

Time and frequency-gated FID: a new approach to study the vibrational dephasing of water

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Abstract. The ultrafast frequency-resolved upconverted vibrational free induction decay (FID) of HDO in D₂O was measured, allowing extraction of the amplitude and phase of the coherent transient. The FID Wigner spectrogram shows evidence of λ -dependent dynamics.

Considerable experimental and theoretical effort has been expended toward understanding the behavior of liquid water at the molecular level, much of it striving to understand the structural and dynamical character of its hydrogen bonding interactions. Investigations of the hydrogen bonding nature of water via vibrational spectroscopy have focused on the OH-stretching band in the 3 μm region. The broad frequency profile of this band and the correlation between stretching frequency and hydrogen bond strength has prompted debate over the possible existence of distinct hydrogen-bonded species and their timescales of interconversion. Recent time-resolved infrared studies of liquid water, primarily in isotopically diluted samples (HDO in D₂O), have shed light on vibrational population [1-3] and rotational [1a, 3] relaxation in the liquid, as well as vibrational Stokes shift [1b] and resonant energy transfer [1c]. These studies do not, however, concur on the nature of the heterogeneity of the OH-stretching band and are limited to resolving dynamics on ≥ 150 fs timescales.

The interplay between H-bond strength and OH-stretch transition frequency suggests value in a mixed time-frequency approach to learning about the influence of H-bonds on the vibrational dynamics of water. Such an approach can be realized in time-resolved experiments using ultrashort (broadband) infrared pulses by determination of the electric fields of the signals. Knowledge of the signal amplitude and phase allows translation of the field into the time-frequency domain via Wigner transformation. [4] The Wigner spectrogram provides a means of visualizing frequency-dependent dynamics as it represents the time-dependent spectrum of the signal. Field measurements of four-wave mixing signals have been accomplished in one-color optical experiments by interferometric techniques. [5] In this paper, we demonstrate the first use of cross-correlation frequency-resolved optical gating (XFROG, [6]) as a means of extracting the amplitude and phase of a spectroscopic signal, that of the free induction decay of HDO molecules in liquid D₂O. This measurement, performed with 55 fs infrared pulses, resolves the complex linear polarization and provides a foundation for similar studies of nonlinear responses such as pump-perturbed FIDs.

Femtosecond mid-infrared (MIR) pulses were generated by a type-I optical parametric amplifier (OPA) based on the nonlinear crystal KNbO₃ (KN). [7] The OPA is pumped by the fundamental of a home-built Ti:sapphire regenerative amplifier and seeded with the near-infrared portion of a white light continuum

generated in a [0001]-cut sapphire plate. The design is similar to that of ref. 8, but is modified for shorter pulse generation. Cross-correlations of the pump pulse with the continuum in the 980-1150 nm range are approximately 60 fs in duration. The pump and continuum are combined collinearly in a 1 mm KN crystal. The center wavelength of the MIR pulses is tunable between 2.9 and 4.2 μm with only minor crystal angle adjustment by varying the temporal overlap of the continuum and pump. Upconversion of MIR radiation for pulse and signal characterization was accomplished by sum-frequency generation in a 300 μm KN crystal using a portion of the 800 nm pump. The gate pulse was characterized by SHG autocorrelation and FROG in BBO. Frequency-resolved signals were detected by a PMT through a monochromator. The sample consisted of a dilute ($\sim 1:200$) solution of HDO in D_2O in a variable-pathlength cell with CaF_2 windows. The OPA was tuned to $\sim 2.94 \mu\text{m}$ to overlap the OH-stretching transition of HDO, and the pulse spectrum spanned the OH-stretch absorption band. The pulses were shortened at the sample location by precompensating the CaF_2 entrance window's dispersion with a Ge window before the sample. The pulses were then re-optimized at the SFG crystal with germanium after the entire empty sample cell.

The XFROG traces of the (empty cell) MIR reference pulse and the HDO FID are shown in Figures 1A and 1B, respectively. Analysis of the XFROG signal of the MIR reference pulse yields a FWHM pulse duration of 55 fs. The FID measurement was made on a 500 μm thick HDO solution by insertion of the sample in the infrared beam with the same dispersion compensation optics. The

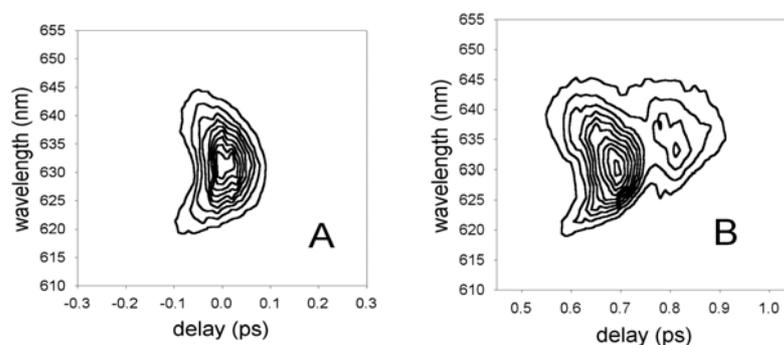


Fig. 1. XFROG data for (A) reference pulse; (B) HDO FID.

XFROG trace of the FID exhibits different temporal behavior on the high and low energy portions of the signal. Analysis of the two-dimensional signals yielded temporal intensity and phase profiles. The phase of the FID of HDO is quadratic in shape for the duration of the free induction decay field.

The amplitudes and phases of the extracted fields were used to construct the Wigner spectrograms (WS) of the MIR reference and FID complex fields as shown in Figures 2A and 2B, respectively. The FID spectrogram exhibits asymmetry along both the time and frequency axes. Simulations show that the general features observed in the FID WS can be reproduced by a superposition of

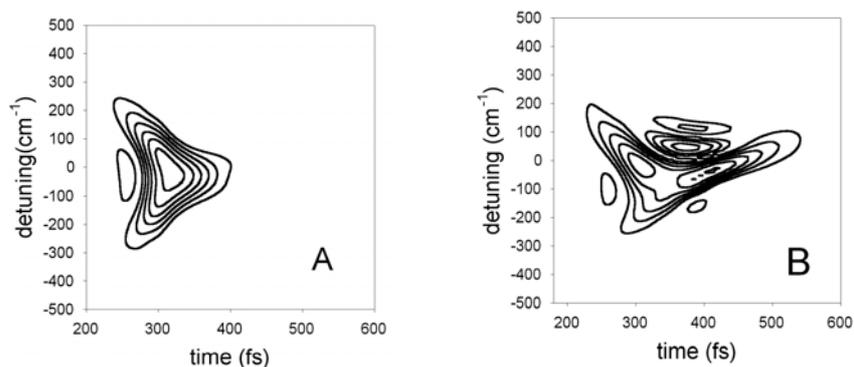


Figure 2. Wigner spectrograms of (A) reference and (B) FID complex fields.

components with different frequencies. Simulations of one- and two-dimensional signals, as well as further experiments with different sample path lengths and concentrations, are in progress to explore the origin(s) of the observed features. These will establish whether the structure in the FID WS is due to true frequency substructure or reflects propagation effects and phase shifts from the dispersion of the index of refraction.

The experiment presented here is a promising approach for the measurement of amplitude and phase dynamics of spectroscopic signals. In the present case we are able to ascertain information from the frequency-resolved upconverted FID that is not accessible from a traditional (frequency-integrated) FID measurement. We are extending this technique to the study of the frequency-dependent dynamics of infrared signal fields of non-equilibrium (pre-pumped) samples, giving access to higher order nonlinear optical information.[9]

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