



Volume 56 (2023)

Supporting information for article:

Promoting X-ray scattering data analysis with two-dimensional correlation spectroscopy

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S1. Fundamentals of 2DCS.

The generalized two-dimensional correlation spectroscopy (2DCS) analysis was developed by Noda (Noda, 1989) to elucidate information in spectral variations of infrared, X-ray, and UV-Vis data obtained under thermal, electrical, optical or chemical perturbations. (Park *et al.*, 2015) Its main advantages include (Noda & Ozaki, 2004) (i) a better understanding of complex spectra with many overlapping peaks, and an enhanced effective spectral resolution by spreading peaks over the second dimension; (ii) unambiguous assignment of peaks through the correlation of bands; (iii) identification of the specific sequential order of spectral intensity changes taking place during the measurement or the value of a controlling variable affecting the spectrum through asynchronous analysis; (iv) so-called heterospectral correlation, i.e., the identification of correlation among bands in two different types of spectroscopy, for example, the correlation between IR and Raman bands.

This work demonstrates the applications of 2DCS in the XrS data analysis, aiming to promote the data analysis and deciphering the structure formation process as a function of variables such as temperature, concentration and time. As shown in Figure 1, for the 2DCS-XrS, the 1D curve of XrS data (i.e., $A(q_j, T_i)$) is obtained as a function of the scattering vector q_j with $j=1, 2, \dots, n$ and temperature variables T_i with $i=1, 2, \dots, m$ during the observation interval between T_l and T_m . The temperature induced dynamic SAXS spectra were transformed into a set of 2DCS-XrS spectra by a cross correlation analysis, which follows the principles detailed in the following.

The dynamic SAXS data $\tilde{A}(q_j, T_i)$ was defined within the observation intervals between T_l and T_m as

$$\tilde{A}(q_j, T_i) = A(q_j, T_i) - \bar{A}(q_j, T_i)$$

Where $\bar{A}(q_j, T_i)$ is the reference spectrum of the system; here we selected the averaged spectrum which is given by

$$\bar{A}(q_j, T_i) = \frac{1}{m} \sum_{i=1}^m A(q_j, T_i)$$

Synchronous (Φ) and asynchronous (Ψ) correlations spectra are given by

$$\Phi(q_x, q_y) = \frac{1}{m-1} \sum_{i=1}^m \tilde{A}(q_x, T_i) \cdot \tilde{A}(q_y, T_i)$$

$$\Psi(q_x, q_y) = \frac{1}{m-1} \sum_{i=1}^m \tilde{A}(q_x, T_i) \cdot \sum_{k=1}^m N_{ik} \tilde{A}(q_y, T_k)$$

Where N_{ik} is the Hilbert-Noda transformation matrix given by

$$N_{ik} = \begin{cases} 0 & \text{if } i = k \\ \frac{1}{\pi \cdot (k - i)} & \text{otherwise} \end{cases}$$

We interpreted the 2DCS-XrS data and determined the sequence of structure formation as a function of external stimuli (i.e., temperature) by following Noda's rules (Noda & Ozaki, 2004):

1. If the intensities of q_x and q_y in the XrS dataset are changing in the same direction, the synchronous 2D cross peak at (q_x, q_y) is positive;
2. if the intensities of q_x and q_y in the XrS dataset are changing in the opposite direction, the synchronous 2D cross peak at (q_x, q_y) is negative;
3. if the change at q_x mainly precedes the change at q_y , the asynchronous 2D cross peak at (q_x, q_y) is positive;
4. if the change at q_x mainly follows the change at q_y , the asynchronous 2D cross peak at (q_x, q_y) is negative;
5. if the synchronous 2D cross peak at (q_x, q_y) is negative, the interpretation of rule 3 and 4 for the asynchronous 2D peak at (q_x, q_y) has to be reversed.

These rules can also be found in the Table S1. In addition, it should be noted that these principles work also if we take the scattering angle (α) instead of the q as the variable.

Table S1. Guidelines for judging the correlations of the peaks' changes based on Noda's rules.

| Synchronous correlation $\Phi(q_1, q_2)$ | asynchronous correlations $\Psi(q_1, q_2)$ | Indication |
|---|---|---|
| + | / | Signal strength of q_1 and q_2 changes in the same direction, i.e., both increase or decrease |
| - | / | Signal strength of q_1 and q_2 changes in the opposite direction |
| + | + | The change in q_1 is mainly before that of q_2 |
| + | - | The change in q_1 is mainly after that of q_2 |
| - | + | The change in q_1 is mainly after that of q_2 |
| - | - | The change in q_1 is mainly before that of q_2 |

S2. Dataset of the 1D XrS curves.

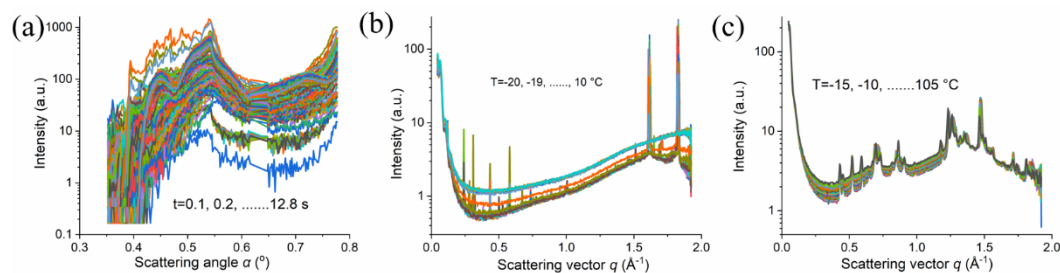


Figure S1. Dataset of the traditional 1D X-ray scattering curves of (a) AuNRs–PEDOT:PSS aqueous dispersion as a function of drying time (t), (b) AuNPs–PEG aqueous dispersion as a function of temperature (T) and (c) ISO/LiTFSI solid electrolyte as a function of temperature (T).

References:

- Noda, I. (1989). *Journal of the American Chemical Society* **111**, 8116-8118.
- Isao, N. & Yukihiro, O. (2004). *Two-Dimensional Correlation Spectroscopy – Applications in Vibrational and Optical Spectroscopy*, pp. 15-38. New York: John Wiley & Sons, Ltd.
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