

Supporting Information for:  
A general approach to combine the  
advantages of collinear and non-collinear  
spectrometer designs in phase-resolved  
second order nonlinear spectroscopy

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## Experimental

A commercial Ti:sapphire based regenerative amplifier is used to create 50 *fs* pulses of 800 *nm* wavelength at a repetition rate of 1 *kHz*. A small fraction is used as the 800 *nm* upconversion beam while the rest is sent to a commercial optical parametric amplifier followed by a difference frequency generation unit. The frequency of the resulting infrared pulses is centered around 3.4  $\mu\text{m}$ . The beam then enters the spectrometer, where it is split into two portions using a Germanium window. The smaller reflected portion (about 5%) is sent through a combination of two free standing wire grid polarizers to yield tunable attenuation and control over its polarization after which the beam is focused onto a z-cut quartz window using a parabolic mirror. En route it passes an incoupling optic consisting of a germanium window coated to be highly transparent in the IR but highly reflective in the visible frequency range. The aforementioned 800 *nm* upconversion beam is reflected at the incoupling optic after which it travels collinearly with the IR. The 800 *nm* pulse is focused as well onto the z-cut quartz where the beams interaction generates the local oscillator (LO). The residual IR is filtered out and the collinear LO/800 *nm* pulses pass a delay stage after which they are reflected at a second incoupling optic of similar type as the first one, where they are collinearly overlapped in space with the second portion of the IR. All three pulses are then focused onto the sample. A series of filters is subsequently used to only let the LO and SFG sample signal pass towards the detectors. On the way the pulses that are orthogonally polarized pass a 1 *mm* thick calcite crystal with a cutting angle of 25° with respect to the optical axis (EKSMA Optics). The calcite crystal is aligned such that the electric field of the signal pulse is orthogonal to the plane defined by the optical axis and the wave vector. Fine control of the timing is achieved by rotating the crystal about the ordinary axis which is orthogonal to the aforementioned plane using a rotational stage (Thorlabs, PRMTZ8 (stage), KDC101 (Servo Motor Controller)). After rotation of the polarization angles of the two pulses by 45° using a Fresnel rhomb (Thorlabs, CCM1-PBS252) the beams pass a polarizing beam splitter cube yielding two outputs which are detected separately using two avalanche photodiodes (Thorlabs, APD410A2). The rejection of the common

mode signals from the two detectors is achieved using a GHz Balun (Marki Microwave), which generates the difference signal between the two inputs. The resulting waveform is integrated by gated integrators (SRS, Boxcar Averager) and finally digitized.

For the Octadecanethiol (ODT) measurements we use a substrate which consists of an evaporated gold film prepared on BK7 glass at our Institute. This film is immersed in a solution of ODT in Ethanol ( $c=5 \text{ mM}$ ) for  $48 \text{ h}$ ,<sup>1</sup> rinsed with pure ethanol and subsequently measured. For the measurement inside the liquid cell the sample is covered with a thin film of deuterated (d3-) acetonitrile and a  $2 \text{ mm}$  thick Calciumfluoride window. A  $20 \mu\text{m}$  thin Teflon wedge acts as a spacer.

## polarization control of the local oscillator

alpha-quartz possesses a non inversion-symmetric crystal structure (D3 symmetry). As a consequence a nonlinear second order signal can be generated inside the bulk. The polarization of the resulting nonlinear signal depends thereby on the polarizations of the incoming beams and the respective orientation of the quartz crystal. A mathematical description of these processes is given in ref.<sup>2</sup> here we will only show the result. For a z-cut alpha quartz crystal where the pump beams are aligned to collinearly traverse the crystal at normal incidence the transmitted second order signal has the following form.

$$\vec{E}_{LO} \propto (\cos(3\Phi) * \vec{e}_x + \sin(3\Phi) * \vec{e}_y) * \chi_{xxx}^{(2)} \quad (1a)$$

$$\vec{E}_{LO} \propto (\sin(3\Phi) * \vec{e}_x - \cos(3\Phi) * \vec{e}_y) * \chi_{xxx}^{(2)} \quad (1b)$$

Equations 1a and 1b describe the cases of parallel and orthogonal pump beam polarizations, respectively.  $\Phi$  represents the angle between the  $x$ -axis in the crystal- and the  $x$ -axis in the laboratory frame and  $\vec{e}_x$  and  $\vec{e}_y$  are the two unit vectors along the  $x$ - and  $y$ -axis in the laboratory frame.  $\chi_{xxx}^{(2)}$  is the only non-vanishing tensor component of the second order susceptibility of

alpha quartz. From equations 1a and 1b we can conclude that the generated nonlinear signal is linearly polarized with a polarization angle  $\gamma$  (in the laboratory frame) of  $\gamma = 3\Phi$  for parallel and  $\gamma = 3\Phi + \pi/2$  for orthogonally polarized pump pulses. The intensity of the nonlinear signal is meanwhile constant for all values of  $\Phi$ . As a consequence of this behavior the polarization of the local oscillator can always be continuously tuned to any value by simply rotating the quartz about its surface normal.

The intensity and the spectral shape of the generated LO will not only depend on the effective second order susceptibility of the alpha-quartz but also on its thickness  $L$ . Due to the necessity to have the pump beams traverse the quartz crystal along its  $z$ -axis it is not possible to achieve any kind of phase matching for the generation of the local oscillator. Because of the resulting dispersion between the pump pulses and the generated LO its intensity only builds up over a short distance inside the crystal to subsequently decrease again in an oscillatory fashion accompanied by increasing modulations in the LO spectrum. The thickness of the quartz crystal should therefore not exceed this short distance of initial intensity growth which given by the coherence length  $L_c$ . Latter can be derived from the wave vector mismatch  $\Delta k^3$

$$L_{coh} = \frac{2}{\Delta k} \quad (2)$$

The coherence length is typically in the range of 10-50  $\mu m$ . A very thin quartz crystal is thus required to maximize the LO output and to avoid the appearance of distortions in the LO spectrum.

## **nonlinear signals from fused silica**

In the main text it is experimentally shown that no background signal is generated inside the fused silica windows which are used to modify the relative pulse timings. This is also supported by theory as shown in the following. Two possible nonlinear contributions that radiate at SFG frequencies are dipolar second order responses and signals which originate from quadrupolar

polarizations.

Due to its amorphous structure the bulk of fused quartz exhibits inversion symmetry. Accordingly  $\chi_{bulk}^{(2)}$  must be zero. At the surface this symmetry is broken so in general  $\chi_{surface}^{(2)}$  is unequal to zero. However, with all beams being collinear and at normal incidence all possible tensor elements of  $\chi_{surface}^{(2)}$  vanish at surfaces with in-plane inversion symmetry. Consequently, no dipolar second order signal can be generated in the window.

Quadrupolar contributions are always polarized along the direction of the wave vector of either one of the pump pulses or the generated signal pulse. In case of these beams being collinear and at normal incidence any quadrupolar contribution inside the fused quartz must therefore have purely longitudinal character and can thus not radiate in transmission direction.

Consequently, no nonlinear signal from quadrupolar sources can arise in this geometry. We can therefore safely assume that no background signal can be generated inside the fused silica window provided that all beams are collinear and travel along the surface normal.

## References

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