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CHAPTER 5

Multidimensional Electronic and Vibrational Spectroscopy: An Ultrafast Probe of Molecular Relaxation and Reaction Dynamics

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Abstract

Multidimensional optical spectroscopy in the visible and infrared is a rapidly developing technique enabling direct observation of complex dynamics of molecules in complex environments such as liquids and proteins. Measuring the correlation between excited and detected frequencies with sub-picosecond resolution has enabled the resolution of long-standing problems such as energy transfer in photosynthesis and the life-sustaining structural rearrangements of liquid water. This chapter aims to provide a bridge between the concepts familiar in the AMO physics community and how those ideas and experimental methods are applied to condensed phase molecular spectroscopy. We outline the technical challenges of these powerful methods while considering a few examples of experiments that showcase the unique perspective offered by 2D electronic and vibrational spectroscopy.

1. INTRODUCTION, BACKGROUND, AND ANALOGIES

Detailed understanding of molecular processes in condensed phases requires spectroscopic probes of short length scales, providing ultrafast time resolution with wavelengths ranging from the far infrared to the ultraviolet. Following extensive progress in pushing temporal resolution to the femtosecond level and below, the current state of the art of optical spectroscopy of molecular dynamics in liquids, solutions, at surfaces, and in complex biological environments, is to extract the greatest possible spectral information while maintaining the traditional time resolution of ultrafast spectroscopy. The approach discussed in this chapter uses methods of photon echoes and hole burning to spread frequency information on to two or more axes, reducing the spectral congestion that results from strong system–bath interactions. Since the first experimental demonstrations a decade ago (Hamm et al., 1998; Hybl et al., 1998; Lepetit & Joffre, 1996; Likforman et al., 1997), multidimensional optical (visible and infrared) spectroscopy has been applied to address many of the most fundamental questions in condensed phase dynamics, and the majority of that progress has been reviewed recently (Cho, 2008; Ganim et al., 2008; Hamm et al., 2008; Jonas, 2003; Wright, 2002; Zheng et al., 2007;
Khalil et al., 2003a). Viewed operationally, multidimensional spectroscopy appears to be nothing more than an adaptation of established atomic and molecular optics techniques to the field of “chemistry.” The aim of this chapter, however, is to outline the points of contact and departure from the experimental methods and conceptual frameworks that underpin the application of multipulse (or multfield) spectroscopy in different regimes.

1.1 Timescales and Orders of Magnitude

In the condensed phase, electronic and vibrational spectral features often are not determined by the lifetime of the excited state. For example, the spectral width of the absorption of a common dye molecule, rhodamine 6G, in ethanol solution is roughly 1400 cm\(^{-1}\) (41 THz, 170 meV), and its broad emission spectrum is \(\sim 6000 \text{ cm}^{-1}\) (170 THz, 745 meV). Despite these very broad line widths, the excited state lifetime is 4 ns, from which one would predict a wholly unphysical Lorentzian line width of 0.0017 cm\(^{-1}\) (50 MHz, 207 neV). Clearly, the relevant system–bath interactions responsible for the spectral line widths are qualitatively distinct from those that determine the population relaxation.

Using traditional language, it is common to separate a spectral width into homogeneous and inhomogeneous contributions, leading naturally to the pulsed photon echo technique or the frequency-domain hole-burning method to dissect the lineshapes experimentally. This approach highlights a key feature of systems studied in the condensed phase: inhomogeneities are not static, and not all systems possess a single homogeneous line width. The most widely used example of inhomogeneity within the context of atomic and molecular optics is Doppler broadening. In the absence of collisions during transit through the measurement apparatus, the distribution is static. In solution, however, a spectroscopically observed molecule constantly interacts with its surroundings leading to fluctuations of its eigenstate energies on a timescale that is comparable to or longer than the “homogeneous” dephasing time. The experimental goal is therefore to determine the timescale for the stochastic sampling of the available microenvironments. Such measurements determine the time taken by a spectroscopically “labeled” subpopulation to randomize, which often connects directly to the degree of system–bath coupling, the magnitude of structural rearrangements and the extent of excitation delocalization. In this context, we refer to “labeling” in the same way that a hole-burning experiment optically tags a subpopulation or transition. The timescale of frequency randomization varies, but for typical condensed phase systems it is generally below a few picoseconds, and often it is subpicosecond. The experimental 2D data, unfortunately, do not uniquely determine an atomistic-level understanding, and it is widely
appreciated that theoretical and computational modeling plays a key role in unpacking the spectral information content (Asbury et al., 2004c; Cho, 2008; Cho et al., 2006; Cho & Fleming, 2005; Corcelli et al., 2004; Dreyer, 2005a,b; Eaves et al., 2005a,b; Fecko et al., 2003; Fleming & Cho, 1996; Hanna & Geva, 2008a,c; Moran et al., 2003a,b; Paarmann et al., 2008; Schmidt et al., 2007; Skinner et al., 1981; Woutersen et al., 2002). Quantum mechanical calculations are required to treat optical excitations and determine transitions frequencies, but extended condensed phase systems are only tractable using classical molecular dynamics simulations. Considerable recent progress is ongoing to embed, self-consistently, a quantum subsystem within a classical simulation, though this is an active area of current research (Hanna & Geva, 2008a,b,c).

1.2 The AMO Perspective: Photon Echoes, Ramsey Fringes, and NMR

Borrowing some ideas from nuclear magnetic resonance, the problem of inhomogeneous broadening has been addressed using nonlinear optical spectroscopy. The Hahn echo, originally observed in nuclear spins (Hahn, 1950), was adapted to atomic systems first in the case of ruby (Kurnit et al., 1964) and later was generalized to gases (Patel & Slusher, 1968). Figure 1 shows the stimulated photon echo pulse sequence along with the $2 \times 2$ density matrix for a two-level system (2LS). The sequence has three time intervals, $t_1$, $t_2$, and $t_3$, where due to interactions with the three fields,
$E_1$, $E_2$, and $E_3$, the system evolves alternately in coherences ($\rho_{jk}$) and populations ($\rho_{jj}$). What makes the sequence an ‘‘echo’’ is the phase conjugation between the two coherence evolution periods. During $t_1$ the density is $\rho_{01}$ and during $t_3$ it is $\rho_{10}$, thus effectively reversing the sign of time in the field-free Green function responsible for the system’s evolution during the second coherence interval. The lower set of density matrices shown during $t_2$ and $t_3$ indicate an alternative pathway where the system returns to the ground state following the second excitation pulse. Both the excited state and ground state paths are required to evaluate the system response to the applied fields. As is typically done in quantum optics, the macroscopic polarization is equal to the number density, $N$, of two-level systems multiplied by the expectation value of the dipole operator $\mu$, viz:

$$P(t_3) = N\text{Tr}[\rho(t_3)\mu].$$

Since the coupling between the external fields and the molecular system is generally weak, the density matrix is typically evaluated perturbatively to third order, though for systems whose low dimensionality permits it there are nonperturbative schemes to evaluate the induced polarization and isolate the terms corresponding to the photon echo signal. It should be noted that in the perturbative regime, one typically considers the $n$th order nonlinear susceptibility, $\chi^{(n)}$, and multidimensional spectroscopy is based on the fact that the entire $n$th order susceptibility can be measured, including the phase. It is customary to define $\chi^{(n)}(\omega_1, \omega_2, \ldots, \omega_n)$ in the frequency domain, and the response function $R^{(n)}(t_1, t_2, \ldots, t_n)$ in the time domain. Both quantities are tensors, and all aspects of the polarizations of the input and output fields are needed to compute the optical properties as well as to understand the underlying microscopic molecular processes.

The conventional interpretation of a photon echo experiment represents the state of the system using a pseudospin vector on the Bloch sphere (Bloch, 1946). By transforming to the rotating frame, each member of the inhomogeneous ensemble precesses away from the origin at a rate proportional to the difference between the specific frequency $\omega_i$ and the frame rotation frequency $\omega_0$. When $t_2 = 0$, the second and third pulses flip the vectors leading to the phase conjugation. The echo is emitted when the vectors precess freely back to the origin, hence the gradual increase and decrease of the echo signal. Choosing $t_2 > 0$ permits incoherent relaxation to occur before the refocusing pulse, providing access to lifetime measurements and observation of spectral diffusion processes due to microscopic site randomization. Indeed, it is precisely the $t_2$-dependence that provides much of the chemical information in condensed phase photon echo experiments.
The most commonly implemented strategy to obtain multidimensional optical spectra is based on the photon echo sequence. Since the goal is spectral resolution, rather than determining dephasing rates by changing the time delays, the information one seeks is generally in the frequency domain. Thus, the emission frequency information is obtained by measuring the emitted signal field in a spectrometer by interferometric combination with a fully characterized reference local oscillator field (Dorrer et al., 2000; Gallagher et al., 1998; Lepetit et al., 1995; Lepetit & Joffre, 1996; Likforman et al., 1997), which is typically derived from $E_3$ (Figure 1). A Fourier transform algorithm can be used to isolate the electric fields using spectral interferometry (Lepetit et al., 1995). Given this ability to measure the signal field as a function of $\omega_3$, the excitation frequency information is obtained by scanning the $t_1$ delay and then Fourier transforming the recorded spectra along this dimension, yielding $\omega_1$. The result of the above procedure is a two-dimensional spectrum correlating the excited frequency $\omega_1$ with the detected frequency $\omega_3$ at a specific value of the so-called “waiting time” $t_2$. Further discussion of the details of obtaining 2D lineshapes that correspond to absorptive processes are described below.

As an illustration using a model of alternatively homogeneously and inhomogeneously broadened 2D spectra, Figure 2 shows simulations of 1D and 2D spectra for a two-level system (Faeder & Jonas, 1999). The 2D spectrum of a 2LS with exponential dephasing is a 2D Lorentzian, and the net 2D spectrum of an ensemble of 2LSs is the sum of the individual 2D spectra. The two models produce similar 1D absorption spectra using the same size ensembles. The two 2D spectra, however, show a clear difference in the shape of the spectrum. For the homogenous model there is essentially no specific dependence of the emission frequency on the excitation frequency, whereas the inhomogeneous model exhibits a clear correlation between excitation and emission frequencies. The spectral correlation, whose signature is the pronounced elongation along the frequency diagonal ($\omega_1 = \omega_3$), directly reflects the underlying inhomogeneous distribution. The asymmetry of the 2D lineshape as seen in the slices (Figure 3) provides a measure of the degree of inhomogeneous broadening. In the discussion so far, dynamics in the system is only contained in the spectral lineshape. As will be discussed below, some of the most chemically relevant information is obtained by observing how the 2D lineshape asymmetry relaxes as the waiting time is increased (Cho, 2008; Faeder & Jonas, 1999; Kwak et al., 2008b; Lazonder et al., 2006). This kind of information is one of the key distinctions between how the photon echo pulse sequence is used in multidimensional spectroscopy and how it is used in atomic physics.

Another experimental method commonly employed in traditional AMO physics is the production of Ramsey fringes with spatially separated fields (Ramsey, 1950). First demonstrated in the microwave spectral
domain, Ramsey fringe spectroscopy (Figure 4) has been adapted to many situations using both linear and Doppler-free, two-photon absorption approaches, temporal pulses, and additional fields (Ramsey, 1995). From the system’s perspective, the coherence induced through the first interaction is read out by a second field whose effective time delay is determined by the transit time between the fields. For an atomic beam at finite temperature the Maxwell–Boltzmann distribution of molecular speeds in the $z$-direction imparts a static inhomogeneity that is manifested as a distribution of transit-time broadening. The phase acquired for an atom moving at a velocity $v_i$ with center frequency $\omega_i$ in transiting the distance $\Delta z$ between the two fields is $\omega_i t_i$, where $t_i = \Delta z / v_i$. As a function of the laser frequency $\omega_0$, which is tuned through the resonance of the atoms, fringes develop in the resulting fluorescence emission measured after the last field. The spectral resolution achievable with the Ramsey fringe method is inversely proportional to the distance between the fields. Clearly the method can only function in systems where the dephasing time—the time for the decay of the initially produced coherence—is much

**FIGURE 2** Model 2D spectra for an ensemble of two-level systems with (left) primarily homogeneous broadening, and (right) inhomogeneous broadening. The inhomogeneous broadening leads to a distinctive frequency correlation parallel to the $\omega_1 = \omega_2$ diagonal. For most systems of interest in condensed phase dynamics, this inhomogeneity is transient and as the waiting time between excitation and detection is increased, the 2D lineshape asymmetry relaxes.
longer than the transit between the two fields. In solution or in liquids, there is no analogous experiment, since diffusion is the limiting transport process. One might imagine, however, that mass-selected clusters may be able to be studied using a Ramsey fringe method in the gas phase. Despite the clear analogy between Ramsey fringes and photon echoes, again the inhomogeneity is static, and the vast majority of the formal theoretical developments of both Ramsey fringes and photon echoes are for static systems of two- or three-levels with very weak coupling to the environment (i.e., via spontaneous emission). Thus the similarities aid in making translations between the molecular questions of condensed phase dynamics and isolated atoms, but the differences highlight the motivation to use multidimensional spectroscopy as a probe of dynamics in complex environments.

**FIGURE 3** Slices through the simulated 2D spectra shown in Figure 2. The blue curves show diagonal slices, and the green curves show the antidiagonal slices passing through the peak maximum. The difference in line width is a measure of the inhomogeneity.
It has been customary to draw analogies between multidimensional spectroscopy and multidimensional NMR spectroscopy (Scheurer & Mukamel, 2002). Despite many parallels in experimental implementation and data processing, however, the key strengths of multidimensional spectroscopy are manifest most clearly when the analogies fail. More specifically, whereas a set of coupled spin-1/2 particles gives rise to a $2^N$-dimensional space of system eigenstates, a simple pair of coupled oscillators gives rise to an infinite dimensional state space. Furthermore, important information regarding the anharmonic nature of the underlying potential surfaces is contained in transitions involving states other than those in the ground and first excited vibrational exciton bands. Calculating the transition frequencies and transition dipoles in the 2D spectra from first principles is far more challenging than in the case of NMR. Spins also interact only very weakly with their environments, so that although the emitted signals are vanishingly small, there is virtually no penalty for increasing the number of pulses in the sequence, enabling the observation of correlations between many different kinds of nuclei. Finally, the existence of a nonlinear optical signal is conditioned by the anharmonic nature of the Hamiltonian. In the case of vibrations, anharmonicities often constitute a relatively small fraction of the overall transition frequencies; they may overlap spectrally with the fundamental transitions thereby diminishing the signal. In electronic systems, there are often overlapping and unintuitive excited states. Such complicated energy level structure does not exist in the case of NMR. The intrinsic time
resolution of NMR is orders of magnitude lower than optical 2D spectroscopy, which is necessarily performed with ultrafast (<100 fs) pulses. Thus, from a practical viewpoint multidimensional spectroscopy can be used as an ultrafast probe of triggered, nonequilibrium chemical events on the femtosecond to picosecond timescale (Baiz et al., 2008; Bredenbeck et al., 2004, 2005, 2007; Cervetto et al., 2008; Chung et al., 2007; Kolano et al., 2006; Smith & Tokmakoff, 2007b).

1.3 Diagrammatic Representation of Dynamical Evolution

Most textbooks on quantum and nonlinear optics describe the system response to a series of pulses using a two-level system and encode the four density matrix elements in three coordinates (Allen & Eberly, 1987). An applied field may be viewed as imparting a torque, \( \Omega \), on the three-dimensional vector, \( s \), as:

\[
\frac{ds(t)}{dt} = \Omega(t) \times s(t).
\]  

(2)

By inserting exponential relaxation of the inversion \( \rho_{11} - \rho_{00} \) with a decay time given by \( T_1 \) and coherences, \( \rho_{12} \) and \( \rho_{21} \), given by \( T_2 \), realistic models of atomic dynamics can be used to predict and interpret multipulse experiments. It is common to obtain results for the generated signal by directly integrating the equation of motion for the Bloch vector, leading to familiar effects of free-induction decay, Rabi oscillations, optical nutation, electromagnetic-induced transparency, and photon echoes (Allen & Eberly, 1987). For situations where the inversion is small, due to large detuning from atomic resonance or because the fields are weak, the time-dependence may be evaluated perturbatively by expanding the system response in powers of the applied field (Borde´, 1983). The perturbative treatment naturally leads to a finite-order signal that appears at a well-defined spatial location \( \mathbf{k}_s = \pm \mathbf{k}_1 \pm \mathbf{k}_2 \pm \mathbf{k}_3 \pm \cdots \) and emission frequency \( \omega_s = \pm \omega_1 \pm \omega_2 \pm \omega_3 \pm \cdots \). For the purposes of enumerating the possible field-matter interaction events and field-free evolution periods, one often graphically represents the given term in the perturbation sum (Berman & Lamb, 1970). Shown in Figure 5, we adopt the convention commonly used in the 2D community and show an energy level diagram where field interactions are represented as vertical arrows, with solid arrows indicating that the interaction raises or lowers a bra-side density matrix element, while the dashed arrows indicate transitions made to the ket side (Ulness et al., 1998). Choosing a particular signal direction fixes the wave vectors of the exciting fields. A diagrammatic method helps to list exhaustively all evolution pathways by representing the density matrix as two vertical lines and the field interactions as arrows that point up and to the right for
positive wave vector, and up and to the left for negative wave vector (Bordé, 1983). In analogy with other diagrams used to sum perturbation series, these diagrams have come to be called “double-sided Feynman” diagrams. To enumerate all paths, all permutations are required such that the arrow direction and time ordering is preserved. For example, a field with wave vector of \(-k_2\) contributes by inducing a downward transition on the left (ket side), and an upward transition on the right (bra side). The only constraint is that the system must terminate in a population after the emission of the signal to ensure a nonzero trace. With these rules, it is straightforward to list all possible pathways to \(n\)th order provided the energy levels and transition dipole moments connecting the levels are known.

Figure 5 shows double-sided Feynman diagrams with the corresponding energy level diagrams for a three-manifold, three-level system. For the first three fields, ket- and bra-side interactions are denoted with dashed and solid arrows, respectively. The emission of the signal field is denoted by a thick solid arrow. Abbreviations used are ground state bleach (GSB), stimulated emission (SE), and excited state absorption (ESA).
leads to a net weight for the induced absorption that is twice that of the ground state bleach signal $|\mu_{\alpha 0}|^2 |\mu_{ba}|^2 = 2|\mu_{\alpha 0}|^4$. The nonlinear signal’s existential dependence on anharmonicity in the molecular potential makes the spectroscopy particularly sensitive to precisely those aspects of the Hamiltonian that linear spectroscopy cannot reveal.

To provide a general description of the types of 2D lineshapes that have been observed in several experimental contexts, Figure 6 shows a schematic spectrum corresponding to the three-level system depicted in Figure 5. The slanted peak with solid contours illustrates the spectrum due to the ground state pathways such as ground state bleach (GSB) and stimulated emission (SE), whereas the dashed contours, which have opposite sign, indicate the excited state absorption (ESA). In most of the vibrational systems that have been studied, the ESA slant appears roughly parallel to the ground state contribution, indicating that the inhomogeneity does not substantially affect the anharmonicity. There may be systems, however, where the correlation between the 0–1 and the 1–2 transitions is more complicated, leading to qualitatively different ground state and excited state lineshapes. In electronic spectroscopy, there are not as simple universal trends in the relationship between the first and second excited manifolds, and the inhomogeneity of ESA has not yet been explored experimentally.

**FIGURE 6** Cartoon 2D spectrum for a three-manifold, three-level system showing the ground state (solid) and excited state (dashed) contributions to the signal. The diagonal elongation indicates inhomogeneous broadening. In a harmonic system, the positive ground state and negative excited state signals overlap spectrally, thus interfering destructively.
Systems with multiple states in the first excited manifold exhibit a characteristic pattern of cross-peaks in a 2D spectrum in the same way that such peaks are observed in 2D NMR spectra. The simplest model where cross-peaks arise is shown in Figure 7 for a two-manifold, three-level system. There are two related phase-matching conditions termed rephasing \((k_R = -k_1 + k_2 + k_3)\) and nonrephasing \((k_{NR} = +k_1 - k_2 + k_3)\). The significance of these two directions is discussed below regarding the 2D spectral lineshape. Here, we briefly mention that in the “rephasing” geometry, the system evolves at conjugate frequencies during the two coherence periods and can therefore produce an “echo.” In the “nonrephasing” case, system evolution occurs at the same frequency during both coherence periods and, therefore, cannot produce a macroscopic rephasing. We point out the two sequences to highlight the differences in the peak locations in a system with strong coupling leading to cross-peaks. For the rephasing sequence there are two paths that lead to a given cross-peak, and two that lead to a given diagonal peak. In the nonrephasing sequence, however, three paths lead to diagonal peaks while only one leads to the cross-peak. It is noteworthy that the paths evolving as coherences contribute differently in their locations in the rephasing and nonrephasing sequences (Khalil et al., 2004; Nee et al., 2008). The rephasing coherence paths involve excitation at one frequency and emission at the other frequency, whereas the nonrephasing coherence paths are due to excitation and detection at the same frequency. Thus, the modulation that is due to these coherences appear on the cross-peaks for the rephasing sequence and on the diagonal for the nonrephasing sequence (Engel et al., 2007; Khalil et al., 2004; Nee et al., 2008; Nemeth et al., 2008, 2009; Tekavec et al., 2009).

A schematic 2D spectrum for the multilevel system depicted in Figure 7 is shown in Figure 8. Although the level diagrams of Figure 7 suppress the second excited state manifold for simplicity, this cartoon spectrum includes the cross-peaks due to ESA (Golonzka et al., 2001). The cartoon shows two diagonal peaks with their corresponding red-shifted ESA peaks of opposite sign, as well as two cross-peaks (solid contours) and the associated cross-peaks (dotted contours) that are due to ESA. By measuring the relative magnitudes of these peaks it is possible to constrain a coupled Hamiltonian model of the underlying eigenstates, including the relative orientations of the transition dipoles (Golonzka et al., 2001).

1.3.1 Causality and the Absorptive Lineshape

Due to the obvious causality of the linear optical response that follows optical excitation, there is a simple relationship between absorption and dispersion via the Kramers–Kronig relations. In higher order response
As in Figure 5, double-sided Feynman diagrams and wave mixing energy level diagrams for a two-manifold, three-level system. The paths leading to coherences during $t_2$ are labeled.
functions the relationship is less transparent (Faeder & Jonas, 1999). Obtaining absorptive lineshapes is of particular interest since the often uninteresting dispersive effects of density and thermal gratings can complicate the extraction of the response due solely to resonant absorption and emission. Separating absorptive spectra from dispersive contributions also maximizes the information content of a 2D spectrum, allowing discrimination of signals such as ESA and GSB that have different relative signs. It has been recognized that the real part of the photon echo signal does not contain the purely absorptive 2D spectrum unless two different experiments are recorded where the roles of the first and second pulses are interchanged (Hybl et al., 2001b; Khalil et al., 2003b). In the conventional echo sequence, the signal is detected in the rephasing ($k_R = -k_1 + k_2 + k_3$) direction. To obtain an absorptive 2D spectrum, it is necessary to also measure the signal that emerges in the nonrephasing ($k_{NR} = +k_1 - k_2 + k_3$) direction and add this to the rephasing signal. Drawing analogies to NMR spectroscopy, Jonas and coworkers have explained the reasoning behind the requirement of measuring both rephasing and nonrephasing pathways (Faeder & Jonas, 1999). Consider the sequence of pulses in the 2D measurement as depicted

![Cartoon 2D spectrum for a three-manifold, three-level system. The solid diagonal and cross-peaks arise from the pathways shown in Figure 10. The additional dashed and dotted peaks are due to excited state absorption. 2DIR spectra typically show both diagonal (dashed) and off-diagonal (dotted) anharmonicity.](image)

**FIGURE 8** Cartoon 2D spectrum for a three-manifold, three-level system. The solid diagonal and cross-peaks arise from the pathways shown in Figure 10. The additional dashed and dotted peaks are due to excited state absorption. 2DIR spectra typically show both diagonal (dashed) and off-diagonal (dotted) anharmonicity.
in Figure 9. Prior to excitation by the third pulse, the system is in a population; causality dictates that the 2D signal we seek should be zero, implying a Kramers–Kronig relationship with respect to the time variable $t_3$ (assuming delta function pulses). However, a similar causal relationship does not hold with respect to the time variable $t_1$, during which the system is in a coherence. Here, a negative $t_1$ delay corresponds to an inversion of the time ordering of the first two pulses, with signal being present at positive and negative $t_1$ values, regardless of the pulse ordering. Thus, collecting the signal in a single phase-matching direction for a fixed value of the waiting
time $t_2$ amounts to truncating the signal at $t_1 = 0$, resulting in a mixing of real and imaginary components in the Fourier transform with respect to $t_1$. To avoid this problem, symmetric recording of the signal with respect to $t_1$ is needed, permitting a complex Fourier transform over the full range $-\infty < t_1 < \infty$ (Faeder & Jonas, 1999; Hybl et al., 1998). Obtaining this full range to successfully separate absorptive and dispersive spectra can be achieved experimentally using a number of different approaches that will be discussed in further detail in Section 2. We note that for large values of $t_2$ if the system evolution is slowly varying, a scan over positive and negative $t_1$ delays in a single phase-matched direction should suffice for collecting both rephasing and nonrephasing pathways, as illustrated in Figure 9.

Depending on the experimental approach used for obtaining rephasing and nonrephasing signals, an additional step may be required to unambiguously assign the absorptive and dispersive components of the 2D spectrum. This ambiguity arises unless the absolute phase of the radiated signal is known. Since many experimental implementations measure the complex rephasing and nonrephasing signals by spectral interferometry with a reference field, only phase differences are directly measured, leaving an undetermined phase offset. The solution that is commonly used is to rely on the projection slice theorem (Faeder & Jonas, 1999), which states that the real part of the projection of the 2D spectrum along the $w_1$ axis is equal to the spectrally resolved pump-probe signal (Hybl et al., 2001b). This method requires a separate acquisition of the spectrally resolved pump-probe signal for the appropriate $t_2$ delay. Several alternative approaches have recently been developed to measure the absolute phase directly (Backus et al., 2008a; Bristow et al., 2008). Alternately, the pump-probe implementation of 2D spectroscopy avoids this problem altogether and will be discussed in Section 2.2.

1.4 Molecular Perspective

Since $n$th-order multidimensional spectroscopy essentially involves the measurement of the $n$th-order optical response function, there are clearly many parallels with the experiments and formalism developed within the context of AMO physics. Here we outline the types of molecular phenomena that are particularly well suited to study with multidimensional spectroscopy.

1.4.1 Coupling

Any spectroscopic technique measures transitions between energy eigenstates, and these eigenstates do not always correspond to spatially localized excitations. The inherent freedom granted by quantum mechanics to choose
any convenient basis often allows one to use a basis that is structurally intuitive. Upon choosing a \(N\)-dimensional basis, it is possible to express the potential energy in the Hamiltonian in terms of the \(N\) coordinates expanded about a reference configuration \(\mathbf{q}_0 = (q_0^1, q_0^2, \ldots, q_0^N)\):

\[
V(q_1, \ldots, q_N) = \sum_{j,k=1}^{N} \frac{\partial^2 V}{\partial q_j \partial q_k} |_{\mathbf{q}_0} (q_j - q_j^0)(q_k - q_k^0) \\
+ \sum_{j,k,l=1}^{N} \frac{\partial^3 V}{\partial q_j \partial q_k \partial q_l} |_{\mathbf{q}_0} (q_j - q_j^0)(q_k - q_k^0)(q_l - q_l^0) + \ldots,
\]

where the first sum of terms includes the harmonic \((j = k)\) contribution as well as the bilinear \((j \neq k)\) coupling. A nonzero nonlinear optical response requires terms in the potential beyond second order, and the lowest of these appear in the second sum. The diagonal anharmonicity \((j = k = l)\) accounts for the anharmonicity along each of the basis coordinates, whereas the off-diagonal anharmonicity accounts for coupling through the anharmonicity. In principle, an \(n\)th-order spectroscopy can only measure terms to \(n\)th-order in the potential, but the eigenenergies will generally be sensitive to higher order terms as well as the finite basis size in any practical calculation. Provided the system permits sufficient spectral isolation for a reasonable number of spectroscopic modes, it is possible to determine the parameters of the potential. In general, coupling between transitions appears as cross-peaks in the 2D spectrum, and one may extract the parameters of the potential using the energies and relative amplitudes of the peaks (Bredenbeck & Hamm, 2003; Ding et al., 2005; Golonzka et al., 2001; Woutersen & Hamm, 2001).

The model described above for a nominally vibrational problem can be easily adapted to treat the multiple chromophores in strongly coupled electronic systems. In molecular aggregates, branched polymers, quantum wells and natural photosynthetic protein assemblies, the electronic degrees of freedom are often coupled by the strong interactions between neighbors (Axt & Mukamel, 1998). The strong interactions lead to splittings in the electronic eigenstates. In close analogy to the strong coupling in vibrational states in molecules, the specific eigenenergies are especially sensitive to distance and orientations of the constituent units. Thus spectroscopic information is also structurally sensitive, though the link between spectrum and structure is often difficult to establish quantitatively. Both electronic and vibrational multidimensional spectroscopy can elucidate the underlying degree and nature of coupling, as well as the sensitivity to the environment and its fluctuations (Cho, 2008).
1.4.2 Line Broadening

Line broadening has long been understood as resulting from the effects of lifetime and frequency fluctuations. In contrast to the case of isolated gas atoms, in the condensed phase line widths are rarely determined by excited state life time due to the overwhelming significance of environmental fluctuations. Considering the system–bath interactions to produce a time-dependent instantaneous energy gap expressed as a frequency $\omega = \Delta E/\hbar$:

$$\omega(t) = \langle \omega \rangle + \delta \omega(t), \quad (4)$$

the absorption lineshape can be viewed as a consequence of the time-correlation function of the frequency fluctuations (Kubo, 1969):

$$C(t) = \langle \delta \omega(t) \delta \omega(0) \rangle. \quad (5)$$

Within the Gaussian–Markov model for fluctuations, fast fluctuations decay exponentially, leading to Lorentzian lineshape functions, whereas slow fluctuations decay as a Gaussian, corresponding to Gaussian spectral lines. Such a model permits smooth transit from homogeneous (Lorentzian) to inhomogeneous (Gaussian) limits of spectral features. As described above, a linear spectrum in the condensed phase lacking perfectly isolated spectral features cannot distinguish unambiguously between these two microscopically distinct underlying dynamics (Loring & Mukamel, 1985; Tanimura & Mukamel, 1993). Using the 2D lineshape, however, it is possible to determine more rigorously the dynamical origin of a broadened line.

1.4.3 Orientation

Condensed phase molecules seldom rotate freely; instead the orientational evolution is diffusive. Since the nonlinear response function is fundamentally a correlation function of the dipole operator, using fields with different polarization combinations it is possible to isolate both the orientation between coupled transitions as well as the orientational relaxation of the whole molecule (Tokmakoff, 1996). Neglecting for the moment dynamical reorientation, the nonlinear optical signal results from four light-matter interactions mediated by the dipole operator. A peak in a 2D spectrum at the location $(\omega_a, \omega_b)$, where both states are in the first excitation manifold for simplicity, is weighted by the following product of transition dipole moments: $\vec{\mu}_{0a} \vec{\mu}_{a0} \vec{\mu}_{0b} \vec{\mu}_{b0}$. Assuming an isotropic distribution of molecular orientations, the ratio of this cross-peak to the $(\omega_a, \omega_a)$ and $(\omega_b, \omega_b)$ diagonal peaks may be used to deduce the orientation of the $0\rightarrow a$ and...
0→b transitions. The orientations of the transitions may be associated with structural constraints provided one has a structural correspondence with the spectroscopically bright eigenstates (Hochstrasser et al., 2002; Wang et al., 2006).

Since there are four total field polarizations in a third-order experiment, it is also possible to use different combinations of laser polarizations and selection of signal polarization by an analyzer to enhance the orientational information in a 2D spectrum. Although there is initial preferential excitation of molecules whose transition moments are parallel to the laser polarization direction, as these molecules diffusively reorient, the generated signal will decrease. Thus, by increasing the waiting time \(t_2\) delay, orientational dephasing will lead ultimately to a re randomized sample. The timescale for orientational diffusion is often measured using transient absorption anisotropy. Measuring the pump-probe signal with parallel \((\Delta A_{\|})\) and perpendicular \((\Delta A_{\perp})\) polarizations, the ratio \((\Delta A_{\|} - \Delta A_{\perp})/(\Delta A_{\|} + 2\Delta A_{\perp})\) characterizes the anisotropy of the transient absorption signal. Since transient absorption spectroscopy can be derived from a full 2D spectrum, this information is naturally contained within 2D spectra (Tokmakoff, 1996).

1.4.4 Coherence

The first and third time periods \((t_1 \text{ and } t_3)\) are often referred to as coherence periods because in all cases the system must evolve as a coherence (off-diagonal density element) to produce a third-order signal. There is no requirement, however, that the system evolve in a population (diagonal density element) during the so-called "population" time \(t_2\). Indeed, the very short pulses used to perform impulsive, Fourier transform 2D spectroscopy with the photon echo sequence are typically broad in frequency and able to excite many different transitions. When two or more transitions are accessible within the laser bandwidth, the second interaction may connect the ground state with a different excited state. The sequence can be represented with the density matrix for a three-level system as:

\[
\begin{pmatrix}
\rho_{00} & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\overset{\mu_{0a}}{\longrightarrow}
\begin{pmatrix}
0 & \rho_{0a} & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\overset{\mu_{0b}}{\longrightarrow}
\begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
\rho_{ba} & 0
\end{pmatrix}
\overset{\mu_{0b}}{\longrightarrow}
\begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}.
\]

(6)

where the system is excited at the frequency \(\omega_{0a}\) and emits at \(\omega_{0b}\). During the population time, the system is in the coherence \(\rho_{ba}\), thus the \(a\rightarrow0\) transition probability will oscillate at the frequency \(\Omega_{ba} = \omega_{0b} - \omega_{0a}\). These coherences have in fact been observed since the development of femtosecond pump-probe spectroscopy, but their appearance at specific locations in
the 2D spectrum enables more direct assignments of the constituent eigenstates (Khalil et al., 2004; Nee et al., 2008). The time dependence of coherences can provide additional information about the frequency–frequency cross-correlation involving pairs of states. Coherence is a generic property of nonlinear spectroscopy and will be discussed below in several contexts of purely electronic, vibronic and purely vibrational transitions.

1.4.5 Spectral Diffusion

Hole-burning double resonance spectroscopy has enabled isolation of the homogeneous line width hidden within an inhomogeneous band by burning a hole and probing the resulting loss of absorption. In a transient hole-burning experiment, a moderately narrow band laser excites a small subpopulation and a time-delayed broadband probe interrogates the sample; the absorption difference in the presence and absence of the pump is monitored. In a statically inhomogeneous system, the transient hole does not change in time. If the system is dynamically inhomogeneous, however, the hole will fill in as the initially excited molecules adopt different conformations or experience different local solvent environments. Since the filling in of the hole is analogous to how a concentration hole fills in by diffusion, the stochastic sampling of all energetically accessible substates is referred to as spectral diffusion (Klauder & Anderson, 1962). Multidimensional spectroscopy provides a direct probe of spectral diffusion since a dynamically inhomogeneous system will display a diagonally elongated 2D lineshape at short waiting times, followed by a loss of this initial correlation (Figure 10). As the correlation is lost, the 2D lineshape will become less asymmetric, and the decay of the asymmetry provides a direct measure of spectral diffusion (Hybl et al., 2001a; Lazonder et al., 2006).

FIGURE 10 Cartoon representation of spectral diffusion. At short waiting time (left) the signal displays inhomogeneity as a diagonal elongation. With increased waiting time the spectrum relaxes to a symmetrical 2D shape as each initially excited subpopulation stochastically samples all the available local environments or conformations.
Spectral diffusion is a sensitive measure of solvation dynamics and slow structural rearrangements, allowing a spectral window into the dynamical rigidity or floppiness of hydrogen bonded complexes (Elsaesser et al., 2007), liquids (Cowan et al., 2005; Eaves et al., 2005a; Zheng et al., 2007; Kraemer et al., 2008) and key locations within proteins (Bandaria et al., 2008; Fang et al., 2006, 2008; Lim et al., 1998).

1.4.6 Chemical Exchange

It is a cornerstone of chemical dynamics that at equilibrium the rate of formation of the product is equal to the rate of formation of the reactant such that the overall ratio of both species’ concentrations maintains a constant value: the equilibrium constant. Using transition state theory, it is possible to derive an expression for the forward and backward rate constants, whose ratio yields the equilibrium constant. The values of the rate constants are determined by the relative energy differences of the reactant, product, and the transition state. For transition state barriers that are sufficiently low, the transit of a molecule from reactant to product, and vice versa, may be monitored using ultrafast spectroscopy while the system remains essentially at equilibrium (Cahoon et al., 2008; Fang et al., 2006; Finkelstein et al., 2007; Ishikawa et al., 2008; Kim & Hochstrasser, 2005a, 2006; Kim et al., 2008; Kwak et al., 2008a; Woutersen et al., 2001; Zheng & Fayer, 2007; Zheng et al., 2005, 2007). An extension of the ideas discussed in the context of spectral diffusion—where there is not assumed to be an energetic barrier between the substates—is that of ultrafast chemical exchange. Figure 11 shows a schematic chemical exchange measurement, indicating the loss of inhomogeneity as well as the growth of exchange cross-peaks. By exciting a sample of species A and B that are in equilibrium, at early waiting time before appreciable numbers of molecules have reacted, the 2D spectrum appears as a simple mixture of two components whose proportions determine the equilibrium constant. As the waiting time is increased, more reactants become products and more products become reactants. Initial excitation at \( \omega_A \) of the reactant leads to emission at \( \omega_B \) of the product. At the same time, initial excitation at \( \omega_B \) of the product leads to emission at \( \omega_A \) of the reactant. By monitoring the growth of the exchange cross-peak, it is possible to determine the rate of interconversion. More specifically, the \( t_2 \)-dependent growth of the cross-peak yields the sum of the forward and reverse rate constants (Perrin & Dwyer, 1990). The individual rate constants can be determined provided one knows the equilibrium constant, which can be obtained from steady-state measurements. By repeating the experiment at different temperatures, the Arrhenius law provides an estimate of the energy gap between the transition state and the reactant and product. The key experimental requirement is that the signal persists long enough to observe the interconversion,
limiting the method to particularly fast reactions or to those which have very long lived vibrational markers. Additionally, it remains a question to what extent the vibrational excitation itself modifies the equilibrium or the kinetics of exchange. Chemical exchange is an established technique in the toolbox of NMR spectroscopy, and its recent extension to the IR illustrates the generality of the experimental approach. Although there is no a priori prohibition against electronic chemical exchange spectroscopy, electronic transitions typically are even more poorly characterized as near-equilibrium than are their IR counterparts. Additionally, structural changes such as complexation to form a dimer often lead to quenching of the electronic excited state. Nevertheless, small electronic chromophore probes attached to a larger macromolecular complex may prove practical in observing large-scale equilibrium fluctuations of the underlying support.

1.4.7 Energy Transfer

There are few useful generalities about the microscopic details of energy transfer in condensed phase systems. Both vibrational and electronic energy can transfer according to an array of mechanisms, not all of which can be understood simply using Fermi’s Golden Rule. Clearly the system studied must possess a spectral marker for energy transfer, and provided one exists, the waiting time dependence of a 2D spectrum enables one to map the disappearance of excitation energy in one spectral
region to the appearance at another. In vibrational systems spatial correlations can be extracted by exploiting the identification of spectral signatures with specific structural components. Electronic energy transfer within or between chromophores must be analyzed using quantum chemical calculations since the spectrum-structure link is often indirect (Cho et al., 2005), though the rich history of ultrafast transient absorption offers many examples of electronic energy relaxation.

The following sections will focus separately on the specific implementations of multidimensional spectroscopy in the visible spectrum to study electronic transitions and in the infrared to probe molecular vibrations. Though there are certainly many conceptual and practical differences, the underlying theoretical and conceptual framework is common to both, and advances in the field have seen immediate application in both spectral regimes wherever possible.

2. TWO-DIMENSIONAL ELECTRONIC SPECTROSCOPY

The physical nature of the condensed phase often leads to highly inhomogeneously broadened electronic spectra. Examples of this are many: a dye molecule (chromophore) in solution experiences a unique microenvironment that reflects the local configuration of solvent molecules. A light-harvesting complex, consisting of an arrangement of chromophores in different protein environments with inter-chromophore distances and orientations fixed by the protein architecture, has broadband absorption that suits its function. In its Fourier transform implementation, the combination of high time and frequency resolution makes 2D electronic spectroscopy (2DES) a valuable tool for studying energy and charge transfer and chemical dynamics in the condensed phase. This combination is particularly powerful for studying inhomogeneously broadened systems where spectral changes reflecting the dynamics of the chromophore and its environment occur on rapid timescales. In this respect 2DES offers distinct advantages over single molecule spectroscopies that currently suffer from limited time resolution.

In contrast to the numerous theoretical and experimental 2DIR studies, work at visible frequencies has been lacking. This can in part be attributed to the relatively more difficult experimental implementation of 2D spectroscopy at higher frequencies. Since the early work of the Jonas group (Faeder & Jonas, 1999; Hybl et al., 1998, 2001a,b, 2002; Jonas, 2003), 2DES has being applied to a growing number of problems ranging from the study of solvation dynamics (Hybl et al., 2002; Jonas, 2003), to energy transfer in photosynthesis (Brixner et al., 2005; Engel et al., 2007; Read et al., 2008; Zigmantas et al., 2006) and in semiconductor systems (Borca et al., 2005; Li et al., 2006; Yang et al., 2007; Zhang et al., 2007). Parallel
efforts to simplify experimental implementations of 2DES are ongoing and aim to extend 2DES to new frequency regimes such as the ultraviolet. Here we discuss some of the experimental challenges of 2DES and outline two methods that have been used to meet these challenges. We conclude with several examples from the recent 2DES literature that highlight the capabilities of 2DES.

2.1 Idiosyncrasies and Technical Challenges of Multidimensional Electronic Spectroscopy

The pulse sequence for 2DES, shown in Figure 1 reveals some of the challenges of its implementation at optical frequencies. Being a Fourier-transform-based spectroscopy, interferometric precision of $\sim\lambda/100$, corresponding to timing errors of 0.017 fs at 500 nm is needed to produce accurate Fourier transform frequencies (Jonas, 2003). In the infrared, the requirement is considerably easier to meet: at 5 $\mu$m the same degree of precision requires timing errors of less than $\sim$0.17 fs. Even at infrared frequencies, scanning artifacts from imperfect translation stages can degrade the quality of the spectra (Ding et al., 2006; Volkov et al., 2005). In a well-constructed interferometer, optical pathlength fluctuations and mechanical instabilities introduce timing errors of $\sim$0.1 fs over a 20-min period (Jonas, 2003), limiting the duration of possible experiments. These problems suggest that mechanisms for both stabilizing the phase and precisely measuring time delays are needed for successful 2DES experiments.

The broad features of electronic spectra can be somewhat sharpened by the separation of 2D spectra into absorptive and dispersive components. This separation requires knowledge of the complex signal field, and therefore contains phase information that can distinguish between signal contributions of opposite sign, such as ESA and stimulated emission signals. As discussed in Section 1.4.1, obtaining the absorptive spectrum requires detection of the signal field during the second coherence time $t_3$ and collection of two different phase-matched signals: the rephasing and the nonrephasing contributions. In general, the detection of the signal field can be readily achieved by spectral interferometry with a reference electric field (Lepetit & Joffre, 1996). The proper separation then requires interferometric stability between signal and reference fields, and knowledge of the absolute signal phase.

2.2 Experimental Implementations

2D spectroscopy has been implemented using a number of different methods, and each of them solves the problems of timing precision, phase stability and lack of knowledge of the absolute phase in different ways.
Fully noncollinear measurements are desirable for two reasons: to permit isolation of weak signals from strong excitation pulses, and to facilitate selection of a subset of density matrix elements (Jonas, 2003; Mukamel, 1995). Fully collinear measurements, closer to their NMR cousins, have been developed by the Warren group using pulse-shaping methods (Li et al., 2007; Tian et al., 2003; Wagner et al., 2005). Here phase-cycling rather than phase-matching is used to separate the desired signal components. Fully collinear methods have the advantage of operating in the rotating frame, reducing the required sampling rate. They are also less restricted by the sample size than the fully noncollinear implementations that require coherent buildup of signal. However, the collinear geometry is not background free, requiring 16 different phase settings to isolate the absorptive 2D spectrum. The Marcus group has developed a collinear setup for fluorescence-based 2DES (Tekavec et al., 2007). While they employ standard interferometers, they avoid problems associated with interferometer stability by using a phase modulation method that decouples pulse-pair timing errors from their relative phase (Tekavec et al., 2006). More recently a hybrid, partially noncollinear approach has been adopted by a number of groups (DeFlores et al., 2007; Grumstrup et al., 2007; Myers et al., 2008; Shim et al., 2007; Tekavec et al., 2009). In the following sections we focus on two different experimental approaches to 2DES, providing details of both methods and highlighting the strengths and weaknesses of each implementation.

2.2.1 Diffractive Optics

A simplified solution to implementing 2D Fourier transform spectroscopy is to use diffractive optics (DO) to generate the required pulse sequence and phase-matched geometry. DO have been used previously for implementing fifth-order Raman spectroscopy (Astinov et al., 2000; Kubarych et al., 2003) and transient-grating studies (Goodno et al., 1998; Dadusc et al., 2001; Maznev et al., 1998) where they have permitted passively phase stable heterodyne detection. To extend their use to 2D spectroscopy, the ability to implement a time delay between pulse pairs was needed. This was done by refractive delays that vary the optical path-length by rotating an arrangement of coverslides (Cowan et al., 2004; Ogilvie et al., 2002a) or translating a wedge pair (Brixner et al., 2004). In condensed phase systems at room temperature, the first coherence period \( t_1 \) is very short-lived, with typical dephasing rates that are often commensurate with the pulse duration (~20–50 fs), meaning that refractive delays are practical for scanning such short durations. Cowan et al. (2004) also showed that reflective optics could be used to exploit correlations in phase errors between pulse pairs to achieve overall phase error cancellation (Cowan et al., 2004; Ogilvie et al., 2002a).
2DES experiments are frequently implemented using amplified laser systems, which offer stable and reliable output with appropriate pulse energy and repetition rate for studies of dynamical processes over a broad range of timescales. Our diffractive-optics-based experimental apparatus for 2DES is shown in Figure 12(a). A Titanium sapphire oscillator seeds a 1 kHz regenerative amplifier to produce 40-fs pulses with an energy of 1 mJ at 800 nm. To permit access a broader range of wavelengths, from the visible to the near IR, we divide the output from the regenerative amplifier and pump two noncollinear optical parametric amplifiers (NOPA). These NOPAs produce ~10 μJ, 20 fs pulses over the broad range from ~475–1000 nm (Wilhelm et al., 1997). Having independently tunable pump and probe pulses allows two-color 2DES (2C2DES), which adds flexibility to previous implementations of 2DES by providing access to a broader range of electronic transitions, spanning the visible and near-infrared. We generate the excitation pulse sequence for the experiment by sending the pump and probe beams into a passively phase-stabilized diffractive optics arrangement (Cowan et al., 2004; Ogilvie et al., 2002a). The standard BOXCAR geometry is used, as shown in Figure 12(b). Three of the four beams constitute the excitation pulse sequence, while the fourth beam, which conveniently propagates in the signal direction, is reduced in intensity and sent through the sample prior to the other pulses to act as a reference field for heterodyne detection of the signal. The passive phase-stability of the DO approach is derived from the fact that the first-order diffracted beams from the DO provide beams 1 and 2 from the first NOPA and 3 and 4 from the second NOPA. By passing through almost identical optical pathways between the DO and the sample, timing errors caused by mechanical instabilities are common to the beams hitting the sample.

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**FIGURE 12** (a) Two color 2DES based on the diffractive optics approach. NOPA: noncollinear optical parametric amplifier, PC: prism compressor, PM: parabolic mirror. (b) Phase-matching geometry
the same optical elements. Using refractive delays we have demonstrated a high degree of phase stability ($\lambda/90$) between the relevant pulse pairs, leading to a high degree of phase stability in the signal (Cowan et al., 2004). To scan the $t_1$ delay while maintaining this passive phase stability we use a refractive delay line as previously demonstrated, employing pairs of wedges (Brixner et al., 2004) rather than a tilted coverslip configuration (Cowan et al., 2004). We calibrate this delay by scattering pulses 1 and 2 from a pinhole and performing spectral interferometry, achieving timing precision of several attoseconds. Two pairs of wedges allow us to scan positive and negative values of $t_1$, collecting the rephasing and nonrephasing signals to separate absorptive and dispersive components of the 2D spectra (Jonas, 2003). We use a standard delay line for the $t_2$ delay where interferometric precision is not needed. We spectrally disperse our heterodyned signal in a spectrometer acquiring the signal electric field through spectral interferometry (Lepetit & Joffre, 1996).

Other implementations of fully noncollinear 2DES have solved the phase stability problem by using active phase stabilization (Zhang et al., 2005). The Nelson group has pioneered the use of pulse shapers for fully noncollinear 2DES (Gundogdu et al., 2007; Vaughan et al., 2007), employing a 2D pulse shaper to provide both the phase-matched beam geometry and excellent control of the timing, phase and spectral content of the pulses. Similar to Cowan et al. (2004), a recent implementation by Brixner et al. (2004) (Selig et al., 2008) employs the idea of using pulse pairs arranged to exploit phase error correlations to maintain overall phase stability. Unlike the Cowan method, diffractive optics are not employed in this method, permitting easier extension to broadband applications.

While the DO approach to 2D spectroscopy solves the phase stability problem, it does not provide absolute phase information since it employs spectral interferometry, which only measures the relative phase between signal and reference fields. By acquiring the spectrally resolved pump-probe signal for each $t_2$ delay, the projection slice theorem can be used to extract the absorptive 2D spectrum (Faeder & Jonas, 1999). Alternately, two new approaches have recently been developed that solve the absolute phase problem optically without the need for a supplemental pump-probe measurement (Backus et al., 2008a; Bristow et al., 2008).

2.2.2 The Pump-Probe Geometry

It was pointed out by Jonas and coworkers that a pump-probe geometry would remove some of the technical challenges of 2D spectroscopy (Faeder & Jonas, 1999). With collinear pump beams, rephasing and nonrephasing signals are emitted in the same direction, allowing their simultaneous collection and eliminating the need for separate scans that can introduce phase errors. This approach was identified several years before
the introduction of 2D optical spectroscopy (Cho et al., 1992), but the full power of the method was only recently recognized and properly implemented first using a germanium acousto-optic pulse shaper (Shim et al., 2007), and later using a Mach–Zehnder interferometer (DeFlores et al., 2007). In the case of Zanni’s implementation, a pulse shaper was used to produce the collinear pump pair for excitation. Later Zanni extended the work to the near-IR (Grumstrup et al., 2007), demonstrating the method in rubidium. Pulse-shaping has the advantage of providing excellent control of the timing of the pump pulse pair and permits phase-cycling opportunities that are unavailable with interferometer-generated delays. Being a pump-probe measurement, the transmitted probe acts as a heterodyning field with well-defined timing with respect to the signal. In scattering samples, phase-cycling can be used to discriminate against scattered light and improve signal quality (Shim et al., 2007).

Ogilvie et al. (2002a) have implemented the pulse-shaping method at visible frequencies, with a configuration shown in Figure 13(a) (Myers et al., 2008). The pump beam was sent into an acousto-optic pulse shaper (Dazzler, Fastlite) to create the first two excitation pulses with a variable delay. Unlike a delay produced by an interferometer, the pulse shaper allows the introduction of an arbitrary carrier wave phase shift that permits phase-cycling schemes analogous to those used in NMR (Li et al., 2007). The modulation applied to produce the pulse pair was of the form $|E(\omega)| (1 + \exp[i(\omega t_1 + \varphi_{12})])$ where $E(\omega)$ is the spectral amplitude of the pulse and $\varphi_{12}$ is the relative carrier wave phase shift. Pump and probe pulses are crossed at the sample cell at a small angle ($\sim 2^\circ$). The heterodyne-detected 2D signal was spectrally resolved at 1 kHz, providing the $v_3$ axis of the 2D spectrum. The $t_1$ delay was scanned using the Dazzler, as further detailed in reference Myers et al. (2008).

![Figure 13](image)

**FIGURE 13** (a) 2DES in the pump-probe geometry, using a pulse shaper to generate the pump pulse sequence. NOPA: noncollinear optical parametric amplifier, PC: prism compressor, PM: parabolic mirror. Here a continuum probe pulse, generated by focusing into a sapphire plate is used. Alternatively a second NOPA can provide the probe pulse. (b) Phase-matching geometry.
In the pump-probe geometry, the total signal intensity contains the signal of interest as well as a host of other signals, including the transmitted probe light, the free-induction decay from pulse 3, and the pump-probe signals resulting from the pair-wise interactions of the probe with pump pulse 1 and pump pulse 2 (Faeder & Jonas, 1999). The desired third-order signal $P_{S2D}^{(3)}$ can be partially isolated from the other contributions by chopping every other pump pulse with a mechanical chopper or with the pulse shaper and then computing the difference between consecutive spectra. Alternatively, a phase-cycling scheme, where consecutive pump pulses are given a $\phi_{12} = 180^\circ$ relative phase shift, produces signals that are opposite in sign at every second laser shot. Compared to chopping, this scheme effectively doubles the duty-cycle of the experiment. The signal of interest is then:

$$S(\omega_3, t_2, t_1) \propto - \text{Im} \left[ E_3^*(\omega_3) P_{S2D}^{(3)}(\omega_3, t_2, t_1) \right]$$

$$\propto \text{Re} \left[ E_3^*(\omega_3) \left\{ R^{(R)}(\omega_3, t_2, t_1) e^{-i\phi_{12}} + R^{(NR)}(\omega_3, t_2, t_1) e^{i\phi_{12}} \right\} \right].$$

Because pulses 1 and 2 are essentially interchangeable, for $\phi_{12} = \phi_1 - \phi_2 = 0^\circ$ the time domain signal must be symmetric with respect to $t_1 = 0$ and must therefore be purely real (Faeder & Jonas, 1999). If $\phi_{12} = 90^\circ$, the signal becomes antisymmetric with respect to $t_1 = 0$ and all of the signal amplitude will be present in the imaginary part. In practice, since we only scan positive $t_1$ values, care must be taken when computing and interpreting the final 2D spectrum. We can either symmetrize the data prior to FT along $t_1$, or take the cosine transform (when $\phi_{12} = 0^\circ$) or the sine transform (when $\phi_{12} = 90^\circ$) with respect to $t_1$. Along the $t_3$ dimension, causality requires that there be no 2D signal for $t_3 < 0$. Upon applying the symmetry and causality conditions, Fourier transform with respect to $t_1$ and $t_3$ yields the complex 2D spectrum, the real part of which is purely absorptive.

As recent work has shown, separating rephasing and nonrephasing spectra can be useful for observing vibronic modulation of 2DES line-shapes (Nemeth et al., 2008), as well as for analyzing the joint frequency fluctuations or dephasing time of coupled chromophores (Cheng & Fleming, 2008; Ge et al., 2002). Although these signals are collected simultaneously in the pump-probe geometry, phase-cycling can be used to separate these contributions by collecting data with $\phi_{12} = 0^\circ$ and $\phi_{12} = 90^\circ$ (Myers et al., 2008). A demonstration of the separation is shown in Figure 14, where the rephasing and nonrephasing contributions are shown for a simple laser dye, LDS750 in acetonitrile. At room temperature LDS750 exhibits a large Stokes shift due to a combination of solvation and
intramolecular relaxation processes (Kovalenko et al., 1997). This Stokes shift is evident in the two-color 2D spectrum. We note that the imaginary part of the data shown in the bottom right resembles a dispersive spectrum. However, it contains no new information, being equivalent to a Kramers–Kronig inversion of the absorptive data over a finite frequency range and is therefore not a complete measure of the dispersive susceptibility (Albrecht et al., 1999).

Two-dimensional spectroscopy in the pump-probe geometry is considerably easier to implement than noncollinear approaches. The great benefit of using a pulse shaper to generate the $t_1$ delay is that it removes any uncertainty in the location of $t_1 = 0$, allowing easy measurement of the absorptive 2D spectrum (Grumstrup et al., 2007; Shim et al., 2007). The information content of the absorptive component has been shown to be equivalent to that obtained in the noncollinear geometry (Faeder & Jonas, 1999). Use of a pulse shaper provides access to phase-cycling procedures that can improve the signal-to-noise ratio (SNR) (Shim & Zanni, 2009; Shim et al., 2007) and isolate signals of interest. Another significant benefit of the pump-probe geometry is the straightforward extension to 2C2DES, and the use of a continuum probe, allowing the

FIGURE 14  Separation of the rephasing and nonrephasing contributions for LDS750 in acetonitrile at $t_2 = 500$ fs. The rows contain real and imaginary spectra as indicated. Left column: components of the rephasing signal. Middle column: components of the nonrephasing signal. Right column: addition of the rephasing and nonrephasing signals to give the absorptive spectrum (top right)
exploration of coupling between electronic transitions over a broad frequency range. Ultrabroadband continuum-probed 2DES has recently been demonstrated by the Ogilvie group (Tekavec et al., 2009). While simpler to implement than noncollinear approaches to 2D spectroscopy, the pump-probe geometry is not a background free measurement and as such will have a poorer SNR. As in any pump-probe experiment, the SNR cannot be optimized because the relative intensity of the signal and transmitted probe (which acts as the heterodyning reference field) cannot be independently controlled. For some of the tensor components, it has been shown that polarization schemes can remove this difficulty, allowing signal to noise that should approach that of background-free measurements (Myers et al., 2008; Xiong & Zanni, 2008).

2.3 Examples of 2D Electronic Spectroscopy Experiments

2.3.1 Energy Transfer in Light-Harvesting Systems

The light-harvesting systems responsible for photosynthesis in plants and bacteria exploit a common architecture that resembles an energy “funnel.” Photons are absorbed by light-harvesting complexes consisting of antennae arrays that surround a reaction center, to which the solar energy is transferred and stored as stable charge separation (Blankenship, 2002; van Amerongen et al., 2000). The high efficiency with which this energy transfer occurs (>95%) has generated intense interest in these systems and a desire to understand their design principles for use in artificial devices. In light-harvesting complexes, the geometric arrangement of light absorbing pigments and the local protein environment tune the absorption properties and direct the flow of energy. What makes them particularly challenging spectroscopic subjects is their mixture of disorder induced by different conformations and microenvironments and the electronic coupling of the closely spaced pigments (van Amerongen et al., 2000). The effects of coupling and disorder produce broad electronic spectra that are difficult to interpret. Mapping the energy and charge transfer pathways in photosynthetic systems and understanding the underlying design principles are part of an ongoing effort for which 2DES is uniquely suited to provide (1) the high time resolution necessary to follow the early events of energy transfer; (2) a more direct view of electronic coupling; and (3) the ability to dissect the inhomogeneously broadened lineshapes to separate disorder and electronic coupling effects.

Figure 15 depicts a simple case of two coupled chromophores exchanging energy and describes how the coupling and energy transfer process is observed with 2DES. Two extremes of the strength of dipole–dipole coupling are considered. When the coupling is weak, excitations are localized on the individual chromophores and energy transfer can be
described by Forster theory as an incoherent hopping between chromophores. In the 2D spectrum, as the waiting time $t_2$ is increased, this appears as an increase in the amplitude of both the lower energy diagonal peak and the cross-peak below the diagonal, indicating net population flow into the lower energy transition, often referred to as “downhill” energy transfer. In the strong coupling limit an excitonic picture is used, where excitations are delocalized. In this case, as a function of the waiting time $t_2$ the cross-peaks carry the information about energy transfer. By recording 2D spectra at different $t_2$ values, the dynamics and pathway of energy flow can be mapped out. A 1D spectroscopy measurement would integrate over the $\omega_{\text{exc}}$ axis of the 2D spectra leading to overlapping contributions that complicate interpretation of the data. In particular, the cross-peaks that provide information about coupling and energy transfer may be buried beneath other contributions.

The Fleming group has used 2DES to study a number of light-harvesting systems, some of which has been recently reviewed by Cho (2008). They have focused much of their work on the Fenna–Matthews–Olson complex (FMO) (Brixner et al., 2005; Cho et al., 2005; Engel et al., 2007; Read et al., 2008): a pigment/protein structure in green sulfur bacteria that serves as bridging structure to transfer energy between larger peripheral antennae and the reaction center. The structure of a
single FMO subunit is shown in Figure 16, which illustrates its arrangement of seven bacteriochlorophyll molecules. Its relatively small number of chromophores and well-characterized structure has made FMO a good model system for studying energy transfer in photosynthesis (Camara-Artigas et al., 2003). Previous work had proposed an excitonic model of energy transfer (Cho, 2008; Vulto et al., 1999). This model derived the exciton states from linear spectroscopic measurements and the known crystal structure to estimate site energies for the different pigments, and electronic coupling between them. An excitonic model combined with transient absorption measurements permits kinetic modeling of the exciton state populations to derive a picture of energy flow. However, the $t_2$ dependence of the cross-peaks in a 2D spectrum allows a more direct visualization of excitonic coupling and energy transfer. The intuitive picture of energy flow through FMO that was previously derived from nonlinear spectroscopy involved a stepwise downhill flow of energy into the lowest exciton state 1 (Cho, 2008; Vulto et al., 1999). While consistent with an overall downhill flow, the 2D spectroscopy of the Fleming group refined the model, revealing two dominant energy transfer pathways in FMO. These pathways often skip between states that are adjacent in energy, instead choosing pathways with stronger spatial overlap of the excitonic wavefunctions, as depicted in Figure 16.

In their work on the FMO complex, the Fleming group also observed electronic coherences. These coherences are generated by using excitation pulses with large enough bandwidth to excite multiple electronic transitions and are manifested as modulations in the amplitude of diagonal and
cross-peaks as a function of the waiting time, as depicted in the Feynman diagrams of Figure 7 and discussed in Section 1.4.4. The frequency of the modulations observed in FMO was consistent with the expected exciton difference frequencies used to model the 2D spectra. While the work was performed at low temperature (77K), the coherences were remarkably long-lived, raising intriguing questions about both the role of the protein architecture in preserving the electronic coherence and the possible importance of coherence in maximizing energy transfer efficiency (Engel et al., 2007). Studies on other natural light-harvesting systems at temperatures as high as 180K have shown similar coherences (Lee et al., 2007), as have polymers at room temperature (Collini and Scholes, 2009).

In addition to natural photosynthetic systems, candidates for artificial light-harvesting systems are also beginning to be addressed with 2DES. Kauffmann and coworkers have recently studied bi-tubular J-aggregates, examining energy transfer between the inner and outer walls (Nemeth et al., 2009; Sperling et al., 2008), while the Fleming group has also studied exciton dynamics in a different J-aggregate system (Stiopkin et al., 2006).

2.3.2 Vibrational Wavepacket Dynamics in 2DES

In pump-probe spectroscopies utilizing ultrashort pulses, the incident pump pulse may excite a coherent superposition or “wavepacket” of vibrational states, as in impulsive-stimulated Raman scattering (ISRS) (Merlin, 1997; Mukamel, 1995; Yan & Nelson, 1987a, b). Many experiments have explored vibrational wavepacket dynamics in systems as diverse as semiconductors to proteins (Armstrong et al., 2003; Mukamel, 1995; Zhu et al., 1994). On the excited state, vibrational wavepackets are generated because the excited state geometry is different from that of the ground state; in acquiring the new excited state geometry, the molecule undergoes structural rearrangements that drive vibrational modes. The bandwidth of the excitation pulses determines the highest vibrational frequency that can be excited impulsively; a 10-fs pulse is capable of exciting modes as high as 1500 cm$^{-1}$. In a 2DES experiment, vibrational wavepackets can also be generated, where after the interaction of the second pulse the system evolves in a coherence between vibrational states on the ground or excited electronic state, as depicted in the Feynman diagrams in Figure 7. The vibrational wavepacket motion will be manifested as modulations in the 2D spectra as a function of the waiting time.

Recently Nemeth et al. (2009) have explored the effect of vibrational wavepacket motion on 2D spectra, studying the laser dye N, N’-bis(2,6-dimethylphenyl)perylene-3,4,9,10-tetracarboxylicdiimide (PERY, Figure 17 (a)) dissolved in DMSO (Nemeth et al., 2008). This dye has been studied extensively by other groups using a broad range of nonlinear optical techniques (Larsen et al., 2001; Ohta et al., 2001). A distinguishing feature of
FIGURE 17  (a) Structure of PERY. (b) Absorption (solid) and emission (dotted) spectra of PERY showing the pump (dashed) and continuum (dash-dotted) spectra. (c) Absorptive 2D spectra for PERY in DMSO at different waiting times $t_2$. (d) Ratio of diagonal to antidiagonal widths for the central peak (solid blue), lower peak (dashed red), and upper peak (dotted green), showing modulation with a ~240-fs period. Also indicated are the $t_2$ values corresponding to the 2D spectra shown in (c)
PERY is the progression of a high frequency vibrational mode \((1410 \text{ cm}^{-1})\) that strongly modulates its absorption and emission properties, shown in Figure 17(b). While most spectroscopic investigations of PERY have used pulse durations too long to impulsively excite the \(1410 \text{ cm}^{-1}\) mode, lower frequency intramolecular modes, particularly one at \(139 \text{ cm}^{-1}\), have been seen in three pulse echo peak shift (3PEPS), transient-grating studies (Larsen et al., 2001; Ohta et al., 2001), and the 2D work of the Kauffmann group.

The Ogilvie group has recently studied PERY in DMSO using the pump-probe geometry with a continuum probe to span the broadband absorption and emission features (Tekavec et al., 2009). Figure 17(b) shows the pump and probe wavelengths used in their experiments, while Figure 17(c) shows 2D spectra of PERY in DMSO taken at different waiting times (Tekavec et al., 2009). Three distinct peaks are present in the 2D spectra located at \(\nu_3 = 605 \text{ THz}\), \(\nu_3 = 560 \text{ THz}\), and \(\nu_3 = 520 \text{ THz}\). The central peak arises from a combination of bleach of the ground state and Stokes-shifted excited state emission, leading to a slight shift below the diagonal. The low frequency cross-peak arises from the double-peaked emission characteristic of PERY’s vibronic progression. The origin of the high frequency cross-peak is the common ground state between the \(0 \rightarrow 0\) and \(0 \rightarrow 1\) transitions. Although subtle, a modulation in the ellipticity of the peaks is evident, as shown in Figure 17(d) where we plot the ratio of diagonal to antidiagonal full-width half-maximum (FWHM) of the three peaks as a function of waiting time. All three peaks exhibit ellipticity oscillations with a 240-fs period, in accordance with 3PEPS and transient-grating studies (Larsen et al., 2001; Ohta et al., 2001). These results are also consistent with one-color 2D experiments by Nemeth et al. (2008) who observed modulation of the central peak (Nemeth et al., 2008).

A common problem facing studies of vibrational wavepacket motion is that it is difficult to determine whether the observed vibrational motion occurs on the ground or the excited electronic state (Armstrong et al., 2003; Kobayashi et al., 2001; Kumar et al., 2001). This distinction is often of interest for identifying vibrational modes involved in a chemical reaction. 2DES separates ESA contributions which are opposite in sign and often displaced relative to the other signal components as in Figure 6. Modulation of the amplitude of ESA features of the data must arise solely from vibrational wavepacket motion on the excited state, allowing for a clear separation from ground state contributions. This has not yet been observed in 2DES data.

### 2.3.3 Understanding 2DES Spectra

Descriptions of the quantum dynamics of condensed phase systems remain an unmet challenge. A powerful and extensively used formalism for describing nonlinear spectroscopies is based on the nonlinear response
function. In general, the response of a medium to the application of the three time-ordered excitation pulses is given by the third-order response function $R_{3D}$ (Mukamel, 1995), the frequency-domain analog of which is the third-order nonlinear susceptibility $\chi^{(3)}$ (Butcher & Cotter, 2003). In the impulsive limit, the radiated field emitted in response to the excitation pulse sequence is directly proportional to $R_{3D}$. The problem then becomes one of using the measured $R_{3D}$ to derive a picture of the structural and electronic dynamics of the system. Figure 18 depicts a flowchart of the approach that is often used to obtain an accurate system description to reproduce the amplitudes, positions, and lineshapes revealed by the 2DES spectra (Khalil et al., 2003).

The starting point is a set of generalized coordinates $Q$ that provide an appropriate description of the system. The system properties, such as the site energies of the constituent chromophores, and couplings between chromophores, are described by the Hamiltonian $H_S^e$. In the case of light-harvesting complexes, and other molecular aggregates, the Frenkel exciton Hamiltonian has been extensively used (Davydov, 1971). The degree of coupling between chromophores determines what theory is appropriate to describe the coupling: in the weak-coupling limit Förster theory is adequate, while intermediate to strong coupling requires alternative descriptions such as modified Förster theory, which accounts for the finite spatial extent of the chromophores (Jordanides et al., 2001; Scholes, 2003; Scholes & Fleming, 2000; Scholes et al., 2001). Diagonalizing

![Flowchart](image-url)

**FIGURE 18** Flowchart for using 2DES to derive an accurate description of the structural and electronic dynamics of our system. Modeled after Khalil et al. (2003a,b)
the $\hat{H}_S^E$ Hamiltonian results in the electronic eigenstates whose transition frequencies and lineshapes map onto the peak positions in a 2DES spectrum at $t_2 = 0$.

In the condensed phase the system is constantly interacting with the surrounding bath, causing fluctuations and shifts in transition energies of the eigenstates. The nature of the bath is described by the bath Hamiltonian $\hat{H}_B$, while its interaction with the system is captured by the system–bath coupling $\hat{H}_{SB}$. Because many of the bath degrees of freedom may have little effect on the system, one popular approach to simplifying quantum condensed phase dynamics is based on the reduced density matrix formalism, in which degrees of freedom of the bath that are considered to be irrelevant to the measured observable and are averaged over. Redfield theory, one famous implementation of this procedure (Redfield, 1965), reduces to the Bloch model in the case of a two-level system. Originally developed for NMR spectroscopy where interactions between the system and bath are weak, Redfield theory fails in many condensed phase systems. For example, the solvation of a dye molecule, where the excited state induces reorganization of the surrounding solvent structure, requires a description that captures the effect of the system on the bath coordinates. The secular approximation, which is often used to further simplify Redfield theory, uncouples the diagonal and off-diagonal elements of the density matrix and therefore cannot describe effects such as coherence transfer. Seeking alternate descriptions to condensed phase quantum dynamics is an ongoing effort (Brixner et al., 2005; Cho et al., 2005; Zhang et al., 1998; Zigmantas et al., 2006) that can be refined with the aid of 2D spectroscopy: for any given system description, the third-order response function can be directly computed, allowing calculation of the resulting 2DES spectra and an iterative approach to improving the system description to match 2D experiments.

3. TWO-DIMENSIONAL VIBRATIONAL SPECTROSCOPY

In his first report of two-dimensional NMR spectroscopy, Richard Ernst recognized that the method was general and in principle could be applied to other spectral regions such as “electron spin resonance, nuclear quadrupole resonance, in microwave rotational spectroscopy, and possibly in laser infrared spectroscopy” (Aue et al., 1976). Although it took more than two decades to develop methods of generating ultrashort, broadband IR pulses, and efficient electric field detection techniques, today there are many groups using 2DIR spectroscopy to study a diverse array of molecular systems. This section outlines idiosyncrasies of multidimensional spectroscopy in the infrared, then summarizes the experimental
implementation of 2DIR spectroscopy, and considers several illustrations of both equilibrium and nonequilibrium variations of the technique.

3.1 Idiosyncrasies of Multidimensional IR Spectroscopy

In the infrared, transitions generally correspond to relatively well-localized vibrational excitations that are often associated with specific chemical groups. The trend one expects in electronic transitions—that transitions between states that are extended in space are lower in energy, while those that are localized are higher in energy—are sometimes, but not always maintained (Harris & Bertolucci, 1989). For instance, the O–H stretch, which appears between 3300 and 3500 cm\(^{-1}\), is highly localized when the OH unit is attached to something very different, such as the CH\(_3\) (methyl) group in methanol, CH\(_3\)OH. Likewise, the often studied “amide I” band of proteins and peptides, is largely composed of the C–O stretch and appears around 1650 cm\(^{-1}\), though there is some deformation along the C–N bond. When the molecule has high symmetry, however, the coupling between the local units often leads to delocalized vibrational modes that span the entire molecule, even at very high frequencies. Examples include the \(\sim 2000\) cm\(^{-1}\) CO stretch band in metal carbonyl complexes such as Mn\(_2\)(CO)\(_{10}\) and the \(\sim 3300\) cm\(^{-1}\) CH stretches in benzene.

A key feature of vibrational spectroscopy is that it is possible to shift the energy of a transition by isotopic substitution. For example, the C–O in the amide I band of a helical peptide absorbs at roughly 1650 cm\(^{-1}\), and this band shifts to the red by 60 cm\(^{-1}\) upon substitution to \(^{13}\)C–\(^{18}\)O (Backus et al., 2008b; Bagchi et al., 2007; Bredenbeck & Hamm, 2003; Fang & Hochstrasser, 2005; Fang et al., 2003, 2004, 2006; Ganim et al., 2008; Ihalainen et al., 2008; Kim & Hochstrasser, 2005b; Kim et al., 2005, 2008; Mukherjee et al., 2004, 2006a,b; Pfister et al., 2008; Smith & Tokmakoff, 2007a,b; Wang et al., 2006; Woutersen & Hamm, 2001). Using site specific isotope labels, it is possible to selectively investigate the coupling between a particular pair of amide units. Applying site specific isotope labels to peptides (small chains of amino acids) is straightforward using direct peptide synthesis, but extending the approach to whole proteins is not currently feasible since living systems—bacteria or yeast—are typically used to produce complete proteins. Besides the technical challenges of isotope editing, there are more substantial consequences, particularly when multiple transitions on distinct sites are coupled either through the mechanical anharmonicity or through transition dipole coupling. Shifting one unit out of resonance with the others introduces a defect and qualitatively changes the resulting eigenstate and its associated degree of delocalization. Eigenstate maps have been constructed for large protein systems showing the effect of isotope editing on distant sites (Smith & Tokmakoff, 2007a). In the metal carbonyl dimanganese decacarbonyl (Mn\(_2\)(CO)\(_{10}\), or
DMDC), the 1% natural abundance $^{13}$C amounts to 10% of the sample containing an isotope defect. There are two different CO positions on the molecule, resulting in two different sets of vibrations due to the isotopomers. Using quantum chemistry theory, it is possible to evaluate the fundamental vibrational eigenstate energies for both the pure and isotopomer cases. Thus, isotope editing can be very useful in providing additional spatial information, but the effects are not always local and need to be treated with care.

3.2 Experimental Implementation

Most 2DIR spectrometers employ 1-kHz amplified Ti:sapphire lasers that produce 1–5 mJ pulses with pulse durations <100 fs centered at a wavelength of 800 nm. To generate mid-IR pulses, the 800 nm acts as a pump in a collinear optical parametric amplifier (OPA) seeded by a white-light continuum generated in a Kerr material such as sapphire. Several nonlinear optical materials are available for the parametric amplification, with specific choices based on the desired spectral range. Following two-stage parametric amplification, the signal and idler are difference frequency mixed in another crystal, producing output in the mid-IR (Kaindl et al., 2000). Our implementation (Figure 19) uses a single 4-mm β-barium borate (BBO) crystal for both the first and second stages of the OPA, followed by a 1-mm GaSe crystal for the difference frequency generation. Using beam splitters in the OPA we arrange a second identical OPA alongside the first, permitting a second independently tunable OPA which provides another pair of signal and idler outputs. The dual OPA/DFG provides the capability of exciting and detecting at two different spectral regions to study coupling between different kinds of vibrations (Kumar et al., 2006; Rubtsov et al., 2003a,b, 2005). The first two pulses in the noncollinear three-pulse photon echo sequence are derived in an interferometer using a single CaF$_2$ beamsplitter and the delays are scanned using two pairs of 7.3° apex, 1 inch ZnSe wedges. The wedges are preferred over retroreflectors because of the greatly reduced periodic artifacts induced by slight mirror misalignments (Ding et al., 2006). The wedges are mounted on 1-inch translation stages actuated by optically encoded (7.4 nm resolution) DC motors that are scanned once, giving the $t_1$ axis. The large apex angle offers a maximum delay of 12 ps, corresponding to a Fourier transform resolution of 2.4 cm$^{-1}$, which is sufficient for the majority of IR transitions in the condensed phase. Other implementations of 2DIR spectroscopy employ the pulse-shaping and partially collinear methods described in Section 2.

The features of the above description are common to most implementations of background-free Fourier transform 2DIR spectroscopy. One key practical advantage of visible 2D spectroscopy over the IR counterpart is the ease of single-shot spectral measurements using a silicon CCD camera.
in a spectrometer. In contrast to megapixel cameras for visible light detection, the state of the art of IR array detectors based on mercury–cadmium–telluride (MCT) used to measure the multichannel IR spectrum consist of merely 128 pixels. Moreover, these expensive detectors are not useful outside of the IR spectral range, limiting use of the spectrometer to one purpose. In a series of demonstrations (Baiz et al., 2008; Kubarych et al., 2005; Lee et al., 2008; Nee et al., 2007, 2008; Treuffet et al., 2007; Anna et al., 2009), we have shown that upconverting the IR signal into the visible—where a silicon CCD camera can detect the spectrum—is a feasible and flexible alternative to direct IR detection.

Although it is not strictly required, we have adopted a strategy where the IR signal is mixed with a highly chirped 800-nm pulse that is derived from the uncompressed output of the Ti:sapphire chirped-pulse amplifier system. Chirped pulse powers of 500 μJ are easily produced with modest loss of the amplified output for our 2.5-mJ Spectra-Physics Spitfire Pro system. The linear frequency slope due to the predominantly second-order spectral phase introduced by the stretcher was measured using frequency-resolved cross-correlation with a temporally short IR pulse to
be 0.5 cm\(^{-1}\) ps\(^{-1}\) (0.015 THz ps\(^{-1}\), or 66.7 ps\(^2\), or \(6.67 \times 10^7\) fs\(^2\)). Given that the full, usable, base-to-base bandwidth of the chirped pulse is 200 cm\(^{-1}\), the base-to-base temporal width is 400 ps assuming a purely linear frequency chirp. This base-to-base width corresponds to a Gaussian full-width-at-half maximum of 165 ps. Since the emitted nonlinear signal has a finite temporal extent, there is some inevitable broadening of the spectral resolution due to the overlap with a finite spectral band of the chirped pulse. For a 5-ps exponential decay, which corresponds to a 1.33 cm\(^{-1}\) spectral FWHM, the signal overlaps with 2.5 cm\(^{-1}\) of chirped pulse bandwidth, leading to some degree of spectral convolution. Since the chirp of the mixing pulse is known, however, there is a predictable effect on the upconverted field provided one knows the spectral phase of the chirped pulse. In principle, the spectral distortion associated with the chirped pulse upconversion process can be corrected in a simple way (Anna et al., unpublished).

In practice, the chirped pulse energy is roughly 100 \(\mu J\) and the upconversion crystal is an uncoated 0.2–0.8 mm MgO(5%):LiNbO\(_3\) wedge. The wedge is required to avoid temporal modulations of the chirped pulse as it interferes with itself after two reflections. Due to the very long coherence length of the chirped pulse, even the relatively small Fresnel reflectivity of the uncoated crystal faces induces temporal modulations of the chirped pulse amplitude. These modulations have a period on the order of 5–10 ps for typical crystal lengths (0.2–0.5 mm), leading to both temporal and spectral modulations of the upconverted fields. The wedged crystal both rejects the reflected signal and acts as a variable thickness crystal, enabling an effectively continuously adjustable analog gain of the upconverted signal. There is always a trade-off between phase-matching bandwidth and upconversion efficiency, and the wedge allows a latitude of choice for a specific spectroscopic context. Since we implement upconversion using a noncollinear geometry to avoid a dichroic recombining optic, we arrange the wedge of the crystal to be oriented perpendicular to the phase-matching axis, thus the prismatic effect of the wedge partially compensates the spatial chirp of the noncollinear phase-matching.

Besides the Fourier-transform-based 2D techniques described above, it is also possible to record absorptive 2D spectra using a transient hole-burning implementation, and indeed this was the method first used a decade ago (Hamm et al., 1998). A short path length cavity, low-finesse scanning Fabry–Pérot interferometer produces an exponentially decaying pulse in the time domain, which has a Lorentzian spectral profile. By tuning the cavity length, the center frequency of the étalon shifts, and at each center frequency the differential absorption spectrum (pump-on minus pump-off) of a broad-band probe is measured. Compiling the differential absorption spectra results in an absorptive 2D spectrum without any need for phasing the data. The pump-probe spectrum contains a signal
with a perfectly defined phase relationship with the local oscillator, which is the unabsorbed probe itself. The interference of the reference and the emitted third-order signal produces a purely absorptive 2D spectrum. A limitation of the Fabry–Pérot filter approach is the temporal profile of the pump pulse, which is peaked at early times and decays at later times. To ensure well-separated pulses, the probe pulse cannot enter the sample before the pump pulse has had time to decay appreciably. Thus the spectral resolution of the $\omega_1$ axis is linked to the time resolution during $t_2$ (Cervetto et al., 2004). In practice, the probe is generally delayed roughly 1 ps relative to the pump, allowing the system to vibrationally relax or for the initially excited IR excitation to redistribute among any modes that energetically and spatially overlap the initial excitation. A modification of the temporal profile was implemented using the pulse-shaping approach producing a time-reversed exponential pulse, enabling a closer temporal spacing between pump and probe (Shim et al., 2007). Despite the technical limitation of the hole-burning approach, some of the most definitive and seminal 2DIR spectra, particularly of nonequilibrium systems have been measured using this approach (Hamm et al., 2008).

3.3 Examples of Equilibrium 2DIR Spectroscopy

There have been several reviews summarizing many of the achievements of 2D spectroscopy (Ganim et al., 2008; Hamm et al., 2008; Jonas, 2003; Khalil, 2003a; Wright, 2002; Zheng et al., 2007); particularly noteworthy is a recent comprehensive overview by Cho (2008). Rather than attempt to list all the varied systems that have been studied, we aim here to show a few selections that illustrate some common molecular goals outlined in Section 1.4.

3.3.1 The OH Stretch in Water

The infrared spectra of all hydrogen-bonded molecules—most notably water—are characterized by a signature broad absorption feature between 3000 and 3700 cm$^{-1}$ corresponding to either the OH or NH stretch. This broad feature is much-maligned by chemists due to its lack of specificity, but inside this complex band hides much of the richness of the unusual structural and dynamical properties of liquid water. Although the OH stretch in the gas phase is a very narrow feature, in the liquid it is significantly broadened to roughly 300 cm$^{-1}$ due to the strong hydrogen bonding interactions. From diffuse X-ray scattering, water is known to have short range order, where, on average, each water molecule donates and accepts two hydrogen bonds, leading to a four-coordinate structure (Hura et al., 2000; Sorenson et al., 2000). It has been a long-standing challenge in the study of water dynamics to understand the timescale of the structural rearrangements of liquid water (Rey et al., 2002). From its remarkable spectrum, it is clear that water presents a
spectacular example of inhomogeneous broadening, and this inhomogeneity cannot be static since the liquid is constantly fluctuating. As discussed above in general terms, 2D spectroscopy is particularly well suited to the task of measuring the loss of transition frequency memory due to spectral diffusion. Thus, the development of 2DIR spectroscopy has to a certain extent been guided by the quest to dissect the complex lineshape of water.

The basic description of the water OH stretching band is linked to a rather simple geometrical picture (Figure 20) where the dominant parameter is the distance between the two oxygen atoms involved in the hydrogen bond. In a “long” hydrogen bond, the O atoms are farther apart than the average, leading to a higher OH stretch frequency as it shifts toward the gas phase value where the hydrogen bonds are absent. Conversely, a “short” hydrogen bond, where the O atoms are closer than the average, has a lower OH stretch frequency due to the partial sharing of the H atom between the two O atoms. Although the distance between oxygen atoms is the dominant determinant of OH frequency, recent studies have found that more detailed, multidimensional coordinate spaces are useful for describing hydrogen bond switching, where the motion of the H atom is significantly far from the equilibrium potential minimum (Eaves et al., 2005a; Loparo et al., 2006b). The OH stretch in water illustrates a prototypical case where there is a well-defined structure-spectrum relationship, but the underlying dynamics are entirely hidden beneath the structureless lineshape.
Pure water at room temperature and atmospheric pressure has a concentration of 55.6 mol l$^{-1}$ (33.4 molecules nm$^{-3}$), making the concentration of OH stretch vibrations 111.2 mol l$^{-1}$. Faced with the difficulty of assembling a practical sample cell of pure water, coupled with the analytical complexity of a liquid composed entirely of the same spectroscopic entity, the first ultrafast 2D measurements were performed on the related isotopomers, HOD in a solution of H$_2$O (HOD:H$_2$O) (Asbury et al., 2004a, b,c) and HOD in a solution of D$_2$O (HOD:D$_2$O) (Eaves et al., 2005a,b; Loparo et al., 2006a,b). Using dilute isotope substitution, the spectroscopic mode—either OD in (HOD:H$_2$O) or OH in (HOD:D$_2$O)—is shifted from the H$_2$O absorption, lowering the optical density and permitting the use of typical 10–100 μm path length samples. Besides the practical advantages of using the isotope substituted water systems, they also permit the study of a single OH or OD stretch, effectively in spectroscopic isolation, as a probe of the surrounding liquid dynamics.

The most striking feature of the isotopically substituted water systems is shown schematically in Figure 20 as the underlying lineshapes. From the measured 2DIR spectra, both Fayer and coworkers and Tokmakoff and coworkers observed that the blue side of the band had a broader line width than the red side of the band. These line widths are obtained by considering antidiagonal slices as depicted in Figure 3. The appearance of the blue-broadened lineshape is surprising if one imagines that in the limit of an infinitely long hydrogen bond one recovers the gas phase picture. While the frequency is shifted toward the blue as expected, the line width is inconsistent with the narrow gas phase width. On the red side, the line width is actually narrower despite greater interactions with the surroundings due to the shorter hydrogen bond. These heterogeneous lineshapes indicate that the longer hydrogen bonds have faster short-time dynamics due to the orientational freedom gained by the decreased interaction with surrounding molecules (Kwak et al., 2008a,b). Conversely, the shorter hydrogen bonds are more rigid since they are essentially held in place by the stronger association with the adjacent hydrogen bond acceptor (Loparo et al., 2006a,b; Steinel et al., 2004). In HOD:H$_2$O, the asymmetry decay due to spectral diffusion occurs on a timescale of roughly 3 ps (Asbury et al., 2004a,b,c; Corcelli et al., 2004), whereas in HOD:D$_2$O, the relaxation is roughly twice as rapid (Loparo et al., 2006a,b). These hydrogen-bond rearrangement dynamics reflect the well-known timescale for solution phase phenomena such as solvation dynamics (Castner & Maroncelli, 1998; Stratt & Maroncelli, 1996).

Inspired by the experimental results, theoretical investigations have pointed to the importance of another aspect of condensed phase systems that has no obvious isolated-atom analogue, namely the independence of the transition dipole moment on the solvent coordinate. The so-called Condon approximation (Condon, 1926) treats the transition dipole as an
operator solely in the system’s Hilbert space and neglects the influence of bath degrees of freedom. Because coupling to the bath is often weak—so weak that it is almost always treated perturbatively—it is generally reasonable to assume that the solvent does not strongly affect the system’s coupling to the electric field. Nevertheless, using models that account for non-Condon effects to varying degrees, it was shown that a model employing the pure Condon approximation was in poorer agreement with the data than one which does not invoke the approximation at all (Schmidt et al., 2005, 2007). Although non-Condon effects are manifested in the linear spectrum, the added frequency axis and temporal dynamics of nonlinear spectroscopy enable more highly constrained feedback to the theoretical analysis. Non-Condon effects have also been predicted theoretically for a model of proton transfer in solution (Hanna & Geva, 2008a), where the transition state geometry actually enjoys a much larger transition moment—in effect magnifying the transition state. It is a holy grail of ultrafast spectroscopy to be able to observe transition states, and such fortuitous enhancement of the transition state region due to non-Condon effects may aid in achieving this long-standing goal.

The spectroscopy of pure water is not the same as what one observes in the isotope substituted systems for the simple reason that the line between “system” and “bath” is very hard to draw since the two are essentially fully resonant. The resonant interaction between the optically excited mode and its surroundings introduces two significant complications: (1) energy transfer can become qualitatively more efficient due to resonant coupling (Woutersen & Bakker, 1999) and (2) the spectroscopic mode is less well defined due to the spatial delocalization of the energy eigenstates (Paarmann et al., 2008). Förster coupling between nearby oscillators is virtually assured, as well as an efficient energy relaxation process that passes through the second overtone of the HOH bending vibration ($\omega = 1650 \text{ cm}^{-1}$) (Ashihara et al., 2007; Lindner et al., 2006). Notwithstanding the technical difficulties of studying an ultra-high optical density sample, the pure water system posed a daunting challenge.

Using an ingenious nanofabricated SiC flowing sample cell with a 400 nm pathlength, combined with the passive phase stability of a diffractive optics-based 2D spectrometer, Miller and coworkers succeeded in recording the 2DIR spectrum of pure water (Cowan et al., 2005; Kraemer et al., 2008). While they did observe a heterogeneous lineshape with a broader blue side, they also observed a dramatically increased 50-fs decay of the inhomogeneous asymmetry. Such a rapid loss of frequency memory could not simply be due to structural rearrangements of the hydrogen bonded network, since it is the same network in both pure water and the isotope substitutes—only the spectroscopic probe has changed. The most current interpretation, based on temperature-dependent measurements as well as mixed
quantum-classical simulations, points to eigenstate delocalization as the principal mechanism for the loss of frequency memory, as well as rapid anharmonic coupling to lower frequency intermolecular modes (Ashihara et al., 2007; Paarmann et al., 2008). Due to the strong degree of resonant coupling the instantaneous eigenstates span multiple OH chromophores, much in analogy to the multichromophoric systems involved in natural and artificial light harvesting (Cho et al., 2005; Cheng et al., 2007; Cheng & Fleming, 2008; Scholes & Fleming, 2000; Scholes et al., 2001; Zigmantas et al., 2006). As the liquid fluctuates to a degree that might be imperceptible using the local probe of an isotope substitute, the composition of the spectroscopically addressed state changes spatially and energetically. Thus, there are effectively two classes of spectral diffusion, one at the longer range length scale of the hydrogen bond network, and another at the shorter range of eigenstate delocalization and anharmonic coupling. The eigenstates are viewed as fragile markers of a much more detailed set of fluctuations relative to the coarse hydrogen bonding rearrangements probed in HOD:H₂O and HOD:D₂O. Liquid water illustrates the powerful capabilities of multidimensional spectroscopy to dissect a complex spectral lineshape that has stood for years as one of the most important puzzles in condensed phase spectroscopy.

3.3.2 Vibrational Coherence

Uncovering the heterogeneous dynamics of water illustrates a fundamental strength of 2D spectroscopy to elucidate underlying dynamics that make up a spectral lineshape. The 2D water experiments reported to date, however, focus specifically on one single band and do not reflect directly the coupling of multiple spectral features. Besides the lineshape, 2D spectroscopy is designed to measure couplings through the observation of cross-peaks in the spectrum. One aspect of coupling is the possibility of observing coherent modulation of cross-peak amplitudes as a function of the waiting time $t_2$. The observation of coherence in ultrafast spectroscopy is by no means new (Elsaesser & Kaiser, 1991), but multidimensional spectroscopy provides a clear window to observe the individual states involved, as well as to determine their precise dephasing dynamics. Considering for simplicity a three-state system (Figure 7), composed of a common ground state and two optically accessible excited states, following the first two field interactions the possible system densities are $\rho_{00}$, $\rho_{aa}$, $\rho_{bb}$, $\rho_{ab}$ or $\rho_{ba}$. For the rephasing sequence, the $t_2$ coherences appear at the locations of the cross-peaks since the coherence during $t_1$ is at one frequency, $\rho_{0a}$ or $\rho_{0b}$, and the coherence during $t_3$ (bold arrow) is at the other frequency, $\rho_{0b}$ or $\rho_{0a}$, respectively (see Figure 7). For the
nonrephasing sequence, both pathways that go through a coherence during $t_2$ involve the same $t_1$ and $t_3$ coherences, thus, the $t_2$-dependent coherences appear on the diagonal.

Since the system may evolve in a coherence during the waiting time, the signal will oscillate at the difference frequency of the two constituent levels. The modulation can be easily verified by considering both the coherent and ground state paths. The coherent paths are represented by the following density matrix:

$$\rho^{(\text{coherent})} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \rho_{ab} \\ 0 & \rho_{ba} & 0 \end{pmatrix}. \tag{8}$$

A full derivation of the coherence appearing in cross-peaks that arise from a common ground state is given in the Appendix. We find the total signal at the cross-peak ($\omega_1 = \omega_{0b}$, $\omega_3 = \omega_{0a}$) to be given by the sum of the coherence path and the ground state path:

$$S^{(\text{total})} = S^{(\text{coherence})} + S^{(\text{ground})} = e^{-i\omega_{ab}(t_2 - t_1)} + 1 |\mu_{0a}|^2 |\mu_{0b}|^2 \tilde{\rho}_{00}, \tag{9}$$

where $\tilde{\rho}_{00}$ is the initial ground state density (which could be a thermal distribution, for example), $\mu_{0a}$ and $\mu_{0b}$ are the transition dipole moments between $|0\rangle$ and $|a\rangle$ and $|b\rangle$, respectively. The two constants are identical and are given by the square magnitudes of the individual transition dipole moments between the ground state and the two states involved in the coherence. At this point it is straightforward to include the dephasing of the coherence through a phenomenological damping factor, $\gamma$. Including the dephasing yields:

$$S^{(\text{total})} = e^{-i(\omega_{ab} + i\gamma)(t_2 - t_1)} + 1 |\mu_{0a}|^2 |\mu_{0b}|^2 \tilde{\rho}_{00}. \tag{10}$$

A characteristic curve of the coherence cross-peak is shown in Figure 21 for parameters typical of metal carbonyl complexes. This feature is observed experimentally and will be described below.

It is possible to observe $t_2$-coherences in several ways using multidimensional spectroscopy. In an absolute-value rephasing spectrum, the cross-peaks are modulated according to the discussion above, whereas in an absolute-value nonrephasing spectrum the diagonal peaks are modulated. In a purely absorptive spectrum, where both a rephasing and nonrephasing spectrum are measured and their real parts added, both the diagonal and cross-peaks oscillate. Depending on the spectral
congestion, and the added difficulty of having to record many 2D spectra to track the full timescale of the coherence, absolute-value rephasing spectra have proved capable of resolving complex coherent dynamics (Nee et al., 2008).

Since third-order multidimensional spectroscopy is a four-wave mixing process, it is possible to view the signal generation as a phase and amplitude grating written in the material (Eichler et al., 1986). In a transient-grating experiment, two temporally overlapped pulses arrive at a sample and are tuned to match a resonance in the material. The angle between the beams leads to a spatial interference pattern that encodes excited state and ground state molecules in the bright and dark fringes, respectively. The diffraction efficiency of a time-delayed probe pulse decreases as the molecules return to the ground state, and the diffraction can be due to a combination of refractive and absorptive changes via a Kramers–Kronig relation (Dadusc et al., 1998; Ogilvie et al., 2002b). To measure separately either the refractive or absorptive components of the signal, one requires a phase-sensitive method based on interfering the signal with a local oscillator reference, as has already been described above for 2D spectroscopy (Dadusc et al., 2001). From the perspective of a transient-grating experiment, the importance of the ground state pathways is evident: the signal relies equally on the presence of molecules in an excited state population as it does on those that remain in a ground state population.

The grating picture also helps to clarify how to imagine $t_2$-coherences from a macroscopic perspective. Since the coherence necessarily involves two different excited states, the grating is written with two fields of different frequency, generating a traveling wave. As the waiting time

![Figure 21](image-url)  
**Figure 21** Simulated cross-peak decay due to introducing a dephasing of the coherence with a frequency of 62 cm$^{-1}$ and a dephasing rate of 0.5 ps$^{-1}$
between writing and readout is increased, the diffraction pattern due to the coherence moves across the sample at a rate proportional to the difference frequency, leading alternately to overall constructive and destructive interference with the static population grating (Figure 22). Although the simple grating experiment performed with broadband pulses does not permit correlation of an excitation and detection frequency, the generation of coherences can still be viewed within the macroscopic and physically intuitive context of a transient diffraction grating.

The experimental and theoretically predicted linear infrared (FTIR) spectrum of the metal carbonyl complex Mn$_2$(CO)$_{10}$ (dimanganese decacarbonyl, DMDC) is shown in Figure 23 along with the molecule’s structure. The largest features are the three bands centered at 1982, 2013, and 2045 cm$^{-1}$. The central peak is due to two degenerate modes of $E$ symmetry, thus the feature is roughly twice the magnitude of the other two. Based on the molecule’s symmetry, one predicts and observes four IR active vibrations, leaving six Raman active modes that are invisible in the IR (Cotton & Kraihanzel, 1962). That there are more dark modes than bright modes immediately points to a key complication in a system such as DMDC since the anharmonic potential is unrelated to the spectroscopic activity, indicating that vibrational energy is free to flow between bright and dark modes. A full accounting of the relaxation processes in DMDC requires the inclusion of the dark modes, though they are not directly observed in the 2DIR experiment. In the experimental spectrum there are small-amplitude peaks in addition to the three main bands, and these are assigned to the presence of $^{13}$C. The most clearly visible feature due to $^{13}$C in the FTIR spectrum shown in Figure 23 is that at 2002 cm$^{-1}$. The natural abundance of $^{13}$C is 1.1%, indicating that 10% of the sample is Mn$_2$(CO)$_9$^{13}CO. Since the modes are delocalized throughout the molecule, one $^{13}$CO will have an effect on essentially all of the vibrational modes, changing the linear and nonlinear spectrum in a generally unintuitive manner. There are two structurally distinct carbonyl locations in DMDC, 8 are equatorial and 2 are axial. Assuming statistical independence of the isotope substitution site, 8% of the sample has an equatorial isotope defect, while 2% has an axial defect. Since the heterodyne detected 2DIR
signal has linear scaling with number density, contributions from species present in these ratios are certainly observable. The isotope contribution adds some complexity to the spectrum, and in principle can be removed either by chemical enrichment with $^{12}$CO or by direct synthesis of an isotopically pure sample. Alternatively, it has long been a technique in characterizing metal carbonyl compounds to purposefully introduce $^{13}$CO to break the symmetry, thus relaxing the selection rules.

The absolute-value rephasing 2DIR spectrum of DMDC is shown in Figure 24 for a waiting time of ~100 fs. As is expected from a three-peaked linear spectrum, the 2D spectrum has nine major peaks corresponding to all of the excitation/detection pairs. Besides these nine peaks, which correspond to transitions between the ground state and the first excited manifold, there are additional peaks that arise from ESA. The ESA peaks reflect directly the frequencies of the second excited manifold, and are therefore due to the diagonal and off-diagonal anharmonicity initially introduced in Section 1.4. From all of these peak positions and their relative magnitudes, it
is possible to devise a Hamiltonian that is consistent with the data, but the number of fitting parameters is so large that it would be difficult to find a unique solution. The approach we have taken is to compute the harmonic vibrational frequencies using \textit{ab initio} quantum chemistry, and then use vibrational perturbation theory to compute the vibrational anharmonicities. Particularly when we wish to include all 10 carbonyl modes (6 of which are Raman active), diagonalization of a 10-dimensional problem is intractable given that each dimension requires on the order of 10 basis vectors to reach convergence. In general if one requires $n_B$ basis vectors for each of $D$ dimensions, the number of total vectors in the tensor product space is $n_B^D$, and the Hamiltonian matrix has dimension $n_B^{2D}$. Thus, for a 10 mode system with 10 basis vectors per dimension, the Hamiltonian contains $10^{20}$ elements, or 400 exabytes of memory for single precision.

The 2D spectrum shown in Figure 24 was recorded by one single scan of the $t_1$ delay, which required only 10 s of acquisition time. This rapid measurement enables a fine sampling along the $t_2$ axis, recording a separate 2D spectrum at each waiting time point. Figure 25 shows four 2D spectra taken at various waiting times, showing that the cross-peaks
exhibit modulations as a function of $t_2$. These modulations are due to the creation of coherences among the excited eigenstates. The $t_2$-dependence can be seen more clearly by following individual cross-peaks in the $t_2$ domain. Figure 25 also shows the modulation of three cross-peaks taken from 180 2DIR spectra recorded from $t_2 = 0$ to 18 ps in 100-fs steps (Nee et al., 2008). It is noteworthy that the temporal profile of the modulations exhibits cusps near zero-amplitude and smoother changes near the maximum amplitude, in agreement with the derivation above. Fourier transforms of the coherence signals with respect to $t_2$ are also shown. The highest frequency coherence centered near...
62 cm\(^{-1}\) (2045–1983 cm\(^{-1}\)) has a spectral width that is very narrow, whereas the other coherences are broader. The broadening of the lower-frequency coherence is likely due to spectral overlap with other transitions, possibly from the isotopomers. Based on the most cleanly resolved 62-cm\(^{-1}\) feature, the dephasing time of the coherence is comparable to that of the fundamental transitions as determined from the line width of the 1D FTIR spectrum (assuming homogeneous broadening) or from the antidiagonal width of the 2D spectrum.

Since the frequency of the coherence can be straightforwardly predicted from the linear spectrum, the key new information obtained in the \(t_2\)-dependent measurement is the line width (or dephasing rate) of the coherence. It is possible to derive a relationship between the line width of the “excited state” coherence, \(\rho_{ab}\), in relation to the line width of the “fundamental” coherence \(\rho_{0a}\) and \(\rho_{0b}\). The instantaneous energy gap between the states \(|a\rangle\) and \(|b\rangle\) and the ground state \(|0\rangle\) is (in terms of frequency) (Nee et al., 2008):

\[
\omega_{0a}(t) = \langle \omega_{0a} \rangle + \delta \omega_{0a}(t), \quad \omega_{0b}(t) = \langle \omega_{0b} \rangle + \delta \omega_{0b}(t),
\]

where the angled brackets denote the average transition frequency, and \(\delta \omega\) is the time-dependent fluctuation. The frequency–frequency correlation functions that determine the “fundamental” coherence line widths are:

\[
c_{0a}(t) = \langle \omega_{0a}(t) \omega_{0a}(0) \rangle = \langle \delta \omega_{0a}(t) \delta \omega_{0a}(0) \rangle, \\
c_{0b}(t) = \langle \omega_{0b}(t) \omega_{0b}(0) \rangle = \langle \delta \omega_{0b}(t) \delta \omega_{0b}(0) \rangle,
\]

(12)

With the Fourier transforms of these correlation functions it is possible to obtain the lineshape functions (Kubo, 1969). Following the same approach, we consider a frequency trajectory of the “excited state” coherence \(\Omega_{ab}(t)\):

\[
\Omega_{ab}(t) = [(\langle \omega_{0a} \rangle + \delta \omega_{0a}(t))] - [(\langle \omega_{0b} \rangle + \delta \omega_{0b}(t)] \\
= \langle \Omega_{ab} \rangle + \delta \omega_{0a}(t) - \delta \omega_{0b}(t)
\]

(13)

and the corresponding time correlation function:

\[
C_{ab}(t) = \langle [\delta \omega_{0a}(t) - \delta \omega_{0b}(t)][\delta \omega_{0a}(0) - \delta \omega_{0b}(0)] \rangle,
\]

(14)

which can be expanded as:

\[
C_{ab}(t) = \langle \delta \omega_{0a}(t) \delta \omega_{0a}(0) \rangle + \langle \delta \omega_{0b}(t) \delta \omega_{0b}(0) \rangle \\
- \langle \delta \omega_{0a}(t) \delta \omega_{0b}(0) \rangle - \langle \delta \omega_{0b}(t) \delta \omega_{0a}(0) \rangle.
\]

(15)
The first two terms are simply the same correlation functions that determine the lineshape of fundamental coherences. The second two terms, however, are frequency–frequency cross-correlation functions. The lineshape of the excited state coherence in principle contains additional information since it reports the degree of mutual correlation between two different transitions. In the limit of fully un-cross-correlated fluctuations, the coherence line width should equal that of the fundamental coherences. Conversely, in the fully cross-correlated limit, the excited state coherence may be much narrower than the line widths of the fundamentals (Engel et al., 2007). In the case of the system described here, DMDC, the lineshape of the excited state coherence is very similar to that of the underlying transitions, suggesting that the two modes involved fluctuate essentially independently, despite their sharing of identical local CO units.

Figure 26 shows the isolated 62-cm$^{-1}$ coherence with a simulation of the feature using the result of Equation (10) multiplied by a biexponential overall damping that describes the orientational relaxation of the cross-peak amplitude. The parameters of the simulated cross-peak amplitudes were a 0.33 ps$^{-1}$ coherence dephasing rate and a fast 5.2 ps$^{-1}$ and a slow 0.019 ps$^{-1}$ damping. Since the scanned waiting time was not sufficient to

---

**FIGURE 26** Trace (blue) of the cross-peak at $\omega_1 = 1985$ cm$^{-1}$, $\omega_3 = 2045$ cm$^{-1}$ showing clearly the coherence signal. The data are reproduced well using a single coherence dephasing rate of 0.33 ps$^{-1}$, and a biexponential decay of the overall cross-peak amplitude with rates of 0.019 and 5.2 ps$^{-1}$.
include the overall vibrational relaxation to the ground state, which is known to be on the order of 100 ps, the biexponential relaxation is due essentially entirely to orientational relaxation. The fast 5.2 ps$^{-1}$ rate is due to intramolecular vibrational redistribution, and leads to an orientational relaxation because the different transitions are oriented in different directions, thus appearing as if the molecule were reorienting. The slower 0.019 ps$^{-1}$ rate arises from the diffusive reorientation of the whole molecule in the liquid. The observation of vibrational wavepackets through these coherent oscillations serves to highlight the inherently three-dimensional information contained in the full, third-order response function. More recently, we have used the observation of coherent cross-peak modulations to isolate the signature of chemical exchange in a flexible molecule with a highly congested spectrum (Anna et al., 2009).

4. FUTURE DIRECTIONS

A growing number of research groups are employing 2DES for the study of coupled electronic transitions in condensed phase systems ranging from light-harvesting systems to quantum-well structures. As the technical barriers to implementing 2DES continue to fall and further applications prove the utility of 2DES, this number will surely increase. In particular, the relative ease of transforming a pump-probe experiment into a 2DES experiment may speed the process (Grumstrup et al., 2007; Myers et al., 2008; Shim et al., 2006; Shim & Zanni, 2009; Tekavec et al., 2009).

While numerous polarization 2DIR experiments have been performed, the use of polarization control has been limited to a handful of 2DES experiments (Read et al., 2008; Zhang et al., 2007). This degree of freedom promises enhanced structural information and the ability to suppress unwanted signal contributions. Alternative pulse sequences that probe multiple quantum coherences promise new ways to separate Liouville-space pathways and isolate spectroscopic signals sensitive to electronic correlations in many-electron systems (Li et al., 2008; Yang & Mukamel, 2008).

Although the visible frequency regime currently represents the high-frequency limit at which 2D spectroscopy has been experimentally realized, it is unlikely to remain that way for long. Theoretical work is already showing the promise of extending 2D spectroscopy into the ultraviolet regime (Abramavicius et al., 2006), which accesses the electronic resonances of the basic constituents of proteins and DNA, promising new structural probes of conformational dynamics and energy and charge transfer in biological systems. At ultraviolet frequencies, the technical challenges of 2D spectroscopy can be readily met by pulse-shaping methods, so it is likely that 2DUV spectroscopy is on the horizon. Looking even further ahead, multidimensional X-ray spectroscopies for
exploring coupling between core-electron transitions have also been proposed and may become feasible with the development of high-intensity coherent X-ray sources (Schweigert & Mukamel, 2007).

In the decade since two-dimensional spectroscopy was first demonstrated in the visible and infrared spectral regions, there has been substantial progress in its application to condensed phase dynamics. The overwhelming majority of experiments have focused on systems that are at equilibrium. That is, although the optical spectroscopy is by definition nonequilibrium, it is viewed as a small perturbation permitting a nearly noninvasive probe of equilibrium fluctuations. An alternative avenue has also been pursued using photoswitches (Hamm et al., 2008), temperature jumps (Chung et al., 2007), and photochemical (Baiz et al., 2008) and photophysical (Bredenbeck et al., 2004) triggers to use 2DIR spectroscopy as a probe of an inherently nonequilibrium process. These experiments are essentially higher-order optical processes where an additional correlation enables comparison of a differential 2D spectrum in the presence and absence of some auxiliary optical modulation. It is a long-standing challenge in molecular spectroscopy and electronic structure to obtain detailed information about the vibrational potential surface of excited electronic states. Using 2DIR spectroscopy as a probe of dynamic, nonequilibrium excited electronic states will enable application of the powerful spectral decongestion already demonstrated at equilibrium.

These new approaches provide access to a vast range of timescales, offering site-specific, ultrafast dynamical snapshots of, for example, large-scale structural changes in a protein as it switches from an active to a passive state. With the wider adoption of pulse-shaping techniques, wavelength regions can be combined yielding essentially arbitrary combinations of UV, visible and IR frequency axes in novel multidimensional spectroscopy methods. Key problems in light harvesting, organic light-emitting diodes, photocatalysis, as well as biological photochemistry are often found to possess and exploit transitions in several spectroscopic windows, and a combined approach will be needed to understand and design new materials as we search for replacements to finite energy resources.

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APPENDIX: DERIVATION OF THE $T_2$-DEPENDENT COHERENCE

This density matrix evolves freely according to the matter Hamiltonian, $H_0$, until $t_3$, when the third pulse arrives. Immediately before the third pulse arrives, the density matrix is:

$$
\rho^{(\text{coherent})}(t_3-) = G_0(t_2) \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & \rho_{ab} \\
0 & \rho_{ba} & 0
\end{pmatrix}
= \theta(t_2 - t_1) \exp \left[ -\frac{i}{\hbar} H_0(t_2 - t_1) \right] \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & \rho_{ab} \\
0 & \rho_{ba} & 0
\end{pmatrix},
$$

where $G_0$ is the field-free Green function, $\theta$ is the Heaviside function, and the subscript "3-" on the time indicates this is the time just before $t_3$. Written in terms of frequency differences $\omega_{jk} = (E_j - E_k) / \hbar$, the propagator can be inserted into the matrix giving:

$$
\rho^{(\text{coherent})}(t_3-) = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & \rho_{ab} \\
0 & e^{i\omega_{ab}(t_2-t_1)}\rho_{ba} & 0
\end{pmatrix}.
$$

The effect of the next pulse is another application of the dipole operator, and the signal is proportional to the expectation value of the dipole operator. Since we only consider here the rephasing pathway, the third density operator acts from the right according to the double-sided Feynman diagram in Figure 7.

$$
\langle \mu(t_3) \rangle = \text{Tr} \{ \mu [G(t_3) \rho^{(\text{coherent})}(t_3-)] \mu \}
= \text{Tr} \left[ \mu \begin{pmatrix}
0 & 0 & 0 \\
e^{i\omega_{ab}(t_3-t_2)}e^{-i\omega_{ab}(t_2-t_1)}\mu_{b0}\rho_{ab} & 0 & 0 \\
e^{i\omega_{ab}(t_3-t_2)}e^{i\omega_{ab}(t_2-t_1)}\mu_{a0}\rho_{ba} & 0 & 0
\end{pmatrix} \right],
$$

where $\mu$ is given as

$$
\mu = \begin{pmatrix}
0 & \mu_{0a} & \mu_{0b} \\
\mu_{a0} & 0 & 0 \\
\mu_{b0} & 0 & 0
\end{pmatrix}.
$$
yields

\[
\langle \mu(t_3) \rangle = \text{Tr} \left( e^{i\omega_a(t_1-t_2)} e^{i\omega_b(t_2-t_1)} \mu_{0a} \rho_{0b} \rho_{ba} + \epsilon e^{-i\omega_a(t_2-t_1)} \mu_{0a} \rho_{0b} \rho_{ba} \right) \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}.
\] (A.5)

Fourier transform of the signal with respect to \(t_3\) yields peaks at \(\omega_{0a}\) or \(\omega_{0b}\) that are modulated by the coherence frequency \(\omega_{ab}\). The above treatment clearly neglects all relaxation, and is merely intended to explain the location of the modulated cross-peaks for a rephasing spectrum. Choosing one of these peaks, that centered at \(\omega_{0a}\), the \(t_2\)-dependence is:

\[
S^{(\text{coherence})}(\omega_{0a}, t_2) \propto e^{-i\omega_{ab}(t_2-t_1)} \mu_{0a} \rho_{0b} \rho_{ab}.
\] (A.6)

Following the same reasoning as above, the contribution to the signal at the same cross-peak due to the path that returns to the ground state during \(t_2\) is:

\[
S^{(\text{ground})}(\omega_{0a}, t_2) \propto \mu_{0a} \rho_{00},
\] (A.7)

where \(\rho_{00}\) is the ground state density matrix element during \(t_2\). The total signal at the cross-peak is given by the sum of the two paths:

\[
S^{(\text{total})} = S^{(\text{coherence})} + S^{(\text{ground})} = e^{-i\omega_{ab}(t_2-t_1)} \mu_{0a} \rho_{0b} \rho_{ab} + \mu_{0a} \rho_{0a} \rho_{00}.
\] (A.8)

Since the signal is of the form \(f(\phi) = A e^{i\phi} + B\), not only do the real and imaginary parts of the signal oscillate as a function of \(\phi\), so does the absolute value. Depending on the relative amplitudes of the dipole moment matrix elements and the density matrix elements, the absolute value modulations will have varying degrees of visibility as shown in Figure A.1.

To determine the correct relative amplitudes \(A\) and \(B\), we must examine in detail the terms \(\rho_{ab}\) and \(\rho_{00}\) by explicitly accounting for the first two pulse interactions. Again we consider the \(t_2\)-coherence and \(t_2\)-ground state paths separately. Both pathways, since we restrict ourselves to rephasing diagrams, begin with the dipole operator acting from the right on the initial density:

\[
\rho(t_1+) = \begin{pmatrix} \tilde{\rho}_{00} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & \mu_{0a} & \mu_{0b} \\ \mu_{a0} & 0 & 0 \\ \mu_{b0} & 0 & 0 \end{pmatrix}
\]

\[
= \begin{pmatrix} 0 & \mu_{0a} \tilde{\rho}_{00} & \mu_{0b} \tilde{\rho}_{00} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},
\] (A.9)
where $t_{1+}$ indicates the density immediately after application of $\mu$; this density will evolve according to the field-free Hamiltonian between $t_1$ and $t_2$ as

$$
\rho(t_1) = G_0(t_1) \begin{pmatrix} 0 & \mu_{0a} \tilde{\rho}_{00} & \mu_{0b} \tilde{\rho}_{00} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & e^{-i\omega t_1} \mu_{0a} \tilde{\rho}_{00} & e^{-i\omega t_1} \mu_{0b} \tilde{\rho}_{00} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (A.10)
$$

For the $t_2$-coherence pathway, the second pulse acts from the left:

$$
\rho(t_2^-) = \mu \begin{pmatrix} 0 & e^{-i\omega t_1} \mu_{0a} \tilde{\rho}_{00} & e^{-i\omega t_1} \mu_{0b} \tilde{\rho}_{00} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & e^{-i\omega t_1} \mu_{0a} \tilde{\rho}_{00} & e^{-i\omega t_1} \mu_{0b} \tilde{\rho}_{00} \\ 0 & 0 & 0 \\ 0 & e^{-i\omega t_1} \mu_{0b} \tilde{\rho}_{00} & e^{-i\omega t_1} \mu_{0b} \tilde{\rho}_{00} \end{pmatrix} \quad (A.11)
$$

Thus, we see that the terms we originally identified as $\rho_{ab}$ and $\rho_{ba}$:

$$
\rho_{ab} = e^{-i\omega t_1} \mu_{0b} \mu_{a0} \tilde{\rho}_{00}, \quad \rho_{ba} = e^{-i\omega t_1} \mu_{0a} \mu_{b0} \tilde{\rho}_{00} \quad (A.12)
$$

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{figure.png}
\caption{Absolute value of the cross-peak signal for three different values (0.1, 0.5, 1.0) of the relative amplitude of the ground state and coherent pathways. For the 1:1, the signal shows a distinct cusp which is observed experimentally. As the coherence dephases, the oscillations become more symmetric.}
\end{figure}
Inserting these into the expression found for the signal

\[ S^{(\text{coherence})}(\omega_{0a}, t_2) \propto e^{-i\omega_0 t_1} e^{-i\omega_0 (t_2 - t_1)} |\mu_{0a}|^2 |\mu_{0b}| \tilde{\rho}_{00} \]  

(A.13)

and we find that, indeed, the \( t_1 \) dependence shows that this signal is peaked at \( \omega_1 = \omega_{0br} \) corresponding to a cross-peak at \( (\omega_{0br}, \omega_{0a}) \).

Next, we consider the pathway where the system returns to the ground state. Following the common initial dipole application from the right, we operate with the second field from the right as well:

\[ \rho(t_{2-}) = \begin{pmatrix} 0 & e^{-i\omega_0 t_1} \mu_{0a} \tilde{\rho}_{00} & e^{-i\omega_0 t_1} \mu_{0b} \tilde{\rho}_{00} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \]  

(A.14)

\[ \mu = \begin{pmatrix} e^{-i\omega_0 t_1} \mu_{0a} \tilde{\rho}_{00} + e^{-i\omega_0 t_1} \mu_{0b} \tilde{\rho}_{00} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \]

and thus we identify the density matrix element, \( \rho_{00} \):

\[ \rho_{00} = e^{-i\omega_0 t_1} \mu_{0a} \mu_{0a} \tilde{\rho}_{00} + e^{-i\omega_0 t_1} \mu_{0b} \mu_{0b} \tilde{\rho}_{00} \]  

(A.15)

and insert it into the expression for the signal at \( \omega_{0a} \) due to the ground state propagation:

\[ S^{(\text{ground})}(\omega_{0a}, t_2) \propto \mu_{0a} \mu_{0a} \tilde{\rho}_{00} = \mu_{0a} \mu_{0a} \left[ e^{-i\omega_0 t_1} \mu_{0a} \mu_{0a} \tilde{\rho}_{00} + e^{-i\omega_0 t_1} \mu_{0b} \mu_{0b} \tilde{\rho}_{00} \right]. \]  

(A.16)

Focusing attention on the specific cross-peak \( (\omega_{0br}, \omega_{0a}) \), we consider the term centered at \( \omega_{0br} \) during \( t_1 \):

\[ S^{(\text{ground})}(\omega_{0a}, t_2; \omega_1 = \omega_{0br}) = \mu_{0a} \mu_{0a} \mu_{0b} \mu_{0b} \tilde{\rho}_{00} = |\mu_{0a}|^2 |\mu_{0b}|^2 \tilde{\rho}_{00}. \]  

(A.17)

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