Polarization shaping in the mid-IR and polarization-based balanced heterodyne detection with application to 2D IR spectroscopy

Chris T. Middleton, David B. Strasfeld, and Martin T. Zanni
Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706-1396, USA

Abstract
We demonstrate amplitude, phase and polarization shaping of femtosecond mid-IR pulses using a germanium acousto-optical modulator by independently shaping the frequency-dependent amplitudes and phases of two orthogonally polarized pulses which are then collinearly overlapped using a wire-grid polarizer. We use a feedback loop to set and stabilize the relative phase of the orthogonal pulses. We have also used a wire-grid polarizer to implement polarization-based balanced heterodyne detection for improved signal-to-noise of 2D IR spectra collected in a pump-probe geometry. Applications include coherent control of molecular vibrations and improvements in multidimensional IR spectroscopy.

1. Introduction
Femtosecond pulse shaping is now finding use as a tool for collecting multidimensional spectra [1-7]. Multidimensional optical spectroscopies are a relatively new set of techniques that correlate coupled electronic or vibrational eigenstates, separate lineshapes into their homogeneous and inhomogeneous components, and measure energy transfer, among other capabilities [1]. Two-dimensional versions are the most common, but no matter the dimensionality, a series of pulses are needed to collect the spectra. Compared with standard techniques, pulse shaping is a more convenient and more flexible method of generating the needed pulse sequences. The relative phases of the pulses are easily set so that experiments can be performed in the rotating frame or phase cycling can be utilized to remove scatter [3, 8]. The center frequencies and shapes of the pulses can be designed to perform either time- or frequency-domain experiments [3]. Because the phase stability of the pulse trains is excellent, data can be averaged for long periods of time. Elimination of mechanically based optical delay lines dramatically reduces acquisition times. In this paper, we demonstrate polarization pulse shaping in the mid-infrared, which we anticipate will further improve the utility of pulse shaping for 2D infrared (IR) spectroscopy and the control of ground-state vibrational motions [9,10].

Polarization pulse shaping was first implemented using two layered liquid-crystal spatial light modulators [11]. This approach is not feasible in the mid-IR because current liquid crystals are only transparent between 400 and 1800 nm. Currently, the only method for pulse shaping directly in the mid-IR, which we developed a few years ago, uses an acousto-optical modulator.
made of germanium (Ge AOM) [12]. However, other polarization shaping approaches, recently
developed in the near-IR and visible regions [13,14], are compatible with our Ge AOM. These
new methods permit control of the phase, amplitude and polarization of the shaped pulses
through a very simple modification of a standard 4f pulse shaping geometry. Two identical
beams are sent through the shaper along different paths such that their frequency-dependent
amplitudes and phases can be programmed independently. The polarization is then rotated by
90° for one of the two beams, which are then recombined so that they propagate collinearly.
These two orthogonally polarized beams are the projections of the desired electric field. In the
visible and near-IR, the beam recombination can be performed using Wollaston prisms, cube
polarizers, or diffractive optics, but such optics for the mid-IR are rare. Instead, we use a wire-
grid polarizer to recombine the orthogonally polarized pulses with high efficiency, much like
a cube polarizer.

Wire-grid polarizers also permit us to implement balanced heterodyne detection when the
signal field is emitted collinear with, and polarized orthogonal to, the local oscillator. Balanced
heterodyne detection is a useful way of improving the signal-to-noise in heterodyne-detected
experiments [15]. It is most commonly implemented by combining a local oscillator with the
signal field from orthogonal spatial directions using a 50/50 beamsplitter so that two sets of
collinearly propagating beams are created (Fig. 1b). The interference term between the local
oscillator and signal fields in the two beams are 180° out-of-phase, while the homodyne terms
are independent of phase. Thus, by subtracting the signals from the two detectors, the
interference terms add while the homodyne terms, which are the largest source of noise, are
subtracted. However, 2D spectroscopies collected in a pump-probe geometry, like when
performed using a pulse shaper, have collinearly propagating signal and local oscillator fields,
and thus cannot be easily combined on a beam splitter. In this paper, we demonstrate that
balanced heterodyne detection can still be implemented in pump-probe geometries using
polarization to create out-of-phase terms. This improvement makes the signal levels and signal-
to-noise of 2D spectra collected in a pump-probe geometry equivalent to a four-wave mixing
beam geometry.

2. Experimental setup

The optical layout of our polarization shaper, shown in Fig. 1a, is based on the method used
by Lindinger and associates for visible pulses [14]. A 50/50 beam splitter is used to split the
mid-IR into two beams which are sent into the shaper at different angles such that the diffracted
beams are centered on different halves of a Ge acousto-optical modulator at the focus of the
4f setup. Thus, the amplitudes and phases of the frequency components in each beam can be
controlled independently. The two shaped beams exit the shaper at different angles, the
polarizations of the beams are rotated to be orthogonal using zero-order λ/2 MgF\textsubscript{2} waveplates,
and the two beams are recombined using a wire-grid polarizer. An optical delay line and a pair
of ZnSe wedges are used for coarse and fine adjustment of the temporal overlap, respectively.
The two pulses are dispersion compensated by the shaper to near transform-limited pulse
durations. Additional MgF\textsubscript{2} waveplates are used as shown in Fig. 1a to increase the throughput
efficiency due to differing polarization dependences of the 50/50 beam splitter, gratings and
AOM as well as to create equal pulse energies in the two beams, although these will not be
necessary in future designs with customized optics. Our current design allows about 100 units
of frequency to be independently controlled in each of the two beams, although this resolution
can be improved with tighter focusing at the AOM.

3. Results and discussion

To demonstrate polarization shaping in the mid-IR, we have created 4 simple pulse shapes,
which are shown in Fig. 2. More complicated pulse shapes, reported in a separate publication,
have been used to control ground-state vibrational motions [10]. The pulses were characterized by linear cross-correlations with a ~50 fs reference pulse which was split from the main mid-IR beam before the shaper and passed through a λ/2 waveplate to set its polarization at 45° relative to the orthogonally polarized shaped pulses. The beams were then sent through a wire-grid polarizer and focused onto a mercury cadmium telluride (MCT) detector. The reference pulse was scanned in time using a ZnSe wedge pair. For each pulse shape, cross-correlations were performed with the polarizer set to 0° and 90° to obtain the temporal profile of the two orthogonal projections of the polarization vector. Using the same reference beam for the two polarization measurements allows the relative phase of the two orthogonally polarized electric fields to be measured. The cross-correlations at these two polarizer angles are shown as projections onto the two polarization planes in Fig. 2. The 3D representations of the pulses shown in Fig. 2 were generated through vector addition of the two projections. The pulse shapes shown in Fig. 2 are generated by using the shaper to control the relative time delay between the two orthogonal components, Δt, and their relative phases, Δφ. Setting Δt = 0 ps and Δφ = 0 creates a 45° linearly polarized pulse; Δt = 0.7 ps and Δφ = 0 creates a double pulse in which one pulse is polarized perpendicular to the other; Δt = 0.1 ps and Δφ = 0 generates a pulse whose linear polarization rotates from 0° to 90° during its duration; and Δt = 0 and Δφ = π/2 creates a right-circularly polarized pulse. Slight variations in the ~200 fs pulse durations are caused by the shaper resolution and the rise/fall times of the radio-frequency amplifier for the AOM, which we have not considered in generating the pulse shapes. Pulse shapes like these would be useful in measuring rotational anisotropy, eliminating diagonal peaks from 2D spectra [16], and for measuring vibrational circular dichroism spectra [17,18]. Since the Ge AOM acoustic wave can be updated every 10 μs, a new shape can be generated with every laser shot up to a 100 kHz repetition rate.

Once the polarization-shaped pulses are generated, they can be used in any number of experiments. One particularly appealing use is in 2D IR spectroscopy. Two-dimensional infrared spectroscopy is at least a 3rd-order technique, meaning that there are a minimum of 4 interactions between the sample with the incident and emitted electric fields. Pulse sequences with various polarization conditions are useful in 2D IR and 2D visible spectroscopies because they can be used to measure the relative orientations of transition dipoles [19], remove unwanted diagonal peaks in order to better resolve cross peaks [16], and reduce background signals [20]. In this paper, we use the notation <a,b,c,d> to represent the polarizations of the 4 electric fields in the laboratory frame, with a, b, and c being the excitation fields and d is the electric field emitted by the sample. The brackets represent the ensemble average over the orientations of all the molecules in the sample. In what follows, we show that pulse sequences utilizing <90°,0°,90°,0°> and <90°,0°,0°,90°> are especially useful for collecting 2D IR spectra when using pulse shaping or a pump-probe beam geometry because these polarization conditions enable balanced heterodyne detection of the signals by using projected polarizations.

The schematic layout for the polarization-based heterodyne detection is shown in Fig. 1c. Balanced heterodyne detection requires that the local oscillator and signal fields be combined in such a way that two sets of out-of-phase signals are generated, e.g.,

\[
\frac{1}{2} |LO \pm PE|^2 = \frac{1}{2} |LO|^2 + \frac{1}{2} |PE|^2 \pm \text{Re}(LO \cdot PE),
\]

where LO is the local oscillator electric field and PE is the signal field (also called a photon echo) emitted due to the 3rd-order polarization of the sample. A free-induction decay is also emitted in the pump-probe phase matching direction used here. As mentioned above, subtracting these two signals doubles the oscillating term LO·PE while removing the |LO|^2 and
$|PE|^2$ terms. These latter terms are a major source of noise, but can be extremely well subtracted with balanced heterodyne detection since their intensity fluctuations are well correlated. For balanced heterodyne detection of the signals in the pump-probe beam geometry, we create the out-of-phase signals using a polarization-based method [21]. First, a polarization scheme, such as $<90^\circ,0^\circ,90^\circ,0^\circ>$, is used in which $PE$ is emitted with a polarization perpendicular to $LO$ and then a wire-grid polarizer is used to project $LO$ and $PE$ onto mutually orthogonal axes (see Fig. 1c). The beam containing $LO$ and $PE$ must be incident on the face opposite the wire-grid or an additional $180^\circ$ phase shift will occur upon reflection, canceling the phase difference caused by the polarization projection.

The two sets of collinearly propagating beams are separately focused into a spectrometer and onto two 64-element MCT arrays for detection in the frequency domain. The signals on the two arrays, respectively, are given by

$$|LO\sin\Theta + PE\cos\Theta|^2 = |LO|^2\sin^2\Theta + |PE|^2\cos^2\Theta + 2\sin\Theta\cos\Theta\text{Re}(LO \cdot PE)$$
$$|LO\cos\Theta - PE\sin\Theta|^2 = |LO|^2\cos^2\Theta + |PE|^2\sin^2\Theta - 2\sin\Theta\cos\Theta\text{Re}(LO \cdot PE),$$

where $\Theta$ is the angle of the wire-grid polarizer with respect to $LO$ or $PE$ (Eq. (2) neglects the Fourier transform preformed by the spectrometer). When $\Theta = 45^\circ$, the oscillatory signals on the two detectors are equal in magnitude but opposite in sign and Eq. (2) reduces to Eq. (1). A $\lambda/4$ waveplate can be used to eliminate the dependence on $\Theta$ [22]. In practice, the reflected and transmitted signals are not exactly equal due to slightly different divergences and intensities of the two beams, so we empirically set $\Theta = 52^\circ$ to balance the static offsets on the detector. Subtraction is currently performed on the computer after digitization, so that balancing the two signals can be refined computationally, but the preferable method is to electronically balance the pre-amplifier signals which improves the sensitivity.

To collect a 2D IR spectrum, we use the polarization shaper to create an orthogonally polarized pulse pair like in Fig. 2b, and step $\Delta t$ from 0 to 3.98 ps in 20 fs steps with $\phi = 0$, recording the signals transmitted through and reflected from the wire-grid polarizer simultaneously. The thin and dashed lines in Fig. 3 show, respectively, the transmitted and reflected signals for the two pixels corresponding to 1978 cm$^{-1}$, which is the absorption maximum for the model compound we report here, W(CO)$_6$ in chloroform. Notice that the fast oscillations are $180^\circ$ out-of-phase, but that the slow oscillations of the baseline are in-phase. The drift in the baseline is caused by laser intensity fluctuations. The difference of the two signals is also shown as a thick line in Fig. 3, where it is apparent that the oscillations become approximately twice as large and the baseline drift is much smaller, demonstrating that the signal-to-noise is improved. Figure 4a-c shows 2D IR spectra at $\omega_1 = 1940$-2000 cm$^{-1}$. Figure 4a-b shows the two 2D IR spectra generated from Fourier transforming the signals from each row of the detector. Each spectrum consists of an out-of-phase doublet created from nonlinear processes between the $\nu = 0$-1 and 1-2 transitions, respectively. The doublet in the two spectra are $180^\circ$ out-of-phase and their difference gives rise to the 2D IR spectrum shown in Fig. 4c. Figure 4d-f show the same spectra, respectively, as in Fig. 4a-c except for $\omega_1 = 0$-150 cm$^{-1}$. In addition to the baseline offsets caused by $|LO|^2$ and $|PE|^2$, each of the individual 2D IR spectra are superimposed on a low-frequency transient absorption background which is intrinsic to the pump-probe beam geometry [1]. This transient absorption background is also automatically subtracted. The increase in signal-to-noise is easily apparent near zero frequency (compare Figs. 4d-e with 4f). Reduction in low-frequency noise is especially advantageous for collecting data in the rotating frame which requires scanning fewer time delays, but also shifts the observed vibrational frequencies towards zero.
One issue that must be addressed with this polarization pulse shaper design is the drift in the relative phase of the two shaped mid-IR beams. Since the beams do not follow identical optical paths, small changes in path length cause a drift in relative phase (the changes in time delay are small compared to the pulse width, so it manifests itself primarily as a change in phase). To monitor the phase drift, we used polarization-sensitive heterodyne detection, as described above, but with a single-channel detector that measured the interference between the two shaped beams. The detector monitored a small amount of the beam intensities from the opposite side of the wire-grid polarizer that recombined the two shaped beams (WGPI in Fig. 1a). Thus, the phase drift can be monitored while simultaneously collecting 2D IR data sets. For demonstration, we monitored the phase drift using three masks initially corresponding to minimum interference ($\Delta \phi = 0$), maximum interference ($\Delta \phi = \pi$) and a single-beam mask where the amplitude for one of the shaped beam is set to zero. The masks were alternated at ~1 Hz and the intensities monitored for several hours (Fig. 5). As observed previously for a four-wave mixing beam geometry [23], the phase drift is slow. Thus, it can be recorded during the course of the measurement and then used to passively correct the phase drift during data processing [23]. The relative phase could also be actively corrected on-the-fly by continuously adjusting the relative path length of the two shaped beams, as done previously [24]. Alternatively, the arbitrary waveform generator itself can correct the phase on-the-fly, which is a method we demonstrate in Fig. 5. Here, the relative phase is measured every 13 min. and the phase is adjusted with the shaper, giving a long-term relative phase stability of $\sim \lambda/10$. Higher sampling rates can be used for better phase stability. Although not readily available at mid-IR wavelengths, birefringent polarizers or birefringent prisms could be used to eliminate the relative phase instability as in common-path designs previously demonstrated in the visible [25,26].

4. Conclusion

We have presented a means by which the complete electric field of mid-IR pulse sequences can be computer controlled using a Ge AOM. Complete control over the electric fields allows for 2D or higher dimensionality IR experiments to be performed without having to modify the optical setup. Since time delays are scanned using the shaper, there are no moving parts involved in collecting spectra. Furthermore, the optical setup is much easier to align than a four-wave mixing beam geometry. Mid-IR polarization shaping has already proven beneficial for the control of molecular vibrations [10] and future applications are numerous. For example, it could be used to selectively enhance desired features of pump-probe [27] or multidimensional spectra [28]. The polarization shaper opens the door to 3rd-order measurements of vibrational optical activity in chiral systems [17] particularly because of its ability to create, and rapidly alternate between, mid-IR pulses with right- or left-circular polarization [18].

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Fig. 1.
(a) Optical layout of mid-IR polarization shaper. (b) Schematic layout of traditional balanced heterodyne detection. (c) Schematic layout of polarization-based balanced heterodyne detection. WGP: wire-grid polarizer, WP: MgF2 zero-order λ/2 wave plate, ZW: ZnSe wedge pair, AOM: Ge acousto-optical modulator, BS: 50/50 ZnSe beamsplitter, S: signal, LO: local oscillator. Polarization vectors indicate relative directions but not relative magnitudes.
Fig. 2. Cross-correlations of demonstrative polarization-shaped pulses with a reference pulse: (a) a 45° pulse, (b) two perpendicular pulses with a delay, (c) a pulse with time-dependent linear polarization rotating from 0° to 90°, (d) a right-circularly polarized pulse. Traces are colored based on instantaneous polarization angle.
Fig. 3.
Polarization-based balanced heterodyne detected 2DIR signals in the time domain. Signals were obtained from the polarization components transmitted through (thin line) and reflected from (dashed line) the wire-grid polarizer in Fig. 1c. The difference signal (thick line) was obtained by subtracting the reflected signal from the transmitted signal.
Fig. 4.
Polarization-based balanced heterodyne detected 2DIR signals in the frequency domain. Spectra were obtained from the polarization components (a,d) transmitted through and (b,e) reflected from the wire-grid polarizer in Fig. 1c. (c,f) The difference spectrum is obtained by subtracting the reflected spectrum from the transmitted spectrum. Panels a-c and d-f show the same respective data sets but at different values of $\omega_1$. 
Fig. 5.
Interference intensity of the shaped pulses (left) without and (right) with active phase correction. The thin and thick lines correspond to interference intensities with and without, respectively, an additional $\pi$ rad phase shift applied to one pulse. The data has been smoothed to better show the long-term trends.