Multidimensional Optical Spectroscopy

Conventional spectroscopy is one dimensional: signals are recorded vs. a single frequency or time parameter yielding valuable information on energy levels, transition dipole moments and electronic and nuclear motions. In multidimensional spectroscopy the signals are measured as a function of several parameters. Multidimensional optical spectroscopy uses sequences of laser pulses 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 cross peaks provide valuable information on their interaction. Multidimensional NMR has a remarkable structural resolution and enabled the determination of the conformation of numerous complex (bio) molecular 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 different degrees of freedom than spins, thus providing complementary information on the structure and dynamics of (bio) molecular systems. 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 intermolecular 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 from the infrared 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. 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, the directions of the wave vectors, etc., thus resulting in a rich phase space of possible multidimensional techniques.

This special issue presents an overview of the present status of the exciting and developing field of multidimensional optical spectroscopy. 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, reviews ultrafast spectroscopy in the Terahertz regime. In the second tutorial Two-Dimensional Electron-Electron Double Resonance and Molecular Motions: The Challenge of Higher Frequencies, 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 vibrational coherences. Other applications include biexciton formation in semiconductor nanostructures and colloidal quantum dots, polaritons in trapped ions, conjugated polymers, dye aggregation, organic monolayers at metal-liquid Interfaces.

In another group of articles of this issue the response of the molecular vibrations of complex condensed-phase systems are 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, three-dimensional spectroscopy, quantum process tomography by 2D fluorescence spectroscopy, pulse-shaping, and multidimensional signals from single molecules in open junctions.

We hope that this issue will be a valuable source for experts in the field and will help newcomers to enter this exciting field.

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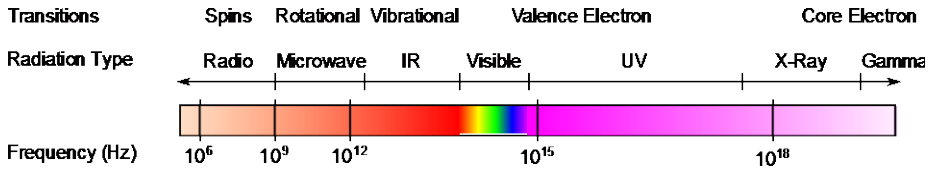

Radio	NMR, atomistic structure, slow (millisecond) dynamics
Microwave	Rotational structure of molecules
Infrared	Protein structure and folding, picosecond kinetics, hydrogen bonding
	THz spectroscopy: Low frequency motion in liquids, intersuband transitions in semiconductors
Visible	Charge and energy transfer in photosynthetic complexes, solvation dynamics, femtosecond relaxation, quantum wells and dots
UV	Protein structure through backbone (FUV) and aromatic side chain (NUV) transitions, base stacking and photophysics in nucleic acids, DNA
X-Ray	Attosecond dynamics of core and valence electrons, atomistic structure
Gamma ray	Nuclear structure

Coherent Nonlinear Optical Spectroscopy in Multiple Dimensions