency relationship of laser pulses more in the following section; however, note that herein we refer to the narrowband laser sources as a "picosecond" laser to maintain convention with the VSFG field. While many of the core applications of VSFG can be achieved with spectrometers built with either picosecond or broadband laser sources, certain experimental considerations and capabilities will vary.

In this article, we provide specific examples where picosecond VSFG spectrometers can be successfully leveraged to study the molecular structure at extended planar interfaces. Focus is centered on the picosecond VSFG systems because, at the time of this writing, a variety of picosecond VSFG spectrometers are commercially available, whereas broadband systems are not. "Commercially available" is defined as a spectrometer system where all the major components (oscillator, amplifier, OPA, etc.) and the initial construction/installation phase of the system are handled by the manufacturer. In contrast, all broadband VSFG spectrometers will be "homebuilt," meaning that the positioning of all the primary components on an optical table and the experimental setup is assembled by the research team wishing to use VSFG. While not all picosecond VSFG spectrometers found in the literature are commercial systems, it is the commercial availability of these laser systems that have the potential to move access to VSFG experimental capabilities to be more akin to that of benchtop FTIR or Raman systems. This can be an incredibly advantageous model for laboratories not interested in investing, in the financial resources, and time required to build a custom VSFG spectrometer. The choice of a picosecond laser source in the spectrometer design does not impact the ability to successfully implement VSFG spectroscopy in one's research, though it will restrict access to the newer applications of VSFG spectroscopy that are at the leading edge of nonlinear optical development and require a broadband laser source.

We begin by describing the picosecond VSFG spectrometer before providing examples of how this system can be used to study the molecular structure of a wide array of interfaces. This will be followed by a discussion of the capabilities and costs of the picosecond and broadband VSFG spectrometers to provide insight into where the spectrometer designs are similar and how they diverge from one another. Finally, a model decision tree is presented to illustrate how someone interested in acquiring a VSFG spectrometer can decide if the picosecond or broadband systems are sufficient for their specific research goals.

II. DEFINING PICOSECOND AND BROADBAND IN THE CONTEXT OF VSFG

As mentioned in Sec. I, laser pulse duration and bandwidth are linked (via the time-bandwidth product).[2,3] In general, as laser pulses broaden in frequency space, they will become narrower in temporal duration and vice versa. This relationship is illustrated in Fig. 1. Under certain experimental scenarios, the physics underlying the time/frequency representations of laser pulses will become incredibly important to the success and interpretation of experiment results. However, these issues, mostly appear when using femtosecond pulses generated by broadband laser sources. Since this article is primarily focused on understanding the general capabilities of VSFG spectrometers built with different laser sources, we will refer the reader to other sources for an in-depth look at the physics relevant to the time/frequency representations of ultrafast laser pulses.[3]

In the context of VSFG spectroscopy, the reference to ***picosecond*** versus ***broadband*** always refers to the properties of the infrared (IR) pulse, since the visible (VIS) pulse will nearly always have a pulse duration in the picosecond regime for reasons mentioned in Sec. IV. For both spectrometers, the properties of the IR pulse will be determined by the laser source pumping an optical parametric amplifier (OPA), where the IR pulses are generated. In a ***picosecond*** VSFG spectrometer, the IR pulse is produced by an OPA pumped with a laser source possessing a picosecond temporal pulse width. As a result, the IR pulse will possess picosecond pulse durations. ***Broadband*** VSFG spectrometers have IR pulses with shorter pulse widths (~100 fs). These IR pulses are also produced using OPAs, albeit with slightly different construction to the picosecond variants that are pumped by laser sources with femtosecond pulses. The interested reader can find information elsewhere to further explore OPA operation and function with respect to IR pulse generation.[4] In VSFG spectroscopy, the ***broadband*** nomenclature arises from the reference to the IR pulses' broad frequency distribution.

One important consequence to note stemming from the bandwidth of the IR beam involves the manner in which the vibrational modes of surface molecules are excited. The broad frequency distribution of broadband IR pulses can simultaneously excite molecular vibrations across broad spectral regions (>200 cm^{-1}). The narrowband nature of the IR pulses in picosecond VSFG systems, however, requires the IR frequency to be sequentially tuned across the spectral region of interest in order to measure a VSFG spectrum. The experimental impacts of simultaneous excitation versus frequency scanning will be further discussed in Sec. IV.

III. VSFG SPECTROSCOPY WITH PICOSECOND LASER SOURCES

A. Design of picosecond VSFG spectrometers

Two different picosecond VSFG designs are shown in Fig. 2, corresponding to a commercially available picosecond spectrometer (Ekspla, Lithuania)[5,6] and a home-built experimental setup.[7,8] These diagrams demonstrate the physical layout of the picosecond VSFG experimental setup. For a deeper discussion on the construction of home-built VSFG systems, the reader is referred elsewhere in this tutorial series.[9]

The commercially available system [Fig. 2(a)] utilizes an Nd: YAG based oscillator that produces an intense 1064 nm beam that is frequency doubled to produce a 532 nm beam. This second harmonic beam is recombined with the residual 1064 nm beam in an OPA to produce an IR pulse. The OPA is capable of tuning the IR wavelength across a broad frequency range (1000–4000 cm^{-1}), allowing numerous vibrational regions to be probed. The polarization state of the IR beam is controlled by sending the beam through a series of mirrors (not illustrated) before it enters the "experimental bridge." Within the bridge, the VIS beam is polarization selected using a half-wave plate and overlapped with the IR beam at the sample stage to generate a sum-frequency response at the sample surface. The reflected VIS and IR beams are blocked, while the SF beam is polarization selected using a half-wave plate/polarizer cube combination before being frequency selected by a monochromator and detected with a photomultiplier tube (PMT). The software needed to run this spectrometer is provided by the spectrometer manufacturer along with the VSFG spectrometer system.

The home-built picosecond VSFG spectrometer [Fig. 2(b)] possesses all the same primary components and experimental capabilities as the commercially available system, however, the experimental details vary slightly due to a different gain medium (Ti: Sa) used in the oscillator. In the home-built system, illustrated here, the oscillator produces a weak 800 nm beam that is amplified in power before being sent on to pump the OPA. The principles of operation governing the function of this OPA will be the same as those in the commercial system; however, the specific construction of this OPA varies slightly from the OPA found in the commercial system. The IR pulses produced by this OPA can also be tuned across a wide range of frequencies (1000–4000 cm^{-1}). Both the VIS and IR

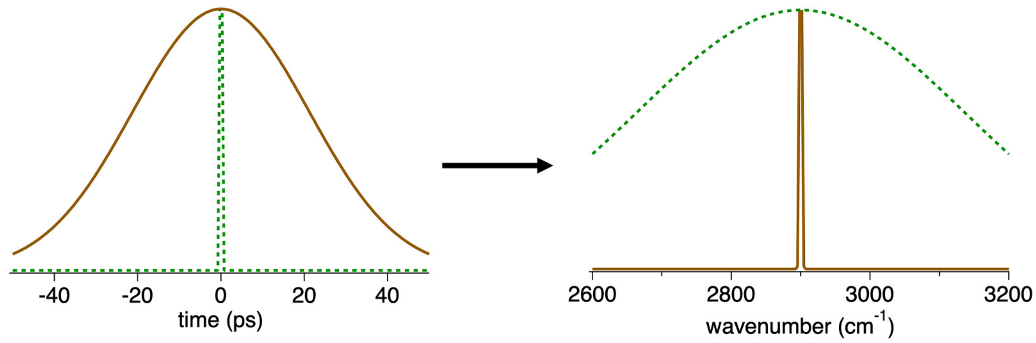

FIG. 1. Illustration of the relationship between pulse duration (left) and bandwidth (right). A Gaussian shaped 100 fs pulse (dashed green) will broaden to have large bandwidth, shown here to be centered over the CH stretching region (2800–3000 cm^{-1}). In contrast, a Gaussian shaped 30 ps pulse (solid brown) has a longer pulse duration, which results in a narrow bandwidth.

beams are polarization selected in similar manner to the commercial system before they enter the experimental bridge. The SF response generated at the sample stage is polarization selected before being sent directly onto a CCD detector. No monochromator exists in the detection line of this specific system and, thus, the CCD functions similar to a PMT. With no frequency selection by a monochromator, a daily frequency calibration of the OPA output (i.e., the IR beam) is performed. This VSFG spectrometer is operated by a home-built software created in LabVIEW.

For these two systems, the temporal duration is approximately the same for the pulses driving the OPA, in the picosecond regime, in each spectrometer design. This result in picosecond temporal properties and narrow frequency bandwidth for the IR pulses is utilized in each spectrometer. Despite some differences in the spectrometer design (VIS wavelength, detection system, etc.), they function nearly identically and have both been successfully utilized in producing publishable VSFG results.[6,7]

B. Probing interfacial molecular structure with picosecond VSFG

For the moment, we place a hold on comparing the picosecond and broadband spectrometer and exclusively focus our discussion on the experimental capabilities of the picosecond VSFG spectrometer. This spectrometer design has been successfully leveraged to study molecular structure and reactivity at the air–water,[10–13]

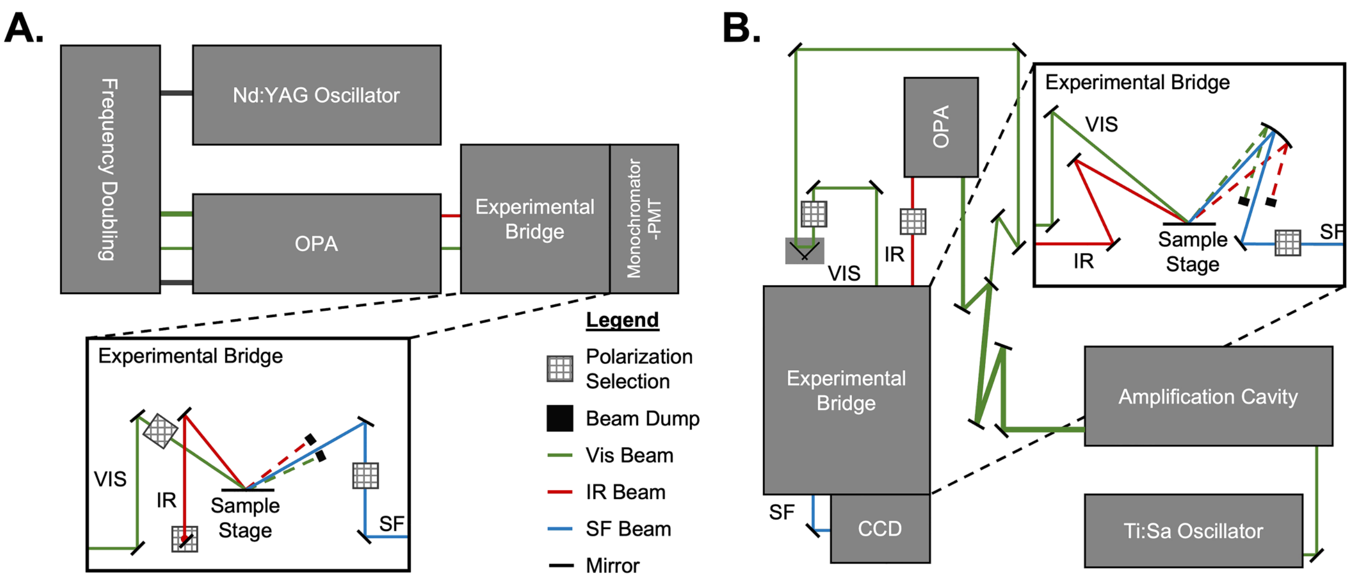

FIG. 2. Schematic layouts of the (a) commercial picosecond VSFG spectrometer (Ekspla, Lithuania) (Refs. 5 and 6) and a (b) home-built picosecond VSFG spectrometer (Refs. 7 and 8). For scale, the system on the left sits on a single 8 × 12 in. optical table, while the system on the right spans two 8 × 12 in. optical tables.

oil–water,[14–17] and solid–water[18–21] interfaces. These VSFG studies, and many others, have significantly contributed to our understanding of interfacial water structure, chemical reactivity of interfacial species, conformational arrangement of interfacial species, biomolecular orientations, and much more. Herein, we illustrate several applications of a commercial picosecond VSFG spectrometer to probe the molecular structure at the air–solid and air–liquid interfaces, isolate the spectroscopic signatures of protein secondary structure, and monitor for time-dependent conformational changes within a surfactant monolayer. It is worth noting that the broadband spectrometer is capable of these sorts of experiments; however, our intention with this section is to sample a small set of experimental capabilities that are available when using a picosecond VSFG spectrometer due its potential ease of implementation to newcomers in the field.

At the air–solid interface, we have used VSFG to probe the molecular structure of a nonthrombogenic material engineered for medical applications. This material is composed of a fluorinated n-alkanethiol film on a mixed dopamine–cyclic olefin copolymer substrate. The vibrational features observed in the spectrum shown in Fig. 3(a) correspond to a wide array of C–C, C–F, and C–O vibrations.[22] The interpretation of spectral signatures can be particularly tricky when considering the multiple chemical layers, complicated further by the C–F stretches being particularly difficult to interpret.[23] However, this spectrum can provide preliminary constraints on the molecular structure and chemical composition that can then be verified with additional VSFG experiments and other complementary surface analytical techniques. For instance, the sharp peak at 1375 cm^{-1} can be assigned to the asymmetric CF_3 stretch.[22,23] Specific polarization combinations (e.g., PPP, referenced in order of sum-frequency, visible, infrared beams) will probe dipoles oriented in certain directions relative to the interfacial plane and carry much more spectral information. A more complete discussion on these topics can be found elsewhere.[1,24] The presence of the asymmetric CF_3 stretch across multiple polarization combinations can be used to calculate the average tilt angle of the methyl group at the end of the fluorothiol.[25] Another, albeit tentative, assignment of in-plane ring deformations below 1600 cm^{-1} provides constraints on the chemical composition of the polymerized dopamine layer, which has been hotly debated.[26,27] This ring deformation suggests the presence of polymer rings lying within the interfacial plane. It is observations like these that can provide substantial aid in the characterization of material layers.

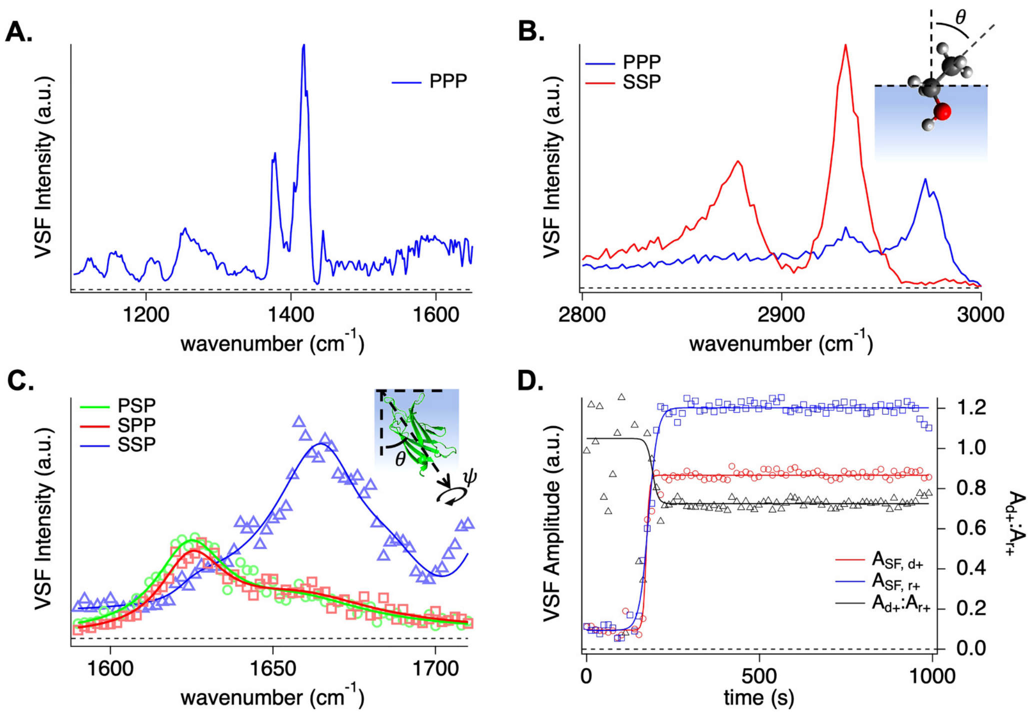

FIG. 3. VSFG data were taken using a commercially available picosecond VSFG spectrometer (Ekspla, Lithuania). (a) VSFG spectrum of the air–solid surface of a teflon-like material was recorded in the PPP polarization combination. (b) At the air–ethanol surface, VSFG spectra were measured in the SSP (red) and PPP (blue) polarization combinations. The inset is an illustration of the orientation information obtained from these spectra. (c) The achiral, SSP (blue triangles), chiral, PSP (green circles), and SPP (red squares) polarization combinations were measured in the protein dysferlin's C2A domain at the air–water interface. Solid lines are spectral fits using a series of Lorentzian line shapes. The inset provides an illustration of a kind of protein structure information that can be calculated with these data. (d) VSF amplitudes of the methylene (2850 cm^{-1}, A_{d+}, red circles) and methyl (2875 cm^{-1}, A_{r+}, blue squares) modes were recorded in the SSP polarization combination as a function of time for an aqueous solution of sodium dodecyl sulfate. The calculated ratio (black triangles) between the two values (A_{d+}:A_{r+}) is provided as a function of time. Solid lines are a guide to the eye. In all panels, the dashed horizontal line denotes zero sum-frequency intensity.

Turning to the air–liquid interface, we show the sum-frequency spectrum of ethanol (absolute, anhydrous, 0.22 μm filter, Pharmco-Aaper) surface in the SSP and PPP polarization combinations [Fig. 3(b)]. The strong SF signal present in multiple polarization combinations indicates that the interfacial ethanol molecules possess a preferred orientational ordering at the alcohol surface.[28] The presence of different vibrational features in the different polarization combinations is the consequence of the projection of those vibrational dipoles onto the interfacial plane. Using these vibrational features and multiple polarization combinations, one could calculate the average orientation of the vibrational groups and, thus, determine the orientation of the molecule itself.[24,25,29] This, then, provides an ensemble averaged view of the orientational ordering of solvent molecules at the liquid surface. A significant amount of VSFG research has occurred at air–liquid interfaces, where researchers focused on the structural organization of interfacial solvent molecules. In particular, intense focus has been placed on utilizing VSFG spectroscopy to study the structure of interfacial water molecules at these liquid surfaces.[11,30–32] Beyond interfacial solvent structure, VSFG has been extensively applied toward understanding the structural organization of molecules adsorbed to liquid surfaces, as seen in the next series of experiments.

One significant promise of VSFG is the capability of probing the structure of biomolecules at model membrane surfaces. For proteins, the spectral region associated with the amide I vibrations originating from the amino acid chain backbone has proven a valuable source of information on protein adsorption,[12,33,34] aggregation,[35,36] and binding geometry[37–39] at liquid and lipid surfaces. Pioneering work by the Chen and Yan research groups has shown how VSFG photons can be detected from amide groups organized around a chiral center.[12,13] This "chiral" VSFG allows one to isolate the spectral response from protein secondary structures.[40] Chiral VSFG spectra are shown in Fig. 3(c) along with an "achiral" spectrum of the same protein. The achiral spectrum was recorded in one of the four common polarization combinations, SSP.[24] When coupled with advanced spectral analyses[34] or computer simulations,[37] these spectra can allow researchers to calculate the binding geometry of proteins at lipid surfaces (tilt and twist angle) and study the chemistry that influences lipid–protein binding. As a result, VSFG has significant potential to aid in structure determination when proteins are bound to lipid surfaces, an area where current biophysical methods struggle.[41]

The final example we present from our picosecond spectrometer is the time-dependent observation of the interfacial structure of surfactant alkyl chains. The amplitude ratio between the symmetric methylene (A_{d+}) and symmetric methyl (A_{r+}) vibrations of a surfactant or the lipid alkyl chain is a useful metric for assessing changes in the conformational ordering of the linear carbon chains.[10,15,24] Measuring these responses as a function of time allows one to monitor for changes in the alkyl chain conformational structure. In Fig. 3(d), the VSFG response is measured as a function of time for the symmetric methylene and methyl vibrational modes. The calculated A_{d+}:A_{r+} ratio between the sum-frequency amplitudes is then plotted as a function of time. The rapid rise in sum-frequency amplitude (blue and red traces) occurs after the addition of surfactants to the aqueous subphase as the molecules adsorbs to the air–water interface. The subsequent plateau in VSFG amplitudes is indicative of an equilibrated surfactant monolayer, with the unchanging ratio (black trace) revealing that there are negligible changes in the conformational ordering of the surfactant alkyl chain over the time period measured. Such time-dependent experiments can be generalized beyond surfactant monolayers and concentrated on monitoring molecular adsorption and conformational/orientational changes of many interfacial species.

These experimental results from the air–water and solid–water interfaces are intended to provide context and inspiration as to some of the kinds of interfaces that can be probed and the information that is accessible when using picosecond VSFG spectrometers. This set of experiments is nonexhaustive and further examples can be found for picosecond VSFG experiments of the oil–water interface[42–45] and picosecond heterodyne setups,[46–48] among many other examples.

IV. PICOSECOND VERSUS BROADBAND VSFG

Having illustrated how picosecond VSFG spectrometers can provide important insight into the molecular structure of several interfacial systems, we now turn to compare some experimental features of the picosecond VSFG system with a broadband VSFG spectrometer. Table I contains a list of "features" that could affect one's choice of which spectrometer would be best suited for their research needs. This table is not meant to be an exhaustive list of every consideration warranting attention but is intended to paint broad contours of the costs and capabilities of the two spectrometer designs to aid a researcher in their decision of which VSFG laser system will be sufficient or necessary for their research program.

Again, the features listed here are only some of the considerations a researcher will need to contemplate as they purchase their VSFG spectrometer. While this list implies that the broadband spectrometer is more versatile when it comes to the range of VSFG experiments, one can perform on this system, there exist hidden

TABLE I. Potential features to consider when choosing to purchase a picosecond or broadband VSFG spectrometer.

Feature	Picosecond spectrometer	Broadband spectrometer
Commercially available?	Yes	No[a]
Laser gain medium	Nd:YAG, Ti:Sa	Ti:Sa, Yb
VIS pulse wavelength	532, 800	515, 800, 1030
Spectral resolution[a]	2–6 cm^{-1}	0.6–20 cm^{-1}
Minimum price[b]	<$ 400 000	>$ 700 000
Laser source repetition rate	10 Hz–1 kHz	kHz–MHz
Vibrational lifetime experiments?	No	Yes
SFG scattering?	No	Yes

[a]To the best of the authors' knowledge as of April 2022.
[b]Minimum prices are *rough estimates* based on the authors' personal knowledge as of April 2022 and are presented in USD.

costs specific to the broadband VSFG spectrometer. In what follows, we will discuss these trade-offs before reframing the discussion as a model decision tree, through which we will follow the decision pathways of several representative researchers as they work to determine which spectrometer is best for their laboratory.

A. Picosecond versus broadband: Is one best?

When it comes to the question of whether one laser source is better than the other, the answer becomes quite subjective. We have already illustrated how the picosecond system can be used to extract structural insight from several different interfacial systems and provided references to ever more diverse examples. Broadband VSFG spectrometers can perform all the same experiments we illustrated above, but with IR pulses possessing shorter temporal durations comes a whole new set of experimental considerations.

To start, the use of broadband IR pulses can noticeably shorten spectral acquisition times as a result of their broad frequency distribution and, typically, higher laser repetition rates. While this is more of a convenient feature, typical broadband IR pulses can simultaneously excite a frequency region spanning ≥200 cm^{-1}, eliminating the need to "scan" the IR frequency across a frequency region such as when using the picosecond spectrometer. Broadband laser sources also have repetition rates of 1 kHz and greater, reducing the time required to achieve a reasonable signal-to-noise ratio in the measured vibrational spectrum. For instance, the picosecond VSFG spectrometer took ∼25 min to record each amide I spectrum shown in Fig. 3(c). A broadband VSFG spectrometer could have made similar measurements in minutes or less, depending on the particular spectrometer used.

Yet, a potential downside to the broad frequency distributions is that, unless care is taken in the pulse shaping of the VIS pulse, the broadband spectrometer can come with a reduction in spectral resolution relative to the picosecond spectrometer. This is the result of resolution in VSFG experiments being determined by the bandwidth of the VIS beam. An excellent example of broadening effects was illustrated by Velarde and Wang, who measured the VSFG spectrum of a cholesterol monolayer at the air–water interface using different spectrometer designs.[49] Figure 4 shows a reproduction of spectra they recorded using a high-resolution broadband spectrometer (dotted trace, 0.6 cm^{-1} resolution), a standard broadband spectrometer (dashed trace, 15 cm^{-1} resolution), and a picosecond VSFG spectrometer (solid trace, 6 cm^{-1} resolution). Providing the best resolution is the high-resolution broadband spectrometer, followed by the picosecond spectrometer, followed finally by the broadband spectrometer. With higher resolutions, the multiple peaks near 2950 cm^{-1} become resolved, with a similar obscuring effect seen in the broadening of the methylene (2850 cm^{-1}) and methyl vibrational modes (2875 cm^{-1}). Spectral broadening has the potential to obscure important vibrational bands that will complicate interpretation and can lead to misinterpretations in structural analyses that rely on accurate fitting procedures.

Thankfully, the past decade or two has witnessed advances in pulse shaping technology that can largely mitigate resolution issues in broadband VSFG spectrometers. Pulse shaping is a process by which the laser pulse profile in the frequency or time representation can be altered to researchers' preference. Relevant application to VSFG spectroscopy, one could narrow the VIS pulse, in frequency space, to improve spectral resolution. In modern broadband VSFG experimental setups, pulse shaping is most often accomplished using commercially available Fabry–Pérot etalons[50,51] or home-built 4f pulse shapers.[47,52] These methods routinely push the spectral resolution below 10 cm^{-1}. The subwavenumber resolution seen in Fig. 4 (dotted trace), and referenced in Table I, was accomplished by an alternative approach. This method involves combining a broadband laser source for IR generation with a separate long picosecond laser source for a narrowband VIS beam. While this experimental approach illustrates how broadband spectrometers can possess superior resolution to the picosecond variant, new practitioners in the VSFG field are unlikely to be interested in coupling multiple laser sources together. Therefore, if a broadband spectrometer is used, the first strategy set is more likely to be desirable in order to achieve a comparable resolution to the picosecond spectrometer system. Note, however, that pulse shaping methods require maintenance of beam alignment through the pulse shapers; otherwise, the VIS bandwidth and frequency can shift, impacting experimental results.

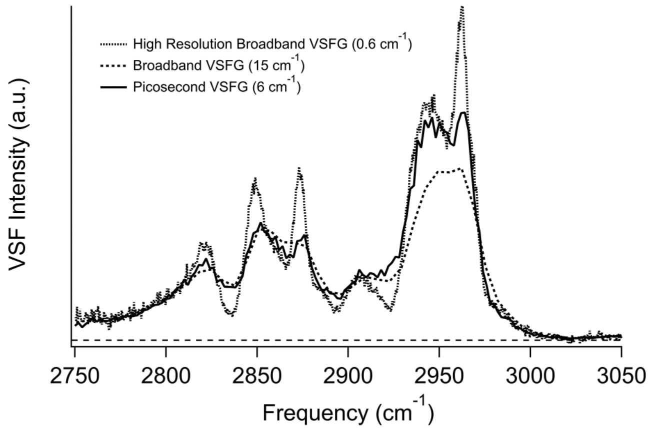

FIG. 4. VSFG spectra of a cholesterol monolayer were recorded with a picosecond (solid trace, 6 cm^{-1} resolution), broadband (dashed trace, 15 cm^{-1} resolution), and high-resolution broadband (dotted trace, 0.6 cm^{-1} resolution) spectrometer. The figure has been adapted with permission from Velarde and Wang, Phys. Chem. Chem. Phys. **15**, 19970 (2013). Copyright 2013, Royal Society of Chemistry.

Related to any discussion on VSFG bandwidth and resolution needs to be a mention of the methods by which SFG photons are detected and the normalization procedures used in broadband and picosecond VSFG spectroscopy. The method of detection in broadband VSFG experiments requires a need to spectrally resolve the sum-frequency signal onto a CCD camera. Spectrally resolving many frequencies of light simultaneously is often achieved using an optical spectrometer to spatially disperse the frequencies of light onto the CCD detector. The necessity of this detection method is due to the broad IR pulse simultaneously exciting an entire spectral region, which leads to the emission of the full VSFG spectrum. Meanwhile, since the picosecond system "scans" across a frequency region, the sum-frequency spectrum is the frequency resolved by the scanning of the IR frequency. Often monochromators will be incorporated into the detection line to improve frequency filtering of the detected sum-frequency light; however, this is not a necessity as one can see in the home-built spectrometer design we highlighted in Sec. III A.

Critically, both spectrometer designs require normalization of sum-frequency spectra as OPAs do not emit IR photons with equal energy at every wavelength. In the case of broadband VSFG spectrometers, the broadband IR pulses will have Gaussian-esque intensity distributions as a function of IR frequency. As a result, sum-frequency spectra need to be corrected for the frequency dependent IR excitation of these broad pulses. Experimentally determining the effects of changing IR intensity is most commonly accomplished by measuring a nonresonant sum-frequency response off of a gold surface. Since the nonresonant sum-frequency response is frequency independent,[53] any variations in the sum-frequency intensity are the result of changes in the IR intensity. Sum-frequency spectra of the sample of interest are then normalized to this nonresonant spectrum. This same normalization approach is necessary for many picosecond VSFG spectrometers. However, another, alternative, normalization method exists for some commercial picosecond systems, where the VIS and IR beam energies are coincidently measured at every data point in the scanned sum-frequency spectrum.[54] Due to the frequency scanning method of detection, these energy measurements provide a shot-by-shot measurement of how the IR and VIS energies are changing as a function of IR frequency. This information becomes equivalent to that which a nonresonant spectrum provides as long as there is a negligible change in the IR/VIS overlap at the surface as a function of frequency.

Moving beyond issues of spectral resolution and toward the experimental capabilities of these spectrometer variants, broadband IR pulses have the advantage of opening the door to new interfacial spectroscopies beyond what we have demonstrated above. These include the ability to measure the vibrational lifetimes of interfacial molecules[32,55,56] and determine the structure and dynamics of molecules adsorbed to the surface of nanoparticles.[57–61] Femtosecond excitation pulses are an absolute necessity for vibrational lifetime measurements, such as time-dependent or multidimensional VSFG spectroscopies. Typical vibrational lifetimes are on the order of hundreds of femtoseconds to picoseconds.[62,63] Therefore, femtosecond (broadband) IR pulses are required to follow the dynamics of vibrational excitations. For example, multidimensional VSFG spectra are also capable of providing critical information of the conformational structure of proteins at surfaces.[64,65] The use of VSFG *scattering* spectroscopy also requires the use of broadband IR pulses, as a demonstration of this experiment with a picosecond VSFG spectrometer has yet to be accomplished. The vast majority of published VSFG work has focused on extended planar interfaces, VSFG scattering spectroscopy measures the vibrational spectrum of molecules adsorbed to nanoparticle surfaces. From these spectra, the molecular structure and bonding environment of polymer nanoparticles,[62,66] liposomes,[67,68] and, most extensively, nanoemulsions have been studied.[60,69–72] It is worth noting that while the broadband VSFG spectrometer opens the door to these experimental techniques, the ever increasingly popular heterodyne detected (phase-sensitive) VSFG technique can be performed with either spectrometer design, and phase-sensitive picosecond VSFG spectrometers can also be found commercially.

Even though one could reasonably conclude broadband spectrometers offer increased experimental versatility over the picosecond spectrometer, this does not come without a cost. Likely the most immediate cost researchers will think of is monetary. With the commercial availability of the picosecond VSFG spectrometer, a *rough* estimate of the cost of acquiring basic SFG capabilities for a research laboratory at the time of this writing is ≤$400k USD. This estimate includes the cost of all the equipment associated with the laser system, an optical table, and other potential incidentals associated with installing the system. A broadband VSFG system will be more expensive, with a minimum cost north of $700k USD, nearly twice that of the picosecond system. The broadband laser source, OPA used for generating broadband IR pulses, and spectrometer/detector system make up much of this cost. The increased cost of the broadband VSFG system can place an increased burden on the pool of start-up funds or instrumentation grants that a laboratory has to work with. The question a researcher interested in VSFG must ask themselves is whether the increased experimental versatility is required for their research program and worth the increased price tag.

Beyond the start-up cost of purchasing the spectrometer and associated equipment, the acquisition of a broadband system will incur other costs. Generally, the hidden costs of labor and expertise requirements to establish VSFG experimental capabilities will be more heavily weighted for broadband spectrometers. These should also be factored into the decision of which spectrometer design is best suited for one's research laboratory. Since the picosecond spectrometer is commercially available, the installation and initial setup can be carried out by technicians who are trained to set up the VSFG system. Furthermore, these technicians can then provide a short initial training for researchers and aid in troubleshooting for those who may not have previous expertise in the area of nonlinear optics or VSFG. This eliminates the expertise cost of building the experiment and significantly reduces the installation time. As a result, the laboratory will need to work hard to gain the expertise in designing their VSFG experiments and interpreting spectra, but the lag time of building and calibrating the experimental setup is largely eliminated.

When it comes to building a broadband VSFG spectrometer, the above is simply not true. Due to lack of commercial availability, these spectrometers will be home-built systems. Thus, the build-phase of acquiring a broadband spectrometer will require expertise in nonlinear optics that not all laboratories may have and, if this is the case, will need to be gained through hiring of a grad student or postdoctoral associate with the necessary skill set. Depending on the previous experience of such personnel and the complexity of the experimental setup, the build time will vary. We recognize that longer build-times and requiring personnel with expertise in nonlinear optics are not inherently negative downsides. However, for research group leaders with little previous experience and who are interested in incorporating VSFG into their research, these factors should be considered.

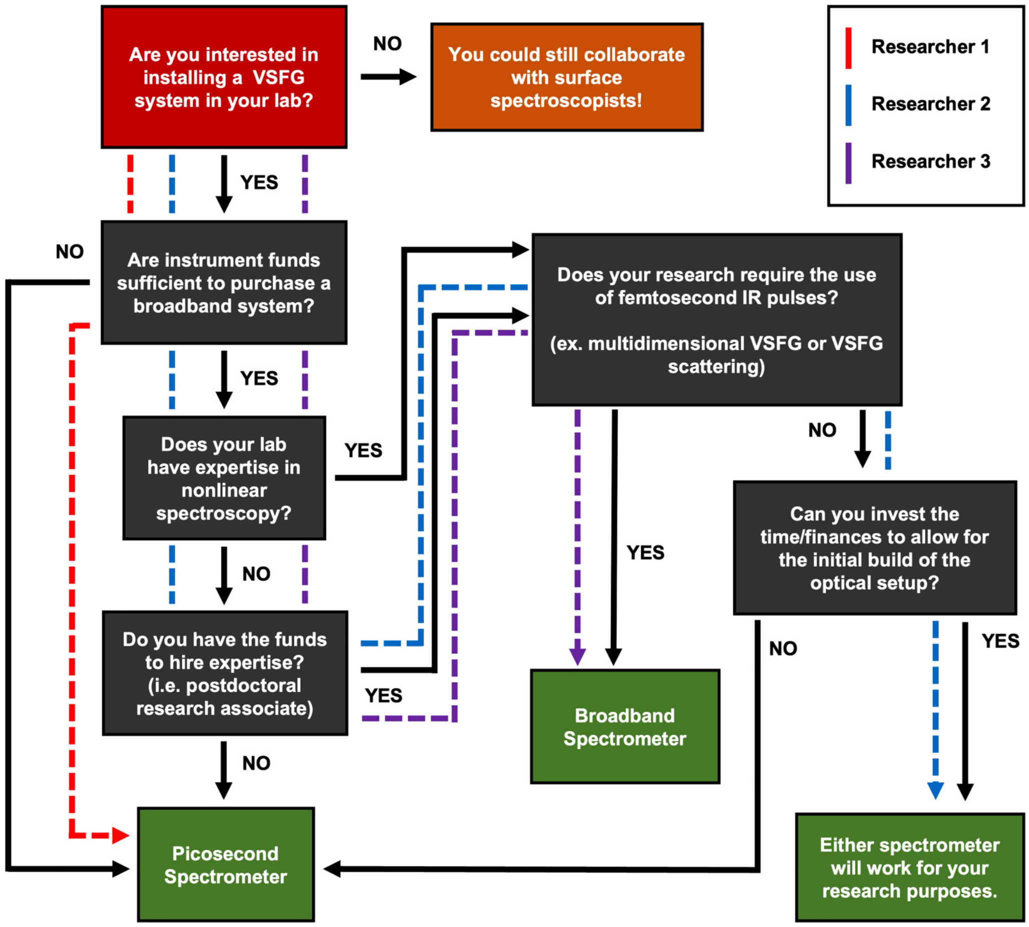

FIG. 5. Model decision tree illustrating some of the decision pathways different researchers might take to determine whether a picosecond or broadband VSFG spectrometer is right for them.

B. Decision time: Deciding the best spectrometer for you

To provide support to those new to the field of VSFG in identifying the spectrometer that will be sufficient for their research program, we have built a model decision tree (Fig. 5) and worked through this decision tree for several example scenarios. We will, again, stress that this discussion is intended to provide the broad contours of the kinds of input that need to go into making the decision of acquiring a picosecond or broadband spectrometer and is not meant to be a full summary of all the considerations one must make. In the tree below, we do not describe rigid rules, but simply provide an example of how one might work out if their research program requires one spectrometer over the other.

The tree begins with the financial consideration of whether the funds exist to consider a broadband VSFG spectrometer. The assumption is made that some funds (laboratory start-up funds, instrumentation grants, etc.) do exist that at least allow for the purchase of a picosecond spectrometer. If the funds do not exist for a broadband system, then it does not make sense to consider it as an option. The picosecond spectrometer will be more than adequate to enable the study of the physicochemical properties of interfaces. After the initial financial consideration, the issue of VSFG and/or nonlinear optical, expertise is considered. If this expertise does not exist in the laboratory and it cannot be hired, then the commercially available picosecond spectrometer makes for an excellent option that will enable the researcher's laboratory to utilize VSFG with minimal previous experience. Once the initial financial and expertise considerations have been examined, the topic of specific experimental capabilities is scrutinized. While broadband spectrometers are necessary to enable some interfacial spectroscopy experiments, if none of these are within the scope of the research plans, then the researcher is left to make the decision based on preference as both the picosecond and broadband spectrometers are sufficient to study the structure of interfacial systems.

We will now maneuver through the decision tree alongside three model researchers. For the sake of good storytelling and to help place oneself in the position of these templates, let us assume each of these researchers has just accepted a professorship and is building their research laboratory at the start of their career. Our first researcher (red path, Fig. 5) is developing a research program that leverages VSFG spectroscopy in their studies of air–water interfacial systems relevant to atmospheric chemistry but does not have access to the start-up funds required to purchase all the equipment necessary for a broadband VSFG spectrometer. Their decision is made quite easy as the convenient acquisition of a picosecond VSFG spectrometer will allow them to successfully incorporate interfacial vibrational spectroscopy into their research program.

Moving onto our second researcher (blue path, Fig. 5), they have not had any personal experience with VSFG, but have previously collaborated on projects with a VSFG laboratory. As they begin building their own research laboratory, they would like to bring the technique in house and have the funds available to pursue a broadband system. Without the personal expertise of building a VSFG system, they have budgeted to hire a postdoctoral research associate that will aid in the initial build-phase and training graduate students in the system's operation, so expertise is not an issue. When considering their research plans, which include the study of biomacromolecular structure at model cell membranes, the information provided by vibrational dynamics studies is interesting but not necessary for their work. They have also considered exploring the use of vesicles as membrane models, but decided against it, so VSFG scattering is not being considered. They are aware that both picosecond and broadband spectrometers have been successfully leveraged in this field of research, so they find themselves in the position to make the decision based on personal preferences and other considerations we may not have directly addressed in this article.

Our final early career researcher (purple path, Fig. 5) is just finishing a postdoctoral research position where they built and utilized multidimensional spectroscopies. Their research is centered on understanding how the chemical structure of electrode surfaces impacts interfacial chemical dynamics as these electrodes are used in different catalytic reactions. Researcher 3 has the funds available for a broadband system and they have the personal expertise in building advanced nonlinear optical systems. The research program they are building requires the ability to probe the time domain so they opt for the broadband VSFG spectrometer in order to take advantage of the temporally short infrared pulse durations.

V. CONCLUSION

In this article, we focused our discussion on the use of the picosecond VSFG spectrometer, highlighting several example use cases, and discussed several practical issues researchers should consider when deciding between purchasing a picosecond or broadband VSFG spectrometer. This discussion is intended to be for researchers new to the field of nonlinear optics, vibrational sum-frequency, in particular, and is purposed toward helping them navigate some of the differences between the different VSFG spectrometer designs. It is the authors' belief that this discussion will be of practical use to those wishing to explore the application of VSFG in their own research and the choice of laser source they will eventually need to make when purchasing equipment.

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AUTHOR DECLARACTIONS

Conflict of Interest

The authors have no conflicts to disclose.

Ethics Approval

No ethics approval was required for this work.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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