Two-Dimensional Femtosecond Spectroscopies of Coupled Chromophores

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Abstract. The coupling pattern of vibrational or electronic excitons as probed by multidimensional techniques provides a unique view into structure and dynamics of proteins and molecular aggregates.

1. Introduction

The elementary excitations of interacting localized chromophores may be described by the Frenkel exciton model. This applies to infrared vibrational transitions (e.g. the amide band of polypeptides [1,2]) as well as to optical electronic transitions (e.g. photosynthetic antenna complexes [3]). Two-dimensional four wave mixing spectroscopies of these systems, based on the application of sequences of carefully shaped and timed femtosecond pulses provide a novel multidimensional view of molecular structure as well as vibrational motions, interactions, and relaxation processes. Spreading the spectroscopic information in more than one dimension makes it possible to resolve congested spectra, selectively eliminates certain static broadening mechanisms, and provide structural and dynamical information unavailable from one-dimensional measurements. The basic ideas are analogous to multiple-pulse NMR techniques [4]. However, the resulting information is very different and complimentary [5,6]. The possible 2D resonant four wave mixing pulse sequences are studied.

2. Exciton Model of Localized Vibrations or Molecular Aggregates

The third order optical susceptibility of a system of coupled chromophores may be calculated by solving the nonlinear exciton equations (NEE) [6-8]

$$\chi^{(3)}(-\omega_s;\omega_a,\omega_b,\omega_c)=\frac{1}{3!}\sum_{p}\sum_{nm_1m_2m_3}\sum_{n'n''}\mu_n\mu_{m_1}\mu_{m_2}\mu_{m_3}$$

$$\times G_{n'm_1}(\omega_a)G_{n'm_2}(\omega_b)G^{+}_{m_3n''}(\omega_c)G_{nn''}(\omega_a+\omega_b-\omega_c)\bar{\Gamma}_{n''n'}(\omega_a+\omega_b)+c.c.$$

where G is the one exciton Green function and $\bar{\Gamma}$ is the exciton-exciton scattering matrix. The p summation represents all possible frequency permutations.

Reprinted from *Ultrafast Phenomena XI*, edited by T. Elsaesser, J. G. Fujimoto, D. A. Wiersma,
W. Zinth, (Singer-Verlag Berlin Heidelberg) (1998).

In a two-dimensional four wave mixing experiment, two of the three pulses are time-coincident and only differ by their wavevectors. Figure 1 shows the double-sided Feynman diagrams for all four possible techniques which survive the rotating wave approximation. Each technique is represented by two diagrams, with and without the participation of the two-exciton states.

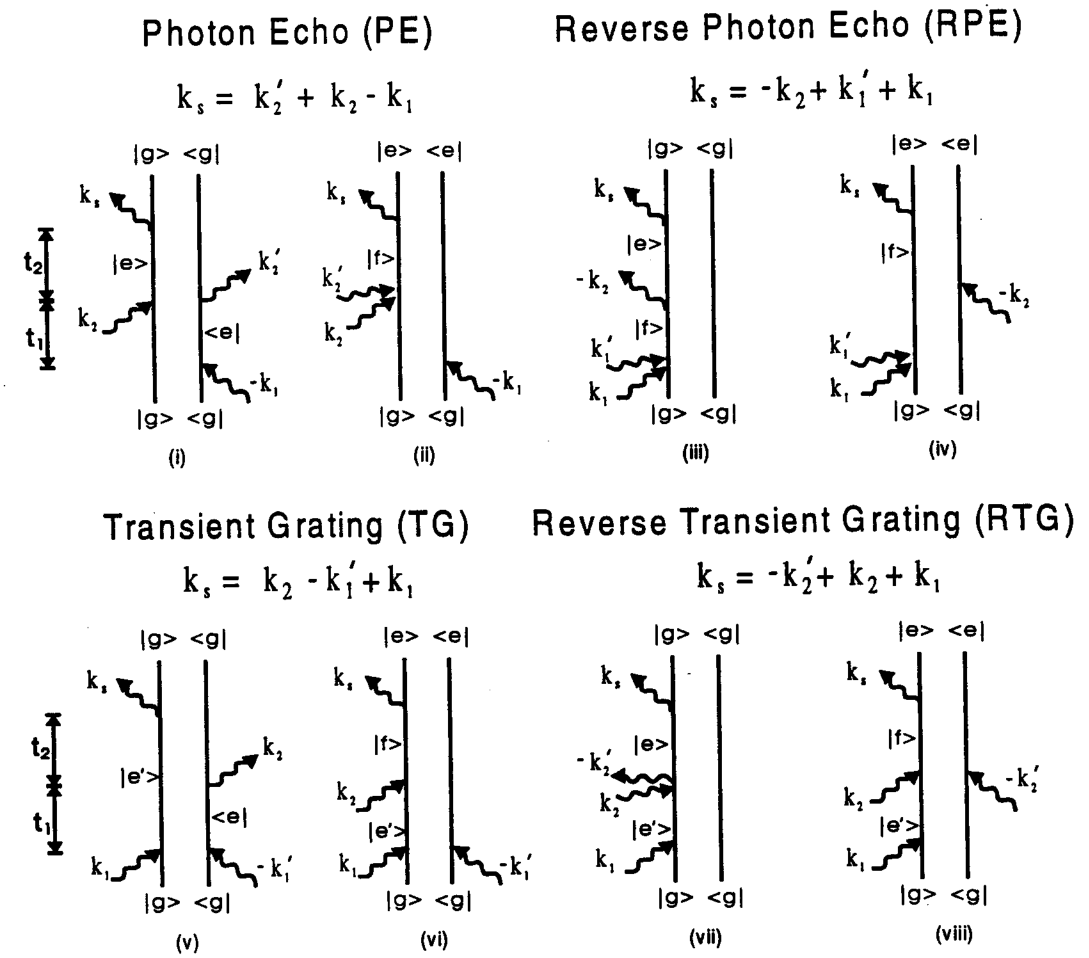

Fig. 1. Feynman diagrams of the four possible resonant 2D techniques. |g>, |e>, and |f> represent the ground, the one-exciton, and the two-exciton states, respectively.

Figure 2 shows model calculations for a system made out of 8 interacting vibrations [6]. Frequencies are given in units of the lowest transition frequency. Fig. 2(a) shows the linear absorption. Fig. 2(b), (c), (d) give the corresponding two-dimensional PE, TG and RTG infrared spectroscopies, respectively. Shown is the double Fourier transform of the heterodyne signal (Ω_1 and Ω_2 are the frequency variables conjugate to t_1 and t_2 respectively). Cross off-diagonal peaks reflect intermolecular couplings. The reverse photon echo (not shown) vanishes for non-interacting two level systems. This calculation demonstrates how two-dimensional spectroscopy can be used to directly probe the coupling pattern of interacting chromophores through the two-exciton manifold. It should be possible to extract useful structural and dynamical information by inverting such 2D signals.

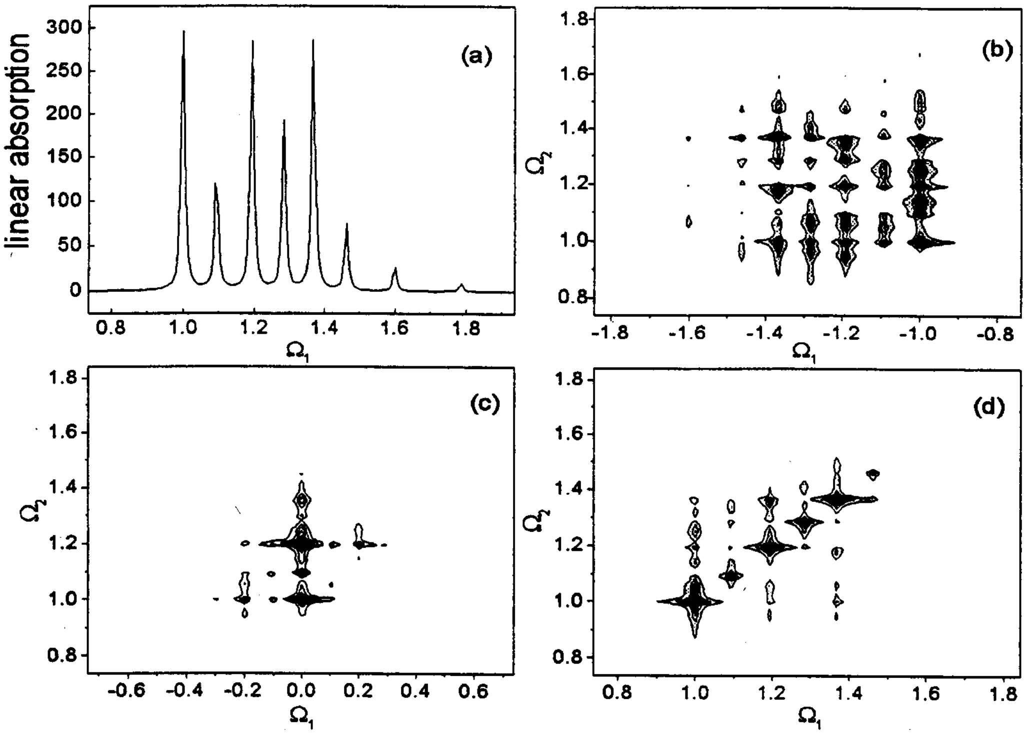

Fig. 2. (a) linear absorption of a coupled 8 chromophore aggregate. Panel (b) (c) (d) display the 2D spectroscopies of this aggregate. (b) PE, (c) TG, (d) RTG.

Acknowledgements. We wish to thank the support of the National Science Funcdation and the United States Air Force Office of Scientific Research.

References

1 H. Torii and M. Tasumi, *J. Chem. Phys.*, **96**, 3379 (1992).
2 P. Hamm, M. Lim, and R. M. Hochstrasser, "The Structure of the Amid I Band of Peptides Measured by Femtosecond Nonlinear IR Spectroscopy", *JCP*, preprint.
3 R. van Grondelle, J. P. Dekker, T. Gillbro, and V. Sundström, *Biochim. Biophys. Acta.* **1187**, 1 (1994).
4 R. R. Ernst and G. Bodenhausen and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, Clarendon Press, Oxford, 1987.
5 Y. Tanimura and S. Mukamel, *J. Chem. Phys.* **99**, 9496 (1993)
6 W. M. Zhang, V. Chernyak, and S. Mukamel, "Multidimensional Femtosecond Correlation Spectroscopies of Electronic and Vibrational Excitons", *J. Chem. Phys.*, submitted.
7 S. Mukamel, *Principles of Nonlinear Optical Spectroscopy,* Oxford, New York, 1995.
8 V. Chernyak, W. M. Zhang, and S. Mukamel, "Multidimensional Femtosecond Spectroscopies of Molecular Aggregates and Semiconductor Nanostructures; the Nonlinear Exciton Equations", *J. Chem. Phys.*, submitted.