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Preface: Special Topic on Multidimensional Spectroscopy

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Multidimensional signals are generated by subjecting molecules to sequences of short optical pulses and recording correlation plots related to the various controlled delay periods. These techniques which span all the way from the THz to the x-ray regimes provide qualitatively new structural and dynamical molecular information not available from conventional one-dimensional techniques. This issue surveys the recent experimental and theoretical progresses in this rapidly developing 20 year old field which illustrates the novel insights provided by multidimensional techniques into electronic and nuclear motions. It should serve as a valuable source for experts in the field and help introduce newcomers to this exciting and challenging branch of nonlinear spectroscopy. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4921015>]

Conventional spectroscopy is one dimensional: signals are recorded vs. a single frequency or a time parameter yielding valuable information on energy levels, transition dipole moments, and electronic and nuclear motions. In multidimensional optical spectroscopy, the signals are measured as a function of several parameters. Sequences of laser pulses are used to perturb or label the electronic and vibrational degrees of freedom and to probe correlated events taking place during several well-defined time intervals. The resulting correlation plots can be interpreted in terms of multipoint correlation functions that carry considerably more detailed information on dynamical events than the two-point functions provided by any 1D technique.

Multidimensional Spectroscopy has its origin in Nuclear Magnetic Resonance (NMR) spectroscopy where sequences of short radiowave pulses interact with nuclear spins. The information obtained is often presented in two dimensional plots with two frequency axes. The diagonal peaks in these plots represent the energies of the nuclear spins and the off diagonal cross peaks provide valuable information on their interaction. Multidimensional NMR has a remarkable structural resolution and enabled, e.g., the determination of the conformation of complex biomolecular systems. Over the past 20 years, the concepts of multidimensional NMR have been extended to the optical regime. The use of light at optical frequencies enables the probing of degrees of freedom other than spins, thus providing complementary information on the structure and dynamics of complex molecules and aggregates. In addition, the use of optical pulses dramatically enhances the temporal resolution from the millisecond to the femtosecond regime. The necessary control over the phase of some or all of the laser pulses, which is straightforward for radio waves (NMR), is considerably more challenging at optical frequencies.

The first multidimensional optical experiments focused on highly nonlinear off-resonant Raman spectroscopy of intermo-

lecular nuclear motions in molecular liquids, but it was soon realized that resonant signals are much easier to detect and can provide more direct information on the molecular dynamics. As a result, after the first wave of 2D Raman studies, the field gradually evolved to the infrared and then to the visible. At present, many multidimensional optical spectroscopic studies have been reported providing important structural and dynamical information that was not accessible with conventional 1D optical techniques. Nowadays, UV technology exists in few labs, and attosecond x-ray pulses suitable for nonlinear measurements are on the horizon.

The field of multidimensional optical spectroscopy is now rapidly expanding, as shown in Fig. 1. There are many parameters of the interacting light beams that can be varied: the primary ones are the delays between short pulses. These can be supplemented by numerous other parameters like the carrier frequencies, the pulse shapes, the optical phases, the polarization directions, and the directions of the wave vectors, thus resulting in a rich phase space of possible multidimensional techniques.

This special issue presents an overview of the present status of this exciting and rapidly developing field. Both experimental and theoretical developments are covered. Two focus articles are included to introduce related fields, the first, Phase-resolved nonlinear terahertz spectroscopy—From charge dynamics in solids to molecular excitations in liquids by Thomas Elsaesser, Klaus Reimann, and Michael Woerner,¹ reviews ultrafast spectroscopy in the terahertz (THz) regime. In the second tutorial, Two-Dimensional Electron-Electron Double Resonance and Molecular Motions: The Challenge of Higher Frequencies,² Jack Freed reviews pulsed Electron Spin Resonance (EPR) studies in the microwave regime.

One group of articles presented in this special issue focuses on two-dimensional electronic spectroscopy of aggregates in the visible. These studies report on energy and charge separation in photosynthetic antenna complexes and reaction centers, carotenoid-to-bacteriochlorophyll energy transfer, exciton models, vibronic coupling, and the interplay of electronic and

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Multidimensional Spectroscopy

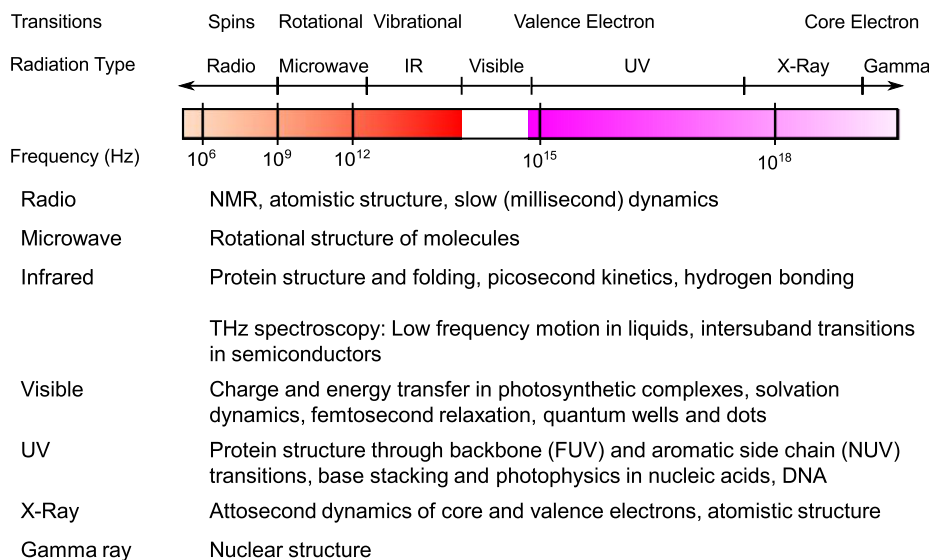


FIG. 1. Summary of multidimensional signals across the electromagnetic spectrum.

vibrational coherences. Other applications include biexciton formation in semiconductor nanostructures and colloidal quantum dots, polaritons in trapped ions, conjugated polymers, dye aggregation, and organic monolayers at metal-liquid interfaces.

Another group of articles of this issue covers the response of molecular vibrations of complex condensed-phase systems as studied by two-dimensional infrared (2DIR) spectroscopy, stimulated Raman, and sum-frequency generation. The measured responses provide valuable information on hydrogen bonding in water, alcohols, and molecular complexes; the secondary structure of proteins; solvent dynamics; chemical reaction rates; and the properties of the vapor/water interface and ionic liquids.

This special issue also presents the latest advances in the techniques. These include coherent multidimensional optical spectroscopy using incoherent light, multidimensional protocols based on multiple perturbations and measurements, phase-resolved nonlinear terahertz spectroscopy in solids and molecular liquids, 2D Raman-THz spectroscopy of molecular liquids, quantum process tomography by 2D fluorescence spectroscopy, pulse-shaping, and multidimensional signals from single molecules in open junctions.

¹T. Elsaesser, K. Reimann, and M. Woerner, *J. Chem. Phys.* **142**, 212301 (2015).

²J. M. Franck, S. Chandrasekaran, B. Dzikovski, C. R. Dunnam, and J. H. Freed, *J. Chem. Phys.* **142**, 212302 (2015).