Relevance of Multi-dimensional Spectroscopy for the Study of Sun-light-driven Processes

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It seems obvious that time-resolved **ultrafast spectroscopic experiments study** photosynthesizing (light-harvesting) molecular **systems under conditions different from those found in their operational environment**. In particular, in the laboratory, the **excitation condition is substantially different from Sun-light illumination**, and the individual component systems of light-harvesting systems might not be connected to the charge separating part of the apparatus; hence the **excitation is not drained** from the light-capturing antenna. These profound differences provoke **questions about the relevance of** the experimental insights into the primary processes of photosynthesis obtained by **ultrafast time-resolved spectroscopy**. In this contribution, we review the answers to these important questions by minimalistic models and general theoretical considerations based on non-linear response theory. Time-resolved spectroscopy comes out remarkably well from this questioning. The **difference in the excitation condition turns out to be an advantage** (at least from a theoretical point of view); **the difference between the drained and the undrained non-equilibrium states** of the photosynthetic systems **seems to be small** for typical light-harvesting parameters. Besides some conceptual details and a need for care in overinterpreting coherent aspects of the dynamics observed in time-resolved experiments, **ultrafast time-resolved spectroscopy**, including its multi-dimensional variants, **is the right tool to build a big picture of the Sun-light driven processes**.
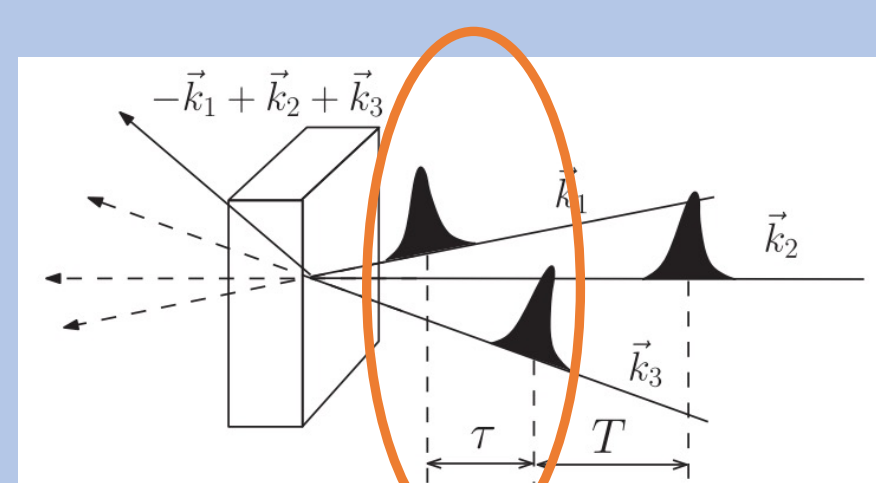
Main Possible Objections against Time-resolved Spectroscopy

Issue	Time-resolved spectroscopy	Operational Conditions	How to Resolve the Problem
Strenght of Illumination	Strong?	Weak	S1
Light driving	Impulsive/ Multiple Pulses	Steady	S2, S3
Illumination type	Coherent	Incoherent	S2
Load/Drain	Yes/No	Yes	S4

Strength of Illumination/Order of Response　S1

Third order spectroscopies observe dynamics induced by **second order excitation**

Second-order excitation serves as an initial condition for excited state propagation both in non-linear spectroscopy and in the light-harvesting function.

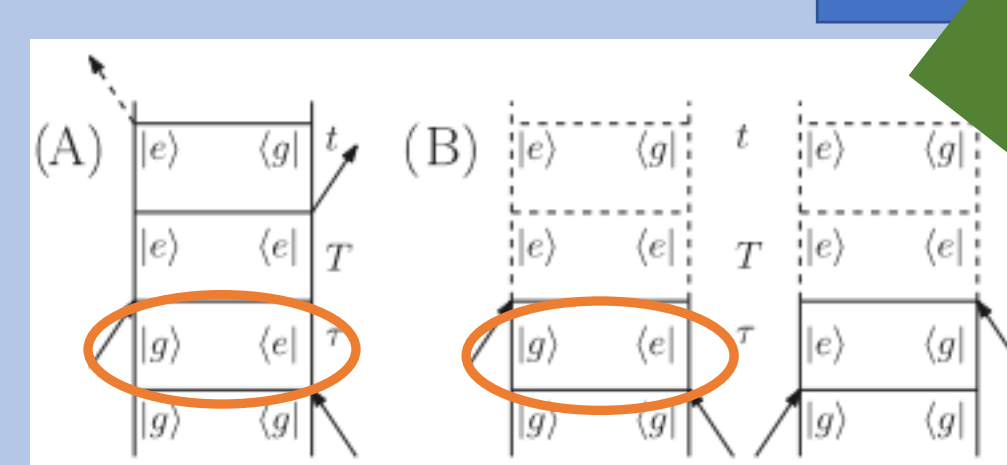Delay τ between the two light-matter interactions appears in both situations.

Fig 1: Typical non-colinear scheme of Fourier Transformed 2D (FT2D) Spectroscopy .

Fig 2: Third order response continues the second order diagrams that set the τ−dependence of the initial condition for the excited state dynamics.

- Weak response to light corresponds to **second-order perturbation theory**
- Validity and reproducibility of non-linear spectra are bound to the observation of the correct non-linear order
- **Third-order spectroscopies** do not represent a strong illumination regime

Driving by Incoherent Light　S2

Ideally, we want to know what happens when light-harvesting machinery is "struck by a photon from Sun." This is, however, **not a question compatible with quantum mechanics.** The theory formulated in terms of the **quantum mechanical state of light** weakly driving the excitation in a molecular system [1] finds the excited state to depend on a **second-order response operator** convoluted with the **second-order field correlation function of the light**. For steady illumination (Sunlight), the later quantity does not depend on time.

Ref. [1]

Derivation of second order excitation

A steadily driven state with excitation trapping and drain (charge separation) will reach saturation, where **no time-dependence occurs**. In particular, all dynamic coherence is washed away.

Second-order excited state dynamics under arbitrary driving can be **constructed** from the second-order response operator – **second-order Liouville pathways.**

Non-linear optical spectroscopy gives unique access to the second-order response operator (via the third-order response). However, **dynamics occurring in the laboratory is not the dynamics occurring under Sunlight**. The latter can be reconstructed from laboratory measurements. The difference is illustrated in Fig. 3.

$$\hat{\rho}_e(t) = -\frac{1}{\hbar^2}\int_0^t d\tau'\int_0^{\tau'} d\tau\ \mathrm{tr}_B\{U_0(t-\tau')\hat{\mu}|g\rangle\hat{w}_{\mathrm{eq}}$$
$$\times\langle g|\hat{\mu}U_0^\dagger(t-\tau'+\tau)\}G_E(t-\tau',t-\tau'+\tau)+\mathrm{h.c.}.$$

$$G_E(t-\tau',t-\tau'+\tau)=\langle\hat{E}(t-\tau')\hat{E}(t-\tau'+\tau)\rangle$$

Second order field correlation function. Light coherence properties enter here.

Fig. 3: Steady driving of oscillatory systems leads to dynamics different from impulsive driving. This property is not limited to quantum systems or quantum driving (from Ref. [5])

To describe arbitrary weak-light-driven dynamics
- We need response operator for δ−pulse excitation
- We need the field correlation function of the light
- Coherent or incoherent is not of crucial importance

Multi-dimensionality　S3

In the non-linear response, each response interval requires its own equations of motion [2]. Excited state dynamics is not the same for different values of the delay τ.
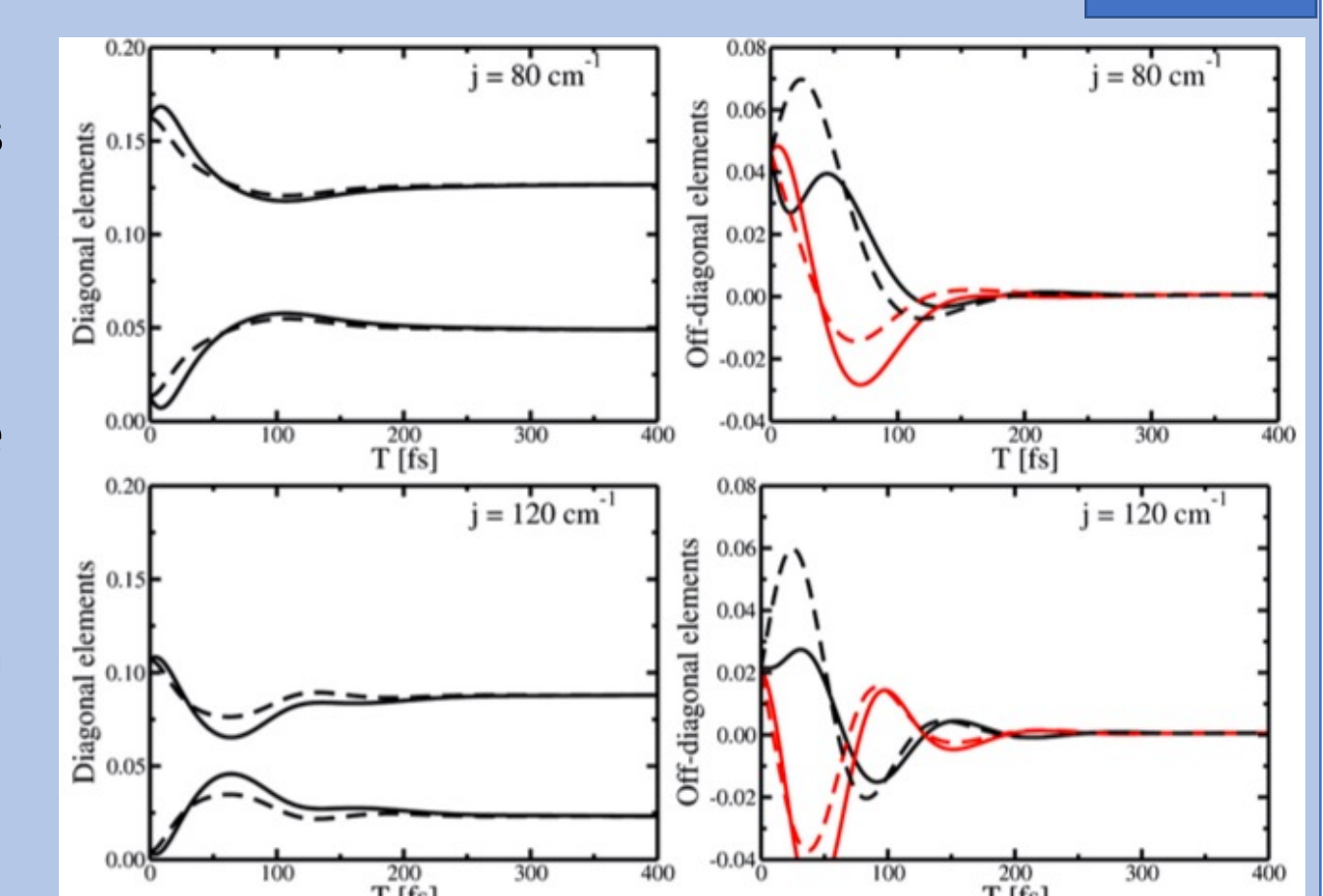
For systems with non-trivial bath (underdamped vibrations, long bath correlation time, …), it is not an issue of a simple phase factor.

In principle, the knowledge of τ dependence of the system dynamics is required to construct the correct driven state.

For Sun-light, τ is extremely short.

Fig. 3: Populations (left column) and coherence (right column) of a dimer excited by two pulses with $\tau = 0$ (full line) and $\tau = 60$ fs (dashed line). From Ref. [3].

Ref. [3]

- 2D Fourier Transformed Spectroscopy observes an average of dynamics corresponding to different "bath" initial conditions (different τ delays)
- The effects are relatively small, and the magnitude of contributions decays quickly with increasing τ [3].
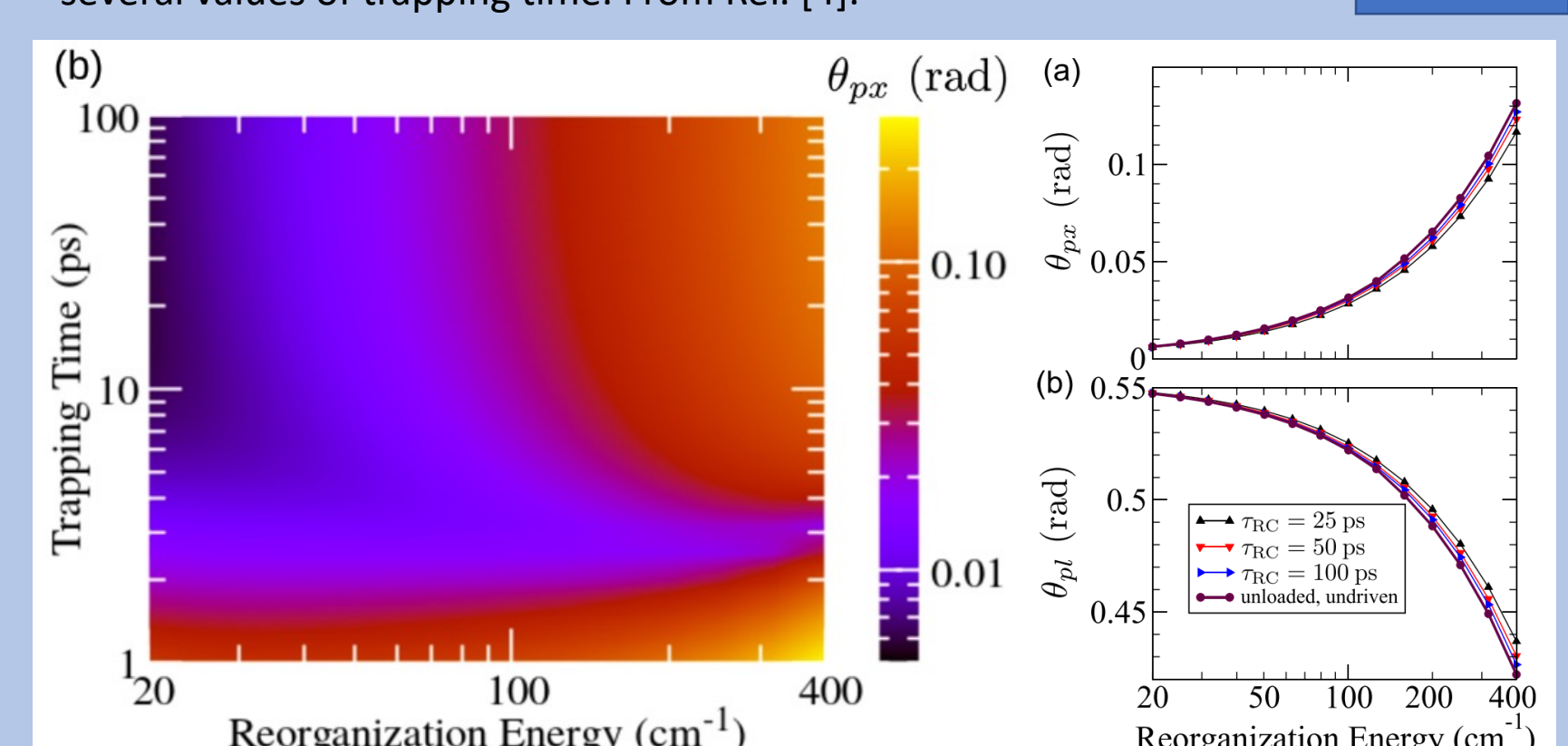
Effects of Load/Drain　S4

Spectroscopy provides information about the states that can be resonantly excited – it informs us about the **preferred basis (PB) of the embedded electronic system**. Fast trapping and excitation drain can shift this basis. The resulting **non-equilibrium steady state** (NESS) **might not be related to the spectroscopically observed dynamics.**

How is trapping changing PB?

Fig. 4: Left (b): Basis rotation with respect to the excitonic basis of a dimer as a function of trapping time and bath reorganization energy. Right (a): Dependence of basis rotation on reorganization energy for several values of trapping time. From Ref. [4].
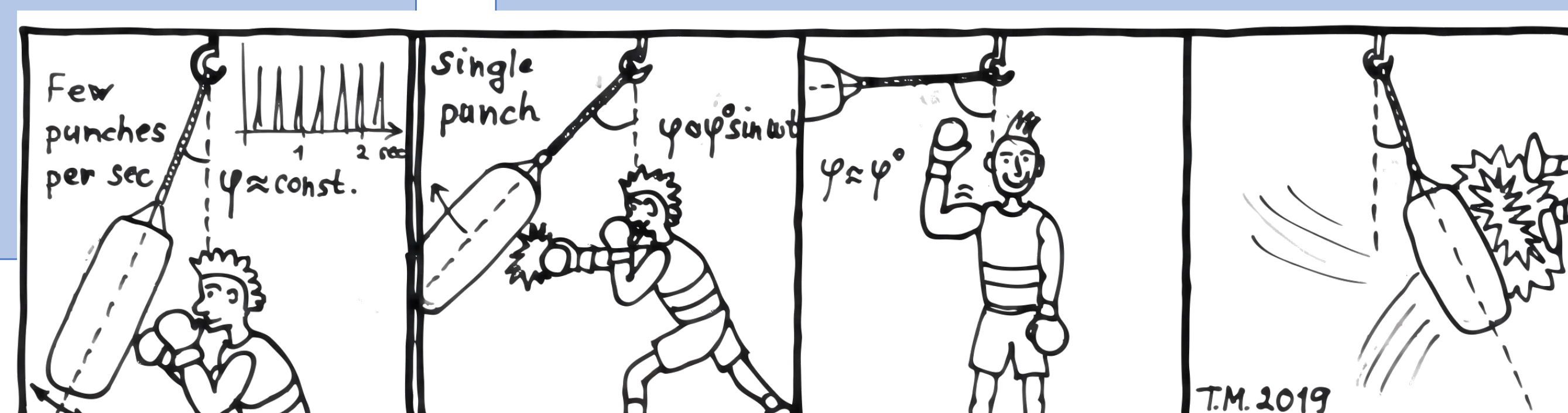
Ref. [4]

For the parameter region typical for natural light-harvesting
- Driven NESS is structurally similar to undriven equilibrium [4]
- Effects of load/drain are **negligible for picosecond trapping time** [4]

Summary

- **Non-linear spectroscopy** contains the **complete information** necessary **to reconstruct dynamics** under arbitrary weak light driving, including light **with different coherence properties and temporal dependencies**.
- **Under Sun-light illumination**, the system enters a non-equilibrium steady state (NESS), which does not display "dynamics" but exhibits **non-zero currents.** Photo-induced dynamic coherence does not play a role [4,5]
- For parameters typical for natural light-harvesting (slow excitation trapping), the NESS is structurally similar to the expected equilibrium state.

Literature

[1] T. Mančal and L. Valkunas, New J. Phys. **12** (2010) 65044
[2] T.Mančal and F. Šanda, Chem. Phys. Lett. **530** (2012) 140
[3] J. Olšina and T. Mančal, Chem. Phys. **404** (2012) 103
[4] V. Janković and T. Mančal, J. Chem. Phys. **153** (2020) 244110
[5] T. Mančal, Chem. Phys. **532** (2020) 110663
[6] J. Cao *et al.*, Sci. Adv. **6** (2020) eaaz4888

Ref. [5]

Few punches per sec　Single punch　$\varphi \propto$ const.　$\varphi \approx \varphi°\sin\omega t$　$\varphi \not\approx \varphi°$　T.M. 2019