

Utilizing Coherence to Enhance Function in Chemical and Biophysical Systems

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Coherence phenomena arise from interference, or the addition, of wave-like amplitudes with defined phase. While coherence has been shown to yield transformative new ways for improving function, advances have been limited to pristine matter, as quantum coherence is considered fragile. Recent evidence of coherence in chemical and biological systems, however, suggests that the phenomena are robust and can survive in the face of disorder and noise. Here we survey the state of recent discoveries, present viewpoints that suggest coherence can be used in complex chemical systems, and discuss the role of function as a design element in realizing coherence.

Introduction

Coherence often hides in complex systems, and its presence is deemed too fleeting to be relevant for robust function. As such, chemists and biologists have not traditionally considered coherence as a powerful tuning element for enhancing or explaining function. But is coherence a passing detail or is it a potential force?

The presence of coherence, and its dominance over an incoherent background, is revealed by a phenomenon known as coherent backscattering. This occurrence is apparent when we view Saturn's rings from Earth. The rings of this celestial body are notably brighter when the sun is aligned along the direction from Earth to the planet. The principle is that when the light waves enter this disordered medium, they can be scattered precisely in a backward direction. Those precisely backscattered light waves exit the medium so that they line-up in step with each other, causing their amplitudes to sum perfectly. As a result, the intensity of this back-scattered light is twice that of light dispersed in other directions¹. This amplification-like effect is astounding considering the complexity of the scattering process, through millions of randomly arranged ice crystals that comprise Saturn's ring, and then return over the same path. Adding wave amplitudes in phase is a

more powerful concept than would be anticipated, and gives rise to the notion of harnessing coherence as an element of design.

Coherent backscattering can be seen on much smaller spatial scales too, such as when it is used to improve light absorption in solar cells² or when the effect enables lasing in disordered media of plastic or powdered semiconductors^{3,4}. Likewise, scattering in periodic structures leads to ‘localized light’ that is deployed by photonic crystals and presents a novel way to control light transmission⁵. Other kinds of correlations produce striking enhancement of interactions between nanoscale systems. For example, when charge density fluctuations are correlated over long length scales, exceptional long-range van der Waals forces result⁶. Such attractive forces are impossible to attain by an incoherent sum of interactions from local fluctuations along the breadth of the materials.

We are accustomed to viewing functional biological systems as operating classically, so when quantum coherence appears, it seems surprising. However, recent discoveries of coherence phenomena in various biological and materials systems⁷⁻¹¹ suggest the viability of coherence-enhanced function. In addition, coherence has been widely discussed as a means of improving transport in disordered and complex systems¹². Examples include long-range transfer of electronic excitation—light harvesting—in photosynthesis and efficient, almost unidirectional charge separation at donor-acceptor interfaces in organic photovoltaics. While it is stimulating to consider unique microscopic protocols for employing coherence and quantum effects, greater inspiration lies in how to leverage these effects to yield new ways of optimizing materials, energy transduction, multi-molecular machines, or whether new and potent routes for chemical synthesis might be conceived.

Now is the time to evaluate opportunities to harness electronic and nuclear coherences to realize energy transduction or chemical transformation including, but not limited to, reactions driven by light. In this report, we explore: What are current examples that indicate how function has been enhanced by engineering dynamics in a coherent regime? How does coherence change the way we approach designing for function? While we build our discussion around some select examples from the literature, we do not attempt to review the full scope of work that has been published in the past few years.

Defining and Detecting Coherence

Coherence can be classical or quantum mechanical and comes from well-defined phase and amplitude relations where correlations are preserved over separations in space or time. While an intuitive picture for classical coherence is a recurring pattern, quantum mechanical coherence is exemplified by superposition states. The distinction between classical and quantum coherence is not always obvious, but is indicated by special correlations—a notable example is photon bunching and anti-bunching¹³. Quantum superposition states thereby have properties that are not realized in classical superpositions¹⁴.

We are likely more familiar with quantum mechanical coherence than we realize. For example, chemists know there are two ways of drawing the alternating double and single bonds in a benzene ring and that these two structures, φ_1 and φ_2 , are in ‘resonance’, meaning that, from the perspective of classical valence bond theory¹⁵, the electronic ground state is a quantum mechanical superposition state that includes resonance of these Kekulé structures: $c\varphi_1 + c\varphi_2 + \dots$. More limited delocalization can mix the wavefunctions of an electron donor and acceptor into an intervening bonding bridge. When this occurs, the bonding bridge enables remarkably long-range electron transfer (20–30 Å) reactions through chemical bonds in supramolecular systems, or through proteins to instigate biological redox chemistry¹⁶⁻¹⁸.

Coherence effects that result from strong resonance interactions are robust and decisive in their roles for function because these states are little perturbed by disorder and fluctuating interactions. Other coherences are fragile, as it is difficult to maintain states in lock-step when the system is subject to strong random fluctuations—this process where phase coherence is lost is called decoherence. Coherence and decoherence are, therefore, competing processes, **Box 1**. To understand conceptually how energy gap fluctuations affect resonances and, upon appropriate averaging, give rise to decoherence the example of “flickering resonance” can be helpful¹⁹.

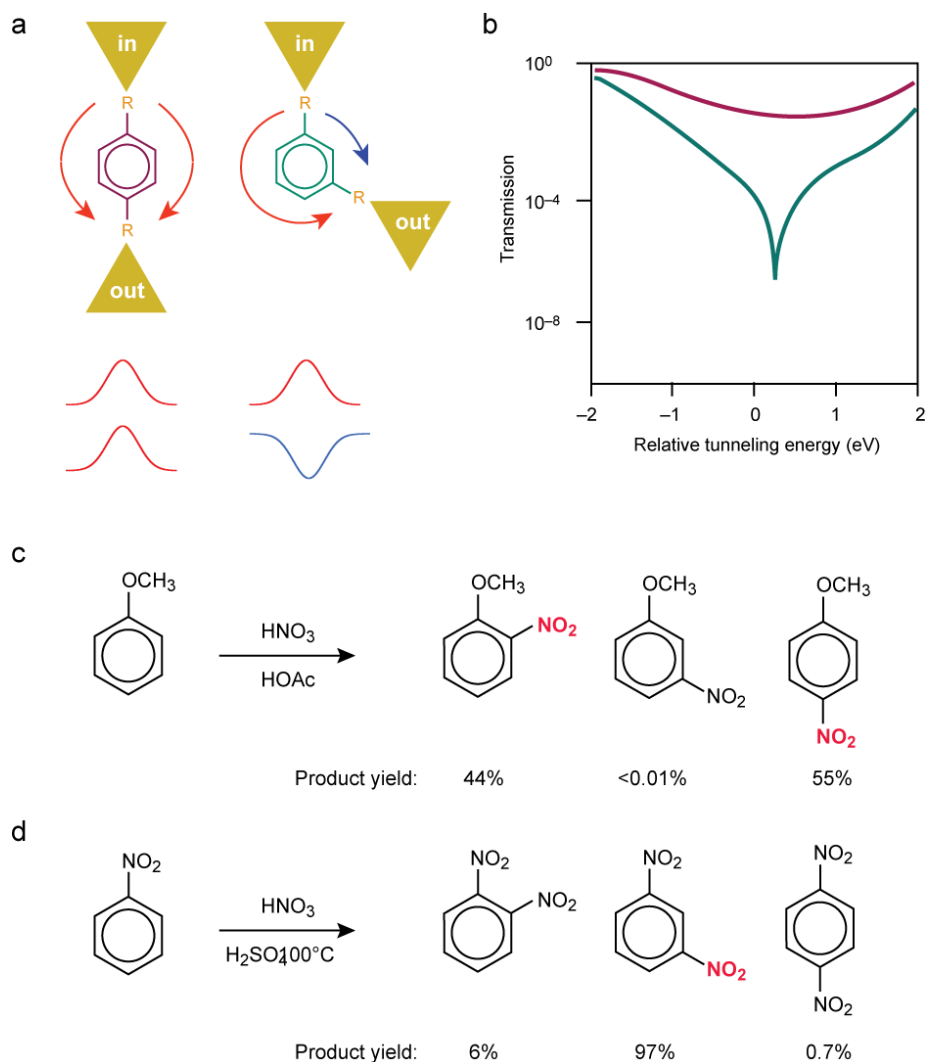


Figure 1. Coherence phenomena. a. Conceptual illustration of the electron wavefunction amplitude for two alternative transmission paths through the molecule, R = thianoethyne. The gold triangles represent the electrical contacts of the molecular transport junction apparatus. b. Current transmission curves predicted for the para-configuration molecule, red, and the meta-configuration molecule²⁰, green. c, d. Examples of prototypical electrophilic aromatic substitution reactions.

Adding wave amplitudes, or interference phenomena, have dramatic consequences. For example, when a molecule spans two electrodes^{21,22} transport junctions form to reveal striking differences in current according to interference of the pathways by which electrons can be routed through a molecule^{23,24}. As the electron tunnels through the molecule it traverses physical, structural pathways according to the amplitudes and

energies of molecular orbitals^{20,25,26}. Quantum interference between pathways through the π -system can prevail, despite competing pathways through the σ -bonds. We illustrate in **Figure 1a,b** representative calculations from this rich field of investigation. We show of two contrasting cases of tunneling through di(thioethyne)benzene molecules—the electron tunnels from one electrode through the benzene ring to the other electrode, via the input and output thioethyne linkers. Linkers can be positioned at different relative positions on the 6-fold symmetric benzene ring. In the para-linked molecule, the two principal pathways are identical and, therefore, interfere constructively and ensure high transmission. In contrast, meta-linking the two thioethyne groups in the same chemical moiety results in the electron traversing two different pathways around the aromatic ring. Destructive interferences result and are evident in the transmission spectrum as markedly suppressed transmissions at various energy resonances. These observations contrast with predictions from circuit analogs where resistors are wired in parallel²⁴.

A similar partitioning of ortho/para versus meta pathways is well known in synthetic chemistry, and is widely exploited in electrophilic aromatic substitution reactions. The withdrawal or addition of electron density by a substituent defines a particular pattern of electron density at the ortho, meta and para positions and primes them for directed attack by the reagent. In this case, electron donating reagents yield ortho or para substitution, while electron withdrawing reagents direct meta substitution, **Figure 1c,d**. This serves to show how quantum interference might have wider implications, but we note that there is a broad literature on aromatic C-H activation chemistry that does not easily connect with the elegant explanations of single molecule conductance.

In many systems, such as complex molecules or even single electrons or photons, coherence can be difficult to measure. Standard measurements tend to hide coherence as they only measure probabilities—that is, diagonal elements of the density matrix—either in a particular basis that is unique to the experiment or in a basis that changes with time, for instance as excitons localize. Despite this challenge, it is important to assess coherence for feedback on design principles. Function comes from dynamics, a transformation from reactants to products, and optimal microscopic dynamics results

from a balance between coherence and dissipation. Between the limits of this interplay, there must be a maximum in the rate²⁷.

Coherence can be detected reasonably easily using specialized measurements. For example, short laser pulses can excite ladders of states in phase, thereby making a superposition that can be detected using two-dimensional spectroscopy, [Box 2](#). A cross-peak in the 2D map labels the excited and detected transitions, while oscillations in the cross-peaks as a function of pump-probe waiting time reveal coherences involving those transitions marching together in time. This does not last forever—the oscillations damp away as a function of waiting time as a consequence of dephasing, giving a lower bound for the decoherence time of the quantum superposition. An example of electronic coherence is shown in [Figure 2a–c](#). Broad-band femtosecond pulses overlap the first two exciton states, heavy-hole exciton (HX) and light-hole exciton (LX), of a semiconductor ‘nanoplatelet’ colloid dispersed in ambient temperature solution²⁸. The amplitude of the cross-peaks, HX-LX and LX-HX, in the 2D signal map oscillate as a function of excitation-detection time delay, showing that the amplitude of HX and LX bands indeed are correlated until the superposition dephases. This dephasing of this ensemble happens with a time constant of 13 fs. Electronic coherences at ambient temperature typically decohere with a time constant of ≤ 100 fs.

Similarly, vibrational ladders in molecules can be impulsively excited as superposition states (vibrational coherences) by short laser pulses, [Figure 2d,e](#). In [Figure 2d](#) the transient absorption spectrum of a chromophore cresyl violet in solution as a function of pump-probe time delay is shown. Notice the ripples on top of the spectrum—these indicate the in-step phase of the vibrational coherence synchronously swinging backwards and forwards in the vibrational potential of each mode²⁹. The coherences are better revealed by removing the slowly changing signal amplitude due to population kinetics, [Figure 2e](#). Vibrational coherences typically decay with time constants in the picosecond range.

An outstanding challenge is to relate the detected coherence to its role in function, and this goal likely requires more detailed characterization of wavefunction amplitudes and phases. The challenge comes down to how to reconstruct essential features of a

wavefunction by a series of measurements of observables. For example, even for a simple light wave, four carefully referenced unique measurements of the transmitted intensity of a light beam through various polarizers and waveplates are needed to measure the polarization state³⁰. That inspires a strategy for characterizing quantum superpositions³¹. Clearly new kinds of characterization tools for complex molecular systems are essential. Recently, it has been demonstrated that a technique known as weak measurement allows for direct access to the wavefunction³² or density matrix of a system³³. In a weak measurement the system is only very weakly perturbed in each measurement trial and a correspondingly small amount of information about its state is learned. Averaging over repeated measurements on an ensemble allows the density matrix to be pieced together. Monitoring biological and chemical systems by weak measurements thus offers a new way to study the role of coherence in their function, **Box 3**.

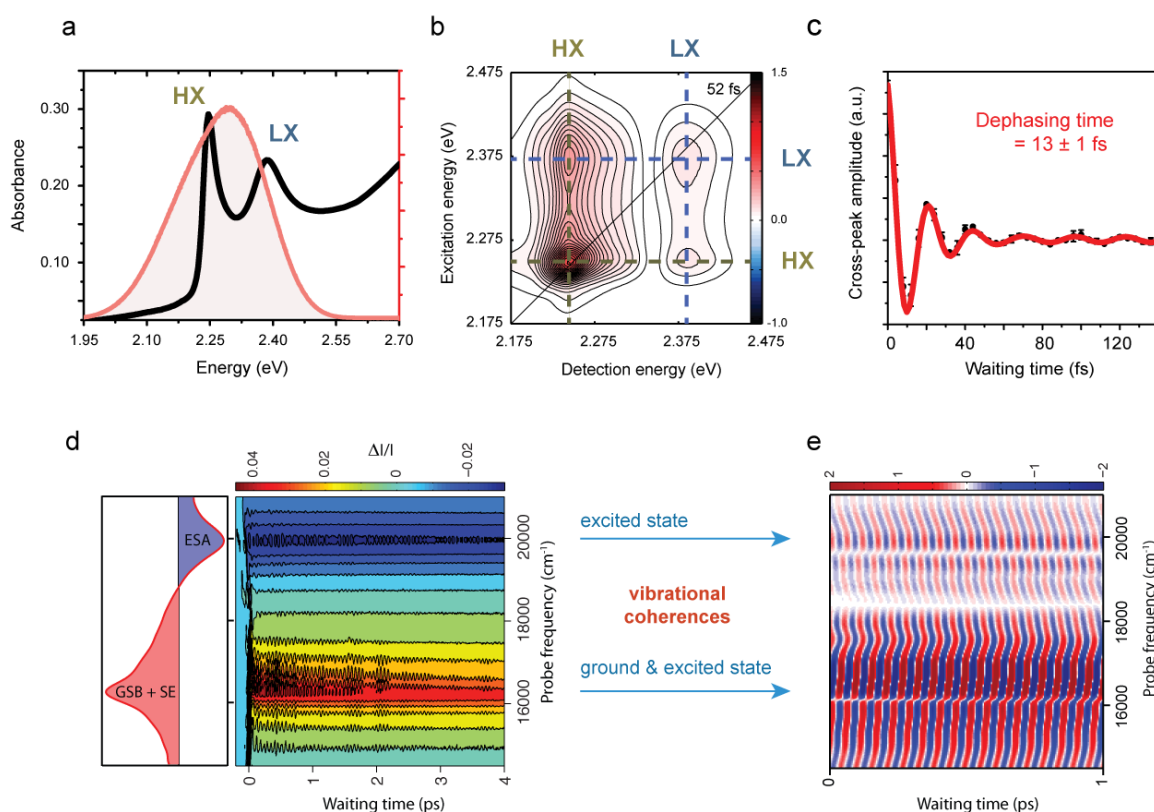


Figure 2. Coherences Revealed by Experiment. a. Absorption spectra of CdSe nanoplatelets (black line) showing the HX and LX exciton transitions²⁸. Spectrum of the laser pulses used in the 2D spectroscopy experiments is the orange shaded band. b. Two-dimensional electronic spectrum recorded at a pump-probe delay time of 52 fs. c. Amplitude oscillations in the lower

cross peak of the rephasing 2D spectrum for a CdSe/CdZnS nanoplatelet (real part with population relaxation subtracted) as a function the waiting time. d. A contour map of broad-band pump probe data for cresyl violet solution showing the oscillatory modulation on top of ground and excited state population dynamics³⁴. e. Fourier filtered pump-probe data revealing coherent oscillations of the strong Franck-Condon active modes.

Vibronic coherence

As molecules are complex, their spectroscopy is often not well described as a simple ladder of states. Instead, the interplay among electronic and nuclear motions can lead to quite complicated vibronic levels and mixing between electronic and vibrational wavefunctions³⁵⁻³⁸. This mixing is important for understanding spectroscopy, intramolecular dynamics, and chemical reactions³⁶, and it changes the intuitive translation from spectroscopy to dynamics. Simulations and experiments are needed to identify electronic and vibrational coherence, and combinations known as vibronic coherence where it is impossible to otherwise discriminate electronic from vibrational energy ladders.

A range of phenomena result, collectively called vibronic coupling. Delocalization via vibronic coupling can be robust to environmental fluctuations and it provides an opportunity for chemical design because the underlying vibrational resonances are readily be tuned by structure. The recognition of functional vibronic coherence in biological and chemical systems has been inspired by the discovery and subsequent investigation of surprising coherent oscillations revealed by 2D electronic spectroscopic studies of photosynthetic systems^{7,9,10}, **Figure 3a,b**.

To illustrate how interaction between molecules changes an intuitive ladder of vibrational levels into a more complicated set of states, model calculations of two interacting molecules³⁶ (electronic coupling 50 cm^{-1} , energy gap 650 cm^{-1} , and vibrational frequency of 600 cm^{-1}) are plotted in **Figures 3c,d**. When the vibrational reorganization energy is large, **Figure 3c**, it is clear that the spectroscopy is a simple sum of those of the individual molecules. When the displacement is smaller, **Figure 3d**, the vibronic transitions become delocalized across the two molecules. This is the case where exciton-vibration delocalization is amplified by resonance between the excitonic gap(s) and vibrational

frequencies³⁹. Physically, the displacement represents a change in geometry of the molecule along each normal mode upon photo-excitation, as equilibrium geometries are different in each electronic state.

Vibronic transitions are crucial for enhancing energy transfer rates, as evident in the Förster spectral overlap, because they provide many combinations of energy differences. Similarly, vibronic states provide a manifold of donor and acceptor states that can bridge large free energy differences and increase rates of electron transfer immensely⁴⁰.

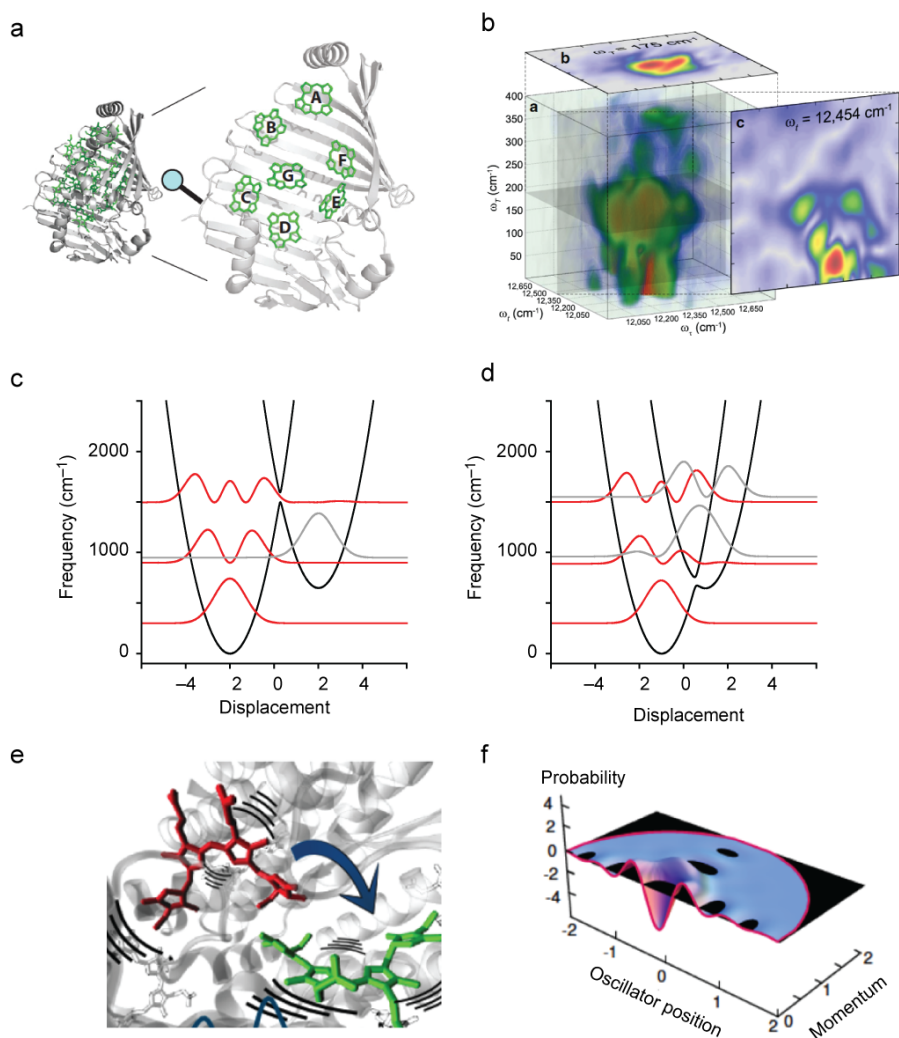


Figure 3. Vibrations change the picture. a. Structural model of the FMO complex from a green sulfur bacterium. The 7 (of a total of 8) resolved chromophores are indicated. b. Quantum beating signatures for a 77K FMO 2D spectrum show the frequencies associated with the energy differences among the excitons. The waiting time axis has been Fourier transformed to frequency, see ref ⁴¹. c. Vibronic wavefunctions of two weakly interacting molecules, showing that

excitations are independently localized on each molecule (electronic coupling 50 cm^{-1} , mode frequency 600 cm^{-1} , energy gap 650 cm^{-1} , dimensionless displacement 4.0). d. As coupling to vibrations becomes weaker (dimensionless displacement 2.0), the vibronic densities delocalize across the two molecules. e. Model dimer of bilin molecules from the light harvesting complex PE545, where excitonic states are quasi-localized. f. Regularized Glauber-Sudarshan P distribution, which is a phase space distribution used to write the density matrix of the state of the vibrations in the basis of coherent states. Rather than true probability, negative values make this a *quasi-probability* distribution in phase-space. Such negative values cannot be exhibited by the state of any classical system—are unambiguous signatures of the state’s quantum character⁴².

Recent work has examined the implications of these delocalized vibronic states for 2D spectroscopy and light harvesting mechanism^{39,43-46}. It has been proposed that discrete vibrational modes of electronically coupled chromophores may generate and regenerate coherence against a background of dephasing if the exciton-vibration coupling is sufficiently strong⁴⁷. Other work suggested coherent vibronic energy transfer has signatures of quantum mechanical probability laws⁴², **Figure 3e,f**. In this case, when analyzing the collective nuclear motions coupled to the excited state dynamics, it was found that the distribution of the occupation number of the vibrational motion driving energy transfer between molecules is much narrower than predicted for a classical coherent system. Such small fluctuations can only be described by quantum phase-space quasi-probability distributions that have negative values, **Figure 3f**, which is a feature impossible to find in a classical system. Experimental approaches that certify the non-classical nature of coherence in chemical and biophysical systems are essential if we are to understand what functionalities can be enhanced or achieved only via quantum coherence.

Studies of other systems ranging from organic photovoltaics to photosynthetic reaction centers associated with the oxygen evolving complex photosystem II (PSII) have revealed notable coherent oscillations using ultrafast spectroscopy⁴⁸⁻⁵⁰. Many of these oscillations have frequencies of vibrational modes identified in resonance Raman and fluorescence line-narrowing spectra, and some of these frequencies also match frequency differences between the exciton states. The key result in the case of PSII is that resonance between

excitons and vibrational levels in charge-transfer states leads to vibronic mixing that is hypothesized to optimize the flow of population to the terminal charge separated state⁵¹.

As well as modifying spectral band progressions, vibronic coupling can localize excitation or charge. The manifestation of vibronic coupling in spectra of molecular aggregates can therefore be utilized to measure exciton delocalization by relating the mean delocalization length of excitons to the ratio of the electronic photoluminescence band intensity (I^{0-0}) and the first vibronic band (I^{0-1})^{52,53}. The photoluminescence ratio analysis reveals the extraordinary coherent delocalization of the exciton along disorder-free polydiacetylene chains^{52,54}, **Figure 4**, estimated to be $\sim 30\text{--}50$ nm at 15K.

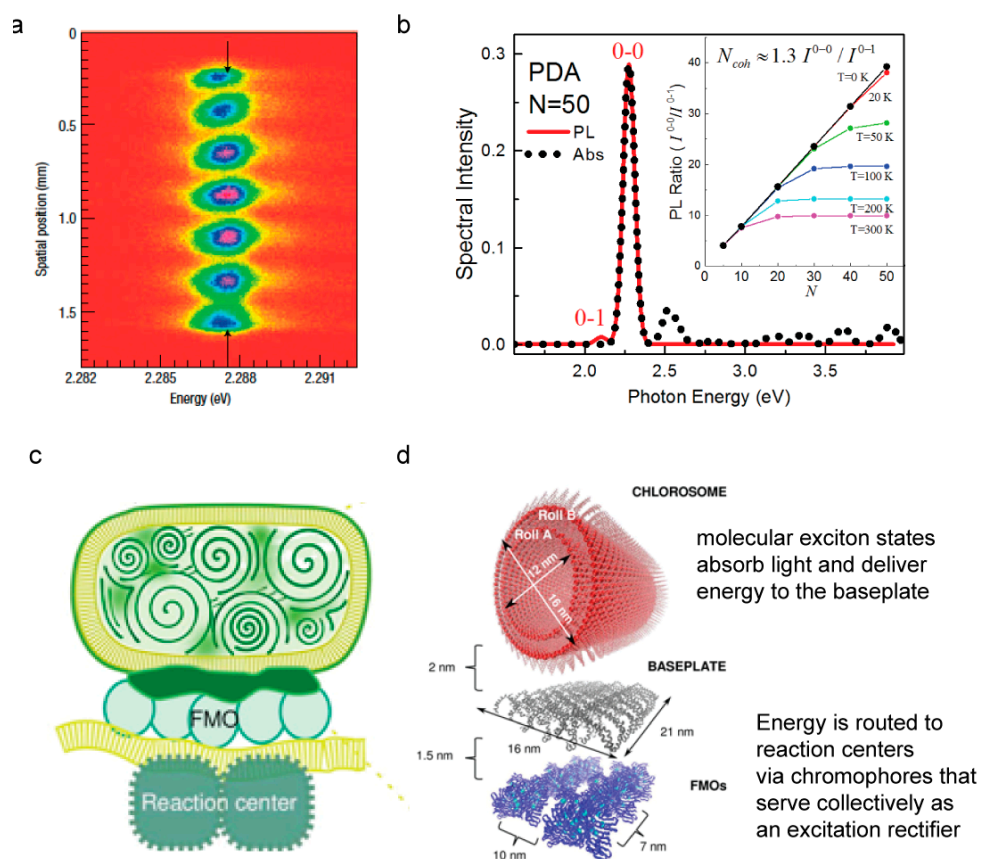


Figure 4. Long-range Excitons. a. Fluorescence interference pattern obtained from two 1- μm -wide emitting regions of a 10- μm -long chain of polydiacetylene, suggesting an extraordinary coherence length for the exciton⁵⁴. b. Absorption spectra (black dot) and emission spectra (red line) predicted for polydiacetylene chains with $N=50$ repeat units at $T = 0$ K calculated numerically using the multiparticle basis set⁵². Inset shows how the calculated photoluminescence ratio I^{0-0}/I^{0-1} depends on N for various temperatures. The linear behavior at

low temperatures saturates at higher temperatures, indicative of a convergent coherence number, with $N_{coh} < N$. c. Illustration of the chlorosome light harvesting complex and associated proteins the transport excitation energy to the reaction center in green sulfur bacteria d. The atomistic model used for simulations. It includes the chlorosome, baseplate and FMO complexes.

Coherent Excitons are Prevalent and Robust

Coherence is certainly used in photosynthetic light harvesting⁵⁵ as evidenced by strong electronic coupling that delocalizes excitation to produce new effective chromophores that span multiple molecules. These effective light-absorbing states are known as molecular excitons⁵⁶. Delocalization in molecular exciton states is a kind of coherence that is robust to dephasing between excitons because energy fluctuations at individual molecular sites are averaged away⁵⁷—that effect is observed as narrow spectral line shapes. Molecular excitons can have significant functional implications for materials⁵⁸.

Light is absorbed and emitted collectively by these delocalized states, and the interplay of phases in the light absorbing units that decide the properties of molecular excitons can be effectively modeled by scattering of standing waves⁵⁹, emphasizing how the excitonic optical properties derive from coherence. Energetic disorder disrupts this perfect wave-like properties underpinning exciton states, thereby diminishing their delocalization through space^{12,60}. Delocalization competing with localization is seen in experimental data and well illustrated by recent studies of various supramolecular systems⁶¹⁻⁶³ as well as in natural ring-shaped light harvesting complexes from purple bacteria⁶⁴. Superradiance is the collective fluorescence emission from two or more interacting chromophores, which lead to shorter radiative rates for reasons much like the explanation for coherent backscattering described in the introduction. Superradiant enhancement of emission reveals the robustness of exciton delocalization⁶⁵.

Exciton states have significant consequences for light harvesting because energy donor and/or acceptor are not single molecules, like the case treated in normal Förster theory. Instead, the energy donor and/or acceptor comprise the exciton states shared between strongly interacting chromophores. New effective chromophores for light harvesting can thus be constructed, or in nature they can evolve based on pigments already employed by

a photosynthetic organism—amply demonstrated by the B850 ring in the LH2 light harvesting complex of purple bacteria⁶⁶. A modified version of Förster theory accounts for the way these non-additive effects in excitonic donors and acceptors promote energy transfer, and we call this Generalized Förster Theory (GFT)⁶⁶⁻⁶⁸.

In GFT, the donor and/or acceptor states are delocalized—this is strong electronic coherence—but owing to a separation of time scales (energy scales of electronic couplings) the energy transfer from donor to acceptor is treated as incoherent, just as in Förster theory. Keeping in mind the interplay between delocalization and decoherence (Box 1), states can be much more delocalized when serving as excitation acceptors than donors. The delocalization of excitation within donor and/or acceptor manifolds enable remarkable acceleration of the energy transfer rate because the collective transition dipoles are much larger than molecular transition dipoles. Also, in marked contrast to Förster theory, dark exciton states are often similarly good excitation donors or acceptors because of how the dipole approximation fails in the case of molecular aggregates⁶⁶. For B800 to B850 energy transfer in LH2, the rate is predicted to be ten times faster than the simulations that assume excitation is localized on bacteriochlorophyll molecules⁶⁷. A similar example of how delocalization can enhance energy transfer is found in the chlorosome antenna complex of green sulfur bacteria⁶⁹, [Figure 4c,d](#).

The complexity of theory needed to predict energy transfer depends on a balance of frequency scales, as discussed in Sec. 2, necessitating development of sophisticated theories to describe details of the energy transfer mechanism⁷⁰⁻⁷⁴. What evidence is there that these complicated theories are necessary? One important ongoing advance is to develop experiments that record not only rates of energy transfer, but provide insight into the mechanism and provide stronger tests for theoretical models. Two-dimensional electronic spectroscopy⁷⁵⁻⁷⁷ has enabled significant contributions in this direction. For example, long-lived coherent oscillations—whatever their precise origins—observed in 2D electronic spectra of the Fenna-Matthews-Olson (FMO) complex, [Figure 3a,b](#), as a function of pump-probe waiting time⁴¹, challenge the predictive power of theories for assessing the competition, or cooperation, of coherent and incoherent reaction mechanisms^{7,10}.

Coherent Charge Transport

In the sense of long-range periodic electronic states (Bloch functions), coherence is the basis for describing charge transport in crystalline solids. In such solid state systems, decoherence can be caused by phonons, collective vibrations of the lattice that include vibrations that couple to optical transitions. When electron-phonon coupling is much weaker than electron-electron interactions, as is the case for most crystalline inorganic semiconductors and metals, an electronic wavefunction is delocalized over the extended lattice and is well described in momentum space by the single particle band structure. Coherent movement of a low energy electron or hole can be described by ballistic motion of a free electron or hole with effective mass determined by the band curvature near the conduction band minimum or valence band maximum. Scattering by phonons and charged defects disrupts the coherent motion of these carriers, leading to diffusive transport when the scattering is strong.

The discoveries of highly efficient solar cells from hybrid organic-inorganic perovskites (HOIPs) have led to feverish research activities with no slow-down in sight⁷⁸. HOIPs are easily formed from solution at room temperature and, therefore, should contain a high density of structural defects. Surprisingly, photophysical and transport measurements reveal behavior expected for intrinsic and defect-free semiconductors⁹¹ including long-lived charge carriers with lifetimes more than three orders of magnitude longer than those in conventional semiconductors, suggesting drastically reduced electron-phonon scattering rates⁷⁹. The exceptional properties of HOIPs are hypothesized to arise from coherent transport of carriers and the way carriers couple to lattice vibrations to form polarons. The size difference between polarons results in markedly different transport properties^{79,80}. A large polaron moves coherently and its mobility depends inversely on temperature. The large polaron may provide the essential protection mechanisms to shield charge carriers from each other and from charged defects⁸¹.

Is coherent charge transport important in disordered molecular systems? This is a question that has been examined in the context of conjugated materials for solar energy conversion⁵⁸ and charge transport along DNA strands⁸².

Transition metal complexes

From biochemistry to catalysis (both thermal and photochemical) to solar energy conversion, transition metal complexes play an important role. Their relevance comes about due to the interdependent electronic and structural features that arise from the involvement of *d* orbitals in the valence configurations of such compounds. The Jahn-Teller distortion—ubiquitous in transition metal complexes—is closely related to the vibronic exciton model discussed above⁸³. For instance, the D_{2d} symmetric bis(diimine)copper(I) complex flattens to D_2 symmetry upon photoexcitation. The sequence of motions involved has been followed in experiments detecting coherent vibrational wavepackets⁸⁴, **Figure 5a**. It was found that the b_1 symmetry 290 cm^{-1} vibration decoheres as its vibrational energy flows to the low frequency b_1 flattening mode and the molecule changes shape.

Structural motion can drive coherent changes to electronic structure when it modulates metal-metal interactions. For example, the di-Pt(II) complex, $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ (ppy = 2-phenylpyridine; $^t\text{Bu}_2\text{pz}$ = 3,5-di-*tert*-butylpyrazolate), undergoes a metal-metal-to-ligand-charge-transfer transition upon photoexcitation and, subsequently, the Pt–Pt equilibrium distance contracts. For this reason, electronic coupling between the two halves of the molecule is modulated by metal-metal vibrational motion⁸⁵, **Figure 5b**.

Persistent coherence through an electronic state change is afforded from studies of chromium acetylacetonate,⁸⁶ where excitation into the lowest-energy spin-allowed ligand-field absorption of this compound results in rapid intersystem crossing from a quartet to doublet spin excited state in $<100\text{ fs}$. Coherent oscillations produced by excitation of the initial quartet state do not decohere during the radiationless transition, **Figure 5c**. Studying these coherent motions in the context of wave packet dynamics may suggest ways to reengineer molecules so as to manipulate the excited-state dynamics.

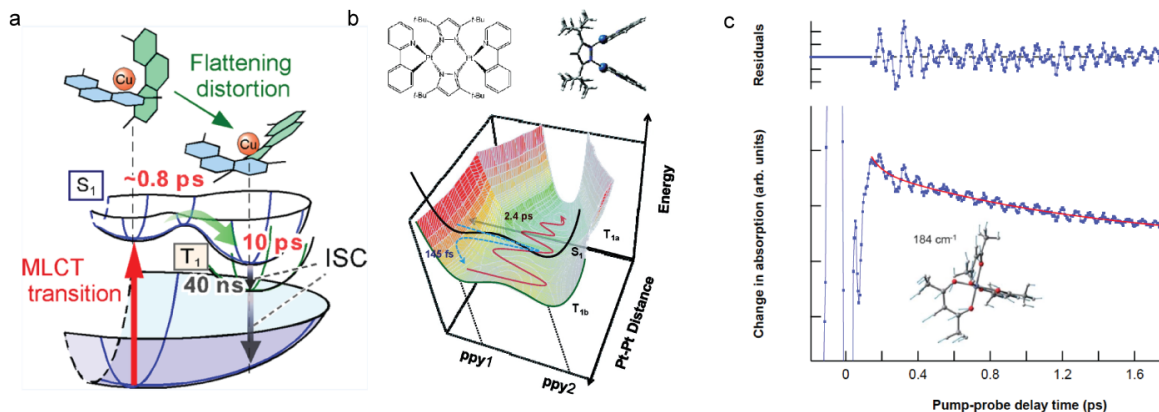


Figure 5. Coherent motion in transition metal complexes. a. Schematic diagram of the mechanism of the photoinduced structural change of $[\text{Cu}(\text{dmphen})_2]^+$ and the concomitant coherent vibrational wavepacket motion⁸⁴. b. Energy relaxation diagram for $[\text{Pt}(\text{ppy})(\mu\text{-}^i\text{Bu}_2\text{pz})_2]$ elucidated from femtosecond pump-probe anisotropy data superimposed on potential energy curves⁸⁵. c. Transient kinetics measured for $\text{Cr}(\text{acac})_3$ following excitation into the lowest energy spin-allowed ligand-field state⁸⁶.

Function from Coherence

While coherence comes in many forms and modifies dynamics in different ways, it often involves complex correlations and might be hidden from the experimenter. Regardless, exploiting coherence clearly enables new ways to enhance properties or even to produce functions not conceivable by other routes. Designing chemical or synthetic biological systems that use coherence optimally is a difficult challenge and a goal that needs specific systems in mind.

When designing for function, we should ask: (i) Will we take a modular approach and design building blocks that work using coherence and then assemble them? Will these building blocks perform the desired function or will the desired function emerge collectively only once the units are coupled? (ii) How will the system scale? How will the macroscopic function that will likely appear—and be explainable classically—be enabled by coherence at the microscopic level? (iii) What sorts of materials will enable scaling?

Highlighting quantum interference effects requires a nonintuitive balance of factors at the molecular scale⁸⁷ and suggests that scaling the design to more complex systems is challenging, but has great potential. One of the issues to address is the question of time

scales, in particular how long the coherence needs to be sustained (see **Box 1**) to provide function before the phase information is lost. While the relevant time scale is not always the rate of the dynamical process, it is useful to consider for molecular transport junctions, for instance, how long the electron resides on the molecule as it passes from one electrode to another⁸⁸. When the electron tunnels, this so-called contact time is very short (~1 fs), but it increases markedly in the resonance regime and, in tandem, the scattering becomes inelastic.

Decoherence is not always detrimental —indeed, it can be deployed to achieve function. Recent work for instance has predicted that fluctuations can produce coherence that drives the production of mobile carriers in organic solar cells⁸⁹. An example of quantum effects interplaying with kinetics and decoherence is the *quantum ratchet*, or rectifier⁹⁰⁻⁹². The principle is, essentially, that coherence helps defeat the efficacy of back reactions otherwise enabled by the detailed balance condition. The concept is that a fast-forward reaction involves free evolution in the basis of delocalized states, the next fastest process is decoherence that localizes the product state, and then the even slower back reaction is suppressed because it is limited to incoherent dynamics. This ensures unidirectional transfer, which causes a rectifier action, and has been suggested to be especially relevant for the Fenna-Matthews-Olson (FMO) complex that functions as a quantum wire or diode for excitons. A hypothesis for charge separation in conjugated oligomer-fullerene blends is also such an example⁹³.

Whether coherence can be harnessed in synthetic chemistry is an interesting, and immensely challenging, question. Chemical transformations are often considered based on electronegativity arguments, where reactive groups (e.g. electron rich or poor) attack molecules, and form new bonds. At first glance, such mechanisms involve multiple electrons in the structure but, in practice, they typically occur as one-electron steps via transition states. Since energetic barriers for making and breaking bonds are high, these reactions proceed relatively slowly. To analyze the time scales and seek opportunities where coherence could be used in optimization, we propose that defining a contact time would be useful, analogous to that described for the molecule transport junctions.

Quantum chemical dynamics calculations have predicted roles for coherence underpinning catalysis, specifically the role of molecules interfacing with a semiconductor⁹⁴. Many important photo-induced reactions require redox steps (e.g., water oxidation). The redox flexibility of transition metal complexes combined with the sensitivity of their geometry to oxidation state presents opportunities for coupling light absorption with multi-electron chemistry. Whether or not multielectron transfers can be achieved coherently is an unanswered question, although one- versus two-electron transfer processes have been studied theoretically⁹⁵. A hint as to the difficulty of the problem can be seen by comparing the energy scales in a molecule of orbital energies (one particle energies) to the electron correlation corrections for the electronic states, which are much smaller.

As a specific example, consider the Diels-Alder cycloaddition reaction that cyclizes a diene together with an alkene. Two pathways are conceivable⁹⁶. One where the reaction happens in two incoherent intermediate steps—the reactants are hinged together, then tethered to complete the cyclization. The other pathway forms these partial bonds synchronously, yielding a cyclic intermediate that subsequently relaxes geometrically and electronically to the product. It has been established that the activation barrier for this latter mechanism is lower than the sequential pathway, but only slightly. Ultrafast spectroscopic studies in the gas phase have suggested that both concerted and sequential pathways can be involved⁹⁷. What is not clearly resolved is whether the concerted mechanism can be classed as coherent.

Proton-coupled electron transfer (PCET) is ubiquitous in biology and is also important for realizing difficult chemical transformations, including production of solar fuels^{98,99}. An opportunity for coherence is in the coordination of the electron and proton transfer, where quantum effects are relevant because these are light particles. Evidence suggests they can be concerted¹⁰⁰, but to what extent are they quantum-mechanically coherent? Interestingly, many of the principles discussed in this report are relevant to mechanistic details of PCET reactions¹⁰¹.

Open Questions and Forecast

Coherence and how it affects function are not as mysterious as sometimes perceived. While, to date, much of the experimental work has been devoted to demonstrating its existence in specific physical, chemical, or biological systems, there are many examples of coherence phenomena from synthetic chemistry to coherent scattering phenomena to van der Waals forces. These examples illustrate that employing coherence for function can be practical and is not limited to exotic materials at low temperature.

We suggest that the focus should now shift from confirming the existence of coherence to exploring the connection between coherence and function. This area of investigation will require extensive feedback between theory and experiment, synthesis and measurement, and the development of systematic methods to quantify the influence of coherence in specific processes or devices.

Exploration of function requires controlled perturbation and establishing this essential methodology requires new control mechanisms and clear assessment tools. For instance, new experimental techniques need to measure delocalization of wavefunctions as well as the collapse of delocalized states that will serve to elucidate quantum-ratchet like effects. Initial steps in this direction have been reported, showing that the ratio of vibronic intensities we described in Sec. 3 can be used to track localization in time by measuring the time-evolving fluorescence spectrum⁶².

Attosecond laser sources have already opened up the ability to study coherent electronic motion, like charge migration and quantum interference between electrons^{102,103}. Attosecond lasers may enable studies of electron-nuclear wave packet motion¹⁰⁴. Similarly, advances in time-resolved X-ray spectroscopies open up new probes of electronic structure^{105,106}. Inspired by coherent multiple scattering and molecular transport junctions, reactivity of metal centers might be directed or redox chemistry tuned by interference effects to modify the electron density at an active site of a catalyst.

Is coherence a potential force for enhancing function? Reflecting on coherent backscattering, which provides scattering that is two times brighter than diffuse scattering, significant gains are possible when robust coherence phenomena are exploited. This level of gain warrants the aim of future research. Yes, while many fundamental

problems remain to be investigated, we conclude that the prospects for coherence-enabled function are bright—like Saturn’s rings when viewed with zero phase angle.

Acknowledgements

The authors gratefully acknowledge the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy. We thank Mark Spitler and Jeff Krause for leading the organization of the Basic Energy Sciences workshop on *Optimal Coherence in Chemical and Biophysical Dynamics*. G.D.S. thanks Erik Sorensen for explaining electrophilic aromatic substitution reactions. We thank Eileen D. Foszcz for providing Figure 5c. We thank Lee Truly Rumbles, freelance writer, for improving the manuscript.

Author contributions

L.X.C. proposed the workshop to the Department of Energy Council for Chemical and Biochemical Sciences. G.D.S. and G.R.F. wrote the paper with substantive input from all co-authors. All the authors formulated and discussed the content of the paper and commented on the manuscript.

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Box 1: Quantum Mechanical Coherence and Decoherence

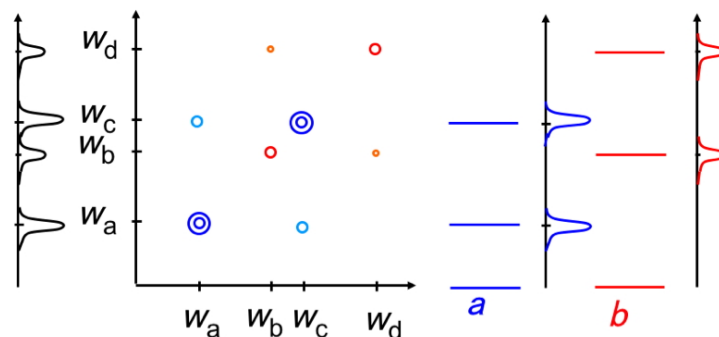
Chemists are familiar with the concept and importance of quantum mechanical coherence in the context of magnetic resonance. In that case coherence means that spins are **superposition** states—wavefunctions of the form $\psi_i = c_\uparrow|\uparrow\rangle \pm c_\downarrow|\downarrow\rangle$, manifest as net spin polarization perpendicular to the magnetic field. Usually ensembles of (non-interacting) spins are observed in an experiment, and can be thought of as a collection of independent spins with individual coherences (provided the spins are considered to be distinguishable) between their orientations $|\uparrow\rangle$ and $|\downarrow\rangle$.

The full information on the system is encoded in the associated statistical operator or **density matrix**. Since nothing more is to be known about the quantum state of the spin, the density matrix (note this is an ensemble average) is directly associated with the system state and itself often simply called “the state”. Probabilities of finding populations of a spin state are indicated in diagonal elements of this matrix, $|\uparrow\rangle\langle\uparrow|$ and $|\downarrow\rangle\langle\downarrow|$. However, this matrix encodes decisively more than probabilities, namely coherences. Coherences are indicated by “off-diagonal” values, that in this example include $|\uparrow\rangle\langle\downarrow|$ and $|\downarrow\rangle\langle\uparrow|$. Note that coherence is the property of a state and it is dependent on the choice of basis because it is defined with respect to a certain basis (here the spin basis comprising $|\uparrow\rangle$ and $|\downarrow\rangle$). Other kinds of measures that do not depend on the representation basis can be used to analyze the coherence properties of a given state, for example ‘purity’—defined as the trace of the square of the density matrix.

Coherence will generally diminish with time following its creation by, for example, an ultrashort light pulse. The loss of coherence is referred to as **decoherence** or **dephasing**, and although these terms mean different things they are often used interchangeably. Decoherence may be understood as a purely quantum mechanical phenomenon that arises from the observed system becoming quantum mechanically entangled with the unobserved bath (environment) degrees of freedom. Averaging over the latter leads to an irreversible decay of the off-diagonal elements of the system’s density matrix, which can also be induced by classical noise. The system thus irrevocably loses its ability to exhibit interference phenomena. Dephasing, on the other hand, has contributions from both decoherence and from an ensemble effect that arises because different ensemble members evolve slightly differently, so that phase correlations across the ensemble are progressively reduced on average, even though the coherence may be significantly longer lived in each individual member of the ensemble. Even after complete dephasing, phase correlations and the ability to display interference can then often be resurrected by spin-echo like experiments. We usually understand dephasing to come from a statistical average over an environment comprising many degrees of freedom that couples to the system but which cannot be observed directly. A bath relevant to chemistry is the solvent—physically all the solvent molecules jiggling around randomly and coupled to the system (a solute) by solvation forces.

Box 2. Two-dimensional electronic spectroscopy

The information content of the simplest absorptive 2D spectra can be appreciated by considering an experiment in which a tunable laser excites the sample and changes in the sample's absorbance spectrum are measured for all detection frequencies as a function of the tunable excitation frequency. Like a topographic map, the 2D spectrum shows contours indicating the decrease in absorbance as a function of the excitation and detection frequencies. In the example above, the sample with linear absorbance spectrum shown at left has 4 peaks that could arise from 4 molecules with one peak each, one molecule with 4 peaks, or any intermediate combination. The 2D spectrum shown has 8 peaks: 4 diagonal peaks with $w_{\text{excitation}}=w_{\text{detection}}$ plus 4 off-diagonal "cross-peaks". To understand this 2D spectrum, consider the 2D spectrum of the molecule *a* with energy level structure and spectrum shown at the right in blue. The sample will be unaffected for $w_{\text{excitation}} < w_a$, so the 2D spectrum shows no change in absorbance. However, when $w_{\text{excitation}} = w_a$, some *a* molecules are transferred out of their ground state and into their first excited state. Because this decreases the concentration of *a* molecules in the ground state, the Beer's law absorbance decreases for every transition starting in the ground state of *a*, generating 2D peaks at $w_{\text{detection}} = w_a$ and $w_{\text{detection}} = w_c$. The diagonal 2D peak at (w_a, w_a) is stronger than the cross peak because of stimulated emission from the population transferred to the first excited state, which further decreases the absorbance change detected at w_a , but not at w_c (since no molecules were transferred to the second excited state by excitation at w_a). As the tunable laser frequency is increased, nothing happens to *a* until *a* is excited to its second excited state at $w_{\text{excitation}} = w_c$. The decrease in Beer's law absorbance again generates 2D peaks at $w_{\text{detection}} = w_a$ and $w_{\text{detection}} = w_c$, and this time the diagonal 2D peak at (w_c, w_c) is stronger because of stimulated emission. The 2D spectrum of *b* can be understood in the same way as that of *a*. Because *b* molecules are completely unaffected by excitation of *a*, and vice versa, the 2D spectrum of their mixture is the sum of the 2D spectra of the individual components. The presence and absence of 2D cross-peaks are equally informative: the presence of 2D cross-peaks at (w_a, w_c) and (w_c, w_a) proves that the peaks at w_a and w_c in the linear absorption spectrum come from the same molecule; the absence of cross-peaks at (w_a, w_b) and (w_b, w_a) proves that the peaks at w_a and w_b in the linear absorption spectrum come from different molecules. Thus, the 2D spectrum directly separates the linear absorbance spectrum of the mixture at left into the spectra of its components at right. In general, 2D spectra are more complicated than this simple example, which neglects the possibility of absorption transitions originating from the excited states.



Box 3. Measuring and Assessing Coherence

While coherence is theoretically well-defined and also accessible to experimental quantification, it is more difficult to ponder the actual role of the coherence detected in a dynamically evolving reaction or transport process, against that of stochastic activation and transfer processes. Often dynamical coherence can prevail only on shorter scales. We then need to understand how coherence on these short scales can condition functionality on large scales. In such scenario we would like to monitor the interplay of coherent and incoherent processes in real time, without disrupting their actual progress. While, given the intricate structure and the complexity of interactions between molecules and the environment, considerable conceptual and experimental advances will still be needed. The technique of *weak measurement* allows direct access to a quantum system's density matrix or state, without considerably perturbing it. A challenge is to port the method, so far employed in quantum optical contexts, to truly complex molecular assemblies.

In **weak measurement** two quantum systems are weakly coupled by some interaction. This interaction is typically used to model how measurement generally works (hence “weak measurement”). That is, one system is considered the system under study and the other the measurement apparatus¹⁰⁷. In practice, often these two systems are actually just two different degrees of freedom of the same system, e.g. the spin and position of an electron.

If the coupling were strong, the two systems would become strongly correlated (in fact, entangled). For example, the indicator reading on the measurement apparatus would correlate exactly and unambiguously with the value of the measured parameter in the system under study. If one observes the indicator, it will collapse to a particular reading and the system under study will collapse the corresponding basis state. On the other hand, if the coupling is weak, the two systems are imperfectly correlated; each distinct indicator reading now corresponds to many states of the system under study. In this case, although an observation of the indicator would give ambiguous results, this ambiguity is precisely what maintains the superposition of states in the system under study, thereby avoiding collapse. And, remember, collapse in a particular basis destroys coherence between the basis states. A small amount of the coherence of the system under study is transferred to the measurement apparatus. Then by averaging over many trials and performing a tomographic reconstruction one can in many cases extract the real and imaginary parts of the full density matrix.

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