

Fluorescence-Detected Two-Dimensional Electronic Coherence Spectroscopy by Acousto-Optic Phase Modulation

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Abstract. We present a robust and high signal-to-noise strategy for phase-selective ultrafast electronic coherence spectroscopy. We demonstrate our approach using atomic Rb, isolating specific non-linear signal contributions to the excited state population.

Introduction

Two-dimensional electronic coherence spectroscopy (ECS) is an important method to study the coupling between distinct optical modes of a material system [1-3]. Such studies often involve excitation using a sequence of phased ultrashort laser pulses. In conventional approaches, the delays between pulse temporal envelopes must be precisely monitored or maintained. Here we introduce a new experimental scheme for phase-selective non-linear ECS, which combines acousto-optic phase modulation with ultrashort laser excitation to produce intensity modulated non-linear fluorescence signals. We isolate specific non-linear signal contributions by synchronous detection, with respect to appropriately constructed references. Our method effectively decouples the relative temporal phases from the pulse envelopes of a collinear train of four sequential pulses. We thus achieve a robust and high signal-to-noise scheme for phase-selective ECS to investigate the resonant non-linear optical response of photo-luminescent systems. We demonstrate the validity of our method using a model quantum three-level system – atomic Rb vapor. Moreover, we show how our measurements determine the resonant complex-valued third-order susceptibility.

Experimental Methods

In our approach [4, 5], we use continuously driven acousto-optic (AO) Bragg cells to impart time-varying phase shifts to consecutive incident pulses of a laser pulse train. By placing two such AO cells, each in separate arms of a Mach-Zehnder interferometer and operating at well-defined and distinct frequencies (Ω_1 and Ω_2), we create a train of collinear pulse pairs with relative phase modulated at the AO difference frequency ($\Omega_{21} = \Omega_2 - \Omega_1$). Based on the above technique, we construct a train of four collinear pulses consisting of two independently phase modulated pulse-pairs ($\Omega_{21}/2\pi \sim 5$ kHz and $\Omega_{43}/2\pi \sim 8$ kHz; see figure 1).

When this train excites a quantum system, such as the D-line transitions of atomic Rb vapor, the excited state population depends on both linear and non-linear coherences, which contribute to the fluorescence signal. While the linear signal terms oscillate at the fundamental frequencies Ω_{21} and Ω_{43} , the non-linear terms oscillate at

the combination (side-band) frequencies $(\Omega_{43} - \Omega_{21})/2\pi \sim 3$ kHz and $(\Omega_{43} + \Omega_{21})/2\pi \sim 13$ kHz.

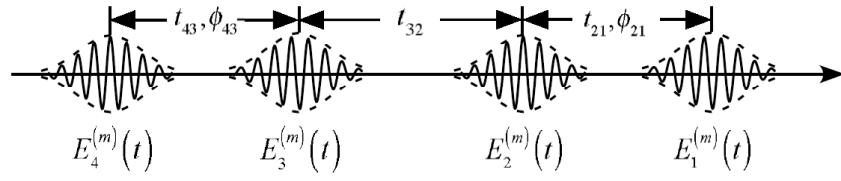


Fig. 1. Train of four sequential phase-modulated pulses. Each pulse sequence is labeled by the superscript m ; individual pulses are labeled by the subscripts 1 – 4. A pulse sequence is characterized by the interpulse delays t_{21} , t_{32} , and t_{43} , and the relative temporal phases ϕ_{21} and ϕ_{43} .

We synchronously detect the fluorescence signal using “sum” and “difference” frequency reference waveforms, which we generate from the pulse spectral densities. This approach, combined with a consistent phase calibration method, ensures that the signal phase is measured relative to that of the excitation pulses. We use the resulting de-modulated signals to construct complex-valued interferograms, proportional to overlaps between third-order wave packets excited by three of the four pulses, and first-order wave packets excited by the remaining pulse. These fluorescence-detected “difference” and “sum” frequency signals are, respectively, analogous to the rephasing and non-rephasing third-order polarizations, characterized in four-wave mixing experiments and excluding the effects of non-resonant interactions.

Results and Discussion

In figures 2 and 3, we compare our measurements of the rephasing and non-rephasing

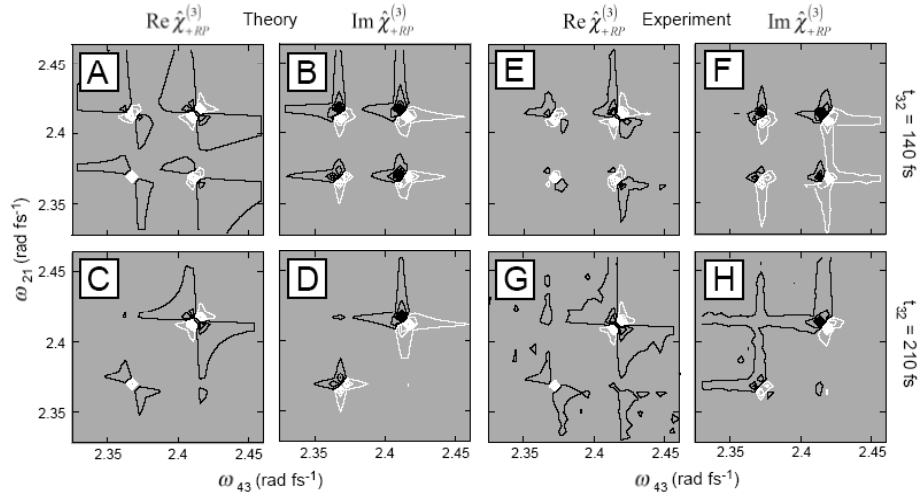


Fig. 2. Comparison between theoretical calculations [panels (a) – (d)] and experimental data [panels (e) – (h)] for the rephasing susceptibility obtained by phase-modulation ECS.

third-order susceptibilities to theoretical calculations, which are based on the known three-level Hamiltonian for the Rb system. We determine the susceptibilities by Fourier transforming the “sum” and “difference” frequency interferograms.

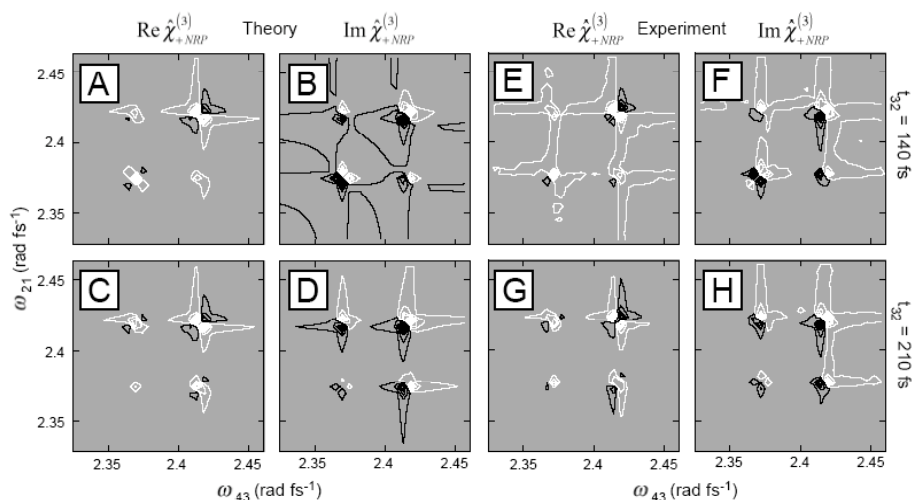


Fig. 3. Comparison between theoretical calculations [panels (a) – (d)] and experimental data [panels (e) – (h)] for the non-rephasing susceptibility obtained by phase-modulation ECS.

Both rephasing and non-rephasing susceptibilities agree quantitatively with our calculations. We emphasize that both the real and imaginary parts of the spectra are accurately described, confirming that the data are properly phased.

Conclusions

We have developed a phase-selective technique for two-dimensional femtosecond spectroscopy, called phase-modulation electronic coherence spectroscopy (PM-ECS). PM-ECS provides a straightforward route to measure the complex-valued resonant third-order susceptibility. The establishment of this method is an important step toward future experiments on photo-luminescent molecular systems, in which the optical nonlinearity results from direct coupling between optical transitions.

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- 1 R. M. Hockstrasser, Proc. Nat. Acad. Sci. **104**, 14190, 2007.
- 2 J. C. Vaughan, T. Hornung, K. W. Stone, and K. A. Nelson, J. Phys. Chem. A **111**, 4873, 2007.
- 3 D. M. Jonas, Annu. Rev. Phys. Chem. **54**, 425, 2003.
- 4 P. F. Tekavec, T. R. Dyke, and A. H. Marcus, J. Chem. Phys. **125**, 194303, 2006.
- 5 P. F. Tekavec, G. A. Lott, and A. H. Marcus, J. Chem. Phys. **127**, 214307, 2007.