



Modified two-dimensional correlation spectra for streamlined determination of sequential order of intensity variations



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ABSTRACT

Modified forms of two-dimensional (2D) correlation spectra, i.e., sign-adjusted asynchronous spectrum and merged correlation spectrum, are discussed. They are developed for the streamlined determination of the sequential order of spectral intensity variations using only one 2D map by combining the pertinent information of synchronous and asynchronous spectra. Development of small side lobe artifacts near the peripheral of a cross peak is sometimes noted, especially for highly overlapped bands which are changing intensities in the opposite directions. The merit of the ease of interpretation afforded by the modification of correlation spectra probably outweighs the introduction minor artifacts, but some care certainly is required to avoid misinterpretation. Modified spectrum provides additional characteristic signature to the butterfly pattern cluster of cross peaks for the unambiguous identification of the presence of a band with position shift.

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1. Introduction

Two-dimensional correlation spectroscopy (2DCOS) has gained widespread popularity in the spectral analysis of various physical, chemical and biological systems under the influence of some form of external perturbations [1–4]. By spreading spectral peaks along the second dimension, apparent spectral resolution is often enhanced. Synchronous and asynchronous cross peaks are used to identify the presence or lack of coordinated spectral responses induced by the given perturbation. Because of the general and versatile applicability of the technique for many different types of sample systems under the influence of a variety of dynamic and static perturbations, which are also probed by diverse selection of spectroscopic probes, 2DCOS has become a part of the standard analytical tools for many researchers [5–7].

One of the interesting features of 2DCOS analysis is the ability to determine the sequential order of spectral intensity variations along the perturbation variable axis by simply examining the signs of cross peaks appearing on 2D spectral maps [1,4]. In other words, one can deduce which spectral band is changing its intensity in comparison to the others. The mathematical basis for such assertion arises from the nature of the complex cross correlation formalism derived from the classical time-series analysis [1,8,9].

This type of sequential order information turned out to be surprisingly useful in gaining rapid insight into mechanistic understanding of processes involving multiple stages of events which are often found in a number of real world systems.

Although the basic cross peak sign rules for determining the sequential order of intensity variations seem to be relatively simple, actual implementation is sometime tedious and prone to errors, especially if a large number of cross peaks must be examined from highly congested 2D correlation spectra. The goal of this note is to examine alternative approaches to the standard practice of sequential order determination by 2DCOS analysis to seek a more streamlined procedure. More specifically, sign-adjusted asynchronous spectrum, originally proposed by Czarnecki and coworkers [10–12], and a related idea called merged correlation spectrum are discussed with their utility, as well as limitations and potential issues.

2. 2DCOS and 2DCDS analyses

2.1. Dynamic spectra

It is helpful to briefly go over the standard practice of 2DCOS analysis first before discussing the possible alternative approaches to the procedure. 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

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spectral intensities. The spectral variable ν_j with $j=1, 2, \dots, n$ may be for example wavenumber, frequency, scattering angle, wave length, etc., and the other variable t_k with $k=1, 2, \dots, m$ represents the effect of the applied perturbation, e.g., time, temperature, concentration 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 should be understood that use of other physical variables is equally valid.

Dynamic spectra used in 2D correlation spectroscopy are explicitly defined as

$$\tilde{A}(\nu_j, t_k) = \begin{cases} A(\nu_j, t_k) - \bar{A}(\nu_j) & \text{for } 1 \leq k \leq m \\ 0 & \text{otherwise} \end{cases} \quad (1)$$

where $\bar{A}(\nu_j)$ is the spectrum of the reference state of the system [4]. In the absence of the a priori knowledge of the reference state, the reference spectrum is often taken as the averaged spectrum over the observation interval between t_1 and t_m .

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

With this specific choice of the reference spectrum, the portion of dynamic spectra within the observation interval essentially becomes equivalent to the mean-centered spectrum.

To assist further discussion, a set of eleven ($m=11$) simulated time-dependent IR spectra observed every minute for the duration of 10 min ($t_1=0$ and $t_{11}=10$) are created as an illustrative model and shown in Fig. 1a. Each spectrum of the set consists of four distinct absorption peaks with evolving intensities, designated respectively as A, B, C, and D, located around 1490, 1470, 1460 and 1450 cm^{-1} . Pseudo-random noise of about 0.1% is also injected into each trace. The evolution of the peak maximum intensities along the time axis during the observation interval is shown in Fig. 1b. The reference spectrum (Fig. 1c) taken as the time average according to Eq. (2), and resulting dynamic spectra are shown in Fig. 1d.

2.2. Synchronous 2D correlation spectrum

Synchronous 2D correlation intensities in terms of dynamic spectra is given by

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

If the reference spectrum is chosen as the average spectrum over the observation interval, and spectral traces are sampled evenly at a fixed increment, synchronous correlation intensity becomes essentially the same as the covariance of spectral intensity changes induced by the applied perturbation.

The map of correlation intensity $\Phi(\nu_1, \nu_2)$ as a function of two independent wavenumber axes ν_1 and ν_2 is the synchronous 2D correlation spectrum, which is a symmetric plot consisting of auto-peaks located at the main diagonal position (i.e., $\nu_1=\nu_2$) and cross peaks located at off-diagonal positions. The intensity of an auto-peak corresponds to the extent of spectral intensity variations of the band induced by the applied perturbation. Thus, if the spectral intensity is greatly affected by the perturbation, the corresponding auto-peak becomes strong and more contour lines appear. In contrast, an auto-peak becomes weak with less contour line if the band intensity is less affected by the perturbation.

Cross peaks of synchronous 2D spectrum located at the off-diagonal positions represent the coordinated or simultaneous

changes of spectral intensities observed at two different wavenumbers, ν_1 and ν_2 . The sign of a synchronous cross peak becomes positive if the spectral intensities measured at the two wavenumbers change mostly in the same direction along the perturbation variable t_k , 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. The latter case is useful in identifying the different origins of even highly overlapped spectral bands.

Fig. 2a shows the synchronous 2D IR spectrum constructed for the simulated dynamic spectra of Fig. 1d. This plot and subsequent 2D spectra were all generated with a homebuilt software. Different intensities of auto-peaks at the main diagonal indicate that the magnitudes of spectral signal changes during the observation period are ranked in the decreasing order of: D>A>C>B. In other words, the spectral intensity for the band D changes the most, while that for B changes the least. Signs of the cross peaks are consistent with the overall relative directions of spectral intensity changes. For example, the positive cross peak at (1490, 1450) indicates that intensities for A and D are changing in the same direction, i.e., both decreasing, while the negative peak at (1470, 1460) indicates that band B is decreasing but band C is increasing. Interpretation of a synchronous spectrum is usually very much straightforward.

Cross peaks are typically observed in a synchronous correlation spectrum for every band pairs even if patterns of spectral intensity changes are not completely matched and behaving slightly asynchronously. Some synchronous correlation intensity is usually observed as long as the spectral intensities at corresponding wavenumbers are changing, which is indeed the case for this model system. For example, although Fig. 1b shows that bands A and B have clearly different variation patterns of spectral intensities, a positive cross peak is still observed at (1490, 1470). In short, mere presence of a synchronous cross peak by itself does not guarantee the complete synchronization of spectral intensity variations.

2.3. Asynchronous 2D correlation spectrum

Asynchronous 2D correlation intensity is given by

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

The term N_{ij} is the element of the so-called Hilbert-Noda transformation matrix [2] given by

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

The map of correlation intensity $\Psi(\nu_1, \nu_2)$ becomes the asynchronous 2D correlation spectrum.

Asynchronous correlation intensity represents the out-of-phase or sequential changes of spectral intensities measured at two different wavenumbers. It is possible to determine the sequential order of spectral intensity changes by observing the signs of cross peaks appearing on 2D correlation spectra [1,4]. The so-called Noda's rules of sequential order dictate that 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. If we have the condition of $\Psi(\nu_1, \nu_2)=0$, the variations of spectral intensities at two wavenumbers, ν_1 and ν_2 are completely synchronized. Finally, if we have a rare but possible situation such that $\Phi(\nu_1, \nu_2)=0$, the sequential order of intensity variations cannot be determined. It should be pointed out as a caution that some very weak cross peaks may not

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