Short Communication

Dipole–dipole interactions in solution mixtures probed by two-dimensional synchronous spectroscopy based on orthogonal sample design scheme

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HIGHLIGHTS

- "Orthogonal Sample Design Scheme" was used to construct 2D spectroscopy.
- Dipole–dipole interactions of DMF/$CH_3COOC_2H_5$, $C_{60}/CH_3COOC_2H_5$ in CCl_4 were probed.
- Interactions were studied using FT-IR and combination of UV–Vis/FT-IR spectra.
- 2D synchronous spectrum can be used to characterize dipole–dipole interaction.

GRAPHICAL ABSTRACT
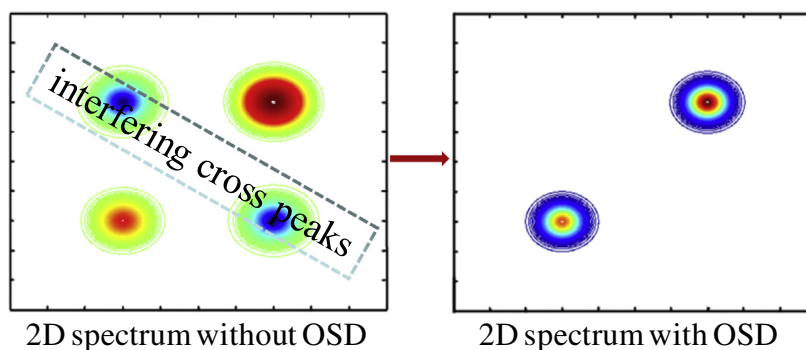
2D spectrum without OSD → 2D spectrum with OSD

ARTICLE INFO

ABSTRACT

Two-dimensional (2D) synchronous spectroscopy together with a new approach called "Orthogonal Sample Design Scheme" was used to study the dipole–dipole interactions in two representative ternary chemical systems (N,N-dimethyllformamide (DMF)/$CH_3COOC_2H_5$/CCl_4 and $C_{60}/CH_3COOC_2H_5/CCl_4$). For the first system, dipole–dipole interactions among carbonyl groups from DMF and $CH_3COOC_2H_5$ are characterized by using the cross peak in 2D Fourier Transform Infrared Radiation (FT-IR) spectroscopy. For the second system, intermolecular interaction among π–π transition from C_{60} and vibration transition from the carbonyl band of ethyl acetate is probed by using 2D spectra. The experimental results demonstrate that "Orthogonal Sample Design Scheme" can effectively remove interfering part that is not relevant to intermolecular interaction. Additional procedures are carried out to preclude the possibilities of producing interfering cross peaks by other reasons, such as experimental errors. Dipole–dipole interactions that manifest in the form of deviation from the Beer–Lambert law generate distinct cross peaks visualized in the resultant 2D synchronous spectra of the two chemical systems. This work demonstrates that 2D synchronous spectra coupled with orthogonal sample design scheme provide us an applicable experimental approach to probing and characterizing dipole–dipole interactions in complex molecular systems.

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Introduction

Intermolecular dipole–dipole interaction is caused by permanent or instantaneous electrostatic forces [1,2], which have been presumed and used to explain the structure, physical–chemical properties of many molecular systems [3-11]. However, there are few approaches for the direct detection of dipole–dipole interactions, especially the experimental approaches available for the direct observation of the occurrence of intermolecular interactions are still quite limited.

Two-dimensional (2D) synchronous spectroscopy was established and rapidly promoted with the contribution of Noda [12-20] and Ozaki [13,17,20-25]. Many important spectral features that are not readily accessible in the original set of one-dimensional (1D) spectra can be clearly visualized in the 2D spectra. Two-dimensional correlated spectroscopy has attracted extensive interests for a broad range of applications in a variety of research fields and provided a new avenue to the study of intermolecular interactions. However, interfering cross peaks due to other sources of correlation may also arise even if there is no intermolecular interaction. This problem makes it difficult to use the cross-peaks as a reliable criterion to judge whether intermolecular interaction actually occurs or not.

In our previous works, a new method nominated "Orthogonal Sample Design Scheme (OSD)" was established to construct 2D synchronous spectroscopy which could get rid of interfering cross peaks caused by accidental synchronicity so that intermolecular interaction between two components dissolved in a solvent can be characterized in a reliable manner [18], which had been used effectively to confirm the weak interactions between lanthanide (III) ions with organic ligands in solutions mixtures [19]. In recent years, the OSD scheme has been optimized by our group so that we can probe the intermolecular interactions in various ways [26-32]. Several scheme, such as double orthogonal sample design (DOSD) [28], asynchronous orthogonal sample design (AOSD) [29-31], double asynchronous orthogonal sample design (DAOSD) [32], had been introduced to remove interfering cross peaks in 2D spectra. In this paper, we apply the OSD scheme on two ternary chemical systems (DMF/CH$_3$COOC$_2$H$_5$/CCl$_4$ and C$_{60}$/CH$_3$COOC$_2$H$_5$/CCl$_4$) to show this approach can be used to characterize dipole–dipole interaction between molecules with permanent dipole moments.

Experimental

Materials

DMF, ethyl acetate and CCl$_4$ were of A.R. grade and purchased from Beijing Chemical Company. CCl$_4$ was purified according to the protocol described in Ref. [33]. C$_{60}$ was a gift provided kindly by Prof. Zhou Xi-Huang, College of Chemistry and Molecular Engineering, Peking University. It was prepared by arc method and purified through wet process, the purity was more than 99% [34].

Instrument

The FT-IR spectra were collected on a Bio-Rad FTS-65A Fourier transform infrared spectrometer equipped with an attenuated total reflection accessory. All the spectra were recorded at a resolution of 4 cm^{-1} and 32 scans were co-added. The UV–Vis spectra were recorded on a Varian Cary 1E UV–Vis spectrophotometer and the spectra were measured at a scanning rate of 60 nm/min.

The 2D synchronous spectra were calculated based on the algorithm by Noda [20] using the software of MATLAB (The Math Works Inc.).

General procedure for constructing 2D mixed solutions synchronous spectrum

We now use an example listed in Table S1 (Supplementary material) to show the general procedures of constructing a 2D synchronous spectrum based on the orthogonal sample design scheme from a chemical system containing solute P and solute Q.

Step (i): Four solutions containing P and Q are prepared, and the concentrations of P and Q (denoted as $_{PQ}C_P^i, _{PQ}C_Q^i, i = 1, 2, 3, 4$) are set as listed in Table S1. The selection of the concentrations of $_{PQ}C_P^i, _{PQ}C_Q^i (i = 1, 2, 3, 4)$ meet the requirement of Eq. (1).

$$\sum_{i=1}^{m} \left(C_P^i - \overline{C}_P \right) \left(C_Q^i - \overline{C}_Q \right) = 0 \tag{1}$$

where $\overline{C}_P$ and $\overline{C}_Q$ are, respectively, the average of the initial concentrations of species P and Q. The difference between the initial concentration of individual species and their average value is called the dynamic concentration, as shown in Eq. (1).

Step (ii): Four 1D spectra denoted as ai (i = 1, 2, 3, 4) are recorded for the four solutions obtained in step (i).

Step (iii): A 2D mixed-solutions synchronous spectrum of P/Q is then generated based upon the four 1D spectra obtained in step (ii). The cross peak at (x, y) in the 2D mixed solutions spectrum can be used to characterize the presence of intermolecular interactions between P and Q.

Other considerations

Before we use the cross peak in the 2D mixed-solutions spectrum, other factors that may bring about additional interfering cross peaks should be considered. Accordingly, an appropriate pretreatment should be adopted to make sure that the observed cross peaks are not artifact.

Interference caused by solvent–solute interactions

Every chemical system studied here is a solution consisting of solvent and solutes. Although the contribution from the solvent to the characteristic peaks of the solutes could often be safely neglected, some levels of solvent–solute interactions become inevitable, since a solvating layer often occurs around each solute molecule. Such interactions may lead to a deviation from the linearity between absorbance and concentration of the solutes. This type of a deviation may also produce cross peaks that reflected solute–solvent interactions rather than solute–solute interactions. Therefore, something should be done to remove the interference caused by solvent–solute interactions before we use cross peaks to identify the existence of intermolecular interactions strictly between different solutes.

The solute and its solvating layer can be regarded as a separate entity (solvated-solute complex). Within a suitable concentration range of the solutes, the integrity of the solvated-solute complex remains virtually undisturbed, and the solvated-solute complex also follows the Beer–Lambert Law. Consequently, the interference caused by the solvent–solute interactions can also be effectively removed.

Experimentally, a series of solutions are prepared first by dissolving each solute separately in the corresponding solvent for spectral measurement. Based on the experimental results, we then determine the suitable concentration ranges where good linear relationships between the absorbance of the characteristic peaks and concentrations of the solutes are obtained (R > 0.99, see Supplementary material).

Accordingly, we select the afore-mentioned concentration ranges to construct 2D synchronous spectra, thereby excluding