Implementation of Broadband near-UV Pump Pulses for Ultrafast 2D Electronic-Vibrational Spectroscopy

Jason W. Sandwisch[1], James D. Gaynor[1,2], Munira Khalil[1]
[1] *Department of Chemistry, University of Washington, Box 351700, Seattle, Washington, 98195, USA*
[2]*Current Affiliation: College of Chemistry, University of California, Berkeley, California, 94720, USA*
Email: mkhalil@uw.edu

Abstract: We present the generation of efficient, tunable sub-20 fs broadband near UV pulses. The tunable pulses are used in two-dimensional electronic-vibrational spectroscopy and reveal additional vibronic states in an excited state intramolecular proton transfer process.

INTRODUCTION. Two-dimensional electronic-vibrational spectroscopy (2D EV) is an emerging third-order nonlinear, multidimensional Fourier transform (FT) spectroscopy technique utilizing a sequence of optical and infrared femtosecond (fs) electromagnetic fields (Fig. 1a) resonant with electronic and vibrational transitions in the system of interest. The 2D EV spectrum provides a map of vibronically coupled electronic and vibrational degrees of freedom in complex systems. [1-3]. Recent examples of 2D EV spectroscopy highlight its ability to provide microscopic insight into the role of vibronically mediated ultrafast photochemical processes [4,5].The success of 2D EV experiments hinges on the availability of broadband (BB) pump pulses that can excite multiple electronic transitions in the sample of interest (Fig. 1b). The generation of temporally compressed, broadband pump pulses with μJ levels of pulse energy is challenging in the near UV (nUV) region (370-440 nm), which is home to charge transfer absorptions in light harvesting and π-conjugated molecular complexes. Here, we report the generation and use of stable 20 μJ, sub-20 fs BBnUV pulses, which to our knowledge, have the highest compressed pulse conversion efficiency of reported nUV pulse generation schemes [6-8]. We use the BBnUV pulses as pump pulses in a 2D EV experiment to study the role of vibronic coupling during ultrafast intramolecular excited state proton transfer (ESIPT) in 10-hydroxbenzo-[h]-quinolone (HBQ), an intramolecular hydrogen-bonded molecule with a π-conjugated backbone. The tunability of the BBnUV pulse is crucial to show that two vibronic states in HBQ are resonantly excited during the 2D EV experiment. The advancements in pulse generation lay the foundation for further studies on: Light harvesting, ESIPT, π-conjugated, and nanomaterial systems.

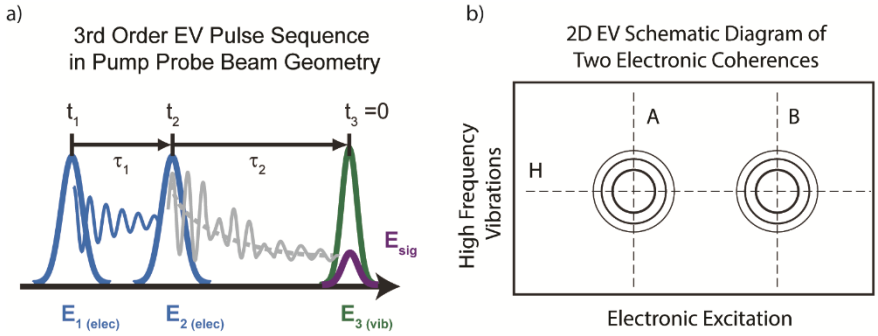

Fig. 1. a) The 2D EV heterodyne pulse sequence consisting of BBnUV pump pulses (E_1 and E_2) and a mid-IR probe pulse (E_3). The pump pulses are separated by the pump delay (τ_1), with the typical pump-probe delay (τ_2) separating E_2 and E_3. The signal is spectrally dispersed using a spectrometer. b) A cartoon 2D EV spectrum obtained by Fourier transforming along the time delay (τ_1) and spectrally dispersing the probe pulse (ω_3). The 2D EV spectrum directly maps the correlations between the electronic transitions (A, B) which lie within the bandwidth of the BBnUV pulse with the high frequency vibrational modes (H) resonant with the mid-IR probe.

EXPERIMENTAL METHODS. The 2D EV experiment utilizes an acousto-optic programmable dispersive filter (Dazzler™) to generate a phase stable pump pulse pair. The pulse shaper has a conversion efficiency of ~12% in the nUV region and places a tight constraint on the pulse energy requirement for the BBnUV pulses used in the experiment. The experimental layout for BBnUV generation is shown in Fig. 2a and relies on self-phase modulation (SPM) in optically transparent media. Briefly, a ~ 233 μJ portion of the 800 nm output of a Ti:Sapphire regenerative amplifier (38 fs, 1 kHz) is focused over 1 meter focal distance using a concave mirror into a series of 5 fused silica plates (25 x 25 x 0.1 mm) set at Brewster's angle. We estimate a fluence of 27 TW/cm^2 at the focus of our 800 nm pulse, which is sufficient to achieve SPM in thin fused silica plates and results in the generation of a broadband 800

nm pulse (BB800). Before frequency doubling the BB800 pulse, the chirp induced by the SPM process is corrected from two reflections of chirped mirrors (Newport, 10Q20UF.42) to optimize frequency doubling in a 100 µm thick Type I BBO. A prism compressor independently controls the chirp of the BBnUV pulse and is optimized using feedback from transient grating cross correlation frequency resolved optical gating (TG XFROG) measurements [9]. The resultant BBnUV pulses are compressed to as short as ~18 fs with pulse energy of up to 20 µJ/pulse with ~1% RMS intensity fluctuations over 12-16 hours of operation (Fig. 2b). This corresponds to a compressed pulse conversion energy efficiency of 8.8%, obtained by comparing the compressed energy of the BBnUV pulses with the input 800 nm pulse energy. This efficiency is significantly higher than other nUV generation schemes [6-8]. We note that due to phase mismatch bandwidth conditions during frequency doubling, using a 50 µm thick BBO result in BBnUV pulses with bandwidths to support 6.3 fs Fourier limited pulses (Fig. 2c). The BBnUV pulses were incorporated as pump pulses into our 2D EV spectrometer, details described elsewhere [10]. The pump pulses generated for 2D EV experiments of HBQ were compressed down to 22 fs with pulse energies of 800 nJ/pulse to avoid photodissociation of the system (Fig 3a.).

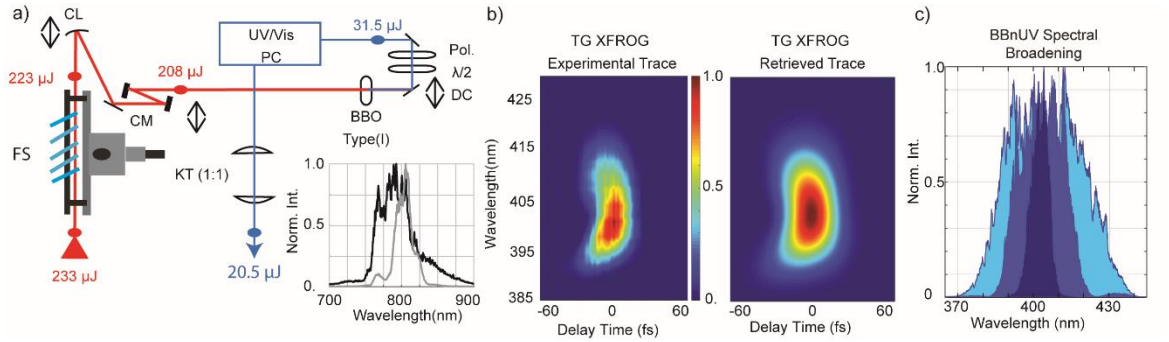

Fig 2. a) BBnUV pulse generation set up with measured pulse energies at various locations along the beam path. Inset: Normalized intensity spectrum of broadened 800 nm pulse (black) with FWHM 55.4 nm and incident fundamental pulse (gray) with FWHM 21.4 nm. Black arrows denote a translation stage. FS: Fused Silica. CL: Concave Lens. CM: Chirped Mirrors. DC: Dichroic Mirror. UV/vis PC: two prism, prism compressor. KT: recollimation Keplerian Telescope. b) TG XFROG measurements of BBnUV pulse characterization *Left panel:* Experimentally collected TG XFROG trace. *Right Panel*: Retrieved TG XFROG trace minimum FROG error of 0.00950 using a 256 grid size, with a temporal FWHM of 18 fs and spectral FWHM of 18.5 nm. c) Normalized nUV pulse spectra comparison. *Dark Blue*, nUV pulse generated without spectral broadening in a 100 µm BBO, FWHM 8.4 nm centered at 400 nm. *Blue*, BBnUV pulse generated in a 100 µm BBO, FWHM 18.5 nm centered at 402 nm. *Light Blue,* BBnUV pulse generated in a 50 µm BBO, FWHM 36.0 nm centered at 405 nm.

RESULTS AND DISCUSSION. The advantage of spectral tunability of the BBnUV pulses is shown by 2D EV experiments of HBQ. Here two different spectrally tuned BBnUV pulses near the lowest energy transition of HBQ were used as pump pulses for 2D EV, denoted red and blue shifted (Fig. 3a). We note that after pulse shaping, pulse energies of 1.1 µJ were available before attenuation. The 2D EV experiments were conducted with a mid-IR probe centered ~1450 cm^{-1} to investigate the 1447 cm^{-1} excited state vibrational mode, a ring bending motion that shortens the proton donor-acceptor distance. In HBQ, ESIPT occurs rapidly following photoexcitation [11]. The excited electronic state resembles a proton transferred state and is vibronically coupled to the 1447 cm^{-1} mode. The tunable pump pulses allowed for spectral overlap of two vibronic states coupling to this mode to be resolved for the first time.

Comparison of the 2D EV excitation axis (ω_1) slices in Fig. 3b highlight the key result. When a slightly broader, red shifted pump pulse is used, two vibronic states are clearly resolved, at 25522 cm^{-1} and 25971 cm^{-1}. By comparison, the blue shifted pump spectrum only resolves the latter higher frequency vibronic state. The peak splitting of 449 cm^{-1} directly reports on the separation of the vibronic states. Comparison of additional probe frequencies (ω_3) in the 2D EV correlation map of the red shifted pump (Fig. 3c) reveal different vibronic coupled modes with strikingly different peak positions along ω_1. The different ω_1 peak position informs reveals the excitation frequency dependent vibronic coupling for each high frequency mode. We have reported the use of efficiently generated, tunable BBnUV pump pulses for 2D EV spectroscopy, which has enabled the discovery of multiple vibronic states participating in the ultrafast ESIPT in HBQ. We expect that 2D EV spectroscopy with BBnUV pulses will find a wide use in the study of ultrafast vibronic processes in molecular and material systems.

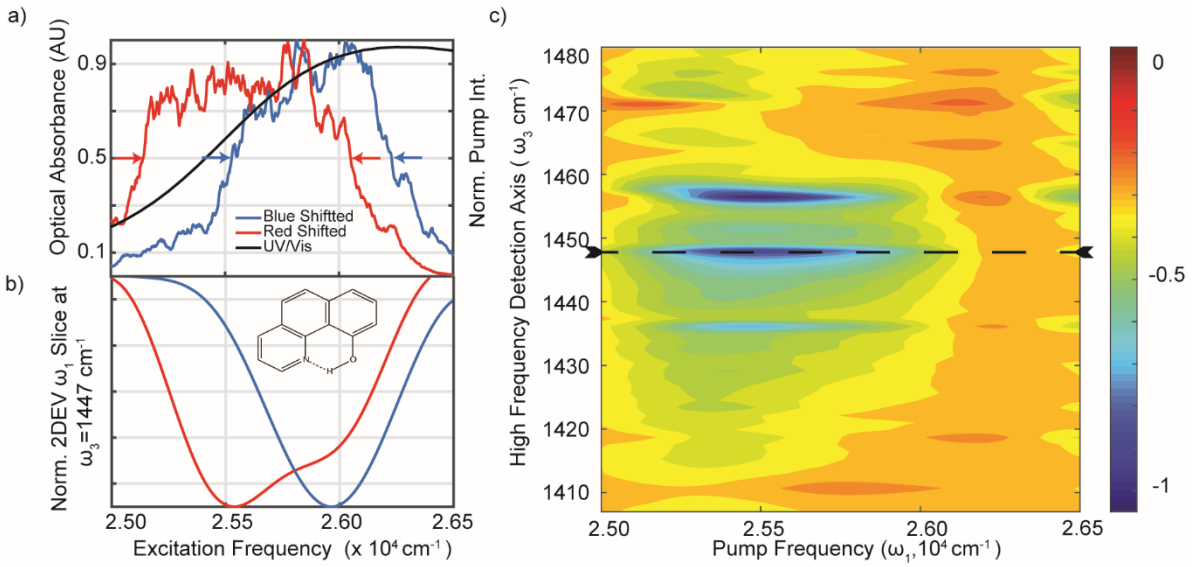

Fig 3. a) Ground state electronic absorption spectrum of HBQ and corresponding normalized pump pulses used in the 2DEV experiment. The absorption spectrum corresponds to a sample concentration of HBQ of 50 mM dissolved in tetrachloroethane solution with a 50 μm pathlength (solid black). The red shifted pump spectrum (solid red) is centered at 25,594 cm^{-1} with a FWHM of 910 cm^{-1} while the blue shifted pump spectrum is centered at 25880 cm^{-1} with a FWHM of 698 cm^{-1}.b) 2D EV ω_1 slices at an ESA feature at 1447 cm^{-1} collected at a probe delay time of 200 fs. Each slice is normalized to itself between 0 and -1. The ω_1 slice obtained with a red shifted pump (solid red) depicts a double-well structure indicating two features contribute to the 2DEV spectrum centered at 25522 cm^{-1} and 25971 cm^{-1}, while the that obtained with a blue shifted pump (solid blue) displays a single feature centered at 25971 cm^{-1}. c) Normalized 2D EV correlation map obtained with red shifted pump pulses. Black dashed line indicates ω_1 slice used in b). Contour map is constructed using 20 equally spaced contour levels between 0 and 1.

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