

Two-Dimensional Ultrafast Fourier Transform Spectroscopy in the Deep Ultraviolet

Chien-hung Tseng, Spiridoula Matsika¹ and Thomas C. Weinacht

*Department of Physics and Astronomy, Stony Brook University,
Stony Brook, NY, 11794-3800*

¹*Department of Chemistry, Temple University,
Philadelphia, PA, 19122*

tweinacht@sunysb.edu

<http://ultrafast.physics.sunysb.edu/>

Abstract: We demonstrate two-dimensional ultrafast fourier transform spectroscopy in the deep ultraviolet (~ 260 nm) using an acousto-optic modulator based pulse shaper. The use of a pulse shaper in the ultraviolet allows for rapid scanning, high phase (time) stability (~ 0.017 rad) and phase cycling. We present measurements on the DNA nucleobase Adenine.

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References and links

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1. Introduction

Two-dimensional (2D) ultrafast infrared (IR) and electronic spectroscopies have become powerful techniques for studying biological and physical systems. 2D spectroscopies provide information on molecular structure and energy transfer, e.g. protein-folding, electronic couplings in photosynthesis and semiconductor carrier dynamics [1, 2, 3]. In 2D spectroscopies, one measures the third order polarization generated by a pair of excitation pulses. It is crucial to maintain the phase (time) stability between these excitation pulses. Experiments have maintained the phase stability between excitation pulses via diffractive optics [4, 5], active interferometric stabilization [6] and most recently by generating phase-locked pulses in the collinear or boxcar geometry with a pulse-shaper [7, 8, 9, 10]. Performing 2D spectroscopy with a pulse shaper in a pump-probe geometry allows doing the measurements with a very simple experimental setup [9]. In this approach, one measures the absorptive spectra and is able to work in a rotating frame and implement phase-cycling [7, 11] for relaxed sampling requirements in the excitation pulse sequence, selectivity in the couplings measured, and improved signal to noise.

While there have been many advances made in 2D spectroscopy over the past few years, 2D spectroscopies have been limited to the IR and visible regime although many molecules of interest absorb in the UV and deep UV. The phase stability required for 2D UV spectroscopy is over an order of magnitude greater than what is required for 2D IR spectroscopy because of the difference in wavelength. For 1/100 of a cycle phase stability between pulses, one requires a timing jitter between excitation pulses of less than 10 attoseconds, which is quite demanding using a conventional interferometer-based setup, but not using a pulse shaper. Here, we demonstrate pulse shaper assisted 2D UV (~ 260 nm) spectroscopy at the S_0 - S_1 transition band for many interesting molecules.

We present 2D UV measurements on the DNA base adenine. The DNA and RNA bases absorb strongly in the UV (200 \sim 300 nm), yet are highly stable to photochemical decay [12, 13, 14]. Generally, excited states of molecules are more reactive than the ground states, and when the DNA bases are driven to singlet excited states by the UV, they become prone to damage. Non-adiabatic processes can convert the electronic energy to vibrational energy, but they have to compete with other harmful photochemical mechanisms that take place on

ultrafast timescales. It has been suggested that there exist low-lying S_0 - S_1 conical intersections which provide effective channels for deactivation of the electronic excitation [13, 15] and bring the molecule from the excited state back to the ground state rapidly. Prior ultrafast studies on the DNA bases include UV transient absorption [12, 16], resonance-enhanced multiphoton ionization (REMPI) [18], femtosecond fluorescence upconversion [17], pump-probe mass spectrometry [19], and time-resolved photoelectron spectroscopy [20]. We expect that 2D UV spectroscopy will serve as an important complement to these established techniques.

2. Experimental apparatus

Figure 1 shows our experimental setup. A standard amplified titanium sapphire laser system produces pulses at 780 nm with 1 mJ of energy at a repetition rate of 1 kHz. The pulses from the amplifier have a duration of 30 fs, as measured using second harmonic generation frequency resolved optical gating. We generate pulses in the UV via second harmonic generation and sum frequency generation. We first use a BBO crystal to generate the second-harmonic (390 nm) of the fundamental. Group velocity mismatch between the second-harmonic and the fundamental inside the BBO crystal results in the second-harmonic trailing behind the fundamental pulse as they leave the crystal. A calcite crystal is used after the doubling crystal to compensate for the difference in group delay. Finally, the third-harmonic (260 nm) is generated via sum-frequency-generation in another appropriately cut BBO crystal. The UV pulse energy is about $13\mu J$, and the bandwidth is 13 THz. The uv pulses duration (50 fs) is measured with self-diffraction frequency resolved optical gating [21].

The UV and the IR are separated with a dichroic mirror and sent into a Mach-Zender interferometer. The UV arm goes through a computer controlled acousto-optic modulator (AOM) based ultrafast pulse shaper [22]. The pulse-shaper generates the phase-locked pump-pump pulse pair for the 2D spectroscopy. Unlike an interferometer, the pulse shaper can independently control the delay (τ) and phase between pulses and naturally produces phase stable pulse pairs. The phase mask of the pulse shaper for a pump-pump pulse-pair can be expressed as

$$M(\omega) = \frac{1}{2}[exp(i\omega\tau)exp(i\phi_1) + exp(i\phi_2)] \quad (1)$$

where $\omega\tau + \phi_1$ and ϕ_2 correspond to the phase of pulses at $t = \tau$ and $t = 0$ respectively. The 2D signal is the sum of two third-order nonlinear responses and its phase depends on the relative phase between the two excitation pulses $\Delta\phi_{12} = \pm(\omega\tau + \phi_1 - \phi_2)$. The pulse-shaper can be programmed such that ω corresponds to the central frequency of the laser (non-rotating frame), or it can be shifted to any lower frequency (partial rotating frame) [11], which therefore lowers the required sampling rate (in order to meet the Nyquist criterion) and can transfer the signal to less noisy region in the frequency domain.

Furthermore, cycling the phase between pump pulses can reduce the background noise induced by pump-probe transient absorption and scattering [7, 11]. The phase of the 2D signal depends on the phase difference between the pump pulses, ϕ_{12} , while the transient absorption signal doesn't. Signal with $\phi_{12} = 0$ ($S(\phi_{12} = 0)$) and that with $\phi_{12} = \pi$ ($S(\phi_{12} = \pi)$) have 2D signals with opposite signs but identical transient absorption. As a result, subtracting $S(\phi_{12} = 0)$ from $S(\phi_{12} = \pi)$ removes contribution from transient absorption. The scattering from each pump pulse depends on the phase of a single pulse (ϕ_1 or ϕ_2). Adding up $S(\phi_1 = 0, \phi_2 = 0)$ and $S(\phi_1 = \pi, \phi_2 = \pi)$ preserves the 2D component and eliminates the scattering noise. Generally, we collect four spectra ($S(\phi_1 = 0, \phi_2 = 0)$, $S(\phi_1 = 0, \phi_2 = \pi)$, $S(\phi_1 = \pi, \phi_2 = \pi)$, $S(\phi_1 = \pi, \phi_2 = 0)$) sequentially at each delay τ , and obtain our final spectrum by combining the four measurements:

$$S_{total} = S(\phi_1 = 0, \phi_2 = 0) - S(\phi_1 = 0, \phi_2 = \pi) + S(\phi_1 = \pi, \phi_2 = \pi) - S(\phi_1 = \pi, \phi_2 = 0) \quad (2)$$

We used spectral interferometry to measure the relative phase between the two pump pulses, measuring the spectrum of the pump pulse pair and recovering the relative phase between the pulses every 20s for 30 minutes. The delay between the two pulses was kept constant as 400 fs. The RMS deviation for the retrieved relative phase is 0.017 rad, which corresponds to a timing jitter of about 2 attoseconds. This measurement is limited by the signal to noise of our spectrometer, and places an upper limit on the phase (time) stability between the pump-pump pulses.

After the pulse shaper, the UV pulse energy is about $1.3\mu J$ for an unshaped pulse. The IR arm of the interferometer contains a prism pair for dispersion compensation, a delay stage for adjusting the pump-probe delay (T), and a second set of tripling nonlinear crystals to generate the UV probe pulse. The probe pulse energy is about 100 times weaker than the pump. The probe can be centered at 260 nm or shifted slightly (± 4 nm) by adjusting the angles of the BBO crystals used for generating the UV. The uv pump-pump and probe pulses are combined non-collinearly and focused into a 2 mm pathlength fused silica cuvette by a 1 m focal length curved enhanced Aluminum mirror. In our geometry, the pulses overlap over a longitudinal region of several mm, and are thus well overlapped throughout the sample. The IR and the second harmonic residuals in the probe beam are filtered out by reflection from two dielectric mirrors (YL4, CVI) after the curved mirror. The Adenine solution is prepared by dissolving adenine (Sigma-Aldrich) in distilled water. The solution has 70% transmission at 260 nm. After the sample, the pump-pump beam is blocked, and the probe spectrum is measured with a spectrometer (USB2000, Ocean Optics) as a function of the pump-pump delay τ for each pump-probe delay T . We then Fourier transform the spectrum data along τ at each probe wavelength. The 2D data is then constructed from the probe spectrum (ν_{probe}) and Fourier transformed pump-pump delay (ν_{pump}).

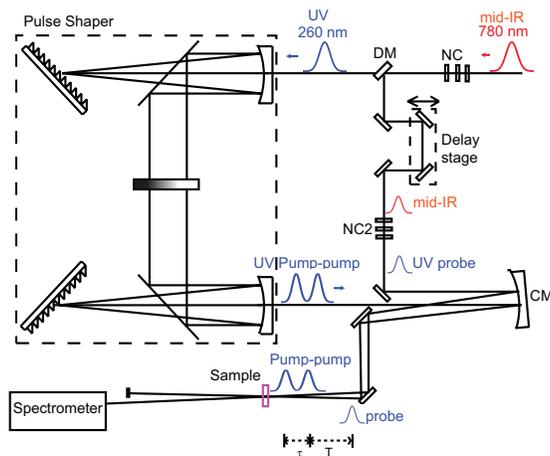


Fig. 1. Experimental Setup. The IR is converted to UV (~ 260 nm) by nonlinear crystals (NC1). The UV-pump and IR are separated by the dichroic mirror (DM). The UV-pump goes into the pulse shaper and becomes a phase-locked pump-pump pulse pair. The IR passes through the second set of nonlinear crystals (NC2) to generate the UV-probe. The UV pump-pump and probe pulses are focused into the sample by the curved mirror (CM). The probe spectrum is detected with a spectrometer as a function of the pump-pump delay τ for each pump-probe delay T .

3. Results

We demonstrate UV 2D spectroscopy on adenine in solution. The absorption of adenine starts at around 285 nm and extends to the vacuum violet [23], making UV 2D spectroscopy an ideal tool for studying its excited state dynamics. Figure 2 shows the real value of the 2D spectrum for different pump-probe delays as well as the real value of the spectrum for the pump-pump excitation pulse pair. Figure 2 panels (a), (b) and (c) show the real (absorptive) components of adenine 2D spectrum for pump-probe delays of $T = 50, 200$ and 400 fs respectively. To make sure that any diagonal features are not due to pump-pump scattering into the spectrometer, we performed the 2D scans with increased spectrometer integration time and blocked the probe to detect only the scattered signal. We measured the scatter from the pump pulses to be less than 1 part in 10^4 of the probe signal. Figure 2 panel (d) shows the real value of the Fourier transform of the pump-pump spectrum for different delays to illustrate our intrinsic instrumental resolution. The 2D spectra reveal dynamics on S_1 taking place on sub 100 fs timescales, consistent with measurements from time resolved photoelectron studies [20]. A detailed interpretation of these measurements is the subject of a forthcoming publication.

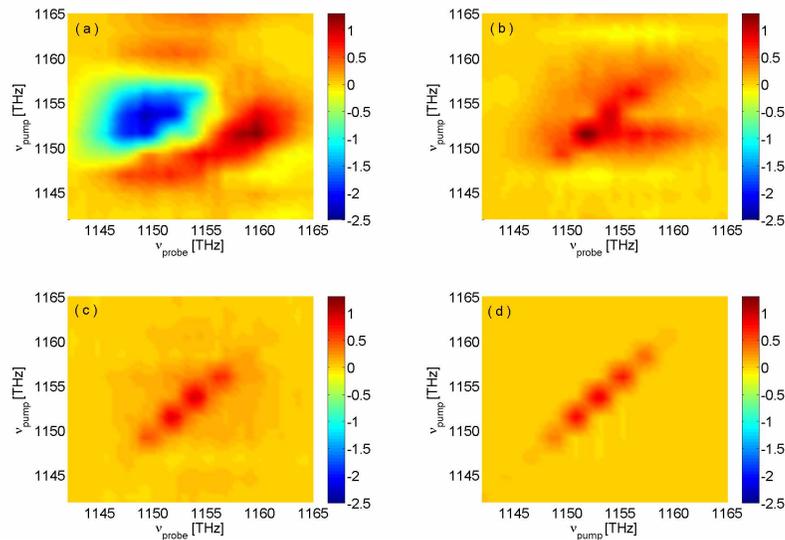


Fig. 2. Real component of the 2D spectrum of Adenine in water at (a) $T = 50$ fs, (b) $T = 200$ fs, (c) $T = 400$ fs, and (d) the real component of the Fourier transform of the pump-pump spectrum.

Figure 3 compares the 2D spectrum with and without phase cycling. Panel (a) shows data taken without phase cycling and panel (b) shows data taken with four phase cycling. Both data sets were taken with the same number of laser shots and pulse energies, so they can be compared directly. Phase cycling improves the signal to noise ratio in the data by a factor of 2 and can be used in future experiments to select particular nonlinear polarizations in the sample.

The resolution of our spectrometer is about 2 THz, and we used a pump-pump delay range of 1000 fs, yielding a resolution of about 2 THz along the pump-pump delay axis. Collecting the data with a higher resolution spectrometer and larger pump-pump delay range would allow us to easily improve the resolution by a factor of 2 or 3. It is not clear that further improvements in resolution would yield more details given the timescale of the dynamics and the damping of

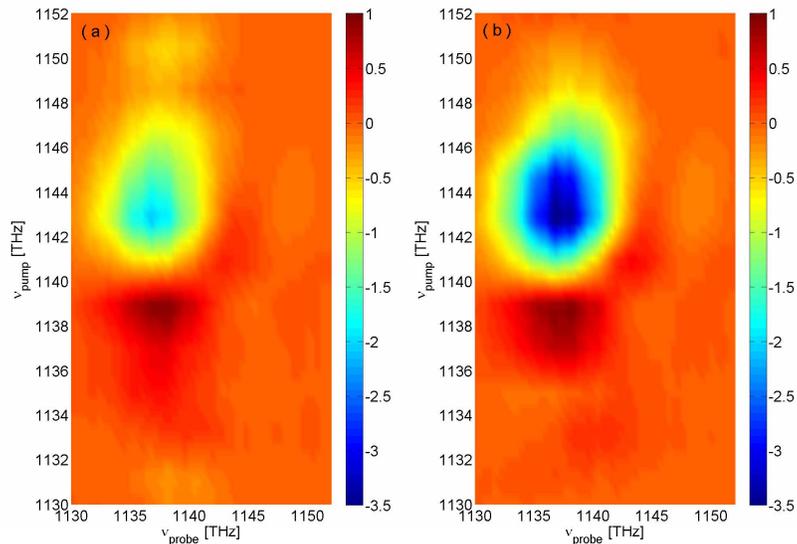


Fig. 3. Real component of the 2D spectrum of Adenine in water (a) without phase cycling, (b) with four-phase-cycling at $T \approx 50 fs$.

the molecular coherences in solution.

The pump pulse fluences were an order of magnitude below the saturation fluence, ensuring that our measurements were performed in the weak field regime. This was confirmed by pump probe measurements for different pump pulse energies. Thus, even though the probe pulse can ionize the molecule in addition to driving stimulated emission (since the ionization potential is less than twice the UV photon energy), the changes recorded in the 2D spectra as a function of pump-probe delay encode dynamics in the excited neutral state rather than the molecular cation.

4. Conclusion

In conclusion, we have demonstrated 2D Fourier transform spectroscopy in the deep ultraviolet using an AOM based ultrafast laser pulse shaper. The technique is ideally suited for studying the excited state dynamics of the many molecules whose S0-S1 transition lies in the deep ultraviolet. By using a UV pulse shaper to perform the measurements, we naturally have excellent phase (time) stability and can perform rapid phase cycling, enhancing the data quality and isolating desired nonlinear polarizations in the 2D spectrum. This research was performed with support from the Department of Energy under award numbers DE-PS02-08ER08-01 and DE-FG02-08ER15984.