A Non time Ordered Pulse Scanning Protocol for Multidimensional Spectroscopy with Entangled Light

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Abstract Quantum light can induce correlations in photo excited molecules and probe them with unusual spectral and temporal resolution. A new non-time-ordered pulse delay scanning protocol in multidimensional signals reveals resonances not accessible by standard techniques. This protocol allows to understand how entanglement of the light field is imprinted into entanglement of matter.

1 Introduction: Spectroscopy with Entangled Light

Quantum spectroscopy utilizes the quantum nature of light to reveal matter properties not available with classical light [1]. Entangled photons offer several advantages. First, the signals scale to lower order in the incoming intensity [2]. The pump-probe signal e.g. scales linearly rather than quadratically. This allows to perform nonlinear spectroscopy with lower intensity, limiting damage in e.g. imaging applications. Second, time-and-frequency entanglement allows to obtain higher temporal and spectral resolutions. The temporal resolution Δt depends on the entanglement time T, determined by the length of the nonlinear crystal, while the spectral resolution $\Delta\omega$ is determined by the pump envelope. These are independent control variables, not Fourier conjugates, and are thus not bound by the uncertainty $\Delta\omega\Delta t > 1$. The nonlinear response of the system is governed by a matter correlation function of the dipole operator windowed by a corresponding correlation function of the electric field. For instance the two photon absorption (TPA) signal given by a

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K. Yamanouchi et al. (eds.), *Ultrafast Phenomena XIX*,
Springer Proceedings in Physics 162, DOI 10.1007/978-3-319-13242-6_106

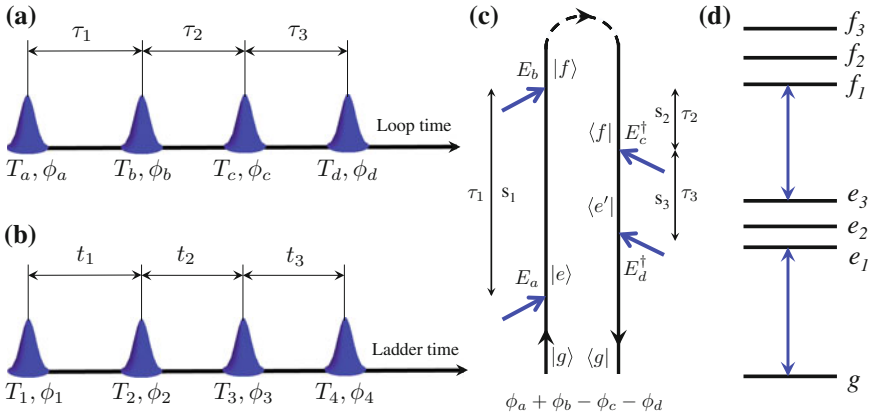

Fig. 1 The pulse sequence for unrestricted LOP (**a**), LAP (**b**). Loop diagrams for the TPA process with indicated loop delays for the phase cycling selected the signal with $e^{i(\phi_a+\phi_b-\phi_c-\phi_d)}$ (**c**). Level scheme for the molecular timer (**d**)

population of a double-excited state ρ_{ff} in an aggregate (Fig. 1d) can be read off the loop diagram in Fig. 1c

$$S(\Gamma) = \frac{1}{\hbar^4}\int_{-\infty}^{\infty} dr_a \int_{-\infty}^{\infty} dr_b \int_{-\infty}^{\infty} dr_c \int_{-\infty}^{\infty} dr_d \left\langle E_d^\dagger(r_d) E_c^\dagger(r_c) E_b(r_b) E_a(r_a) \right\rangle \times \left\langle \mathcal{J} V(r_d) V r_c) V^\dagger(r_b) V^\dagger(r_a) \right\rangle. \quad (1)$$

Depending on the state of the light, the four-point correlation function in (1) may couple different interaction times between the bra- and/or the ket-. It would therefore be useful to define a delay scanning protocol for multidimensional signals that utilizes these properties.

2 LOP—A New Non time Ordered Delay Scanning Protocol

Multidimensional optical signals are commonly recorded by varying the delays between time ordered pulses t_j, j = 1, 2, … (see Fig. 1b). Spectra are displayed vs the Fourier conjugates $\tilde{\Omega}_j$ to these variables which describe the evolution of the density matrix and are represented by ladder diagrams. We denote it as the ladder delay scanning protocol (LAP). Here we propose a new non-time-ordered loop delay scanning protocol (LOP) obtained by following the time evolution of the

wavefunction and described by loop diagrams [3]. We demonstrate that this protocol allows to observe different types of resonances and reveal information about intraband de-phasing not readily available by the LAP. The TPA signal (1) is given by the single loop diagram in Fig. 1c. a, b, c, d denote the pulse sequence ordered along the loop (not in real time); a represents "first" on the loop etc. To realize the LOP experimentally, the indices a–d are assigned as follows: first by phase cycling we select a signal with phase $\phi_a + \phi_b - \phi_c - \phi_d$. The two pulses with positive phase detection are thus denoted a, b and with negative phase—c, d. In the a, b pair pulse a comes first. In the c, d pair pulse d comes first. The time variables in Fig. 1c are $\tau_1 = T_b - T_a$, $\tau_2 = T_c - T_b$, $\tau_3 = T_c - T_d$, where T_j, $j = a, b, c, d$ corresponds to the central time of the j-th pulse, $\Omega_{\mathbf{j}}$ are frequency conjugates to τ_j. With this choice τ_1 and τ_3 are positive whereas τ_2 can be either positive or negative. The loop delay variables s_j in Fig. 1 are centered around $|\tau_j|$. The LOP protocol can be realized experimentally using a pulse shaper [4] or e.g. Franson interferometer [5].

3 Probing Intraband Dephasing Rates of Excitons in Aggregates

We consider a model aggregate with intraband dephasing rate $\gamma_{ee'}$ between excitonic states using LOP as shown in Fig. 2. Figure 2a shows the two photon fluorescence signal for a classical light with narrow intraband dephasing $\gamma_{ee'} = 1$ meV. It gives a diagonal cross peak $e = e'$ and one pair of weak side peaks parallel to the main diagonal at $(e,\ e') = (e_2,\ e_3)$ Fig. 2d shows that the signal obtained using

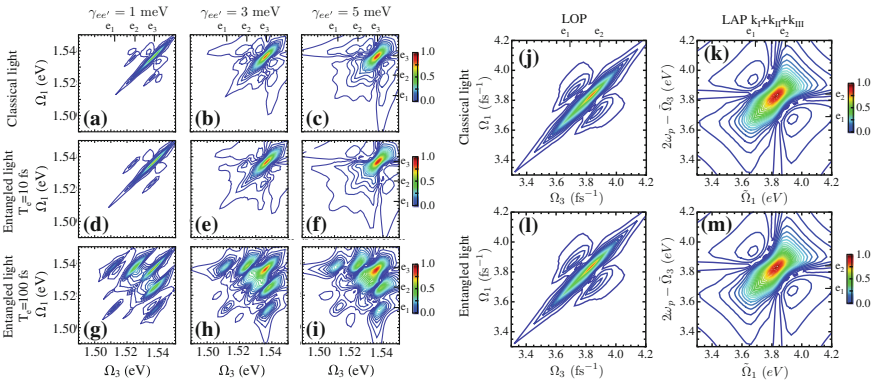

Fig. 2 *Left side* of the plot: TPA signal using LOP for a model of molecular trimer using classical light—*top row*, entangled light with entanglement time T_e = 10 fs—*middle row* and T_e = 100 fs—*bottom row*. Intraband dephasing $\gamma_{ee'} = 1$ meV—*left column*, 3 meV—*middle column* and 5 meV—*right column*. *Right side* of the plot is comparison between LOP and LAP protocols for a molecular dimer. LOP signal calculated using classical light (**j**), and entangled light (**l**). Corresponding LAP signal shown in *panels k* and *m*, respectively

entangled photons with short entanglement time T_e = 10 fs is similar to the classical signal in panel (a). For T_e = 100 fs in Fig. 2g we observe two additional strong side cross peak pairs with $(e,\ e') = (e_1,\ e_3)$ and $(e,\ e') = (e_1,\ e_2)$. The weak peak at $(e,\ e') = (e_2,\ e_3)$ is significantly enhanced as well. Thus, the LOP display (Ω_1, Ω_3) allows for effective determining of the intraband dephasing for distinct pair of e and e' states even if intraband dephasing is broad. The two right columns of the Fig. 2 compare the signals for LOP and LAP protocols. The LOP spectra for classical and entangled light are given in panels j and l. The corresponding LAP spectra are shown in the panels k and m. Entanglement makes no difference in this parameter regime (the two rows are virtually identical). However the signals of two scanning protocols are very different. The LOP signals are narrow and clearly resolve the e_1 and e_2 states whereas the corresponding LAP signals are broad and featureless.

Acknowledgements We gratefully acknowledge support from the National Science Foundation (Grant No. CHE 1361516), and the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, and (U.S.) Department of Energy (DOE).

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