A Coherent White Paper

Simplified One-Beam 2D Electronic Spectroscopy using a Millijoule Amplifier and HCF

Coherent two-dimensional spectroscopy (CMDS) represents a powerful group of spectroscopic techniques with the unique ability to reveal couplings between different states of a system, as well as their relaxation timescales. These methods range from two-dimensional infrared (2DIR) used to probe vibrational states, to 2D electronic spectroscopy (2DES) that examines electronically excited states in molecules, semiconductors and nanoparticles. The complexity in practice – optical, mechanical, electronic – of these methods has limited their use to a relatively small group of developers and users. However, the situation is rapidly changing with the advent of rugged ultrafast amplifiers, turnkey pulse shapers, and other off-the-shelf components. Now a group based at McGill University, led by Professor Pat Kambhampati, have combined one of these amplifiers – a Coherent Legend Elite HE – with a hollow core fiber (HCF) compressor from few-cycle Inc., along with several other key innovations, to demonstrate a system based on a single collinear beam geometry, providing a much simpler route to 2DES data.

2D Spectroscopy Basics

In traditional (one-dimensional) spectroscopy, the interaction of light and a sample is normally acquired and shown as intensity as a function of frequency (wavelength) on a one-dimensional plot. In the case of infrared absorption, this then provides information about structure and form. For example, infrared spectra are widely used by chemists to identify molecular species and to interpret their geometry, bond strengths and so forth. (Since the 1980's infrared absorption has been mostly studied using Fourier transform – FTIR – where time domain data is converted to frequency domain plots.)

As its name suggests, in two-dimensional spectroscopy, the sample is simultaneously interrogated by light at two wavelengths (frequencies). A second frequency axis is added to the usual one-dimensional plot and the data is represented as a 2D correlation map, as a function of two different frequencies. This is exemplified in figure 1.

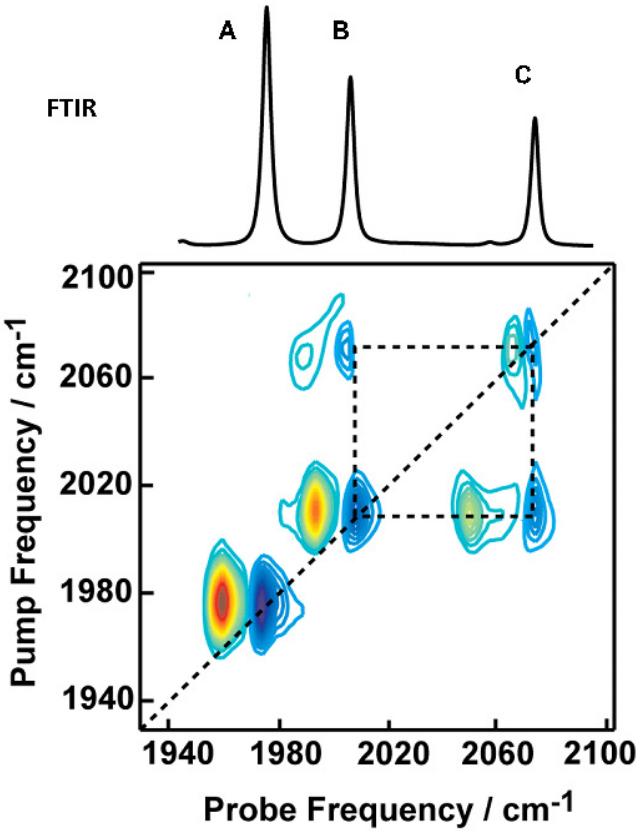


Figure 1: *Experimentally measured FTIR (top) and 2D IR (bottom) spectra for a mixture of compounds. From the FTIR spectrum, one cannot determine how many types of molecules are contained in the mixture. The 2D IR spectrum exhibits a pair of diagonal peaks for each of the peaks in the FTIR spectrum. The cross peaks in the 2D IR spectrum reveal that the two higher frequency peaks are coupled to each another, indicating their belonging to the same molecule. In fact, these spectra were collected for a mixture of two compounds. (See "2D infrared spectroscopy moves towards mainstream use," Laser Focus World - July 2013 - by M. Zanni, C. Middleton, M. Arrigoni, and J. Henrich.)*

When the two frequencies are the same, then the diagonal plot is the conventional one-dimensional spectrum. But, now consider if the pump frequency is fixed at absorption peak B of the sample. This will excite a vibration, just as in FTIR, *and* will also perturb the absorption of peak C, if *the two transitions B and C are coupled*. Any pair of vibrations linked by common atoms in this way are called coupled vibrations, and will give rise to so-called cross peaks, displaced from the diagonal (one-dimensional) spectral line. So at the very least, 2D spectroscopy can tell us which vibrations are coupled. (As shown in figure 1, the peaks are usually plotted as intensity contours and two contrasting colors, e.g., blue and red, are used to indicate the relative sign of the peaks.)

Although this is an important capability, in theory this information could be obtained by other analytical means, such as isotopic substitution. However, the shape, linewidth and intensity of coherences observed by 2D absorption spectroscopy can provide a wealth of both structural and dynamic (e.g., intramolecular energy flow) information beyond this.

Moreover, just as with one-dimensional IR, 2D spectra are today recorded by an effective Fourier transform from the time domain. This entails using closely spaced broadband pulses that cover the entire wavelength range of interest. Importantly, these pulses are coherent in phase and completely controllable in time and, ideally, in polarization also. The entire sequence of pulses is illustrated schematically in figure 2.

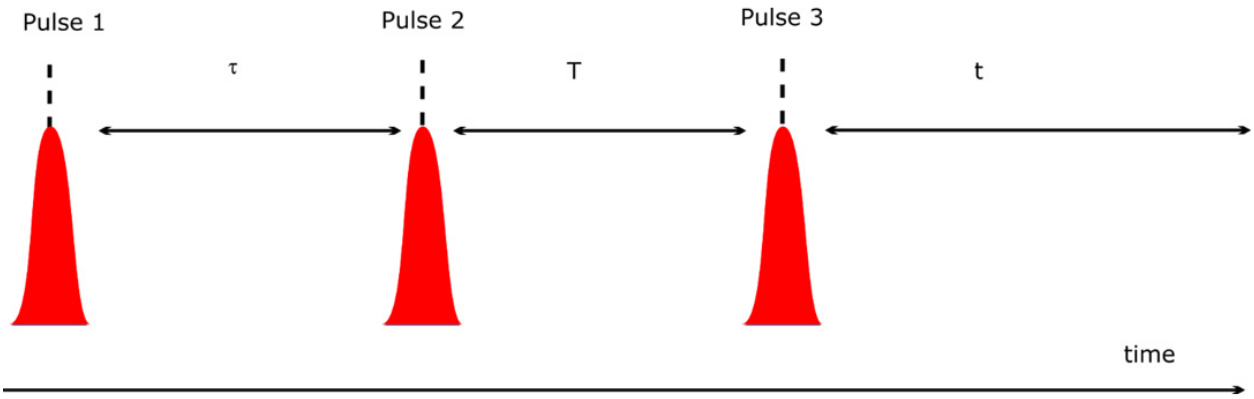


Figure 2: *Coherent pulse sequence. Pulse 1 creates a coherence, Pulse 2 creates a population or a double quantum coherence, Pulse 3 creates a coherence which is measured as the non-linear optical signal of interest. Specific signals corresponding to specific quantum pathways are selected via the phase of the pulses. Earlier implementations selected the wavevectors rather than the phases.*

The sample is irradiated with three pulses, eventually triggering the sample to produce a fourth signal pulse which is separated by a spectrometer and typically measured using heterodyne detection with a reference pulse from the laser source. The temporal separation between the first two pulses (the pump pulses) is called the coherence time and is usually labeled τ. The Fourier transform of τ converts the time domain data into excitation frequency (ω1). The spectral separation provided by the detection spectrometer provides the signal frequency (ω3). Data like figure 1 are then created by plotting ω1 versus ω3. The delay between pulses 2 and 3 (the probe pulse) is called the population delay time (T) and is typically greater than τ. Because all three laser pulses are coherent, recording data as a function of T provides information about dephasing times and similar dynamic information about the excited state population created by pulses 1 and 2. Because of this temporal information, the methods are sometimes collectively called coherent multidimensional spectroscopy (CMDS). Here a full dataset is typically acquired by slowly stepping T and scanning τ at each fixed T.

Electronic Spectroscopy – White Light Continuum

One-dimensional electronic spectroscopy uses visible or ultraviolet light to excite electrons in a sample to create excited states in isolated molecules or various types of localized or diffuse excitons in condensed phase samples. Two-dimensional electronic spectroscopy – optical CMDS – provides additional information ranging from coherences in molecular chromophores to many-body interactions in quantum-confined materials. Nanoparticles in solid phase (e.g., quantum dots) or solution (i.e., colloids) represent one of several areas of research currently being studied by Professor Pat Kambhampati at McGill University (Toronto, Canada). He explains, "Optical CDMS provides quantum dynamic information we could not access any other way, even by using pump-probe techniques. It is enabling our group to study electronic couplings in quantum dots and other model systems; this puts us on a path to answering fundamental questions about the fate of excitons generated by photon absorption or charge injection. Ultimately, this information should enable the development of material systems with optimized properties for applications such as solar energy, communications and next generation displays."

Obtaining optical CMDS data with the widest possible set of information requires stable, coherent pulses with a bandwidth sufficient to address all the relevant excited levels. While in principle, two tunable CW sources would fulfil the task, in practice broadband femtosecond pulses are the method of choice. In addition, the use of short pulses enables also to study the dynamic of sample, by varying the delay of one of the pulses. The most common accepted method of obtaining these broadband "white light" pulses is to use a non-collinear optical parametric amplifier (NOPA). NOPAs are typically pumped with a 100-150 fs amplifier and are able to produce a broad spectrum that provides some level of tunability. Although NOPAs are able to produce sub-10 fs pulses, pushing their bandwidth to an extreme makes them more difficult to operate in a stable and repeatable fashion – a clear impediment in experiments that may last hours.

Hollow Fiber Compressor

Part of Kambhampati's research emphasis is technological development – creating new methods and tools to provide simpler access to a broader audience, particularly for complex techniques such as optical CMDS. To this end, Kambhampati and graduate student Hélène Seiler decided to investigate the use of a hollow core fiber to generate the requisite white light continuum.

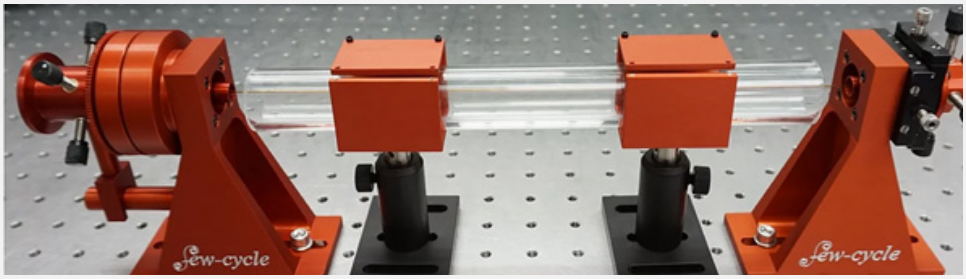
A hollow core fiber is a narrow glass or quartz capillary that acts as a waveguide. In this case, it is filled with an inert gas. It is well-known that when a high energy femtosecond laser pulse from an ultrafast amplifier is injected into such a fiber, the high peak power drives non-linear optical effects in the inert gas. Under optimum conditions, the output is a broadband continuum that can be compressed to a much shorter pulse width than the original input pulse. Until recently, these hollow core fiber (HCF) compressors have been used mainly to reach short (a few fs) pulse widths and to drive high harmonic generation in gases. However, Seiler wanted to investigate whether the spectral properties, and phase/intensity stabilities were suitable for optical CMDS.

Specifically, Seiler and Kambhampati wanted to use input pulses from the Coherent Legend Elite HE, a 1 kHz/8 mJ titanium:sapphire amplifier formerly used in their lab to pump a NOPA. The use of a regenerative amplifier architecture means that the Legend Elite HE delivers high-quality spatial beam profiles and extremely stable pulses, which are requisites for controlled non-linear processes as planned with the HCF. Moreover, this amplifier had been configured for ~120 fs pulse width for NOPA pumping. NOPAs are ideally driven with long pulses that are easy to generate. The HCF approach is generally driven by short pulses. Hence there is interest in using milder driving pulses which are easier to generate. In terms of the inert gas fill, helium can handle the highest input power whereas neon can deliver the broadest visible continuum. Based on the 8 mJ pulse energy from the Coherent Legend Elite HE, the McGill group decided to use argon as a best match for these pulses. The key then is to match the fiber core diameter to the pulse characteristic in order to maintain a low enough intensity, and then to use a long propagation length (i.e., long fiber).

Seiler obtained a HCF from few-cycle Inc., a company that is a leading supplier of this technology. Based on various parameters, few-cycle recommended a 2.5 meter HCF with a 0.4 mm core diameter.

Hollow Core Fibers – Short Pulses, Wide Bandwidth

The use of hollow core fibers for ultrafast pulse compression and spectral broadening is enabled by several commercial vendors. As used by the Kambhampati group, the new flexible fiber system produced by few-cycle Inc. is a modular product line that allows researchers to choose various fiber lengths and inner diameters to achieve a desired nonlinear effect. Experimentally measured transmission for multi mJ femtosecond pulses ranges between 50% - 80%, depending on the application. The work here highlights the ability to generate broadband continua for 2D spectroscopy. Moreover, the few-cycle Inc. system can routinely deliver temporal compression up to 15X. This enables the use of next generation ytterbium based ultrafast amplifiers to reach sub 20 femtosecond performance, expanding the research enabled by these flexible femtosecond sources.



Single Beam Optical CMDS Methodology

Generating three addressable coherent pulses with controllable time delays and then detecting a low signal (relative to the intense laser pulses), all on the femtosecond timescale, is a considerable challenge. For instance, in the early days of the technique, this entailed co-aligning three separate beams. The Kambhampati group is on a relentless mission to borrow some concepts from FT NMR to simplify this challenge and thus broaden the utility of optical CMDS. As Kambhampati states, "You can buy commercial solutions for pump-probe 1D spectroscopy, and we want to show that this can be possible for 2D spectroscopy also." The switch from a NOPA to a stable HFC is just one of three key innovations that they have combined for the first time in their latest experimental setup as summarized schematically in figure 3. These are:

1. HCF for simple generation of stable broadband pulses.
2. A collinear single-beam geometry that eliminates complex alignment challenges
3. A direct optical readout of the signal using a gated spectrometer with CCD

The keys to success with a HCF are beam quality and laser stability. A HCF is a highly non-linear device which will amplify any unwanted phase or amplitude noise and changes in beam profile and pointing associated with the input pulses. Seiler notes, "We have demonstrated that the HCF can deliver broadband pulses with the requisite low phase noise with higher stability than a NOPA. But to maximize this advantage, it is critical to have a low noise amplifier like the Legend Elite HE."

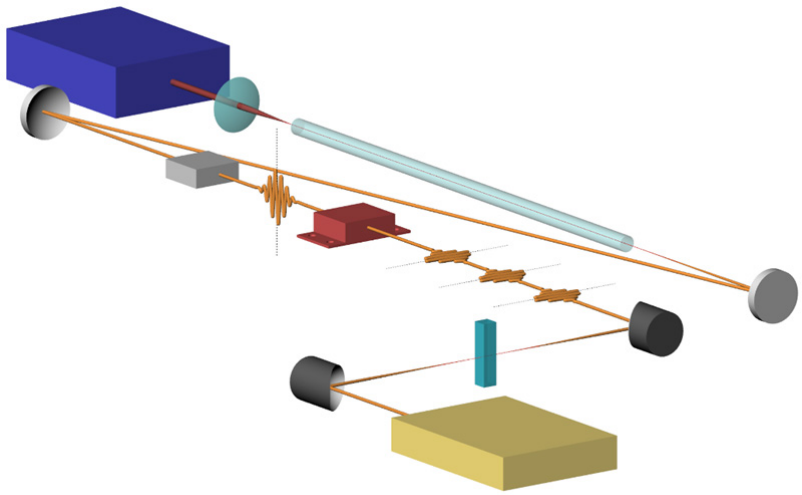


Figure 3: *Schematic of Kambhampati single beam setup. In the simplest implementation, the Ti:sapphire system forms the power source which drives the short pulse generation in the HCF (few-cycle Inc.). These pulses are then sent to a grism-based compressor, followed by an acousto-optic modulator to generate the coherent pulse trains which are directly fed into a spectrometer for readout. Other variations have been implemented with new ones being currently tested.*

The key to (2) and (3) is the clever use of a programable acousto-optic pulse shaper (Dazzler, Fastlite). Kambhampati explains, "In a collinear geometry, all signals are emitted in a single direction. This makes it impossible to rely on wavevectors to single out pathways. However, the *phase dependency* of the non-linear signals can be exploited instead of the wavevectors." Experimentally, this is enabled by the pulse shaper's ability to independently control the constant phase and delay. In simplified terms, the general idea of phase-cycling is to repeat a pulse sequence with given delays while varying the constant phases of the pulses (φi for pulse i). The signal of interest can then be retrieved by judiciously summing the raw data with appropriate prefactors. For example, in the pump-probe geometry, the purely absorptive signal is contaminated with pump-probe contributions. However, since these pump-pump contributions do not depend on the phase between the two first pulses, they can be eliminated by repeating the pulse sequence twice while cycling the phase of the second pulse through 0 and π. Blocking of alternate pulses in the spectrometer is easy at the 1 kHz repetition rate (i.e., millisecond timescale) of the system.

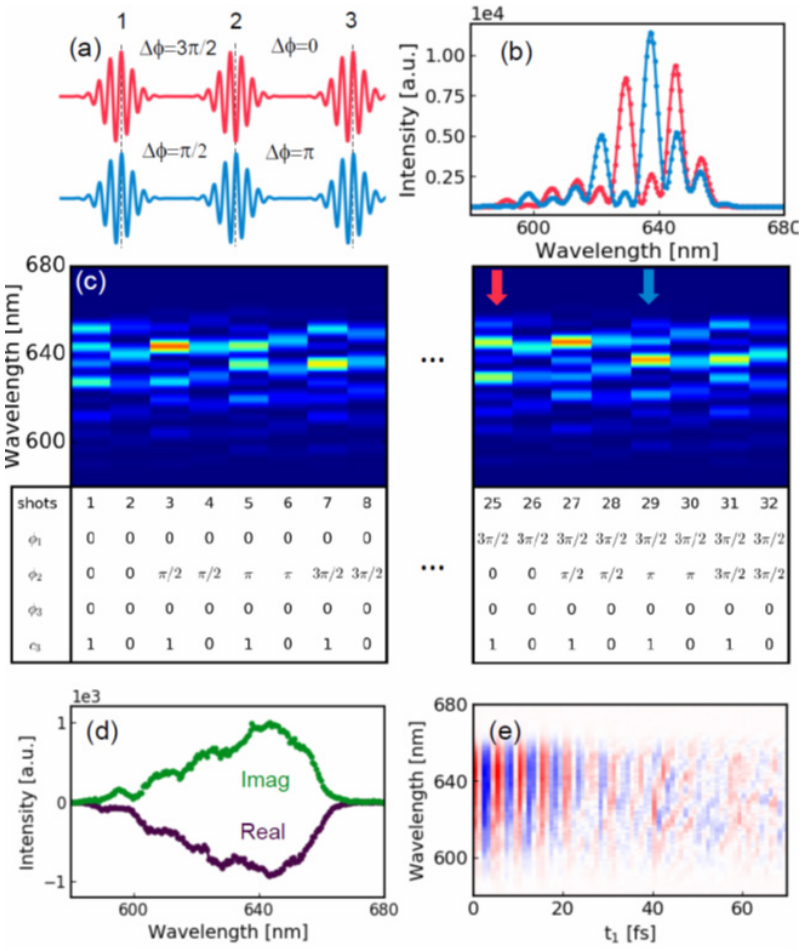


Figure 4: *Demonstration of using phase cycling to obtain 2DE signals. Shown are pulse sequences (a), spectral interferograms (b), phase sequences required to obtain signals of interest (c), complex signals in the frequency domain (d), and in the time domain (e). From J. Chem. Phys. 147, 9 (2017).*

The raw data reaching the spectrometer consists of an interferogram (see figure 4). This is recorded for different phases of pulses 1 and 2 while the probe pulse is chopped. The entire data set consists of 16 different combinations with and without the probe pulse, for a total of 32 pulses for each data point. These are combined to obtain the basis data set. The computer can then Fourier transform this to obtain a 2D spectra plot. Kambhampati notes, "This sounds complicated but once it is programed into the instrument, the actual use of that instrument is then remarkably straightforward."

Some Recent CMDS Data

The first test data obtained with this setup were recorded using the dye Nile Blue as the sample, since the 2D spectral characteristics of this compound are already well-known. Kambhampati explains, "While 2DIR has proved useful for unraveling couplings in molecular spectroscopy, 2DES can provide similarly unique information for electronic materials. We are particularly interested in quantum dots in the semiconductor CdSe, which is a well-known model system." This well-studied system is used for investigations in photo-physics relevant to displays, photovoltaics, detectors and next-generation LEDs. The Kambhampati group has used 1D pump/probe spectroscopy to unravel the structure and dynamics of electronic excitations in CdSe quantum dots (Acc. Chem. Res. 44, 1 (2011)). Figure 5 shows some typical CdSe data that illustrates how 2D spectroscopy produces insights not possible from 1D spectroscopy. The spectra are congested, which makes it impossible to disentangle effects of interest for understanding electronic materials. The spectral congestion problem is clearly resolved by projecting out the system along two frequency axes for detailed analysis.

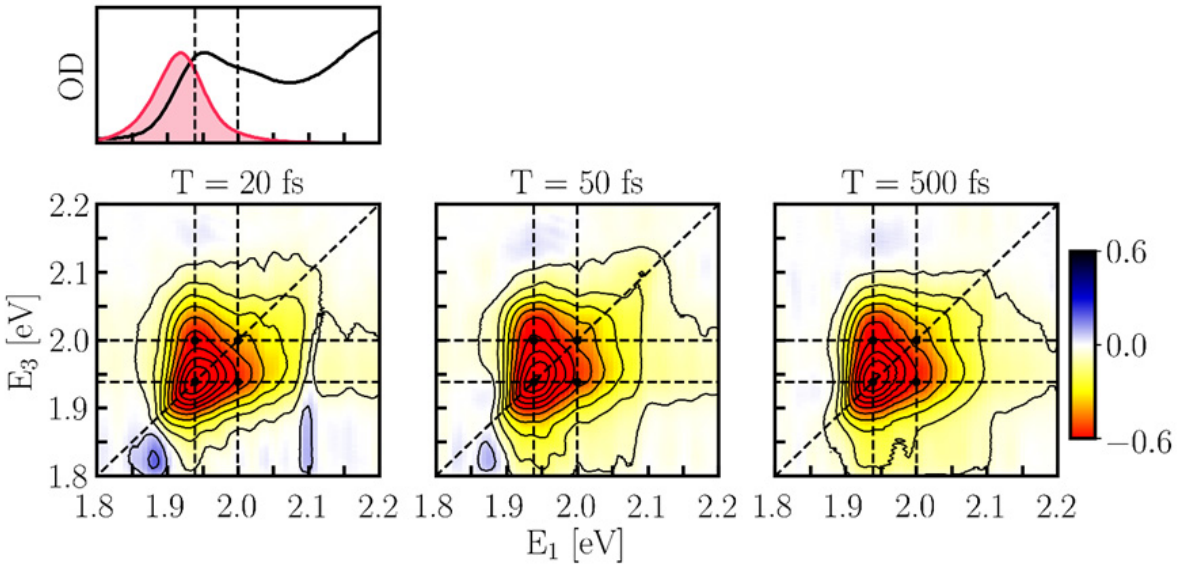


Figure 5: *Some representative 2DE data on CdSe quantum dots.*

Summary

A generation ago, 1D pump-probe spectroscopy in the femtosecond domain was considered state of the art and was rewarded with a Nobel chemistry prize for Ahmed Zewail. Today, it is just a routine tool that is exploited by many people to study molecular energy states and interstate transitions. For 2D spectroscopy to make the same progress, experimental simplicity will be key to commercial solutions. This work at McGill University is surely an important step down that path.