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Simplified and economical 2D IR spectrometer design using a dual acousto-optic modulator

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ABSTRACT

Over the last decade two-dimensional infrared (2D IR) spectroscopy has proven to be a very useful extension of infrared spectroscopy, yet the technique remains restricted to a small group of specialized researchers because of its experimental complexity and high equipment cost. We report on a spectrometer that is compact, mechanically robust, and is much less expensive than previous designs because it uses a single pixel MCT detector rather than an array detector. Moreover, each axis of the spectrum can be collected in either the time or frequency domain via computer programming. We discuss pulse sequences for scanning the probe axis, which were not previously possible. We present spectra on metal carbonyl compounds at 5 μm and a model peptide at 6 μm. Data collection with a single pixel MCT takes longer than using an array detector, but publishable quality data are still achieved with only a few minutes of averaging.

1. Introduction

A 2D IR spectrum is a correlation of two vibrational frequency axes. When Hamm, Lim and Hochstrasser collected the first 2D IR spectrum, they collected the data in the frequency-domain by scanning the center frequency of a narrowband pump pulse to generate one axis and frequency-resolved a femtosecond probe pulse for the second axis [1]. A few years later, Hochstrasser and coworkers collected the first time-domain 2D IR spectrum, followed closely by Tokmakoff and coworkers, by using four femtosecond pulses, two to generate the pump axis and two for the probe axis [2,3]. When originally implemented, it took many hours to collect a single 2D IR spectrum. Nonetheless, the information contained in 2D IR spectra is so valuable that the technique was soon applied in fields as diverse as chemical dynamics, material science, and molecular biophysics, regardless of the time consuming data acquisition [4–15]. Now, due to improvements in the technology and a better understanding of the scientific underpinnings of the technique, 2D IR spectra with high signal-to-noise can be generated in seconds [16–18].

One of the most important developments for fast data collection was the use of spectral interferometry, in conjunction with an array detector, to collect the data for the probe axis of the spectra [2,3,19]. To generate the probe axis, the electromagnetic field emitted from the sample must be time-resolved and Fourier transformed. The measurement can be done in the time-domain, by scanning the fourth laser pulse (called the "local oscillator") and performing a digital Fourier transform or in the frequency-domain by utilizing a spectrometer to optically perform the Fourier transform [20]. With a spectrometer, followed by an array detector, all of the frequencies contained in the emitted field are measured simultaneously. This frequency-domain approach is called spectral interferometry. With spectral interferometry, one only needs to incrementally scan the pump axis, which leads to fast data acquisition of the 2D IR spectrum.

Data acquisition with an array detector also has a few practical drawbacks. The drawbacks included grating losses in the spectrometer that leads to lower signal strength, detector noise from each of the many pixels in the array, and a frequency resolution that is ultimately limited by the pixel size. But the biggest drawback may be its cost. The array detector, spectrometer and associated electronics altogether cost about 1/3 the price of a Ti:Sapphire regenerative amplifier. The high price certainly limits the number of researchers that can utilize 2D IR spectroscopy in their laboratories, even if they already own a regenerative amplifier.

In this article, we present a design for a 2D IR spectrometer that utilizes two germanium acousto-optic modulators (AOM). Previously, we reported a 2D IR spectrometer with a single AOM that modulated the pump beam [17,18,21]. The AOM could be used to generate and scan the time delay between a pair of pulses to collect data in the time-domain or it could generate and scan the center frequency of a spectrally narrow pulse to collect data in the frequency-domain. Interferometric methods have also been developed to generate the pump axis data [22]. For all of these methods, a spectrometer and array detector were used to generate the probe axis. With the addition of a second AOM, these two

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expensive components are no longer needed. The second AOM can create a femtosecond pulse pair to measure the probe data in the time-domain, or it can be spectrally narrowed to measure in the frequency-domain. Either way, a single channel detector replaces the array detector, which greatly simplifies the experimental layout and reduces the cost of the 2D spectrometer since an AOM is significantly less expensive than an array detector, monochromator and the associated electronics. Data collection is still very rapid, because a new pulse sequence can be generated with every laser shot even at multiple kHz repetition rates. In this paper, we demonstrate that even without an array detector, our dual AOM design can collect high signal-to-noise 2D IR spectra in a few minutes.

Rapid time-domain scanning using translation stages has been receiving an increased amount of attention in the past few years [16,22,23]. Continuous scanning of the delay between the two pump pulses, rather than stopping and restarting the translation stages, increases the accuracy and decreases the acquisition time of the pump axis data. Rapid scanning of the pump axis in a style similar to that used in commercial Fourier transform infrared (FTIR) spectrometers has been shown to improve the signal-to-noise [22]. Rapid scanning of the delay between two pump pulses still requires an array detector. Recently, a rapid scan approach has been used for the probe pulse [23]. That method is similar to ours in that a single channel detector is used rather than an array detector, but they used a four-wave mixing phase matching geometry which necessitates a more difficult alignment procedure and requires both the rephasing and non-rephasing spectra to be independently collected, added and phased. Using AOMs in the pump–probe beam geometry, these steps are all done automatically. But there is also an intrinsic difference between delay scanning with translation stages and an AOM. With an AOM, one can precisely control the number of points per period to be collected of the vibrational coherence and thus easily set the frequency bandwidth of the measured spectrum. In contrast, with continuously moving translation stages, the number of points per period is tied to the repetition rate and the speed of the translation stages (a HeNe interferometer is also necessary for calibration of each axis). Thus, moving to higher repetition rates adds more points per period, but those points mainly sample frequencies outside of that spanned by the laser bandwidth unless the scanning speed is also increased. Thus, higher repetition rates do not necessarily correlate with faster data collection. With dual AOMs, data collection time shortens linearly with increased repetition rate. In addition, one can also scan the probe in the frequency-domain, which requires far fewer data points than time-domain data collection. We demonstrate the unique abilities of our spectrometer by collecting 2D IR spectra using various combinations of time and frequency-domain scanning without any mechanical adjustments to the spectrometer.

2. Experimental implementation

A home built optical parametric amplifier (OPA) is pumped by 1.3 mJ, 45 fs transform limited pulses from a 1 kHz Ti:Sapphire regenerative amplifier. The 800 nm output is downconverted into signal and idler pulses (200 μJ combined) in a type II BBO crystal ($\theta = 28.0°$, 2 mm thick) in two stages with collinear alignment. Mid-IR pulses are generated by difference frequency mixing the signal and idler pulses in a type II $AgGaS_2$ crystal ($\theta = 45.4°$, 1 mm thick or $\theta = 41.8°$, 1 mm thick). The resulting pulses have FWHM bandwidths of approximately 185 cm^{-1} at 5 μm or 6 μm respectively, and pulse energies of about 5 μJ.

The spectrometer used for experimentation is shown in Fig. 1. A single mid-IR pulse is brought into the spectrometer where it first passes through a custom periscope assembly in order to generate two parallel vertically displaced pulses (inset). The periscope contains a plane parallel CaF_2 window that reflects about 3% of the mid-IR light at both the front and back faces, while the transmitted light is reflected by a gold mirror. All three beams are reflected off a gold mirror at the bottom of the periscope to bring them back parallel to the optical table. The light coming from the front reflection of the CaF_2 window is discarded, leaving two parallel vertically displaced pulses for the pump ($0.94*I_{input}$) and the probe ($0.03*I_{input}$) beam paths.

The two parallel vertically displaced pulses are reflected off a gold mirror and sent into a 4-f pulse shaper setup. First, the pulses are frequency dispersed using a gold-coated grating (200 grooves/mm, 5.0 μm blaze or 150 grooves/mm, 5.4 μm blaze) in a near-Littrow configuration. The frequency components are then collimated with a custom 12.5 cm focal length CaF_2 cylindrical lens. A folding mirror reflects the light and sends each pulse through its own germanium acousto-optic modulator (AOM). The first-order diffracted light from the AOM is reflected toward a second CaF_2 lens, where the frequency components are focused down at a second grating. The second grating recombines the frequencies of each individual pulse, transforming them back into the time-domain. Theoretical throughput of the spectrometer for the pump pathway is between $0.37*I_{input}$ and $0.47*I_{input}$, but in practice is heavily dependent on the efficiency of the grating pair used. Experimental throughput of the pump is typically measured to be between $0.3*I_{input}$ and $0.4*I_{input}$.

The pump and probe beams are reflected off stacked gold mirrors toward a 90° off-axis parabolic gold focusing mirror (2 in. focal length). The stacked mirrors are horizontally offset to compensate for differences in time delays. The probe beam passes through a ZnSe wedge pair that is positioned using a translation stage for controlling the pump–probe delay time. With this arrangement we can vary the waiting time, t_2 in the 2D IR experiment from 0 to 15 ps.

Following the sample, a second 90° off-axis parabolic gold mirror collimates the pump and probe beams. The pump beam is blocked with an iris, while the probe beam is detected by either a spectrometer and an array detector, as is usual with spectral interferometry detection, or by rotating the spectrometer grating to zero-order so that it acts as a mirror and use only a single pixel on the array for detection (in practice, we sum three pixels to account for slight frequency dispersion). With this detection arrangement, we can quickly switch between array and single channel detection in order for comparison studies. The spectrometer is 150 mm focal length with either a 150 or 75 grooves/mm grating followed by a 64-channel array detector, which results in a frequency resolution of 2.5 or 5 cm^{-1} per pixel, respectively. We use the spectrometer to calibrate the AOMs, but one could use other calibration methods instead, which we are currently devising. Windowing functions are not used in this paper as to not complicate the method comparisons.

3. Results

Fig. 2(a) and (b) show two common ways of collecting 2D IR spectra. They both utilize a femtosecond probe pulse, a spectrometer, and an array detector. They differ in that (a) one has its pump axis collected in the time-domain while (b) the other is collected in the frequency-domain. In time-domain data collection, the delay (t_1 for the pump axis) is incremented and the resulting data computationally Fourier transformed. For frequency-domain data collection, the center frequency of a narrowband pump is scanned while measuring the transient absorption. For the frequency-domain pulse sequence, we draw the pulse envelope as if it were generated by an etalon as Hamm, Lim and Hochstrasser first used, although more optimized pulse shapes are now available with pulse shapers [1,17].