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GUEST EDITORIAL

Coherent Multidimensional Optical Spectroscopy

Multidimensional optical techniques, the focus of this special issue, are analogues of their NMR counterparts; that is, rather than using spin transitions as little spies within a molecule, we use vibrational or optical transitions. Similar to NMR, the spectroscopic states often respond in a very sensitive way to their chemical environment. By modeling the coupling of one of these states to either other states within the same molecule, another molecule, or the solvent, we can extract a wealth of information about molecular structure and dynamics. The interpretation and analysis of these signals requires support from extensive electronic structure calculations as a function of molecular configuration. These provide some critical tests for the accuracy of state of the art methods of theoretical chemistry, and stimulate future developments. The most notable difference from NMR is the greatly-improved temporal resolution, which changes from milliseconds to about 100 fs for vibrational spectroscopy, and even into the 20 fs range for electronic spectroscopy. Looking at the comparison between NMR and optical multidimensional spectroscopy in more detail, we find that many other technical and conceptual differences exist. Hence, NMR ideas may not be directly transferred to the optical regime and new methods and tools are required for the design of novel optical pulse sequences. Multidimensional optical techniques provide a very different window into molecular structure and dynamics that is complementary to NMR spectroscopy.

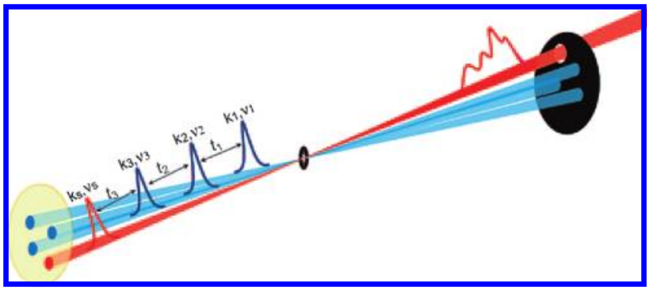

FIGURE 1. Pulse configuration for a heterodyne-detected multidimensional four-wave mixing experiment. Signals are recorded vs the three time delays, t_1, t_2, and t_3, and displayed as 2D correlation plots involving two of the time delays, holding the third fixed.

Conventional optical spectroscopy techniques, such as ordinary infrared, Raman, and UV-visible spectroscopies, provide a one dimensional (1D) projection of the available molecular information of a sample onto a single frequency axis. In contrast, optical multidimensional (2D, 3D) spectroscopy techniques provide a multidimensional projection of the relevant molecular motions offering dramatically more information. In 1D spectroscopy, the linear electrical polarization of the sample induced by the optical field is probed, while in the nonlinear 2D and 3D spectroscopic techniques, the coherent higher order polarization of the sample induced by the sequence of optical pulses is projected in multidimensions. The parametric dependence of the signals on the time intervals between pulses carries a wealth of information. Signals are typically displayed as two-dimensional correlation plots with respect to two of these intervals, say t_1 and t_3, holding the third (t_2) fixed (see Figure 1). The signal is double Fourier transformed with respect to the two desired time variables to generate frequency/frequency correlation plots such as $S(\omega_1;t_2;\omega_3)$ where ω_1 and ω_3 are the frequency conjugates to t_1 and t_3. Just like in NMR, heterodyne-detected (i.e., stimulated) signals record the signal field itself (both amplitude and phase), rather than just its intensity. We can thus display both the real (in-phase) and the imaginary (out-of-phase) components of the response. Coupled vibrational or electronic chromophores generate new resonances, cross-peaks, whose magnitudes and line shapes give direct zero-background signatures of the correlations between transitions. The resulting correlation plots of dynamical events taking place during controlled evolution periods can be interpreted in terms of multipoint correlation functions. These carry considerably more information than the two-point functions of linear 1D spectroscopy. The positions and profiles of the peaks in the 2D contour maps of the signals reflect the variations of the nonlinear response functions on a selected time window, which are sensitive to fine details of the molecular motions and couplings.

The origin of multidimensional vibrational spectroscopy can be traced to the picosecond, electronically off-resonant, coherent anti-Stokes Raman spectroscopy (CARS) measurements of

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vibrational dephasing performed in the 1970s. These were believed to have the capacity to distinguish between fast and slow fluctuations of the environment, which cause homogeneous and inhomogeneous line broadening, respectively, of the spectroscopic transitions. Linear (1D) absorption line shapes are convolutions of the two and cannot tell them apart. It was believed that CARS signals, like the photon echo technique, which is the analogue of the NMR spin echo proposed by Erwin Hahn, can eliminate the inhomogenous broadening and reveal the homogeneous part.

By formulating the problem in terms of multipoint correlation functions of the electronic polarizability, Loring and Mukamel have shown that this is not the case. The key lesson was that optical signals are better classified by their *dimensionality*, that is, the number of externally controlled time intervals, rather than by the nonlinear order in the external laser fields. Both photon echo and time-resolved CARS are four-wave mixing signals, which scale to third order in the external field. However, the latter only has a single control time variable, t_2. The other times t_1 and t_3 are very short, as dictated by the Heisenberg uncertainty relation for electronically off-resonant transitions, and carry no molecular information. The technique is thus one-dimensional (1D), carries identical information to the spontaneous Raman, and cannot in principle distinguish between the two broadening mechanisms.The CARS analogue of the photon echo requires seven, rather than four, pulses. Tanimura and Mukamel then proposed a "simpler" five-pulse, multidimensional impulsive off-resonant Raman technique and showed how it can be interpreted using 2D frequency/frequency correlation plot, as in NMR.. They demonstrated that various models that have the same 1D response can be clearly distinguished by the 2D signals. This work had triggered an intense experimental and theoretical activity. Experiments performed on low-frequency (<300 cm^{-1}) intermolecular vibrations in liquid CS_2 were initially complicated by cascading effects (sequences of lower order processes). It took 10 years to overcome these enormous challenges and carry out the fifth-order Raman experiments, as finally reported by the groups of Fleming and Miller. The extension to resonant 2D spectroscopy of coupled electronic and vibrational chromophores was discussed by Chernyak, Zhang, and Mukamel. Resonant techniques are easier and require fewer pulses, since each transition involves a single field, rather than two for Raman. Resonant vibrational spectroscopy in the infrared was first carried out by Hamm and Hochstrasser and electronic spectroscopy in the visible was demonstrated by Jonas and by Fleming.

The Accounts in this special issue survey the rapid progress in this field. Two-dimensional techniques have been applied to many fields of physics, physical chemistry, and biology, exploring the equilibrated structure of biomolecules, monitoring picosecond−nanosecond peptide folding dynamics, studying hydrogen-bonding structure and dynamics in liquid water and the electrostatic environment and its fluctuations around a chromophore, investigating the vibrational energy transfer pathways, and retrieving information on reaction rates, mechanisms, and yields. Infrared 2DIR techniques provide direct information about the transition-state geometry, time scale, and reaction mechanisms. Nonequilibrium exchange spectroscopy was employed to map light-triggered protein ligand migration.

Much 2DIR activity had focused on liquid water and water in confined biological environments. The Accounts by Fayer; Elsasser; la Cour Jansen, Wiersma, and Pshenichnkov; Tokmakoff; and Saito report novel applications to hydrogen bonding and intramolecular and intermolecular motions in water. Other hydrogen-bonded systems are described in the Account of Tominaga. Advanced theoretical and simulation techniques currently employed in the modeling of 2DIR signals of complex molecules are surveyed by Tanimura, and applications to peptides are given by Cho. Efficient computational techniques of time- and frequency-resolved four-wave mixing signals is presented by Gelin, Egorova, and Domcke. Signatures of nonequilibrium solvation dynamics on multidimensional spectra are simulated by Geva. Exciting recent analytical applications are surveyed by Wright, and biological and biomedical applications to proteomics, imaging, and structural analysis are given by Klug. Interface-specific ultrafast two-dimensional vibrational spectroscopy is reported by Bredenbeck and Bonn. Thermal conductance of molecules at interfaces is studied by Dlott.

It is increasingly harder to maintain the phase stability at higher frequencies. Only a handful of laboratories have so far carried out electronic spectroscopy by employing visible pulses. Applications to photosynthesis complexes are reported by Fleming and to other aggregates by Kauffmann. Two-dimensional electronic double-quantum coherent spectroscopy for probing electron correlations is described by Scholes and Mukamel. Relaxation-assisted 2DIR and measuring bond connectivity patterns are demonstrated by Rubtsov. Two-dimensional infrared spectroscopy of metal carbonyls is reported in a joint experimental and theoretical study of Geva and Kubarych. Waiting time relaxation dynamics has been probed by La Cour Jansen and Knoester. Extensions to 3D-IR spectroscopy are shown by Garrett-Roe and Hamm. Many-body electron hole dynamics in semiconductor quantum wells is reported by Cundiff. The perspective of a global multidimensional response function to femtosecond spectroscopy is developed by Joffre. Diffractive optics technology based four-wave and six-wave techniques, which greatly simplify the implementation of multidimensional techniques, are reported by Miller.

The first experimental realizations of Coherent Multidimensional Optical Spectroscopy have been demonstrated some 10 years ago. In the meantime, many research groups have joined the field, a large number of which are represented in this special issue. A broad range of possible applications of these new spectroscopies is presented. By now the technique has matured and a consistent language in terms of quantum pathways of the density matrix and an intuitive diagrammatic representation was developed for describing the signals. This special issue gives only a glance into possible applications of Coherent Multidimensional Optical Spectroscopy and provides an outlook into further developments. For sure, many other exciting applications will appear in the near future building upon developments in technology and simulation techniques.

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