Progress in Quantum Electronics 55 (2017) 1–34

Contents lists available at ScienceDirect

Progress in Quantum Electronics

journal homepage: www.elsevier.com/locate/pqe

Coherent multi-dimensional spectroscopy: Experimental considerations, direct comparisons and new capabilities

Jonathan O. Tollerud [a], Jeffrey A. Davis [a,b,*]

[a] Centre for Quantum and Optical Science, Swinburne University of Technology, Hawthorn, Victoria, 3122, Australia
[b] ARC Centre of Excellence for Future Low-Energy Electronics Technology, Swinburne University of Technology, Hawthorn, Victoria, 3122, Australia

A B S T R A C T

Optical Coherent Multidimensional Spectroscopy (CMDS) has been developed to probe the electronic states of a diverse range of complex systems. The great advantage of CMDS over linear spectroscopy is the ability to separate and quantify different types of interactions. To do this, multiple carefully controlled femtosecond laser pulses drive a non-linear response in the sample. A specific component of this non-linear response is selected and its amplitude and phase measured. There are many challenges for the experimental realization of optical CMDS, yet there have been several different approaches developed, each with their own advantages and limitations. Identifying the best approach then becomes dependent on the sample and the information being sought. Here we review the various experimental considerations and different approaches that have been developed. We consider the advantages and limitations of each of these, specifically in the context of experiments on solid state systems such as semiconductor nanostructures and 2D atomically thin materials. Two important considerations that are difficult to compare independently of other extraneous factors are the stability and sensitivity of the system. Here, we describe the experimental implementation of two different approaches that experience otherwise identical conditions and present an unbiased comparison of the stability and sensitivity. Furthermore, we demonstrate that by merging these two approaches we are able to combine the advantages of both into a single experiment.

1. Introduction

Quantifying the dynamics and interactions of electronic systems is crucial for understanding the mechanisms that drive functionality. From light harvesting in photosynthesis, to semiconductor-based devices, and much in-between, dynamics on the femtosecond time-scale play an important role [1–9]. The development of femtosecond lasers has enabled an array of ultrafast spectroscopy techniques, which have been applied with great success for over 3 decades [6,10,11]. Different experiments have been used to probe population dynamics (e.g. time-resolved photoluminescence pump-probe/transient absorption) and coherent dynamics (e.g. coherent control, four-wave mixing [2,7,12–16]), yielding insight into energy and charge transfer [2–5,17,18], excitonic interactions [19–22], quantum coherence [14,23,233,234] and more. Coherent multi-dimensional spectroscopy (CMDS) is an extension of four-wave mixing (FWM) and transient absorption, both of which probe the third-order response of the sample to the applied electric field [6,24–32]. In both, there are effectively three light-matter interactions. For third-order CMDS, each of these interactions are carefully controlled in time and the phase and amplitude of the third-order signal is measured. This provides an ability to separate the response into a 2 (or higher)-dimensional spectrum, which in-turn, provides simpler access to details that are often inaccessible in linear spectroscopy. The success of this approach has enabled greater insight into photosynthetic light-harvesting [30,31,33–35], interactions between excitons [36–38], multi-particle correlations [39–42] and many-body effects in semiconductor nanostructures [33,36,43–45], fundamental properties of atomically thin 2D materials [9,46,47] and more.

* Corresponding author. Centre for Quantum and Optical Science, Swinburne University of Technology, Hawthorn, Victoria, 3122, Australia.
E-mail address: jdavis@swin.edu.au (J.A. Davis).

http://dx.doi.org/10.1016/j.pquantelec.2017.07.001

Available online 14 July 2017

This type of approach was originally developed in nuclear magnetic resonance (NMR) experiments, where radio-frequency pulses excite and probe nuclear spin transitions [29,48–50]. In NMR, the interactions between nuclear spins can provide information on molecular structure and is frequently used to do so. Over the 50 years since 2D-NMR was first demonstrated, many different schemes, with different pulse sequences, have been established to access specific information [51–53]. The extension of these approaches to higher and higher order (e.g. modern pulse sequences can have hundreds of pulses) has led to the use of multidimensional for revealing the structure of large complex molecules and proteins [52,53].

The development of the analogous techniques for optical spectroscopy is enticing but limited by various experimental challenges and by the nature of electronic interactions [49,50]. Chief among the experimental challenges is the requirement to measure the signal phase and maintain phase stability between all pulses. At RF and IR wavelengths this is relatively straightforward [54–58], but for optical fields, the higher frequency makes this more challenging. Nonetheless, many different approaches have been developed and applied successfully. Each of these approaches has advantages and drawbacks; none are able to realise all desirable capabilities. The choice of which technique to use is then very dependent on the sample and the information sought. In this review we describe the most commonly used approaches, their advantages and their limitations.

For the purpose of determining what are the most important capabilities, we concentrate on the needs as related to solid state systems, including semiconductor nanostructures and the increasing array of atomically thin materials. In these systems, it is frequently the coherent dynamics and the interactions that are of interest and which can be uniquely accessed by these approaches. Over the past decade, development in optical CMDS and the data analysis has been used to measure homogeneous broadening and radiative linewidths in the presence of substantial inhomogeneous broadening [45,59–63]; to identify and quantify coherent coupling between different types of excitation [36,37,60,64–68]; to reveal and identify many body effects such as excitation induced shifts and excitation induced dephasing [33,36,43–45]; to reveal and quantify weakly interacting type-II excitons and parity forbidden excitons [69]; and to identify multi-body correlations between two and three excitons, (but not between four excitons) [39,42,70]; to measure the coherent dynamics of and interactions between excitons, trions and inter-valley coherences in monolayer transition-metal dichalcogenides [46,47,71–75]; and to measure the interactions, correlations, and coupling between exciton polaritons [76–79].

The development of new materials with new applications such as 2D semiconductors [80], 2D topological insulators [81,82], Weyl semi-metals [83], polariton and exciton condensates [84–86], and other strongly correlated materials [87] is continuing to transform condensed matter physics and needing new ways to measure and understand different types of interactions. CMDS has been developed with the aim of measuring interactions, and together with continued extensions of the capabilities provides an excellent experimental tool for understanding many of these systems.

In this review we focus on the experimental aspects of CMDS and how they can be used to access the important information. We begin with a brief overview of CMDS and a discussion of some of the different types of multi-dimensional spectra that can be obtained, and the information they provide. We then detail the experimental considerations and the different approaches to overcoming the various challenges. One important consideration that is difficult to compare across different techniques is the stability and sensitivity. This is challenging not only because there is no established standard method used to determine the relevant quantities, but also because these measurements are so dependent on the laboratory environment and may not represent the intrinsic stability or sensitivity of a specific approach. In the second half of this review we directly compare two approaches, one regarded to be among the most stable and one among the least. By merging these two approaches we also demonstrate a hybrid experiment that is able to combine the advantages of both.

2. CMDS of electronic transitions

CMDS of electronic transitions has been developed over the last two decades, with several different types of experiments being realized. However, due to technical challenges and inherent limitations (which will be discussed in detail in Section 3), CMDS has been limited primarily (with a few exceptions) to third-order experiments. Nonetheless, these approaches have been able to provide significant insight into a range of different phenomena across a range different sample types. In this section, we briefly describe the nature of the nonlinear signal and the most common types of 2D spectra that have been realized to date.

2.1. Generation of the nonlinear signal

The excitation pulses used in CMDS experiments are typically interpreted as a perturbation of the system Hamiltonian, and the nonlinear signal is thus represented as a perturbative expansion of the light-matter interaction up to the order of the experiment. We briefly describe the salient elements of this interpretation necessary for a general understanding, while more detailed general [88] and rigorous [32] explanations can be found elsewhere.

Each pulse acts on the system Hamiltonian with an electric field of the form:

$$\mathbf{E}_{\mathbf{j}}(\mathbf{r},t) = E_j(t)e^{+\left(i\mathbf{k}_{\mathbf{j}}\mathbf{r}-i\omega t+\phi_j\right)} + E_j(t)e^{-\left(i\mathbf{k}_{\mathbf{j}}\mathbf{r}-i\omega t+\phi_j\right)} \tag{1}$$

where j is the pulse label, E_j is the pulse envelope function, $\boldsymbol{k}_{\mathbf{j}}$ is the wavevector, and ω is the carrier frequency. The response of the system is given by the Liouville variation of the Schrodinger equation:

$$\dot{\rho}(k,t) = [\mathbf{H}, \rho(k,t)] \tag{2}$$