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A fast-scanning Fourier transform 2D IR interferometer

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ABSTRACT

Ultrafast two-dimensional infrared spectroscopy (2D IR) allows for the characterization of vibrational couplings and chemical dynamics. The fastest method of acquiring a Fourier transform 2D IR data set involves spectrally dispersing the signal field onto an infrared array detector. However, use of this method carries disadvantages, including the high cost of IR arrays and the decrease of signal intensity due to dispersion. As an alternative, we demonstrate a readily implemented full time-domain 2D IR detection method in which data from a pulsed laser source is rapidly acquired by scanning an interferometer delay at constant velocity. The stage's position is determined with high accuracy on a shot-to-shot basis by quadrature detection of HeNe tracer interference fringes.

1. Introduction

The past decade has witnessed intense growth in the use of two-dimensional infrared vibrational spectroscopy for applications in chemistry, physics, and molecular biology [1–3]. 2D IR is powerful as a result of simultaneously having sensitivity to molecular structure and femtosecond time-resolution for studying dynamics, which has led to successful applications in areas as varied as hydrogen bond exchange in water, [4,5] chemical reaction kinetics, [6,7] and peptide and protein structure and dynamics [8–11]. A 2D IR spectrum, plotted as a function of two frequency axes, is related to the joint probability of exciting a vibrational transition with frequency, ω_1, and then detecting it at a different frequency, ω_3, after a set waiting period, τ_2. Vibrational couplings give rise to cross peaks between coupled transitions whose intensities are related to the coupling strength and dipole orientation [2]. 2D lineshapes provide information on structural variation and fluctuations. In addition, as the waiting time between excitation and detection, τ_2, is varied, one can observe time-dependent changes in structure, and resolve the flow of population from one state to another [12].

In a 2D IR experiment, a time-varied sequence of three femtosecond infrared pulses coherently drive the vibrations of the sample, stimulating the emission of a signal field (Fig. 1A, inset). The amplitude and phase of the signal is characterized interferometrically by beating it against a known reference field, the local oscillator (LO). The interference between the overlapped signal/LO pair can be detected by spectral interferometry (time–frequency detection) using a spectrometer coupled to a multichannel infrared array detector, or by scanning the LO in time with respect to the signal field (temporal interferometry or time–time detection). This process is repeated as a function of delay between the incident fields, and Fourier transformation allows the signal to be represented as a 2D spectrum in the frequency-frequency domain. The major advantage that spectrally dispersed detection holds is that of multiplex detection. For each τ_1 data point, all ω_3 frequencies are acquired simultaneously. In contrast, the entire τ_3 axis must be scanned in time–time acquisition. This is particularly taxing when high spectral resolution is needed, since the time–time acquisition period scales as the inverse square of the resolution. Further, interferometrically accurate stage positioning is required for the τ_3 axis.

Despite these apparent disadvantages, time–time detection possesses a number of beneficial aspects that make it attractive with respect to time–frequency detection. By spectrally dispersing the signal in time–frequency detection, the total energy of the signal is spread along the elements of the infrared array detector, decreasing the intensity measured per pixel with respect to that on a single channel detector. This intensity/pixel loss coupled with the fact that many infrared gratings are inefficient suggests that weak signals can be more easily detected using time–time detection. Additionally, time–time detection offers the benefit of adjustable spectral resolution since this parameter is determined by the time scanned in the τ_3 dimension and the signal sampling rate, which can be altered to meet experimental needs. In time–frequency detection, the spectral resolution and detected bandwidth in ω_3 is set by the grating dispersion and the pixel spacing in the array detector, which are not adjustable parameters. However, the largest disadvantage to infrared array detectors is the prohibitively high cost, generally 30–80 times that of a single element detector.

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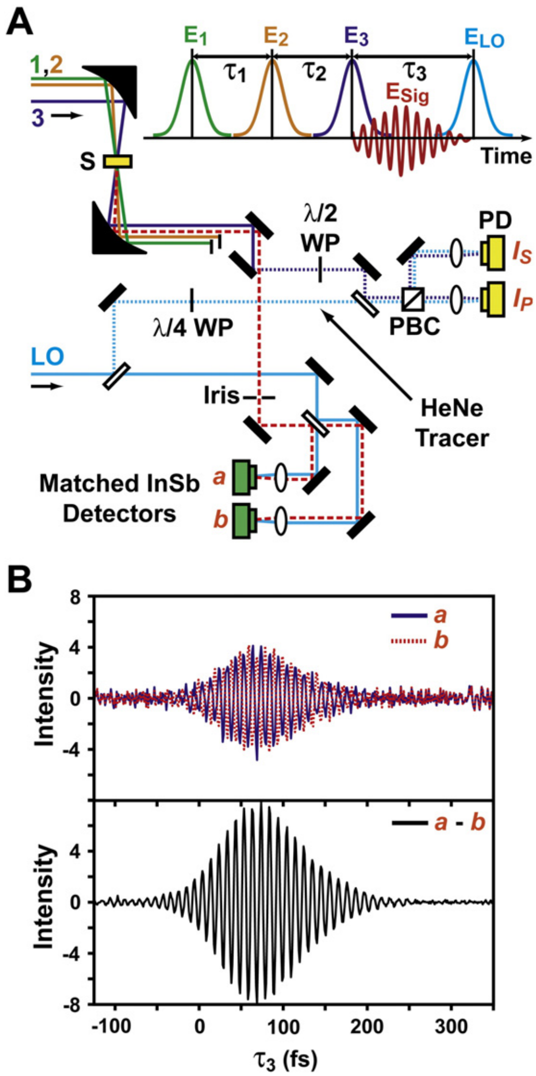

Fig. 1. (A) Schematic descriptions of the experimental layout used to record 2D spectra through time–time detection. The portion of the 2D interferometer used to generate the excitation fields and LO is pictured in Ref. [21]. The signal emitted by the sample is denoted by the long dashed red line, while the HeNe tracer that copropagates with the third IR excitation field and the LO are represented by the dotted blue and cyan lines respectively. S—Sample. LO—Local oscillator. PCB—Polarizing beam cube. WP—Wave plate. PD—Photodiode. (inset) Pulse sequence for 2D IR spectroscopy. (B) Demonstration of balanced detection in the time domain. The solid blue and red dashed traces correspond to the interference measured at the two InSb detectors, *a* and *b*. As τ_3 is scanned, the interference between the signal and LO measured by *a* and *b* is out of phase. Subtraction of the two measured signals allows removal of much of the scatter and LO intensity fluctuations, yielding the clear interferogram shown in black.

To exploit these advantages, we have devised a method that allows us to rapidly acquire 2D spectra in the time domain. Fast scanning techniques for time domain interferometric measurements have previously been implemented to great success [13–15]. Within the context of 2D IR spectroscopy, approaches for rapid time domain scanning have been demonstrated, but these techniques generally require either high precision delay stages [16] or infrared pulse shapers [17]. In contrast, our fast scanning technique uses optics and electronics that are readily present in many labs performing 2D IR experiments and is analogous to the operation of many commercial FT-IR interferometers that operate using constant velocity scanning [18]. In our experimental setup, a temporal interferogram is measured by moving one arm of the interferometer at constant velocity as data are continuously collected. The interference fringes of a HeNe tracer that copropagates with the infrared light are measured at the repetition rate of the ultrafast infrared laser source and used to determine timing. This approach is similar to that recently employed by Lee et al., [19] but avoids the need to modulate one of the arms of the interferometer using a piezoelectric stack.

The detection optics are diagrammed in Fig. 1A. A 1 kHz amplified Ti:sapphire multipass amplifier is used to pump a BBO/$KNbO_3$-based OPA, generating 45 fs pulses centered near 3 μm [20]. For alignment and timing purposes, the OPA output is mode matched with a HeNe laser using a thin Ge plate, and fed into a four-arm Mach–Zehnder interferometer that splits the three excitation pulses and LO for the 2D IR experiment [21]. After the sample, the signal field is overlapped with the LO by combining them from opposite sides of a 50/50 CaF_2 beamsplitter (Thin Film Laboratory). The two matched signal/LO pairs (*a* and *b*) generated by the beam splitter are detected using two matched liquid nitrogen cooled InSb detectors (Infrared Systems Development). Due to the π phase shift upon reflection, the *a* and *b* interference signals are out-of-phase (Fig. 1B) [21]. Detection of the difference signal *a*–*b* removes any homodyne signal and reduces scatter common to the signal/LO pairs. Through proper balancing of the *a* and *b* signal levels, homodyne contributions can be removed from the measured temporal interferograms by subtraction of the signals alone. This eliminates the need to modulate the signal field using an optical chopper as the LO is scanned, and results in an order of magnitude improvement in signal-to-noise over single-channel detection.

Instead of step scanning the τ_3 time delay for a given τ_1 value, we rapidly acquire data along this time axis by moving the LO stage (Aerotech ANT-25L, 50 nm reproducibility, ±150 nm resolution) at constant velocity starting from a negative τ_3 value (typically 200–300 fs before the emission of the signal field) to the final positive time delay. As the stage moves, the interference between the signal and LO is measured for each laser shot using a 250-kilo-samples per second DAQ card (National Instruments). Once a rapidly scanned τ_3 data set is measured, τ_1 is incremented and another rapid τ_3 scan is performed until a full (τ_1, τ_3) data set is obtained.

Since linear stage encoders typically offer inadequate resolution for artifact-free 2D spectroscopy, we determine the value of τ_3 that corresponds to each individual laser shot through quadrature detection [22–24] of the interference between the HeNe alignment beams that copropagate with the LO and the third excitation pulse. One arm of the HeNe is passed through a λ/4 wave plate to circularly polarize it, while the other HeNe arm travels through a λ/2 wave plate before it is recombined with the circularly polarized HeNe beam on a 50/50 beamsplitter. The recombined beam is then passed through a polarizing beam cube that allows detection of the interference in both the horizontal and vertical directions on two matched photodiodes. Both HeNe interferograms are acquired at 1 kHz, locked to the pulse repetition rate of the ultrafast laser, using the DAQ card described above. The angle of the λ/2 wave plate is adjusted to ensure that the fringe depth measured by both detectors is equal. Due to the phase shift between the horizontal and vertical components in one arm of the interferometer due to the λ/4 wave plate, the detected S and P components of the interference correspond to the sine and cosine of the accumulated phase between the two arms. This phase can be extracted by taking the inverse tangent of the ratio of two measured interferograms:

$$\phi = \tan^{-1}\left(\frac{I_P}{I_S}\right), \quad (1)$$

where I_P and I_S correspond to the measured S and P components of the interferogram.

An example section of a HeNe interferogram acquired during the measurement of a 2D surface is given in Fig. 2A. For ease of presentation, the constant offset due to the CW component of each interferogram was removed by subtracting the average of each trace. The velocity of the