Journal of Molecular Structure 1124 (2016) 53–60

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Two-dimensional correlation spectroscopy (2DCOS) analysis of polynomials

Isao Noda

Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716, USA

ARTICLE INFO

Article history:
Received 13 December 2015
Received in revised form
28 January 2016
Accepted 29 January 2016
Available online 3 February 2016

Keywords:
Two-dimensional correlation spectroscopy
2DCOS
Polynomials
Curve fitting

ABSTRACT

2DCOS analysis of dynamic spectra, which can be approximated in the form of a polynomial function by the least squares curve fitting method, is carried out. Curve fitting provides a practical way of condensing a large spectral dataset in terms of a small number of fitting parameters and filtering out noise and superfluous spectral intensity variations from the raw spectra. Pertinent features of the findings are illustrated by using a simple simulated spectral data subjected to curve fitting with polynomials. Closed-form analytical expressions for 2D correlation spectra are obtained from the polynomial functions used for the curve fitting and their Hilbert transform counterpart. Such analytical expressions provide useful insight into the inner working of 2DCOS analysis, especially the role of slope and curvature of spectral intensity variations, in determining the signs of cross peaks used in the interpretation of 2D spectra.

1. Introduction

The basic methodology of generalized two-dimensional correlation spectroscopy (2DCOS) is well established today [1–4]. Dynamic spectra, i.e., spectral intensity variations induced in response to an external perturbation applied to the system, are examined with the aid of complex cross correlation analysis to generate 2D maps defined by two independent spectral axes. It is often pointed out that apparent spectral resolution is substantially enhanced by spreading peaks along the second dimension. Furthermore, seemingly convoluted spectral intensity variations are effectively sorted out by using 2D correlation spectra. Synchronous 2D correlation spectrum characterizes the coordinated or simultaneous responses, and asynchronous spectrum reveals sequential or out of phase nature of certain responses. A simple set of rules based on the signs of cross peaks are used to interpret the responses of system constituents to the perturbation.

Efficient numerical computational method makes it straightforward to obtain 2D correlation spectra from practical dynamic spectra in the form of discretely sampled and digitized spectral dataset [2,3]. The ease of generating 2D correlation spectra, along with the general applicability of the technique to a very broad field of science with various spectroscopic probes, perturbation methods, and sample systems, has made 2DCOS a very popular data analysis tool [5–7]. Rigorous treatment of underlying mathematical concept behind 2DCOS analysis, based on the classical theory of time-series complex cross correlation using the Fourier transform description of spectral intensity variations, is also available [1,8,9]. However, somewhat more intuitively understandable description of 2DCOS concept is always desired.

2DCOS analysis of spectral intensity variations, which can be adequately described in terms of polynomial functions, is explored here. A simple least squares curve fitting method, for example, will generate such a dataset based on polynomials from the raw spectral data. Purpose of the 2DCOS analysis of polynomials is twofold. Firstly, the fidelity of replicating 2D correlation spectra must be examined when a model polynomial function instead the actual spectra is used. In the accompanying paper appearing in this issue [10], it is demonstrated that even a simple representation of dynamic spectra in terms of a quadratic polynomial can adequately capture most of the pertinent feature of original spectral data to generate useful 2D correlation spectra. The merit of condensing a large spectral dataset in terms of a smaller number of fitting parameters is obvious. It is further expected that the properly conducted least squares curve fitting operation should have an overall positive effect by removing the noise and other superfluous contributions, such as baseline fluctuations, from the original spectra. Here the polynomial reconstruction of raw spectral data may be viewed simply as the data pretreatment prior to the 2DCOS analysis.

The second motivation behind this work is to obtain the explicit

---

E-mail address: noda@udel.edu.

http://dx.doi.org/10.1016/j.molstruc.2016.01.091
0022-2860/

closed-form analytical expressions for 2D correlation spectra based on the polynomials. In the past, explicit analytical solutions were derived for spectral intensity variations having the waveforms of sinusoids, exponential decays, and Lorentzian distributions [1,4]. Solutions to polynomials will be a useful addition to the list. Once the analytical solutions are obtained in terms of a small set of model parameters used in the polynomial fit, it is hoped to provide valuable insight into the inner workings of how 2DCOS analysis really operates. More specifically, how patterns of intensity variations defined by a set of parameters can be compared to each other to support the rules commonly used in interpreting 2D correlation spectra.

2. Model system

To illustrate the efficacy of the 2DCOS analysis based on polynomial fitting, a simple simulation model system is considered. Two parallel and independent first order reactions are assumed with the rate constants of 0.2 and 0.1 min^{-1}.

Faster reaction : $A \rightarrow D \quad k_1 = 0.2\ \text{min}^{-1}$ (Scheme 1)

Slower reaction : $C \rightarrow B \quad k_2 = 0.1\ \text{min}^{-1}$ (Scheme 2)

Species A, B, C and D, respectively, have their corresponding characteristic absorption bands at 1800, 1600, 1400 and 1200 cm^{-1}, each having a Lorentzian band profile with the half width at the half height of 33 cm^{-1}. The evolution of the band intensities are then observed for the initial 10 min. The resulting simulated spectra are shown in Fig. 1a. Peak intensities of individual bands shown in Fig. 1b follow the expected first order reaction profiles of $e^{-k_1 t}$, $1 - e^{-k_2 t}$, $e^{-k_2 t}$, and $1 - e^{-k_1 t}$.

2D correlation spectra of the model reaction system are shown in Fig. 1c and d. They are calculated by the well-established numerical method [2]. Average spectrum is provided at the top and side of each 2DCOS map as the reference. Synchronous spectrum (Fig. 1c) depicts the intensity variations of the four bands associated with the species and relationships between the decrease in the reactants A and C and increase in the products B and D. The difference in the reaction rates is clearly manifested in the development of asynchronous cross peaks in Fig. 1d. Spectral intensity variations of species A and D occur earlier during the observation interval compared to those of B and C. The consumption of reactant and generation of product for each reaction scheme are completely synchronized, such that no asynchronous cross peak is observed between A and D bands or B and C. The results deduced from the 2DCOS analysis are consistent with the premise of the simulated reaction model.

3. Continuous dynamic spectra and reduced perturbation variable

3.1. Reference and dynamic spectra

2DCOS analysis nowadays is carried out almost exclusively with digitally stored spectral data sampled discretely. Numerical computation of 2D correlation spectra using a well-established algorithm based on the discrete Hilbert transform method is a standard practice in the field. However, it is sometimes useful to go back to the early notations based on using continuous functions for 2DCOS analysis [1]. This situation is especially true for the detailed mathematical analysis when explicit closed-form analytical expressions are conveniently available. Such was indeed the case for 2D correlation study of time-dependent IR dichroism signals induced in a polymer film by sinusoidal dynamic deformation [11–13].

Consider a set of spectra $A(\nu,t)$ with the spectral variable ν measured under the influence of an external perturbation represented by the variable t. The spectral variable can be wavenumber, frequency, wave length, etc., and the perturbation variable can be temperature, time, concentration, etc. They will be referred to, respectively, as wavenumber and time here for convenience. The 2D correlation analysis of $A(\nu,t)$ is carried out within an explicitly determined observation interval between t_{min} and t_{max}.

Dynamic spectra are given by

$$\tilde{A}(\nu,\ t) = \begin{cases} A(\nu,\ t) - \overline{A}(\nu) & \text{for } t_{min} \le t \le t_{max} \\ 0 & \text{otherwise} \end{cases} \tag{1}$$

with the reference spectrum $\overline{A}(\nu)$, which is taken as the time average spectrum

$$\overline{A}(\nu) = \frac{1}{t_{max} - t_{min}} \int_{t_{min}}^{t_{max}} A(\nu,\ t)dt \tag{2}$$

Dynamic spectra are viewed as the manifestation of the deviation from the reference state induced by the imposed perturbation. For time t outside of the observation interval, the actual value of $A(\nu, t)$ may or may not be known. In contrast, because of the mathematical consistency required for the correlation analysis, the value of $\tilde{A}(\nu,\ t)$ is set explicitly to zero outside of the observation interval.

3.2. 2D correlation spectra

We now introduce the dimensionless reduced perturbation variable $\theta(t)$ as

$$\theta(t) = \frac{t - \frac{(t_{max}+t_{min})}{2}}{t_{max} - t_{min}} \tag{3}$$

to replace the original perturbation variable t. This simple transformation of variable makes the rest of the mathematical treatment straightforward. The observation interval in terms of θ is now bound between -1 and 1, and Eq. (1) is rewritten as

$$\tilde{A}(\nu,\ \theta) = \begin{cases} A(\nu,\ \theta) - \overline{A}(\nu) & \text{for} -1 \le \theta \le 1 \\ 0 & \text{otherwise} \end{cases} \tag{4}$$

Choosing the time average as the reference spectrum in Eq. (2) leads to the constraint to the dynamic spectra as

$$\int_{-1}^{1} \tilde{A}(\nu,\ \theta)d\theta = 0 \tag{5}$$

which becomes useful later.

Combining the previously derived results for the generalized 2DCOS [1,2] with this newly introduced reduced variable, synchronous and asynchronous 2D correlation spectra $\Phi(\nu_1,\nu_2)$ and $\Psi(\nu_1,\nu_2)$ for the dynamic spectra are obtained as

$$\Phi(\nu_1,\nu_2) = \frac{1}{2} \int_{-1}^{1} \tilde{A}(\nu_1,\ \theta)\cdot\tilde{A}(\nu_2,\ \theta)d\theta \tag{6}$$

$$\Psi(\nu_1,\nu_2) = \frac{1}{2} \int_{-1}^{1} \tilde{A}(\nu_1,\ \theta)\cdot\tilde{H}(\nu_2,\ \theta)d\theta \tag{7}$$

and $\tilde{H}(\nu_2,\ \theta)$ is the Hilbert transform of $\tilde{A}(\nu_2,\ \theta)$ given by