

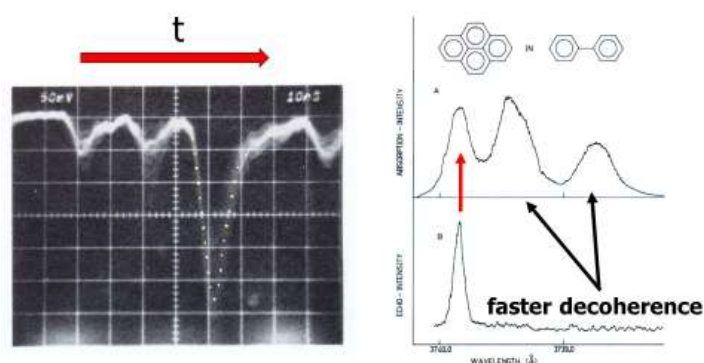
# Echoes of the past, flashlight on the future

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**Abstract** A brief history of photon echo spectroscopy, which led to femtosecond multidimensional spectroscopy, is given. Several 2D-experiments are discussed. The rapidly advancing use of femtosecond optical and X-ray pulses opens new avenues for exploration of excited-state structural dynamics, especially during conical intersections.

All life-sustaining chemical processes on our planet proceed in condensed phases: from proteins moving around in cells and optical excitons finding their way to the reaction center through an energetically-rugged landscape of pigments, embedded in a scaffold of proteins, to protein-embraced molecules reacting to an impinging photon with an ultrafast twist or transfer of a proton; dynamical processes that trigger follow-up reactions along a desired pathway. In the case of mammalian sight, vision starts with an ultrafast *cis-trans* isomerization, eventually leading to a series of electric pulses that tickle specific brain neurons to create a visual image. “We are such stuff that dreams are made on”, wrote William Shakespeare. Molecular spectroscopists around the globe *all* share the dream that someday nuclear and electronic motions of reacting molecules can be followed in real time and that this will generate a much deeper insight into chemical reactivity. Great progress towards that goal was made by George Porter using flash photolysis on a microsecond timescale and by Ahmed Zewail using fs pump-probe experiments to probe the nuclear dynamics of molecules undergoing dissociation or isomerization in the gas phase. In condensed phases, *dephasing* plays a dominant role in the broadening of optical spectra, leading to a loss of spectrally-resolved vibrational structure and inter- and intra-molecular couplings, which reflect and

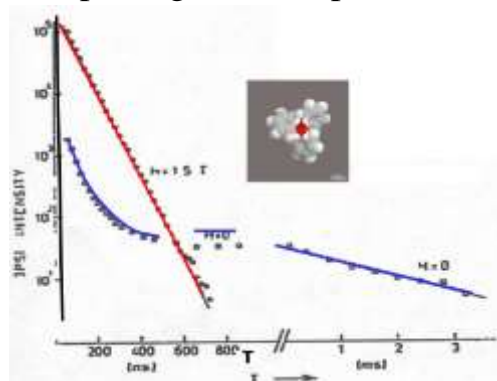


**Figure 1.** Photon echo of pyrene (*P*) in biphenyl at 1.5 K. Echo is the third pulse from the left. The absorption and echo-excitation spectrum of the three *P*-sites are shown at the right-hand side.

govern the molecule's excited-state dynamics. Erwin Hahn showed that multiple pulse (echo) experiments (1) can overcome most of the effects of dephasing and also expose internuclear couplings. Richard Ernst (2) showed that by Fourier transforming the time-encoded multiple pulse data, a 2D-spectrum is generated from which detailed structural information can be

extracted. Ernst also suggested (2) that this 2D-mapping technique should be

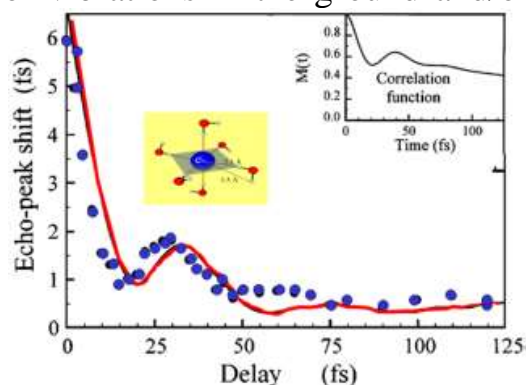
applicable to IR spectra. Sven Hartmann, a student of Hahn, succeeded in generating optical echo's from a ruby crystal at liquid He temperature (3). This was an important milestone in coherent optical spectroscopy and published in the New York Times of November 9, 1964. Generation of photon echoes in molecular systems had to wait for the invention of tunable dye lasers. Our group succeeded in reporting the first photon echo experiments on a condensed phase molecular



**Figure 2.** Stimulated photon echo decay of triphenylmethyl at 1.5 K with and without magnetic field. The 1<sup>st</sup>-2<sup>nd</sup> delay is 40 ns.

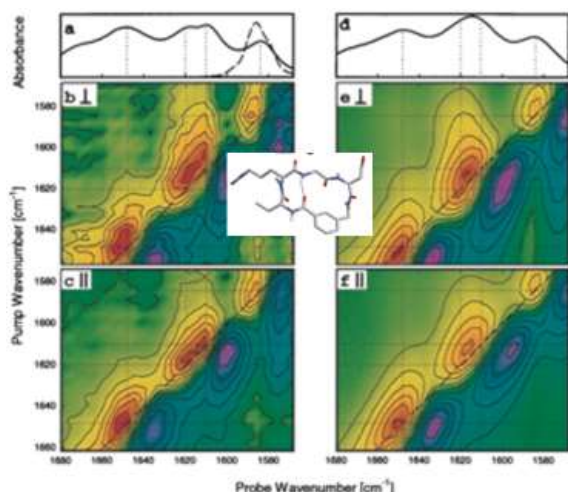
the triphenylmethyl radical (TPM) (5). The dramatic effect of a magnetic field on the stimulated photon echo-decay results from *spin entanglement*. In zero magnetic field the electron-nuclear spin states in the ground and excited state are entangled through the anisotropic hyperfine coupling. In a high magnetic field these states are disentangled and the optical transition behaves like an inhomogeneously broadened two-level system, as shown by the echo decay, which is exactly half the fluorescence lifetime (130 ns) (*There are 65536 electron-nuclear spin states underlying the TPM's doublet-doublet transition!*). Note that the storage of optical coherence in spin states implies that optical coherence can also be stored in vibrational states, leading to a long-lived decay-component in the stimulated photon echo with lifetime(s) of vibrations in the ground and/or excited state. In the decades following these nanosecond photon echo experiments, we reported the first time-resolved picosecond (6) and femtosecond photon echo experiments in solution -*clearly showing non-Markovian dynamics* (7)- and echo-peak shift measurements (Fig. 3 & Refs. 8, 9), showing the great potential of photon echo to gather new information on electronic and vibrational decoherence and dynamics. For instance, the underdamped motion in the correlation function  $M(t)$  of the solvated electron-deduced from echo-peak shift

system (4). Figure 1 shows the results of this – *measured on the late evening of Christmas eve in 1975-* photon echo experiment on pyrene in biphenyl at 1.5 K, demonstrating *that identical molecules in different environments can show very different decoherence*. With this experiment, which marks the transition from *classical to quantum (coherent) spectroscopy*, **photon echo spectroscopy** of condensed-phase molecular systems got a start. Soon thereafter stimulated photon echoes (t-2D) in different mixed crystals were studied, the most spectacular result (Fig. 2) being obtained from



**Figure 3.** Echo-peak shift of the electron in water. Blue dots data, red line is the simulated echo-peak shift, based on  $M(t)$  (inset).

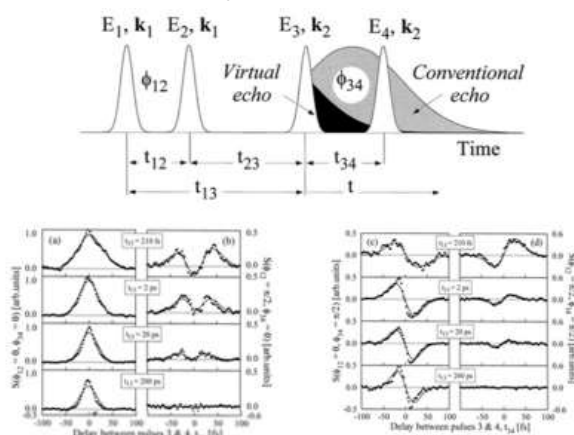
*measurements*- was assigned to a  $\sim 850 \text{ cm}^{-1}$  libration of a water molecules, caging the solvated electron (9). Fayer's group, using a Free Electron Laser for infrared- pulse generation, were the first to report on vibrational echo experiments of a C=O stretching band in a hexacarbonyl (10). Shortly thereafter, Tanimura and



**Figure 4.** 2D pump-probe spectra of a penta-peptide (inset) in  $D_2O$ . b and c are experimental, e & f theoretical fits.

this technology, Hochstrasser's group took the lead in 2D-IR spectroscopy (13) for structural determination of proteins in solution (Fig. 4). At about the same time, the Jonas group reported the first 2D-visible-range spectra of a dye (14). Fleming's group was the first to report on 2D-experiments of a photosynthetic light-harvesting complex (15). Since these first 2D-experiments, coherent multi-dimensional spectroscopy has taken off with many innovations, both in experimental approach (16) and in theoretical analysis (17,18,19). Several notable 2D-experiments will be discussed at the Symposium. We contributed to this development by reporting the first phase-controlled heterodyne-detected stimulated photon echo (HSPE) experiments (20), using a cavity-dumped Ti:Sa-laser system that was phase-stable for over 24 hrs. We further showed (21) that with a full set of orthogonal HSPE signals a separation into rephasing and non-rephasing contributions to the HSPE-signal could be made (Fig.5), which is the basis for 2D-spectroscopy. Figure 5 shows the HSPE-pulse sequence and some typical HSPE-signals obtained

Mukamel reported calculations on two-dimensional femtosecond vibrational spectroscopy in liquids (11), laying with it the foundation for 2D-IR and 2D-VIS spectroscopies. For a long time photon echo experiments were considered an esoteric business and very difficult to perform. That perspective changed with the development of solid state femtosecond Ti:sapphire lasers (12), which could be hands-off operated for a very long time. With a Ti:Sa laser also intense  $\sim 150 \text{ fs}$  infrared pulses could be generated by parametric amplification and difference frequency mixing. Using



$$R^{\text{echo}} \propto \{S_{\text{HSPE}}(0,0) + S_{\text{HSPE}}(\pi/2, \pi/2)\} + i\{-S_{\text{HSPE}}(0, \pi/2) + S_{\text{HSPE}}(\pi/2, 0)\},$$

$$R^{\text{virt. echo}} \propto \{S_{\text{HSPE}}(0,0) - S_{\text{HSPE}}(\pi/2, \pi/2)\} - i\{-S_{\text{HSPE}}(0, \pi/2) + S_{\text{HSPE}}(\pi/2, 0)\}$$

**Figure 5.** Pulse sequence for HSPE-experiments. HSPE-signals for 4 orthogonal phase combinations at increasing waiting times; third-order nonlinear response function  $R$  for real echo and virtual echo.

for four orthogonal phase settings, in our study of solvation dynamics. The fits were made using the celebrated multimode Brownian oscillator model developed by Mukamel (19) who made extremely important contributions to the development of multi-dimensional spectroscopy by publishing dozens of papers on the subject and by publishing a book on non-linear optical spectroscopy (19) that gained the status of ‘The Bible of Nonlinear Optical Spectroscopy’. Recently Mukamel proposed a novel technique called TRUECARS (22), combining fs optical excitation with a (sub)fs X-ray interrogation pulse to probe, by Raman scattering, the *electronic coherence* generated during passage of a wave packet through a conical intersection. This is a promising new tool to get a better grasp of the electronic and nuclear dynamics at conical intersections, which are so ubiquitous in Nature. Another promising avenue concerns the effort to generate videos of atomic movements during a chemical reaction by ultrafast diffraction using either bright electrons or fs X-ray pulses (23). The use of *quantum process tomography* to quantify coherence transfer dynamics in molecular systems, and in pigment-protein complexes, also presents a future and grand challenge (24).

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