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Two-dimensional codistribution spectroscopy to determine the sequential order of distributed presence of species

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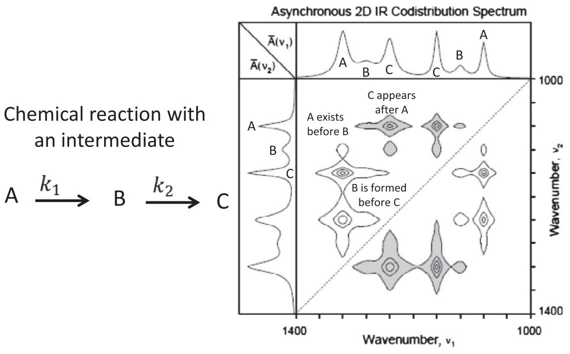
HIGHLIGHTS

- Two-dimensional (2D) codistribution spectroscopy for population dynamics of species.
- Determination of the sequential order of distributed presence of species.
- Different from the order of intensity variations analyzed by traditional 2D correlation.
- Moment analysis for the center of gravity and spread of distributions along the perturbation axis.

GRAPHICAL ABSTRACT



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ABSTRACT

Two-dimensional codistribution spectroscopy (2DCDS), a technique designed specifically for the analysis of population dynamics, such as temporal distributions of species during a chemical reaction, is described. 2D codistribution analysis focus on the signal features reflecting the distributed presence of species, instead of the variation patterns of perturbation-induced deviations from the reference state, which has been traditionally analyzed by two-dimensional correlation spectroscopy (2DCOS). This technique is derived from the moment analysis of spectral intensity distributions along the perturbation variable axis within a well-defined observation interval. Derivation and properties of 2D codistribution spectra are provided, and comparison is made to 2D correlation spectroscopy with the help of simulated IR spectra generated from model chemical reactions.

1. Introduction

Generalized two-dimensional (2D) correlation spectroscopy is a broadly applicable data analysis technique based on the cross-correlation of spectral intensity variations induced by an external perturbation, which is imposed on the system of interest [1–4]. The technique has gained popularity due to its versatility in selecting a number of analytical probes (e.g., IR, Raman and X-ray), perturbation methods (e.g., thermal, chemical, mechanical, and electrical) and type of samples to be analyzed [5–7]. Some well-recognized advantages of 2D correlation spectroscopy include the enhancement of apparent spectral resolution by spreading overlapped peaks along the second dimension and unambiguous band assignment assisted by the coordinated behavior of intensity variations among bands sharing similar molecular structural origins or environments.

One of the very unique features of 2D correlation analysis is its ability to determine the sequential order of spectral intensity variations within the well-defined observation period of the experiment by using a set of simple rules associated with the signs of correlation peaks [1,4]. This feature becomes especially useful in

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sorting out a complex set of perturbation-induced spectral intensity variations, which are often progressing more or less in parallel, to provide a clearer mechanistic insight into a number of phenomena encountered in physical, chemical and biological systems.

The sequential order rule is derived from a well-established mathematical consideration of time-series signal analysis [8,9]. The order of signal variations is assigned simply based on the determination of relative phases of the dominant Fourier components comprising the signals to be compared [10]. The underlying assumption in 2D correlation spectroscopy is that the spectral intensity variations of a system to be studied represent the specific responses to a commonly shared perturbation, which in turn should exhibit relatively similar distributions of the Fourier components in their waveforms by the constraint of the causal relationship. In other words, the waveforms of perturbation-induced intensity variations compared in a properly conducted 2D correlation spectroscopy experiment may not arbitrarily follow independent patterns.

Although the determination of the sequential order of spectral intensity variations along the perturbation variable is based on a solid mathematical theory, and this procedure seems to work consistently well in a number of reported studies, there exists some persistent misunderstanding about the type of information provided by 2D correlation spectroscopy. Most importantly, one should remember that 2D correlation provides the sequential order of intensity variations but does not directly tell the order of the distributed existence, i.e., population demographics, of specific species. The confusion seems to be especially common in the chemical kinetics studies, where sequential order of spectral intensity variations is erroneously equated with the order of the presence of specific species.

The primary goal of this article is to clarify the distinction between two types of sequential order information, i.e., variation vs. distributed presence. To this end a new type of data analysis tool called two-dimensional codistribution spectroscopy (2DCDS) is introduced, which is designed to directly provide the sequence of distributed presence of species along the perturbation variable axis. The technique can be used as a complementary tool to augment the deficiency of traditional two-dimensional correlation spectroscopy (2DCOS) in directly identifying the presence of intermediate species.

2. Background

2.1. 2D correlation spectroscopy

The theory of generalized 2D correlation spectroscopy has been well-established in the last 20 years [1,4]. Detailed background information concerning 2D correlation analysis, including the mathematical derivation and properties of correlation spectra and their applications, are described elsewhere [1–4,10]. In this section, only a very brief summary of the pertinent development, which will be used later for further discussion, is provided.

Suppose a discretely sampled set of spectra $A(\nu_j, t_k)$ is obtained for a system measured under the influence of an external perturbation, which induces changes in the observed spectral intensities. The spectral variable ν_j with $j = 1, 2, \ldots, n$ may be for example wavenumber, frequency, scattering angle, etc., and the other variable t_k with $k = 1,2,\ldots,m$ represents the effect of the applied perturbation, e.g., time, temperature, and electrical potential. Only the sequentially sampled spectral dataset obtained during the explicitly defined observation interval between t_1 and t_m will be used for the 2D correlation analysis. For simplicity, we use wavenumber and time to designate the two variables, but it is understood that use of other physical variables is equally valid.

Dynamic spectrum used in 2D correlation spectroscopy is explicitly defined as

$$\widetilde{A}(\nu_j, t_k) = \begin{cases} A(\nu_j, t_k) - \overline{A}(\nu_j) & \text{for } 1 \leqslant k \leqslant m \\ 0 & \text{otherwise} \end{cases} \tag{1}$$

where $\overline{A}(\nu_j)$ is the spectrum of the reference state of the system. In the absence of the a priori knowledge of the reference state, the reference spectrum is typically set as the time-averaged spectrum over the observation interval between t_1 and t_m.

$$\overline{A}(\nu_j) = \frac{1}{m}\sum_{k=1}^{m} A(\nu_j, t_k) \tag{2}$$

With this specific choice of the reference spectrum, the portion of dynamic spectra within the observation interval essentially becomes equivalent to the mean-centered spectra.Synchronous and asynchronous 2D correlation spectra, $\Phi(\nu_1, \nu_2)$ and $\Psi(\nu_1, \nu_2)$, are given by

$$\Phi(\nu_1, \nu_2) = \frac{1}{m-1}\sum_{j=1}^{m} \widetilde{A}(\nu_1, t_j) \cdot \widetilde{A}(\nu_2, t_j) \tag{3}$$

$$\Psi(\nu_1, \nu_2) = \frac{1}{m-1}\sum_{j=1}^{m} \widetilde{A}(\nu_1, t_j) \cdot \sum_{i=1}^{m} N_{ij}\widetilde{A}(\nu_2, t_i) \tag{4}$$

The term N_{ij} is the element of the so-called Hilbert–Noda transformation matrix given by

$$N_{ij} = \begin{cases} 0 & \text{if } i = j \\ \frac{1}{\pi(j-i)} & \text{otherwise} \end{cases} \tag{5}$$

Synchronous spectrum $\Phi(\nu_1, \nu_2)$ represents the coordinated or simultaneous changes of spectral intensities observed at two different wavenumbers, ν_1 and ν_2, along the perturbation variable t_k. The sign of the synchronous correlation intensity becomes positive if the spectral intensities measured at the two wavenumbers mostly change in the same direction, either increasing or decreasing. On the other hand, if one is increasing while the other is decreasing, the sign of $\Phi(\nu_1, \nu_2)$ becomes negative.

Asynchronous spectrum $\Psi(\nu_1, \nu_2)$ represents the out-of-phase or sequential changes of spectral intensities. If we have $\Psi(\nu_1, \nu_2) = 0$, the variations of spectral intensities at two wavenumbers, ν_1 and ν_2 are completely synchronized. If the signs of $\Phi(\nu_1, \nu_2)$ and $\Psi(\nu_1, \nu_2)$ are the same, the overall spectral intensity variation observed at ν_1 predominantly occurs prior to that at ν_2. If the signs are different, the order is reversed. Finally, if we have $\Phi(\nu_1, \nu_2) = 0$, the sequential order of intensity variations cannot be determined. It is important to emphasize that 2D correlation spectra only give the sequential order of spectral intensity variations but not the order of the distributed presence of species responsible for the spectral signals.

2.2. Binary one-step chemical reaction

We start with a simple demonstration of why the traditional 2D correlation spectroscopy may not be the best tool for the determination of the order of the distributed presence of different species. Let us consider a first-order one-step reaction system comprising only two components, the reactant **A** and product **B**. The reaction rate constant k_1 is set arbitrarily to 0.2 min^{-1}.

$$\mathbf{A} \xrightarrow{k_1} \mathbf{B} \quad k_1 = 0.2\ \text{min}^{-1}$$

Simulated IR spectra of pure **A** and **B** are given in Fig. 1a, and the set of mixture spectra representing the first 10 min of the reaction process are given in Fig. 1b. Isosbestic points characteristic of a binary reaction system are clearly observed for the spectra.