

Fluorescence-detected two-quantum and one-quantum-two-quantum 2D electronic spectroscopy of Rhodamine 700

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Abstract. We demonstrate the simultaneous acquisition of three fourth-order nonlinear signal contributions using a shot-to-shot-modulating pulse shaper and fluorescence detection. Beside the 1Q photon echo, two different species of two-quantum contributions can be isolated without any background via phase cycling.

1 Introduction

Coherent two-dimensional (2D) spectroscopy is a versatile technique that reveals detailed information about molecular systems via probing their dynamics with ultrashort laser-pulse sequences. Besides well-established one-quantum (1Q) 2D spectroscopy enabling, e.g., the study of exciton transport in light-harvesting systems, two-quantum (2Q) 2D spectroscopy correlates doubly-excited vibrational or electronic states with their constituent singly-excited (1Q) states [1, 2]. It was shown that the obtained coherently-detected signals are suitable for quantifying electron correlation energies [3], which were believed to be unmeasurable for a long time. The core idea is to measure the energy shift of a 2Q state with respect to twice the energy of the 1Q state, reflecting the magnitude of interaction between the two involved electrons [2, 3]. Significant challenges are that 2Q signals are typically weak and that there is a strong background from scattering and nonresonant solvent contributions. This may have precluded a more widespread application of the method.

Here we solve these problems by introducing a new approach for 2Q 2D spectroscopy that measures fluorescence instead of coherent four-wave mixing signals. While incoherent detection is already used for 1Q 2D spectroscopy [4-6], studies for 2Q signals are scarce. We obtain a background- and scattering-free signal employing only one broadband excitation beam. Utilizing an acousto-optic pulse shaper on a shot-to-shot basis [6, 7] and phase cycling [4, 8] we extract various signal contributions from the same raw data set. In addition, we experimentally introduce 1Q-2Q spectroscopy [8] with less congested spectra than in the 2Q case.

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2 Coherent two-quantum signals from an incoherent observable

In our approach, we create a final fourth-order excited-state population via phase-coherent pulse sequences and utilize the unique phase dependency of different nonlinear signal contributions in order to extract them via phase cycling [4, 8]. It was theoretically shown [8] that by cycling the phases of a three-pulse sequence 16 times, one should be able to recover the photon echo, the 2Q signal and also a so-called 1Q-2Q signal. The key difference between the latter two population-based techniques lies in the different time ordering of the twice-interacting pulse. This can be illustrated by double-sided Feynman diagrams [Fig. 1(a)], where arrow directions represent interaction phase $+\varphi$ (right) or $-\varphi$ (left). For a three-level system with ground (g), singly excited (e), and doubly excited state (f), three pathways Q_1 , Q_2 , and Q_3 , which are weighted with quantum yields Φ_e and Φ_f [Fig. 1(a)] are present. Two coherence times, τ and t , are scanned and then a 2D Fourier transform is performed. We simulate the 2Q [Fig. 1(b)] and 1Q-2Q [Fig. 1(c)] spectra for a system with 100 meV correlation energy (Δ) between the first ($|g\rangle \rightarrow |e\rangle$, $\hbar\omega_{eg} = 2.0$ eV) and the second ($|e\rangle \rightarrow |f\rangle$, $\hbar\omega_{fe} = 2.1$ eV) 1Q transitions using the Lindblad master equation.

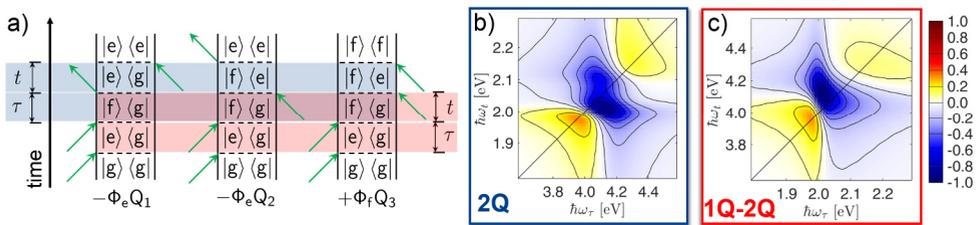


Fig. 1. Theory. (a) Feynman pathways provide the basis for (b) 2Q and (c) 1Q-2Q simulated real parts of 2D spectra of a three-level system. The signal phases are $\varphi^{2Q} = 2\varphi_1 - \varphi_2 - \varphi_3$ and $\varphi^{1Q-2Q} = \varphi_1 + \varphi_2 - 2\varphi_3$.

It is evident that 1Q-2Q spectroscopy scans the $|e\rangle\langle g|$ 1Q coherence only [red τ interval in Fig. 1(a)], while 2Q spectroscopy probes the $|e\rangle\langle g|$ and $|f\rangle\langle e|$ 1Q coherences [blue t interval in Fig. 1(a)]. Thus, the latter signal may suffer from interference between different 1Q coherences [distortions in Fig. 1(b) as compared to Fig. 1(c)]. All obtained data have in common that, because fluorescence is the observable, nonresonant solvent responses or scattering are absent. This is especially important for 2Q signals because the resulting artefacts would be strong compared to the naturally weak 2Q signals.

3 Experimental setup and results

We use a commercial Ti:Sa chirped-pulse amplifier (800 nm, 1 kHz, 35 fs) to generate a long-term stable supercontinuum output via focusing a spatially stabilized beam into an argon-filled hollow-core fiber [Fig. 2(a)]. Second- and third-order dispersion control is granted by a dual grism compressor and the pulse shaper. Phase-coherent and time-delayed pulse sequences are streamed shot-to-shot by an acousto-optic programmable dispersive filter (AOPDF, Dazzler) [6, 7]. A 0.1 mM solution of Rhodamine 700 in ethanol is pumped through a flow cuvette, into which we focus the beam. The resulting fluorescence signal is collected via microscope objectives and detected by an avalanche photodiode in a linear range. For data analysis, we remove potential artefacts which may arise from imperfections of the pulse shaper by subtracting normalized time-domain data acquired with low pulse energy (0.7 nJ) from those with high pulse energy (19 nJ).

The extracted real-valued nonlinear contributions from one measurement are shown in Fig. 2 and contain the 1Q photon-echo (b), the 2Q (c), and the 1Q-2Q signals (d). Via phase cycling, we directly obtain the real-valued signals so that no additional phasing is required.

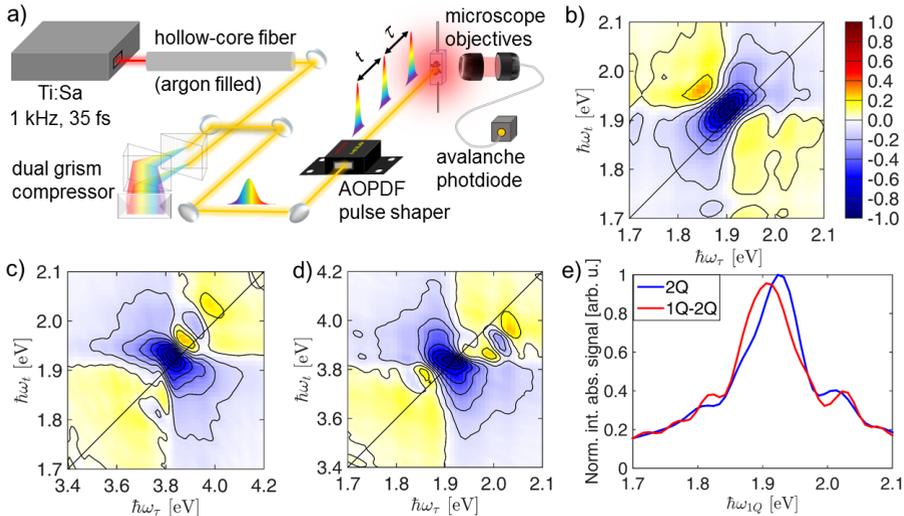


Fig. 2. Setup and experimental results. (a) An acousto-optic pulse shaper generates phase-coherent pulse sequences on a 1 kHz shot-to-shot basis. We recover, from a single raw data set, the (b) 1Q photon echo, (c) 2Q, and (d) 1Q-2Q 2D spectra of Rhodamine 700 in ethanol. Five-fold zero padding was applied, and all plots are normalized to their highest absolute value. (e) Projections of the 2Q and 1Q-2Q spectra onto the 1Q axes (normalized to the highest absolute value of the 2Q projection).

Both 2Q-associated spectra [(c) and (d)] look very similar. However, by analyzing the absolute-valued projections onto their respective 1Q axes [Fig. 2(e)], it is evident that the $|e\rangle \rightarrow |f\rangle$ transition manifests as a blueshift of the 2Q lineshape. This indicates a low value for Φ_r , so that path Q_2 contributes significantly [see Fig. 1(a)]. By simulating the 2D spectra with varying Δ , best agreement with experiment is obtained for $\Delta = 30$ meV.

4 Conclusion

We introduced a single-beam setup for fluorescence-detected two-quantum (2Q) 2D electronic spectroscopy with broadband excitation. Our approach is free of scattering artefacts or nonresonant background and further gives access to 1Q-2Q 2D spectroscopy which is less congested than the 2Q variant. For Rhodamine 700, a comparison between these two spectra revealed a blue-shifted second 1Q transition into a 2Q state with a very low quantum yield, indicating nonradiative relaxation channels into the ground state.

References

1. E. C. Fulmer, P. Mukherjee, A. T. Krummel, and M. T. Zanni, *J. Chem. Phys.* **120**, 8067-8078 (2004)
2. S. Mukamel, R. Oszwaldowski, and L. Yang, *J. Chem. Phys.* **127**, 221105 (2007)
3. J. Kim, S. Mukamel, and G. D. Scholes, *Acc. Chem. Res.* **42**, 1375-1384 (2009)
4. P. Tian, D. Keusters, Y. Suzaki, and W. S. Warren, *Science* **300**, 1554 (2003)
5. P. F. Tekavec, G. A. Lott, and A. H. Marcus, *J. Chem. Phys.* **127**, 214307 (2007)
6. S. Draeger, S. Roeding, and T. Brixner, *Opt. Express* **25**, 3259-3267 (2017)
7. S. Mueller, S. Draeger, X. Ma, M. Hensen, T. Kenneweg, W. Pfeiffer, and T. Brixner, *J. Phys. Chem. Lett.* **9**, 1964-1969 (2018)
8. H.-S. Tan, *J. Chem. Phys.* **129**, 124501 (2008)