FEMTOSECOND TRANSIENT ABSORPTION DATA ANALYSIS: 2D-CORRELATION SPECTROSCOPY PERSPECTIVE

Progress Report in Partial Fulfilment of the Requirements for the

Chemistry Minor Project (CHY 450)

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DECLARATION

I, **Manasi Vyahalikar (IMS21245)**, hereby declare that the progress report on the research work entitled **"Femtosecond Transient Absorption Data Analysis: 2D-Correlation Spectroscopy Perspective"** submitted to School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram, towards partial requirement for the Chemistry Minor Project (CHY 450) is an original work carried out by me under the supervision of **Dr. Adithya Lakshmanna**.

In keeping with the general practice of reporting scientific observations, due references have been made in the report. Any omission that might have occurred by oversight or error is regretted.

Thiruvananthapuram **Manasi Vyahalikar**

Date: 30th April, 2025 Signature

CERTIFICATE

This is to certify that the research work contained in this progress report entitled "**Femtosecond Transient Absorption Data Analysis: 2D-Correlation Spectroscopy Perspective**" submitted by **Manasi Vyahalikar (IMS21245)** to Indian Institute of Science Education and Research Thiruvananthapuram towards partial requirement for the Chemistry Minor Project (CHY 450) is an original work carried under my supervision and has not been submitted elsewhere for the award of any degree.

Thiruvananthapuram **Dr. Adithya Lakshmanna**

Date: 30th April, 2025 Signature (with date and official seal)

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RESEARCH ABSTRACT

Two-dimensional correlation spectroscopy (2D-COS) is a model-free analytical technique for investigating kinetic data without requiring prior assumptions about the system. In the context of ultrafast spectroscopy, 2D-COS facilitates the construction of correlation plots that reveal key characteristics of dynamic processes. As such, it serves as an effective preliminary tool for subsequent model-based approaches, such as global analysis. In this study, direct absorption spectra of dimethylamino stilbene in acetonitrile were utilized to generate synchronous and asynchronous 2D contour plots across various time windows. Asynchronous correlation spectra were computed using the Hilbert–Noda transformation, enabling a more detailed understanding of the underlying spectral dynamics.

RESEARCH OVERVIEW

Various analytical methods are employed to investigate the dynamics of a system and its constituent species, most of which rely on fitting kinetic models to experimental data. However, in many cases, the system is not well understood a priori, and extensive trial-and-error approaches can be time-consuming. To address this, two-dimensional correlation spectroscopy (2D-COS), a model-free technique, was introduced by Noda in 1986, with a generalized version proposed in 1993 [1]. 2D-COS analyzes the effect of external perturbations, such as temperature, pH, and concentration changes, on spectral data [13].

In systems where model assumptions are difficult to establish, 2D-COS provides a crucial starting point for model-based methods like global analysis [3]. Consequently, it has found wide applications across fields such as environmental science and nanomaterials. Moreover, it is compatible with various spectroscopic techniques, including IR, NMR, and UV spectroscopy [15].

In this work, 2D-COS was applied to correlate kinetic data (wavelength, time, and optical density values) obtained from time-resolved transient absorption spectroscopy. Correlation analysis reveals how two variables (here, OD values at different wavelengths) change simultaneously, enhancing spectral feature visualization [3], revealing relationships [2], and helping determine the sequential order of spectral events [4]. It can also be used the identify the band in the 1D spectra [14].

Synchronous and asynchronous 2D-COS plots were generated to distinguish concurrent (synchronous) from sequential (asynchronous) spectral changes [5]. A set of established rules was used for interpreting these correlations [6]. Recent advancements have introduced software tools compatible with MATLAB and Origin, enabling more intuitive visualization through contour maps [1]. A key advantage of 2D-COS is its ability to resolve highly overlapping spectral features by examining differential responses to perturbations [7]. Additionally, the spectral data can be mathematically represented using methods like least-squares curve fitting [6].

Contour plots (λ vs. λ) for various time windows were generated using Python in VSCode. The asynchronous matrices were calculated via the Hilbert–Noda transformation after mean-centering the data. These plots enable the visualization of subtle but significant spectral dynamics, offering insights at the molecular level [1].

RESULTS AND DISCUSSION

The goal was to analyze the time-resolved Transient Absorption Spectra data of dimethylaminostilbene (DAS) in ACN using 2D-COS. Using the dynamic changes in optical density (OD) over time, synchronous and asynchronous correlation data are extracted and plotted for different time windows. This allows for a deeper investigation into the temporal changes of the spectral dynamics. The plots obtained can be used to gain insights into the excited-state evolution and the dynamics.

1) 3D plot (OD vs Wavelength vs Time)

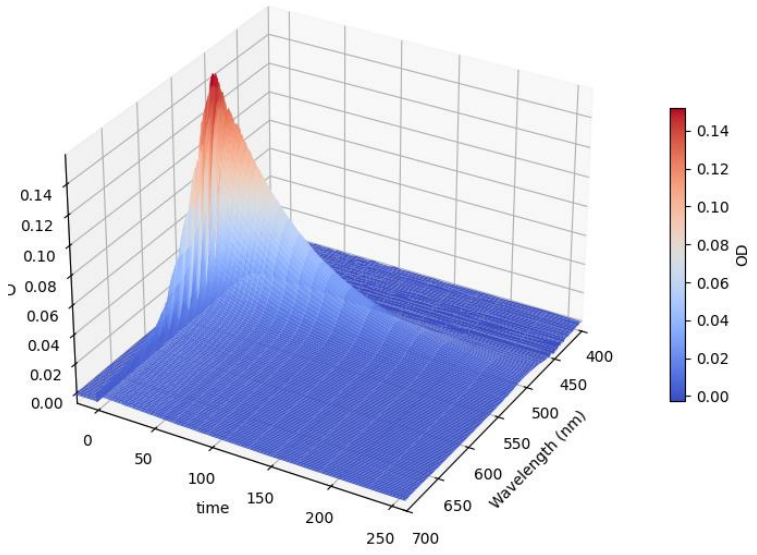


***Figure 1**. 3D plot of transient kinetic data*

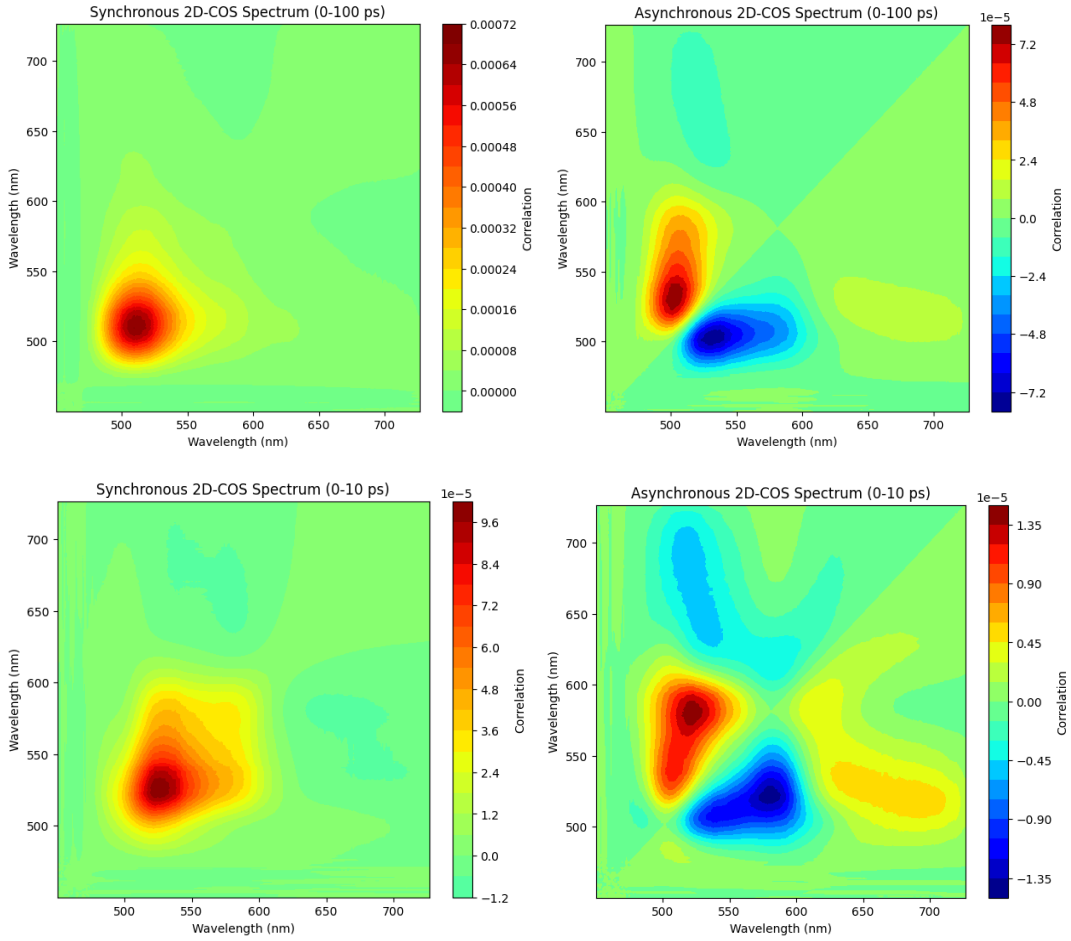
The surface plot obtained shows the intensity evolution across wavelengths and time. It was observed that the maximum absorbance (peak) is around 510nm. Hence, the 450-700nm range is used to plot the synchronous and asynchronous correlation data.

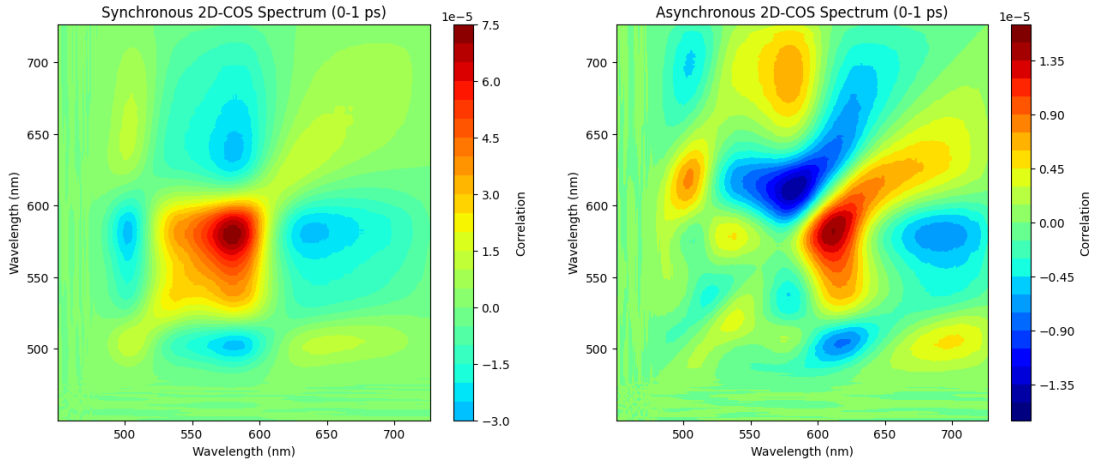
2) Contour Plots

The synchronous correlation map shows a strong autopeak along the diagonal. The autopeaks correspond to the autocorrelation function [3]. This indicated the most

responsive wavelengths. From Fig 2, it is observed that the correlation is positive around 500-600nm for synchronous spectra. This dictates the simultaneous intensity changes, suggesting coordinated behaviour.

The correlation intensity reveal tells us about the strength of the process [4].





a) *b)*

***Figure 2**. Contour maps of a) Synchronous Spectrum b) Asynchronous Spectrum obtained from 2D-COS*

- **Hilbert-Noda Transformation**

  It is used to generate the asynchronous data. In the asynchronous plot, higher intensity regions reveal that more than one process are in action [4].

3) Effect of Time Windowing

The evident spectral changes evolve over time by comparing the contour maps at different time windows. Only those ranges are considered where significant intensity can be observed. The rest of the data remains constant.

Time windowing can also be useful in identifying the number of processes describing the behaviour of the system. The different patterns in the synchronous plot for different time windows indicate the different processes taking place [4].

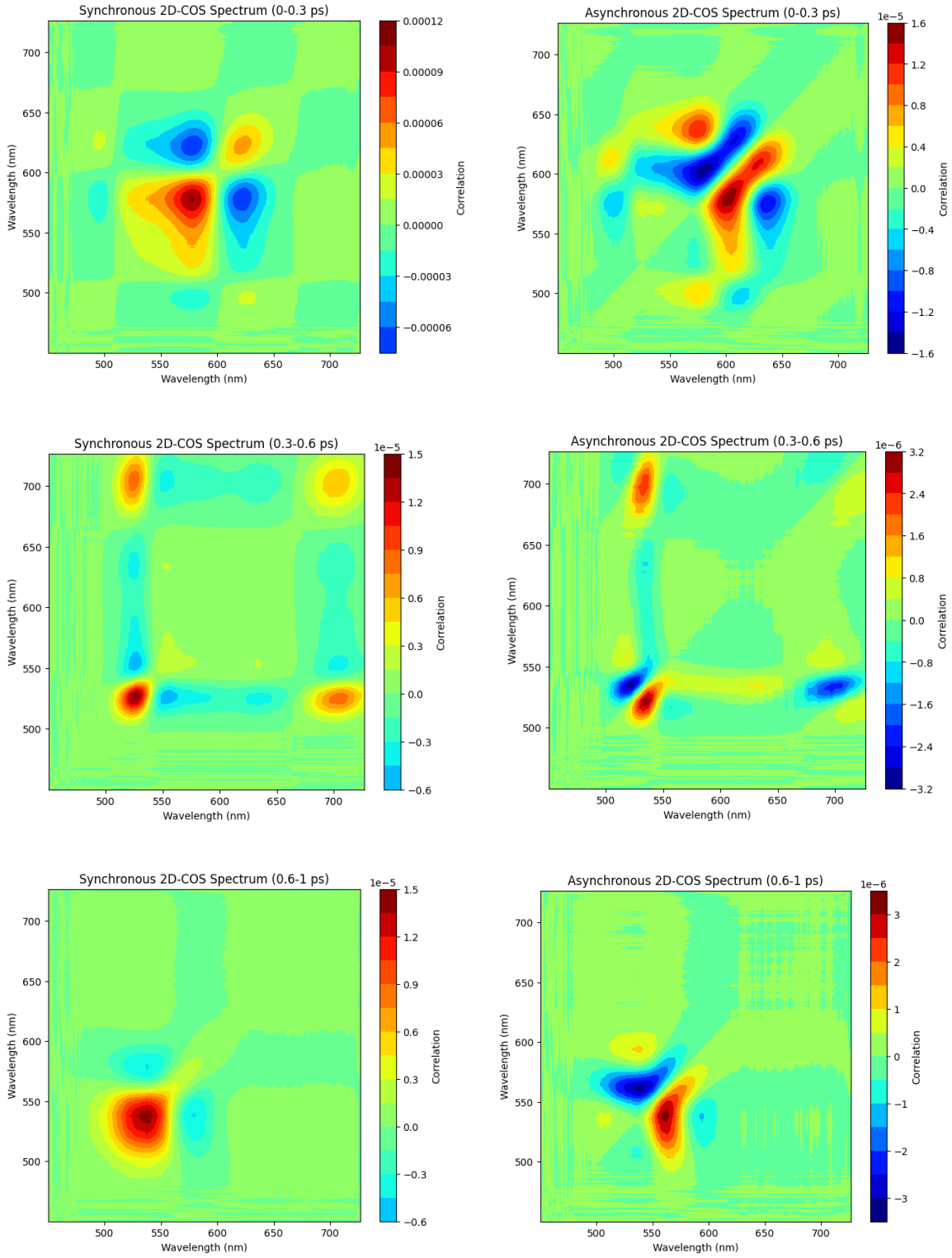


Figure 3. *Contour maps for various time windows*

The evolution of correlation across different time windows can be seen. We can observe that the spectra for various time windows look significantly different. Notably, the synchronous spectra for various time intervals exhibit significant differences, indicating

that distinct processes are active in each window. From this, we can deduce that multiple processes contribute to the overall spectral evolution in these time windows.

In the asynchronous spectra, the dominance of off-diagonal peaks is particularly evident. These off-diagonal features are characteristic indicators of sequential spectral changes, where different processes occur one after another rather than simultaneously. The presence and intensity of these peaks provide critical information about the time ordering of spectral events.

By analyzing the asynchronous spectra, it becomes possible to disentangle overlapping spectral features, which often pose a major challenge in complex systems. Specifically, sequential changes can be resolved, allowing the separation of contributions from different molecular species or reaction pathways.

- **0 – 0.3 ps**

  More rapid changes can be seen. Multiple cross-peaks are observed away from the diagonal, suggesting sequential changes in asynchronous spectrum.

- **0.3 – 0.6 ps**

  A strong correlation is observed at one point, and the less intense parts move far, indicating changes are taking place. In the asynchronous spectra, the two off-diagonal points remain, while the other two have moved, meaning the sequence of changes is there but slow in nature.

- **0.6 – 1 ps**

  A very strong correlation is observed at one point in synchronous spectra. The off-diagonal peaks in the asynchronous spectrum are present, but the intensity has been highly reduced, indicating that the rate of sequential change has slowed down.

EXPERIMENTAL/ THEORETICAL DETAILS

2D-COS is an analysis technique used to interpret the spectra under external perturbations like pressure, temperature, and time. It is a very powerful method, as it helps analyze the overlapping spectra by increasing the resolution of molecular dynamics. Hence, this method has been used here.

The Transient Absorption Spectroscopy is performed on DAS in ACN, and the data obtained is used. The data consists of wavelengths in the first row and time in the first column, with the corresponding OD values. A 3D plot of OD vs wavelength vs time was plotted. It is observed that the peak lies (maximum absorption) in the range 450-700 nm.

1. **Data Extraction**

   The data for various time windows is extracted in csv file format. By starting at a much larger range and then minimizing it, the plot for different time windows is obtained.

2. **Codes**

   The code was developed taking reference from [8].

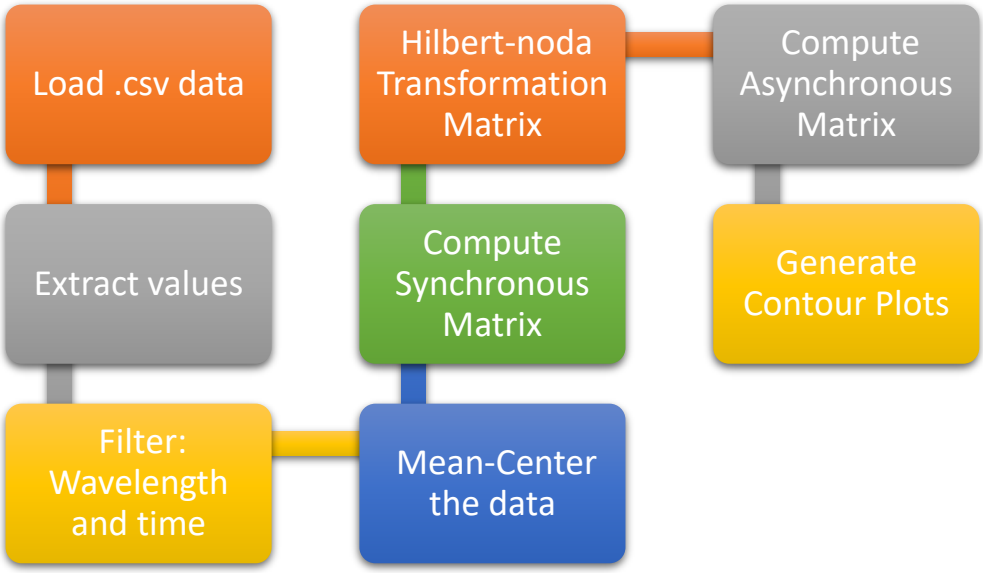


Figure 4. *Code Flowchart*

3. Mathematical Framework

Two sets of 2D spectra are produced: Synchronous (Φ) and Asynchronous (Ψ). Synchronous spectrum describes intensity changes occurring simultaneously between two wavelengths, while Asynchronous spectrum describes intensity changes happening out of phase, i.e., the phase changes from 0° to ±90° [9]. The OD values were mean-centered to plot the spectra. This ensures that we compare variations and not the absolute values.

The mean-centered values are given by [18]:

$$\mathrm{X}_{ij} = OD_{ij} - \frac{1}{N}\sum_{k=1}^{N} OD_{kj}$$

The synchronous matrix is calculated using the formula

$$\Phi = \frac{X^T X}{N-1}$$

where, N is the number of time points

The asynchronous matrix is calculated using the formula

$$\Psi = \frac{X^T H X}{N-1}$$

where H is the Hilbert-Noda Transformation matrix

Hilbert-Noda Transformation Matrix is a skew-symmetric matrix having zero as diagonal elements. For a function T(x), the Hilbert transform is given by [10].

$$\mathcal{H}[T(x)] = \frac{1}{\pi}\lim_{\varepsilon\to 0}\int_{|\xi|>\varepsilon} T(\xi - x)\,\frac{1}{x}\,dx$$

It is a convolution integral that can be solved by discretizing it into matrix form.

$$\mathcal{H}[T(x)] = \sum_{k=1}^{L} N_{jk}\cdot T(\xi_k), \quad j = 1,2,\dots,L$$

Computation of the discrete Hilbert transform provides a computational advantage over the Fast Fourier Transform (FFT). There is a mathematical equivalence between the Hilbert Transform and the Fourier Transform, which can be utilised to gain insights into the underlying properties of asynchronous spectra [11].

4. Interpretation

The synchronous spectra correspond to the covariance of the spectral variations. The diagonals give autocorrelation portions, where $\lambda_1 = \lambda_2$. These values are always positive. On the other hand, the off-diagonal peaks are called cross peaks, where $\lambda_1 \neq \lambda_2$. They reflect synchronized changes [2] and help characterize intermolecular interactions [16].

- The positive cross-peaks indicate that the intensity changes in the same direction for λ_1 and λ_2, i.e., they increase or decrease together.
- The negative cross-peaks indicate that the intensity changes in the opposite direction for λ_1 and λ_2.

The asynchronous spectra do not have autopeaks. Only cross-diagonal peaks can be observed, which are antisymmetric with respect to diagonal [12].

- The positive cross-peak indicates positive phase shift, i.e., variation in λ_1 occurs before λ_2.
- The negative cross-peak indicates that variation in λ_2 occurs before λ_1.

Furthermore, the use of covariance requires that variation in spectral response be either reasonably linear or non-linear. The synchronous correlation should be considered linear. Hence, it can be used to correlate the spectral bands [2].

5. Tools

The code was implemented using Python. Various Python libraries were used, such as Numpy, Scipy, Pandas, and Matplotlib. The contour plots were visualized using Visual Studio Code.

CONCLUSIONS

The 2D-COS has been adapted to decode the transient absorption spectral data of dimethylaminostilbene in acetonitrile solution, and analyze the spectral dynamics without depending on any a priori model. Global analysis are typically analyzed through model-based methods. By analyzing spectra at different time windows, we can gain insights into the timing and behavior of different species. However, some information between overlapping processes may be lost. In the future, improving and expanding the code could make 2D-COS an even more powerful tool to support kinetic analysis across various systems.

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