

Broadband Electronic Two-Dimensional Spectroscopy in the Deep UV

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Abstract: We developed an all-reflective fully-noncollinear setup for two-dimensional electronic spectroscopy in the broadband UV (2DUV) with great phase stability ($\Lambda/150$) and applied it to the UV-chromophores dissolved in ethanol using 8-fs UV-pulses, generated in the 245-300 nm range.

We are able to resolve 2D-spectra in the $\sim 6000 \text{ cm}^{-1}$ spectral window.

OCIS codes: (320.7100) Ultrafast measurements; (320.7150) Ultrafast spectroscopy

1. Introduction

Ultraviolet electronic two-dimensional spectroscopy of dissolved chromophores and DNA requires broadband transform-limited UV-pulses in the 240-300 nm range. It is dictated by the spectral width of their absorption spectra which normally have a FWHM of $\sim 30 \text{ nm}$ or more ($\geq 3000 \text{ cm}^{-1}$). Such UV-pulses can be generated from the broadband VIS-spectra using achromatic frequency doubling (ASHG) combined with a pulse shaper for reducing the phase distortions [1]. However, managing and manipulating these ultrashort pulses in the UV-domain, especially in the 240-300 nm spectral range, requires the use of explicitly reflective optics since any refractive optical elements will heavily disturb their phase profiles and will thus significantly perturb measured 2D-spectra. Using reflective diffractive optics (DO) [2] allows to overcome these difficulties and creates the possibility for the design of a four-beam interferometer with high phase stability necessary for acquiring correct 2D-spectra in a fully-noncollinear geometry ("background-free" heterodyne measurement). In order to avoid parasite phase distortions in the UV-pulses, we developed a fully reflective photon-echo-based 2DUV setup capable of measuring 2D-spectra in the UV spectral range of 230-350 nm (spectral window $\sim 15000 \text{ cm}^{-1}$).

2. Experimental setup

Figure 1 (left) shows a layout of developed all-reflective 2DUV setup based on the reflective DO (crossed grating, custom designed by Holoeye) which diffracts the incoming beam into 4 first-orders with an efficiency of 60%.

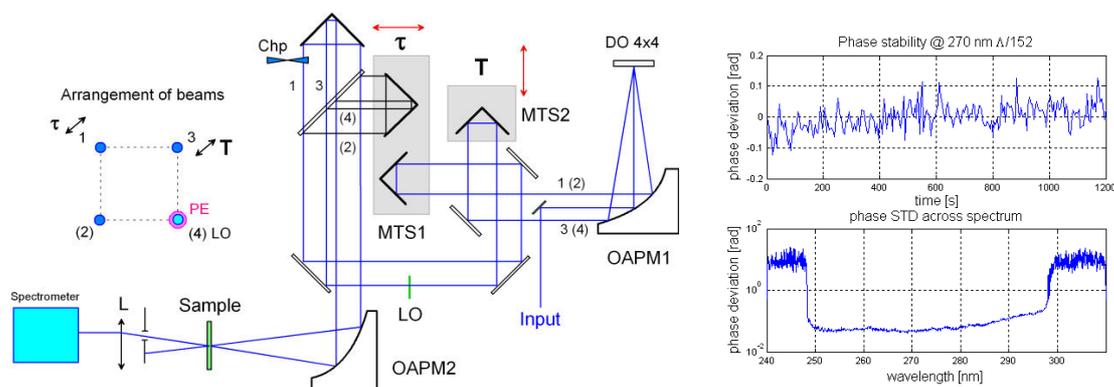


Fig. 1. Schematic layout of 2DUV setup (right) and phase stability, monitored within 20 min (left).

Generically it is similar to the 2D-setup developed earlier [3]; the main difference is the use of a DO and roof mirrors instead of conventional beam splitters and retroreflectors (to minimize the number of reflections and thus transfer more energy to the sample). The construction is similar to the design published in [4]; however, uncoupling of translation stages MTS1&2 (XMS-50, Newport) is achieved by an additional pass of beam #2 through MTS1 but in the opposite direction, allowing an independent scan of "waiting" delay T and "dephasing" delay τ which leads to an increase of phase stability and overall robustness of this four-beam interferometer. Figure 1 (right) demonstrates the phase deviations monitored within 20 min (for treatment details, see [3]) and the achieved phase stability of $\Lambda/150$ is even better than for the VIS 2D-setup published in [3]. Note that the acquisition of a single 2D-spectrum

with a good SNR takes typically 5 min. For heterodyne detection of the generated photon echo signal, a 200- μm neutral density filter with OD = 2 was placed into local oscillator beam (4).

The 8-fs UV-pulses (measured *in situ*) have been generated using ASHG (the design is similar to the one published in [1]) of broadband VIS-pulses, generated by a two-cascade home-built non-collinear optical parametric amplifier (NOPA) pumped by a Coherent Elite USP laser system. The NOPA delivers light pulses with a spectral width of 490-600 nm and energy of 8 μJ , while the energy of UV-pulses was 600-700 nJ at the output of ASHG and ~ 5 -7 nJ per beam at the sample position. In order to minimize light scattering and pulse broadening, we developed and used a wire-guided jet for the circulation of samples, dissolved in ethanol. The thickness of the working area was maintained at ~ 250 μm (can be varied by changing the speed of the jet); the OD of the samples used was 0.3-0.35 in maximum absorbance.

3. Results and discussion

We investigated several UV-chromophores dissolved in ethanol. As an example, Fig. 2 a-c show representative 2D-spectra of *para*-Terphenyl (PTP) at waiting times of $T = 100, 300$ and 1000 fs, respectively, measured in a 34000 - 41000 cm^{-1} spectral range. At shorter T the contribution to the photon-echo signal from ethanol increases significantly and prevents correct measurement of 2D-spectra (at $T = 0$ it is ~ 200 times larger than the PTP-signal).

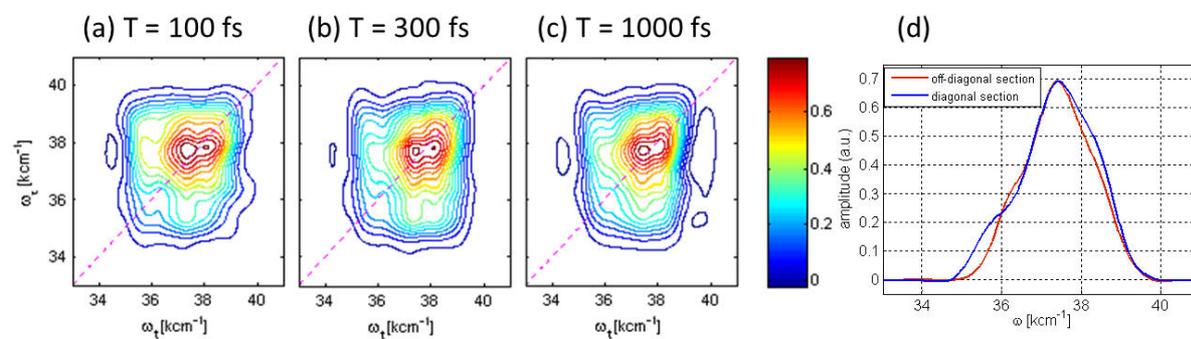


Fig. 2. Absorptive parts of 2D-spectra at different waiting times T (a-c) and cross-sections at $T = 100$ fs (d).

At all waiting times the 2D-spectra exhibit homogeneous broadening of PTP in ethanol (see comparison of on- and off-diagonal cross-sections of 2D-spectrum at $T = 100$ fs, Fig. 2 d); however, there are some dynamics in these spectra - a structure, viewed at $T = 100$ fs, disappears by increasing T . We can speculate that this fine structure reflects underlying vibrational transitions in the PTP-molecule not resolved in the absorption spectrum. The FWHM of cross-sections corresponds to a 6 fs dephasing time, thus we can conclude that the observed homogeneous broadening of PTP is caused mainly by very strong coupling between electronic transitions and the solvent.

It should be noted that in the present study, due to very short UV-pulses, the achieved spectral window (~ 6000 cm^{-1}) is more than one order of magnitude larger than was reported previously for this UV spectral range [4-6].

4. References

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