

# Two-dimensional infrared (2D IR) correlation spectroscopy study of self-assembly of oleic acid (OA) in conjunction with partial attenuation of dominant factor by eigenvalue manipulating transformation (EMT)

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## ARTICLE INFO

### Article history:

Received 13 September 2011

Received in revised form 1 December 2011

Accepted 12 January 2012

Available online 21 January 2012

### Keywords:

Two-dimensional (2D) correlation spectroscopy

Infrared

Eigenvalue manipulating transformation (EMT)

Oleic acid

Self-assembly

## ABSTRACT

Highly selective two-dimensional (2D) correlation analysis, achieved by attenuating a major principal component in spectral data with eigenvector manipulating transformation (EMT) technique, was demonstrated. A spontaneous evaporation process of a binary mixture solution of oleic acid (OA) and carbon tetrachloride (CCl<sub>4</sub>) was monitored by attenuated total reflection infrared (ATR-IR) spectroscopy. Fine details of the dynamic behavior of OA molecules undergoing self-assembly into smectic liquid crystals were analyzed by 2D correlation spectroscopy scheme in conjunction with EMT technique. Correlation feature derived from the original spectral data is dominated with the contribution from the major dimer components of OA. On the other hand, 2D correlation spectra generated from the reconstructed data by attenuating the first principal component (PC1) showed selective enhancement of the correlational feature associated with the minor monomer component, which makes it possible to identify distinct populations, each having different dynamic behavior during the self-assembly.

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## 1. Introduction

Main feature of two-dimensional (2D) correlation spectrum is often dominated with the intensity variation arising from unwanted signals arising from interfering constituents in system. One of the important benefits derived from chemometric analysis combined with 2D correlation analysis is the ability to rationally reject such irrelevant information presented in the spectral data [1]. For example, 2D correlation analysis in conjunction with data reconstruction based on principal component analysis (PCA), known as PCA-2D, was proposed by Jung et al. to improve the quality of the analysis [2]. The basic hypothesis of PCA is that the improved proxy of the original data matrix can be reconstructed from only a limited number of significant factors, namely principal components (PCs). 2D correlation analysis based on the data reconstructed by rejecting unnecessary PCs makes it possible to effectively elucidate the most important features presented in the data without being hampered by noise or insignificant minor components. Thus, PCA-2D may be viewed as a form of denoising technique for the pretreatment of data.

Recently, another type of PCA-based data transformation for 2D correlation analysis, called eigenvector manipulating transformation (EMT), was proposed by the same group [3–5]. EMT produces a new reconstructed data by systematic substitution of individual factors. By partially attenuating specific PCs with EMT scheme, it becomes possible to suppress the unwanted contribution from selected components in the system. A characteristic advantage of EMT lies in the fact that rejection of the contribution from noise or insignificant minor components as well as selective enhancement of certain correlational features becomes possible by systematically manipulating the weight on PCs.

In this study, the effect of the attenuating major PC was demonstrated with time-dependent attenuated total reflection infrared (ATR-IR) spectra of a binary mixture solution of oleic acid (OA) and carbon tetrachloride (CCl<sub>4</sub>). The understanding of the nature concerning self-assembling of OA is of great scientific interest, from fundamental research and practical technological points of view [6–8]. Spectroscopic study of self-assembling of OA provides interesting opportunity to derive adequate molecular level insight into the underlying mechanisms of the system.

Transient evaporation of binary mixture solution of OA and CCl<sub>4</sub> was monitored by ATR-IR spectroscopy. During the evaporation of CCl<sub>4</sub> from the system, OA molecules substantially go through several transitions. For example, it is believed that the isolated monomers of OA show spontaneous organization of

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molecular units into a certain kind of ordered structure. This process includes the formation of dimer based on hydrogen bonding of carboxyl group and aggregation of dimer units into tightly packed smectic liquid crystals. Such phenomenon is closely related to the degree of hydrogen bonding of the carboxyl group and segmental movements of carbon atoms along the alkyl chain [9–13]. Consequently, the variation of the time-dependent ATR-IR spectra of the binary mixture solution substantially reflects such transition of OA molecules. Thus, in turn, the detailed analysis of the dynamic behavior of the spectra provides useful background information on how the OA molecules aggregate into the smectic liquid crystals during the evaporation of the  $\text{CCl}_4$ .

## 2. Background of EMT

Assume a spectral data matrix  $\mathbf{A}$  of  $m$  by  $n$  dimension, where  $m$  is the number of spectral traces and  $n$  is the number of data points per spectrum. Reconstructed matrix  $\mathbf{A}^*$  by singular value decomposition (SVD) is given as follows

$$\mathbf{A}^* = \mathbf{U}\mathbf{S}\mathbf{V}^t \quad (1)$$

The superscript  $t$  indicates the transpose of matrix. The  $m$  by  $r$  so-called left singular matrix  $\mathbf{U}$  contains the first  $r$  eigenvectors of the matrix  $\mathbf{A}\mathbf{A}^t$ , and the  $n$  by  $r$  right singular matrix  $\mathbf{V}$  contains the first  $r$  eigenvectors of  $\mathbf{A}^t\mathbf{A}$ . The  $r$  by  $r$  matrix  $\mathbf{S}$  is a relatively small diagonal matrix. The diagonal elements of  $\mathbf{S}$  are the first  $r$  singular values of  $\mathbf{A}$ , which are the positive square roots of the eigenvalues of either  $\mathbf{A}\mathbf{A}^t$  or  $\mathbf{A}^t\mathbf{A}$ , arranged in the decreasing order.

The new EMT-reconstructed data matrix  $\mathbf{A}^{**}$  is obtained by manipulating and replacing eigenvalues of  $\mathbf{A}^*$ . The reconstructed data matrix  $\mathbf{A}^{**}$  based on general form of PC attenuating EMT is given by

$$\mathbf{A}^{**} = \mathbf{A}^* - \sum_i k_i s_i \mathbf{U}_i \mathbf{V}_i^t \quad (2)$$

This form indicates that the data matrix  $\mathbf{A}^{**}$  is reconstructed by attenuating the contribution from  $i$ th singular values. The attenuation parameter  $k_i$  can be chosen individually for different PCs. The value of individual  $k_i$  can be set to 0 (no attenuation), 1 (full elimination) and so on, depending on the specific strategy of EMT. For example, it is possible to suppress the effect of PC1 by setting  $i = 1$ . The reconstructed data are then analyzed with conventional 2D correlation spectroscopy scheme to elucidate the dynamic behavior of the components presented in the data [1,14,15].

## 3. Experimental

Time-dependent ATR-IR spectra of a binary mixture solution of OA and  $\text{CCl}_4$ , undergoing a spontaneous evaporation process were measured by a NEXS 870 FT-IR spectrometer equipped with a MCT detector (Thermo Nicolet). The initial mole fraction of the OA in the mixture solution was 0.02. The 20  $\mu\text{L}$  sample solution was analyzed by depositing it on a horizontal ZnSe ATR plate. The sample was exposed to open atmosphere at room temperature (24 °C), and sets of IR spectra were collected at intervals of 4 s, with each set consisting of eight coadded scans at a 4  $\text{cm}^{-1}$  resolution. Once the solution mixture was exposed to air,  $\text{CCl}_4$  started evaporating. Eventually,  $\text{CCl}_4$  was completely removed from the system and only oleic acid remained behind.

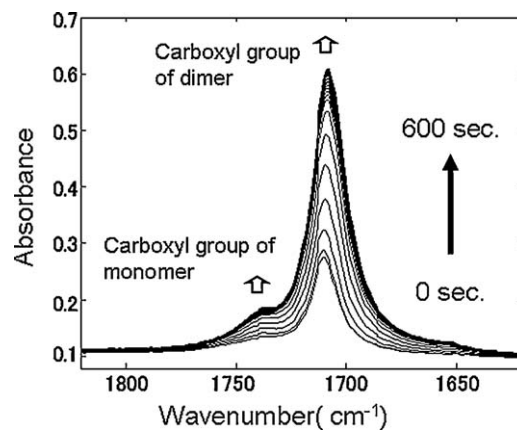


Fig. 1. Time-dependent ATR-IR spectra of binary mixture solution of OA and  $\text{CCl}_4$ .

## 4. Results and discussion

### 4.1. 2D correlation analysis of original data matrix

Fig. 1 represents the time-dependent ATR-IR spectra of the binary mixture solution. Peaks observed in this region are specific to vibrational modes of carboxyl group of OA. For example, a minor peak observed at 1740  $\text{cm}^{-1}$  is assignable to the monomer of OA [16]. A major peak observed at around 1710  $\text{cm}^{-1}$  exhibits gradual increase in the spectral intensity and shift in position from 1714 to 1708  $\text{cm}^{-1}$  [16]. Such variation of the spectral feature in this region may be explained as the co-existence of the contributions from the dimers with disordered orientation and the dimers forming quasismectic liquid crystals in which the dimers are tightly packed together and have only short-range positional order. Iwahashi et al. reported that OA tends to form a specific self-assembled model, which provides most condensed packing form of the dimers of OA due to the segmental movements of carbon atoms along the alkyl chain [10]. The variation of the spectral intensity here substantially reflects the structural alternation of OA induced by the change in the concentration. Thus, the detailed analysis of the change in the spectral feature may, in turn, provide useful information on how OA molecules undergo the self-assembly. However, it is not straightforward to investigate these spectral changes from the conventional one-dimensional stack of the spectra. The application of 2D correlation analysis becomes useful to elucidate such subtle but pertinent information.

Fig. 2(A) represents synchronous correlation spectrum calculated from the set of IR spectra shown in Fig. 1. The synchronous correlation spectrum provides only one specific auto-peak at around 1710  $\text{cm}^{-1}$ , indicating the gradual increase in the concentration of the OA during the evaporation. It is important to point out that some minor synchronous correlation peaks, for example an auto-peak and cross peaks arising from the monomer, do not show up in this synchronous correlation spectrum. Having a band with a large magnitude of intensity variations creates the problem in simultaneously displaying the fine features of bands exhibiting only small amount of intensity variations. Consequently, the generation of such seemingly simple correlation pattern suggests that large portion of the variation of the spectral feature is dominated with the intensity change of the dimer peaks.

The corresponding asynchronous correlation spectrum is shown in Fig. 2(B). The generation of a negative cross peak between 1708 and 1714  $\text{cm}^{-1}$  reveals that the change in the dimer occurs before the change in the monomer cluster. Thus, it is likely that formation of the dimer is followed by the aggregation of the dimer units into a certain cluster structure. Such sequential order of the events agrees well with the development of smectic liquid

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