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Wei-Chen Yang and Dennis K. Hore

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Broadband models and their consequences on line shape analysis in vibrational sum-frequency spectroscopy

Wei-Chen Yang and Dennis K. Hore^{a)}

Department of Chemistry, University of Victoria, Victoria, British Columbia V8W 3V6, Canada

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Vibrational sum-frequency generation (SFG) spectroscopy can provide valuable qualitative and quantitative information about molecular species at surface and buried interfaces. For example, the resonance frequency of a particular chemical function group is revealing of the surface environment, especially when compared to what is observed in bulk IR absorption or Raman scattering spectra. Furthermore, the amplitude of the mode can be related to the molecular orientation, providing a detailed quantitative account of the surface structure. Each of these attributes, however, requires fitting the spectra to some vibrationally resonant line shape. This is particularly challenging when the modes of interest co-exist with broad resonance features, such as water O–H stretching. In this perspective, we examine the merits and consequences of different approaches to fitting homodyne SFG data. We illustrate that, while any model can provide a useful description of the data, no model can accurately and consistently provide even the relative phase deeply encoded in homodyne data without the use of additional information. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5053128>

I. INTRODUCTION

Second-order nonlinear surface spectroscopy is valued for its ability to selectively probe molecules at interfaces when the same species are present in one or both of the adjacent bulk phases. This is the result of the symmetry requirement for non-zero achiral second order susceptibility tensor elements $\chi_{ijk}^{(2)}$ where i, j , and k are Cartesian coordinates. Under the electric dipole approximation and in the absence of appreciable surface charges, signal originating from $\chi^{(2)}$ processes such as sum-frequency generation (SFG) is observed only in the absence of inversion symmetry.^{1,2} That is, there can be no macroscopic inversion center that creates a point $(x, y, z) \rightarrow (-x, -y, -z)$. This occurs to some extent for purely mathematical reasons. For example, at the polymer–water interface, if we imagine a Fresnel-type interface where a semi-infinite polymer phase meets a semi-infinite water phase, no inversion centers exist at the plane $z = 0$. If the polymer is amorphous, there is an effective inversion center in the isotropic bulk, as there is in the bulk aqueous phase. If a methyl symmetric stretch is observed at PMMA–water, we therefore know that no methyl groups in the bulk polymer phase have contributed to the measured response. In addition to this geometric symmetry-breaking, the anisotropic forces acting on a methyl group with a bulk polymer phase located at $z < 0$ and a bulk water phase at $z > 0$ likely result in a preferred organization of the chemical functional groups. This creates an additional symmetry breaking in a chemical sense. As a final note, if there are species in solution that contain methyl groups, they will also not contribute to the vibrational $\chi^{(2)}$ spectrum since their orientational

average is isotropic unless they interact with (are adsorbed on) the surface.

Without any additional considerations or further analysis, SFG spectra therefore present useful qualitative information such as the presence of ordered species at the surface, the surface environment as revealed by the resonant frequency (shifts) compared to the bulk phase IR or Raman values,^{3,4} heterogeneity of the surface environment from the linewidths, and the polarity of the functional group orientation from the direction in which the bands point in the case of interference with significant non-resonant modes or in an explicit heterodyne measurement. However, further evaluation may be performed in order to extract quantitative information, such as a ratio of mode amplitude in two different polarization schemes to gain information on the molecular orientation.^{5–10} Also, it is often necessary to fit the observed bands to a model even if just to extract the resonant frequency as the peak value may be shifted due to interference. Many schemes have been proposed for such line shape analysis.^{11–17} This perspective will take a look at a few of the common approaches and discuss their relative merits and consequences.

II. VIBRATIONAL LINE SHAPES

It may be known from chemical intuition, or from the results of a normal mode analysis, that an observed peak in an SFG spectrum contains only a single vibrational mode. In such cases, the homogeneous component of the line shape is represented in the frequency domain by a Lorentzian function

$$f_L(\omega) = \frac{A}{\omega_0 - \omega - i\Gamma}, \quad (1)$$

^{a)}Author to whom correspondence should be addressed: dkhore@uvic.ca

where A is the amplitude, ω_0 is the resonant frequency, and Γ is the homogeneous or intrinsic linewidth, proportional to the reciprocal vibrational dephasing time T_2 .^{18,19} If multiple such modes are observed, regardless of whether they are well-separated in frequency or overlapping, the frequency dependence of the second-order susceptibility may be described by

$$\begin{aligned}\chi^{(2)}(\omega) &= \chi_{\text{NR}}^{(2)} + \sum_q \chi_q^{(2)} \\ &= A_{\text{NR}} e^{i\phi_{\text{NR}}} + \sum_q \frac{A_q}{\omega_q - \omega - i\Gamma_q},\end{aligned}\quad (2)$$

where each of the q modes has a corresponding Lorentzian amplitude A_q , resonance frequency ω_q , and width Γ_q and $\chi_{\text{NR}}^{(2)} = A_{\text{NR}} e^{i\phi_{\text{NR}}}$ represents any vibrationally non-resonant contribution, if present. We note that for dielectric materials, $\chi_{\text{NR}}^{(2)}$ is real since $\phi_{\text{NR}} = \pm 180^\circ$, but in the case of materials that are not transparent to the visible and SFG beams such as metals, $\chi_{\text{NR}}^{(2)}$ may be complex-valued. In all of our model spectra that follow, we have set $\chi_{\text{NR}}^{(2)} = 0$ for simplicity. The sign conventions^{20–22} in the Lorentzian denominators appearing in Eqs. (1) and (2) have their origin in the time-domain second-order response function

$$R^{(2)}(t) = A_{\text{NR}} e^{i\phi_{\text{NR}}} \delta(t) - i\Theta(t) \sum_q e^{-i\omega_q t} e^{-\Gamma_q t}, \quad (3)$$

where $\Theta(t)$ is the Heaviside step function and

$$\chi^{(2)}(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} R^{(2)}(t) dt. \quad (4)$$

In theory, there should also be line broadening due to instrumental considerations (laser and spectrograph bandwidth) and distribution of molecular environments. Such broadening mechanisms are well-described by a Gaussian function

$$f_G(\omega) = A \exp\left[-\frac{(\omega - \omega_0)^2}{2\Gamma_G^2}\right], \quad (5)$$

where A is the peak amplitude, ω_0 is the resonance frequency, and Γ_G is the net inhomogeneous linewidth. In practice, the signal-to-noise ratio is often insufficient to distinguish whether a band has a pure Lorentzian profile. In the case of IR absorption and spontaneous Raman scattering spectra, fitting may be performed using a purely Gaussian line shape, as there are no interference effects. Those bulk spectroscopic techniques directly measure the imaginary component of the first- and third-order susceptibility, respectively. In the case of SFG spectroscopy, however, Gaussians alone do not provide the phase contribution to account for spectral interference. In cases of low signal-to-noise or insufficient spectral resolution in SFG, the default approach is to fit using purely Lorentzian line shapes, letting Γ be as wide as necessary to fit the bands reasonably well. In such cases, one could report widths as large as 10–15 cm^{-1} , even though previous measurements of the dynamics reveal that the homogeneous linewidth should be much narrower.^{11,12,23,24}

A more rigorous approach is to employ a line shape that uses the known homogeneous width Γ_L and fit to the experimental data to obtain the inhomogeneous component Γ_G . A popular example is the Voigt function

$$\begin{aligned}f_V(\omega) &= f_L(\omega) \otimes f_G(\omega) \\ &= \int_0^\infty \frac{A}{\omega_L - \omega - i\Gamma_L} \exp\left[-\frac{(\omega_L - \omega_0)^2}{2\Gamma_G^2}\right] d\omega_L\end{aligned}\quad (6)$$

derived from a convolution of Lorentzian and Gaussian line shapes by introducing an additional inhomogeneous decay term in Eq. (3).^{25,26} When the spectral resolution and signal-to-noise are sufficiently high, it may be possible to determine both $\Gamma_{L,q}$ and $\Gamma_{G,q}$ from a fit to the data.^{27,28} This is especially true in heterodyne experiments, since simultaneous fitting of the real and imaginary $\chi^{(2)}$ spectra facilitates this separation of homogeneous and inhomogeneous components.^{29,30}

III. GENERATION OF MODEL SPECTRA FROM MOLECULAR SIMULATIONS

We now turn to the case of a distribution of molecular vibrations that is so broad that a single value of A cannot capture the line shape with any of the functions described above. A typical case is that of the water interfacial hydrogen-bonded O–H stretching that covers a nearly 1000 cm^{-1} range from approximately 2800–3800 cm^{-1} . Depending on the particular system, at least two distinct bands are observed, centered near 3200 cm^{-1} and 3400 cm^{-1} . Although the origin of these features is still under discussion, there is considerable interest in characterizing changes in the spectral shape in a manner that captures the 3200/3400 cm^{-1} ratio in response to external perturbations such as the addition of salt or alteration of bulk pH.^{31–33}

When dealing with experimental data, any description of the O–H bonded region is a model. Even simple models that do not capture the underlying dynamics of different water populations are useful in that they provide a means to describe and monitor changes in the spectral appearance. For example, fitting the spectrum to a sum of two Lorentzians, two Gaussians, or two Voigt functions—one centered at 3200 cm^{-1} and one at 3400 cm^{-1} —all provide a description of the spectral shape. The difference between the three approaches, however, lies in the resulting amplitude and phase of the spectral response. A description based on two Lorentzians or two Gaussians is more straightforward since the line shapes have only a single width parameter to fit. If a Voigt profile were to be used, it is necessary to choose a homogeneous linewidth, making further assumptions about the population of water molecules.

In order to further evaluate the choice of resonant $\chi^{(2)}$ line shape, we need to compare against $\chi^{(2)}$ spectra for which both $\text{Re}\{\chi^{(2)}\}(\omega)$ and $\text{Im}\{\chi^{(2)}\}(\omega)$ are known. For this, we employ a simple classical simulation of SPC (simple point-charge) water next to a model hydrophilic surface, where the water oxygen–surface interaction is described by a Steele 10-4 potential^{34,35} with $\sigma = 0.3$ nm and $\varepsilon = 0.55$ kJ mol⁻¹. We employ an instantaneous normal mode approach as developed

for interfacial water simulations by Morita and Hynes.³⁶ For each of approximately 5300 water molecules in a $4 \text{ nm} \times 4 \text{ nm} \times 10 \text{ nm}$ box, the net force along the O–H bond vector was used to calculate the frequency of the low- and high-energy vibrational eigenmodes. These would correspond to the symmetric and antisymmetric stretch in the gas phase, but do not possess the same symmetry in the condensed phase. The forces are also used to determine the coupling constants (c_1, c_2) that are used to create the two water vibrations from the dipole moment $d\mu/dQ$ and polarizability derivatives $d\alpha^{(1)}/dQ$ of an uncoupled O–H oscillator, where Q is the normal mode coordinate. We can then create the water molecular properties

$$\left. \frac{d\alpha^{(1)}}{dQ} \right|_{\text{low}} = c_{1,\text{low}} R_1 \frac{d\alpha^{(1)}}{dQ_1} R_1^{-1} + c_{2,\text{low}} R_2 \frac{d\alpha^{(1)}}{dQ_2} R_2^{-1}, \quad (7a)$$

$$\left. \frac{d\alpha^{(1)}}{dQ} \right|_{\text{high}} = c_{1,\text{high}} R_1 \frac{d\alpha^{(1)}}{dQ_1} R_1^{-1} + c_{2,\text{high}} R_2 \frac{d\alpha^{(1)}}{dQ_2} R_2^{-1} \quad (7b)$$

and

$$\left. \frac{d\mu}{dQ} \right|_{\text{low}} = c_{1,\text{low}} R_1 \frac{d\mu}{dQ_1} + c_{2,\text{low}} R_2 \frac{d\mu}{dQ_2}, \quad (8a)$$

$$\left. \frac{d\mu}{dQ} \right|_{\text{high}} = c_{1,\text{high}} R_1 \frac{d\mu}{dQ_1} + c_{2,\text{high}} R_2 \frac{d\mu}{dQ_2}, \quad (8b)$$

where R is a direction cosine matrix that considers the individual bond orientations with respect to the surface and R^{-1} is its inverse. We finally create the second-order susceptibility for the collection of molecules using

$$\chi_{\text{yyz}}^{(2)}(\omega) = \sum_{\text{molecules}} \left[\frac{1}{2m\omega_{\text{low}}} \cdot \frac{d\alpha_{\text{yy}}^{(1)}}{dQ} \cdot \frac{d\mu_z}{dQ} \right]_{\text{low}} \frac{1}{\omega_{\text{low}} - \omega - i\Gamma} + \frac{1}{2m\omega_{\text{high}}} \cdot \frac{d\alpha_{\text{yy}}^{(1)}}{dQ} \cdot \frac{d\mu_z}{dQ} \left[\frac{1}{\omega_{\text{high}} - \omega - i\Gamma} \right], \quad (9)$$

where we have fixed $\Gamma = 2 \text{ cm}^{-1}$ for every mode, and the inhomogeneous contribution to the line shape naturally results from the multitude of water species that are sampled using this method, each contributing a unique value of ω_{low} and ω_{high} in the $2800\text{--}3800 \text{ cm}^{-1}$ range. One can see that the form of Eq. (9) is exactly that of Eq. (2). The only difference is that the number of Lorentzians in Eq. (9) is large, with $2N$ terms originating from each of the $N \approx 3500$ water molecules in each time step of the simulation. This results in an intensity spectrum indicated with black dots in the top row of Fig. 1 and phase spectrum retrieved from $\text{Re}\{\chi^{(2)}\}$ and $\text{Im}\{\chi^{(2)}\}$ (red and blue dots in Fig. 1, respectively) using a quadrant-preserving arctangent,

FIG. 1. Points (same across all panels) indicate the $|\chi^{(2)}|^2$ spectrum (top row), real (red) and imaginary (blue) $\chi^{(2)}$ spectrum (middle row), and phase spectrum (bottom row) obtained from the results of our molecular dynamics simulation using Eq. (9). A maximum entropy method was used to extract the phase. The resulting intensity, real, imaginary, and phase spectra are shown with solid lines using (a) a fixed $\phi_{\text{offset}}(\omega) = -7^\circ$ chosen to match the known phase in the region of the sharp 3700 cm^{-1} feature and (b) $\phi_{\text{offset}}(\omega) = 34^\circ$ to reproduce the low frequency end of the spectrum. We have also considered (c) a linear variation of ϕ_{offset} that does a reasonable job of accounting for the actual data.

$$\phi(\omega_{\text{IR}}) = \begin{cases} \tan^{-1} \left[\frac{\text{Im}\{\chi^{(2)}\}}{\text{Re}\{\chi^{(2)}\}} \right] & \text{if } \text{Re}\{\chi^{(2)}\} > 0, \\ \tan^{-1} \left[\frac{\text{Im}\{\chi^{(2)}\}}{\text{Re}\{\chi^{(2)}\}} \right] + 180^\circ & \text{if } \text{Re}\{\chi^{(2)}\} < 0 \text{ and } \text{Im}\{\chi^{(2)}\} \geq 0, \\ \tan^{-1} \left[\frac{\text{Im}\{\chi^{(2)}\}}{\text{Re}\{\chi^{(2)}\}} \right] - 180^\circ & \text{if } \text{Re}\{\chi^{(2)}\} < 0 \text{ and } \text{Im}\{\chi^{(2)}\} < 0, \\ 90^\circ & \text{if } \text{Re}\{\chi^{(2)}\} = 0 \text{ and } \text{Im}\{\chi^{(2)}\} > 0, \\ -90^\circ & \text{if } \text{Re}\{\chi^{(2)}\} = 0 \text{ and } \text{Im}\{\chi^{(2)}\} < 0 \end{cases} \quad (10)$$

plotted with green dots in the bottom row of Fig. 1.

IV. DATA FITTING STRATEGIES

A. Local field corrections

Experimental data from a homodyne SFG experiment representing $|\chi^{(2)}|^2$ may be fit to the magnitude squared of Eq. (2). Note that if the dispersion of the local field corrections is not significant over the measured spectral range, it is possible to fit $|\chi_{\text{eff}}^{(2)}|^2$ using Eq. (2) and then apply local field corrections $\mathbf{L}$ to the extracted A_q .^{37,38} For example, in the case of SSP (s-polarized SFG, s-polarized visible, and p-polarized infrared) and SPS polarization schemes,

$$\chi_{\text{SSP}}^{(2)} = L_{yy}(\omega_{\text{SFG}})L_{yy}(\omega_{\text{vis}})L_{zz}(\omega_{\text{IR}})\chi_{yyz}^{(2)}, \quad (11a)$$

$$\chi_{\text{SSP}}^{(2)} = L_{yy}(\omega_{\text{SFG}})L_{zz}(\omega_{\text{vis}})L_{yy}(\omega_{\text{IR}})\chi_{yzy}^{(2)}. \quad (11b)$$

Each of these polarizations probes only a single element of $\chi^{(2)}$ in a sample with axial ($C_{\infty v}$) symmetry about the surface normal. As a result, if the peak amplitudes in Eq. (2) $A_{q,yyz}$ and $A_{q,yzy}$ are desired for an orientation analysis, there are two options. The first is to extract $\chi_{yyz}^{(2)}$ and $\chi_{yzy}^{(2)}$ from the spectra (or $|\chi_{yyz}^{(2)}|^2$ and $|\chi_{yzy}^{(2)}|^2$ in the case of homodyne data) by calculating $L_{ii}(\omega_{\text{SFG}})L_{jj}(\omega_{\text{vis}})L_{kk}(\omega_{\text{IR}})$ (or the magnitude squared of this quantity for homodyne data) and then correcting the measured intensity. The second option is to fit the intensity data to Eq. (2) directly to obtain $A_{q,\text{eff}}$ and then use the appropriate ratio of $L_{ii}L_{jj}L_{kk}$ elements when interpreting the $A_{\text{SSP}}/A_{\text{SPS}}$ ratio to extract the molecular orientation dependence of the underlying A_{yyz}/A_{yzy} . It should be emphasized, however, that Eq. (2) is an expression for $\chi^{(2)}$ itself and not $\chi_{\text{eff}}^{(2)}$. Any dispersion in $\mathbf{L}$ alters the line shape and is therefore best handled prior to fitting. Note that fitting the effective susceptibility is the only option available when treating PPP spectra since the relative weighting of the four contributing $\chi^{(2)}$ elements (xxz , xzx , zxx , and zzz) is generally not known in advance.

Finally, we note the $\mathbf{L}$ factors are real off resonance for external reflection experiments and in the case of internal reflection below the critical angle. Since we are intrinsically dealing with vibrational resonances, $\mathbf{L}_{\text{IR}}$ are necessarily complex-valued. However, it is not always easy to have knowledge of the complex refractive index in the infrared region. For this reason, it is common to use real refractive indices for all three beams to calculate each of the requisite $\mathbf{L}$ contributions. In an internal reflection experiment above the critical angle,³⁹ however, the complex nature of $\mathbf{L}$ cannot be ignored when

PPP measurements are performed, as this affects the relative weighting of the contributing $\chi^{(2)}$ terms.

B. Selection of fitting algorithm

Before moving to options for fitting broad vibrational features that result from a highly heterogeneous molecular environment with many sub-populations, we comment on fitting even relatively simple cases such as spectra consisting of a few isolated resonances. Optimizers can generally be separated into categories depending on whether they require only function evaluations or first derivatives as well (these can always be numerically evaluated using additional function evaluations if analytical forms are not tractable), whether they are bounded (including the option of permitting and/or requiring upper and lower bounds for each parameter), their performance (speed and accuracy), susceptibility to local minima, and sensitivity to initial conditions. When fitting IR or Raman spectra, the amplitudes of all modes are positive and nearly any algorithm can be used to obtain the same results. It is therefore not typical to discuss the algorithm although common choices are nonlinear least squares techniques such as Levenberg-Marquardt.⁴⁰ When fitting SFG spectra, however, the situation is much less straightforward and not all algorithms will return the same result. There are two problems: the first is that, on resonance ($\omega_{\text{IR}} = \omega_q$), each Lorentzian has a value of A_q/Γ_q . A small change in Γ_q to increase the width of the line shape will require A_q to be increased accordingly in order to have only a small change in the residual. In other words, depending on the sequence in which the parameters are adjusted, and whether they are varied individually or in pairs/groups, the fitting may converge prematurely. The second and more serious issue is that, if the relative sign of A_q between two peaks is not known (as is generally the case), it is very difficult to “force” an optimizer to explore both options with the same effort, i.e., varying the resonant frequencies, amplitudes, and widths in order to determine the best fit combination with all sign combinations in the numerator of Eq. (2). Almost all optimizers struggle with this, and approaches based solely on least squares algorithms are likely to give up early. The most serious consequence is that there is little (and often no) indication of this. The residuals may be small and the fit may be qualitatively decent in comparison to the experimental data—but the global minimum, or a deeper local minimum, may exist when one of the resonant modes

is phase shifted by 180° . This is critical not only for obvious applications such as bond polarity determination but also for basic analysis such as peak amplitude ratios and resonance frequency determination, as these parameters are all affected by the presence of neighboring vibrational resonances.⁴¹ One approach that has been employed in our laboratory is to first generate all combinations of signs for the number of peaks to be employed in the fitting and then explore them exhaustively for simple cases, or sampled randomly (Monte Carlo techniques can be employed here) when the parameter space is too large.⁴² For each combination, a quick optimization can then be employed using a technique such as truncated Newton's method,⁴³ followed by a clean-up in the vicinity of the minimum using a steepest descent optimizer like a simplex routine.

It should be emphasized, however, that all of the above approaches rely on a *convenient* amount of interference between vibrational modes. When both the spectral resolution and signal-to-noise are sufficient, it should be possible to extract the relative phase. We are referring to a situation where

FIG. 2. Illustration of the effect of relative phase on neighboring vibrational modes. (a) $|\chi^{(2)}|^2$ intensity, (b) $\text{Re}\{\chi^{(2)}\}$ and $\text{Im}\{\chi^{(2)}\}$ spectra in red and blue, respectively, and (c) phase for two modes with same (solid line) and opposite signs, i.e., phase shifted by 180° (dashed line) on resonance with respect to each other. One notices that while $\text{Re}\{\chi^{(2)}\}$ and $\text{Im}\{\chi^{(2)}\}$ immediately display the relative (and absolute) phase, the relative phase information is subtle in the $|\chi^{(2)}|^2$ spectra.

the spectral overlap between neighboring modes is enough to notice whether the resulting interference pattern originates from modes that are in-phase or out-of-phase, but the resonant frequencies are not so close together to again obscure this information.⁴⁴ Figure 2 illustrates the case where two neighboring modes have the same separation in their resonant frequencies, same homogeneous linewidths, and same magnitude of their amplitudes, but opposite sign. One can see that while the absolute and relative phase is clearly revealed in the real and imaginary $\chi^{(2)}$ spectra from heterodyne data, the homodyne data show a difference in the shape that requires sufficient resolution and signal quality to differentiate. The challenge is to use the correct number and type of resonant line shape functions, as the fitting routines at best will simply return the parameters associated with those functions. We note that, in some cases, such challenging situations are greatly assisted by the measurement of spectra in multiple beam polarizations. For example, Zhang *et al.* have illustrated that it is possible to distinguish cyano mode vibrations that are 6 cm^{-1} apart by using all three unique polarization schemes (SSP, SPS, and PPP) available to achiral systems with $C_{\infty v}$ symmetry.⁴⁵

V. TECHNIQUES FOR HANDLING EXPERIMENTAL DATA

A. Kramers-Kronig approaches

If only intensity data are available, there are techniques available to extract the phase that do not assume any particular model for the line shape and therefore do not require prior knowledge of the nature or number of resonant modes. One such option uses the causality relationship in the dispersion of the real and imaginary components of $\chi^{(2)}$ in the form of a Kramers-Kronig transformation^{46–52}

$$\text{Re}\{\chi^{(2)}\}(\omega) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\text{Im}\{\chi^{(2)}\}(\omega')}{\omega' - \omega} d\omega', \quad (12a)$$

$$\text{Im}\{\chi^{(2)}\}(\omega) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\text{Re}\{\chi^{(2)}\}(\omega')}{\omega' - \omega} d\omega', \quad (12b)$$

where P is the Cauchy principal value and ω' is a dummy spectral variable over which the integration is performed. The quality of the approximation may be assessed by computing $|\chi^{(2)}|^2 = \text{Re}\{\chi^{(2)}\}^2 + \text{Im}\{\chi^{(2)}\}^2$ and minimizing the residuals compared to the experimental intensity data. There are two caveats associated with this approach. The first is that the integration must be performed over a finite frequency domain in practice, resulting in an unknown offset to $\text{Re}\{\chi^{(2)}\}(\omega)$. For systems with no significant non-resonant contribution, this offset is readily evaluated. The more serious difficulty is that, as only *relative* phase information is encoded in the homodyne data, there is an overall phase offset

$$\chi^{(2)} = |\chi^{(2)}| \exp[i(\phi + \phi_{\text{offset}})] \quad (13)$$

that affects the real and imaginary components. If one is willing to assume that ϕ_{offset} is independent of ω in the frequency region of interest, then some additional information can be used to resolve this ambiguity. For example, perhaps the phase of the non-resonant response is known, or the polarity (and hence phase) of a well-separated resonant mode is known.

B. Maximum entropy methods

Another option for phase retrieval is to use a concept from information theory, the maximum entropy method (MEM).^{15,53–57} This technique seeks to add features to the time domain response function $R^{(2)}(t)$ in Eq. (3) that is related to the second-order susceptibility through a Fourier transform

$$R^{(2)}(t) = \int_0^\infty \chi^{(2)}(\omega) e^{-i\omega t} d\omega. \quad (14)$$

The objective is to add features without increasing the spectral entropy h defined by

$$h = \int_0^1 \log[\chi^{(2)}(\nu)] d\nu, \quad (15)$$

where

$$\nu = \frac{\omega - \omega_1}{\omega_2 - \omega_1}$$

is defined such that $0 \leq \nu \leq 1$ in the frequency region between $\omega_1 = 2800 \text{ cm}^{-1}$ and $\omega_2 = 3800 \text{ cm}^{-1}$ in our example. In the first step, a $|\chi^{(2)}|$ spectrum of $2N + 1$ frequencies is Fourier transformed to obtain $R^{(2)}(t)$. One then solves the matrix equation

$$\begin{bmatrix} R_0^{(2)} & R_1^{(2)*} & \cdots & R_N^{(2)*} \\ R_1^{(2)} & R_0^{(2)} & \cdots & R_{N-1}^{(2)*} \\ \vdots & \vdots & \ddots & \vdots \\ R_N^{(2)} & R_{N-1}^{(2)} & \cdots & R_0^{(2)} \end{bmatrix} \begin{bmatrix} 1 \\ a_1 \\ a_2 \\ \vdots \\ a_N \end{bmatrix} = \begin{bmatrix} b \\ 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix}, \quad (16)$$

where N values of a and a single value b are sought. The complex spectrum is finally generated from

$$\chi^{(2)}(\nu) = \frac{be^{i\phi_{\text{offset}}}}{1 + \sum_{n=1}^N a_n e^{i\nu n}}. \quad (17)$$

Just as in the case of Kramers-Kronig transformations, we note that there is a phase offset ϕ_{offset} that is left unresolved. This is to be expected for any method that takes only the magnitude $|\chi^{(2)}|$ into consideration, as any $\phi_{\text{offset}}(\omega)$ will reproduce the magnitude or intensity spectrum. In our water example, since the true phase is known, we can evaluate the $\phi_{\text{offset}}(\omega)$ required in the MEM. Figure 1(a) illustrates the case of a fixed $\phi_{\text{offset}}(\omega) = -7^\circ$, chosen to match the known phase in the region of the sharp 3700 cm^{-1} feature. In Fig. 1(b), $\phi_{\text{offset}}(\omega) = 34^\circ$ to reproduce the low frequency end of the spectrum. Figure 1(c) illustrates a simple linear variation in ϕ_{offset} that reasonably captures the true phase over the observed frequency region. A detailed discussion about the application of MEM to phase retrieval in SFG spectroscopy, including the inner workings of the technique is found in Ref. 53. A discussion of cases where MEM is most successful in SFG spectroscopy and a consideration of its limitations appear in Ref. 55.

VI. FITTING BROAD RESONANCE FEATURES IN HOMODYNE DATA

A. Fitting water spectra in the absence of localized vibrations

The model water intensity profile obtained from our molecular simulations using Eq. (9) is shown with black dots

in all three panels in the top row of Fig. 3. We now attempt to fit the spectrum using an arbitrary number of Lorentzians to arrive at the $\chi^{(2)}$ line shape [Eq. (2) with no non-resonant component]. The resulting $|\chi^{(2)}|^2$ is shown with the overlaid gray line in the top row of Fig. 3 when either 4, 6, or 8 Lorentzians are used. Here we can compare the fit phase (solid green lines in Fig. 3) to the true phase (green points) obtained using Eq. (10). The residuals of the intensity spectra are plotted in the third row. One can see that, as the number of Lorentzians increases, the residuals decrease in a predictable manner. We conclude that, even though the homodyne data can be fit to an arbitrary degree of precision, there is no pattern to the shape of the phase spectrum that results from such a procedure. In other words, the predicted phase does not merely differ from the known phase by a constant, or even a slightly varying shift. The scores (sum of the squares of the residuals) are shown in the bottom row of Fig. 3 for all $(2^n)/2$ tests. The black dashed line indicates the test that yielded the best fit, whose results are displayed in the panels above. Since it is difficult to gauge how much the best score differs from others for large n , we have expanded the scale in the neighborhood of the global minimum and overlaid those values in red. Inspection of the scores shows that as n increases, even though the residuals get smaller, there are many random combinations of phase reconstructions that result.

We are concerned about performing the fitting in a way that rigorously explores the various combinations of the sign of the amplitudes $\pm A_q$ in Eq. (2). As a result, we want to have the optimizer constrained in its search by specifying the sign of A_q . For n components, there are 2^n combinations of signs for the Lorentzians amplitudes. Of these, half of the combinations represent the same solution, but shifted by 180° . For example, when we evaluate the combination $\{+, +, -, +, -\}$ belonging to $n = 5$, then we do not need to also study the combination $\{-, -, +, -, +\}$. In the absence of any nonresonant contribution, we therefore have $(2^n)/2$ possibilities to explore. In the top three rows of Fig. 3, we have plotted the results of the fitting from the sign combination that provided the best score (smallest sum of the squares of the residuals). In the bottom row, we plot the scores for all $(2^n)/2$ tests in black, with an expanded region about the global minimum (indicated by the vertical black dashed line) plotted in red. Sign combinations that did not return any level of acceptable fit are indicated by the short dashed gray lines. An important conclusion from these scores is that there are many solutions that have scores nearly as good as the global minimum. With real experimental data, the error in each data point would introduce a further uncertainty that would make even more of the solutions (perhaps all of red points in Fig. 3) virtually identical. In other words, although models are certainly useful when fitting homodyne data, there is no further advantage to choosing a model line shape that incorporates a phase, as the phase profile resulting from a fit to broad homodyne SFG data is arbitrary.

Since we will continue to use such figures as we refine our analysis, it is worth mentioning why we plot the phase spectrum rather than the more readily interpretable $\text{Re}\{\chi^{(2)}\}$ and $\text{Im}\{\chi^{(2)}\}$ spectra. Since we are ultimately comparing to homodyne data, it is important for us to distinguish whether

FIG. 3. Results of fitting a model water line shape to a sum of Lorentzian functions. A broad line shape was created from a sum of three Gaussians, indicated by the identical set of points in the top row. This shape was then fit to a sum of n Lorentzian functions, with $|\chi^{(2)}|^2$ plotted in gray in the top row and the phase spectrum plotted in green in the second row. The residuals between the original data and the fit are plotted in the third row. For each combination of peak amplitude sign/phase chosen, the score is shown in black points in the bottom row. A zoomed in version close to the minimum (best fit value, indicated by the vertical dashed black line) is indicated with red points. Combinations that did not yield acceptable fitting results are indicated by short dashed gray lines, as seen in test 22 for the $n = 8$ case.

the phase profiles returned by our fit to various models differ in *shape* or only by a fixed offset. In other words, we want to know whether ϕ_{offset} has a frequency dependence. Figure 4 plots the real (red), imaginary (blue), and phase (green) spectra for a line shape created from four Lorentzians (dashed lines, same in all columns). Superimposed on these plots are the same data, but shifted in phase by 180° [drawn with lines in Fig. 4(a)], 45° [Fig. 4(b)], and -45° [Fig. 4(c)]. Although the offsets in phase are clearly visible in panels (b), (d), and (e), it is not obvious when studying $\text{Re}\{\chi^{(2)}\}$ and $\text{Im}\{\chi^{(2)}\}$ spectra. When the phase shift is a multiple of 90° , this may be somewhat apparent, but even in this relatively simple example with only three modes, the $\pm 45^\circ$ cases are too complicated to analyze without looking at the phase spectra directly.

Finally, we illustrate the result of fitting the same model water data to an arbitrary number of Voigt functions with the

homogeneous linewidth fixed at 5 cm^{-1} and the inhomogeneous linewidth optimized in the fit. Figure 5 illustrates that when using $n = 4, 6$, or 8 Voigt functions, the accuracy to the fit of the homodyne data increases as n increases, but this does not bring us any closer to approximating the known phase (green dots).

B. Influence of broad resonances on isolated vibrational modes

We are now in a position to address the topic of how any of these approaches to fitting a broad continuum of resonances influences fitting of sharp isolated modes in the same spectral region. A common situation in vibrational SFG spectroscopy is one where C–H and O–H modes co-exist. An example is that of an organic surfactant at the air–water interface. In such cases, the appearance of the C–H stretching modes often indicates some interference with the underlying water background.⁵⁸

FIG. 4. Real (red), imaginary (blue), and phase (green) spectra for a line shape created from four Lorentzians (dashed lines, same in all columns). Superimposed on these plots are the same spectra, but shifted in phase by (a) 180° , (b) 45° , and (c) -45° .

FIG. 5. Results of fitting the model water line shape to a sum of Voigt functions. See caption of Fig. 3 for an explanation of all the panels.

TABLE I. Returned amplitude, resonant frequency, and width for the narrow (mode 2 of 7) vibrational mode among the broad resonances for 3 of the 64 tested combinations of amplitude signs. The combinations are labeled to facilitate further inspection using the additional data presented in S1 of the [supplementary material](#).

Combination	Signs of A_q	A_2	ω_2/cm^{-1}	Γ_2/cm^{-1}	Score
5	{+, +, +, -, -, +, +}	3.21	3100	7.13	0.0268
14	{+, +, +, -, -, +, -}	3.35	3100	7.17	0.0175
19	{+, +, -, -, +, -, +}	6.29	3100	7.33	0.0191

In such situations, it is often sufficient to have some qualitative discussion of the water band shape, but quantitative information on the organic resonant modes is desired. For example, the ratio of methyl symmetric stretch amplitudes obtained with different polarization schemes may be needed to analyze the orientation of the molecule. As the organic modes are not free of the water background, some model needs to be used to account for the water contribution.

We have taken the $\chi^{(2)}$ spectrum from the molecular dynamics simulation (points in the top row of Fig. 3) and added a single mode at 3100 cm^{-1} with an amplitude of 6 and a width of 7 cm^{-1} corresponding to the ω_q , A_q , and Γ_q parameters in Eq. (2). Previously, we were not concerned with any sharp resonant features, and so it was not critical to determine exactly where the n values of ω_q were placed. However, it is reasonable in this case to position each of the broad features some distance away from the mode of interest. We therefore introduce 6 additional modes to comprise the broad spectral response, with one of them at ω_1 well below the resonance of interest and the other 5 (ω_{3-7}) well above the frequency of interest that we refer to as ω_2 . We then go about fitting the spectrum in the usual way, considering all $(2^7)/2 = 64$ combinations of positive and negative signs for A_q . This time, however, rather than plotting the score (sum of the squares of the residuals) obtained in the best fit for each combination, we are more concerned with whether we can reproduce the known values

of ω_2 , A_2 , and Γ_2 . The results of all 64 trials are shown in S1 of the [supplementary material](#), along with plots over the complete spectral region from 2800 to 3800 cm^{-1} . We highlight three of those combinations here, with best fit parameters in Table I and intensity and phase information shown in Fig. 6. Among these three results, the best scores (smallest sum of the squares of the residuals) were obtained for combination 14 with $A_2/\Gamma_2 = 0.467$, followed by combination 19 with $A_2/\Gamma_2 = 0.858$. We compare this to the known result of $A_2/\Gamma_2 = 0.857$ and observe that this ratio can deviate from its expected value by nearly a factor of two with a negligible difference in the residuals.⁵⁹ It should be noted that, although the phase returned by the fitting appears to be matched to the known result for sign combination 19, the fitting performed over the entire 2800 – 3800 cm^{-1} range reveals discrepancies in the phase (S1 of the [supplementary material](#)). The reason for this is by now apparent: The broadband spectra on their own are capable of being fit with a large variation in the resulting phase spectrum; the interference between the resonant mode and the continuum bands is sensitive to the phase in the region of the 3100 cm^{-1} mode.

VII. FITTING HETERODYNE DATA

The focus of this perspective was on the fitting of SFG intensity (homodyne) data, illustrating the consequences of different models as a result of the underlying phase spectra. It is interesting to briefly contrast this situation with the case where explicit experimental phase data are available from a heterodyne experiment. Several schemes have been proposed to obtain the SFG phase spectrum.^{30,60–80} Regardless of the experimental method employed, the result is that we now have knowledge of the black and green dots in our figures. In the case of the broad resonances without any isolated modes in the same spectral region, simultaneously fitting the magnitude and phase with either Lorentzian or Voigt line shapes produces the same results, as any model line shape is now fully constrained.

FIG. 6. Three of the 64 combinations of 7 peaks used in the fitting of broadband resonances including a narrow mode at 3100 cm^{-1} . Although several of the $2^7/2 = 64$ combinations have similarly small residuals, the outputs vary dramatically in the returned amplitude and phase of the narrow mode. See the text and S1 of the [supplementary material](#) for additional details.

In such cases, fitting for the sake of monitoring changes in spectral intensity of the broad features has a further advantage in that the phase profile must be consistent with the change in amplitude.

The larger advantage of heterodyne data may be realized in the case of an isolated resonance superimposed on a broad water O–H background. With reference to Fig. 6, the reason why differences in the A_2/Γ_2 ratio are obtained is precise since the phase profile of the background is unknown. Fitting to a model that simultaneously constrains the phase in the bottom row of Fig. 6 would recover A_2/Γ_2 so long as there are no resonances too close to ω_2 . In other words, the challenge of overlapping resonances illustrated in Fig. 2 also applies in the case of a sharp spectral feature together with a broad background. This is because there is no difference whether interfering spectral features originate from water or organic functional groups that are close in frequency. So long as the model used to create the water background has resonances that are sufficiently far from the isolated mode of interest, the known phase spectrum is sufficient to constrain the fit to reliably return A_2/Γ_2 . In this sense, the results and discussion we have presented for water apply to any congested spectral region. In S2 of the [supplementary material](#), we have revisited the same 64 combinations of amplitudes for 7 Lorentzian functions, now simultaneously fitting the real and imaginary $\chi^{(2)}$ spectra obtained from the $\chi^{(2)}$ magnitude and phase. In general, this is preferable to fitting phase spectra since the real and imaginary components are necessarily on the same scale (and therefore their residuals are weighted equally) and we avoid challenges due to discontinuities resulting from phase angle wrapping. This time, the best fit value (combination 10 in S2 of the [supplementary material](#)) returns $A_2/\Gamma_2 = 0.860$, illustrating that one can rely on the heterodyne data for the task of analyzing the line shape in the neighborhood of multiple resonances.

VIII. CONCLUSIONS AND OUTLOOK

When using vibrational sum-frequency generation to study broad resonance features, typically water in the 2800–3800 cm^{-1} spectral range, it is often useful to model the line shape in order to monitor the change in those features with respect to an external perturbation,³³ for example, when tracking the 3200/3400 cm^{-1} intensity as a function of the solution pH or ionic strength. We have illustrated that, in general, simple line shapes such as pure Lorentzians are equally as useful as Voigt profiles. We note that, when using complex-valued functions, although the interferences between neighboring modes can be captured in the intensity profile, nothing is gained from an analysis of the resulting phase spectra, since even the *relative* phase cannot be retrieved when fitting homodyne data. We have contrasted this with model-free approaches to line shape analysis in the form of Kramers-Kronig and maximum entropy methods. These techniques have the advantage of not requiring any assumption of the frequency, amplitude, or width of underlying resonant modes and are capable of retrieving the relative phase. It should be noted, however, that these techniques are only applicable in cases where the signal-to-noise ratio is sufficiently high; when the spectral intensity is weak,

direct fitting approaches may be preferable. We further note that, when using either set of techniques, it is important to distinguish between background intensity (that can be experimentally corrected) and true non-resonant contributions to the signal, as both fitting and model-free approaches interpret interference between resonant modes based on the amount of non-resonant signal. Our second conclusion concerns the fitting of spectrally narrow features in the presence of such broad line shapes—for example, organic surfactant C–H stretching modes that lie in the tail of the water O–H stretching. We have illustrated that, even when only the amplitude of the narrow resonances is desired, fitting homodyne data in general cannot reliably retrieve that amplitude, as a result of the uncertainty in the phase of the underlying broad resonances. Finally, none of these results should detract from the utility of fitting spectra to simple physical models; they simply illustrate that obtaining phase information from broad resonances is relegated to heterodyne SFG experiments.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for detailed results of the fitting of all 64 trials in the case of an isolated resonant mode superimposed on a broad background. The sign combinations of the underlying bands are shown in detail, along with plots over the complete spectral region from 2800 to 3800 cm^{-1} next to the expanded region about the narrow resonance. This is illustrated for the case of homodyne fitting in S1 and in the case of explicit phase data available in S2.

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