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Conceptual understanding of optical multi-dimensional coherent spectroscopy

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Abstract In this tutorial review, the machinery of optical (visible and infrared) two-dimensional coherent spectroscopy has been discussed from a conceptual point of view, emphasizing the necessity along with few practical applications of this state-of the art spectroscopic technique.

Keywords Two-dimensional spectroscopy, Inhomogeneous broadening, Photon-echo, Spectral diffusion, Cross-peak beating

Introduction

Almost all chemical and biological phenomena take place in condensed phase (solids and liquids) and the initial steps of many fundamental processes of great importance to us occur within ultrafast time scale (from few tens of picoseconds down to few tens of femtoseconds) where the early time dynamics drives all other dynamical events that follow. For example, the primary energy transfer and subsequent charge separation in photosynthesis is over within few picoseconds and it controls the overall efficiency of energy harvesting and storage crucial for sustaining life on earth. Optical (visible and infrared) multi-dimensional coherent spectroscopy has been developed as a spectroscopic probe to study condensed phase phenomena in complex chemical and biological systems with ultrafast time resolution inaccessible by its predecessor multi-dimensional nuclear magnetic resonance (NMR) spectroscopy. In this review article a conceptual discussion on the simplest form of optical multi-dimensional coherent spectroscopy, *viz* optical two-dimensional (2D) coherent spectroscopy (henceforth called simply as 2D-CS), is presented. Only the basic principles of 2D-CS has been discussed with two examples of its practical applications; for a detailed theoretical description the reader is referred to many excellent texts [1-3] and reviews [4-9].

2D-CS is a type of non-linear optical spectroscopy (a variant of *four-wave mixing technique*) developed for mapping time-resolved correlation between absorption and emission frequencies. To understand how 2D-CS helps us deciphering condensed phase dynamics, it is important first to understand a dynamical description of linear absorption and its limitations in describing condensed phase dynamics.

Linear absorption

The familiar text-book picture of linear absorption that immediately crops up in our mind is: atoms and molecules have discrete or 'quantized' energy levels and when photons of right energy are 'absorbed' the atoms or molecules make a transition from lower energy states to higher energy states. This is a frequency domain picture of light absorption considering only conservation of energy. However, light is a spatially and temporally varying electromagnetic field and light-matter interaction is a time-dependent process. According to the general time domain description of light absorption the time-dependent electric field of light sloshes the polarizable electrons inside matter creating a time-dependent 'induced' dipole moment or macroscopic polarization (under the *electric dipole approximation*) which radiates a coherent secondary filed in the same direction (due to conservation of linear momentum) but with opposite phase compared with the driving field;

destructive interference of the secondary emitted field with the driving field results in attenuation of the filed which we call as linear absorption. Thus (linear) absorption is fundamentally a coherent secondary emission interfering with the incident wave. In 2D-CS we record the correlation between two such coherent emission frequencies (*i.e.* between absorption and emission frequencies) at different times, which is a direct time-domain measurement of the ultrafast temporal evolution of the system under study.

Line-broadening in condensed phase

Consider a two-level system (TLS) consisting of a ground state and an excited state; any two energy levels (electronic or vibrational) of an isolated atom or molecule in gas phase may be approximated as a TLS. If we optically excite the system, a *quantum superposition* or *coherence* between the two levels is created which is equivalent to the 'classical' induced dipole moment as already described. The induced coherence has a 'life-time' and the decay of the coherence is known as (linear) *free induction decay* (FID) which results in a decaying coherent secondary emission as explained earlier. The frequency spectrum of the FID (*i.e.* the *Fourier transform* of the FID) has a *Lorentzian line-shape* and its width is limited only by the lifetime of the coherence; this width is known as *natural line-width*. Typical life-time for (electronic) transitions in atoms is 1 ns or longer corresponding to a frequency width of 1 GHz (~0.03 cm^{-1}) or smaller.

Now imagine what happens if we put our TLS inside a crystal. The lattice vibrations tend to shift the transition frequency of the TLS. The equivalent time-domain picture is coupling to the lattice 'dissipates' the induced coherence and the FID has a faster decay. In frequency domain this causes a broadening in addition to natural line-width which is known as *homogeneous line-width* or (more rigorously) as *dynamic line-width*. In an experiment dealing with a collection of millions of TLSs in a crystal (*e.g.* a 'transparent' crystal doped with chromophores), we observe the same absorption profile for every TLS as long as the crystal is 'perfect', *i.e.* all lattice sites in the crystal are identical. This is highly unlikely and in reality every crystal is 'imperfect' in the sense that at any instant of time one site has a slightly different local environment than the other. If we take a 'snap-shot' we observe a variation of transition frequencies among the collection or 'ensemble' of TLSs. The equivalent time-domain picture is: following optical excitation the induced coherence of each TLS in the ensemble evolves at a phase set by its own transition frequency and due to variation of transition frequencies the oscillations eventually go out of phase causing a 'global decay' of the collective oscillation known as *ensemble dephasing* or *inhomogeneous dephasing*. In frequency domain this leads to further broadening of the overall line-width known as *inhomogeneous line-width* or (more rigorously) as *static line-width* whereas the overall absorption profile has a *Gaussian line-shape*. In condensed phase typical ensemble dephasing time-scale is less than 1 ps corresponding to a frequency width for inhomogeneous broadening of 1 THz (~30 cm^{-1}) or larger.

As illustrated in Figure 1, consider three types of TLSs with distinct transition frequencies (red/green/blue); if we collect a linear spectrum of such an ensemble of TLSs, we cannot simply disentangle the individual line-broadening contributions to the total line-width (*i.e.* the red/green/blue features are hidden within the grey envelope).

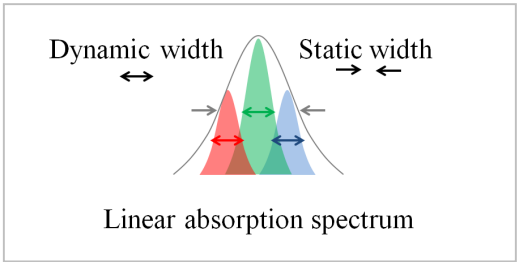

Figure 1: Schematic of spectral profile of a collection of TLSs in condensed phase.

Note that this separation of homogeneous and inhomogeneous line-widths is quite arbitrary which entirely depends on short- and long-time environmental fluctuations (here, the lattice-vibrations) respectively: if we record the absorption spectrum of a particular TLS over shorter period of time (or take a 'snap-shot'), we see a homogeneous spectrum centered on a particular transition frequency; however, if we record a series of absorption spectra of the same TLS over longer period of time, we see a 'wandering' of its transition frequency across the inhomogeneous profile. This phenomenon, known as *spectral diffusion*, has been observed in single molecule spectroscopy [10]. Therefore, 'time-averaging' is equivalent to 'ensemble-averaging' (if the system is completely 'ergodic').

Thus, one of the major challenges in understanding condensed phase dynamics is to measure the spectral features arising from short- and long-time fluctuations separately, which is not possible by simple linear spectroscopic measurements. Liquids have similar dynamics except that they are structurally less ordered and more fluctuating than solids, and hence more difficult to deal with.

2D-CS: Dynamics of diagonal peaks

Separating the contributions of homogeneous and inhomogeneous broadening to the total line-width in condensed phase was an active area of research in the 80's and 90's when a number of different spectroscopic methods were developed. One direct approach is to measure the line-width of a single TLS at a time by linear absorption/fluorescence measurements and repeat this for other TLSs ('ensemble-averaging') or for the same TLS at different times ('time-averaging') to build-up statistics that resemble ensemble behavior; this is what has been rendered by spectroscopy of isolated (immobilized) single molecules [10]. The other approach is still dealing with an ensemble of TLSs at a time but separating the contributions by non-linear optical methods (as linear methods do not apply). In frequency domain this has been done by *spectral hole burning* where a narrowband laser saturates an optical transition which is followed by a broadband absorption probing the spectral hole (with homogeneous line-width) created by the saturating excitation [11]. On the other hand, in time domain it has been done by *photon-echo* which is analogous to *NMR spin-echo* [12].

The simple tricks played in a three-pulse photon-echo (3PPE) experiment (where the electric field of each of the three optical pulses interacts only once with the system) are: 1) creating a coherence with the first pulse equivalent to a 90-degree RF pulse in spin-echo, 2) turning the coherence into a population by a time-delayed second pulse and 3) 'immediately' re-exciting the system by a third pulse to create a new coherence; the second and third pulse together equivalent to a single 180-degree RF pulse in spin-echo. The coherence created after the third pulse evolves either in the same phase (*non-rephasing* or *anti-echo* signal) or in the opposite phase (*rephasing* or *echo* signal) with respect to the initial coherence. For the echo signal, execution of the 180-degree RF pulse reverses the direction of the initial coherent oscillations (created by the the first pulse) so that they trace back their phase evolution and eventually come into phase to cause a 'global enhancement' of the collective oscillation (hence called 'echo').

In a spin echo experiment, spatially 'collinear' RF pulses are used and the signal FID can be isolated by *time-gating* with electronics. Unfortunately, this does not hold for a photon-echo experiment as there is no control over the number of interactions executed by a single optical pulse and electronics do not respond in ultrafast time-scale to isolate the signal FID. This problem was circumvented by using pulses reaching the system a 'non-collinear' spatial geometry: due to momentum conservation the signal, resulted from just one interaction from each of the three pulses, is emitted in a background-free spatial direction; also, the echo and the anti-echo signals are emitted in different directions. This is known as *phase-matching*. Instead of measuring

the signal FID directly in real time (again, as electronics fail), temporal or spectral interferometric methods (using a fourth *local oscillator* pulse interfered with the signal FID) are used to retrieve the amplitude as well as phase for the emission spectrum while the Fourier transform of the temporal interferogram recorder by delaying the first two pulses provides the amplitude and phase for the absorption spectrum.

Considering our ensemble consisting of three types of TLSs with distinct transition frequencies, the 2D spectrum shows diagonally elongated line-shape as each type of TLS absorb and emit at .

its own characteristic frequency; this is shown in the left panel of Figure 2 (red/green/blue retains its identity during emission). To observe photon-echo in a 3PPE experiment the time-delay between the second pulse and the third pulse (called as *waiting time* or *population time*) should ideally be 'zero', otherwise owing to *spectral diffusion* each TLS eventually loses the 'memory' of its oscillation frequency and the correlation between excitation and emission frequencies is lost. In 2D spectrum, this is observed as a circularization of the diagonally elongated line-shape, as shown in the right panel of Figure 2 (red/green/blue loses its identity during emission and emits everywhere)

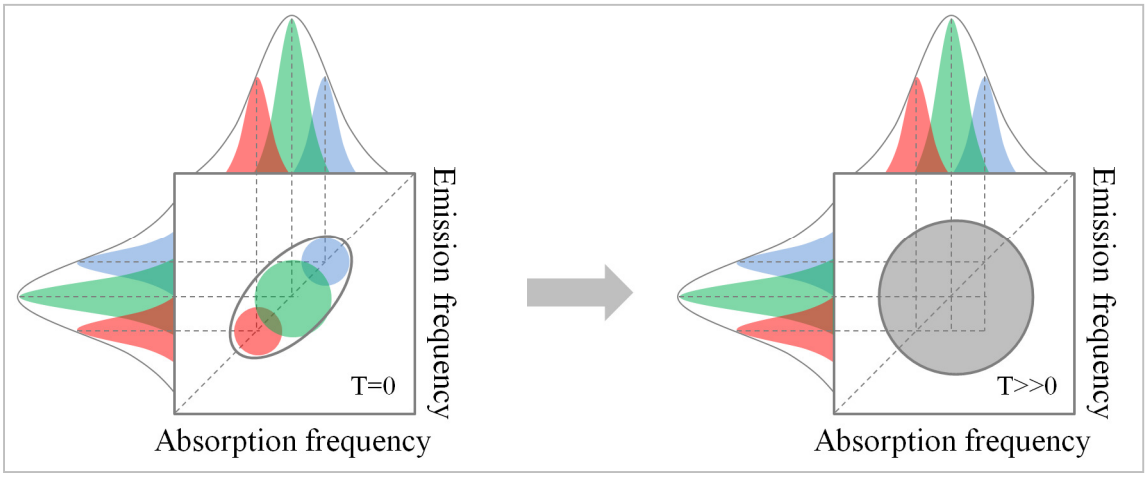

Figure 2: Schematic of 2D spectra of an ensemble of TLSs showing (left panel) diagonally elongated line-shape at zero waiting time (T=0) and (right panel) spectral diffusion as the waiting time is increased (T>>0). Note that this diagonal elongation refers to the diagonally elongated real *relaxation spectrum* which is the sum of real parts of echo and anti-echo spectra; we haven't, however, explained this in the main text to keep the simplicity of our discussion.

2D-CS: Dynamics of cross peaks

The hallmark of multidimensional spectroscopy does not lie in separating the different contributions of line-widths but rather in exploring the 'coupling' between excited states that furnish ultrafast structural and dynamical information. To illustrate, consider a collection of pairs of TLS that share a common ground state and their excited states are coupled (for example, a collection of 'coupled dimer's). In a 2D spectrum this coupling is manifested as a cross-peak as shown in Figure 3; note that each TLS has a diagonally elongated feature at zero waiting time as explained before.

For example, these cross-peaks may manifest the relative coupling between two carbonyl moieties corresponding to the two peptide bonds in a tri-peptide when studied by infrared 2D-CS [6] or they may reveal the coupling between electronic (excitonic) states within a photosynthetic pigment-protein complex (PPC) when studied by visible 2D-CS [13]; thus if we take a time-series of 2D spectra and observe the evolution of the cross-peaks, we can track the orientation dynamics of the peptide linkages that leads to the folding/unfolding of the tri-peptide or the excitation energy transfer (EET) between the states that leads to photosynthetic light harvesting, respectively.

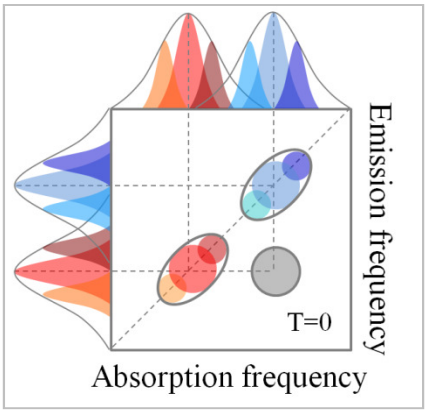

Figure 3: Schematic of a 2D spectrum of an ensemble of coupled pairs of TLS showing cross-peaks.

It is noteworthy to mention here that in recent times long-lived time-dependent beating of the cross-peaks in a PPC has been observed [14]; this has given birth to a new field of research, namely *quantum biology* [15] and has fuelled the research in exploring the possible role of microscopic origin of quantum effects in photosynthetic EET efficiency [16-17] and many other chemical and biological phenomena.

Summary

To conclude, a simple description of the basic working principles of optical two-dimensional coherent spectroscopy is presented avoiding any theoretical rigor. The usefulness of 2D-CS in understanding condensed phase dynamics is emphasized and two important practical applications are discussed.

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