

# Two-dimensional infrared correlation spectroscopy: Global phase angles for specific analytical systems

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## Abstract

In this paper we discuss further properties of 2D correlation spectroscopy using the global phase angle intensity normalization method. The 2D global phase angle analysis method has been shown to discriminate against arbitrary signal amplitude changes not related to real correlation intensities. We have confirmed that the positive or negative sign of a global phase angle 2D correlation peak is a direct expression of the sequential order of signal intensity changes. We have derived analytical solutions for 2D correlation algorithms using the global phase angle based on sinusoidal, exponential decay, and Lorentzian model functions. These derivations show that the experimental determination of the global phase angle can provide a quantitative measurement of sequential order when using these specific analytical models.

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## 1. Introduction

The concept of generalized two-dimensional (2D) correlation spectroscopy has previously been described [1–7]. Using this method, one can systematically analyze complex spectral signal variations in infrared, Raman, ultraviolet–visible, or other optical spectra having different waveforms [8–13]. The advantages of the general 2D method can be summarized as: (i) identification of various inter- and intramolecular interactions through selective correlation of bands; (ii) examination as to which spectral responses are in-phase and which are out-of-phase relative to one another; and (iii) assignment of bands based on their correlation response.

While generalized 2D correlation spectroscopy has many advantages, interpretation of 2D correlation spectra can be far from straightforward. This is because spectral intensity variations within a dynamic data set can have different amplitudes, which give complicated generalized 2D

correlation maps. This leads to the situation in which the positions and the signs (positive or negative) of the 2D correlation peaks can be accurately determined and used in molecular interpretation, but where the intensity values of the 2D correlation peaks may have no physical meaning.

In order to overcome this limitation, a practical 2D correlation method using a global phase angle intensity normalization procedure (i.e. a global 2D phase map) has been proposed [14]. The use of a 2D global phase angle correlation method enables researchers to discriminate against arbitrary signal amplitude changes that are not related to physically meaningful correlation peaks. In addition, the global phase angle method effectively incorporates a filtering algorithm based on the standard deviation spectrum that removes the effects of small amplitude noise. The global 2D phase mapping analysis has been applied to experimental data [15–17]. For instance, temperature-dependent infrared spectra of an electrically conductive Langmuir–Blodgett film have been studied using the global 2D phase mapping analysis to examine overlapping, shifting, and broadening features of absorption components in the CH<sub>2</sub> symmetric stretching band region [17].

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Our objective in this paper is to discuss further properties of generalized 2D correlation spectroscopy, especially: (i) the use of the 2D global phase angle analysis method as it relates to determining the sequential order of signal intensity changes, and (ii) the derivation of analytical solutions for 2D correlation methods using the global phase angle based on sinusoidal, exponential decaying, and Lorentzian model functions. We have found that the positive or negative sign of a 2D global phase angle correlation peak is a direct indicator of the sequential order of signal changes, and we have confirmed that the use of the global phase angle provides a quantitative measurement of sequential order for specific analytical systems. The results reported here will enable us to broaden the quantitative aspects of the generalized 2D correlation spectroscopy method.

## 2. Background

The calculation of the global 2D phase mapping intensity normalization method was proposed in previous publications, based on the theoretical framework of synchronous and asynchronous correlation functions [1–7,14].

Briefly described, two-dimensional correlation analysis using global phase mapping begins with a set of dynamically varying spectra. We assume a series of spectra measured as a function of variable  $t$ , i.e.  $y(v, t)$ . The variable  $t$  is referred to as “time” for convenience, although the parameter  $t$  can be any reasonable measurement of a physical quantity, e.g., temperature, pressure, concentration, etc., including chronological time. The parameter  $v$  is usually a proper spectral variable (e.g., wavenumber, wavelength, Raman shift, etc.). In addition, we assume that  $y(v, t)$  is observed in the period of  $T$  ( $T: T_{\min} \leq t \leq T_{\max}$ ). The dynamic spectra of  $y(v, t)$ , denoted as  $\tilde{y}(v, t)$ , are then given by

$$\tilde{y}(v, t) = \begin{cases} y(v, t) - \bar{y}(v) & \text{for } T, \\ 0 & \text{otherwise,} \end{cases} \quad (1)$$

where  $\bar{y}(v)$  is a reference spectrum, which corresponds to the static, non-varying component of  $y(v, t)$ . The selection of  $\bar{y}(v)$  is arbitrary, but the reference spectrum is usually defined as in the following equation:

$$\bar{y}(v, t) = \frac{1}{T} \int_T y(v, t) dt. \quad (2)$$

The synchronous 2D correlation spectrum  $\Phi(v_1, v_2)$ , and the asynchronous 2D correlation spectrum  $\Psi(v_1, v_2)$ , are defined in the following equation:

$$\Phi(v_1, v_2) + i\Psi(v_1, v_2) = \frac{1}{\pi T} \int_0^\infty \tilde{Y}_1(\omega) \tilde{Y}_2^*(\omega) d\omega. \quad (3)$$

In this expression  $\tilde{Y}_1(\omega)$  and  $\tilde{Y}_2^*(\omega)$  are the Fourier transforms to the frequency ( $\omega$ ) domain, calculated from the dynamic components of  $y(v_1, t)$  and  $y(v_2, t)$ , i.e.

$$\tilde{Y}_1(\omega) = \int_{-\infty}^\infty \tilde{y}(v_1, t) e^{-i\omega t} dt, \quad (4)$$

$$\tilde{Y}_2^*(\omega) = \int_{-\infty}^\infty \tilde{y}(v_2, t) e^{+i\omega t} dt. \quad (5)$$

Here, we recognize that  $\tilde{Y}_1(\omega)$  and  $\tilde{Y}_2^*(\omega)$  are the conjugates of one another. The global phase angle is simply given by

$$\Theta(v_1, v_2) = \arctan \frac{\Psi(v_1, v_2)}{\Phi(v_1, v_2)}. \quad (6)$$

Eq. (6) indicates that the calculation of the global phase angle automatically cancels the information about the amplitudes of signal intensity changes in  $y(v_1, t)$  and  $y(v_2, t)$ . The “amplitudes” are the values that can be obtained by calculating the standard deviation of the signal intensity changes.

The global phase angle does not provide any concrete physical meaning beyond a mathematical projection; however, it does serve as a convenient correlation index that is invariant to changes in signal amplitudes. A signal filtering method to mask the amplified noises in the baseline region was proposed in the general use of the global phase map [7,14], however, we do not include a discussion of this filtering method in the current study.

## 3. Further properties of the global phase angle

### 3.1. Direct expression of sequential order of signal intensity changes

The positive or negative sign of the global phase angle can be utilized as a direct expression to determine the sequential order of signal intensity profiles. The rule to determine the sequential order was given in the generalized 2D method [1,2], which is simplified by the global phase angle as follows:

- (i) If  $\Theta(v_1, v_2) > 0$ ,  $y(v_1, t) \rightarrow y(v_2, t)$ : if the sign of the global phase angle becomes *positive*, the intensity change at  $v_1$  occurs predominantly *before* that at  $v_2$ .
- (ii) If  $\Theta(v_1, v_2) < 0$ ,  $y(v_1, t) \leftarrow y(v_2, t)$ : if the sign of the global phase angle becomes *negative*, the intensity change at  $v_1$  occurs *after* that at  $v_2$ .

While the determination of the sequential order of signal intensity changes is one of the most remarkable features of the generalized 2D correlation analysis, there are a few exceptions [7]. For instance, the rules cannot be applied to the signal intensity changes with extremely different waveforms.

### 3.2. Analytical solutions for sinusoidal, exponential decay, and Lorentzian functions

In this section, analytical solutions that can be applied to 2D correlation analysis using the global phase angle

normalization procedure are derived, corresponding to sinusoidal, exponential decay, and Lorentzian model functions. The selected three waveforms are frequently utilized as model functions to simulate signal intensity changes that accompany physical or chemical phenomena. For instance, sinusoidal functions are used to express the responses that undergo a repetitive external perturbation. In addition, exponentially decaying curves can be seen in the chemical kinetics monitored by spectroscopy. Also, a time-domain Lorentzian type waveform can be a proper model function response for chromatographs equipped with a spectroscopic detector.

To simplify the analytical expressions, several variable substitutions will be made in this section. For example, the expressions  $y(v_1, t)$ ,  $y(v_2, t)$ ,  $\Phi(v_1, v_2)$ ,  $\Psi(v_1, v_2)$ , and  $\Theta(v_1, v_2)$  will be simplified to  $f(t)$ ,  $g(t)$ ,  $\Phi_{fg}$ ,  $\Psi_{fg}$ , and  $\Theta_{fg}$ , respectively.

### 3.2.1. Sinusoidal functions

Let us suppose such a sinusoidal intensity change  $f(t)$  that is observed in the period of  $T$  ( $T: -\infty \leq t \leq +\infty$ ). The dynamic component of  $f(t)$  is given by

$$\tilde{f}(t) = A_f \cos(\Omega t + \beta_f), \quad (7)$$

where  $A_f$  determines the amplitude of the sinusoidal intensity change and  $\beta_f$  is the phase of the sinusoidal function with the frequency  $\Omega$ . The global phase angle  $\Theta_{fg}$  corresponding to the synchronous  $\Phi_{fg}$  and asynchronous  $\Psi_{fg}$  values of the sinusoidal functions of  $f(t)$  and  $g(t)$  [4,7] is given by

$$\Phi_{fg} = \frac{A_f A_g}{2} \cos(\beta_f - \beta_g), \quad (8)$$

$$\Psi_{fg} = \frac{A_f A_g}{2} \sin(\beta_f - \beta_g), \quad (9)$$

$$\Theta_{fg} = \beta_f - \beta_g. \quad (10)$$

### 3.2.2. Exponential decay functions

An exponential decay intensity profile  $f(t)$  is assumed to be observed in the period of  $T$  ( $T: 0 \leq t \leq +\infty$ ). The dynamic component is expressed as

$$\tilde{f}(t) = A_f \exp(-k_f t), \quad (11)$$

where  $A_f$  and  $k_f$  correspond to the  $f(t)$  value at  $t = 0$  and the rate constant of the exponentially decaying process, respectively. The signal amplitude is determined by the parameter  $A_f$ . For exponential functions  $f(t)$  and  $g(t)$ , the synchronous  $\Phi_{fg}$  and asynchronous  $\Psi_{fg}$  values [4,7], and the global phase angle  $\Theta_{fg}$  are given by

$$\Phi_{fg} = \frac{A_f A_g}{T} \cdot \frac{1}{k_f + k_g}, \quad (12)$$

$$\Psi_{fg} = \frac{A_f A_g}{\pi T} \cdot \frac{\ln(k_f/k_g)}{k_f + k_g}, \quad (13)$$

$$\Theta_{fg} = \arctan \frac{\ln(k_f/k_g)}{\pi}. \quad (14)$$

### 3.2.3. Lorentzian type functions

A Lorentzian-shaped profile  $f(t)$  is assumed to be observed in the period of  $T$  ( $T: -\infty \leq t \leq +\infty$ ). The dynamic component is expressed as

$$\tilde{f}(t) = \frac{A_f}{1 + (t - \tau_f)^2}, \quad (15)$$

where  $A_f$  and  $\tau_f$  are the peak value and the peak position of the Lorentzian function, respectively. In this simplified model, we have fixed the bandwidth of the Lorentzian function such that the half-width at half-height equals one, however, the function can be generalized. The signal amplitude is determined by  $A_f$ . The synchronous  $\Phi_{fg}$  and asynchronous  $\Psi_{fg}$  values [4,7], and the global phase angle  $\Theta_{fg}$  corresponding to Lorentzian functions  $f(t)$  and  $g(t)$  are given by

$$\Phi_{fg} = \frac{\pi A_f A_g}{T} \cdot \frac{2}{4 + (\tau_g - \tau_f)^2}, \quad (16)$$

$$\Psi_{fg} = \frac{\pi A_f A_g}{T} \cdot \frac{\tau_g - \tau_f}{4 + (\tau_g - \tau_f)^2}, \quad (17)$$

$$\Theta_{fg} = \arctan \frac{\tau_g - \tau_f}{2}. \quad (18)$$

### 3.3. Common feature among the analytical solutions

For each specific analytical case, the global phase angle is related only to the target parameters (i.e.,  $\beta_f$ ,  $\beta_g$  for sinusoidal,  $k_f$ ,  $k_g$  for exponential, and  $\tau_f$ ,  $\tau_g$  for Lorentzian functions), and not influenced by the signal amplitude information caused by the parameters of  $A_f$  and  $A_g$ . This feature indicates that determination of the global phase angle in actual spectroscopic measurements will allow us to estimate the quantitative relation of the target parameters (i.e.,  $\beta_f - \beta_g$ ,  $k_f/k_g$ , and  $\tau_g - \tau_f$ ).

## 4. Summary

We have discussed further properties of the global phase angle normalization procedure as it applies to generalized 2D correlation analysis. The properties of the global phase angle method can be categorized as follows.

- (i) In general, the global phase angle serves as a semi-quantitative correlation index. The global phase angle serves as a universal correlation index invariant to signal amplitude information with the ability to determine the sequential order of signal intensity changes. However, it does not itself have any concrete physical meaning such as a fixed time delay in sinusoidal systems (Sections 2 and 3.1).
- (ii) Under certain circumstances, the global phase angle can become a fully quantitative correlation index. This happens in the specific cases where analytical solutions to the global phase angle function exist. Such solutions exist for model functions that simulate

a series of experimentally measured spectroscopic data. In general, the global phase angle can be considered a quantitative correlation index when the target parameters of the model function can be estimated quantitatively (Sections 3.2 and 3.3).

The quantitative applications of the generalized 2D correlation spectroscopy method that have been reported to date are limited by the lack of an objective, external standard. The relative nature of these analyses originates from the model-free approach utilized by the generalized 2D correlation analysis method; that is, the general 2D method calculates correlation intensities independently of a defined external model.

We are currently working on methods to eliminate the relative nature of the current quantitative analysis methods used in generalized 2D correlation spectroscopy. Previously, our research group has proposed modified, model-based approaches to extend the techniques of 2D infrared correlation spectroscopy. These new model-based techniques incorporated correlations using sinusoidal and exponential functions [18,19]. At present, we are in the process of extending these model-based approaches so that they can be applied to a generalized system. A generalized model-based approach to 2D correlation spectroscopy will hopefully provide a means to quantitatively analysis spectral response in a dynamic data set.

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