

## Diffractive Optics Based Four-Wave, Six-Wave, ..., $\nu$ -Wave Nonlinear Spectroscopy

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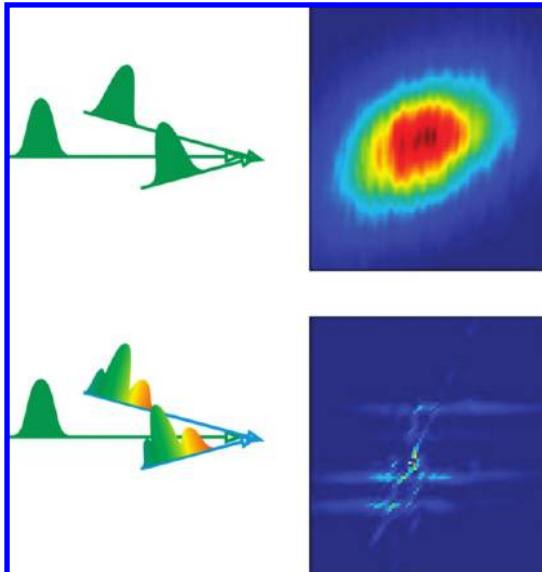
### CONPECTUS

A detailed understanding of chemical processes requires information about both structure and dynamics. By definition, a reaction involves nonstationary states and is a dynamic process. Structure describes the atomic positions at global minima in the nuclear potential energy surface. Dynamics are related to the anharmonicities in this potential that couple different minima and lead to changes in atomic positions (reactions) and correlations. Studies of molecular dynamics can be configured to directly access information on the anharmonic interactions that lead to chemical reactions and are as central to chemistry as structural information. In this regard, nonlinear spectroscopies have distinct advantages over more conventional linear spectroscopies. Because of this potential, nonlinear spectroscopies could eventually attain a comparable level of importance for studying dynamics on the relevant time scales to barrier crossings and reactive processes as NMR has for determining structure.

Despite this potential, nonlinear spectroscopy has not attained the same degree of utility as linear spectroscopy largely because nonlinear studies are more technically challenging. For example, unlike the linear spectrometers that exist in almost all chemistry departments, there are no “black box” four-wave mixing spectrometers.

This Account describes recent advances in the application of diffractive optics (DOs) to nonlinear spectroscopy, which reduces the complexity level of this technology to be closer to that of linear spectroscopy. The combination of recent advances in femtosecond laser technology and this single optic approach could bring this form of spectroscopy out of the exclusive realm of specialists and into the general user community. However, the real driving force for this research is the pursuit of higher sensitivity limits, which would enable new forms of nonlinear spectroscopy. This Account chronicles the research that has now extended nonlinear spectroscopy to six-wave processes and to a completely generalized “ $\nu$ -wave” mixing form to fully control state preparation and coherences.

For example, direct observation of global protein motions and energetics has led to the collective mode coupling model to understand structure–function correlations in biological systems. Direct studies of the hydrogen bond network of liquid H<sub>2</sub>O have recently shown that both intramolecular and intermolecular degrees of freedom are strongly coupled so that the primary excitations of water have an excitonic-like character. This fundamentally different view of liquid water has now resolved a 100-year-old problem of homogeneous versus inhomogeneous broadening of the vibrational line shapes. By adding programmable pulse shaping, we can access new information about the many-body interactions directly relevant to chemical reaction dynamics. We can also steer the course of the reaction along multidimensional surfaces to provide information about fluctuations far from the equilibrium, which are most relevant to chemical reactivity.



## Nonlinear Spectroscopy: Unique Window on Chemistry

To provide a general overview, it is useful to discuss what advantages are accrued by using nonlinear spectroscopic methods. Several comprehensive sources can be consulted for the necessary background.<sup>1,2</sup> Each wavelength range accesses a different type of transition that in itself is sensitive to different nuclear degrees of freedom and length scales of correlations. As a simple primer, the basic information content can be examined for each wavelength range without getting involved in the details. The induced polarization ( $P$ ) can be described as an expansion of the material susceptibility ( $\chi$ ) in terms of the field ( $\mathbf{E}$ ) dependence. For an instantaneous medium response (dielectric)

$$P(t) = \chi^{(1)}\mathbf{E}(t) + \chi^{(2)}\mathbf{E}(t)^2 + \chi^{(3)}\mathbf{E}(t)^3 + \dots \quad (1)$$

whereas for an absorptive medium, the response is always delayed and thus

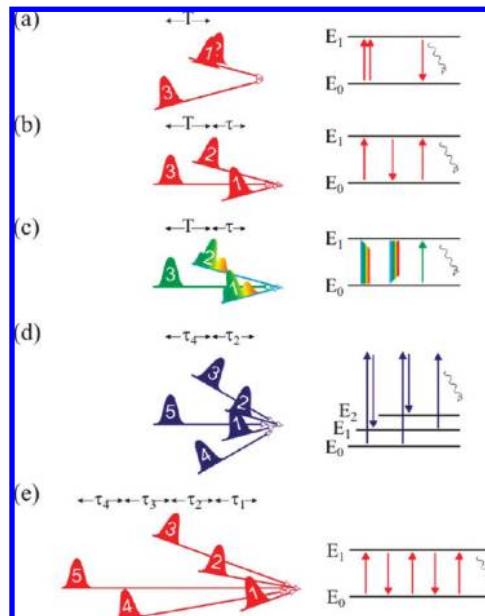
$$P(t) = \chi^{(1)} \otimes \mathbf{E} + \chi^{(2)} \otimes \mathbf{E} \otimes \mathbf{E} + \chi^{(3)} \otimes \mathbf{E} \otimes \mathbf{E} \otimes \mathbf{E} + \dots \quad (2)$$

where the different power-dependent contributions to the susceptibility are denoted by  $\chi^{(n)}$ , and  $\otimes$  denotes a convolution integral. In general, the susceptibilities are complex tensors of  $n+1$  rank with respect to the input fields and generated signal field. Linear spectroscopy is described by the  $\chi^{(1)}$  term:  $P(t) = \chi^{(1)} \otimes \mathbf{E} \equiv \int d\tau \chi^{(1)}(t-\tau)\mathbf{E}(\tau)$ ; the Fourier transform of which gives the frequency response for absorption (Im term of  $\chi^{(1)}$ ) and dispersion or index of refraction (Re term of  $\chi^{(1)}$ ). The odd terms are of most interest to this Account because these nonlinear polarizations are capable of probing isotropic as well as anisotropic materials (e.g., liquids, proteins, polymers).

The induced polarization driven by the input fields with well-defined geometries ultimately leads to constructive interference in a specific direction and radiation of the signal field  $\mathbf{E}_s$  (proportional to  $P$ ). A four-field interaction leads to the generation of an induced polarization in a specific geometry:

$$\omega_s = \pm \omega_1 \pm \omega_2 \pm \omega_3, \quad \vec{k}_s = \pm \vec{k}_1 \pm \vec{k}_2 \pm \vec{k}_3 \quad (3)$$

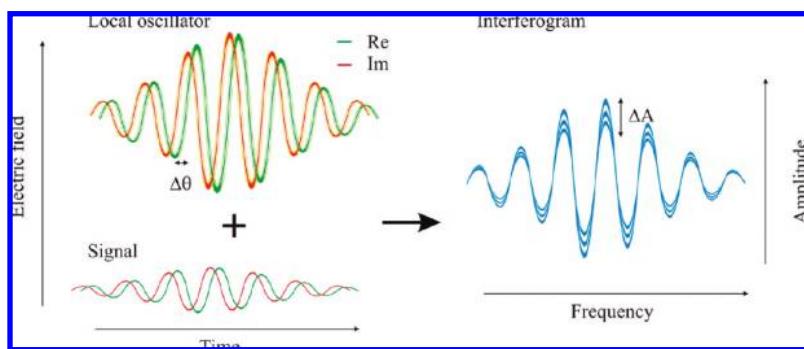
The latter condition (eq 3) provides selectivity over the specific order of the nonlinear interaction. Note that for all nonlinear processes there is a time and a frequency variable, offering a great deal of versatility in probing different aspects of the material response. For pulsed laser fields, it is possible to delay the timing between excitation pulses with all combinations possible. The number of different timing and field combinations increases with the dimensionality of the nonlinear spectroscopy and opens up enormous



**FIGURE 1.** Schematic representation of the many different possible nonlinear spectroscopies realized through different beam combinations with respect to phase matching and time/wavelength multiplexing. Panels a–c show different forms of four-wave mixing or  $\chi^{(3)}$  spectroscopy: pump–probe with the probe delay,  $T$ , monitoring population relaxation; noncollinear four-wave mixing for coherent spectroscopies, and general pulse shaping or coherent control 2D spectroscopy to select initial state preparations, respectively. Six-wave-mixing experiments shown are 2D Raman (d) and resonant  $\chi^{(5)}$  (e) spectroscopies.

flexibility over what microscopic processes can be selectively probed, as shown schematically in Figure 1 within a time domain picture.

At the  $\chi^{(3)}$  level, there are three input fields and a signal field generated or four fields in total, and hence the general term four-wave mixing. If the time delay between the excitation pulses is set to zero, the spectroscopy is referred to as transient grating spectroscopy (or pump–probe if both excitation pulses are collinear, see Figure 1a). In this case, the time evolution of the third-order polarization gives information on the population dynamics through the enhanced sensitivity to accompanying changes in the Re part of the complex index of refraction (e.g., direct observation of nonradiative channels or photodark states). By using an angle between the excitation beams, the signal field from the induced nonlinear polarization is radiated in a direction that conserves momentum (eq 3), spatially isolating the signal from the incoming pumping and probing fields. Since the signal is spatially isolated from the incoming fields, this experiment is as close to zero background as possible for an all optical experiment and imparts tremendous sensitivity to even a nonlinear process.



**FIGURE 2.** Schematic diagram of optical heterodyne detection and importance of phase stability. The phase noise ( $\Delta\theta$ ) translates to amplitude noise ( $\Delta A$ ) and reduction in SNR.

There are additional capabilities with the extra degrees of freedom in pulse sequencing. Scanning the time delay between the excitation pulses ( $\tau$ ) enables one to probe the coherence in the induced polarization. This ability is essential to the removal of inhomogeneous broadening effects that mask the dynamics of interest. This feat is made possible by explicitly monitoring the induced polarization involving multifield interactions with the initially prepared state. A phase conjugate or  $180^\circ$  phase-shifted polarization is driven that leads to rephasing of the initial polarization. This pulse protocol and rephasing process is identical to spin echos used in NMR. There is however an important distinction in that nonlinear laser methods are capable of observing the rephasing process in the small pulse area limit due to the much higher sensitivity imparted by the spatially isolated signal and much larger population differences between field-coupled states. The additional dimension introduced by the excitation pulse delay makes this form of spectroscopy two-dimensional. The observable provides direct information on the molecular/bath couplings through homogeneous dephasing mechanisms. Higher order processes access additional dimensions and correspondingly more information. In principle, it is possible to use different combinations of frequencies from UV to IR to probe couplings between different degrees of freedom, that is, electronic, vibrational, and bath couplings, as well as coherent interactions involved in energy transfer. Essentially, one can excite a particular coherence, label it, and monitor it in time as the system evolves, with specific information on the relaxation dynamics of the labeled state and its couplings to various degrees of freedom. *It is precisely this information that is needed to understand chemical reaction dynamics and the underlying processes governing reaction branching ratios.*

## Diffractive Optics: Single Optic Approach for Phase Sensitive Spectroscopy

With the advent of diffractive optics, highly specialized equipment is no longer a prerequisite for conducting nonlinear spectroscopic studies. Any arbitrary beam pattern for a given nonlinear process of interest can be Fourier transformed to a spatial phase profile of a diffractive optic (DO), reducing otherwise complex optical systems essentially to a single optic.

The first work to employ diffractive optics to generate arbitrarily complex beam patterns for phase matching and realize the inherent passive phase stability possible in relay imaged interferometer designs was the work of Goodno et al.<sup>3</sup> The most important development was that diffractive optics could in fact achieve passive phase stabilization on the order of  $\lambda/100$  or better, enabling true heterodyne detection. Independently, the Nelson group demonstrated the application of DOs<sup>4</sup> and has since focused on fully programmable solutions for even greater flexibility.<sup>5</sup>

Figure 2 shows schematically the importance of phase stability. Prior to the implementation of simple passive phase stabilized means for heterodyne detection, information on the third-order induced polarization was generally acquired by monitoring the signal intensity (homodyne detection). In this case, the changes in the Re and Im terms of the susceptibility are detected in quadrature; that is, for four-wave mixing, the diffracted signal intensity,  $I_s$  or  $|E_s|^2 \propto (\Delta OD)^2 + (\Delta n)^2$ . Certain dynamics affect the  $Re(\Delta n)$  part of the signal without affecting the  $Im(\Delta OD)$  term. Terms such as solvent relaxation, protein motions, and density changes associated with thermalization of molecular processes all contribute to changes in the index of refraction (Re part) with undetectable contributions to the changes in the optical absorption (Im part). Due to the quadratic nature of the signal detection, these terms will form the cross terms with other potential contributions from

excited state processes. This complication can be disentangled with proper controls, but in certain cases, there will always be some ambiguity in the sign and amplitude of the different signal source terms. In contrast, heterodyne detection involves the mixing of the signal field,  $\mathbf{E}_s$ , with a local oscillator field,  $\mathbf{E}_r$  at the detector,  $I_s \propto |\mathbf{E}_r|^2 + |\mathbf{E}_s|^2 + \mathbf{E}_r[\text{Im}(\mathbf{E}_s)\sin(\theta) + \text{Re}(\mathbf{E}_s)\cos(\theta)]$ , where  $\theta$  is the phase difference between the signal and reference (local oscillator) fields. Differential detection leaves the amplified cross term of interest  $\mathbf{E}_r[\text{Im}(\mathbf{E}_s)\sin(\theta) + \text{Re}(\mathbf{E}_s)\cos(\theta)]$ . The signal is now linear in the signal field, significantly amplified by the cross term with the reference field, and the relative magnitudes of the Re and Im terms contributing to the signal can be isolated by adjusting the phase of the reference field. Both the amplification in signal-to-noise ratio (SNR) and isolation of the Re and Im parts depend on the phase stability. *The ability of the signal field linearization and selective determination of the Re and Im components to the nonlinear susceptibility is the key enabling feature of DO-based nonlinear spectroscopy.*

Ideally, all interacting fields should be phase stabilized to better than  $\lambda/100$  to give commensurate gains in signal-to-noise. In optical spectroscopy, the central carrier wavelength is approximately 500 nm such that the required path length stability is on the order of 50 Å. For four-wave mixing alone, active feedback to phase lock all four laser fields on a routine basis is a significant challenge that has only recently been solved using a unique combination of well-engineered electronics and optomechanics.<sup>6</sup> In general, one needs to phase lock each field involved in a nonlinear interaction (four fields for four-wave mixing, six fields for six-wave mixing, etc.) such that this condition becomes even more problematic as one goes to higher order spectroscopies. In contrast, the required degree of phase stabilization has been achieved through the use of a simple DO in which both the complex beam patterns for phase matching and phase locked signal detection can be encoded in a single optic.<sup>3,7</sup>

*The new concept exploited in this work is not to eliminate noise but to generate correlations in the noise between the different interacting beams and have the noise cancel in the detection process.* Two topologically different interferometer designs have been developed both of which provide high phase stability and independent time delays for multidimensional spectroscopy. In one manifestation, all the beams are generated from the same DO using our previous approach<sup>3</sup> with one minor modification: variable glass delays are introduced for the various time dimensions.<sup>8–10</sup> The low-frequency noise is the same or correlated on all four beams such that the relative phase differences are passively stabilized. Second, it is

also possible to introduce anticorrelated noise in the excitation and probe/reference pulse pairs such that the noise exactly cancels in the signal detection.<sup>10</sup> This is a rather amazing effect that arises from the phase correlations imposed on the signal field through the interaction with the medium. We showed explicitly that by passing excitation/probe and excitation/reference pulse pairs down different arms of the interferometer that the difference in phase noise exactly cancels upon signal detection (Figure 2 of ref 10). The use of delayed pulse pairs is thus a general solution to phase stabilization and will dramatically improve the stability of any interferometer design for nonlinear spectroscopy. This design is also capable of introducing independent time variables without any intervening dispersive optics and has now made it possible to execute fully programmable pulse shaping in combination with nonlinear spectroscopy for both studying and controlling molecular coherences, as will be presented below.

**Four-Wave Mixing with Unique Applications to Protein Response Functions.** Proteins are highly effective “nanobearers” for facilitating chemical reactions. The specific three-dimensional structure is critical to control barrier heights and thereby various biochemical rates. Proteins are not static, and there is a spatial/temporal relationship between the proteins’ dynamics and their functions. In many cases, the global structure of the protein changes in response to chemical reactions at the receptor site as part of its biological function. The forces driving these structural changes are often derived from the formation of a single bond (receptor binding or dissociation). From the observed time scales, it is clear that the protein is not sampling its entire potential energy landscape but must be coarse grain sampling this surface along a highly constrained reaction coordinate.<sup>11</sup> Effectively, biological molecules have been exposed to evolutionary pressures that have led to an extraordinary degree of mode selective coupling over length scales not possible with our current level of chemical sophistication. The question is: what is the so-called director that leads to strongly correlated atomic motions in biological response functions?<sup>11,12</sup> Since proteins in general lack inversion symmetry, the most pronounced signature for mode selective coupling would be a change in the protein shape under the influence of a chemical reaction. Such motions are extremely small. In this application, DO-based four-wave mixing gives direct access to the protein motions through interferometric detection of the Re part of the complex susceptibility with high sensitivity. Detection of changes in protein radius of less than  $10^{-5}$  nm is possible.

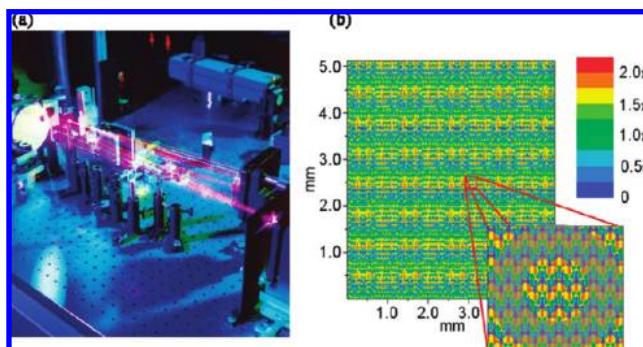
The functionally relevant motions of myoglobin with respect to the ligand binding coordinate were selectively stud-

ied through the isolation of the phase anisotropy induced by the very process of protein motion in executing its biological function. The structure change was photoinduced by breaking the Fe–CO bond (as a model for O<sub>2</sub>) that has been shown to dissociate along a repulsive surface within a half-period (26 fs) of the Fe–CO vibration with 100% quantum efficiency.<sup>13,14</sup> The protein was observed to be literally changing its shape within 500 fs.<sup>15</sup> The observed dynamics are consistent with the reaction forces at the heme site coupling to strongly damped collective motions of the protein. These results are our strongest evidence to date of the collective mode coupling mechanism providing the coarse grain sampling process (the “director”) of protein reaction coordinates.<sup>11</sup> The time base has been extended out to milliseconds using CW probes in which both dynamics and energetics of ligand escape out of the protein were fully resolved.<sup>11,16</sup> Other key problems in protein dynamics are now approachable in which even the most minute energetics driving biological processes can be resolved.

There are similar problems in understanding liquid dynamics where recent use of DOs has been able to significantly enhance the study of isotropic and anisotropic equilibrium fluctuations in liquids,<sup>3,17</sup> selectively study liquid solvation/repolarization dynamics around excited states and photoinduced reaction processes,<sup>18–20</sup> and use a four-wave mixing analogue of kinetic hole burning to observe solute–solvent relaxation dynamics.<sup>21</sup>

## Phase-Locked Multidimensional Coherent Spectroscopies: Approaching NMR Standards

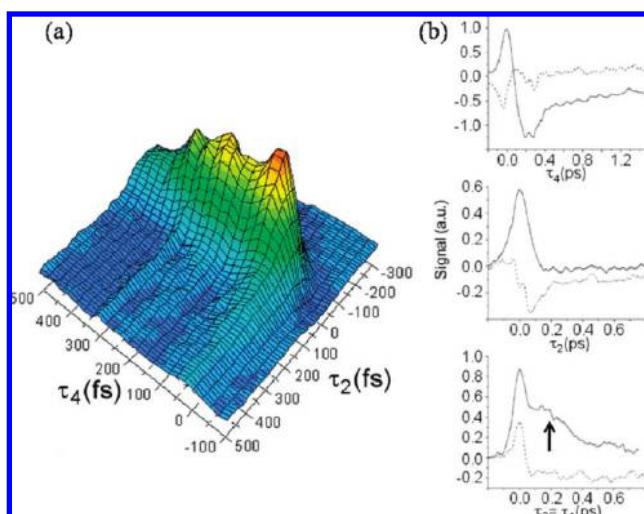
**Six-Wave Mixing: The Ultimate Challenge?** Using femtosecond laser pulses to impulsively excite low-frequency intermolecular Raman modes, a direct measure of the two-time correlation of the bath is obtained that can be connected to the many-body potential pertinent to the liquid state. Multi-time correlation functions can provide a direct determination of the intermolecular couplings. With the present limitations in peak power possible with pulsed terahertz methods, impulsive Raman is currently the only method capable of characterizing the highly anharmonic molecular motions defining the liquid state. It is this context that the original proposal of Tanimura and Mukamel for fifth-order Raman spectroscopy should be viewed as particularly illuminating.<sup>22</sup> This seminal work pointed out the important connection to the bath correlation function of liquids and identified a novel rephasing process involving a two-quantum transition, as shown schematically in Figure 1d.



**FIGURE 3.** (a) Photograph of six-wave mixing DO setup to show the compact nature of the interferometer and (b) phase profile of the six-wave mixing DO. The inset shows an expanded view and the requirement of the probe to spatially overlap with multiple Fourier components in the induced polarization to conserve the signal.

This spectroscopy holds the intriguing possibility of observing a bath echo, the rephasing of otherwise stochastic fluctuations defining the liquid state. The main experimental challenge is that the signals are extremely small. The rephasing process involves a Raman overtone that is by itself a small signal. This experiment is also particularly prone to cascaded lower order nonlinear  $\chi^{(3)}$  processes that only give information on the nuclear free induction decay and do not remove inhomogeneous broadening effects on the signal response.<sup>23</sup> This complication led to erroneous initial assignments and long debate on the origins of the signal response. There is a particularly valuable lesson in the scientific process here: what could be considered as a setback actually led to major advances in nonlinear spectroscopy. Once the problem was properly identified,<sup>23</sup> new concepts in phase-matching beam geometries with differential contrast between low- and high-order nonlinearities were introduced,<sup>24</sup> dependence on wavelength, path length, polarization, distinct tensor properties of the susceptibility, and signal phase were all exploited to solve this problem.<sup>25–27</sup> There have been similar advances in theory where the fifth-order nuclear response function has been shown to be an extremely sensitive test of intermolecular potentials used for modeling liquid state dynamics.<sup>26–28</sup>

The different experimental and theoretical approaches have now converged on the general form of the 2D Raman signal.<sup>27</sup> In this effort, the true power of the passive phase-locking properties of DO-based nonlinear spectroscopy was fully demonstrated. An otherwise extremely complex nonlinear experiment that would require active locking of the six interacting fields was reduced to a single optic (see Figure 3) and led to the first fully isolated fifth-order nuclear response function.<sup>7,27</sup> The DO element designed to perform this class of experiments is instructive in its own right. To attain good



**FIGURE 4.** (a) Two-dimensional Raman of  $\text{CS}_2$  for the  $R_{121211}$  polarization tensor element. The strong focusing of the signal along the  $\tau_4$  probe delay axis and absence of signal along the  $\tau_2$  excitation delay axis agrees with theoretical expectations. (b) Different slices for signal observed in the  $R_{122111}$  tensor element or Dutch Cross configuration that eliminates cascades as a test of signal purity. The rephasing or “bath echo” (indicated by arrow) is observable along the diagonal and shows the short-lived nature of a modal description of the liquid state (ref 25).

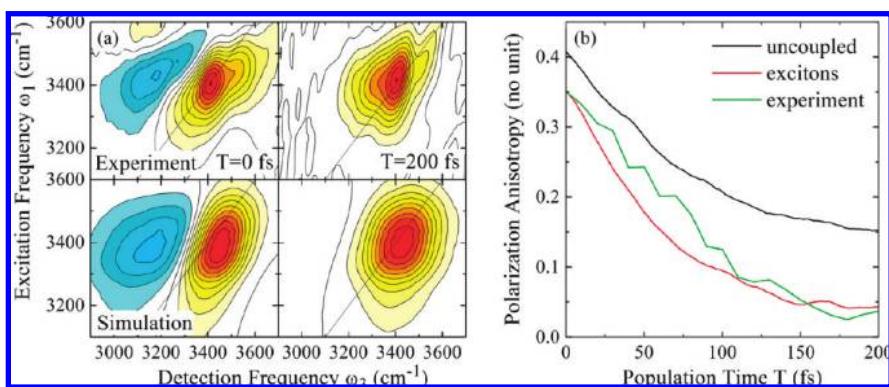
diffraction efficiency over the entire bandwidth, we had to systematically adjust up to 20 different Fourier components to achieve near optimal performance. The phase profile of the diffractive optic is directly related to the spatial profile of the induced nuclear polarization that leads to the generation of the fifth-order signal. Figure 3 shows the six-wave mixing diffractive optic surface relief in terms of a phase profile and gives a nice means to visualize the real space polarization induced in the sample.

With the DO approach, the 2D fifth-order Raman spectra of liquid  $\text{CS}_2$ <sup>7,25</sup> (see Figure 4 for first heterodyne-detected response), benzene,<sup>29</sup> and more recently the highly hydrogen-bonded liquid formamide have been obtained.<sup>30</sup> These experiments are the first steps toward direct studies of the intermolecular potential of liquid water where very distinctive differences in the 2D fifth-order Raman signal were predicted that will help refine our understanding of liquid water.<sup>27</sup> The small Raman polarization in water makes this experiment extremely challenging as the current approach has reached its limit, and the predicted signal from water is more than an order of magnitude smaller yet.<sup>27,28</sup> The intermolecular 2D spectrum of water remains an illusive target, requiring still more ingenuity from the spectroscopy community to reveal its secrets.

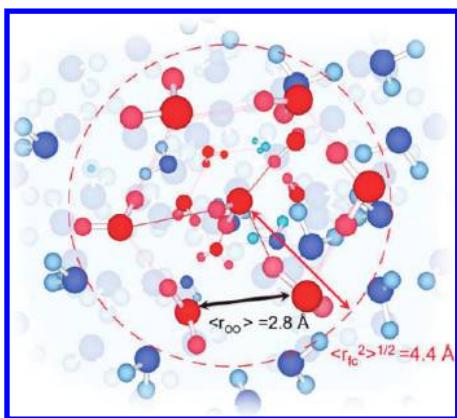
## Two-Dimensional IR: New Insights into the Hydrogen Bond Network of $\text{H}_2\text{O}$

An alternative approach to investigate the intermolecular forces within the hydrogen bond network of liquid water is coherent two-dimensional infrared (2D-IR) spectroscopy. The special properties of liquid water are attributed to the stronger, yet highly anharmonic, intermolecular forces arising from hydrogen bonding. Since the frequency of the OH oscillator is extremely sensitive to the local environment, the OH stretching vibration is the most direct probe of the hydrogen bond network. This correlation has been known for over 100 years since one of the first recorded IR spectra of water showed an anomalously broad vibrational bandwidth.<sup>31</sup> The issue as to whether the all important OH vibrational line shapes are inhomogeneously or homogeneously broadened has been one of the longest standing problems in spectroscopy, a glaring issue given the importance of water. The uncertainty in the degree of inhomogeneous broadening makes it impossible to infer the time scales for correlations within the hydrogen bond network or the relaxation dynamics among the different degrees of freedom. Two-dimensional IR spectroscopy directly gives information on the anharmonic terms in the intermolecular water potential and an immediate resolution of the inhomogeneous versus homogeneous nature of the line shape. The major technical stumbling blocks to resolving this issue are the incredibly strong absorption of water at vibrational resonances and the requirement of exceedingly high time resolution to fully resolve the dynamics of interest. To finally address this issue, we recently introduced nanofluidics for spectroscopic studies to obtain 400 nm pathlengths to solve the high OD problem and remove nonresonant window contributions from nonlinear spectroscopy that mask the fastest dynamics.<sup>32,33</sup> The use of the delayed pulse pairs/DO interferometer was essential to this experiment because the increased SNR was critical to keeping the excitation level at the small perturbation limit (5% excitation, effective temperature jump <6 °C).

The 2D-IR studies of liquid  $\text{H}_2\text{O}$  are shown in Figure 5, where the resolution to this long-standing problem was immediately apparent.<sup>32–34</sup> The elongation along the diagonal at zero waiting time clearly demonstrates that the water spectrum is inhomogeneously broadened. However, water can be counted on for more surprises. The loss in the frequency correlations occurred within 50–100 fs on the red side of the spectrum, within a period of the highest frequency librational components, effectively at the fundamental limit for loss in



**FIGURE 5.** (a) Experimental 2D data (top, ref 33) is compared with a theoretical calculation using a split-operator formalism (ref 34) to explicitly take into account the dipole–dipole coupling between water molecules, as obtained from fitting the experimental time-dependent anisotropy in panel b.



**FIGURE 6.** Combining the vibrational coherence time with the energy hopping time (Figure 5 from ref 33) allows estimation of the spatial delocalization of the OH stretch vibration. Within the coherence time, it is found to be delocalized over several waters (in red), as a disordered exciton schematically represented by the spatial diffusion length (dotted line). Reproduced with permission from ref 33. Copyright 2008, PNAS.

correlations, and more than an order of magnitude faster than isotopically substituted water. There were still more surprises. As the temperature was lowered, the frequency correlation time was found to dramatically increase to the point that the resonant energy transfer between water molecules could be used for the first time to probe the underlying length scale of the frequency correlations in the liquid state (schematically shown in Figure 6), particularly important for the hydrogen bond network of water.

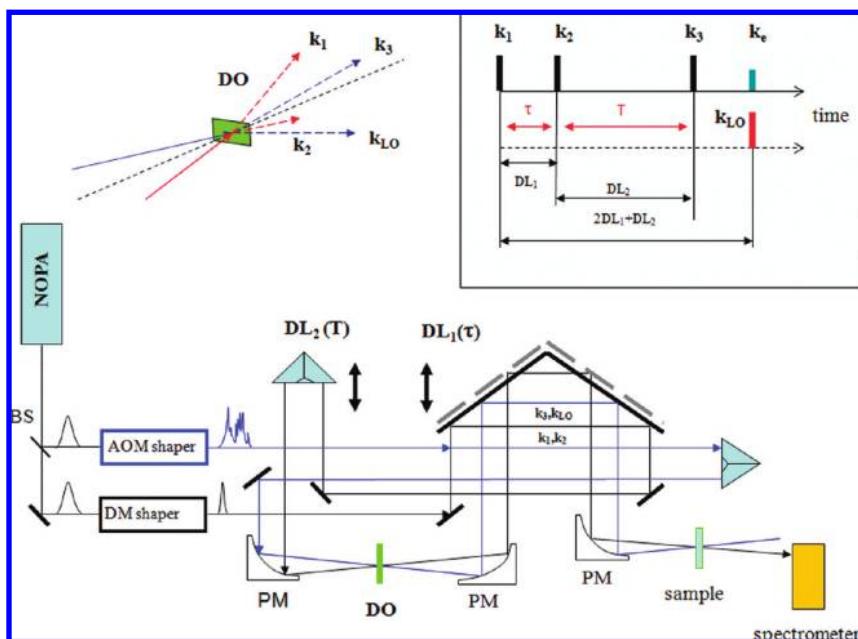
All the various degrees of freedom are found to exchange energy within the time scale of the highest frequency librational motions, the fastest rate possible with respect to energy conservation. There is no clear separation in time scales. All the modes, both intramolecular and intermolecular, are strongly mixed. Not even the highest frequency OH stretch can be defined properly within a molecular basis. The excitation is found to be spatially distributed over many water mol-

ecules to form an exciton-like state, a fundamentally different view of the primary excitations of liquid water.<sup>33,34</sup>

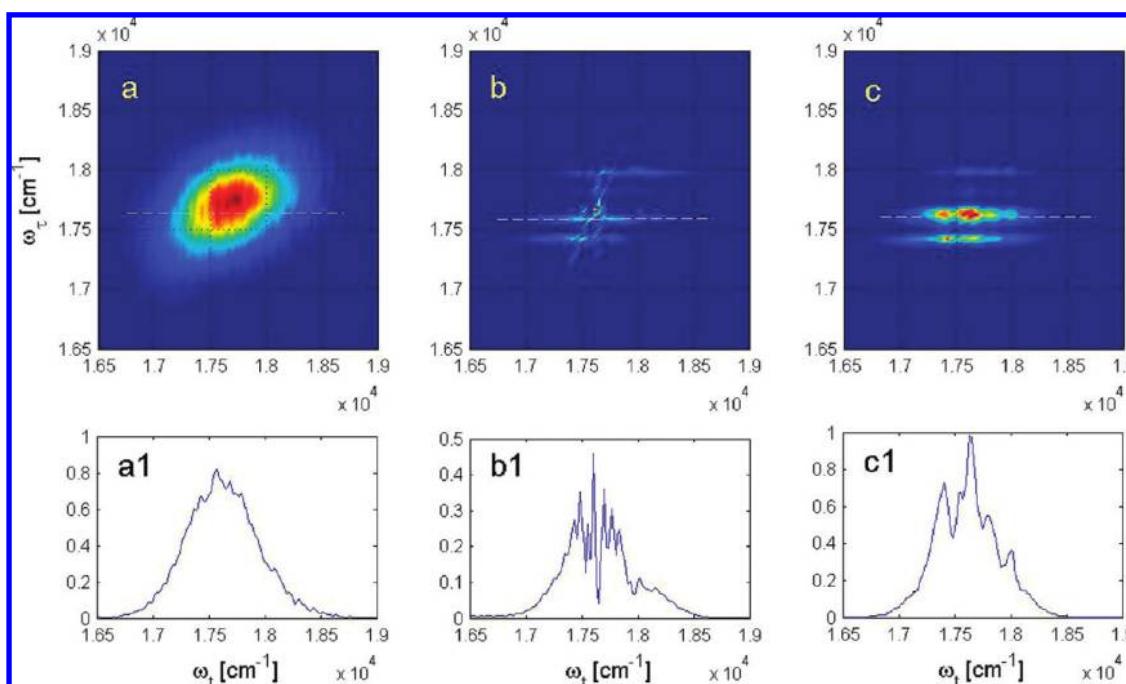
## Coherent Control 2D-Electronic Spectroscopy (2D-E): $\nu$ -Wave Mixing

The most fully generalized extension of 2D-spectroscopy is to combine pulse shaping with existing heterodyne-detected 2D-E spectrometry. Pulse shaping allows controlling the phase and spectrum of the excitation pulse, which enables one (i) to control the coherences, (ii) to control energy transfer flow in conjugated many-body quantum systems, and (iii) to increase the resolution of 2D spectra (sharpness of cross-peaks). The problem in implementing this concept is that embedding a pulse shaper(s) within a 2D spectrometer leads to a significant extension of the interferometer arms needed for the shaper optics and corresponding loss in phase stability. A new optical scheme, shown in Figure 7, solves this problem by fully decoupling the translation stages and using symmetry to effectively make the interferometer more compact. The “dephasing” scan only requires one translation stage to be moved. This is achieved by one additional pass of the “mother” beam for reading ( $k_3$ ) and the local oscillator pulses ( $k_{\text{LO}}$ ) through the “dephasing” translation stage DL1. Excellent phase stability, even for 6 m long interferometer arms, has been achieved with reported phase stability of  $\sim \lambda/100$  (for 20 min).<sup>35</sup> This is a general solution, using delayed pulse pairs for noise correlation/cancellation that can be combined in any standard interferometer design to enhance phase stability.

In the first coherent control 2D-E experiment, we investigated rhodamine 101 in methanol using the “optimal” pulse shape obtained previously from the coherent control of the population transfer in the weak excitation limit.<sup>36</sup> This shaped



**FIGURE 7.** Optical layout of the generalized 2D-MER (molecular electronic resonance) setup with pulse shapers. NOPA = non-collinear optical amplifier (pumped with 150 fs pulses at 775 nm); AOM = acousto-optical modulator; BS = broadband dielectric beam splitter; DM = controllable deformable mirror; DO = diffractive beam splitter; PM = parabolic mirrors with  $F = 15$  cm. Insets show (left) passing of beams through the DO and (right) the pulse timing diagram. The bandwidth of this interferometer exceeds  $6000\text{ cm}^{-1}$  corresponding to a time resolution of better than 10 fs to follow the fastest motions responsible for the underlying dynamics.



**FIGURE 8.** Two-dimensional electronic spectra of rhodamine 101/MeOH at  $T = 0$  measured with a 10 fs pulse (a), “optimal” pulse with both amplitude and phase shaping (b), and “optimal” pulse with amplitude shaping only (c). Panels a1–c1 show corresponding cross sections indicated in panels a–c by dashed lines.

pulse leads to increasing of efficiency of populating the  $S_1$ -state by  $\sim 20\%$  compared with nonshaped (transform-limited) pulses. Figure 8 shows the 2D power spectra at  $T = 0$  obtained with a nonshaped pulse, as well as pulses with both phase and amplitude modulation. The interaction of the

medium with the shaped pulse dramatically changes the 2D-E spectrum; instead of an unstructured spectrum as seen for the unshaped pulse, distinct structure appears in spectra using shaped pulses. Even from the 2D power spectra, one can clearly see that the modulation of the pulse’s amplitude spec-

trum leads to the appearance of fine structure across the 2D-map, whereas the phase shaping additionally gives fine structure along with a central peak with a fwhm of  $\sim 30$  cm $^{-1}$ . In this regard, it is interesting to compare the slice of the 2D spectrum to the pump–probe spectra using the same shaped “optimal” pulse (see ref 36, Figure 12 therein).

We are now able to do state-selective excitation with tailored pulses and control electronic/vibronic coherences via phase modulation to explore detailed excited state dynamics and issues of coherent vs incoherent interactions. Theoretical work treating explicitly phase relationships of coupled states and time orderings is now needed to fully understand the correlation between state preparation and decoherence. However, this first experiment demonstrates how important the application of coherently controlled multidimensional spectroscopy can be for studying the coherence in quantum systems.

## Future Prospect

Diffractive optics provide a single optic approach for simultaneous generation of beam geometries with built in phase matching and the passive phase stabilization of all the necessary laser fields to achieve phase-locked signal detection. Similar objectives are being explored using programmable pulse shaping to even further simplify the optical systems,<sup>5,37,38</sup> albeit with various trade-offs in sensitivity and spectral range. Phase-sensitive signal detection now avails to nonlinear spectroscopy the same kind of phase cycling used to isolate higher order correlation functions in various multidimensional NMR spectroscopies, but with DO-based spectrometers, the entire UV to IR part of the spectrum can be multiplexed. This advance opens up the use of phase contrast to observe distinct aspects of the nonlinear signal with all possible combinations of state preparations and spectral evolution. The new capability of combining this approach with pulse-shaping methods opens up a domain comparable to the riches multidimensional NMR afforded not so many years ago. For example, recent applications of DO-based 2D-E have provided beautiful observations of the importance of coherence in energy transfer observed for light-harvesting systems, self-assembled structures, and conjugated polymer systems.<sup>39–41</sup> The ability to control the phase of the prepared states should provide exquisite control over spatial propagation of the exciton state and site-specific determination of coherent terms in the coupling. From a reaction dynamics perspective, it is now possible to selectively prepare states, even far from equilibrium processes near reaction saddle points, to access information directly relevant to reactive crossings.

With the general philosophy that any problem requires information on structure, dynamics, and energetics, DO-based nonlinear spectroscopy is poised to significantly advance our understanding of the latter two processes and as such is of fundamental interest to chemistry.

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## REFERENCES

- Mukamel S. *Principles of Nonlinear Optical Spectroscopy*; Oxford University Press: New York, 1995.
- Cho, M. Coherent two-dimensional optical spectroscopy. *Chem. Rev.* **2008**, *108*, 1331–1418.
- Goodno, G. D.; Dadusc, G.; Miller, R. J. D. Ultrafast heterodyne detected transient grating spectroscopy using diffractive optics. *J. Opt. Soc. Am. B* **1998**, *15*, 1791–1794.
- Maznev, A. A.; Crimmins, T. F.; Nelson, K. A. How to make femtosecond pulses overlap. *Opt. Lett.* **1998**, *23*, 1378–1380.
- Vaughan, J. C.; Hornung, T.; Feurer, T.; Nelson, K. A. Diffraction-based femtosecond pulse shaping with a two-dimensional spatial light modulator. *Opt. Lett.* **2005**, *30*, 323–325.
- Yang, L.; Zhang, T.; Bristow, A. D.; Cundiff, S. T.; Mukamel, S. Isolating excitonic Raman coherence in semiconductors using two-dimensional correlation spectroscopy. *J. Chem. Phys.* **2008**, *129*, 234711.
- Astinov, V.; Kubarych, K. J.; Milne, C. J.; Miller, R. J. D. Diffractive optics implementation of six-wave mixing. *Opt. Lett.* **2000**, *25*, 853–855.
- Ogilvie, J. P.; Cowan, M. L.; Armstrong, M. R.; Nagy, A. M.; Miller, R. J. D. Diffractive Optics-Based Heterodyne Detected Three-Pulse Photon Echo. In *Ultrafast Phenomena XII*; Miller, R. J. D., Murnane, M. M., Scherer, N. F., Weiner, A. M., Eds.; Springer Series in Chemical Physics; Springer-Verlag, New York, 2003; Vol. 71, pp 571–573.
- Brixner, T.; Stiopkin, I. V.; Fleming, G. R. Tunable two-dimensional femtosecond spectroscopy. *Opt. Lett.* **2004**, *29*, 884–886.
- Cowan, M. L.; Ogilvie, J. P.; Miller, R. J. D. Two-dimensional spectroscopy using diffractive optics based phased-locked photon echoes. *Chem. Phys. Lett.* **2004**, *386*, 184–189.
- Miller, R. J. D. Mother Nature and the molecular Big Bang. *Can. J. Chem.* **2002**, *80*, 1–24.

- 12 Dwyer, J. R.; Hebeisen, C. T.; Ernstoffer, R.; Harb, M.; Deyirmenjian, V. B.; Jordan, R. E.; Miller, R. J. D. Femtosecond electron diffraction: 'Making the molecular movie'. *Philos. Trans. R. Soc., A* **2006**, *364*, 741–778.
- 13 Armstrong, M. R.; Ogilvie, J. P.; Cowan, M. L.; Nagy, A. M.; Miller, R. J. D. Observation of the cascaded atomic-to-global length scales driving protein motion. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 4990–4994.
- 14 Zhang, Y.; Fujisaki, H.; Straub, J. E. Molecular dynamics study on the solvent dependent heme cooling following ligand photolysis in carbonmonoxy myoglobin. *J. Phys. Chem. B* **2007**, *111*, 3243–3250.
- 15 Goodno, G. D.; Astinov, V.; Miller, R. J. D. Femtosecond heterodyne-detected four-wave-mixing studies of deterministic protein motions. 2. Protein response. *J. Phys. Chem. A* **1999**, *103*, 10630–10643.
- 16 Walther, M.; Raicu, V.; Ogilvie, J. P.; Phillips, R.; Kluger, R.; Miller, R. J. D. Determination of the Fe–CO bond energy in myoglobin using heterodyne-detected transient thermal phase grating spectroscopy. *J. Phys. Chem. B* **2005**, *109*, 20605–20611.
- 17 Heisler, I. A.; Meech, S. R. Polarization-resolved ultrafast polarizability relaxation in polar aromatic liquids. *J. Phys. Chem. B* **2008**, *112*, 12976–12984.
- 18 Underwood, D. F.; Blank, D. A. Measuring the change in the intermolecular Raman spectrum during dipolar solvation. *J. Phys. Chem. A* **2005**, *109*, 3295–3306.
- 19 Park, S.; Flanders, B. N.; Shang, X.; Westervelt, R. A.; Kim, J.; Scherer, N. F. Solvent intermolecular polarizability response in solvation. *J. Chem. Phys.* **2003**, *118*, 3917–3920.
- 20 Xu, Q.-H.; Ma, Y.-Z.; Stiopkin, I. V.; Fleming, G. R. Wavelength-dependent resonant homodyne and heterodyne transient grating spectroscopy with a diffractive optics method: Solvent effect on the third-order signal. *J. Chem. Phys.* **2002**, *116*, 9333–9340.
- 21 Khurmi, C.; Berg, M. A. Analyzing nonexponential kinetics with multiple population-period transient spectroscopy (MUPPETS). *J. Phys. Chem. A* **2008**, *112*, 3364–3375.
- 22 Tanimura, Y.; Mukamel, S. Two-dimensional femtosecond vibrational spectroscopy of liquids. *J. Chem. Phys.* **1993**, *99*, 9496–9511.
- 23 Blank, D. A.; Kaufman, L. J.; Fleming, G. R. Fifth-order two-dimensional Raman spectra of CS<sub>2</sub> are dominated by third-order cascades. *J. Chem. Phys.* **1999**, *111*, 3105–3114.
- 24 Blank, D. A.; Kaufman, L. J.; Fleming, G. R. Direct fifth-order electronically nonresonant Raman scattering from CS<sub>2</sub> at room temperature. *J. Chem. Phys.* **2000**, *113*, 771–778.
- 25 Kubarych, K. J.; Milne, C. J.; Lin, S.; Astinov, V.; Miller, R. J. D. Diffractive optics based six-wave mixing: Heterodyne detection of the full  $\chi^{(5)}$  tensor of liquid CS<sub>2</sub>. *J. Chem. Phys.* **2002**, *116*, 2016–2042.
- 26 Jansen, T. I. C.; Swart, M.; Jensen, L.; van Duijnen, P. T.; Snijders, J. G.; Duppen, K. Collision effects in the nonlinear Raman response of liquid carbon disulfide. *J. Chem. Phys.* **2002**, *116*, 3277–3285.
- 27 Milne, C. J.; Li, Y. L.; Miller, R. J. D. Two-Dimensional Fifth-Order Raman Spectroscopy. In *Time-Resolved Spectroscopy in Complex Liquids*; Torre, R., Ed.; Springer-Verlag: New York, 2008; pp 1–72 and references therein.
- 28 Hasegawa, T.; Tanimura, Y. Nonequilibrium molecular dynamics simulations with a backward-forward trajectories sampling for multidimensional infrared spectroscopy of molecular vibrational modes. *J. Chem. Phys.* **2008**, *128*, 064511.
- 29 Milne, C. J.; Li, Y. L.; Jansen, T. I. C.; Huang, L.; Miller, R. J. D. Fifth-order Raman spectroscopy of liquid benzene: Experiment and theory. *J. Phys. Chem. B* **2006**, *110*, 19867–19876.
- 30 Li, Y. L.; Huang, L.; Miller, R. J. D.; Hasegawa, T.; Tanimura, Y. Two-dimensional fifth-order Raman spectroscopy of liquid formamide: Experiment and theory. *J. Chem. Phys.* **2008**, *128*, 234507.
- 31 Aschkinass, E. Absorptionsspektrum des flüssigen Wassers. *Ann. Phys.* **1895**, *291*, 401–431.
- 32 Cowan, M. L.; Bruner, B. D.; Huse, N.; Dwyer, J. R.; Chugh, B.; Nibbering, E. T. J.; Elsaesser, T.; Miller, R. J. D. Ultrafast memory loss and energy redistribution in the hydrogen bond network of liquid H<sub>2</sub>O. *Nature* **2005**, *434*, 199–202.
- 33 Kraemer, D.; Cowan, M. L.; Paarmann, A.; Huse, N.; Nibbering, E. T. J.; Elsaesser, T.; Miller, R. J. D. Temperature dependence of the two-dimensional infrared spectrum of liquid H<sub>2</sub>O. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 437–442.
- 34 Paarmann, A.; Hayashi, T.; Mukamel, S.; Miller, R. J. D. Probing intermolecular couplings in liquid water with two-dimensional infrared photon echo spectroscopy. *J. Chem. Phys.* **2008**, *128*, 191103.
- 35 Prokhorenko, V. I.; Halpin, A.; Miller, R. J. D. Coherently-controlled two-dimensional photon echo electronic spectroscopy. *Opt. Express* **2009**, in press.
- 36 Prokhorenko, V. I.; Nagy, A. M.; Miller, R. J. D. Coherent control of the population transfer in complex solvated molecules at weak excitation. An experimental study. *J. Chem. Phys.* **2005**, *122*, 184502.
- 37 Wagner, W.; Li, C.; Semmlow, J.; Warren, W. S. Rapid phase-cycled two-dimensional optical spectroscopy in fluorescence and transmission mode. *Opt. Express* **2005**, *13*, 3697–3706.
- 38 Grumstrup, E. M.; Shim, S.-H.; Montgomery, M. A.; Damrauer, N. H.; Zanni, M. T. Facile collection of two-dimensional electronic spectra using femtosecond pulse-shaping technology. *Opt. Express* **2007**, *15*, 16681–16689.
- 39 Brixner, T.; Stenger, J.; Vaswani, H. M.; Cho, M.; Blankenship, R. E.; Fleming, G. R. Two-dimensional spectroscopy of electronic couplings in photosynthesis. *Nature* **2005**, *434*, 625–628.
- 40 Collini, E.; Scholes, G. D. Coherent intrachain energy migration in a conjugated polymer at room temperature. *Science* **2009**, *323*, 369–373.
- 41 Milota, F.; Sperling, J.; Nemeth, A.; Kauffmann, H. F. Two-dimensional electronic photon echoes of a double band J-aggregate: Quantum oscillatory motion versus exciton relaxation. *Chem. Phys.* **2009**, *357*, 45–53.