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Dynamics of quantum wave packets in complex molecules traced by 2D coherent electronic correlation spectroscopy

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Abstract

Electronic and nuclear molecular wavepackets are a clear manifestation of the wavelike properties of matter at the very heart of quantum mechanics. In this work we demonstrate how electronic two-dimensional spectroscopy (2D) serves as a highly evolved tool for the simultaneous investigation of both phenomena. In further analysis and theoretical treatments, 2D spectra form an ideal basis for the discussion of electronic decoherence, vibrational relaxation and electron-phonon coupling.

Keywords: Two-dimensional electronic spectroscopy; electron phonon coupling; coherence phenomena

1. Introduction – atomic and bi-atomic molecular wave-packets

Understanding the physics of motional behaviour of elementary excitations in matter is fundamental. For the simplest *alkali-atoms*, pulsed optical *Rydberg* spectroscopy dramatically impacted experimental efforts toward solving the motional mechanics and the generic structure of moving *electronic* excitations over the last two decades [1,2]. In classical mechanics the temporal behaviour of the optical response in these systems is determined by Newton's equation of motion, while in quantum mechanics the corresponding evolution is described by a probability distribution given by the modulus square of a wave-function that is satisfying Schrödinger's equation. The relevance of the one and the other mechanics is usually considered to depend on whether the system is macroscopic or microscopic. However, quantum mechanics is a fundamental theory that should apply to physical systems regardless of size. One of the key theoretical concept to relate these apparently disparate points-of-view is the concept of a coherent wave-packet (WP) in quantum mechanics [3,4]. Such a WP gives a probability distribution that can be related in the correspondence limit to an ensemble of classical orbits [1]. In this picture the motion in quantum mechanics can be represented by a Gaussian WP that is initially localized (confined in space), but spread over positional coordinates as a function of time. Spreading is actually related to classical mechanics or, more strictly

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speaking, WP spreading is an effect that can be perceived classically once the appropriate correspondence with quantum mechanics has been made [1]. As time evolves (and substantial, dissipative damping is absent), the front of the *Rydberg* electronic wave-packet-instead of continuing to spread indefinitely into the future is going to catch its own tail. These back-biting self-interferences thereby trigger an ongoing tendency towards restoring the initial WP on longer time scales. The shape of the primary WP is reconstituted with its original phases after a distinct period [5-8]. These, typically, long-time *revivals* in the asymptotic regime of WP propagation, delicately balanced by the occurrence of additional revivals at rational fractions (*fractional revivals*), are of pure quantum-mechanical origin and do not have any classical analogue.

Going from single-atoms to simple diatomic molecules with moderate bond-strengths and shallow potential minima, femto-second (fs) pulses with widths of 100 fs and below provide the ideal vehicle for intramolecular multi-level excitation. Because of their several tens of THz frequency bandwidths, fs-optical fields coherently prepare a large (*discrete*) number of Franck-Condon (FC) vertical excitations in an *in-phase* superposition of higher harmonics (*vibrational* wave-packet) coupled to the electronic dipole. Since the temporal widths of fs-pulses are generally shorter than the typical periods of WP round-trips, they are at the same time powerful probes of the periodic coordinates of the WPs' (ro)vibronic motion [9-11]. Unlike the electronic WP in alkali-*Rydberg* states, the diatomic (*molecular*) WP prepared in its FC-states is confined to its potential energy surface (PES). However, in an anharmonic potential, the WP's positional coordinates spread as it moves away from the FC-region and propagates. As free evolution proceeds, the (discrete) WP starts to interfere with itself instead of continuing to spread indefinitely into the future. The initial front of the WP becomes split into a number of localized fractions distributed over the motional coordinate. As a result, its intermediate to long-time dynamics deviates dramatically from the behaviour of the corresponding classical ensemble on early fs-times. Such back-biting interferences trigger an ongoing tendency towards restoring the WP's initial shape after distinct periods [6]. The overall time-structure of molecular WP-propagation including both the classical and the quantum-mechanical regime was first experimentally demonstrated for gaseous diatomics (I_2 , Br_2 , NaI , Na_2) by using fs-pump-probe configurations [12,13]. Alternatively, various techniques of wave-packet fluorescence interferometry that probe the spatial interference of population quantum amplitudes from two WPs propagating in the inter-atomic potential were successfully employed [14-17].

With the progress in transformative laser-pulse technology, understanding nuclear structure, electronic features, and dynamics of larger molecular systems has advanced considerably through probing the molecule's higher-order optical response by sequences of pulsed electromagnetic fields. Paralleled by the ability to control various degrees of freedom of the excitation/probing pulses, such as temporal width, sequence, polarization, shape and vector architecture, this has led to a variety of advanced *homodyne* FWM methods in the nineties. These experiments all measure the magnitude of the signal field, $|E^{(3)}|^2$, corresponding to the induced polarization, $E^{(3)} \approx i\omega P^{(3)}$, and include 3-pulse photon-echo peak-shift (3-PEPS), gated photon-echo ($|E^{(3)}(t_g, t_1; t_2)|^2$), monochromator frequency-dispersed echo ($|E^{(3)}(\omega_D, t_1; t_2)|^2$), and transient grating (TG) in time ($|E^{(3)}(t_3, t_2; t_1 = 0)|^2$) or frequency domain ($|E^{(3)}(\omega_3, t_2; t_1 = 0)|^2$) [18-20]. In polyatomic molecules, tiny amplitude-revival oscillations in (multi-dimensional) quantum-mechanical WPs are conceptually allowed. However, from the point-of-view of a realistic experimental assessment they are not detectable even in the absence of an environment. The reason is that a poly-atomic WP starting its motion into the high-dimensional FC-region of the complex molecular structure is instantaneously subject to rapid phase-loss and frequency-spreading, where a potential rebirth of the initial WP amplitude (full revival) would take several hundreds of ns or more. On the other hand low-frequency modulation caused by electron-nuclear coupling between a single FC-excitation dipole and long, low-frequency vibrational wave(s) are conceptually understood as low-energy, vibrational WPs moving in classical recurrences and can be routinely detected via their squared amplitude electronic 3rd-order signals by 1D-homodyne NL 3PEPS and TG, [21,22] preferentially, in simple two-level systems under weak environmental damping. The latter techniques have, in general, the intrinsic time-resolution required for such studies, [23] however, the interpretation of the vibrational beatings is, mostly, ambiguous and information about electron-nuclear coupling is *indirect* and incomplete as all *except* the vibrational couplings can be revealed from these experiments (*vide infra*).

2. The power of two-dimensional (2D) coherent electronic spectroscopy

With the recent experimental advance of two-dimensional FT electronic spectroscopy, 2D-ES, [24-28] cutting edge- heterodyne experiments have come of age that monitor multiple temporal correlations on the time-scale of the optical cycle oscillation in the visible regime. These experiments probe the third order response function, $S^{(3)}(t_3, t_1, t_2)$, which contains all relevant information about the dynamics of the system. Because the diffracted molecular FWM-field $E^{(3)}(t_3, t_1, t_2)$ is recorded under controlled phase at the amplitude level [29], its double FT projection for waiting-time t_2 ($S^{(3)}(\omega_3, t_2, \omega_1)$) gives rise to frequency-frequency correlation spectra ($t_2 = 0$) that are directly sensitive to the presence of intermolecular quantum-coherence and related motional phenomena driven by electronic and vibrational couplings.

2.1. 2D-ES interrogates evolution of quantum systems

Heterodyned Four-Wave-Mixing (FWM) is one of the prime tools for investigation of quantum dynamics in molecular systems. The close-to-classical properties of the coherent laser light greatly simplify the theory and the analysis of non-linear experiments through which the target of investigation – the quantum molecular system – reveals its dynamics. The coherent light acts as a classical parameter of the Hamiltonian and it is therefore possible to assign any observed quantum effects directly to the investigated molecular system.

Semi-classical third order response functions in heterodyned signals have the following general form

$$S^{(3)}(t_3, t_2, t_1) = i^3 \text{tr} \{ \mu G(t_3) V G(t_2) V G(t_1) V W_{eq} \} \quad (1)$$

Here, $G(t)$ is the system's evolution super-operator that contains all information about time evolution of the total density matrix of a multilevel quantum system. Each occurrence of the super- operator $V = [\mu, \dots]/\hbar$ (commutator with transition dipole moment operator) signifies a perturbation of the system by the interaction Hamiltonian $H_{\text{int}} = -\mu E(t)$, which describes the influence of an external classical time dependent field $E(t)$. The system starts from an equilibrium state described by the density matrix W_{eq} .

In a significant class of molecular systems, the energy levels can be grouped into bands that are separated by optical frequency energy gaps. The environment of such molecular systems has often spectral density insufficient to induce sub-picosecond inter-band relaxation, and unless intra-molecular coupling between different bands exists (e.g. in the form of a conical intersection) the time evolution of the bands proceeds independently. The total evolution super-operator thus splits into independent blocks that govern energy transfer, dissipation and de-coherence in individual bands, as well as de-coherence between the bands. The total non-linear response is thus represented by a sum of several contributions of Liouville space pathways, each containing the time evolution of different sections in the total density matrix

$$S^{(3)}(t_3, t_2, t_1) = \sum_n [R_n^{(3)}(t_3, t_2, t_1) - (R_n^{(3)}(t_3, t_2, t_1))^*], \quad (2)$$

The Liouville pathways themselves have a general structure

$$i^3 \text{tr} \{ \mu G_{coh}(t_3) \mu G_{pop}(t_2) \mu G_{coh}(t_1) \mu W_{eq} \}, \quad (3)$$

where $G_{coh}(t)$ and $G_{pop}(t)$ are evolution super-operator blocks corresponding to optical coherence and intra-band dynamics (coherence transfer, population oscillations etc.), respectively. In addition to the time dependence, the response function also carries a spatial factor which enables to limit the number of Liouville pathways interrogated in the experiment by an appropriate selection of the detection direction.

Non-linear spectroscopy takes a great advantage of the fact that, in the limit of ultra-short pulses, the non-linear signal is directly proportional to the non-linear response function with a selected directional phase factor. In an analogy to linear response and absorption coefficient

$$S^{(1)}(t) = \text{tr}\{\mu G(t)\mu W_{eq}\}, \quad (4)$$

$$\alpha(\omega) \approx \text{Re} \int_0^\infty dt S^{(1)}(t) e^{i\omega t}, \quad (5)$$

one can define a quantity

$$\alpha(\omega_3, t_2, \omega_1) \approx \text{Re} \int_0^\infty dt_3 \int_0^\infty dt_1 S_{-k_1+k_2+k_3}^{(3)}(t_3, t_2, t_1) e^{i\omega_3 t_3} e^{-i\omega_1 t_1} \quad (6)$$

which correlates an absorption process as expressed by the first two (from the right) occurrences of the transition dipole moment operator in Eq. (3) and the related process of excited state emission or ground state bleaching as expressed by the other two occurrences of the same operator. A series of two-dimensional plots of $\alpha(\omega_3, t_2, \omega_1)$ reveals the third dimension of this spectroscopic technique, namely the waiting (or population time) t_2 . The time evolution of the signal during the waiting time is governed by evolution of super-operators $G_{pop}(t)$ which describe the time evolution of populations and coherences within bands. The time evolution of the 2D spectrum thus provides direct information about this evolution and enables us, in principle, to reconstruct $G_{pop}(t)$, or more precisely the reduced evolution super-operator $\tilde{G}_{pop}(t) = \text{tr}_{bath}\{G_{pop}(t)W_{eq}\}$, where the degrees of freedom of the environment were averaged over by the trace operation tr_{bath} .

To enable a direct interpretation of the t_2 time evolution of the 2D spectrum in terms of the reduced ES, the environment is required to relax on some faster time scale so that the contributions of the Liouville pathways can be approximated by the reduced ES as

$$i^3 \text{tr}\{\mu G_{coh}(t_3)\mu G_{pop}(t_2)\mu G_{pop}(t_1)\mu W_{eq}\} \approx i^3 \text{tr}\{\mu \tilde{G}_{coh}(t_3)\mu \tilde{G}_{pop}(t_2)\mu \tilde{G}_{pop}(t_1)\mu W_{eq}\} \times R_{bath}(t_3, t_2, t_1) \quad (7)$$

In Ref. [30–32] such separation was found applicable to vibrational modes of PERY dye molecule. In particular, for waiting time larger than certain characteristic bath correlation time, $t_2 > \tau_c$, the contribution of the environment is t_2 -independent, and does not interfere with the determination of the t_2 evolution of the relevant DOF.

2.2. Molecular Electronic Wave-Packets

For excitations into electronic resonances, 2D-electronic coherent spectroscopy 2D-ES has proven an incisive tool to probe *electronic* wave-packets, electronic coupling and coherent motional phenomena between excitonic dipole oscillators in complex multi-chromophore systems. By imaging temporally encoded information, subtle mechanistic details (electronic coupling, quantum-oscillatory motion, and non-perturbative exciton dynamics) could be revealed by this technique from systematic studies on biological light-harvesting complexes [33–39] and in experiments on artificial aggregates. C8O3 [40–44] and C8S3 [45] which are bi-tubular, amphi-philic quantum-systems (“amphi-pipes”) and artificial light-harvesters [46,47]. Culmination of 2D-ES techniques by the very recent advancement in gradient-assisted nD electronic photon-echo-spectroscopy [48] will allow for mapping the evolution of the complete, electronic Hamiltonian with sub-20 fs resolution, thus providing the first real-time recordings of

absolute amplitude-strengths in electronic coupling, and simultaneous monitoring of diagonal/off-diagonal oscillations beyond the secular approximation, i.e. quantum coherence beating/ transfer, and coherent population-oscillations [49].

In photosynthetic complexes, electronic coherence phenomena are long-lived even at room-temperature [38,50], probably, due to a few coherence preserving long-wave modes with weak electron-phonon couplings in their protein-matrix and the protein's unique protecting packing [39]. On the contrary, in synthetic bi-tubular aggregates due to their more pronounced site-disorder, the coupling to high-frequency vibrations in the aggregates' monomeric units and the lack of appropriate low-frequency modulating vibrations, demonstrate only short-lived, sub-100 fs optical inter-band coherence at room temperature. The early low-amplitude off-diagonals at finite coherence times are caused by motional narrowing of excitons in the band stabilized by the hydrophobic/hydrophilic double – cylinder/water interfaces which exceed electron-phonon coupling. Under appropriate solvent induced tuning (water/1-octanol), the C8O3 aggregate forms double-cylinders containing an inner and outer tube. These tubes give rise to two excitonic band-to-band transitions I & II (cf. double-cylinder morphology in Fig.1). The 2D-ES correlation- and relaxation-spectra of C8O3 (Fig.1) illustrate the delicate interrelation between tube-in-tube quantum-interference and the effect of intervening phonon-coupling in this aggregate on a waiting-time scale of $t_2 = 100$ fs [42].

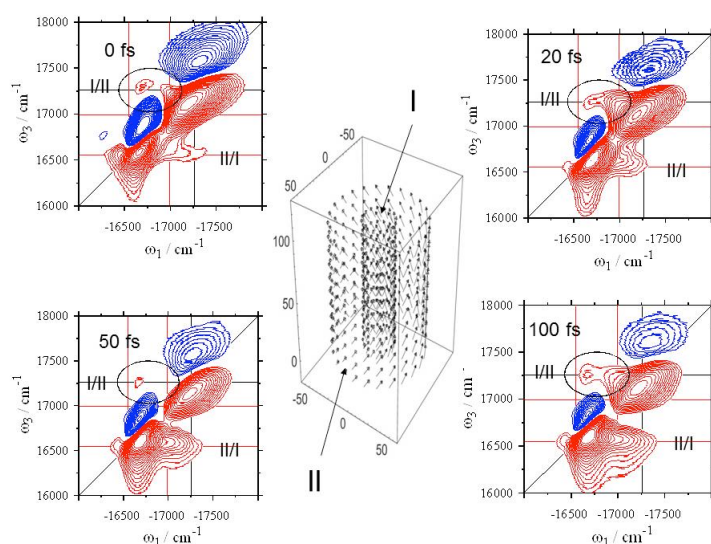


Fig.1. 2D-electronic, absorptive spectra of C8O3/water/1-Octanol recorded at $t_2 = 0, 20, 50, 100$ fs. Spectra are normalized to peak I (electronic band transition of the inner tube). Off-diagonal/diagonal oscillations (see ellipses) between high-energy cross-peak I/II and the *anti-diagonal* of peak II indicate the transition from quantum oscillatory motion to irreversible relaxation. Note that the low-energy off-diagonal peak II/I announces irreversible exciton-dephasing already at $t_2 \geq 0$ and becomes increasingly horizontally elongated along ω_1 as a result of population relaxation [42].

The four snapshots clearly demonstrate quantum-oscillatory motion of the *high-energy* off-diagonal cross-peak I/II ($\omega_3 > \omega_1$) and its delicate balance between early Hamiltonian dynamics and increasingly intervening excitation phonon coupling ($\equiv$ exciton population relaxation). While the off-diagonal low-energy peak II is subject to ongoing relaxation, the sequence of spectra shows that both off-diagonal I/II and the (anti-diagonal regime of) diagonal cross-peak II are oscillatory. Since the anti-diagonal reflects homogeneous broadening, its periodic change $A(t)$ displays the early oscillatory evolution of electron-phonon de-phasing process in the force-field of electronic I-II coupling. Hence, by looking into the evolutions of peaks I/II and II, one observes the *non-stationary* regime of early electron-phonon de-phasing whose evolution rides at the top of the electronic wave-packet until the increasing irreversibility of exciton population relaxation damps-out the wave and makes electron-phonon de-phasing stationary $A(t) \rightarrow A_s$. These snapshots of the periodic breathing behavior ($T \sim 25$ fs) between peaks I/II and II $A(t)$ provide instructive windows that illuminate the early stage of quantum-dissipative de-coherence on the basis of excitation-phonon coupling, but note that $A(t)$ displays an electronic dipole signal such that, clearly, nuclear

damping is only *indirectly* measurable and not proven by simultaneous recordings of *vibrational* motional phenomena in this study.

2.3. Electronic-vibrational wave-packets

Since the dominance of collective *electronic* oscillators in excitonic supramolecular organizations is rather the exception than the rule in molecular world, contributions of nuclear WP motion have to be included in the analysis of 2D-ES experiments for the major class of molecular electronic resonances, both in electronically coupled many-body-systems (c.f. the above synthetic aggregate) and non-excitonic systems. Nuclear motion interacting with an electronic transition by transition-dipole coupled anharmonic oscillator potentials [28,51] is fundamental for understanding vibronic scatter and vibronic coupling as the real underpinnings of intra-molecular motion and chemical change in the excited state. As already addressed, modulations [22,52,53] of electronic 3rd-order signals due to coupled intra-molecular low-frequency vibrations are, in the meantime, ubiquitous in one-dimensional (1D) femtosecond time-resolved experiments [21,22]. However, their underlying physical mechanism of vibronic coupling remains concealed because vibronic degrees-of-freedom cannot be disentangled from these one-dimensional experiments. In particular, measuring coherent high-frequency vibronic motion in an excited-state potential has not yet been directly realized by experimental 2D-ES, due to technical difficulties, and theoretical calculations including a manifold of vibronic states and wave-packet evolution upon FC-excitation are rare [54,55]. Both aspects carrying significant quantum-signatures in the fore-field of this 2D-ES study are, therefore, challenging and have motivated this work.

In this contribution, two-dimensional coherent electronic spectroscopy, 2D-ES, is employed to study typically *non-excitonic* molecules where (non-collective!) electronic transitions are coupled to *nuclear* motional coordinates, exclusively. Two representative molecules (perylene-based dye-molecule *PERY* and *Zn-Phthalocyanine*, *Zn-Pc*) of growing complexity and well known 1D-electronic absorption spectra are described, each of them characterized by a single electronic transition coupled to a set of low-frequency modes, on the one hand (*PERY*) and high-frequency vibronic modes, on the other (*Zn-Pc*). The 2D-experiments are intended (i) to disentangle the puzzle of low frequency vibronic modulation (*PERY*), and (ii) to probe the manifold of *vibronic* couplings spectrally masked in the *Zn-Pc*'s 1D FC high-frequency vibronic progression. The latter measurements are intended to trace the 2D intra-molecular oscillation and dissipation of the vibronic quantum-packet on its pathway to space-energy redistribution and relaxation.

3. 2D-ES experiments on quantum packets

3.1. *PERY* – low-frequency quantum dynamics

As addressed above, the unique advantages of 2D-ES over related one-dimensional third-order nonlinear spectroscopies (transient grating, three-pulse photon echo peak shift, pump-probe spectroscopy) have been demonstrated by studying line-broadening dynamics in solution [56], revealing pathways of energy transfer in molecular aggregates [42] & photosynthetic complexes [33], and probing exciton-exciton interactions in semiconductor quantum wells [57] to name only a few examples. A recently emerging topic of high interest has been the observation of electronic coherences in photosynthetic complexes, an effect that was postulated to increase the energy transfer efficiency in these systems [39]. A correct assignment of oscillations observed in 2D spectra to electronic coherences requires the characterization of modulations arising from vibronic coherences and a way to distinguish these two effects. For performing the former task we have chosen the dye N,N'-bis (2,6-dimethylphenyl)perylene-3,4,9,10-tetracarboxylicdiimide (*PERY*, linear absorption spectrum shown in Fig. 2a) for two reasons: (i) under excitation at 20 000 cm⁻¹ it behaves as an electronic two-level system and (ii) the third-order nonlinear response under this excitation condition is modulated by a low frequency vibrational mode of 140 cm⁻¹ corresponding to a period of 240 fs [21,22,32]. This allows to record 2D spectra at well resolved minima and maxima of the oscillating signal, thereby minimizing effects arising from the finite temporal resolution in the experiment.

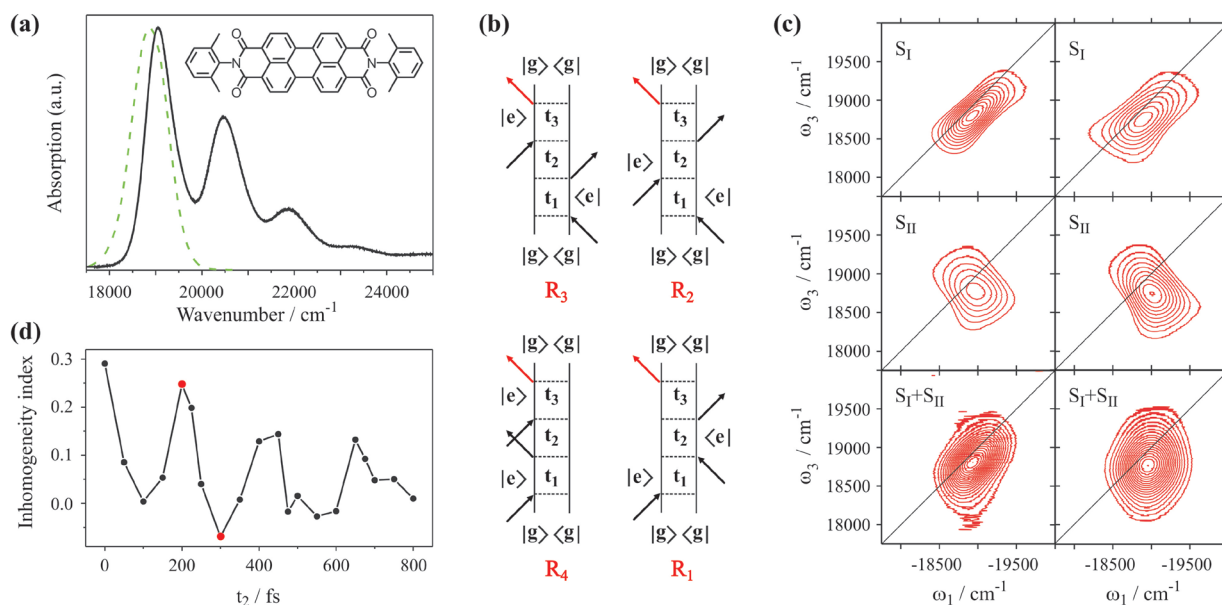


Fig. 2: (a) Linear absorption spectrum of PERY in toluene (black solid line) and spectrum of the excitation pulse (green dashed line). The inset shows the chemical structure of PERY. (b) The four Feynman diagrams graphically illustrating the *Liouville* space pathways contribution to 2D spectra of a two-level system. Diagrams R_3 and R_2 contribute to the re-phasing signal part (S_I), diagrams R_4 and R_1 to the non-re-phasing signal part (S_{II}). (c) Re-phasing (S_I), non-re-phasing (S_{II}) and S_I+S_{II} 2D spectra of PERY for $t_2=200$ fs (left) and 300 fs (right). (d) In-homogeneity index extracted from a series of 2D spectra recorded in the range $0 \leq t_2 \leq 800$ fs.

For a single electronic two-level system only four *Liouville* space pathways contribute to the 2D spectrum (Fig. 2b). They all yield positive signals and can be classified as ground state bleaching (GSB, diagrams R_3 and R_4) and stimulated emission (SE, diagrams R_2 and R_1) depending on whether the system evolves in the ground- or in the excited-state during t_2 . If the excitation pulses are spectrally broad enough to coherently excite two or more vibrational levels, the interaction with the first two pulses creates a vibrational wave packet that evolves during t_2 and is probed by the third pulse. The wave packet evolves with a frequency that is given by the difference in frequency of the two states involved. Modulations of signal intensities induced by vibrational wave packet motion have been observed in 1D spectroscopies [22,52,53]. In 2D-ES the wave packet evolution can be followed by recording a series of 2D spectra for different waiting times t_2 . Fig. 2a) displays the real part 2D spectra of PERY in toluene solution for t_2 -delays of 200 and 300 fs, corresponding to a maximum and a minimum in the one-dimensional third-order nonlinear spectra. The broad line shapes at room temperature and in solution do not allow to resolve individual vibrational levels, however, periodic modulations in the spectral shapes enable to trace the evolution of the vibrational wave packet. For $t_2=200$ fs we observe a peak that is of pronounced elliptical shape with its major axis oriented along the diagonal. For $t_2=300$ fs the major axis becomes nearly parallel to the ω_3 -axis and the peak significantly broadens along the anti-diagonal. The oscillations in the 2D spectra can be assigned to periodic intensity modulations in the rephasing (S_I) and nonrephasing (S_{II}) signal parts. The major axis of the elliptical peak in the S_I and S_{II} spectra is oriented along the diagonal and anti-diagonal, respectively (Fig.2c). The amplitude of these two signal contributions, however, experiences out-of-phase oscillations. These intensity oscillations can be evaluated quantitatively by calculating the inhomogeneity index which is defined as [58]

$$I(t) = (A_R - A_{NR}) / (A_R + A_{NR}) \quad (8)$$

with A_R and A_{NR} denoting the relative intensities of the re-phasing and non-re-phasing signal parts. The inhomogeneity index is related directly to the energy gap correlation function, which provides the connection between experimentally accessible observations and the underlying microscopic molecular dynamics [30,31]. As can be seen

in Fig. 2d, the in-homogeneity index oscillates with a period of 240 fs, thus following the oscillation pattern earlier observed in 1D FWM signals.

Summarizing we note that the experimental signatures of vibrational coherence in 2D electronic spectra can be assigned to periodic changes of the relative amplitudes of the rephasing and non-re-phasing signal parts. Expansion of the vibrational part of the third order response in terms of the Huang-Rhys factor (λ/ω) shows that these enhancements and suppressions are caused by coherent vibrational motion. For an intuitive understanding of the periodic changes, one has to recall the multi-level structure of the quantum mechanical system. Both the ground and excited electronic states of PERY feature levels spaced by vibrational frequency ω , which is smaller than the bandwidth of the pulses. The first two laser pulses thus not only populate vibrational states, but also excite coherences between them. During t_2 -evolution, these coherences modulate the signal by a factor $\exp(\pm i\omega t_2)$. The second-order cumulant approach permits to comprise this coherent dynamics together with solvent induced damping into the energy gap correlation function. Expanding this function of an underdamped vibrational mode in λ/ω we find the most significant changes to oscillate with the cosine of the population time. Given ω is small compared to the electronic energy gap, one finds the re-phasing and non-re-phasing signal parts to oscillate with opposite phase [30,31].

3.2. Zn-Phthalocyanine – high-frequency quantum-packets & vibronic coupling

The Zn-Phthalocyanine, Zn-Pc (Fig. 3), is an artificial system and widely used in nano-technology as a powerful absorber, e.g. in photodynamic therapy of cancer [59]. The 1D-linear absorption spectrum of its low-energy Q-band (in BN-solvent) is shown in Fig. 3 (grey area) covering a spectral region from 14000 to 18000 cm^{-1} . The Q-band ($S_0 \rightarrow S_1$) has a sharp maximum at 14700 cm^{-1} ($S_0^{v=0} \rightarrow S_1^{v=0}$) as well as a low-intense vibronic progression of three distinct vibrational modes at the high-energy side of the spectrum [60-62]. Quantum chemistry [60] predicts four vibrational modes with Huang-Rhys factors in the range of 0.1. By increasing the spectral band width of especially tuned NOPA-pulses down to the sub-10 fs temporal regime [63,64], correlation experiments with wide excitation-emission-probing windows up to 6000 cm^{-1} (0.7 eV) regime with highest time-resolution have become possible, very recently. This technological advance enabled to run for the first time ultra-broadband 2D-ES experiments with nearly transform limited sub-7 fs pulses that spectrally cover the whole frequency range of the Q-band including the entire electronic-vibrational FC-progression [65] and thus allow $\omega_3 - \omega_1$ correlation mapping over a 2D energy-window of 4000 $\text{cm}^{-1} \times 4000 \text{ cm}^{-1}$ with non-overlapping pulses for $t_2 > 10$ fs.

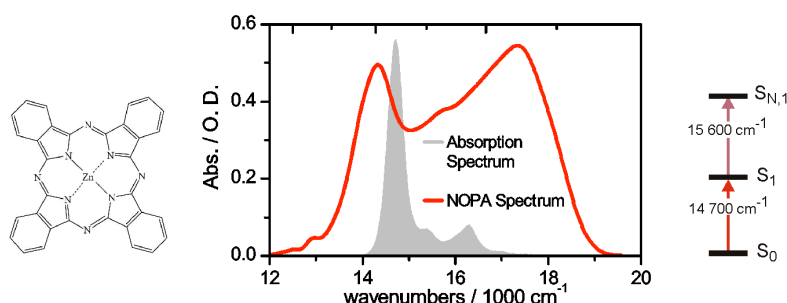


Fig. 3: Structure of Zn-Phthalocyanine (left). Absorption spectrum (grey area) of ZnPc in benzonitrile vs. NOPA-excitation spectrum (red line) and energy level scheme for relevant short time delays, with excited state absorption (ESA) from S_1 to $S_{N,1}$ revealed by 2D-ES, but hidden in conventional 1D spectroscopy.

3.2.1. 2D-Amplitude Spectra

The experimental 2D amplitude spectra proportional to the square root of the squared real and the imaginary part of the respective FT projection $E_s^{(3)}(\omega_1, \omega_3, t_2) = [(E_{\text{abs}}^{(3)})^2 + (iE_{\text{dis}}^{(3)})^2]^{1/2}$ and recorded at delays $t_2 = 0$ (correlation spectrum) and $t_2 > 0$ (relaxation spectra) are shown in Fig. 4a. Sub-7fs broadband excitation, band-to-band t_1 vs. t_3 correlation and FT generates an almost complete 2D Fourier projection of a large-scale vibronic quantum-packet in

terms of a 4 x 4 coherence matrix, with diagonal peaks at $\omega_3 = \omega_1$. Most striking are the off-diagonal cross-peaks both *below* ($\omega_3 < \omega_1$) and *above* ($\omega_3 > \omega_1$) the diagonal trace which are synonymous with the *vibronic* couplings that govern the WP-dynamics of the quantum-packet. A maximum of 16 resonances of varying initial intensity directly maps-out the 2D representation of the Zn-Pc Q-band FC-progression where, theoretically, 12 among them regulate vibronic coupling dynamics and the nature of orthogonal modes decisive in the photochemical dynamics of Zn-PC. Each diagonal element arises from processes occurring within one manifold of fundamental vibrations. The off-diagonal contributions in the cross-peaks represent the processes involving from two different vibronic coordinates via combination transitions into two-quantum states and therefore contain information about the correlation (coupling) between the two vibronic coordinate systems. Their energy-shifts relative to the diagonals (fundamental vibrations) reflect the coupling and an-harmonicity of the system. Spectral positions of the diagonal peaks in the 2D trace ($\omega_3 = \omega_1$) resemble those in the linear absorption (gray-shaded area in Fig. 3) whereas the relative intensities of the 3rd order diagonal peaks are different, since they scale as $\propto |\mu_i|^4$ with the transition moment dipole μ_i , contrary to the $|\mu_i|^2$ -relation for linear absorption.

3.2.2. Real-part (absorptive) correlation – ($t_2 = 0$) and relaxation spectra ($t_2 > 0$)

Contrary to the amplitude spectra in Fig. 4a), the absorptive, real part of the 2D-correlation data (Fig. 4b) is proportional to the diffracted signal field $E_s^{(3)}(\omega_3, t_2, \omega_1)$. The spectrum is constituted by positive (Stimulated Emission SE & Ground State Bleaching GSB, red) and negative (Excited State Absorption ESA, blue) contributions (cf. three-level scheme in Fig. 3) that allow identification of several quantum pathways which interfere to build up the observed 2D patterns.

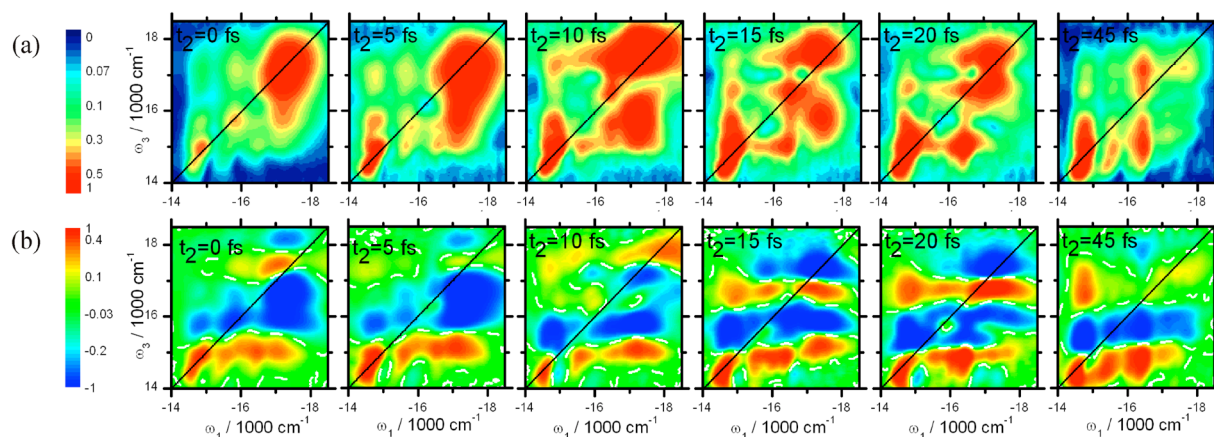


Fig.4: (a) 2D-Amplitude Spectra of ZnPc in benzonitrile recorded for delays of 0, 5, 10, 15, 20 and 45 fs. (b) 2D-Real Part Spectra recorded at the same waiting times

Overall, the absorptive correlation and relaxation spectra provide more information about the subtleties of vibronic coupling phenomena. They spectrally deconvolve the Raman-active positive vibronic couplings from the 1D-FC-vibronic progression and they address the existence of negative ESA-transitions into the S_2 state vibronic manifold. Overall, the recordings of both amplitude and absorptive spectra in tandem with theoretical modeling map-out the *coupled* mode-structure of a prototypical, four-component vibronic wave-packet in a large-scale 2D spectral energy window of $\sim 4000\text{ cm}^{-1}$ (0.5 eV). The entirety of quantum-packet coherence and coherence loss due to dissipation provides a direct look into the landscape of vibronic couplings, their relaxation and motion. Imaging the couplings of the Zn-Pc wave-packet is therefore synonymous with looking into the energy-space trajectory of WP-relaxation which opens, for the first time, a powerful approach to disentangling the quantum-dissipative process of intra-molecular vibronic energy redistribution.

3.2.3. Simulations of Zn-Pc

Care has to be taken in order to bridge the gap between a qualitative and quantitative discussion of the Zn-Pc correlation and relaxation spectra. The high intensity features above 17000 cm^{-1} at $t_2 = 0$ are related to a strong solvent signal. However, the solvent signal rapidly decays on a 20 fs time-scale and appears not to interfere with the evolution of the Zn-Pc signal in the relevant spectral range below 17000 cm^{-1} . The simulations presented in Fig. 5 therefore focus on the *intermediate* regime, where transient features of both pulse overlap and the solvent can be assumed to be substantially relaxed.

The 2D spectrum reveals pronounced *ESA* features indicative of the presence of higher electronic states. The molecular response is therefore expected to correspond to a multi-level system with three bands, the highest of them containing at least two states. Due to the presence of four vibronic modes five levels (commonly a vibronic ground state plus singly excited vibronic states) per electronic state need to be included. The comparison of the theoretical and experimental crosspeak amplitudes strongly suggests the presence of another higher lying excited state with an ESA contribution overlying the GSB and SE. Qualitative agreement with the experimental data at times $t_2 > 25\text{ fs}$ can be obtained with a model containing three vibrational modes. Fig. 5 shows the calculated 2D spectrum of the model system at times $t_2 = 30\text{ fs}$ and $t_2 = 40\text{ fs}$. The simulations demonstrate the progression of the vibronic cross-peaks and the excited state absorption from the singly excited vibronic states of S_1 state to the vibronic states of the S_2 with the same vibrational quantum number. The 2D spectra are calculated at two population times to focus on the time evolution of the cross peak tilt, which is the prime characteristic of the vibronic wave-packet motion. Further studies on disentangling these spectra are in progress.

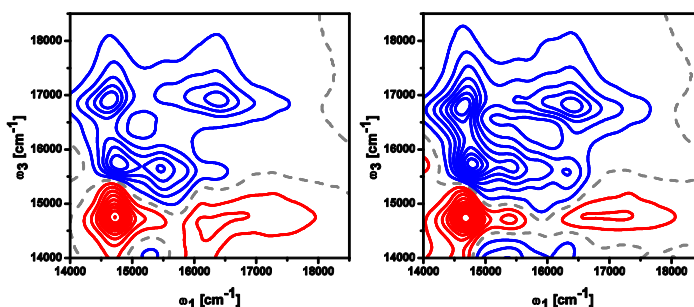


Fig. 5: 2D spectrum of a Zn-Pc model including three vibrational modes with small Huang-Rhys factors at times $t_2 = 30\text{ fs}$ and $t_2 = 40\text{ fs}$. Vibrations with frequencies 680, 1200 and 1600 cm^{-1} and Huang-Rhys factors of 0.1 were used.

4. On the universality of quantum phenomena in multi-level systems - 2D spectroscopy as a tool to distinguish electronic and nuclear wave-packets

2D coherent spectroscopy reveals universal behaviour of multi-level quantum systems, be it electronic or vibrational levels; the same intrinsic quantum dynamics occurs as a precursor in the generation of a macroscopic optical signal. The different origin of the multi-level structure and the apparently different properties of the resulting

2D signal only mirror different special relations between amplitudes of various intrinsic contributions to the 2D spectrum. Thus, in infra-red coherent 2D spectroscopy, *ESA* and ground state contributions exactly cancel for harmonic *PES*, due to a special relation between transition dipole moments for the 0-1 and 1-2 transitions, yet the description of the non-linear signal in terms of quantum mechanics is the same as for any general three level quantum system. However, when the special condition is removed through an-harmonicity, the hidden signal immediately appears. The situation is strikingly similar in electronic 2D spectra of excitonic aggregates. There, the so-called resonance coupling plays a similar role as an-harmonicity in IR [66]. If the resonance coupling is zero, the electronic spectrum of a molecular hetero-dimer contains no cross-peaks. Quantum mechanical description predicts intensive contributions in the 2D spectral region of the cross-peaks, but all the different contributions cancel to zero. The non-zero resonance coupling lifts the cancellation, and could in principle reveal its magnitude through the amplitude of the cross-peaks.

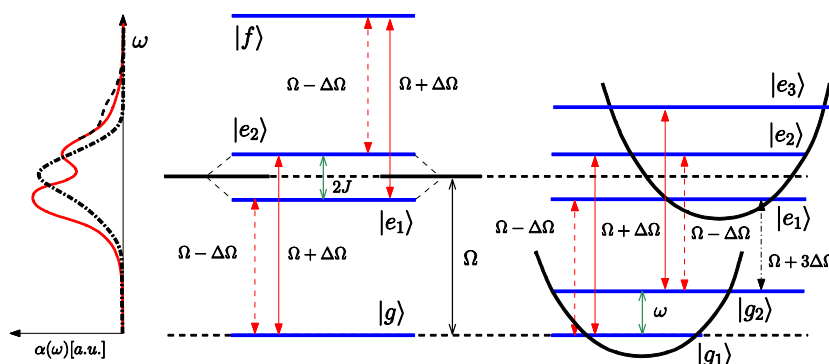


Fig. 6: Energy level scheme of an electronic and vibrational multilevel system and optical transitions involved in 2D electronic spectrum. On the left is a corresponding absorption spectrum in red, and the spectrum of a laser pulse that reduced both models into effective four level systems.

Similarities and differences between electronic and vibrational systems, as the two prominent examples of recently studied multi-level quantum systems, can be exemplified by the example depicted on Fig. 6. From the point of view of molecular spectroscopy, a molecular homodimer with excitonic splitting $2J$, where J is the resonance coupling, can in principle have the same level structure of the first excited state band as a nuclear oscillator with frequency $\omega = 2J$ and a small Huang-Rhys factor. The two-systems are distinguished only by an inevitable presence of a two-exciton state (in homodimer) and a second vibrational state in the electronic ground state (Fig. 7).

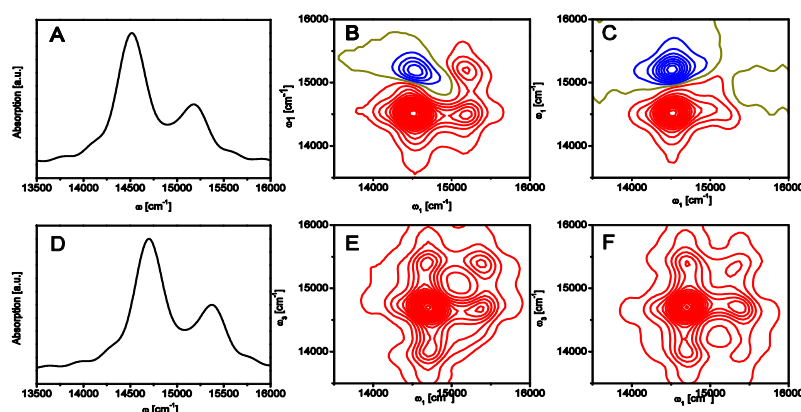


Fig. 7: Comparison of 2D spectra of an electronic (A, B and C) and vibration (D, E and F) few level system with an analogous absorption spectrum (A and D). The 2D spectra are calculated at $t_2 = 50$ fs (B and E) and ($t_2 = 75$ fs) while the period of coherent vibrations is 50 fs in both cases. The orientation of the main peak and of the cross peaks, as well as the intensity of the features, evolve in time.

Provided the relaxation rates between the levels in the first excited state band of both systems are the same, a significant part of the non-linear signal is shared by both systems. No Liouville pathway that would generate an optical signal reaches the level $|e_3\rangle$ and thus the two models effectively consist of four levels. The fourth level appears either as a two-exciton state leading to ESA, or as an additional level in the electronic ground state. Fig. 7 demonstrates the commonalities as well as the differences in the manifestation of the quantum coherence in the 2D signal.

The spectra share some common features due to the three levels that the systems have in common, such as the two diagonal peaks and cross-peaks between them. They also reveal the presence of a higher excited state in the excitonic system (by ESA), and an extra vibronic level in the electronic ground state of the vibronic oscillator system reachable via additional stimulated emission at lower frequencies.

5. Conclusions

Coherent multidimensional spectroscopy gives unprecedented insights into the dynamics of quantum WPs, occurring via coherent preparation of a superposition of quantum states. These states may be eigenstates to the molecular Hamiltonian (nuclear coherences), or of the excitonic Hamiltonian (electronic coherences). While the theory of coherent nD spectroscopy does not distinguish nuclear and electronic coherences, the interpretation of the underlying physics is fundamentally different. Nuclear coherences represent collective and coherent motions of nuclear modes, while electronic coherences represent collective behavior of electronic degrees of freedom. Despite the widely different origins, the two coherences imprint remarkably similar signatures in 2D correlation-spectra. Given the postulated importance of long lived coherences for the efficiency of energy transport, identification of unique signatures of electronic coherences has big impact and this report has outlined the first steps in this direction. The nuclear WPs supply information about motion of nuclear modes localized in the vicinity of a single chromophore. Such nuclear motions are also important for the dynamics of electronic coherences. The destruction of electronic coherence is intimately related to the time dependent loss of correlation of nuclear motions of different sites of an excitonically coupled aggregate. This underlying connection between the nuclear and electronic coherences illustrates the importance of properly characterizing the nuclear motions.

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