



## Effect of visible pulse shaping on the accuracy of relative intensity measurements in BBSFG vibrational spectroscopy



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### ABSTRACT

Quantitative analysis of BroadBand Sum Frequency Generation (BBSFG) vibrational spectra by deconvolution into Lorentzian components has been shown recently to suffer from complications that depend on the spectro-temporal properties and delay of the visible pulse which has to be shaped in order to achieve spectral resolution and possibly temporal discrimination. We present a comprehensive spectro-temporal analysis of BBSFG in order to evaluate quantitatively the consequences of delay dependent spectral changes on the accuracy of BBSFG spectra. We compare purely spectral deconvolution of single spectra and spectro-temporal analysis of multiple spectra obtained with a picosecond visible pulse produced by either a Fabry–Perot (FP) etalon or a 4f pulse shaper (PS). The case of OctaDecaneThiol Self Assembled Monolayer is used for comparison of theory and experiment. Accurate relative intensities can only be obtained from the analysis of multiple spectra generated by the FP-produced visible pulse. Although the spectra obtained with the PS are not delay dependent contrarily to those of the FP, the purely spectral deconvolution does not provide accurate values of the relative intensities. The need for a spectro-temporal analysis is explained by the fact that the first-order IR polarization is distorted both in the time domain by the ps visible pulse shape and in the frequency domain by interferences between the bands that are complicated by a frequency and delay dependent phase shift.

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### 1. Introduction

Sum Frequency Generation (SFG) spectroscopy has the unique advantage to allow simultaneously structural information on adsorbed molecules through vibrational spectroscopy and to probe dynamics at a time scale of  $\approx 100$  fs. This is possible because it is a non-linear optical technique where an IR pulse excites coherently molecular vibrations while a visible pulse up-converts the excited first order IR polarization. In BroadBand SFG (BBSFG) a broadband femtosecond IR pulse is used, which is possible because the spectral resolution is determined by the bandwidth of the visible pulse. The visible pulse is produced by pulse shaping a standard femtosecond pulse to reduce its bandwidth. While BBSFG produces readily vibrational spectra, their quantitative analysis appears to be complicated by spectrum distortion caused by truncation or apodization resulting from the imperfect up-conversion of the first order IR polarization by the visible pulse.

Another feature encountered in SFG of molecules at surfaces as well as in other coherent vibrational spectroscopies is related to the presence of a so-called non-resonant (NR) background generated by the

substrate surface. Numerous materials including metals, semiconductors and insulators give rise to a background through excitation of their electronic states. In particular the gold substrate is well known to give a strong non-resonant response [1]. Although the NR signal greatly helps to detect weak vibrational bands and also contains information on electronic properties of the substrate, interference between resonant (R) and NR contributions complicates the determination of vibrational spectra of molecular adsorbates. NR phase and amplitude depend on the nature of the surface, on the presence of adsorbates and also on the wavelength of the visible light [2]. The phase difference between R and NR contributions is not known and is usually treated as an adjustable parameter in the fitting procedure. The parameters relative to molecular resonances, i.e. peak frequency, width and relative amplitude, can still be in principle obtained from SFG spectra. However Busson and Tadjeddine [3] have shown recently that the set of parameters extracted from deconvolution of resonant spectra from the NR background was not necessarily unique when all parameters are allowed to vary.

In recent years Dlott and his co-workers [4–8] have shown that it is possible to make a temporal discrimination between NR and R contributions thanks to their very different life and dephasing times. As a matter of fact dephasing time of the electronic transitions of metallic substrates is very short, e.g.  $T_2 = 8$  fs for polycrystalline gold [9], so that non-resonant response can be considered as instantaneous and follows the

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excitation pulse ( $\sim 10$ – $100$  fs). In contrast the dephasing time of molecular vibrations at metal surfaces is typically in the ps range, so that both contributions can be separated in time. Temporal discrimination can in principle be achieved by delaying the visible with respect to the IR pulse by  $\sim 300$  fs. However time windowing with a symmetric picosecond pulse does not achieve a sufficiently high level of discrimination. A key innovation originally proposed by Lagutchev et al. [4] consists in using a Fabry–Perot (FP) etalon to produce an asymmetric picosecond pulse.

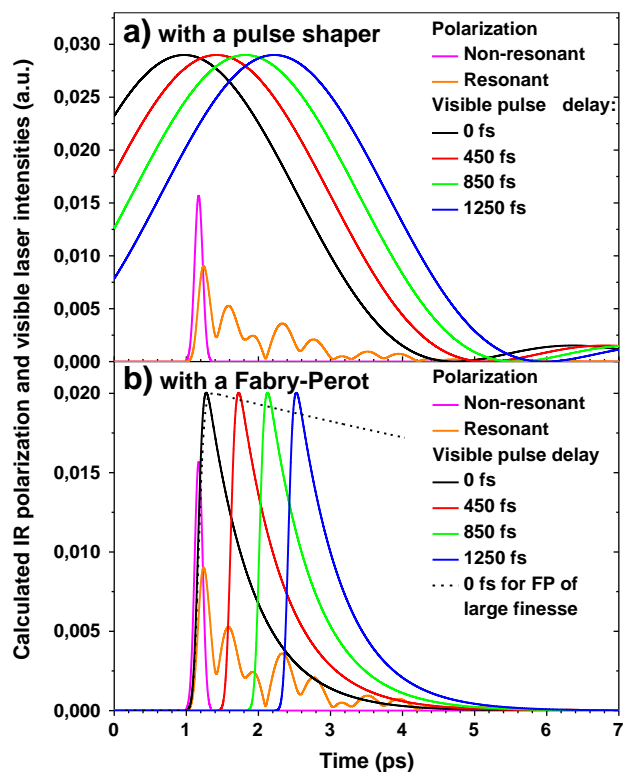
The problems encountered in quantitative analysis of BBSFG spectra have been reported by several authors. Even with a symmetric pulse shape the timing of the IR and visible pulses may significantly affect the BBSFG spectra, as observed by Ishibashi and Onishi [10] and Stiopkin et al. [11], because the typical duration of the visible pulse is still too short with respect to typical  $T_2$  lifetimes to avoid distortion of the first order IR polarization. With asymmetric pulses, Curtis et al. [12–15] have pointed out the fact that any degree of background suppression modifies the sampling of the initial portion of the resonant spectrum. In the case of vibrational modes with different  $T_2$  times, relative intensities vary with the IR-visible time delay. A simultaneous fit of multiple spectra recorded at several time delays was found to dramatically improve the quality of the fit [14] and the determination of resonant parameters, including the number of bands present in the spectrum. Weeraman et al. [16] have proposed a different method of NR suppression involving asymmetric pulses characterized by an exponential rise followed by an abrupt decay. However they did not address the problems related to the temporal profile of the visible pulse. Laaser et al. [17] have pointed out the drawbacks of frequency-domain SFG spectroscopy resulting from the frequency dependent phase shift induced by the time delay between IR and visible pulses. Simulations of the SFG spectra using visible pulses with different temporal profiles have shown that distortion is more pronounced with a FP etalon than with a pulse shaper while it is almost suppressed by time-domain SFG spectroscopy with a scanned femtosecond visible pulse. Recently Shalhout et al. [18] have recorded the SFG spectrum of the methyl-terminated Si(111) surface with a visible ps pulse at two different values of the IR-visible delay (0 and 300 fs). The spectrum consisting of two nearby vibrational resonances spaced by  $\sim 70$   $\text{cm}^{-1}$  and superimposed on a broad NR background was found to be delay dependent. The results and model calculations show that the observed spectral changes should be attributed to a frequency dependent phase shift between the two coherently excited vibrational modes accumulated during the 300 fs delay time due to their different carrier frequencies.

The goal of this paper is to present a comprehensive spectro-temporal analysis of BBSFG in order to evaluate quantitatively the consequences of delay dependent spectral changes on the accuracy of BBSFG spectra. To do this, experimental and simulated BBSFG spectra are compared in the case of a well known model system: OctaDecaneThiol Self Assembled Monolayer (ODT SAM) on gold. Spectra are obtained with a visible pulse produced by either a 4f pulse shaper (PS) or a FP etalon which are compared. ODT is chosen because its main three SFG bands are close enough to each other ( $26$  and  $58$   $\text{cm}^{-1}$ ) to be sensitive to interferences between them. Two deconvolution methods are compared: the first one is the standard deconvolution into Lorentzians, which is purely spectral and cannot include all spectro-temporal effects associated with the SFG process. The second one uses the resolution of the Bloch equations to model the SFG pulse in time domain, followed by Fourier transform into frequency domain. In Section 3 we discuss the effects of visible laser shape and delay both in time and frequency domains, and highlight the shortcomings of the standard deconvolution by comparison with a more general form of deconvolution. In the frequency domain delay dependent interferences between vibrational bands are present and amplified when the visible pulse has broad enough wings. They correspond in the time domain to the quantum beats present in the IR polarization which may be sampled by the visible pulse providing that it is short enough. We illustrate the effect of visible pulse shape and delay by calculations of SFG spectrum and spectral phase as a function of delay for each

pulse shaping method. Two model systems are considered, consisting of either one single band or three bands without NR background. In Section 4 we compare experimental and simulated spectra to examine the degree of accuracy of the relative intensities obtained from the two deconvolution methods and the two pulse shaping methods. We conclude that simultaneous fitting of spectra recorded at several delays with a FP is the only method that allows to extract accurate relative intensities.

## 2. Experimental

SFG spectra of an ODT SAM onto a gold substrate have been measured as a function of the time delay ( $-2$  to  $+2$  ps) between fs IR and ps visible pulses. Tunable IR ( $4$   $\mu\text{J}$ ,  $145$  fs and  $120$   $\text{cm}^{-1}$  bandwidth) and visible ( $809$  nm, adjustable duration  $0.12$ – $6$  ps and bandwidth  $120$ – $2.5$   $\text{cm}^{-1}$ ) pulses generated by a femtosecond Ti:sapphire-based laser system were overlapped at the sample in a collinear co-propagating configuration. The ps visible pulse was obtained by passing the  $120$  fs laser pulse through either a 4f pulse shaper or an air-spaced Fabry–Perot etalon. A 4f pulse shaper is composed of two gratings and two lenses of focal length arranged in a 4f set-up [19]. The spectral components of the input fs pulse are angularly dispersed by the first grating and focused at a particular spot in the Fourier plane by the first lens. Spatial filtering can be simply achieved by inserting a slit in the Fourier plane. The second combination of lens and grating allows for recombination of the remaining frequency components into a single collimated beam. The duration of the time-symmetric output pulse is controlled by the slitwidth. Fig. 1a shows the temporal profile of the PS-produced pulse computed for several



**Fig. 1.** Computed time envelope of the ps visible pulse intensity together with the square modulus of resonant and nonresonant first-order polarizations of ODT SAM on Au induced by the IR laser for several values of the IR-visible delay.

- in the case of the pulse shaper ( $7$   $\text{cm}^{-1}$  bandwidth),
- in the case of the FP etalon ( $R = 95\%$ ,  $\text{FSR} = 448.2$   $\text{cm}^{-1}$ ). The dotted line corresponds to a FP with  $R = 99.9\%$ .

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