Two-dimensional infrared spectroscopy detected by chirped pulse upconversion

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A two-dimensional (2D) infrared spectrum of Mn$_2$(CO)$_{10}$ is measured by using chirped-pulse upconversion (CPU) of the nonlinear signal field plus a reference local oscillator. By converting the spectrum to the visible, a silicon CCD camera can be used. The method offers an attractive alternative to direct IR detection due to the technological maturity of silicon and its greater intrinsic detectivity over HgCdTe. Using CPU, we acquired a rephasing 2D IR spectrum in a few seconds. © 2007 Optical Society of America

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Vibrational spectroscopy offers significant correlation between spectrum and structure in systems ranging from simple diatomic molecules to complex proteins. Multidimensional spectroscopy is well suited to vibrational transitions because pronounced spectral features can be identified with structural elements. The weak link in two-dimensional (2D) IR spectroscopy is in signal detection: to measure the electric field, it is necessary to mix the signal with a local oscillator field, detecting the interference by using a spectrometer. A single-shot, multichannel approach is preferable to reduce measurement time, but, unlike high-pixel-density silicon CCDs, current options for laboratory-scale IR spectroscopy are limited to expensive 1D 64-pixel arrays of HgCdTe (MCT).

By leveraging the multiplex advantage and high sensitivity of a silicon CCD, nonlinear frequency conversion of the IR electric field to the visible spectral region offers a promising alternative to direct IR detection. Although this strategy has been used previously, it has not yet been applied to signal detection in coherent multidimensional spectroscopy. The present implementation is unique in that a highly chirped near-IR ($\lambda_0=800$ nm) field is used to convert the IR signal before entrance into the spectrometer. Chirped pulse upconversion (CPU) enables translation of the IR signal to the visible with small spectral distortion, provided the pulse is adequately stretched. We have previously demonstrated CPU for spectroscopy and mid-IR pulse characterization.

The basic principle of CPU is shown in Fig. 1. Sum-frequency generation (SFG) of a chirped near-IR pulse and a several picosecond IR field occurs in a suitable nonlinear crystal, resulting in visible SFG. Since the chirped pulse duration is much longer than the IR field, a narrow spectral window within the chirped pulse spectrum is gated, leading to SFG with a nearly monochromatic field. The phase of the upconverted field reflects that of the complex IR field and the chirped pulse field, which is essentially constant during the short time window. We note that even in cases where the IR field duration is not negligible relative to that of the chirped pulse, straightforward correction procedures can be applied to avoid any distortion in the retrieved signal. In multidimensional spectroscopy, the IR field to be upconverted consists of the sum of a reference local oscillator and the nonlinear signal. The resulting visible light is

![Fig. 1. (Color online) (a) CPU involves mixing an IR field consisting of signal and reference with a stretched near-IR pulse. (b) Design of the dual-OPA setup that reuses the white-light seed (WLC) and two pump beams ($P_1$ and $P_2$) by using beam splitters ($BS_i$) and high reflectors ($HR_i$) for the pump ($i=p$, bandwidth >50 nm) and seed ($i=s$, bandwidth >100 nm). Pump optics are transparent to the seed and OPA signal. Both outputs are sent to separate difference frequency generators (DFG1 and DFG2). (c) 2D IR pulse sequence.](image-url)
measured by using a conventional silicon-based CCD camera at the focal plane of a spectrometer.

The principles of 2D IR spectroscopy have been described elsewhere. Briefly, three fields \( E_1, E_2, \) and \( E_3 \) with wave vectors \( \mathbf{k}_1, \mathbf{k}_2, \) and \( \mathbf{k}_3, \) respectively, separated by time delays \( t_1 \) and \( t_2 \) generate a third-order nonlinear polarization in a resonant medium, leading to the generation of a signal field, \( E_s(t_3) \), in the background-free directions \( \mathbf{k}_s = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 \), and \( \mathbf{k}_s = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 \), corresponding to rephasing and non-rephasing signals, respectively. At fixed \( t_2, t_1 \) is scanned from zero to positive delay, and the interference between the signal and a reference local oscillator is recorded with a spectrometer. The signal electric field is determined by spectral interferometry.

Fourier transformation of this electric field with respect to \( t_1 \) yields a 2D spectrum in the variables \( \omega_1 \) and \( \omega_2 \).

The collinear 2D IR signal and reference IR local oscillator along with the chirped pulse are focused into a 0.5 mm thick MgO:LiNbO\(_3\) crystal (Castech, 5% doping) by a 10 cm effective focal length 90° off-axis parabolic mirror. To avoid using a beam combiner, the upconversion is done noncollinearly (type I) with a slight 3° vertical angle between the chirped pulse and the IR beam. Following the crystal, a 10 cm lens collimates the visible output, and a short-wavelength pass filter rejects residual 800 nm light. For alignment into the spectrometer, the upconverted reference beam can be seen by eye. The 0.5 m spectrometer with a 1200 grooves/mm grating (TRIAX 550, Horiba) is fitted with a 1340 × 100 pixel, thermoelectrically cooled, back-thinned CCD camera (PIXIS, Princeton Instruments) connected to a personal computer via a USB interface. A combined exposure and readout time of less than 1 ms (single shot) is achieved by limiting the active area of the chip to 1340 × 20 pixels and by vertical binning to provide single-line spectra of 1340 pixels.

Many amplified laser systems automatically have energetic, highly chirped pulses available for CPU through zero-order diffraction in the compressor. The commercial laser system used here—a Spectra-Physics Spitfire Pro outputting 2.5 mJ, 100 fs pulses at 1 kHz centered at 800 nm—yields a beam with 130 \( \mu \)J of total energy. This beam is composed of a train of pulses resembling the leakage through a cavity end mirror in the amplifier. The first pulse in the train is orthogonally polarized relative to the others and is easily isolated by using a polarizing beam splitter. The chirped pulse energy used in the experiments described here is 45 \( \mu \)J. The chirp is dominated by the second-order spectral phase and was measured by frequency-resolved cross correlation to be \( 9 \times 10^6 \text{ fs}^2 \), corresponding to a 350 ps FWHM Gaussian pulse.

The 2D spectrometer is built for dual-frequency operation, though in the present case all three excitation pulses are tuned to the same frequency. The near-IR, white-light-seeded, \( \beta \)-barium borate (BBO) optical parametric amplifier (OPA) and difference-frequency generation (DFG) are standard. One convenient innovation is to reuse all three beams in the OPA by creating a second, parallel OPA with an independently tunable BBO crystal. The dual-OPA design greatly reduces complexity and size and introduces negligible dispersion at the 100 fs level used here. The ability to probe interactions between chemically distinct vibrations by using two-color 2D IR has been shown to offer a convenient shortcut over generating ultrabroadband IR pulses, while eliminating unwanted diagonal (\( \omega_1 = \omega_2 \)) peaks.

Single-shot detection enables \( t_1 \) to be scanned continuously provided the time delay is known for each laser shot. A 25 mm travel DC motor (Newport LTA-HL) driven by a digital signal processor (DSP) controller (Freescale 56F807) actuates a 25 mm travel stage (Newport UMR5.16). Quadrature signals from the 7.37 nm resolution encoder are sent simultaneously to the DSP counter as well as to a data acquisition (DAQ) board (NI PCI-6221) for independent counting. The DAQ is clocked by using the 1 kHz signal from the laser amplifier, where at each laser shot the position determined by the DAQ counter is saved to a memory buffer. The DSP hardware synchronizes an experimental run by logically ANDing a 5 V pulse with the laser trigger pulses. These gated pulses synchronize the CCD camera, providing a one-to-one correspondence between spectra and positions. This approach allows us to measure spectra as we move the \( t_1 \) delay stage continuously.

We applied CPU 2D IR to the metal carbonyl Mn\(_2\)(CO)\(_{10}\). The Mn\(_2\)(CO)\(_{10}\) sample was a 6.5 mmol/L cyclohexane solution in a 100 \( \mu \)m static cell made of 3 mm CaF\(_2\) windows and a Teflon spacer. The 4 cm\(^{-1}\) resolution linear Fourier transform IR spectrum (Fig. 2) shows three principal peaks at 1983, 2013, and 2045 cm\(^{-1}\). Also shown are single-shot dispersed vibrational echoes (DVEs) \((t_1=t_2=0)\)—a nonlinear spectrum integrated over \( \omega_1 \). Figure 2 also shows the single-shot DVE signal for a sample diluted by a factor of 10 in order to indicate the sensitivity of CPU. It has not been possible to determine the absolute upconversion efficiency, but it is possible to record a full 2D IR spectrum with the 0.65 mmol/L sample (not shown). Figure 3 shows a...
spectral interferogram of the DVE signal of the 6.5 mmol/L sample with a reference local oscillator. The spectral bandwidth in this case is limited by the GaSe crystal in the DFG stage and not by the upconversion.

Figure 4 shows the 2D IR spectrum of \( t_2 = 0 \). This spectrum is the absolute value of the rephasing pathway, and, although not formally the pure absolute magnitude spectrum, it nevertheless shows the quality of 2D spectra obtainable by using CPU detection. This spectrum was obtained by using a single 14.5 ps sweep of the \( t_1 \) delay at a 2.28 ps/s rate. Taking only the data for \( t_1 = 0 \) resulted in a spectrum composed of 6352 laser shots and a spectral resolution of 2.3 cm\(^{-1}\). The 2D spectrum is thus recorded in 6.3 s and represents a substantial improvement over traditional measurements, which often require tens of minutes to record a single 2D spectrum.

Because the relative timing between the chirped pulse and the IR signal is generally not precisely known, there is an ambiguity in the absolute frequency of the upconverted IR signal. We add a second, removable beam splitter to the noncollinear interferometer that generates \( E_1 \) and \( E_2 \), effectively transforming it into a Mach–Zehnder interferometer. The pump pulse spectrum is then easily measured with a single MCT detector with time-domain interferometry. The IR spectrum of DFG2 is measured in the same way by interference between the tracer and reference. Upconverted scattered IR light provides a guide for tuning.

MgO:LiNbO\(_3\) crystal absorption restricts detection to frequencies greater than 1800 cm\(^{-1}\). Other crystals such as AgGaS\(_2\) and LiInS\(_2\) can be phase matched and are transparent at longer wavelengths, but the phase matching bandwidth is smaller, forcing the use of thinner crystals. This reduced efficiency can be compensated by using a more powerful chirped pulse. Despite this inconvenience, the overall benefit of CPU for recording 2D IR spectra with much greater frequency content and rapid scanning makes this method a competitive substitute for conventional direct mid-IR detection.

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