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Over the past 15 years, researchers have extended the multidimensional approach (originated with NMR in the 1970s) to infrared and visible coherent spectroscopy. These advances have dramatically enhanced the temporal resolution of coherent spectroscopy from the microsecond to the femtosecond regime.

NMR spectroscopists have developed principles for the design of pulse sequences that enhance selected spectral features and reveal desired dynamical events. Extending these principles to the optical regime offers numerous opportunities for narrowing the line shapes in specific directions, unraveling weak cross-peaks from otherwise congested spectra, and controlling the interferences between quantum pathways. We can achieve these enhancements by shaping the spectral and temporal profiles of the pulses. Pulse polarization shaping may lead to unique probes of time-dependent chirality.

In this Account, we compare two types of signals. The first, the photon echo, is generated in the direction $-\boldsymbol{k}_1+\boldsymbol{k}_2+\boldsymbol{k}_3$, and the second, double quantum coherence, is detected at $+\boldsymbol{k}_1+\boldsymbol{k}_2-\boldsymbol{k}_3$. Here $\boldsymbol{k}_1$, $\boldsymbol{k}_2$ and $\boldsymbol{k}_3$ are the wave vectors of the three incoming pulses in chronological order. We illustrate the novel information extracted from these signals by simulations of three physical systems. In the first system, spectra of GaAs semiconductor quantum wells provide a direct look at many-body electron correlation effects. We directly observe these projections of the many-electron wavefunction, which we can use to test the quality of various levels of computational techniques for electronic structure. Secondly, the spectra of photosynthetic aggregates reveal couplings between chromophores, quantum coherence signatures of chromophore entanglement, and energy-transfer pathways. Using some fundamental symmetries of pulse polarization configurations of nonlinear signals, we can construct specific superpositions of signals that can better distinguish between various coherent and incoherent exciton transport pathways and amplify subtle variations between different species of the Fenna-Mathews-Olson (FMO)

antenna complex. Both of the first two applications require femtosecond pulses of light in the visible range. The third application demonstrates how resonant x-ray pulses may be used to generate core excitations that are highly localized at selected atoms. Such signals can monitor the motions of valence electron wavepackets in real space with atomic spatial resolution

These future x-ray applications will require attosecond bright x-ray sources which are currently being developed in several labs. Common principles underlie these techniques in coherent spectroscopy for spins, valence electrons, and core electronic excitations, spanning frequencies from radiowaves to hard x-rays.