# Multidimensional Spectral Fingerprints of a New Family of Coherent Analytical Spectroscopies

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## Supporting Information

**Abstract**
The supporting information contains an overview of the experimental system and details on the experimental methods and parameters that are important for the experiments. Since the beam pointing and the temporal and spatial overlap of the excitation beams change as a function of wavelength, the system includes adjustable mirrors and delay stages to correct the excitation beams during the wavelength scanning. The relationship between the phase matching angles and the positions of the excitation beams on the focusing mirror are described. Details about the calibration procedure for measuring the temporal overlap are also describe.

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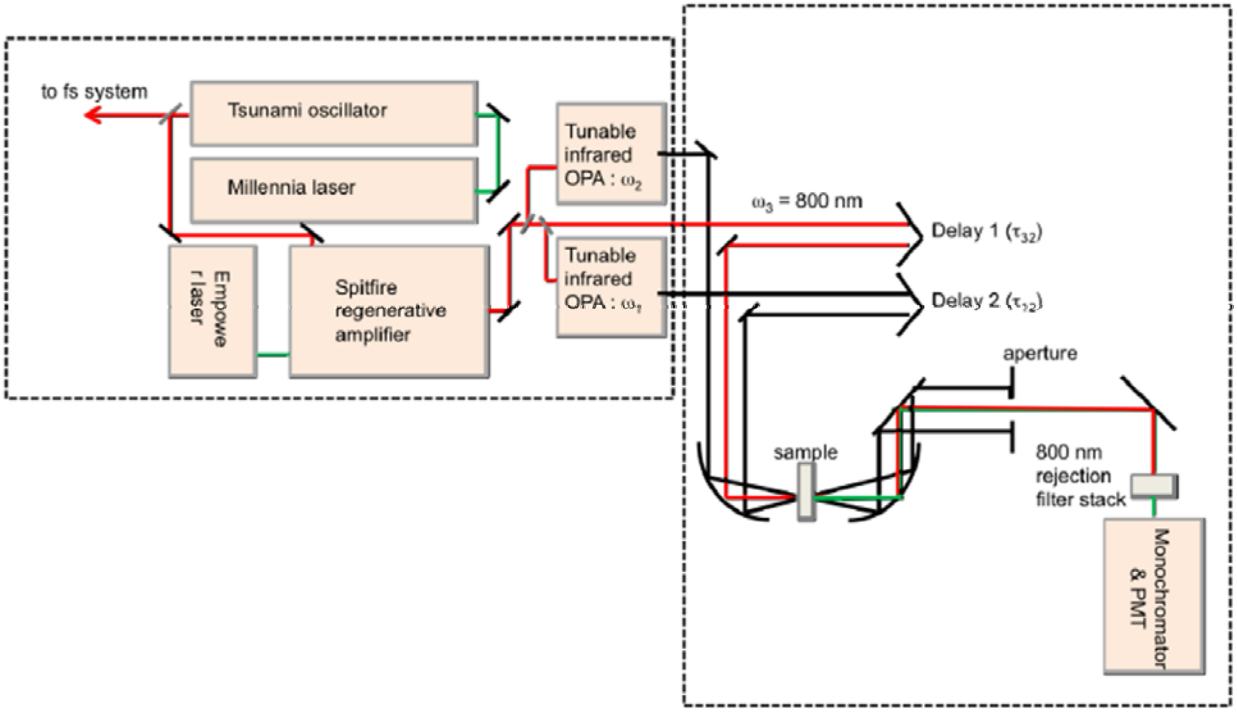
**General Description**

Data were collected on a laser system composed of an oscillator, regenerative amplifier, and OPAs, complete with two additional pump lasers, all purchased from Spectra-Physics (see Fig. S1). A 5 W diode-pumped continuous wave (CW) frequency-doubled Nd:YVO4 \Millennia" pumped the 35 femtosecond, 80 MHz mode-locked Ti:Sapphire \Tsunami oscillator. This output was split between the fs and ps systems, with ~250 mW of power seeding a regenerative amplifier (Spitfire or Spitfire Pro), which was pumped by a 1 kHz, 9 W Nd:YLF Empower. After the stretcher grating inside of the amplifier, a mask was applied to the seed to spatially and spectrally window the spectrum, moving it into the ps regime. The 800 nm, 1.6 ps, 1 kHz output of the amplifier was split to pump two independently tunable optical parametric amplifiers (OPAs) with frequencies $\bar{\nu}_1$ and $\bar{\nu}_2$ in the mid-IR, 15-25 $cm^{-1}$ FWHM Gaussian profiles, ~0.8-1 ps durations, and 1-1.5 μJ pulse energies. A third excitation beam ($\bar{\nu}_3$) with 1-5 μJ/pulse of 800 nm light was created by further splitting of the amplifier output.




The $\bar{\nu}_1$ and $\bar{\nu}_3$ time delays were changed relative to the static $\bar{\nu}_2$ beam by times $\tau_{12}$ and $\tau_{32}$. These two-dimensional delay scans map out each of the coherence dephasing rates. All fields were focused into the sample by either a 50 or 100 mm focal length off-axis parabolic (OAP) mirror. The experimental phase-matching geometry for Triple Sum Frequency (TSF) experiments placed the visible beam normal to the sample plane and the infrared fields at ±10°. For DOVE experiments, the phase matching angles are those that impinge upon the sample. These angles are found by calculating the beam positions as they enter the OAP. OAPs have the property that all beams entering parallel to the optic axis will be focused to the same point. Therefore, we need to convert those desired angles into distances left or right of the optic axis that we can align to. This is done using the equation for the parabola, $y = \frac{x^2}{4f}$, where $f$ is the

focal length of the OAP. The relationship between the phase matching angles and the position of the beams on the surface of the OAP is $x = 2f\left(1-\sqrt{\tan^2\theta+1}\pm\tan\theta\right)$.

The wave vector for the nonlinear output polarization in TSF is the sum of the excitation pulse wave vectors, $\vec{k}_1+\vec{k}_2+\vec{k}_3$ for TSF and $\vec{k}_1-\vec{k}_2+\vec{k}_3$ for DOVE, so the desired output is therefore collinear to the visible field as the momenta of the IR fields will cancel when the frequencies are similar. Spectral discrimination of the signal from the visible input is achieved by a combination of high optical density holographic filters. A monochromator measures the visible signal for experiments with a resolution of the output frequency of 11 $cm^{-1}$ for minimum slit widths. The OPAs and laser table are purged with dry air and maintain a relative humidity of ~2%.

The timing between excitation pulses was defined using the non-resonant TSF signal from a 2 mm ZnSe crystal. It provides a convenient and very intense output that can be used to find the delay positions where the pulses are temporally overlapped. The position of temporal overlap changes when $\bar{\nu}_1$ and $\bar{\nu}_2$ are tuned over the vibrational resonances. Figure S2 shows an example of the dependence of the delay time on the excitation frequency. The large vertical feature at 1480 $cm^{-1}$ is an artifact resulting from the presence of the $\vec{k}_1+\vec{k}_2+\vec{k}_3$ and $2\vec{k}_2+\vec{k}_3$ signals at this position. The delay time changes are largely the result of the path length change in the AgGaS2 difference frequency crystal. The delay changes as a function of tuning range. Calibration of this trend and automated correction of the delay time changes is accomplished by finding the positions for temporal overlap over the entire scan range and then using a computer to change the delay times in direct correlation with the tuning of $\bar{\nu}_1$ and $\bar{\nu}_2$.