

Near-Infrared Molecular Fieldoscopy of Water

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ABSTRACT

We introduce the concept of broadband near-infrared molecular fieldoscopy. In this scheme, molecules are excited by femtosecond pulses in near-infrared spectral range and the complex electric field of their free induction decay is directly measured by means of electro-optic sampling. Few-cycle pulses centered at $2\ \mu\text{m}$ and $1\ \mu\text{m}$ are generated from a 5 kHz, Yb:YAG regenerative amplifier and employed for femtosecond excitation and electro-optic sampling, respectively. We chose water in an acetic acid solvent to demonstrate the first proof of principle measurement with the novel technique. The complex electric field of the combination bond of water molecules at 1930 nm at different molecular concentrations is detected and presented. We show the detection sensitivity of our time-domain technique is comparable to conventional spectral-domain techniques. However, by employing a laser frontend with higher repetition rates, the detection sensitivity can be drastically enhanced. To the best of our knowledge, this is the first detection of the complex electric field of the molecular response in near-infrared spectral range. The new method holds promise for high-resolution overtone spectroscopy and microscopy with unparalleled sensitivity and specificity over the entire molecular fingerprint region.

Keywords: time-domain spectroscopy, femtosecond fieldoscopy, near-infrared spectroscopy, Yb:YAG lasers, femtosecond spectroscopy, water, overtone excitation, background-free detection, femtosecond laser sources.

1. INTRODUCTION

Linear spectroscopy in near-infrared (NIR) spectral range provides information on the molecular composition, structure, and conformation, affording tremendous potential for high-resolution, in-depth, label-free biological spectro-microscopy.¹ In NIR spectroscopy, similar information to infrared spectroscopy is obtained by exciting the first overtone of infrared-active vibrational modes. The intensity and vibrational period of these harmonics depend on the quantity and types of the present molecules in the sample. Quantitative analysis is possible when the changes in the transmitted spectrum are proportional to the concentration of chemical components of the sample under scrutiny. Therefore, NIR spectroscopy has been a popular technique for identification, quantitative and qualitative analysis, and structure-correlation of molecular compositions. In particular, it is routinely used for the detection of the overtone and combination bands of the C-H, O-H, and N-H compositions.² Additionally, as the electric field in NIR spectral region supports a smaller diffraction limit than infrared, molecular information with higher spatial resolution can be obtained. Moreover, the lower cross-section of the overtone excitation allows for deeper penetration of the injected field to the sample, allowing for in-depth spectral imaging.³

Broadband measurements in this spectral region have been carried out mainly in the frequency domain.⁴ This approach suffers from two limitations: I) the detection of small absorption is limited to the intensity noise of the source, and II) the low detection dynamic range. To mitigate above-mentioned constraints, we introduce the concept of molecular fieldoscopy. In molecular fieldoscopy, an ultrashort, phase-coherent pulse is used for molecular excitation and afterwards the transmitted complex electric field that contains the molecular response is directly measured. Here, the electric field is detected in a background-free manner, eliminating the effect of

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the intensity noise of the source. Furthermore, measuring the complex electric field allows for extracting the full spectral phase information of the molecular response, adding a new dimension to the gained spectroscopic data.

It is well known that the interaction of broadband ultrashort pulses with an ensemble of molecules at their resonance frequencies, results in a coherent scattering. The delayed response of the medium, known as free-induction decay (FID), can be explained by the Kramers-Kronig relation. During the interaction, photons at the resonance frequencies are slowed down compared to the other photons and appear at the trailing edge of the excitation pulse, due to the increase of the group refractive index of the medium at the vicinity of the resonance frequencies. The delayed response lasts for hundreds of picoseconds for molecules in the gas phase and down to several picoseconds in liquid phase. The FID carries information about the molecular composition and concentration. Therefore, by temporal detection of the coherent response, valuable spectroscopic information can be gained. Additionally, by using ultrashort pulses, the excitation pulse is confined to a time window of tens of femtosecond, which is significantly shorter than FID of the molecular sample under scrutiny. Here, the response emerging from the sample is separated temporally from the ultrashort excitation pulse, enabling for a background-free detection. As FID after the excitation pulse decreases exponentially, its earlier temporal detection results in a higher detection's signal-to-noise ratio and therefore, sensitivity.

Terahertz time-domain spectroscopy based on electro-optic sampling (EOS) has been a powerful method for the direct measurement of the electric field in mid-infrared and terahertz spectral region.⁵ However, its extension to NIR has been shown just recently, due to difficulties in the generation of short, phase-stable excitation pulses that are temporally synchronized with short sampling probe pulses.⁶

In what follows we report, to the best of our knowledge, the first measurement of the complex electric field of the water's molecular response by using EOS in NIR spectral range.

2. EXPERIMENTAL SETUP

Water plays a prominent role in biological interactions and life, with its first overtone of the symmetric stretch vibration appearing at 1450 nm (6900 cm^{-1}) and a strong $\nu_2 + \nu_3$ combination band near 1930 nm (5180 cm^{-1}). We aimed for the field detection of the water's molecular response at its combination band for various molecular concentration. We chose acetic acid as the background solvent due to its sparse spectral response at this range.

2.1 Near-infrared electro-optic sampling

A home-built, diode-pumped Yb:YAG thin-disk regenerative amplifier operating at 5 kHz repetition rates was used as the frontend.⁷ 1.8 mJ of the output energy of the laser was used to generate a carrier-to-envelope phase-stable, multi-octave, broadband spectrum spanning from 500 nm to 2500 nm.⁸ The broadband spectrum was divided into two portions: i) spectral region covering from 700 nm to 1400 nm, and ii) NIR region with spectral coverage from 1600 nm to 2500 nm. The two portions of the spectrum were amplified to the total energy of 25 μJ in two parallel single-stage optical parametric amplifiers. After amplification each channel was compressed to its Fourier transform limit, resulting in 5 fs pulses centered at 1 μm and 18 fs pulses centered at 2 μm .⁹ The 18 fs, NIR pulses were used for excitation of combination bond of water molecules, while the 5 fs pulses at 1 μm were used as a probe in the EOS setup.

The experimental setup of the EOS is depicted in Fig. 1. First, the NIR beam was focused by a 4 inch focal length off-axis parabolic mirror into the sample. Afterwards, the transmitted beam was collimated by another 4 inch focal length off-axis parabolic mirror. The sample was placed slightly after the focus to avoid filamentation of the NIR pulses. The beam size on the sample was 200 μm full width at half maximum (FWHM). The probe pulses were collinearly combined with the transmitted light from the sample by using an ultra-broadband wire grid polarizer (Thorlabs, WP25L-UB). Subsequently, both beams were focused by a 2 inch focal length off-axis parabolic mirror into a 50 μm -thick BBO (Type II) crystal (CASTECH) at the phase matching angle of $\theta = 25^\circ$. The probe and NIR beams were orthogonally polarized along the ordinary (o) and extraordinary (e) axes of the nonlinear crystal, respectively. By temporal and spatial overlap of the two pulses in the crystal, sum-frequency signal centered at 670 nm was generated. The sum-frequency signal was polarized along the extraordinary (e) axis of the nonlinear crystal and spectrally overlaps with the high-frequency components of the ordinarily polarized probe pulses.

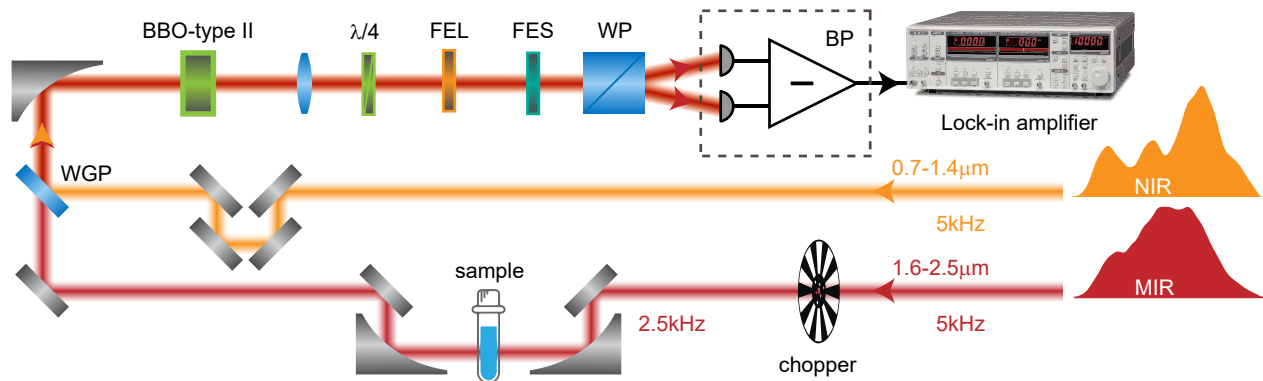


Figure 1. EOS setup consists of a 50 μm -thick BBO (Type II) crystal and an ellipsometer. The NIR beam is chopped at 2.5 KHz and transmits through a 500 μm -thick sample. The sampling beam after the delay line is collinearly combined with the transmitted NIR beam. Thereafter, they are focused in the EOS crystal for sum-frequency generation. The generated sum-frequency signal spectrally overlaps and temporally interferes with the high-frequency components of the probe beam. Appropriate spectral filtering is used to enhance the EOS signal. The polarization rotation of the probe beam as a function of temporal delay is detected by an ellipsometer and read out by lock-in amplifier. WGP: wire grid polarizer, $\lambda/4$: quarter-wave plate, FEL: longpass filter, FES: shortpass filter, WP: Wollaston prism, BP: balanced photodetector.

In order to enhance the EOS signal at the detectors, spectral region between 650 nm and 750 nm was filtered out by using a 650 nm long-pass (Thorlabs, FEL0650) and a 750 nm short-pass (Edmund Optics, 64-324) filters.¹⁰ The generated nonlinear signal induces polarization rotation in the probe pulses as a function of the relative timing of the probe and NIR pulses. The induced electro-optic signal was detected with an ellipsometer consisting of a quarter-wave plate (Thorlabs, AQWP05M-600), Wollaston prism (Thorlabs, WP10), and a home-built balanced detector. In the absence of the NIR beam, the ellipsometer is aligned to equally split and balance the power of the probe pulses at the pair of photodiodes. Therefore, the difference between the photocurrents of the two detectors is equal to zero. In the presence of the NIR pulses, the difference is imbalanced and varies relative to the temporal delay of the probe pulses. The electronic data from the balanced detector is recorded by using a lock-in amplifier (Stanford Research Systems, SR830-DSP) while the NIR pulses were modulated at 2.5 kHz (half of the laser's repetition rate) with a mechanical chopper (Thorlabs, MC2000B-EC).

In parallel for a precise temporal delay scan, the mechanical delay stage (Physik Instrumente, V-528.1AA) was tracked with a Mach-Zehnder-type interferometric delay tracking setup (SmarAct GmbH, PicoScale). The setup employs the beam of a 1.55 μm continuous-wave distributed-feedback laser diode, propagating along the NIR and probe beam-paths.¹¹

A series of measurements were performed to estimate the detection dynamic range of the EOS setup in the absence of the liquid sample. First, the energy of the NIR pulses was attenuated by using a series of neutral density filters with different optical densities (ODs) and afterwards their electric field were measured by EOS. Figure 2 a) illustrates the sampled waveforms for different attenuations. The black curve shows the electric field of the unattenuated NIR pulses. The red curve shows the detectable NIR pulses by EOS with the average power of 650 nanowatts (power attenuation by filters at the OD of 3.1). The corresponding spectra of EOS traces for five different attenuations (OD of 0, 0.8, 1.5, 2.2, and 3.1) are shown in Fig. 2 b). The spectra were obtained by Fourier transformation of the measured electric field. As can be seen, at the highest attenuation the bandwidth of the retrieved spectrum is limited to spectral components with the highest spectral intensity.

2.2 Sample preparation

Acetic acid (Sigma-Aldrich, ReagentPlus, 99%, A6283) and deionized water were used to create solution samples at six different concentrations between 0 Molar to 55.6 Molar (0% - 100%). Afterwards, different mixtures were injected to a sample holder (Harrick Scientific, DLC-M25) consisting of two sapphire windows with a thickness of 2.3 mm. The sample's thickness for all the measurements was 500 μm .

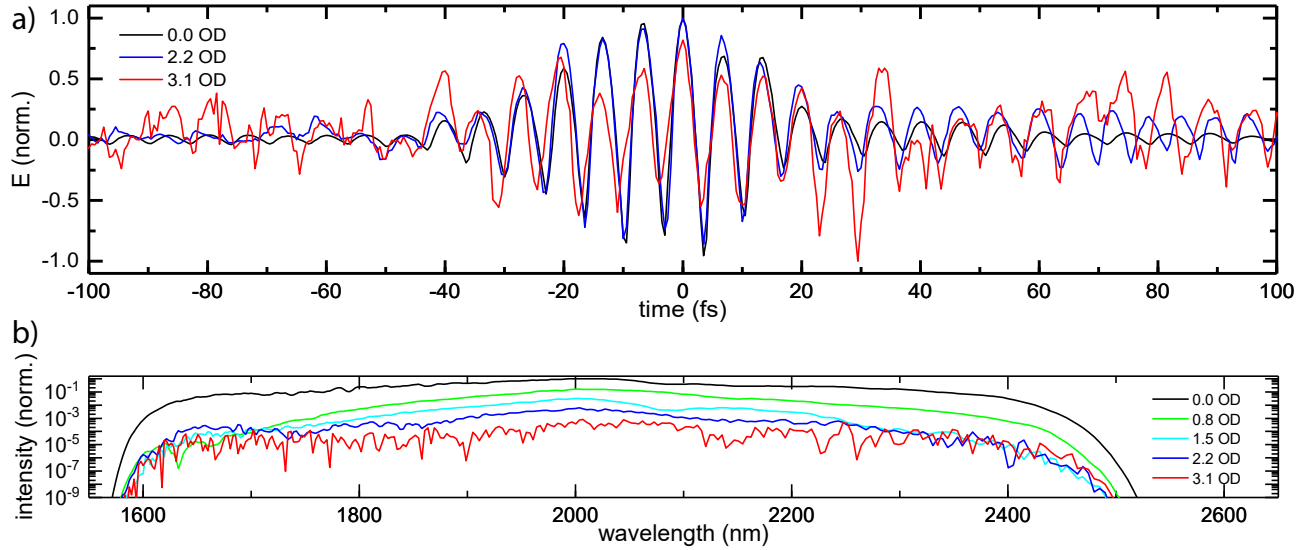


Figure 2. a) Measured electric field of the transmitted pulses in the absence of any sample for three different attenuations (0, 2.2, and 3.1 OD). b) The retrieved NIR spectrum in the absence of any sample for five different attenuations (0, 0.8, 1.5, 2.2, and 3.1 OD). The obtained spectra were normalized then calibrated to the transmitted power.

3. RESULTS AND DISCUSSION

To detect the FID of water molecules, the mixture of acetic acid and water with different concentrations was placed in the sample holder and the transmitted electric field was measured by EOS. The delay stage was scanned over $450\ \mu\text{m}$ with the speed of $1.7\ \mu\text{m}/\text{s}$, corresponding to a single shot detection at each delay position. Background measurements were taken with an empty sample holder and pure acetic acid serving as blank (see Fig. 3 a)). As can be seen in the inset, the amplitude of the excitation pulses goes to zero at temporal delays above 200 fs. By adding the sample, the molecular FID is formed and can be detected free of background at temporal delays beyond 200 fs. Figure 3 b) shows the measured transmitted electric field for the mixture of water and acetic acid at two high concentrations. At high water concentrations the transmitted main pulse is chirped. The NIR response of water molecules is clearly distinguished from acetic acid at 50%, and 100%. To evaluate the sensitivity of the system, measurements of lower water's concentrations (10%, 5%, and 3%) were carried out. As is shown in Fig. 3 c), the molecular response is detectable by naked eye for water concentration as low as 3%.

A similar study¹² was reported in the frequency domain on water molecules in methanol solvent by using a Guided Wave NIR-O Process, fiber-coupled, NIR Spectrometry with the core diameter of $500\ \mu\text{m}$. In this experiment, the water molecules in methanol solvent were placed in a 10 mm-thick sample holder. The combination bond of water molecules could be detected down to 0.1% water concentration. Calibrating our measurements with a $500\ \mu\text{m}$ sample thickness and a $200\ \mu\text{m}$ laser beam size (shown in Fig. 3 c)), to 10 mm of sample thickness and $500\ \mu\text{m}$ of beam diameter, results in 0.075% equivalent detectable water concentration by EOS.

4. CONCLUSION AND OUTLOOK

We presented a novel approach, which we dubbed molecular fieldoscopy, for detection of the complex electric field of molecular response in NIR spectral range. Here, exciting molecules with ultrashort pulses allows for background-free detection of the molecular response. By employing broadband excitation pulses in combination with EOS, the entire molecular vibrations in the fingerprint region can be simultaneously excited and detected.

In this regards, we showed the potential of Yb:YAG thin-disk lasers for generating the required multi-octave spectrum and demonstrated the first proof of principle field-detection of water molecule's vibration at $1.9\ \mu\text{m}$ at different molecular concentrations. Our current detection sensitivity is comparable to the conventional spectroscopy techniques and limited to the stability of the interferometer and the repetition rate of the laser. However,

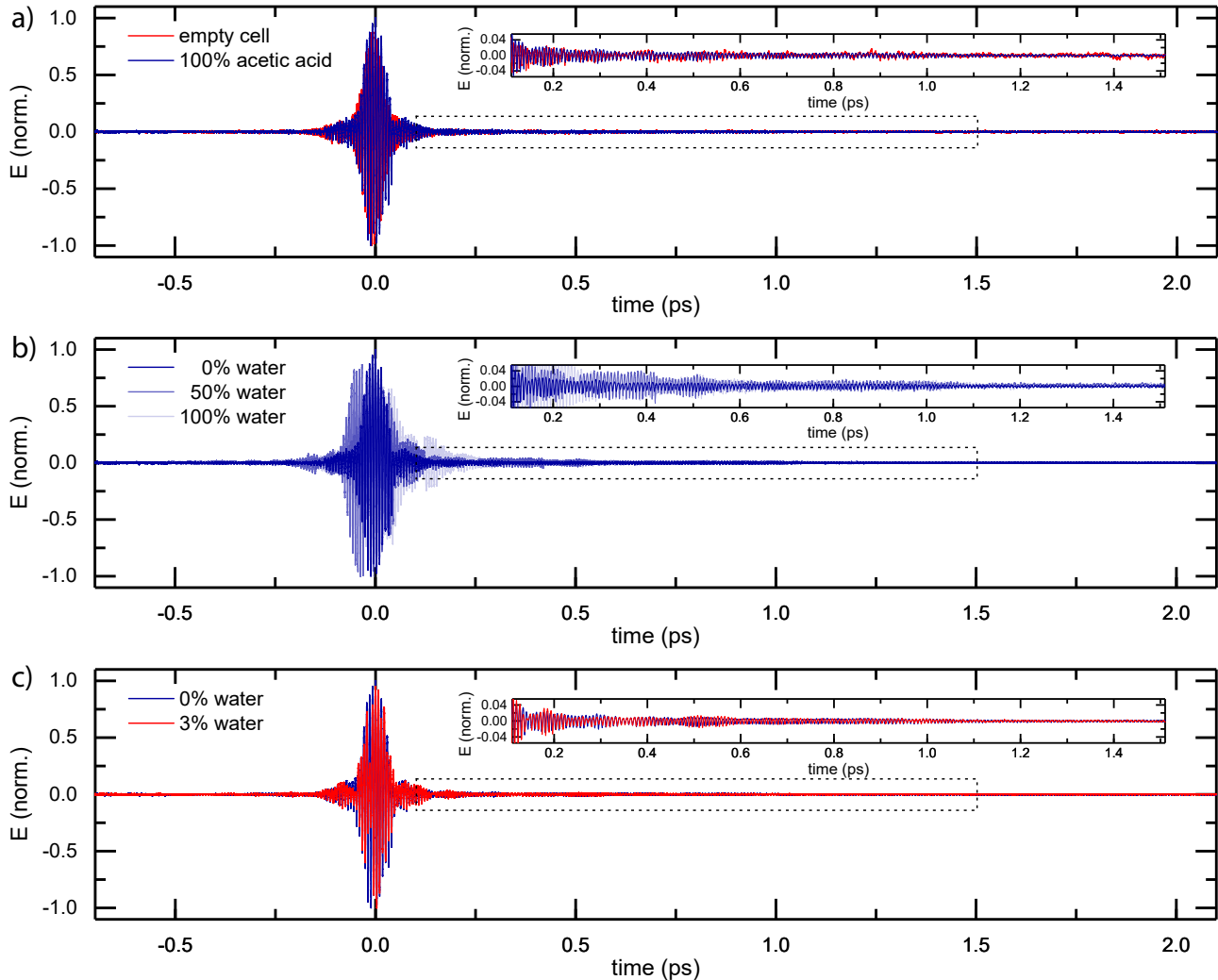


Figure 3. a) Measured electric field of the transmitted pulses in the absence of any sample (red) and 100% acetic acid sample (blue). Inset: zoomed plot for the temporal delays above 100 fs. b) Measured electric field of the transmitted pulses for the mixture of water and acetic acid for three different water's concentrations 0%, 50%, and 100%. Inset: zoomed plot for the temporal delays above 100 fs. c) Measured electric field of the transmitted pulses for the mixture of water and acetic acid for water concentrations 0% (blue), and 3% (red). Inset: zoomed plot for the temporal delays above 100 fs.

employing a frontend at megahertz repetition rates¹³ holds promise for enhancing the detection sensitivity to unparalleled values.

Moreover, combining the concept of molecular fieldoscopy with exciting nonlinear techniques such as two-dimensional spectroscopy, holds promise to increase our understanding of molecular dynamics, for example in water. Water in liquid phase, consists of a molecular network with molecular dynamics at various time scales, from several picoseconds to tens of femtoseconds. The intermolecular OH-bond stretching and bending has the shortest vibrational period at 10 fs and 20 fs, respectively. On a time scale of several hundreds of femtoseconds, librational motions, and the H-bonds stretching and bending occur. Last but not least the exchange of hydrogen-bond partners via breaking and reforming of stable H-bonds occurs in a time range between 1-5 ps.¹⁴ Femtosecond molecular fieldoscopy is capable of detecting the complex electric field of the water response at all above-mentioned time scales with high sensitivity, and may allow for resolving many unknown aspects of water's molecular dynamic.

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