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EDITORIAL | JANUARY 02 2024

## Celebrating 25 years of 2D IR spectroscopy

Special Collection: [Celebrating 25 Years of Two-dimensional Infrared \(2D IR\) Spectroscopy](#)

Carlos Baiz ; Jens Bredenbeck ; Minhaeng Cho ; Thomas Jansen ; Amber Krummel ;  
Sean Roberts 

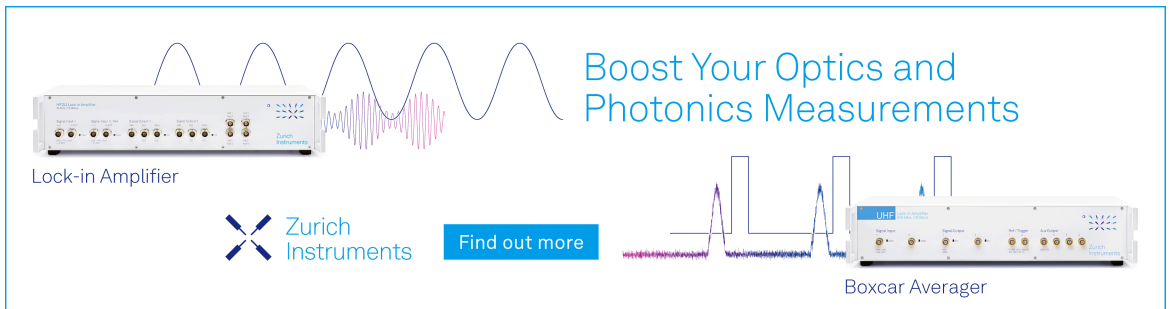


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# Celebrating 25 years of 2D IR spectroscopy

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## I. TWO-DIMENSIONAL INFRARED SPECTROSCOPY

Since its development 25 years ago,<sup>1</sup> two-dimensional infrared (2D IR) spectroscopy has experienced significant advancements in experimental implementations, applications, theoretical models, simulations, and tools for interpreting complex spectra. This momentum, especially in the past decade, has been driven by researchers applying 2D IR spectroscopy to obtain detailed molecular insights across a variety of systems. The evolution of lineshapes during the waiting time provides access to bond-specific dynamics spanning femtoseconds to hundreds of picoseconds. Furthermore, cross-peaks, when detectable, serve as markers of molecular structure and quantitative reporters of chemical exchange or energy transfer, affording a deeper understanding of the mechanisms driving these phenomena, especially when paired with structure-based models.

In terms of optical implementations, the traditional box-CARS configuration has largely given way to more user-friendly “pump-probe” designs. This has been driven primarily by the widespread adoption of pulse shapers.<sup>2</sup> In contrast to optical interferometers, pulse shapers enable independent manipulation of carrier phase and pulse intervals and eliminate phase ambiguities as well as enable measurements in highly scattering samples. Recent 2D IR implementations take advantage of high-repetition-rate lasers, providing a superior signal-to-noise ratio over the original Ti:sapphire-amplifier based approaches.<sup>3</sup>

From a theoretical perspective, 2D IR spectroscopy has benefited from the development of structure-based vibrational maps also

referred to as “frequency maps.”<sup>4</sup> These models translate the evolution of local environments and intermolecular interactions into fluctuating frequencies. Frequency maps are ideally suited to interface with molecular dynamics simulations due to their computational efficiency, providing a granular view of the bath fluctuations, which is often essential for the interpretation of experimental spectra.

This Special Issue in the *Journal of Chemical Physics* spotlights fundamental progress and innovative applications of 2D IR spectroscopy and related methodologies.

## II. ADVANCES IN EXPERIMENTAL METHODS

Most 2D IR studies to date have addressed well-defined solutions of molecular systems with a low number of components. Applications to complex mixtures or solid-state samples are of great interest but pose significant challenges to the 2D IR methodology. Donaldson and co-workers extend the application range of 2D IR spectroscopy to severely scattering solid-state samples by using a bright probe pulse in combination with phase cycling and polarization control.<sup>5</sup> This approach opens access to a wide range of important samples, for example, in heterogeneous catalysis and materials science. Giubertoni *et al.* introduce a powerful approach to disentangling spectra of mixtures of molecules of different sizes by diffusion-ordered 2D IR spectroscopy (2D IR DOSY).<sup>6</sup> In a microfluidic cell, a concentration gradient is generated and spectra are recorded as a function of diffusion time to reveal spectra of monomers and amyloid aggregates in a solution of bovine serum albumin. Daniels and co-workers demonstrate an experimental approach to measuring

high-resolution rovibrational 2D IR spectra of molecules in the gas phase.<sup>7</sup>

### III. APPLICATIONS OF 2D IR SPECTROSCOPY IN MOLECULAR SYSTEMS AND COMPLEX MATERIALS

Excitonic systems, such as nanocrystals and polymer systems, are surprisingly difficult to characterize given the range of timescales observed and the complex interdependence between morphologies, dynamics, and vibrational or electronic lineshapes. Ultrafast 2D IR spectroscopy has emerged as a powerful tool to disentangle the relationship between local conformations, material morphologies, and molecular dynamics, on vibrational states that arise from local site energies and coupling to understand the origin of bulk properties within these complex materials. Li and co-workers interrogate the molecular conformations of the high-mobility copolymer N2200 in two solvents  $\text{CHCl}_3$  and  $\text{CCl}_4$  as well as in films.<sup>8</sup> The authors find that the morphology of the polymers in solution is different in both solvents, but the films cast from either solvent have the same morphology. Rushing *et al.* investigate polymer gel electrolytes using 2D IR spectroscopy, showing that local morphologies and polymer-ion vs polymer-polymer interactions are strongly dependent on the cation concentration.<sup>9</sup> Stingel *et al.* use broadband 2D IR spectroscopy to show that HgSe colloidal quantum dots exhibit a large inhomogeneous broadening and that this broadening is the result of size distribution and doping levels of the quantum dots.<sup>10</sup>

### IV. COMPLEX LIQUIDS AND BIOPHYSICAL APPLICATIONS OF 2D IR SPECTROSCOPY

In biomolecules, spectral congestion of native vibrations due to the biological solvent water is a severe obstacle for 2D IR studies. Isotope labeling schemes, non-native IR labels, and spectrally isolated native vibrations combined with advanced background subtraction approaches are developed to harness the strengths of 2D IR spectroscopy for biophysical applications and the investigation of dynamics in complex liquids using intrinsic vibrations, which provide direct access to a wealth of information.

Obtaining reliable 2D IR amide I spectra in  $\text{H}_2\text{O}$  instead of  $\text{D}_2\text{O}$  is a prerequisite for the application of 2D IR spectroscopy in diagnostics and protein screening. Rutherford *et al.* introduce an according workflow, significantly enhancing the analytical informative value of 2D IR spectroscopy as demonstrated by quantifying the four major protein constituents of blood serum samples.<sup>11</sup> To investigate protein structure and dynamics, Deniz *et al.* unlock the weak cysteine S-H stretching vibration as an expressive vibrational probe that either is intrinsic or can be easily introduced into proteins.<sup>12</sup> With 2D IR setups achieving ever higher sensitivities in recent years, the S-H stretch can now be systematically explored. A selective isotope-labeling strategy allows Chenchiliyan *et al.* to study the chromophore vibrations in a bacterial phytochrome.<sup>13</sup> 2D IR with its ability to analyze spectral inhomogeneity provides insight into the structural heterogeneity of the chromophore environment and might help in the future to better understand the biological role of protein heterogeneity. Isotope labeling of specific amino acids enables Hess *et al.* to study residue-level structural changes in a full-length amyloid peptide upon interaction with nanoparticles.<sup>14</sup> As nanoparticles are increasingly used, understanding their interaction

with biomolecules and their medical implications is vital. Carbohydrates have so far remained difficult to study by 2D IR spectroscopy. Gasse *et al.* open this important class of biomolecules for 2D IR investigations as they introduce and spectroscopically characterize thiocyanate-labeled glucose as the first IR-labelled saccharide.<sup>15</sup> Solvent- and substituent-dependent vibrational energy redistribution in xanthenes has been investigated by Hanes *et al.*, resolving mode specific and statistical relaxation of ring and carbonyl modes with implications for other purine derived biomolecules.<sup>16</sup> Kwon *et al.* study isolated  $\text{D}_2\text{O}$  molecules in chloroform to thoroughly characterize its vibrational states to pave the way for future research on water dynamics.<sup>17</sup> Chatterjee *et al.* investigate the dynamics of a deep eutectic solvent mixture in the vicinity of the eutectic composition by measuring spectral diffusion and anisotropy decay of an intrinsic vibration as well as by MD simulations.<sup>18</sup> Fujii *et al.* study spectral diffusion of the NO stretching vibration of  $[\text{RuCl}_5(\text{NO})]^{2-}$  in  $\text{D}_2\text{O}$ .<sup>19</sup> With support from MD simulations, they concluded that different time scales of spectral diffusion are caused by  $\text{D}_2\text{O}$  molecules located in the proximity of NO and  $\text{D}_2\text{O}$  molecules around the Cl ligands.

### V. ELECTRONIC AND OTHER SPECTROSCOPIES INSPIRED BY 2D IR SPECTROSCOPY

The additional information offered by 2D IR spectroscopy over related ultrafast techniques has led to a push to extend pulse sequences and approaches employed for 2D IR to the study of electronic states that can be accessed using visible or ultraviolet pulses. This has enabled advances to be made in our understanding of electron dynamics in systems ranging from photosynthetic centers to semiconductor nanomaterials and molecular aggregates. Such advances have gone hand in hand with the creation of new methods for identifying and interpreting different processes that contribute to 2D electronic spectroscopy (2D ES), some of which are highlighted by articles contained in this collection.

Lüttig *et al.* present a powerful method for separating different perturbative contributions to 2D ES lineshapes and use their approach to identify the third-order 2D ES lineshape of excitons generated in squaraine oligomers as well as higher-order signals that report on multiexciton interactions.<sup>20</sup> Brosseau *et al.* describe methods for identifying perturbed free induction decay signals that can appear when pulses overlap in 2D ES experiments and could lead to erroneous assignments of observed lineshapes to spectral diffusion and energy transfer if not properly modeled.<sup>21</sup> Horz and co-workers present theory and experiments that introduce a new method, two-photon vibrationally promoted electronic resonance (2P-VIPER) 2D IR spectroscopy, which takes advantage of the long lifetime of electronic states to extend the viewing window for the vibrational dynamics of a system to values significantly longer than what is currently possible using conventional 2D IR methods.<sup>13</sup> Barcaly *et al.* employ ultra-broadband 2D ES spectroscopy in concert with MD simulations to explore different conformations adopted by Cy5 dyes that are commonly used to label DNA and found that these molecules undergo rapid structural fluctuations when bound to single-stranded DNA and DNA Holliday junctions but adopt a range of stable conformations that persist for upwards of hundreds of picoseconds when bound to double-stranded DNA.<sup>22</sup>

## VI. THEORETICAL DESCRIPTIONS OF 2D IR AND 2D ES MEASUREMENTS

While well-established theoretical frameworks exist for describing 2D IR and related spectroscopies, the development of novel theoretical descriptions remains crucial to attain more comprehensive, efficient, and precise descriptions of non-linear optical phenomena. Such advancements enable a deeper fundamental comprehension of observed signals and enhanced modeling capabilities, fostering innovation in experimental design and measurement accuracy while expanding the range of potential applications.

Reppert and Reppert have introduced a diagrammatic representation for 2D IR response functions of weakly anharmonic oscillators, demonstrating that classical and quantum response functions are identical in the weakly anharmonic limit, offering computational advantages for larger systems.<sup>23</sup> Brüggemann *et al.* present an efficient quantum-chemical protocol for predicting static 2D IR spectra without empirical parameters, demonstrating its applicability to various systems and higher-order spectroscopy while highlighting its potential for quantum parameterization.<sup>24</sup> Cina explores the dynamics of equilaterally shaped electronic excitation-transfer trimers, revealing interference phenomena, geometric phases, and stabilization effects, suggesting experimental observation strategies for these dynamic processes.<sup>25</sup> Wu and Xiong introduce a matrix-based approach for deriving non-vanishing tensor elements of physical properties in symmetric systems, demonstrating its validity across various scenarios, including high-order spectroscopy and magnetization.<sup>26</sup> Takahashi and Tanimura construct a model for bulk water, capturing vibrational dynamics and providing a rigorous numerical investigation of quantum dissipative dynamics, demonstrating its applicability through spectroscopic calculations.<sup>27</sup> Gera *et al.* present Dyadic Adaptive HOPS (DadHOPS), a method for calculating linear absorption spectra in large molecular aggregates with size-invariant scaling and the ability to incorporate static disorder, showcasing its effectiveness in complex molecular systems.<sup>28</sup>

## VII. THEORY AND MODELING OF 2D IR AND RELATED TECHNIQUES

Theory and modeling are essential for understanding the underlying principles of 2D IR spectroscopy and related techniques and interpreting experimental data. They can be used to design new experiments, to improve the accuracy of measurements, and to develop new applications for these techniques. For example, theoretical models can be used to calculate the vibrational frequencies of molecules, which can then be used to extract information on the solute-solvent interaction dynamics, spectral diffusion, vibrational excitation transfer, molecular photothermal effect, and chemical reactions from the experimentally measured spectra.

Cho demonstrates that utilizing a thermal diffusion equation and an approximate solution to describe how molecular photothermal effects in IR pump-probe and 2D IR spectroscopy can be used to analyze solute-solvent energy transfer processes and provide insights into mechanisms involved in converting vibrational energy to solvent kinetic energy in solutions.<sup>29</sup> Borkowski *et al.* introduce a method enabling the direct calculation of temperature derivative of 2D IR spectra, which was demonstrated by studying urea's concentration-dependent effects on isotopically dilute aqueous

solutions, revealing a greater sensitivity of temperature-dependent spectral changes to urea concentration and offering insights into various interactions within the system.<sup>30</sup> Considering 2D THz-IR-visible spectroscopy of DMSO, Seliya *et al.* introduce a method to extract accurate couplings between mid-IR frequency modes and low-frequency THz vibrations.<sup>31</sup> Utilizing classical molecular dynamics simulations and model interaction potentials, Töpfer *et al.* study the rovibrational spectra of N<sub>2</sub>O in Xe and SF<sub>6</sub> solvents, showcasing the ability of the 2D IR technique to describe solvent density-induced changes in solute behavior, providing insights into gas-to-liquid phase transitions.<sup>32</sup> Van Hengel *et al.* develop an approach for simulating 2D IR-Raman spectra of proteins by combining molecular dynamics simulations and a map-based Hamiltonian trajectory method.<sup>33</sup> Takahashi and Tanimura employ a multimode Brownian oscillator model and rigorous non-Markovian calculations to simulate complex 2D IR and fifth-order IR-IR-Raman-Raman spectra of bulk water, revealing intricate intermolecular and intramolecular anharmonic interactions among various vibrational modes.<sup>34</sup> Sertcan *et al.*, using DFT quantum chemistry calculation methods, investigate anharmonic couplings in the  $\beta$ -phase of crystalline bromoform, revealing the dominance of electrical anharmonicity in 2D THz Raman response, which confirms the connection between intermolecular and intramolecular mode couplings.<sup>35</sup> Overall, theory and modeling are undoubtedly essential tools for developing and applying 2D IR spectroscopy and related techniques. They have allowed us to understand how these techniques work, interpret experimental data, and design new experiments with specific goals.

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