A new approach to vibrational sum frequency generation spectroscopy using near infrared pulse shaping

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ABSTRACT

We have developed a multipurpose vibrational sum frequency generation (vSFG) spectrometer that is uniquely capable of probing a broad range of chemical species, each requiring different experimental conditions, without optical realignment. Here, we take advantage of arbitrary near infrared (NIR) waveform generation using a 4f-pulse shaper equipped with a 2D spatial light modulator (SLM) to tailor upconversion pulses to meet sample dependent experimental requirements. This report details the experimental layout, details of the SLM calibration and implementation, and the intrinsic benefits/limitations of this new approach to vSFG spectroscopy. We have demonstrated the competency of this spectrometer by achieving an ~3-fold increase in spectral resolution compared to conventional spectrometers by probing the model dimethyl sulfoxide/air interface. We also show the ability to suppress nonresonant background contributions from electrode interfaces using time delayed asymmetric waveforms that are generated by the NIR pulse shaper. It is expected that this advancement in instrumentation will broaden the types of samples researchers can readily study using nonlinear surface specific spectroscopies.

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I. INTRODUCTION

The rapid development of optical pulse shaping^{1–3} methods over the last several decades has opened up new experimental possibilities in a diverse range of fields, spanning high harmonic generation,⁴ nonlinear fiber optics,⁵ nonlinear microscopy,^{6–9} and multidimensional spectroscopy,^{10–13} just to name a few. Recently, we have demonstrated the utility of directly manipulating the phase and amplitude of a femtosecond pulse to tailor waveforms for studies of complex interfaces using vibrational sum frequency generation (vSFG) spectroscopy.¹⁴ In this report, we detail our new vSFG spectrometer that makes use of a low cost 2D liquid crystal on a silicon spatial light modulator (2D LCOS-SLM) to customize near infrared (NIR) up-conversion pulse shapes to meet sample dependent experimental needs. This approach should find use in nonlinear optics labs, especially those making use of surface specific spectroscopies,

to address problems frequently encountered in conventional (and less flexible) spectrometer designs.

Broadband vSFG has become the method of choice for probing chemical species at the interface between two phases.^{11,15–19} The main advantage in broadband vSFG detection lies in simultaneously exciting a wide window of vibrational resonances that are upconverted by a second narrowband laser pulse to generate a complete vSFG spectrum without scanning the IR wavelength. This advantage comes at the cost of comparatively poorer spectral resolution, which is dictated by the bandwidth of the upconverting laser pulse. To achieve modest (~ 10 – 15 cm^{-1}) spectral resolution, researchers often use bandpass filters or 4f-pulse shapers equipped with slits at the Fourier plane.^{2,11,20} While they are convenient to implement, the use of bandpass filters provides neither wavelength nor bandwidth tunability. In contrast, using a slit at the Fourier plane of a 4f-shaper allows for tunable bandwidths and center

wavelengths; however, this approach suffers from challenges in reproducibly specifying the NIR pulse characteristics without extensive recharacterization of the output pulse. Both of these approaches are also only capable of generating time-symmetric pulse shapes, whereas for metallic or semiconducting surfaces, it is often desirable to apply time-asymmetric pulses to suppress nonresonant contributions.^{10,14,15} While powerful, using time asymmetric pulses is not necessarily ideal for studies of insulating samples due to limited spectral/bandwidth tunability (similar to the problems with filters), and spectral artifacts that can arise in the use of time delayed or temporally asymmetric pulses.^{21,22} Thus, the choice of a particular upconversion pulse waveform often predetermines the types of samples that can be optimally studied with a given spectrometer.¹

While different samples have different NIR spectral and/or temporal requirements, there was not, until recently, an avenue to change the pulse shapes in real time without substantial optical realignment. To address this limitation, we have reported the use of NIR pulse shaping methods to achieve a unique ability to probe a diverse set of samples ranging from biomolecules on insulating surfaces to sugar molecules on metallic surfaces in a completely reproducible way without changing any optical alignment.¹⁴ In this report, we expand upon this initial demonstration to detail the entire spectrometer and pulse shaping capabilities in the context of vSFG experiments using a diverse range of samples. Specifically, we use the model dimethyl sulfoxide (DMSO)/air interface as a metric to characterize the spectral resolution improvements afforded by this design and proceed to demonstrate the utility of adaptive pulse shaping to study organic electrolytes at an electrode interface.

II. BACKGROUND AND THEORY

A. vSFG theory

vSFG is a second order nonlinear optical spectroscopy in which one photon (ω_{IR}) induces a vibrational coherence in a molecular sample that is upconverted by a second photon (ω_{NIR}) to produce new light at the sum of the two driving frequencies, $\omega_{\text{SFG}} = \omega_{\text{IR}} + \omega_{\text{NIR}}$. The intensity of the radiated light is proportional to the absolute square of the effective second order nonlinear susceptibility, $\chi_{\text{eff}}^{(2)}$, and the strength of the incident fields ($E_{\text{IR}}, E_{\text{NIR}}$)^{16,22–24}

$$I_{\text{SFG}} \propto |E_{\text{SFG}}|^2 \propto \left| \chi_{\text{eff}}^{(2)} E_{\text{IR}} E_{\text{NIR}} \right|^2. \quad (1)$$

The effective second order nonlinear susceptibility is the sum of a resonant, $\chi_{\text{res}}^{(2)}$, and nonresonant, $\chi_{\text{NR}}^{(2)}$, contribution^{10,14,23,25}

$$\chi_{\text{eff}}^{(2)} = \chi_{\text{NR}}^{(2)} + \chi_{\text{res}}^{(2)} = \chi_{\text{NR}}^{(2)} + \sum_k \frac{A_k}{\omega_{\text{IR}} - \omega_k + i\Gamma_k}, \quad (2)$$

where ω_k is the vibrational frequency, A_k is the amplitude, and $2\Gamma_k$ is the linewidth of the k^{th} -mode. Equation (2) shows that when IR spectral components in the broadband pulse are resonant with a vibrational mode, there is an enhancement in the radiated SFG and thus serves to produce a vibrational spectrum. Given the even-order field interaction within the dipole approximation, vSFG from centrosymmetric and isotropic bulk media cancels on average. In contrast, at interfaces where the local symmetry is broken, the

radiated light coherently adds to produce readily observable signals. This sensitivity to local symmetry makes vSFG a powerful surface specific spectroscopy by providing insight into only the ordered molecular layers at an interface.^{11,15,28–32,16–19,24–27} In the limit that $\chi_{\text{NR}}^{(2)}$ is negligible, the vSFG spectrum is dominated by the molecular resonances at the interface and their interferences with one another. On the other hand, when $\chi_{\text{NR}}^{(2)} > \chi_{\text{res}}^{(2)}$, such as at metallic surfaces, $\chi_{\text{res}}^{(2)}$ becomes relatively small and can become obscured by the background signal from the substrate itself. As mentioned above, this nonresonant background can be suppressed by taking advantage of the ultrafast dephasing of the electronic coherence via a variable time delay between the two driving fields or by changing the temporal shape of upconverting pulses.^{14,15,22}

B. Pulse shaping

To synthesize an arbitrary NIR waveform for vSFG measurements, one needs to control the spectral phase and amplitude of the individual frequency components in an ultrashort pulse. The optics in a 4f-pulse shaper effectively convert a time-domain pulse into the frequency domain, where a mask or modulation function, $M(\omega)$, can be applied that alters the phase and/or amplitudes of the individual frequency components according to the following equation:²

$$E_{\text{out}}(\omega) = M(\omega)E_{\text{in}}(\omega), \quad (3)$$

where the $E_{\text{out}}(\omega)$ represents the frequency domain representation of the desired output pulse shape and $E_{\text{in}}(\omega)$ describes the input pulse. In our pulse shaper, the modulated light exits through the 4f-line in the reverse direction to reassemble the pulse back into the time domain using the same optics, as will be described in more detail below.

III. EXPERIMENTAL

A. Instrument overview

Figure 1 shows the schematic of our new vSFG spectrometer. The light source was a regenerative amplifier system (Spectra Physics Spitfire Ace), which was seeded with a femtosecond Ti:sapphire oscillator (Mai-Tai) to produce ~6 W of average power at a 1 kHz repetition rate with typically 42 fs pulses. Using a fixed ratio beam splitter, ~3.4 W of the 800 nm output was sent to a TOPAS-Prime Plus optical parametric amplifier and a difference frequency mixer to produce broadband mid-IR pump pulses. The spectral bandwidth of the mid-IR pump pulses was typically $\geq 300 \text{ cm}^{-1}$ at the full width at half-maximum (FWHM) when centered at $\sim 2900 \text{ cm}^{-1}$. Although the mid-IR was centered at this particular frequency for all the experiments presented in this work, the optical parametric amplifier (OPA) has a wide tuning range spanning from $\sim 900 \text{ cm}^{-1}$ to $< 4000 \text{ cm}^{-1}$. As such, it is possible to probe a wide range of vibrational modes to meet experimental needs. The ease of implementing this tunability is further facilitated by our use of a collinear excitation geometry (i.e., the NIR and IR beams are combined such that they propagate along the same path), and thus, any changes to IR or NIR center wavelengths do not necessitate realignment of the collection arm. Such realignment is, however, critical in noncollinear geometries due to changing phase-matching conditions. In fact, for our collinear geometry, changing the mid-IR wavelength only requires a slight tuning of the time-delay between pulses owing to wavelength

FIG. 1. Schematic of the vSFG instrument. First, the laser was divided between two optical paths. To generate mid-IR pulses, a majority of the output from the amplified laser system was directed into an OPA with a difference frequency mixer. A portion of the remaining NIR from the amplified laser was sent through an optional bandpass filter, reduced with a telescope, delayed in time, and directed into our compact pulse shaper (picture shown in the green dotted inset). The two paths were polarization purified and rotated before being combined in a dichroic mirror in a collinear geometry. The light was focused onto the sample at a 60° angle with respect to the surface normal. The vSFG signal was collected and dispersed in a spectrometer equipped with a CCD camera. The blue dashed inset shows a cartoon of a modulation pattern applied to the SLM to produce a narrow band symmetric waveform, similar to the function of a slit. The grating pattern applied along the horizontal axis of the SLM is also represented.

dependent indices of refraction in the polarization and focusing optics. Also, small adjustments to the focal position of the excitation lens are needed to optimize signal levels.

Of the remaining light from the amplifier, approximately 1.2 W was directed through a $2\times$ reducing telescope (beam diameter was ~ 5 mm after the telescope) after being filtered with a bandpass filter (Thorlabs, FBH800-10). The reason for this filtering step is twofold: (1) it reduces the intensity of the 800 nm light below the breakdown/self-phase modulation threshold making the telescope design less demanding; (2) since vSFG experiments require narrow-band NIR light, inclusion of a broad spectral window is not necessary and removing the unused components makes alignment safer. Despite these practical reasons to include a bandpass filter for vSFG experiments, we demonstrate below that its inclusion is not essential if one were to want to make, say, ultrashort double pulses, etc. After the telescope and optional filtering, the light was sent into a retro-reflector mounted on a motorized delay stage before being polarization purified with a Glan-laser polarizer and coupled into the pulse shaper itself. The 4f-pulse shaper (Fig. 2) consists of a transmission grating (Wasatch Photonics, WP-1200/840-25.4) in a rotation tip/tilt mount that was used to maximize diffraction efficiency and orientation relative to the optical table (i.e., in the horizontal plane). Next, a flat folding mirror back-reflects the dispersed beam at an

upward angle to the bottom of a silver coated cylindrical mirror (Lambda Research Optics, PAG-CYLC-25.4 $\times$ 25.4B-200) with a focal length of 100 mm that serves to focus individual frequency components along the horizontal dimension of a phase-only 2D liquid crystal on silicon SLM (Hamamatsu, 2D-LCOS-SLM, model X10468-02) positioned at the Fourier plane. The SLM is mounted on a precision linear stage with a tip-tilt-rotation mount to optimize its position and ensure that all SLM pixels are precisely in the Fourier plane. A key aspect of this design is the use of the cylindrical mirror and 2D-SLM, which allows for grating patterns to be applied along the vertical dimension of the SLM to control the amplitude of the frequency components, whereas the spectral phase can be manipulated via masks applied across the horizontal dimension. The entire shaper has a footprint of less than 12×12 in. and costs approximately \$20k (at the time of purchase) making it a very viable and inexpensive alternative to commercial multi-mask SLMs or acousto-optic modulator (AOM) based systems. The light reflected from the SLM is picked off using a square mirror outside of the 4f-line and directed into the vSFG spectrometer. The throughput of the 4f-pulse shaper was measured to be $\sim 70\%$. The alignment of the shaper is optimized by maximizing the second harmonic generation conversion efficiency of the 800 nm light in a β -barium borate (BBO) crystal; this ensures a zero-dispersion design in the absence of an applied

FIG. 2. A simplified drawing of the compact NIR pulse shaper used in this instrumentation. The large black box is the SLM body, whereas the gray rectangular box inside is the active region. A transmission grating disperses the frequency components that are subsequently reflected off a flat folding mirror before being focused onto the SLM with a cylindrical mirror.

mask. A key, but potentially subtle trick in the success of this system lies in the application of a diffraction pattern along the vertical direction of the SLM to divert light to reach our pick off mirror. This serves two key purposes: (1) it allows for the SLM to lie completely in the Fourier plane (i.e., it does not need to be tilted) and (2) it ensures that only light that has been modulated reaches the sample preventing the introduction of unshaped light to the spectrometer.^{33,34} An example of this applied pattern is shown in the inset of Fig. 1 for a slit spanning 8 pixels. Light that does not interact with the liquid crystals or does not see a pattern simply reflects off the modulator and propagates back along the input path.

Independent polarizer/waveplate pairs were used to purify and rotate the polarizations of both IR and NIR beams before being combined using a commercially available dichroic mirror (ISP Optics, BSP-DI-25-2). The collinearly propagating beams were focused onto a breadboard mounted sample stage consisting of an XYZ-stage and a 3-axis goniometer. The sample height was controlled via a stepper motor allowing for precise and reproducible positioning of the sample with respect to the incident and outgoing optical components. The sample stages/environments can be easily changed by swapping breadboards equipped with matching hardware, but differing sample cells.¹⁵ The incident light was focused on the sample using a CaF_2 lens ($f = 150$ mm) mounted on a linear translation stage and angled at 60° with respect to the sample surface normal. The vSFG signal was collected and re-collimated by a 150 mm focal length air-spaced achromatic doublet. This signal was polarization resolved using an achromatic half waveplate followed by a calcite Glan-Taylor polarizer with a 100 000:1 contrast ratio. This approach ensures that the reflection of light from mirrors and gratings is constant, regardless of the polarization of light that is measured. Subsequently, the copropagating signal and residual driving light were separated using a 785 nm short-pass filter (Semrock, SP01-785RU-25). The collimated, polarization resolved, and filtered vSFG signal was then focused into an Acton SpectraPro SP-2300 spectrograph using a pair of quartz ($f = 50$ mm and $f = 15$ mm) cylindrical lenses (Eksma Optics). The dispersed light was detected with a Pixis 256E CCD camera with hardware binning along the vertical direction for a specified region of interest (ROI) that consisted of 10 vertical pixels. The signal and background ROIs were co-specified and recorded at the same time for background/baseline subtraction. The maximum spectral resolution for the spectrograph is $\sim 1.9 \text{ cm}^{-1}$ when using an 1800 line/mm grating centered at 652 nm and 50 μm slit width. The entire instrument was enclosed in a series of gasket sealed purge boxes. Reference IR spectra used to scale vSFG spectra were collected from Au surfaces in the PPP polarization combination.¹⁴ Software was developed in house using LabVIEW to control the SLM, linear stages, rotation mounts, and CCD camera data acquisition. The data analysis was performed offline using LabVIEW and Python scripts.

B. SLM phase calibration

The phase applied to the light incident on each pixel of the SLM was controlled by rotating the liquid crystals with an applied voltage. The dynamic range of the applied voltage on the SLM is 8-bit and specified with grayscale levels from 0 to 256. Thus, a complete phase modulation from 0 – 2π for each spectral component must be contained in the 256 grayscale values for optimal spectral phase

modulation. The calibration of these values to the corresponding phase applied for each frequency was accomplished by using a cross polarizer method in which the spectrum of a phase modulated output pulse was recorded by the spectrometer as a function of each grayscale value. In this calibration procedure, the polarization of the linearly polarized incident beam was rotated 45° to the horizontal axis of the SLM and an analyzer was placed before the spectrometer in such way that its transmission axis was cross polarized to the incident beam's polarization axis. Since the liquid crystals in each pixel of the SLM are aligned horizontally by default, they only interact with the incident electric field component parallel to that dimension while the perpendicular electric field component remains unaffected. Therefore, the polarization of each of the spatially distributed spectral components was rotated by different amounts as the phase of the horizontal electric field component was delayed relatively to the vertical component by the SLM. Depending on the degree of this polarization rotation, the individual frequency components will pass through the analyzer with varying amplitudes. For example, when there is no phase difference applied to the horizontal dimension relatively to the vertical, the output polarization will match that of the input and the light will be blocked by the analyzer. Alternatively, if the applied grayscale value causes a phase shift of π radians to the horizontal component of the incident electric field, the output polarization rotates 90° to the incident polarization and the maximum intensity is transmitted and detected. The resulting spectra are collected for each value of grayscale that was applied over the entire SLM active area.

Spectra from the phase calibration measurement are presented in Fig. 3(a), where the x-axis represents the applied grayscale levels, spanning from 0 to 256, and along the y-axis are the measured spectra. The data for two individual wavelengths, 795 nm (red circles) and 800 nm (grey diamonds), are extracted and plotted in Fig. 3(b) and clearly show a $> 2\pi$ phase modulation for these spectral components across the entire grayscale range. The calibration was completed by fitting the data at each wavelength to the following equation:^{8,34}

$$I(g) = \frac{1}{2} [1 - \cos(\phi_x(g) - \phi_y)], \quad (4)$$

where $I(g)$ is the measured intensity and $\phi_x(g)$ and ϕ_y are the phase along the horizontal and vertical dimensions of the SLM, respectively. The extracted phase, $\phi_x(g)$, can then be fit to a line (or other polynomial), as shown in Fig. 3(c), to produce a look-up table for applying the desired phase. This calibration only needs to be repeated for large changes in the spectrum of the pulse or if the drive voltage of the SLM is changed.

C. Wavelength vs. SLM pixel calibration

Unlike the phase calibration, the wavelength calibration to determine the horizontal position of each frequency component is typically conducted before every experiment. Since the NIR beam and vSFG signal propagate collinearly in our instrument, the same spectrometer optics can be used for this calibration and for signal detection simply by changing the spectrograph grating center wavelength and removing the NIR rejection filter from the signal collection path. The calibration of a given horizontal pixel to the specific wavelength of light it is shaping takes advantage of the

FIG. 3. Phase calibration of the SLM. (a) A false color plot showing the impact of applying a uniform phase, as indicated by varying gray scale values, on the transmitted spectrum, as described in the text. Lineouts from (a) centered at 795 nm (red/circle) and 800 nm (gray/diamond) are shown in (b) along with fits to Eq. (6) described in the text. The extracted wavelength dependent phase is plotted in (c) along with a linear fit that serves as a calibration.

vertical grating pattern that was discussed earlier. In this approach, the grating pattern was only applied along a single vertical array of pixels. This results in only a narrow bandwidth of light being diffracted and subsequently collected by the pickoff mirror and relayed to the spectrometer. The slit pattern was then scanned across the SLM horizontal axis. Figure 4 plots the observed wavelength at which the maximum intensity was measured for each slit position on the SLM. This calibration was repeated for each of the three different spectrograph gratings that were used to achieve different experimental resolutions both with and without the pre-shaper bandpass filter. The blue dots show the data without the bandpass filter where a linear relationship was observed throughout the entire spectral region as expected. With the bandpass filter

in place, the data obtained from the same calibration procedure are shown as red diamonds in Fig. 4 and match the data obtained without using the filter, though over a smaller window dictated by the bandpass filter's bandwidth. Outside of this spectral window, where the spectral components were filtered before entering the pulse shaper, a constant background is detected, regardless of the SLM slit position. Note that the calibration results for all three gratings agree with each other regardless of the application of a pre-SLM bandpass filter or which grating was used in the experiments. The average spectral dispersion was ~ 0.14 nm/pixel as calculated from the calibration for the spectral window spanning from 765 nm to 820 nm. The linear phase shift is calculated by the following equation:³

FIG. 4. Wavelength vs. pixel calibrations for three different gratings in the spectrometer with 600, 1200, and 1800 lines/mm, respectively. A bandpass filter (centered at 800 nm) was used before the pulse shaper to narrow the spectral width of the input pulse. Data points depicted with diamonds and with circles in each plot correspond to the calibrations with and without the band-pass filter, respectively.

$$\varphi = \pm \frac{\lambda_0^2}{2c\Delta\lambda} \text{ fs} = \pm 7619 \text{ fs}, \quad (5)$$

where λ_0 is the center wavelength of the upconverting bandwidth (in nm), $\Delta\lambda$ is the average spectral dispersion (also in nm), and c is the speed of light (299.79 nm/fs). This indicates that the accessible delay range for our pulse shaper is ~ 15 ps.

D. Measured bandwidth vs. applied slit width

Figure 5(a) shows the spectrum of the NIR upconversion pulse at a few representative slit widths. Note that the input pulse shape is not a simple Gaussian profile. A series of slit widths centered at 799.5 nm were applied to the SLM and the light was collected in our spectrometer to directly measure the spectral widths at the FWHM as shown in Fig. 5(a). The measured bandwidths are plotted as a function of slit width in Fig. 5(b). Based on the data, an extrapolated minimum bandwidth of ~ 0.18 nm at 799.5 nm is expected, which leads to a laser limited spectral resolution of $\sim 2.8 \text{ cm}^{-1}$ in the vSFG spectra.³⁵ On the other hand, the optimal spectral resolution we expect to observe with a 1800 line/mm grating in the

FIG. 5. NIR spectra and corresponding bandwidths at different slit widths. In (a), symbols are the measured spectra where double-sided arrows indicate the measured bandwidths at FWHM. (b) shows the measured bandwidths vs. applied slit width on the SLM. The three representative spectra shown in (a) are denoted in (b) by the corresponding color.

spectrometer is $\sim 1.9 \text{ cm}^{-1}$. As such, our maximum spectral resolution is still limited by the upconversion pulse. Despite this limitation, this resolution is $\sim 3\times$ higher than that typically reported for broadband vSFG instruments, but it does not reach the sub- cm^{-1} resolution found in extremely specialized instruments.^{36,37}

E. NIR pulse width characterization

NIR pulse durations were measured as a function of the slit width applied to the SLM via cross-correlation of the shaped NIR pulse with the broadband mid-IR fs pulses using a GaAs window. The NIR time delay with respect to the mid-IR pulse was varied using a linear delay stage taking 10 fs steps to generate the time-traces shown in Fig. 6(a). The convolution of a very short pulse (IR) with the longer NIR pulse serves to map the NIR temporal

FIG. 6. NIR pulse durations determined via cross-correlation measurements are shown in (a). The extracted pulse durations were ~ 4.2 , ~ 2.2 , and ~ 0.6 ps using slit widths of 2, 4, and 12 pixels, respectively. (b) The measured pulse durations are plotted as a function of the measured bandwidth. The expected transform limited pulse widths, using the spectral information from Fig. 5, is shown for comparison. The three-representative cross-correlation measurements, in (a), are indicated in (b) by the corresponding colored circles.

waveform. Spectral bandwidths of ~ 0.22 nm (3.44 cm^{-1}), ~ 0.4 nm (6.25 cm^{-1}), and ~ 1.1 nm (17.2 cm^{-1}) corresponded to the use of slit widths of 2, 4, and 12 pixels, respectively. Pulse durations of ~ 4.2 ps, ~ 2.2 ps, and ~ 0.6 ps were measured at the FWHM of the measured data shown in Fig. 6(a). Assuming a sech^2 pulse shape, which better mimics the top-hat-like spectral shape we obtain from the laser system, as compared to a Gaussian profile, we can calculate the transform limited pulse durations using the previously measured spectral widths (data from Fig. 5). Comparing these transform limited pulse widths to those measured, we arrive at the data in Fig. 6(b) that shows excellent agreement at larger applied bandwidths, whereas for narrower bandwidths, i.e., those smaller than 0.5 nm, the measured pulse durations are longer than the transform limited pulses. This difference is most likely due to the estimation of spectral bandwidths, which is complicated by limitations in the spectral resolution of the spectrograph/CCD and the slight asymmetry in the spectral shapes that are observed when using narrow slit widths.

FIG. 7. Symbolic data points in (a) are the measured cross-correlations obtained by varying the etalon reflectivity; $R = 0.97, 0.98, 0.99$. Solid lines show an exponential fit to the data to estimate decay times. (b) shows the tunability in the center wavelength by varying the virtual tilt angle, θ , of the SLM-generated etalon.

F. Temporally asymmetric pulse generation

An important use of the pulse shaper is the application of arbitrary waveforms for specific experimental needs. In many cases, specifically with metallic and semiconducting surfaces, the nonresonant background dominates the vSFG response. To circumvent this issue, nonresonant suppression methods have been developed using an asymmetric waveform obtained from an etalon that is temporally delayed by a few 100 fs to avoid the ultrafast response of the substrate.^{10,21} To create an etalon waveform using the SLM, we applied the transfer function¹⁷

$$M(\omega) = \frac{1 - R}{1 - R * \exp[i(2d \cos \theta / c)\omega]}, \quad (6)$$

where R is the reflectance, θ is the tilt angle, and d is the distance between virtual etalon surfaces. By tuning the reflectivity of the virtual etalon using the pulse shaper from $R = 0.97, 0.98$ to 0.99 and mapping the cross-correlation, as done in Sec. III E, we arrive at the time-traces shown in Fig. 7(a). These measured waveforms were fit to right-sided exponential decays to extract the decay constants of ~ 0.8 ps, ~ 1.1 ps, and ~ 1.9 ps using R values of $0.97, 0.98$, and 0.99 , respectively. Similarly, adjusting θ allows one to select different spectral windows from the incident pulse, as shown in Fig. 7(b). This provides the aforementioned variable control over central wavelength and the associated spectral resolution that is not possible using a fixed etalon.

IV. RESULTS AND DISCUSSION

The impact of the NIR spectral bandwidth on the vSFG spectral resolution was demonstrated using a neat DMSO/air interface as shown in Fig. 8(a). vSFG spectra were collected using the SSP polarization combination, where the letters describe the polarization of the vSFG, NIR, and IR light fields, respectively. The NIR pulses were symmetric and bandwidths of $11.4, 8.8, 6.2$, and 3.6 cm^{-1} were used to produce these spectra. The average peak position at 2926 cm^{-1} corresponds to the methyl symmetric stretch of DMSO, in agreement with previous vSFG measurements.^{16,38,39} The peak positions, amplitudes, and widths of the vSFG spectra were extracted by fitting the data to Eqs. (1) and (2), using only one resonance to avoid overfitting the data. The linewidths extracted from these fits are compared with the input NIR bandwidths as shown in Fig. 8(b). As expected, the spectral width of the methyl symmetric stretch decreased with narrower NIR bandwidths, with small deviations between the datasets at both high and low resolutions. The differences at narrower bandwidths can be attributed to the importance of inhomogeneous broadening, the convolution of the laser bandwidth with the spectrometer resolution, and interference between closely spaced resonances. At larger bandwidths, the spectral fitting is notably poorer due to the model function used not matching the physical processes being described (i.e., the line shape deviates from a Lorentzian at poor spectral resolutions), making estimates of the line shape smaller than expectations. Despite these relatively minor differences (i.e., only an ~ 1 cm^{-1} difference in widths), it is clear that the vSFG spectral resolution can be reliably changed using our pulse shaper in a completely reproducible and reversible way without realignment or recharacterization.

The difference between using temporally symmetric vs. asymmetric pulse shapes on nonresonant background suppression is

FIG. 8. (a) vSFG spectra acquired from the air/DMSO interface using different bandwidths of NIR pulses. Slit widths of 8, 6, 4, and 2 pixels were used to produce NIR pulses with ~ 11.4 , ~ 8.8 , ~ 6.2 , and $\sim 3.6 \text{ cm}^{-1}$ bandwidths, respectively. The spectra were rescaled and offset for better visual comparison. Recovered linewidths (measured at HWHM) from spectral fitting were found to be ~ 9.4 , ~ 8.3 , ~ 7.7 , and $\sim 4.7 \text{ cm}^{-1}$ for the above mentioned NIR bandwidths, accordingly. The extrapolated NIR bandwidths from the SLM and the recovered spectral linewidths are plotted in (b) as a function of slit widths.

demonstrated in Fig. 9 for the case of propylene carbonate on Au (111) films collected in the SSP polarization combination. Propylene carbonate is an organic solvent routinely used as a high-permittivity component of electrolytes in lithium-ion batteries. The Au surface produces a substantial amount of nonresonant background making

FIG. 9. vSFG spectra of propylene carbonate at an Au interface acquired using two different pulse shapes: a Gaussian and a right sided exponential. Both pulses were temporally delayed by 100 fs with respect to the IR pump pulses. The inset shows the unscaled data.

some molecular vibrations challenging to measure due to the overwhelming background response. Symmetric and asymmetric pulse shapes were generated by applying the appropriate masks to the SLM and delaying them by 100 fs with respect to the driving IR laser pulse. Figure 9 shows the vSFG spectrum of propylene carbonate obtained from an asymmetric pulse shape (blue diamonds) and a symmetric pulse shape (red circles). Time-asymmetric pulses were generated using a reflectance of 0.99, to produce a temporally asymmetric pulse with a decay constant of $\sim 1.9 \text{ ps}$. Notably, the magnitude of the nonresonant signal from the Au substrate is much higher for the symmetric pulse as compared to the asymmetric pulse (see the inset of Fig. 9 for unscaled data). Notably, the edges of the spectrum in Fig. 9 are distorted when using a symmetric pulse, whereas the edges are flat when partially suppressing the nonresonant background using the time-asymmetric pulse. This highlights the problem in collecting small or modest signals interfering with huge background contributions and relying on corrections to quantitatively scale the data. This is illustrated by our measurements that were collected back to back using the same sample, only altering the pulse shapes via the pulse shaper—these results show that the background was well scaled using our normalization procedure for the asymmetric pulse, whereas it was not for the symmetric pulse as the variations in the absolute intensities of the background lead to imperfect scaling. This makes the measured signal easier to analyze, especially in fitting the data, and less susceptible to problems with signal normalization. It is sometimes desirable to keep some of the nonresonant background to enhance weak signals, as was done here. The spectral features measured in both cases agree with one another but are less distorted for the asymmetric pulse.

V. CONCLUSION

Here, we have detailed the design and testing of a multipurpose vSFG spectrometer with the ability to alter NIR pulse shapes without realignment for the study of a wide variety of samples. We have detailed our 4f-pulse shaping design, principles of operation, and characterized its utility on multiple samples spanning

nonlinear media, air/liquid interfaces, and buried electrode/liquid interfaces. It is expected that based on the utility of changing pulse shapes to meet experimental needs, this design will find early adopters keen on expanding the scientific questions that can be addressed using the existing infrastructure while eliminating the down time associated with optical reconfiguration and characterization. Also, applications beyond those demonstrated here, such as multi-pulse generation for time domain vSFG measurements^{11,40,41} or heterodyne detection schemes²⁷ could be readily performed without the need to change experimental geometries.

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