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# Frequency-Domain Two-Dimensional Infrared Spectroscopy using an Acousto-Optic Programmable Dispersive Filter

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## Abstract

We report on multidimensional spectroscopy in the mid-infrared performed using a calomel-based acousto-optic programmable dispersive filter. Although the associated spectral resolution is currently not as good as what has been previously reported using time-domain interferometers or other pulse-shaping technologies, the extreme compactness of the calomel crystal allows a straightforward implementation in a pre-existing pump-probe setup. Furthermore, the frequency-domain approach allows easy measurement of 2D slices of the multidimensional spectrum associated with a given pump frequency. We demonstrate our method with the measurement of the mid-infrared spectrum of carboxy-hemoglobin in three spectro-temporal dimensions.

## 1 Introduction

Two-dimensional infrared (2DIR) spectroscopy has been established in the last two decades as the most advanced form of femtosecond vibrational spectroscopy. Indeed, 2DIR spectroscopy has been shown to be an invaluable tool for investigating vibrational dynamics, as well as couplings between vibrational modes [1]. It shares many conceptual and experimental aspects with the other form of multidimensional spectroscopy, namely two-dimensional electronic spectroscopy (2DES) [2], which is a powerful tool for investigating electronic structure and dynamics using visible or ultra-violet femtosecond pulses. Among the different implementations of multidimensional spectroscopy, the so-called pump-probe geometry is probably the most straightforward [2, 3, 4, 5, 6, 7]. Based on a standard pump-probe setup, this approach yields the multidimensional pump-probe signal  $S(\omega_s, \omega_p, T)$ , resolved as a function of the probe frequency  $\omega_s$ , the pump frequency  $\omega_p$ , and the waiting time  $T$ , also known as the pump-probe delay. Whereas the probe frequency is almost always resolved using a grating spectrometer placed on the transmitted probe beam, two different methods can be distinguished for resolving the pump frequency. In the frequency-domain approach [3], the measured signal is recorded as a function of the center frequency of a tunable narrow-band pump pulse, e.g. using a Fabry-Perot etalon. In the time-domain (or Fourier-transform) approach, the pump-probe signal is recorded as a function of the time delay between two broadband pump pulses, yielding the exciting pump frequency by Fourier-transform spectroscopy [2, 8].

In combination with the pump-probe geometry, another major simplification can be achieved by inserting a programmable pulse shaper in the pump beam, thus allowing to directly filter the incident broadband pulse into a two-pulse sequence (for time-domain multidimensional spectroscopy) or a tunable narrow-band pulse (for frequency-domain multidimensional spectroscopy). Indeed, in the spectral domain extending from the near-IR to the UV, pulse shapers allowing complete control of the spectral amplitude and phase are

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routinely available. The two leading pulse-shaping technologies rely either on a zero-dispersion line (ZDL) including a liquid-crystal [9] or acousto-optic [10] modulator placed in the Fourier plane, or on a more compact acousto-optic programmable dispersive filter (AOPDF) [11]. Applications to 2DES have been successfully demonstrated both with ZDL [12, 13] and AOPDF [7, 14] pulse shapers. In the mid-infrared (MIR) spectral domain, pulse shaping technologies have matured more recently due to an initial lack of suitable modulators. Yet, direct pulse shaping of MIR pulses has been eventually demonstrated with a ZDL using a germanium transverse acousto-optic modulator [15] or deformable mirror [16]. Recently, the availability of suitable calomel ( $\text{Hg}_2\text{Cl}_2$ ) crystals has also made possible the demonstration of a MIR AOPDF pulse shaper in a device of only a few-cm length [17, 18]. However, until now, only the ZDL approach has been applied to 2DIR spectroscopy [6].

In this article, we report on the first application of a calomel AOPDF for 2DIR spectroscopy. By inserting a 22-mm thick calomel crystal and collecting the diffracted beam, we can readily transform a standard pump-probe setup into a 2DIR spectrometer, as previously demonstrated for 2DES [7, 14]. We demonstrate our method with the measurement of 2DIR spectra in carboxy-hemoglobin (HbCO), using the frequency-domain approach.

## 2 Methods

Fig. 1 shows our MIR femtosecond pump-probe setup. As described elsewhere [19], the MIR source consists of a 1-kHz Titanium:Sapphire regenerative amplifier (Libra-HE, Coherent) delivering 4-mJ, 800-nm, 100-fs pulses that are down-converted in a two-stage nonlinear setup in order to deliver horizontally-polarized, 20- $\mu\text{J}$ , 100-fs pulses centered at 5.1  $\mu\text{m}$  (or 1950  $\text{cm}^{-1}$ ). After recombination with a He:Ne alignment laser, a coated ZnSe beam splitter (BS) splits the incoming beam into pump and probe beams, with 16  $\mu\text{J}$  devoted to the pump. With the AOPDF removed and mirror M located in a position suitable for reflecting dotted-line beam (1), the setup shown in Fig. 1 is merely a standard pump-probe setup. Pump and probe pulses are focused on the sample using a  $\text{CaF}_2$  lens L (focal length 40 mm), and the transmitted probe beam is spectrally analyzed using a Chirped-Pulse Up-conversion (CPU) system [20, 21].

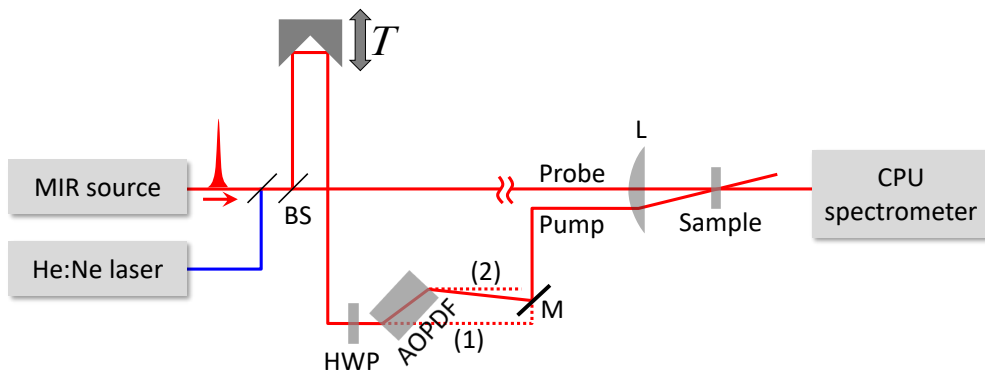


Figure 1: *Experimental setup for 2DIR spectroscopy using an Acousto-Optic Programmable Dispersive Filter (AOPDF). (BS) Beam splitter, (HWP) Half-Wave Plate, (L) lens, (M) Mirror mounted on a motorized rotation stage around the vertical axis and on a translation stage along the direction of the reflected beam. Dotted lines (1) and (2) show alternate paths used during the alignment procedure (see text).*

We first align this standard pump-probe setup and optimize the differential pump-probe signal, measured in HbCO using broadband pump pulses and a 500-Hz mechanical chopper (not shown) inserted on the pump beam. In a second step, we insert the calomel AOPDF (MIR Dazzler, Fastlite) on the pump beam, just after a half-wave plate (HWP) with its neutral axis initially horizontally aligned. Due to the required  $47^\circ$  incidence

angle [17] on the 22-mm long calomel crystal, the beam undergoes a significant lateral displacement. After translation of mirror M in order to collect the beam shown as dotted line (2), and appropriate adjustment of the pump-probe delay, the pump-probe signal is recovered and re-optimized. In a third step, the no-longer needed mechanical chopper is removed and the HWP neutral axis is rotated by  $45^\circ$ , so that the beam incident on the calomel crystal is now vertically polarized, *i.e.* along the crystal ordinary axis. The AOPDF software is parametrized so that an acoustic wave is sent through the transducer to the crystal at a repetition rate of 500 Hz, properly synchronized with the laser amplifier. The acoustic waveform is chosen for diffracting a narrow-band pump pulse centered at  $1951\text{ cm}^{-1}$ , tuned to the  $n = 0$  to  $n = 1$  CO stretch transition in HbCO. After diffraction on the acoustic wave from vertical back to horizontal polarization, the shaped beam acquires an external angle of  $11.0^\circ$  with respect to the incident beam [17] (see solid line in Fig. 1). Mirror M is thus translated accordingly and rotated clockwise by half the diffraction angle, or  $5.5^\circ$ , so that the diffracted beam is sent along the previous direction of the pump beam. The differential pump-probe signal is then monitored by subtracting even (AOPDF OFF) from odd (AOPDF ON) probe spectra, allowing to recover and re-optimize the pump-probe signal by fine adjustment of the pump mirror placed just before the lens (again after proper adjustment of the pump-probe delay). After this straightforward three-step procedure, we are now able to record pump-probe spectra with a pump pulse shape controlled by the AOPDF.

A well-known issue in 2DIR and 2DES is that even a small amount of scattered pump will be strongly enhanced through spectral interference with the probe, thus providing an unwanted contribution to the measured differential pump-probe signal. Furthermore, as the relative phase between pump and probe pulses is not locked, the interference pattern is unstable which makes it more difficult to remove by a mere subtraction. It has been shown previously that phase cycling provides an elegant method to address this issue [6, 7, 22]. This is easily implemented here, by applying with the pulse shaper a  $\pi$  phase shift to every other diffracted pump pulse, thus changing the sign of the interference pattern. The detrimental scattered pump interference then averages out.

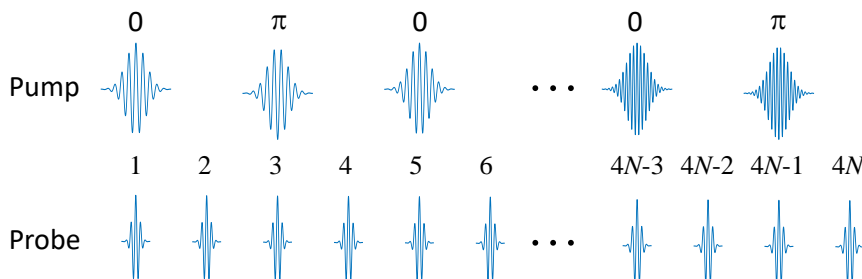


Figure 2: *Schematic view of the  $4N$  pulse sequence used in the 2DIR measurement, where  $N$  is the number of different pump frequencies.*

For frequency-domain 2DIR spectroscopy, we use a convenient feature of the Dazzler known as the “sequence” mode, allowing preloading of a series of waveforms that can be applied on a pulse-by-pulse basis and repeated continuously. As shown in Fig. 2, a scan of  $N$  different pump pulse frequencies can be achieved by preloading a series of  $2N$  pump waveforms, with the pump center frequency changing every other pump pulse and a  $\pi$  phase shift between odd and even pump pulses, as discussed above. This pump-pulse sequence is applied to the AOPDF at a repetition rate of 500 Hz, so that even probe pulses can be used for recording reference spectra, when no pump is applied to the sample. The total pulse sequence thus corresponds to  $4N$  probe pulses, and is repeated every  $4N$  msec for appropriate data averaging of the 2DIR spectrum.

### 3 Results and discussion

We now demonstrate the approach outlined in the previous section with the measurement of a series of 2DIR spectra in HbCO. The preparation of the sample (heme concentration 10 mM, cell thickness 100  $\mu\text{m}$ ) has been described elsewhere [23]. For each value of the waiting time  $T$ , the 2DIR spectrum is averaged by scanning repeatedly the pump center frequency  $\omega_p$  over  $N = 21$  different values ranging between 1920.1 and 1981  $\text{cm}^{-1}$  (with 20 uniform 8-nm steps in wavelength space). The resulting 84-msec acquisition sequence is repeated for 725 frequency scans (corresponding to an acquisition time of about 1 mn), before proceeding to the next time delay. The entire  $T$ -scan procedure is then repeated three times for data averaging, resulting in the series of 2DIR spectra shown in Fig. 3. A continuous series of 2DIR spectra is also available as Visualization 1 (raw data) and Visualization 2 (interpolated data), with  $T$  varying from -3 to +48 ps, by 1 ps steps for  $T \leq 10$  ps and 2 ps steps for  $T \geq 10$  ps.

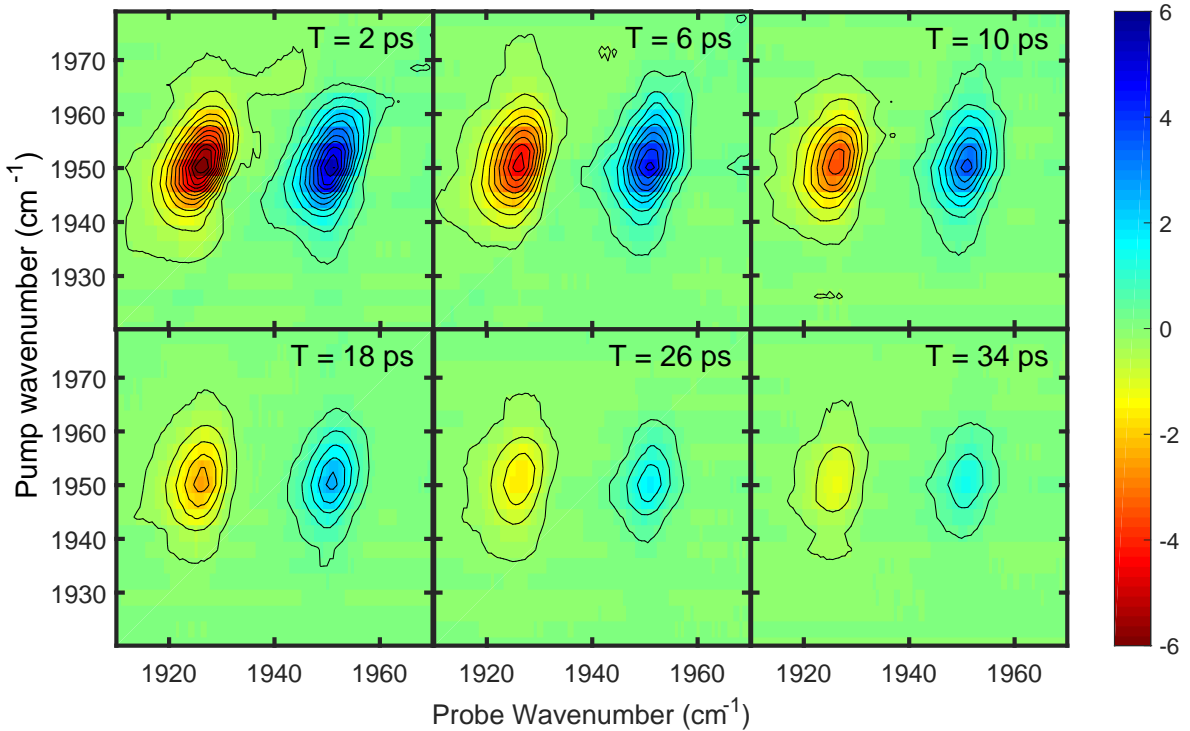


Figure 3: Set of 2DIR spectra measured for the specified values of the waiting time  $T$ . The color scale is common to all plots and shows the relative change in differential transmission (in percents). (Visualization 1) Full 3D set with waiting time  $T$  varying between -3 and +48 ps. (Visualization 2) Full 3D set with linear interpolation on pump wavenumber and waiting time axes.

The spectra shown in Fig. 3 are typical of 2DIR spectroscopy [1], with a positive peak at 1951  $\text{cm}^{-1}$  due to ground state bleaching and stimulated emission ( $n = 0$  to  $n = 1$  CO stretch transition) and a negative peak at 1926  $\text{cm}^{-1}$  due to excited state absorption ( $n = 1$  to  $n = 2$  transition, downshifted due to the 25- $\text{cm}^{-1}$  anharmonicity). The 2DIR signal then decays with increasing waiting time due to vibrational relaxation back to the ground state. At early waiting times, the axis of the elliptic 2DIR response is observed to be only slightly tilted with respect to the vertical, in contrast with high-resolution HbCO 2DIR spectra previously reported [23] where the center line was observed to be almost exactly along the diagonal. This behavior can be attributed to the large spectral-resolution anisotropy in the present measurement. Indeed, the probe spectral resolution is better than 1  $\text{cm}^{-1}$  whereas the pump spectral resolution is limited by the pump spectral width, which we measured to be about 8  $\text{cm}^{-1}$  FWHM. This value is not quite sufficient to resolve the anti-diagonal

width of the 2DIR spectrum, known to be about  $5 \text{ cm}^{-1}$  at early waiting times [23]. However, a change in center line slope can still be observed in Fig. 3 when the waiting time increases, evidencing the expected spectral diffusion at longer time scales.

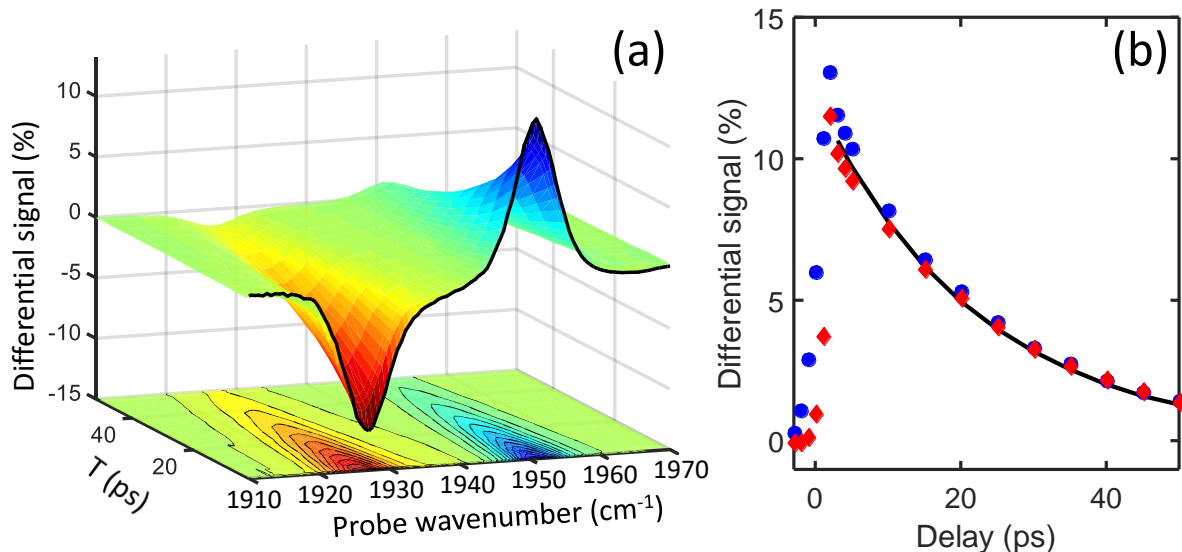


Figure 4: (a) Dependence of the pump-probe signal as a function of time delay, for a pump frequency tuned to  $1951 \text{ cm}^{-1}$ . (b) Time dependence of induced absorption (blue disks) and induced bleaching (red diamonds) peak amplitude. The solid line shows an exponential fit, yielding a vibrational time constant  $T_1 \approx 22.3 \text{ ps}$ .

Although time-domain multidimensional spectroscopy is known to provide in principle a better spectral resolution than frequency-domain multidimensional spectroscopy [4, 6], there are at least two reasons favoring the frequency-domain approach when pulse shaping is achieved using an AOPDF. First, diffraction efficiency is maximized in case of a single-frequency acoustic wave, thanks to the coherent contribution of the entire crystal when a single frequency is diffracted. Second, when an AOPDF is programmed for diffracting a two-pulse sequence, the maximum available delay will be limited by the duration of the acoustic wave associated with each pulse. This results in a compromise between diffraction efficiency (related with the acoustic pulse duration) and spectral resolution (related with the maximum delay), which is not encountered in the frequency-domain approach used here. An additional advantage of the frequency-domain approach is that a 2D slice of  $S(\omega_s, \omega_p, T)$  for a specified pump frequency  $\omega_p$  can be readily obtained by programming the corresponding frequency on the AOPDF and recording the pump-probe spectrum as a function of the waiting time. This is illustrated in Fig. 4(a), showing the time evolution of the pump-probe spectrum with an excellent signal to noise ratio. Fig. 4(b) shows the time dependence of the height of the two peaks, which is observed to be in perfect agreement with an exponential fit with a time constant  $T_1 \approx 22.3 \text{ ps}$ , in good agreement with values previously reported for HbCO [24, 19]. This slicing feature should prove particularly useful for measuring excited state lifetimes using transient 2DIR spectroscopy in a vibrational ladder [19].

## 4 Conclusion

To summarize, we have demonstrated the use of a calomel AOPDF for frequency-domain 2DIR spectroscopy. Thanks to the remarkable compactness of the pulse shaper, a straightforward three-step alignment procedure allows to transform a standard MIR pump-probe experiment into a 2DIR spectrometer. Although the current  $8\text{-cm}^{-1}$  frequency resolution along the pump frequency axis remains modest when compared to time-domain 2DIR spectrometers, the slicing ability of the frequency-domain approach makes it particularly attractive for

transient 2DIR spectroscopy. In particular, the evolution with respect to the waiting time of specific peaks of the 2DIR spectrum can be easily recorded with an excellent signal to noise ratio.

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