Improving signal to noise ratios for transient absorption spectroscopy using an alternative referencing method

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Introduction

Transient absorption (TA) spectroscopy functions by detecting small changes in the transmission of a laser-pumped sample through the measurement of the intensity of a transmitted probe laser beam illuminating a detector. The precision required for detecting these changes can be as low as one part in a million. When sensitivity is limited by laser intensity noise, a separate reference measurement of the probe laser intensity (and noise) can be used to improve signal to noise ratios (SNR) of spectra in TA spectroscopy [1] and variants, including time-resolved multiple-probe spectroscopy [2] or 2D-IR spectroscopy [3]. Referencing reduces the amount of signal averaging required to achieve a given SNR, allowing the detection of weak signals, without an additional time cost. Conventional approaches to referencing can give a 3-10x improvement in SNR. The reference measurement is a measure of the intensity fluctuations of the laser only, which are subtracted from the probe laser data. There are many factors which mean that the probe and reference laser measurements may not be perfectly correlated. In addition to intensity variation, timing, pointing and mode fluctuations also occur in any laser beam and will only yield perfectly correlated reference and probe measurements with identical beam-paths, focusing and detectors. Perfect optical correlation is only possible in practice with great effort.

In this article, we describe an improved referencing scheme implemented at ULTRA, achieved simply by updating software, but without the need for upgraded equipment. The referencing scheme is based on a recently a published algorithm by Ge and co-workers [4-5] that determines the correlation of the laser noise in the probe and reference measurements. We observe that across our facility experiments this algorithm gives an improvement in SNR of 2-5x, compared to conventional referencing.

Referencing

We can think of each spectrum recorded as comprised of the signal to be extracted, as well as the noise to be removed. The dominant source of this noise is laser noise, which scales linearly with spectral intensity and appears as 'baseline wobbling' on the spectrum. While the component of this noise arising from shot to shot intensity fluctuations of the probe can be eliminated using shot-to-shot detection and averaging, using referencing it is theoretically possible to completely remove shot-to-shot noise without the need for long averages, reducing the noise in the data to the detector noise-floor.

Referencing requires a second detector in addition to that recording the transient absorption spectrum S_{sig} of the pumped and probed sample. The probe beam is split before passing through the sample, and the additional beam does not pass through the sample, giving a measure of the reference spectrum S_{ref}, calculated as an 'absorption spectrum'. The two detectors are carefully matched. As the reference beam does not contain any transient absorption signal, and the two detectors are assumed identical, it is also assumed that $S_{ref} = n_{ref} = n_{sig}$, where n_{ref} and n_{sig} are the noise in absorption units on the reference and sample detectors, respectively. The calculation to remove the noise from the signal data is therefore $\langle S_{sig}\rangle - \langle S_{ref}\rangle$, where $\langle\ \rangle$ denotes the mean over a series of laser shots [6]. This is the referencing scheme that has previously been used within Ultra. Using this method alongside signal averaging does give an improvement in SNR. However, matching the signal and reference detectors can be difficult and time consuming, and there is always some small mismatch remaining. Even if the two detectors are perfectly matched, this method gives a theoretical minimum residual noise after referencing (determined by the overall noise floor) $\sqrt{2}\sigma\, n_{sig}^{floor}$, where σ is the standard deviation and n_{sig}^{floor} the noise floor of the signal detector [5].

Correlation Matrix

The alternative method used here eliminates the need for matching the two detectors by instead measuring the correlation between them, without assuming them to be identical [4,5]. There is no need to alter an existing TA setup. The only modifications that are made are to the referencing portion of the data acquisition software. Instead of assuming $n_{sig} \sim n_{ref}$, it is assumed that $n_{sig} \sim \boldsymbol{B}.n_{ref}$, where $\boldsymbol{B}$ is a correlation matrix between the two detectors, with dimensions determined by the numbers of pixels in each detector. Referenced data can then be calculated using $\langle S_{sig}\rangle = \boldsymbol{B}.\langle S_{ref}\rangle$. By minimising the theoretical residual noise after referencing with this method, $\boldsymbol{B}$ is given by [6]

$$\boldsymbol{B} = < n_{sig}.n_{ref}^{T} >.< n_{ref}.n_{ref}^{T} >^{-1}$$

where $n_{\{ref\}}^{T}$ is the transpose of the noise on the reference detector. When acquiring data, the only additional step required by the user is to collect some calibration data prior to taking the data to be referenced, as n_{sig} can only be recorded with the pump beam switched off. Once the calibration data has been collected, $\boldsymbol{B}$ can be calibrated, leaving the actual referencing process identical to the original referencing calculation, other than a single matrix multiplication. The theoretical minimum residual noise using this method is a factor of $\sqrt{2}$ lower than the original method, even before the mismatch between the detectors is taken into account [5]. This is because the overall noise floor is reduced compared to conventional referencing.

The ability to reach this minimum, though, does depend on various factors, including the length of acquisition used to calibrate ***B***, the length of acquisition of the data itself, the distribution of the laser shots used for calibration in relation to those used for data collection, and which variant of TA spectroscopy is being used.

Application

Two examples of the application of ***B*** correlation referencing are discussed here, (i) where strong spectral fluctuations make referencing difficult and (ii) where a very poor match between the signal and referencing spectrometer is used.

In visible probe TA, a typical probe is a white-light-continuum, generated by focusing a femtosecond pulse onto a transparent material such as CaF_2 or sapphire. The non-linear nature of the WLC generation, mean that it can easily become spectrally unstable. With strong spectral instabilities, even near-identical spectrometers struggle with perfect reference subtraction. The example in Fig.1a shows pump on – off noise levels with conventional referencing, but without application of the correlation matrix ***B***. While under this condition, the noise level reaches $\Delta OD < 10^{-4}$ in 2 seconds acquisition (at 10 kHz repetition rate), it is clear that some of the probe laser's spectral fluctuations remain. By generating a correlation matrix, (Fig.1c), the reference spectrum can be modified to better match the probe, and achieve a significant SNR improvement of ~ x5 compared to ordinary referencing, as shown in Fig 1b.

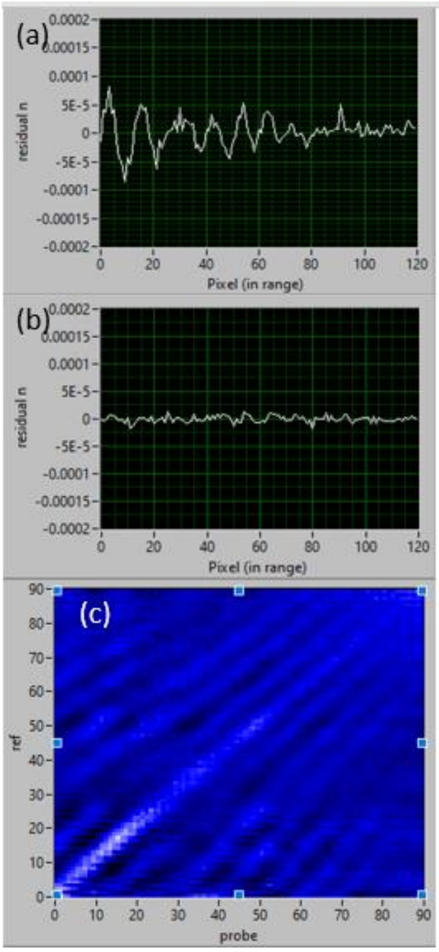

Figure 1. Pump on – off difference spectrum dispersed across 120 pixels of a Si photodiode array from a spectrally unstable WLC probe, referenced. (a) conventional referencing. *(b) spectrum from same data as (a), but with* **B** correlation *referencing applied; (c) the correlation matrix.*

In TA experiments where broadband mid-IR light is used as a probe, costly MCT array detector systems are the most sensitive tool for measuring shot-to-shot mid-IR spectra. A high number of probe pixels will provide maximal spectral resolution for measuring time-resolved spectra. However, spectral resolution is not typically required in the reference spectrum, and one can significantly reduce costs, by using a smaller detector array with a low number of pixels on the reference detector. ULTRA time-resolved IR systems use 2x 128-element probe arrays, with a single 32-element reference array. With quite different detector and spectrometer configurations, the generated correlation matrix matches and corrects the referencing of the 32-element reference spectrum to look like a well matched 2x 128-element reference.

Conclusions

By using the alternative referencing scheme of Nianhui Ge and co-workers [4,5] which calculates the correlation between the probe and reference arrays, an improvement in signal-to-noise ratio of 2-5x compared to conventional referencing has been observed. The referencing scheme has been implemented by updating the existing data acquisition software, without making any changes to the detectors or spectrometers themselves. The need for matching the probe and reference detectors is eliminated, making it possible to use a very different reference detector and spectrometer configurations to those used for the probe. Using this referencing scheme over the conventional method allows for higher SNR values to be achieved, without the need for greatly increased data acquisition time. This can be utilized in TA spectroscopy and its variants, including time-resolved multiple-probe spectroscopy and 2D-IR spectroscopy

References

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