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## Vibrational dynamics via multidimensional electronic spectroscopy

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Vibrational spectroscopy is commonly performed using infrared radiation for direct transitions between vibrational states or using visible radiation in a Raman process. As an alternative to narrowband lasers, broadband femtosecond pulses can be employed to excite vibrational wave packets whose temporal oscillations contain analogous information. In this review article, it is shown that coherent multidimensional electronic spectroscopy provides a generalization of this idea, such that vibrational information can be retrieved together with ultrafast dynamics and correlations between various electronically excited states. In particular, fluorescence-detected coherent two- and three-dimensional electronic spectroscopy is discussed. This can be realized in a single-beam geometry with shot-to-shot pulse shaping that allows for fast data acquisition and simultaneous measurement of 15 (or more) different four- and six-wave-mixing spectra. These provide information on higher electronically excited states, vibrational dynamics, and exciton transport, for example in supramolecular systems. Generalizations of this idea offer additional spatial resolution on a  $\mu\text{m}$  length scale in an optical microscope or even down to the few nm length scale using photoemission electron microscopy. Furthermore, the concept of signal detection was transferred to molecular beams and photoions. A topic of current interest is retrieving the full nonlinear tensor via polarization-shaped laser pulses. In general, multidimensional spectroscopy is a powerful strategy to systematically map out the response of a quantum system for increasing orders of nonlinearity in light-matter interaction. © Anita Publications. All rights reserved.

**Keywords:** Vibrational spectroscopy, Raman process, Photoions, Multidimensional spectroscopy.

### 1 Introduction

The term “vibrational spectroscopy” encompasses various methods that can be used to obtain structural information of molecules and materials via analysis of the transitions between vibrational states. In the common approach of linear vibrational absorption spectroscopy, one induces transitions within the vibrational-state manifold in the electronic ground state of a quantum system by applying infrared radiation and observing the resulting absorption spectrum that indicates resonant excitations. These measurements are usually accompanied by theoretical calculations of the infrared absorption of putative species such that an identification of unknown compounds can be made by comparison [1]. Nowadays this can be carried out in a largely automated fashion in many cases with the help of existing databases of infrared spectra [2]. Applications range from fundamental science and structure determination over quantitative analytics and sensing all the way to material-science and medical applications. Despite the maturity of the field, new ideas are emerging in connection with nonlinear spectroscopy, which is the topic of the present work.

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Apart from the classical approach of linear infrared spectroscopy, there exist a number of variants and extensions (Fig 1) that require more than one light field for interaction and that also provide vibrational information [3, 4]. In transient infrared spectroscopy (Fig 1, top left), the system is excited first by an ultraviolet (UV) or visible (VIS) pump laser pulse (blue arrow) that brings some population from the electronic ground state (e.g., a singlet state  $S_0$ ) to the first excited singlet state ( $S_1$ ), whereupon a subsequent infrared (IR) probe pulse leads to a vibrational transition (red arrow). By varying the time delay between the two pulses (Fig 1, bottom left), one can record the change in IR absorption due to vibrational relaxation or structural changes in the investigated system. This is useful to study the dynamics of structural rearrangements and photochemical dissociation reactions, among others, by observing how the IR spectrum of the reactant evolves into the IR spectrum of the product following the electronic excitation.

As an alternative approach to obtaining vibrational information, one can perform Raman spectroscopy. The Raman effect was discovered and announced by Sir Chandrasekhara Venkata Raman in 1928 (Nobel prize in physics 1930) and has developed into a standard analytical tool. This method is also based on interactions with two different external optical fields, only this time they are typically both in the UV/VIS regime (Fig 1, top middle). If the frequency of the pump interaction is larger than that of the “Stokes” interaction, frequency difference between pump and Stokes corresponds to a vibrational transition and provides the Raman spectrum, often reported as a frequency shift with respect to the excitation light. We will transfer this terminology below to the case of multidimensional electronic spectroscopy.

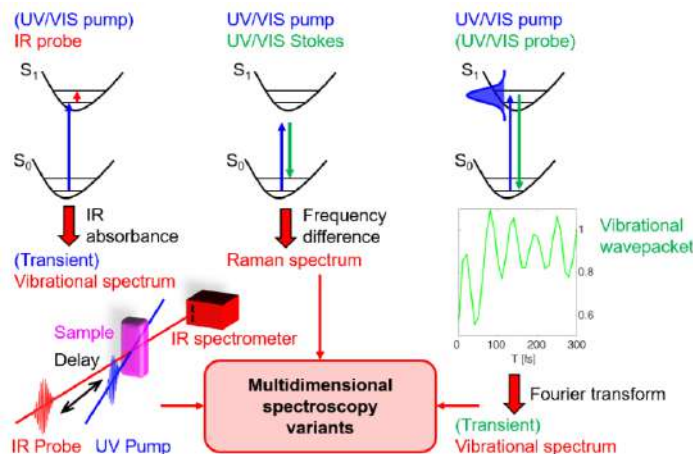


Fig 1. Different types of vibrational spectroscopy.

A third possibility exists by virtue of ultrashort optical pulses and a time-domain description using wave packets (Fig 1, top right). In this case, a femtosecond laser pulse has a broad enough spectrum to excite a coherent superposition of vibrational eigen states in the electronically excited state. Oscillations of such a wave packet may be observed by a time-delayed probe pulse leading to a vibrational spectrum after subsequent Fourier transformation (Fig 1, bottom right).

Combinations among the three techniques are also possible. For example, while a “classical” linear Raman spectrum is obtained with narrow-band excitation in frequency space, it is also possible to use femtosecond lasers and observe and analyze the oscillations of wave packets to get frequency information. This was reported in a coherent anti-Stokes Raman scattering (CARS) experiment by the Kiefer group in 1997 [5]. The idea of the present work builds upon and generalizes this concept by connecting it with multidimensional electronic spectroscopy. In that way, several different frequency axes can be obtained simultaneously, correlating electronic and vibrational transitions in one data set.

Before starting with a description of the background and implementation, it should be pointed out that due to the special nature of this paper as a result of a talk, the literature citations are not as balanced as in a conventional review article and focus largely on own work. Our group develops methods for femtosecond time-resolved and space-resolved spectroscopy and microscopy and applies them to study quantum systems in solution, on surfaces, and in molecular beams. In particular, we seek to establish new variants of coherent multidimensional spectroscopy that correlate various excitation and detection frequencies and provide comprehensive information on the nonlinear response up to a given order in perturbation theory of light–matter interaction. It is emphasized, however, that many groups around the world work on related ideas and have contributed to the substantial advancement of the field in recent years.

## 2 Technique

### 2.1 Basic concept of coherent two-dimensional spectroscopy

The foundation of transient absorption spectroscopy is to vary a time delay,  $T$ , between one pump and one probe pulse, and to observe changes in absorbance,  $\Delta\text{Abs}$ , of the probe pulse in form of a kinetic evolution (Fig 2, green transient). For more information, the probe pulse is usually frequency-resolved, resulting in a specific transient spectrum for each time delay (Fig 2, green spectrum displaying two illustrative peaks). Our group has implemented transient absorption spectroscopy in the ultraviolet [6-8], the visible [9,10] and the infrared [11-14] regions. While this provides valuable insight, the interpretation of spectra is often ambiguous, in particular in cases with many (molecular) species and overlapping spectral contributions.

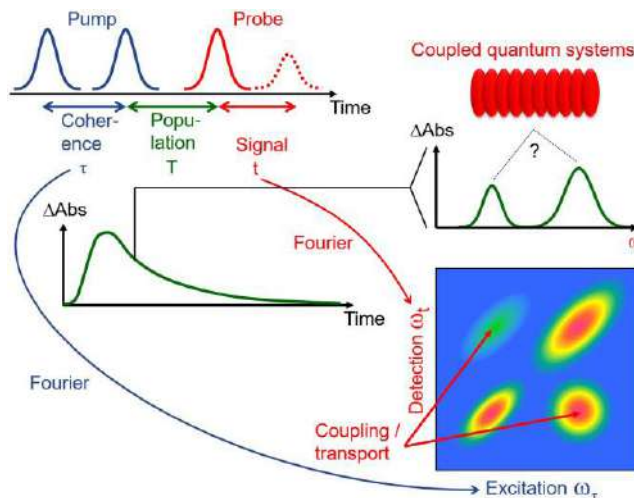


Fig 2. Motivation and principle of coherent 2D spectroscopy.

Following ideas from two-dimensional (2D) NMR spectroscopy [15], optical 2D spectroscopy was suggested in 1993 [16] and then experimentally developed for nonlinear optics [17], near-infrared [18], and infrared [19] molecular excitations. It is a generalization of transient absorption spectroscopy with frequency resolution for both the pump and the probe step and determines the nonlinear third-order response function of a sample after interaction with a sequence of three time-delayed laser pulses [20-22] (Fig 2, top). Thus, the pump interaction is split into two pulses separated by a “coherence time”,  $\tau$ , followed by the “population time”,  $T$ , that takes the role of the time delay in transient absorption, and a “signal time”,  $t$ , in which the field is coherently emitted after interaction with the third pulse. Using Fourier transformation both over  $\tau$  and over  $t$  leads to a 2D spectrum for each  $T$ . 2D spectra correlate the excitation and detection frequencies at a given waiting time. In particular, off-diagonal peaks reveal information on couplings and energy transport that have been exploited extensively to investigate transport phenomena in supramolecular systems.

In previous own work, 2D spectroscopy was pioneered for electronic transitions in the visible [23, 24], with the first application to multichromophore systems in the literature [25, 26]. We have recently derived a mathematical theorem proving that 2D data can recover uniquely the state-to-state population transfer rate matrix under certain conditions [27]. Experimentally, following some technical developments [28, 29] we have determined population dynamics of excitons in several (supra)molecular assemblies [30-37]. In addition to photophysical systems, we have also introduced 2D electronic spectroscopy for photochemical reactions that involve structural rearrangement and bond breakage [38-41]. The 2D approach greatly benefits from broad spectra covering all the relevant electronic transitions, and we have shown how to reach  $\approx 200$  nm of bandwidth in the visible domain and avoid 2D peak-shape distortions at a time resolution of 7 fs [42].

Various implementations of 2D spectroscopy have been developed in the literature [43]. The conventional approach of coherence-detected 2D spectroscopy employs a noncollinear four-wave-mixing geometry in which the desired signal is emitted into a particular direction according to phase matching, i.e., a new coherent beam is created with a wave vector that arises as a linear combination of the wave vectors of the incident fields. For increasing orders of nonlinearity, one has to add more and more beams from various directions (Fig 3, left). Full phase information about the signal is required for Fourier transformation and for constructing a 2D spectrum. This phase is obtained by evaluating the interference of the unknown signal with a known reference laser pulse, the so-called local oscillator (LO) (Fig 3, left, red), as measured in a spectrometer. In addition to the actual signal resulting from resonant excitation of the quantum system (blue), one often has to deal with nonresonant contributions of the solvent and scattered light of the excitation pulses (green) that also interfere with the LO and contaminate the 2D spectrum. This is a drawback when extending the method to higher orders of nonlinearity and higher-order quantum coherences. Also, it is increasingly challenging to retain the required phase stability between all the pulses if they have to be spatially separated and recombined. An alternative solution is described in Section 2.2.

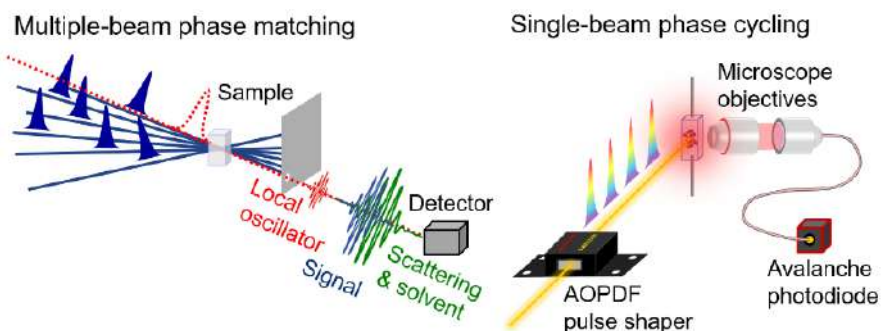


Fig 3. Phase-matching (left) versus phase-cycling (right) geometry of multidimensional spectroscopy.

## 2.2 Fluorescence-detected two-dimensional and three-dimensional spectroscopy

Apart from coherence-detected 2D spectroscopy, it is also possible to employ fluorescence as an observable [44-50] using sequences of collinear pulses and phase cycling [51] to retrieve the desired nonlinear signal contributions. Fluorescence detection offers unique advantages, among them high sensitivity as well as removal of scattering artefacts and non-resonant solvent contributions. In our own work, we developed rapid-scan fluorescence-detected 2D spectroscopy based on shot-to-shot pulse shaping with an acousto-optic programmable dispersive filter (AOPDF) that can be operated at 1 kHz [48] (Fig 3, right). This requires only a single excitation beam and thus avoids the phase instabilities from spatially separated pulses. The full sequence can be programmed electronically into the pulse shaper requiring no mechanically moving parts. Fluorescence is then collected and directed onto a single-pixel detector via a pair of low-numerical-aperture microscope objectives.

This computer-controlled approach offers the advantage of acquiring a full, high-bandwidth, 2D spectrum in only few seconds (plus averaging), and a root-mean-square error of  $< 5\%$  can be reached after just 1 min of measurement time. The number of acquisition steps can be further reduced with compressed sampling [52-56] that we have adapted for 2D fluorescence spectroscopy in an optimal fashion using a genetic algorithm [57].

With the computer control over time delays and phases in place, we can advance to full three-dimensional (3D) spectroscopy. For this purpose, we implemented 125-fold phase cycling that records simultaneously three different fourth-order and twelve sixth-order spectra by applying approximately half a million different pulse shapes within just 8 min of measurement time [58] without averaging (Fig 4).

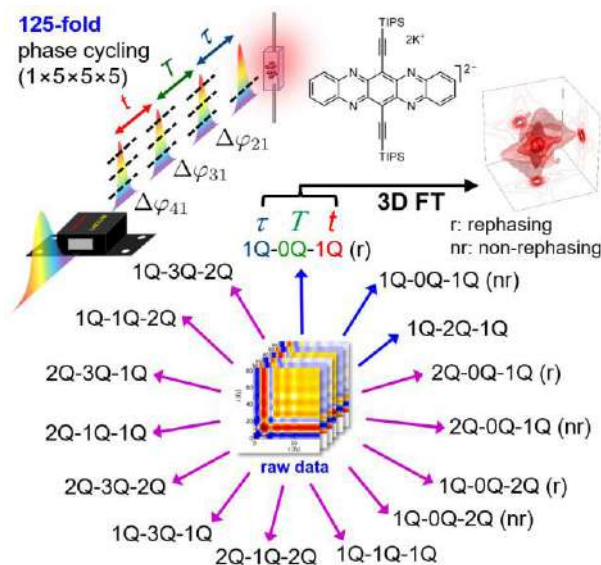


Fig 4. Fourth-order (blue) and sixth-order (violet) signals in fluorescence-detected 3D spectroscopy.

This means that the relative phases of the second, third, and fourth pulse are varied systematically in five steps each, with respect to the first pulse (Fig 4, top left). Using suitable linear combinations of the raw data thus measured provides various available signal types (Fig 4, bottom), labeled according to the number of optical quanta that are coherently excited within the three time periods of the four-pulse sequence. Thus, a zero-quantum (0Q) coherence describes a vibrational wave packet without an additional electronic coherence, a one-quantum (1Q) coherence describes a coherent superposition of the electronic ground state and the first electronically excited state (or a coherence between the first and a higher excited state), and a two-quantum (2Q) coherence relates electronic states two optical quanta apart. After 3D Fourier transformation over all time delays  $\tau$ ,  $T$ , and  $t$ , one obtains a 3D spectrum, here shown exemplarily for the rephasing 1Q-0Q-1Q spectrum on the dianion of the bis(triisopropylsilyl)ethynyl-substituted symmetric tetraazapentacene (TIPS-TAP<sup>2-</sup>) dissolved in tetrahydrofuran (Fig 4, top right) [58], to be further discussed below.

### 3 Results and discussion

#### 3.1 Connecting Raman shift and fluorescence-detected 3D spectroscopy

Let us now analyze the 1Q-0Q-1Q 3D spectrum of Fig 4 more closely in Fig 5 in order to make the connection to Raman spectroscopy proposed in the Introduction. What is the meaning of the three frequency axes? The first pulse creates an electronic coherence (1Q in this case) between ground state and first electronically excited state (Fig 5, top left) that leads to oscillations with a frequency according to the

energy difference between these levels. Fourier transformation over the time delay between first and second pulse thus delivers an excitation frequency axis (Fig 5, right, blue). With the second pulse, a population is created either on the electronic ground state or on the excited state as a vibrational wave packet, i.e., a 0Q coherence regarding the electronic states, as marked in green in Fig 5. Finally, the third pulse creates again a 1Q coherence that is converted by the fourth pulse into a population that, when located on the electronically excited state, can lead to fluorescence that is observed. Thus, the final time delay, when Fourier transformed, provides a detection axis (Fig 5, red).

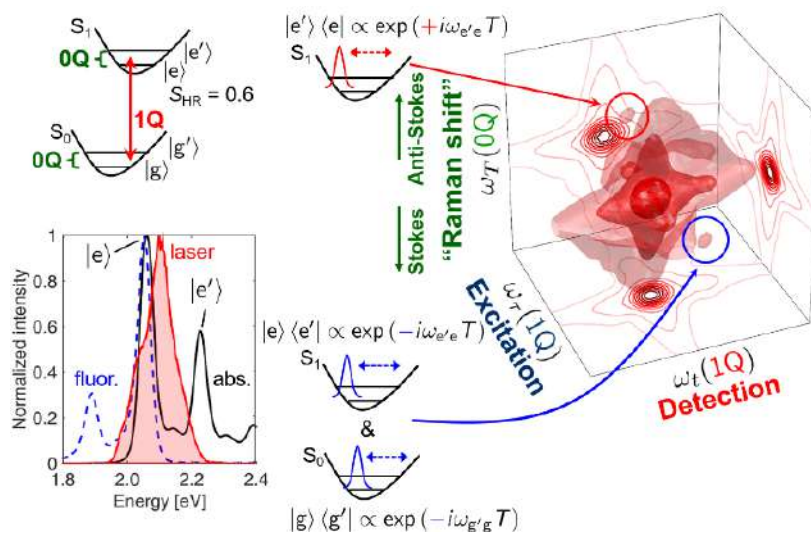


Fig 5. 3D variant of coherent fsresonant Raman spectroscopy.

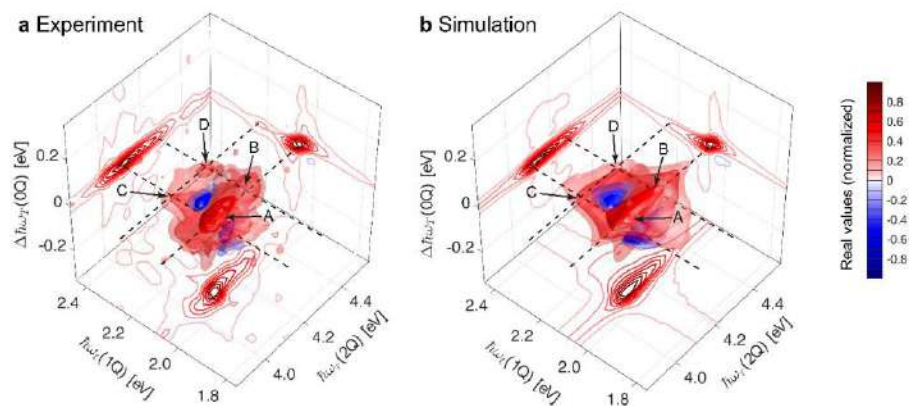
The connection with Raman spectroscopy lies in the 0Q coherence as this corresponds to a vibrational wave packet. Thus, Fourier transformation over  $T$  delivers a frequency axis that can be interpreted as the Raman shift (Fig 5, green) and contains both “Stokes” and “Anti-Stokes” components, i.e., signals shifted to the red or to the blue of the central frequency of the laser. Note that it is not necessary to tune several narrowband lasers to obtain the frequency resolution. Indeed, the opposite is true: We require a broadband laser, and typically the same spectrum is used for all four pulses (although multi-color experiments are feasible as well). The broader the employed laser spectra, the more of the relevant molecular spectrum can be covered. Frequency resolution is inversely proportional to the maximum scanned delay time between the respective pulses for any of the three axes. If conventional mechanical delay stages are used, resolution can be high for sufficiently large delays. In the present, single-beam implementation we are limited by the maximum temporal pulse-shaping window to a few ps. Thus, this approach is particularly suited for elucidating fast dynamics.

Since the excitation spectrum covers two vibrational states in the first electronically excited state (Fig 5, bottom left), the created wave packet oscillates and is thus visible as a 3D cross peak both on the Anti-Stokes (red circle) and on the Stokes side (blue circle). Full analysis of the signal is possible using appropriate modeling [58], but in essence it turns out that contributions to the signal by either ground-state or excited-state wavepackets lead to specific signs in the response, and thus can be at least partially distinguished.

Thus one can obtain femtosecond resonant fourth-order Raman spectroscopic information within 3D spectra, where the Raman shift is correlated both with an optical excitation and an optical detection frequency. In this way, one obtains access to the full nonlinear response function of the quantum system. Apart from the magnitude as shown in Fig 5, one also obtains 3D phase information that indicates the nonlinear change in refractive index, although this component is very rarely analyzed in the literature.

### 3.2 Higher orders and multi-quantum coherences

The results of Section 3.1 provide information on 0Q and 1D coherences. Information about higher-excited states, exciton–exciton binding energies, and electron–electron correlations is available through two-quantum (2Q) 2D spectroscopy as demonstrated in the literature [59–68]. However, in approaches using a phase-matching geometry, there are significant challenges, such as the strong nonresonant background generated by the solvent [69], the inherently small signal, and the lack of a suitable “phasing” strategy that can lead to artifacts [66]. These issues are even more critical for 2Q than for 0Q/1Q-type 2D spectra. We thus introduced fluorescence-based 2Q 2D spectroscopy that remedies these difficulties [70].



**Fig 6.** Sixth-order 2Q-0Q-1Q 3D spectrum (real part) of TIPS-TAP<sup>2-</sup> in tetrahydrofuran solution. (a) Experimental and (b) simulated 3D spectra. The bottom projections of the solids show the purely absorptive 2Q-1Q 2D spectrum at  $T = 0$  fs. The dashed lines in the  $\Delta\hbar\omega_T = 0$  plane denote the energies of the main absorption band and a vibrational progression band along  $\hbar\omega_i$  and the energies of the 2Q levels along  $\hbar\omega_f$ . The letters A–D mark peaks that can be assigned to certain quantum pathways. Figure from [58] with permission.

Accessing multi-quantum correlations is also possible at higher orders of the nonlinear response. Moving from four-wave mixing to six-wave mixing is straightforward in the single-beam geometry of Fig 3 b, as it involves only a suitable programming of the pulse shaper [58]. Indeed, as Fig 4 indicates, we have shown how to obtain three fourth-order and twelve sixth-order spectra at the same time. A sixth-order 2Q-0Q-1Q 3D spectrum is exemplarily shown in Fig 6 a. This provides detailed insight into higher excited states and disentangles quantum pathways. We now routinely carry out simulations of 2D and 3D spectra using a Lindblad formalism (Fig 6 b) and made the code publicly available (<http://www.qd-toolbox.org>). Note the close correspondence of features between experiment and simulation despite the high nonlinear order. Meanwhile we even demonstrated molecular three-quantum coherences [71].

## 4 Combination with spatial resolution and further generalizations

### 4.1 Exciton–exciton-interaction 2D spectroscopy

In Section 3.2 it was shown that coherent six-wave-mixing 3D spectra can be recorded with fluorescence detection. Such information is useful, for example, to characterize exciton transport in extended coupled systems such as molecular aggregates, polymers, or natural light-harvesting systems. While the majority of 2D studies are based on third-order nonlinear response, we recently developed a fifth-order variant called “exciton–exciton-interaction two-dimensional” (EEI2D) spectroscopy (Fig 7 a) [72]. The initial demonstration was done using coherent detection (thus formally a fifth-order process), but we have extended



it now also to fluorescence detection (formally a sixth-order process). It can be shown that both types of experiment probe the same underlying general response function, though there are also some differences [73, 74].

In EEI2D spectroscopy, a signal arises only then when the presence of one exciton influences the behavior of another. Exemplarily, we monitored exciton diffusion by observing annihilation dynamics in a perylene-bisimide-based J-aggregate and determined the exciton diffusion constant (Fig 7b) [72]. In another application, we followed the energy pathways in double-walled tubular dye aggregates and were able to separate the dynamics of outer and inner walls [75]. For disordered systems such as polymers we could show that propagation does not follow the normal diffusion equation as often assumed, but that trapped states lead to sub-diffusive behavior [76].

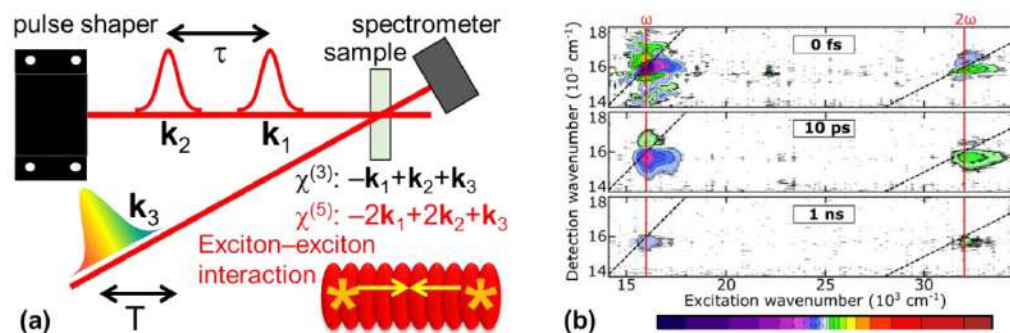


Fig 7. Exciton–exciton-interaction two-dimensional (EEI2D) spectroscopy. (a) In pump–probe geometry, a double excitation sequence is generated with a pulse shaper and the transient white-light absorption recorded. (b) Signals appear near the fundamental and its double and can be separated [72].

#### 4.2 Fluorescence-detected 2D microscopy

Combining femtosecond temporal resolution with direct spatial resolution facilitates the analysis of heterogeneous materials without detrimental averaging over the relevant microstructures. We have developed spectral interference microscopy for full amplitude-and-phase characterization of coherently emitted signals as a function of position with a diffraction-limited optical resolution of  $\sim 260$  nm [77,78]. In this context, we analyzed and controlled propagation in plasmonic nanocircuits [79-85]. As a next step, we then implemented fluorescence-detected 2D microscopy (Fig 8) by connecting a femtosecond pulse shaper with a high-numerical-aperture ( $NA = 1.4$ ) optical microscope (Fig 8 a) [86]. We were able to compensate the dispersion for a broad spectrum (Fig 8 b) such that short pulses of  $\sim 12$  fs duration were realized at the focus of the objective (Fig 8 c). We then observed photoluminescence after excitation with a four-pulse sequence (Fig 8 d). This leads to 2D spectra after double Fourier transformation with additional spatial resolution. We applied this concept to investigate a structured organic film based on a fluorinated Zn phthalocyanine dye. Connecting the observed spectral differences for different spatial positions with the local size of aggregation through the help of time-dependent density functional theory (TDDFT) simulations, we derived a map of the average optical coherence length that varied considerably between two and eight chromophores, and found it to be correlated with the local slope of the microstructured film surface [87]. We are currently exploring the application of this method to other material systems and to concentrations in the single-molecule limit.

#### 4.3 Coherent 2D nanoscopy using photoemission electron microscopy (PEEM)

Spatial resolution can be improved significantly using photoemission electron microscopy (PEEM). In collaboration with Martin Aeschlimann (TU Kaiserslautern) and Walter Pfeiffer (U Bielefeld), we combined PEEM with femtosecond pulse shaping to realize coherent control of spatiotemporal excitation in

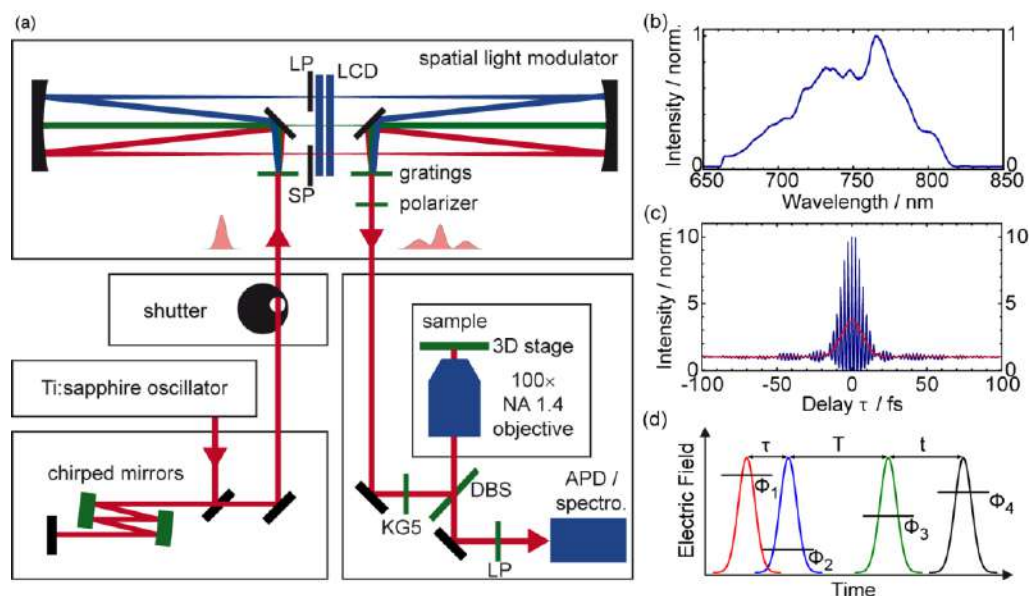


Fig 8. Fluorescence-detected 2D microscopy. (a) Experimental setup; (b) laser spectrum; (c) interferometric autocorrelation in the focus; (d) four-pulse sequence. Figure from [86] with permission.

nanostructured plasmonic systems at  $\sim 30$  nm spatial resolution [88–92]. Applying four-pulse sequences as in Sections 2.2, 3, and 4.2, but detecting electrons instead of fluorescence, we then developed coherent 2D nanoscopy [93], i.e., 2D spectroscopy with nanometer spatial resolution. As an application, we demonstrated Anderson localization of light to be responsible for the efficiency enhancement in thin-film solar cells [94], and we realized strong coupling between plasmonic nanoantennas [95].

Recently, we acquired an aberration-corrected PEEM for our group at Würzburg that delivers  $\sim 3$  nm spatial resolution and combined this with a broadly tunable (215–970 nm) 1 MHz laser at pulse durations of  $< 20$  fs [96]. The characteristics of this system are, to our knowledge, unique. We then investigated a plasmonic nanoresonator [97]. Surprisingly, we detected apparent spatial variations of the Q-factor and resonance frequency that are commonly considered to be global properties for a single mode. By using quasinormal modes we explained these local differences by crosstalk of adjacent resonator modes. Detecting such subtle differences in the femtosecond dynamics of a single system on a nanometer length scale renders the setup as important not only for time-domain studies of plasmon-mediated strong light–matter coupling at ambient conditions but for a vast range of nanostructured surface systems.

#### 4.4 Coherent 2D mass spectrometry

Molecular beams have a long tradition in our group, e.g., the first experiment on coherent control of photodissociation [98] in 1998 and a large body of subsequent related work. We now have developed coherent 2D mass spectrometry in a molecular beam [99]. This complements fluorescence and electrons as incoherent observables in 2D spectroscopy by detecting photo generated ions for the first time in literature, effectively turning off the interactions between the investigated molecules and their environment. Coherent 2D electronic mass spectrometry allows 2D measurements on quantum systems with minimum system–bath interaction and was also applied by others [100]. We recently upgraded our molecular-beam apparatus with a separate preparation chamber that allows us to realize molecular beams with a seed gas, rather than just the effusive beam of the original experiment, making accessible also less volatile substances.

#### 4.5 Tensor response and coherent control

One additional interest of our group lies on chirally selective spectroscopy. We have developed a method for time-resolved detection of photoactivity, i.e., the change of polarization direction of linearly polarized light upon propagation through a chiral sample, and applied this in a pump–probe context [101]. This can, e.g., discriminate racemic from achiral molecular mixtures [102]. Further, we developed a setup for the creation of “laser-pulse enantiomers,” i.e., exact mirror images of the polarization state of any input pulse without requiring wave plates [103]. We apply this setup for time-resolved femtosecond circular dichroism experiments. In connection with chiral light, we also pioneered femtosecond polarization pulse shaping, i.e., the possibility to modify the polarization state of light as a function of time within a single laser pulse [104–106] as applied in quantum control [107]. We also developed full vector-field control that allows independent phase and amplitude shaping of the two transverse field components [108,109] phase, ellipticity, and orientation angle.

The mentioned techniques may in the future be used for tensor analysis of the response function in 2D spectroscopy. Thus one could envision the pulse shaper to automatically deliver the appropriate combinations and permutations of polarizations of the incident pulses to acquire the full polarization-dependent response.

In earlier years, coherent control had been our major research direction, including the first automated control of a photochemical reaction and other work [98,110–113]. While the focus has now shifted towards 2D spectroscopy, we make use of the technology, in particular femtosecond pulse shaping, as outlined above. Another example of technology transfer is the von-Neumann time–frequency phase-space representation that we introduced, together with David Tannor (Weizmann Institute of Science, Israel), to describe shaped laser pulses [114–119]. A current usage in 2D spectroscopy is found in compressed sampling for which a four-dimensional von-Neumann distribution was developed to achieve a sparse representation [57].

One further challenge is to find suitable analysis tools for the large data amounts in multidimensional spectra that can be obtained by the single-beam approach. Applying artificial intelligence schemes such as evolutionary algorithms or neural networks to automatically analyze the data is currently a hot topic.

## 5 Conclusion

This article reviewed work of our group on coherent multidimensional electronic spectroscopy, with a particular focus on the relation with vibrational spectroscopy. It was argued that analyzing the beating patterns observed by probing with broadband optical pulses can deliver information similar to resonance Raman experiments using narrowband lasers. Using a four-pulse sequence and fluorescence detection, it is possible to record fifteen different four-wave-mixing and six-wave-mixing spectra simultaneously within a short time and to plot the result as a three-dimensional (3D) spectrum. Taken together, these 3D spectra provide the full spectroscopic information about the investigated quantum system up to a given nonlinear order of interaction. This can be used, among others, to learn about higher excited electronic states, vibrational wavepacket dynamics, bi-exciton energies, exciton–exciton annihilation, and exciton transport.

Generalizations of the technique of incoherently detected 2D or 3D spectroscopy allow measurements in molecular beams (by detecting photo generated ions), on structured samples with sub-micrometer spatial resolution (by detecting fluorescence in a microscope), or on surfaces even with nanometer resolution (by detecting electrons in a photoemission electron microscope). Current developments aim at detecting the tensor character of the nonlinear response and at automated analysis of multidimensional spectra using artificial intelligence.

Nonlinear spectroscopy is headed for an exciting future with many opportunities for technical development but also applications to more and more complex quantum systems.

## Acknowledgments

I am strongly indebted to my group and many collaborators over the years that made this research possible. It is not possible to list them here. Instead, their names are found as coauthors of the papers in the reference section. It has been a fantastic journey, and I have enjoyed immensely – and still do – working with so many bright students, postdocs, colleagues, and technical and administrative staff whose input, innovative ideas and hard work were indispensable for success. I thank Stefan Mueller for essential scientific contributions and his help in preparing Figs 3 - 6. The research was supported by several funding agencies. The most recent and current projects relevant for the present paper are the European Research Council (ERC) – Grant No. 614623; the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Grant Nos. 220404594 and 423942615; and the Bavarian State Ministry of Science, Research, and the Arts – Collaborative Research Network “Solar Technologies Go Hybrid”. Lastly, I am very much honored by having received the **Dayawati Rastogi Lecture Award 2020** by the *Indian Spectroscopy Society* and the *Asian Journal of Physics*, and I enjoyed very much the generous hospitality at the International Conference on Perspectives in Vibrational Spectroscopy (ICOPVS) in Bengaluru, India, where this prize was conferred.

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