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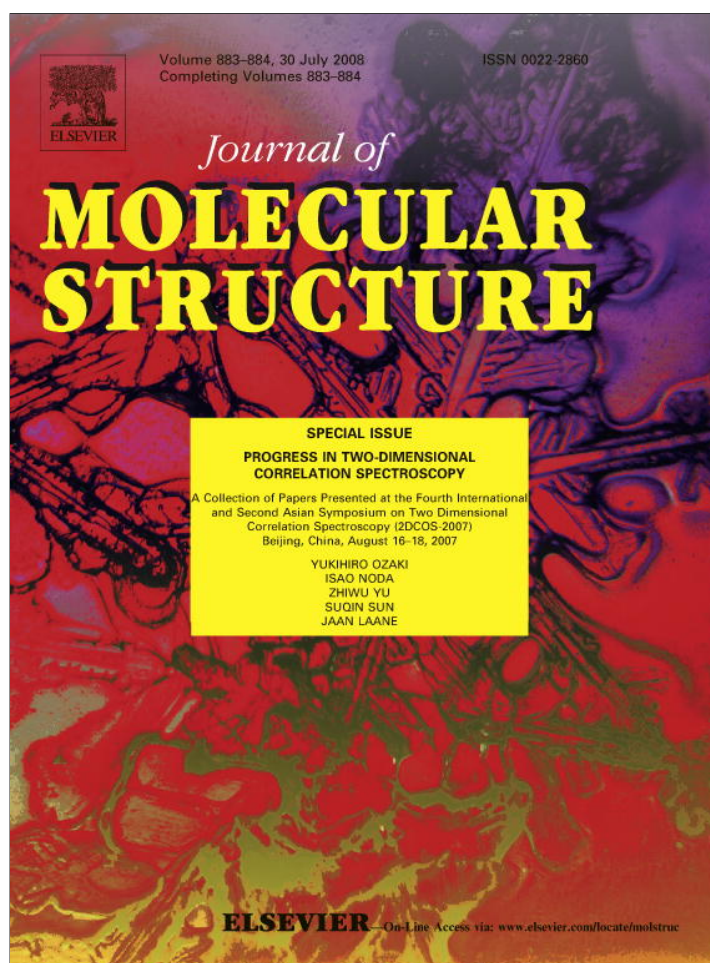


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# Patterns of cross peaks in 2D synchronous spectrum generated by using orthogonal sample design scheme

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## Abstract

A computer simulation is applied on a model chemical system to study patterns of cross peaks in 2D synchronous spectrum generated by using orthogonal sample design scheme. Variations on different spectral parameters, such as peak position, bandwidth, and absorptivity, caused by intermolecular interactions result in rich and complex behavior in 2D synchronous spectrum. Subtle spectral variations that are hard to be observed in 1D spectra can be clear observed in 2D synchronous spectra. The results suggest that the cross peaks in 2D synchronous spectrum generated by using orthogonal sample design (OSD) can act as a resolution enhancement tool that can differentiate highly overlapping bands.

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**Keywords:** Orthogonal sample design scheme; 2D correlation analysis; Synchronous spectrum; Cross peaks; Intermolecular interaction

## 1. Introduction

Two-dimensional correlation spectroscopy, first proposed by Noda in the 1980s [1,2], is a powerful tool for the analysis of multivariable data based on spectral intensity variations induced by an external perturbation. The technique has attracted a scientific interest for a broad range of applications in a variety of research field over the past two decades [3–34]. The introduction of the second spectral dimension provides many new opportunities for the analysis of spectral data. One of the most attractive features in this analysis is that the appearance of a cross peak in 2D synchronous spectra suggests the potential for characterizing intermolecular interactions, which lie the center of many physical, chemical and biological processes. How-

ever, many interfering cross peaks due to other sources of synchronicity, such as concentration variations of solutes, also show up even if there is no evidence of the existence of intermolecular interactions. This interference problem makes it difficult to directly use cross peaks in conventional 2D synchronous spectrum as a reliable criterion to judge if intermolecular interaction actually occurs or not.

In our previous work [35], we propose a new approach called “orthogonal sample design scheme” to solve the problem so that intermolecular interaction between two solutes (denoted as P and Q) dissolved in a solution can be characterized. The scheme works under the framework of 2D synchronous spectroscopy using variable concentrations as an external perturbation. A series of 1D spectra (1, 2, ...,  $m$ ) of P/Q mixtures with varying concentrations of P and Q (denoted as  $C_P^i$  and  $C_Q^i$ , respectively) are recorded and used to construct 2D synchronous spectrum using the algorithm proposed by Noda [4]. The selection of the

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initial concentrations of P and Q should meet the requirement of OSD, i.e., satisfying the following Eq. (1):

$$\sum_{i=1}^m (C_P^i - \bar{C}_P)(C_Q^i - \bar{C}_Q) = 0 \quad (1)$$

where  $\bar{C}_P$  and  $\bar{C}_Q$  are, respectively, the averages 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.

We have demonstrated that this approach can effectively remove interfering cross peaks caused by accidental synchronicity. The approach is based upon the following consideration [35]: under the influence of intermolecular interactions, the spectral behavior of the characteristic bands exhibits systematic deviation from the Beer–Lambert law. This deviation, however, usually occurs in such a subtle manner that it can hardly be observed in conventional 1D spectra. The removal of interfering effects by OSD makes it possible for the deviation from the Beer–Lambert law to be clearly visualized as the formation of cross peaks in 2D synchronous spectrum. The presence of such cross peaks provides a sound basis that allows us to investigate intermolecular interactions in complex chemical systems.

Intermolecular interactions may make the characteristic bands of the solutes undergo versatile spectral changes, such as variations on peak position, bandwidth, and absorptivity. In many cases, the spectral variations caused by intermolecular interaction are subtle and buried by complex spectral envelop. Thus, it is often hard to observe the spectral variation directly in 1D spectrum. The behavior of the cross peak in 2D synchronous spectra generated by OSD may provide some clues to the subtle spectral variation in 1D spectra. Therefore, understanding on the relationship between the spectral variation in 1D spectra and the response in 2D synchronous spectra is of great importance.

In this paper, we have performed a computer simulation on a model chemical system to study the ultimate spectral behavior of the cross peak in 2D synchronous spectra constructed by using OSD under different spectral variation in 1D spectrum.

## 2. Experimental

In the studies of simulated model, two programs compiled using Turbo C 2.0, were written in our lab to generate simulated 1D spectrum which is used as input files to construct 2D synchronous spectra. The 2D synchronous spectra were calculated based on the algorithm by Noda [4] using the software of MATLAB (The Math Works Inc.).

## 3. Results and discussion

The simulated chemical system is a series of solutions containing several chemical species, and each chemical spe-

cies has only one characteristic band in the spectra. To simplify the model, we assume that the solvent does not have any contribution to the simulated spectra. Each trace of simulated 1D spectrum is thus the summation of the peak function of each chemical species dissolved in the solution, as shown in Eq. (2)

$$Y_i^j(v) = \sum_i G_i^j(v) \quad (2)$$

$Y$  is the absorbance,  $v$  is the spectral variable,  $i$  corresponds to the index of a chemical species dissolved in the solution, and  $j$  is the index of a 1D spectrum. Here  $G(v)$  is given as a Gaussian function as shown in Eq. (3):

$$G_i^j(v) = \varepsilon_i L C_i^j e^{-\ln 2 \frac{(v-x_i)^2}{W_i^2}} \quad (3)$$

$L$  is the path-length and set as 1 for convenience in this paper;  $\varepsilon_i$ ,  $x_i$ ,  $W_i$  are the absorptivity, peak position and bandwidth (half-width at half-height, HWHH) of the characteristic band of  $i$ th chemical species;  $C_i^j$  is the equilibrium concentration of the  $i$ th chemical species for the  $j$ th spectrum.

In this paper, it is assumed that two chemical species P and Q are dissolved in the solution and the concentrations of P and Q are used as external variable to construct 2D synchronous spectrum. The initial concentrations of P and Q are listed in Table 1. The selection of the above initial concentrations meets the requirement of the OSD, since the resultant dynamic concentrations satisfy Eq. (1). When there is no intermolecular interaction between P and Q, the dynamic intensities of the characteristic band from P and Q are orthogonal to each other and the cross peaks do not occur accordingly.

When intermolecular interactions between P and Q occur in the solutions, a part of P and Q may undergo subtle structural variation and convert into P' and Q'. The concentrations of P, Q, P' and Q' are governed by the equilibrium shown in Eq. (4):



where  $K$  is the equilibrium constant and arbitrarily set as 0.01 in this paper. The equilibrium concentrations of the four chemical species, which are calculated from the equilibrium constant and the initial concentrations of P and Q are listed in Table 2.

Because of the expected similarities of the spectral parameters, severe band overlapping should occur between the bands of P'/Q' and those of P/Q. Nevertheless, subtle

Table 1  
Initial concentrations of P and Q in the model system

No.	$C_P$ (mol/dm <sup>3</sup> )	$C_Q$ (mol/dm <sup>3</sup> )
1	5.00	4.00
2	4.00	5.00
3	5.00	6.00
4	6.00	5.00

Table 2

Equilibrium concentrations of P, Q, P' and Q' calculated according the initial concentrations listed in Table 1 and equilibrium constant ( $K = 0.01$ )

No.	$C_P$ (mol/dm <sup>3</sup> )	$C_Q$ (mol/dm <sup>3</sup> )	$C_{P'}$ (mol/dm <sup>3</sup> )	$C_{Q'}$ (mol/dm <sup>3</sup> )
1	4.59	3.59	0.41	0.41
2	3.59	4.59	0.41	0.41
3	4.50	5.50	0.50	0.50
4	5.50	4.50	0.50	0.50

spectral variations may indeed occur on the characteristic bands of P' or Q' in comparison with those of P and Q. Consequently, the dynamic intensities of the characteristic bands of P/P' are not orthogonal to those of Q/Q', and cross peaks on 2D synchronous spectra should be produced.

Here, we examine what happens on the cross peaks as a consequence of the variation of the absorptivity, peak position, and bandwidth of the characteristic band of P' and Q'. Since cross peaks are symmetric about the diagonal of 2D synchronous spectra, we discuss only the cross peak at the upper left corner in the following part of this paper.

### 3.1. Effect on the variation of absorptivity of P' and/or Q'

The spectral variables for P, Q, P', and Q' used for the simulation of absorptivity variation are summarized in Table 3. Fig. 1 illustrates the original spectra of the four solutions. In this part, only  $\epsilon_{P'}$  and  $\epsilon_{Q'}$  are variable, while the peak positions and bandwidths of P' and Q' are the same as those of P and Q. Thus the bands for P' and Q' are completely overlapped with those of P and Q. It is very difficult to separate the bands of P'/Q' from those of P/Q in conventional 1D spectra. However, even such a subtle variation can be highlighted by a cross peak at the coordinate (150, 350), and an example is shown in Fig. 2. The cross peak can be either positive or negative. As a matter of fact, the intensity of the cross peak is a function of  $\epsilon_{P'}$  and  $\epsilon_{Q'}$ . Fig. 3 is a contour map to illustrate the relationship between  $\epsilon_{P'}/\epsilon_{Q'}$  and the intensities of the cross peak. The function turns out to be quadratic based on two-dimensional nonlinear regression calculation with  $R^2 = 1$ .

$$Y = 0.0833261\epsilon_{Q'} + 0.0833261\epsilon_{P'} + 0.0083925\epsilon_{P'}\epsilon_{Q'} - 0.1750471$$

where  $Y$  is the intensity of the cross peak.

There arises a problem when  $\epsilon_{P'} < \epsilon_P = 1.0$  and  $\epsilon_{Q'} < \epsilon_Q = 1.0$ . Both of the peaks at 150 and 350 cm<sup>-1</sup> are expected to decrease simultaneously, since some of P/Q are replaced by P'/Q' whose characteristic bands become

Table 3

The spectral variables of P, Q, P', Q' of the model system where the absorptivity of P' and Q' are variable

Spectral variable	Peak position (cm <sup>-1</sup> )	Bandwidth (cm <sup>-1</sup> )	Intensity
P	150	20	1.0
Q	350	20	1.0
P'	150	20	$\epsilon_{P'}$
Q'	350	20	$\epsilon_{Q'}$

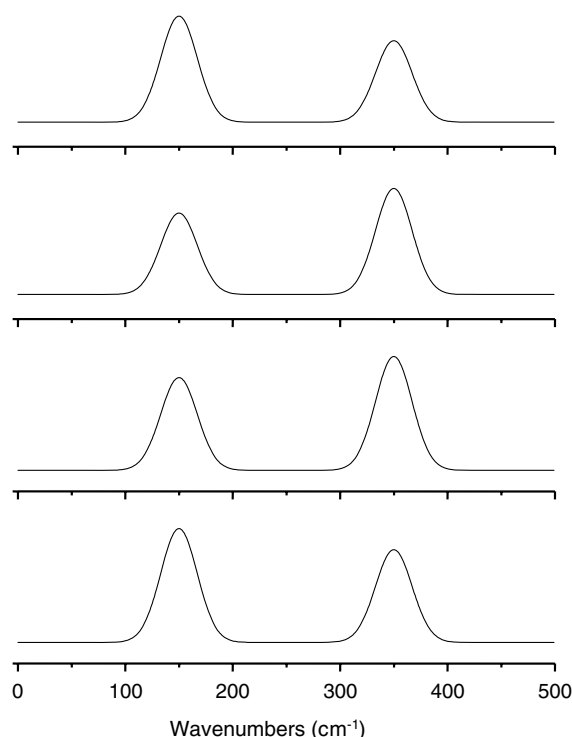


Fig. 1. 1D spectra of the model system. Effect of variation of absorptivity of the characteristic bands of P' and Q'  $\epsilon_P = 1.0$ ,  $\epsilon_Q = 1.0$ ,  $\epsilon_{P'} = 2.0$ ,  $\epsilon_{Q'} = 2.0$ , other spectral parameters are listed in Table 3.

weak. According to the Noda's rule, the cross peak should be positive. However, the cross peak turns out to be negative. To find what happens on the dynamic data, Fig. 4 depicts the intensities of the peak at 150 and 350 cm<sup>-1</sup> versus the index of spectra. The variation of the concentrations of P and Q in OSD brings about fluctuation of the intensities of the bands at 150 and 350 cm<sup>-1</sup>. The amplitude of the fluctuation is larger than the variation of the peak intensity caused by conversion from P/Q to P'/Q'. As a result, the 150

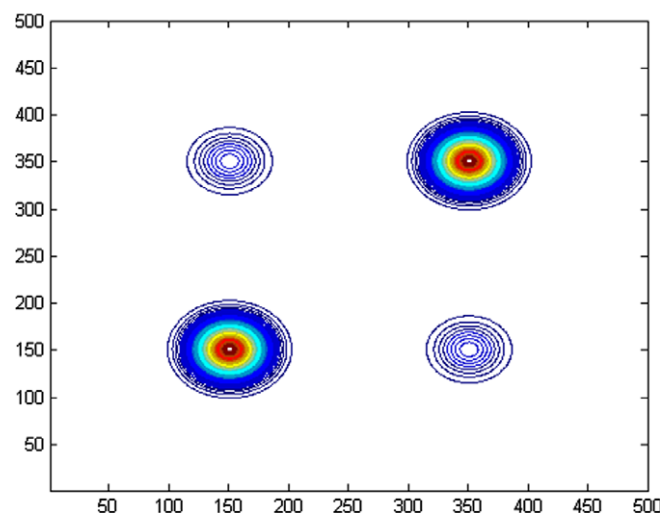


Fig. 2. 2D synchronous spectrum of the model system. Effect of variation of absorptivity of the characteristic bands of P' and Q'  $\epsilon_P = 1.0$ ,  $\epsilon_Q = 1.0$ ,  $\epsilon_{P'} = 2.0$ ,  $\epsilon_{Q'} = 2.0$ , other spectral parameters are listed in Table 3.



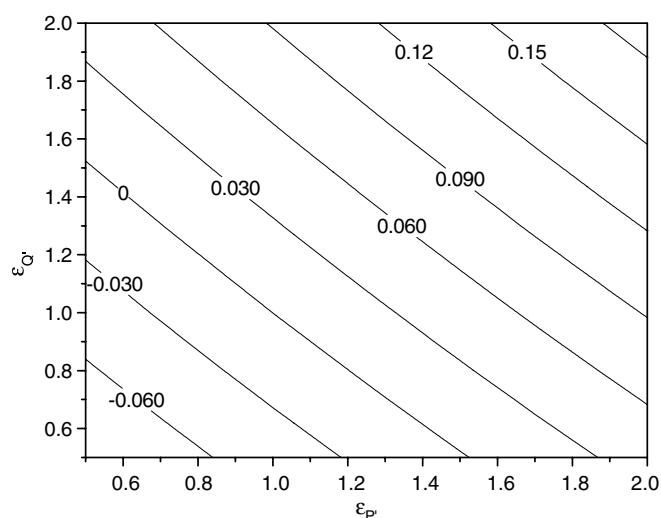


Fig. 3. Contour map that plots the intensity of the cross peak in the 2D Synchronous spectrum as a function of  $\varepsilon_{P'}$  and  $\varepsilon_{Q'}$ .

and  $350\text{ cm}^{-1}$  band intensities actually change in both the same direction and opposite direction within the dynamic data series. Therefore, the unexpected negative cross peak is caused by failure of the prerequisite of the Noda's rule for relatively monotonic signal variations rather than the invalidation of the rule itself.

### 3.2. Effect on the band shift of $P'$ and $Q'$

The spectral variables for  $P$ ,  $Q$ ,  $P'$ , and  $Q'$  for the simulation for band shift are summarized in Table 4. The absorptivities, bandwidths of  $P'$  and  $Q'$  are the same as those of  $P$  and  $Q$ . On the other hand, the peak position

Table 4

The spectral variables of  $P$ ,  $Q$ ,  $P'$ ,  $Q'$  of the model system where the peak positions of  $P'$  and/or  $Q'$  are variable

Spectral variable	Peak position ( $\text{cm}^{-1}$ )	Bandwidth ( $\text{cm}^{-1}$ )	Intensity
$P$	150	20	1.0
$Q$	350	20	1.0
$P'$	$x_{P'}$	20	1.0
$Q'$	$x_{Q'}$	20	1.0

of  $P'$  and  $Q'$  are allowed to be variable. Here the difference in the peak position between  $P$  and  $P'$  are denoted as  $\Delta x_P$ :

$$\Delta x_P = x_{P'} - x_P \quad (5)$$

Similarly, the difference in the peak position between  $Q$  and  $Q'$  are denoted as  $\Delta x_Q$ :

$$\Delta x_Q = x_{Q'} - x_Q \quad (6)$$

In the first case,  $x_{Q'}$  is set to be the same as  $x_Q$ . Additionally,  $x_{P'}$  is set as  $152\text{ cm}^{-1}$ , so  $\Delta x_P$  is quite small in comparison with  $W_P$  ( $\text{HWHH} = 20\text{ cm}^{-1}$ ). Consequently, the peaks for  $P$  and  $P'$  are heavily overlapped, and it is hard to separate the band of  $P'$  from that of  $P$  in conventional 1D spectra, even if the second derivative spectrum technique is used to enhance the resolution of the spectra (Fig. 5).

2D synchronous spectrum manages to reveal the subtle spectral variation. A pair cluster of adjacent cross peaks appear around the coordinate (150, 350) in Fig. 6. One of the pair is a positive peak, while another is a negative peak. The absolute correlation intensities of the two peaks are the same. The spectral coordinates of the two cross peaks are denoted as  $(V_x^1, V_y^1)$  and  $(V_x^2, V_y^2)$ , respectively. We notice that  $V_y^1$  and  $V_x^2$  are the same and this phenomenon is related to the fact that peak position of  $Q'$  is the same as that of  $Q$ . Fig. 7 depicts the variation of the peak position

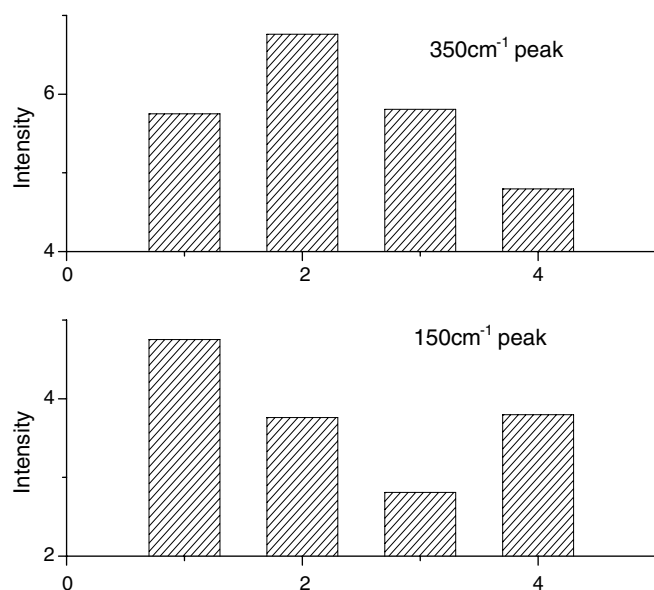


Fig. 4. The fluctuation of the intensity of the peaks at  $150\text{ cm}^{-1}$  and  $350\text{ cm}^{-1}$  versus spectral number. The amplitude of the fluctuation is much larger than the variation of the peak intensity caused by conversion from  $P/Q$  to  $P'/Q'$ .

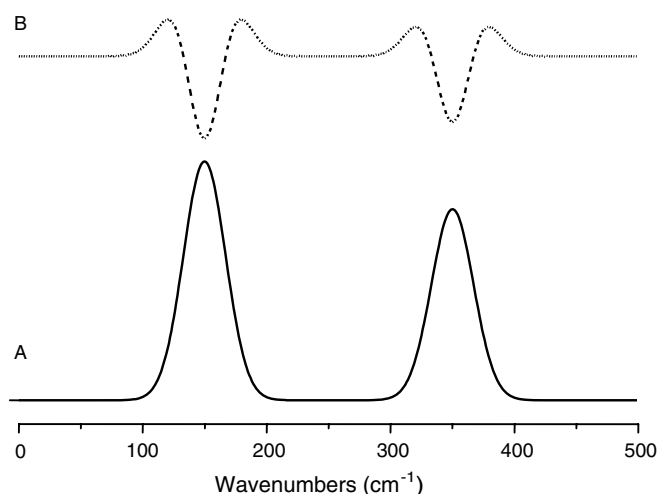


Fig. 5. 1D spectra of the model system. The characteristic peaks of  $P$  ( $x_P$  is 150) and  $P'$  ( $x_{P'}$  is 152) are heavily overlapped. Even second derivative spectral can not separate the overlapping bands. (A) Original spectrum. (B) Second derivative spectrum.

of the positive peak ( $V_x^1$ ) and negative peak ( $V_x^2$ ) as a function of  $\Delta x_P$ . Both  $V_x^1$  and  $V_x^2$  increase monotonically with the increase in  $\Delta x_P$ . If  $\Delta x_P > 0$ , we have  $V_x^1 > x_P$ , while  $V_x^1 < x_P$  is observed when  $\Delta x_P < 0$ . A sudden jump appears when  $\Delta x_P$  is around 0. This phenomenon demonstrates that 2D synchronous spectrum constructed by using OSD possess an ability to enhance resolution of highly overlapped bands with large bandwidths.

In the second case, both  $x_{P'}$  and  $x_{Q'}$  are allowed to be variable. If either  $\Delta x_P$  or  $\Delta x_Q$  are small, a cluster of two adjacent cross peaks appear (Fig. 8). Just as above, one peak is positive and another is negative. However,  $V_y^1$  are not equal to  $V_y^2$  any more. Here we define  $\eta$  as in Eq. (7)

$$\eta = \frac{V_y^1 - V_y^2}{V_x^1 - V_x^2} \quad (7)$$

As shown in Fig. 9, a good linear relationship between  $\eta$  and  $\Delta x_P/\Delta x_Q$  can be observed. This result suggests that  $\eta$  can be used to reflect the ratio of band shifts between peak from P and Q under intermolecular interactions.

When both  $\Delta x_P$  and  $\Delta x_Q$  are quite large, the cross peak exhibits much more complex spectral behavior (Fig. 10). In this case,  $\Delta x_P$  is set to be equal to  $\Delta x_Q$ . When  $\Delta x_P$  increases, the positive cross peak elongates along the direction perpendicular to the main diagonal of the synchronous spectra. Then the elongated peak splits into two peaks.

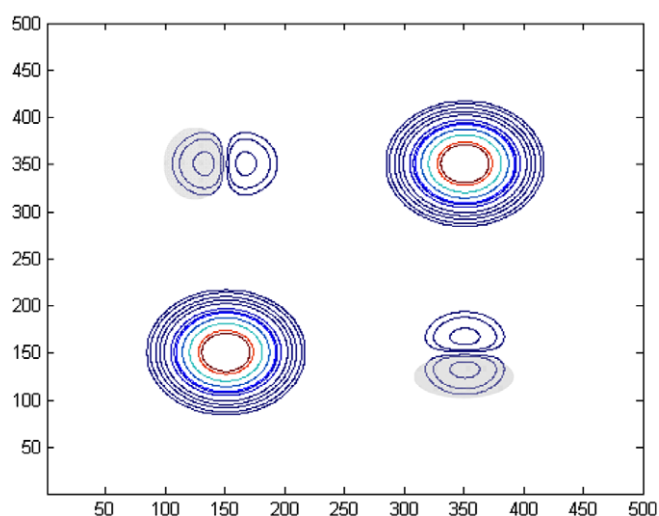


Fig. 6. 2D synchronous spectrum of the model system. Effect of variation of peak position of the characteristic band of P'  $X_P = 150 \text{ cm}^{-1}$ ,  $X_{P'} = 152 \text{ cm}^{-1}$ . Other spectral parameters are listed in Table 4. The cross peaks in the shaded areas mean that the signs of those peaks are negative.

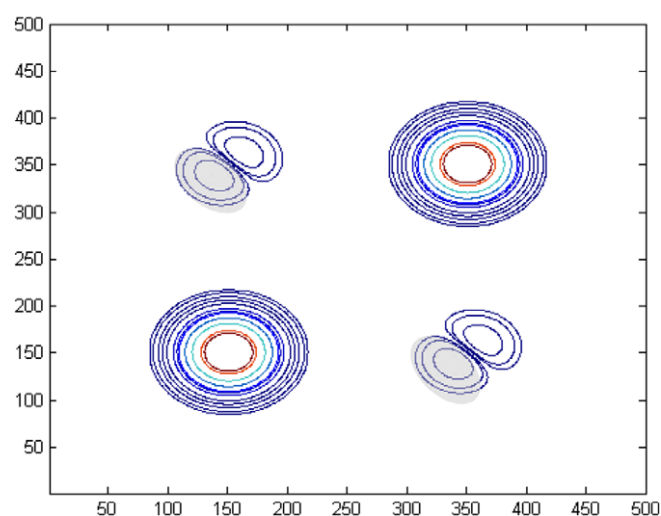


Fig. 8. 2D synchronous spectrum of the model system. Effect of variation of peak position of the characteristic band of P' and Q'. Both  $X_P$  and  $X_Q$  are  $150 \text{ cm}^{-1}$ ,  $X_{P'}$  is  $152 \text{ cm}^{-1}$  and  $X_{Q'}$  is  $352 \text{ cm}^{-1}$ . Other spectral parameters are listed in Table 4. The cross peaks in the shaded areas mean that the signs of those peaks are negative.

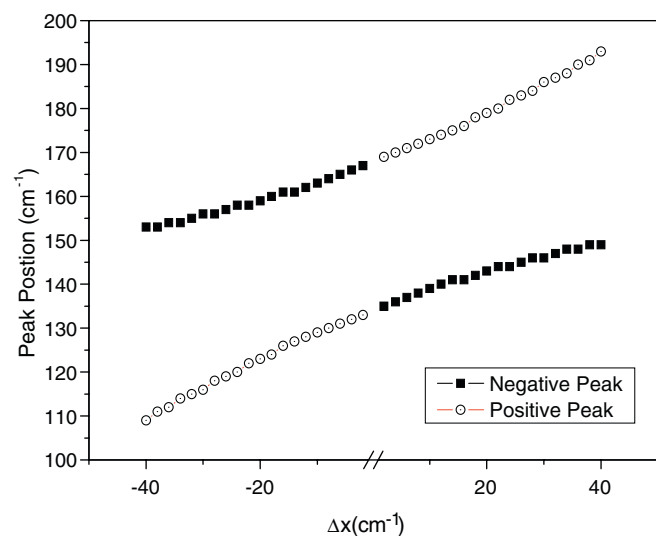


Fig. 7. Relationship between the peak positions of cross peaks and  $\Delta x_P$  when the peak position of P' is changeable. A sudden jump appears when  $\Delta x_P$  is around 0.

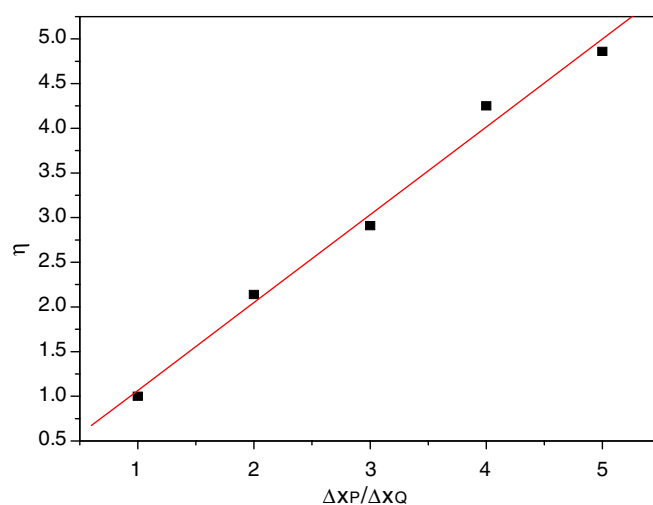


Fig. 9. Good linear relationship between  $\eta$  and  $\Delta x_P/\Delta x_Q$ , demonstrating that  $\eta$  can be used to reflect the ratio of band shifts between peak from P and Q under intermolecular interactions.

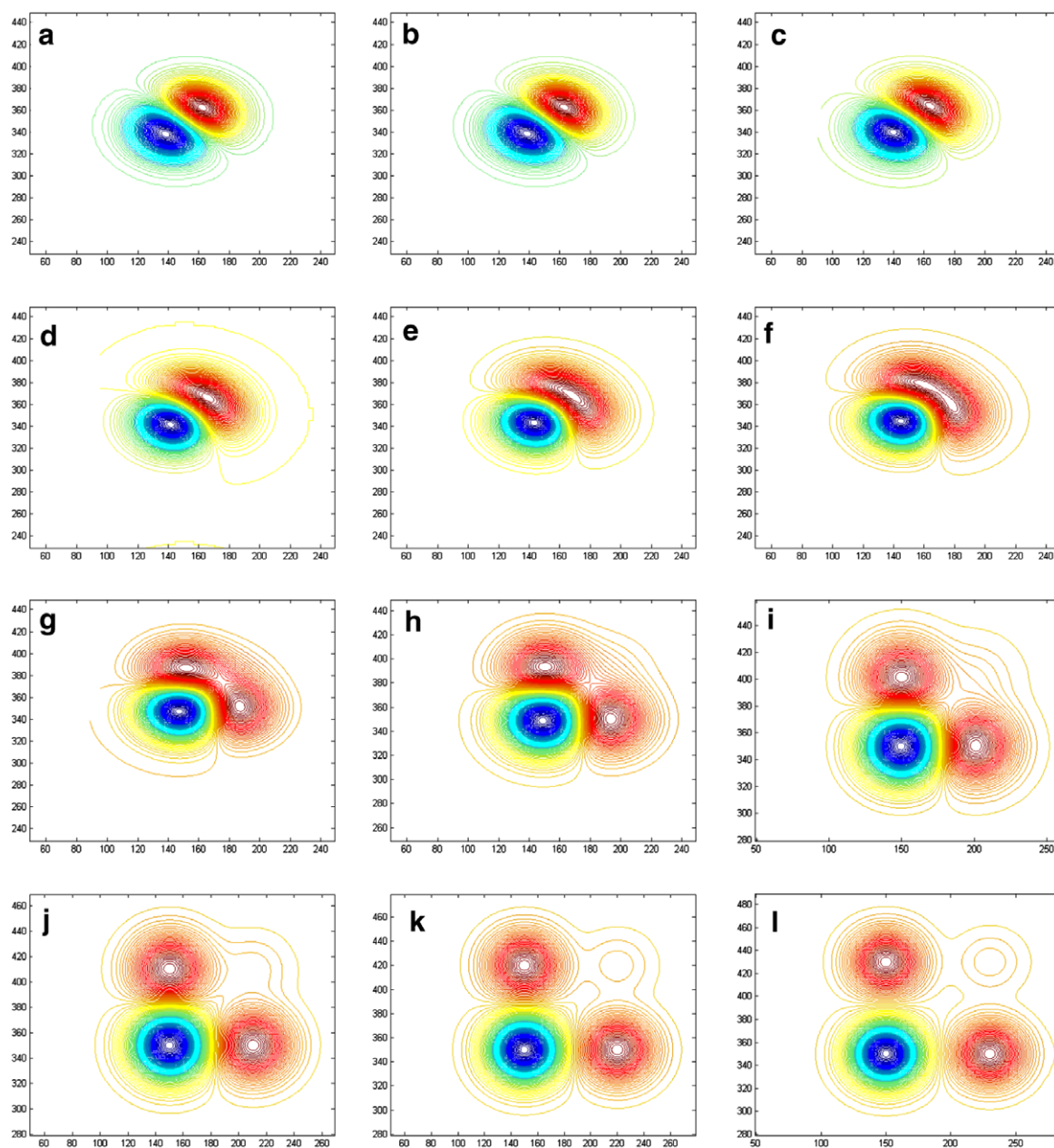


Fig. 10. The spectral behavior of the cross peaks in the model system when the peak positions of  $P'$  and  $Q'$  changes. ( $X_P$  is  $150\text{ cm}^{-1}$ ,  $X_Q$  is  $350\text{ cm}^{-1}$ ,  $\Delta x = \Delta x_P = \Delta x_Q$ , other spectral parameters are listed in Table 4). (a)  $\Delta x = 1\text{ cm}^{-1}$ , (b)  $\Delta x = 2\text{ cm}^{-1}$ , (c)  $\Delta x = 5\text{ cm}^{-1}$ , (d)  $\Delta x = 10\text{ cm}^{-1}$ , (e)  $\Delta x = 20\text{ cm}^{-1}$ , (f)  $\Delta x = 30\text{ cm}^{-1}$ , (g)  $\Delta x = 40\text{ cm}^{-1}$ , (h)  $\Delta x = 50\text{ cm}^{-1}$ , (i)  $\Delta x = 60\text{ cm}^{-1}$ , (j)  $\Delta x = 70\text{ cm}^{-1}$  and (l)  $\Delta x = 80\text{ cm}^{-1}$ .

Eventually, the positive peak changes into three separate peaks. One peak is very weak and other two peaks are quite strong. The two strong peaks are symmetric about a line that links the negative cross peak and the weak cross peak.

### 3.3. Effect on the variation of bandwidths of $P'$ and $Q'$

The spectral variables for  $P$ ,  $Q$ ,  $P'$ , and  $Q'$  for the simulation of bandwidth variations are summarized in Table 5. The absorptivities and peak positions of  $P'$ ,  $Q'$  are the same as those of  $P$  and  $Q$ . In this case, the bandwidths of  $P'$  and  $Q'$  are allowed to be changeable.

Table 5

The spectral variable of the model system where the bandwidths of  $P'$ ,  $Q'$  are variable

Spectral variable	Peak position ( $\text{cm}^{-1}$ )	Bandwidth ( $\text{cm}^{-1}$ )	Intensity
$P$	150	20	1.0
$Q$	350	20	1.0
$P'$	150	$W_{P'}$	1.0
$Q'$	350	$W_{Q'}$	1.0

In the first case,  $W_{Q'}$  is set to be the same as  $W_Q$ .  $W_{P'}$  is arbitrarily set as 22, a little larger than that of  $W_P$ . Fig. 11 shows a typical spectra of a mixture of  $P$ ,  $Q$ ,  $P'$  and  $Q'$ . For



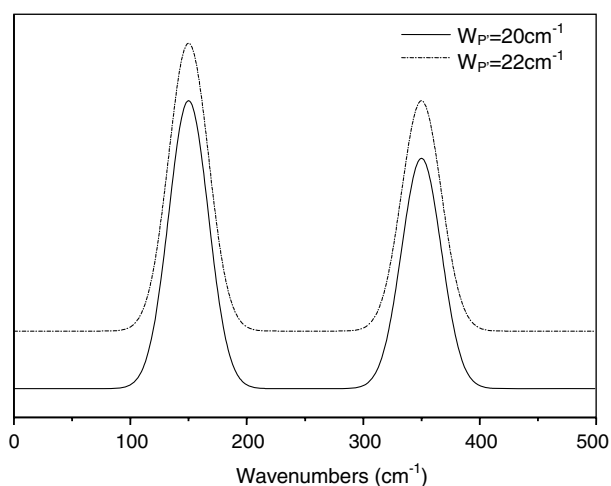


Fig. 11. 1D spectra of mixture of P, Q, P' and Q'. The bandwidths for the characteristic peak of P' are 20 cm<sup>-1</sup> and 22 cm<sup>-1</sup>, respectively. Thus the characteristic bands of P and P' are heavily overlapped.

comparison, a spectra of the model system where  $W_{P'} = 20 \text{ cm}^{-1}$  is also shown. Spectral variation caused by changes in the bandwidth of P' is too subtle to be directly observed in 1D spectra.

A cluster of two adjacent positive cross peaks appear in the 2D synchronous spectra (Fig. 12). The two peaks are symmetric about a point (150, 350). Since the bandwidths of Q and Q' are the same,  $V_y^1$  and  $V_x^2$  are identical. Here the different in bandwidth between the peaks for P and P' are denoted as  $\Delta W_P$ :

$$\Delta W_P = W_{P'} - W_P \quad (8)$$

Similarly, in bandwidth between the peak for Q and Q' are denoted as  $\Delta W_Q$ :

$$\Delta W_Q = W_{Q'} - W_Q \quad (9)$$

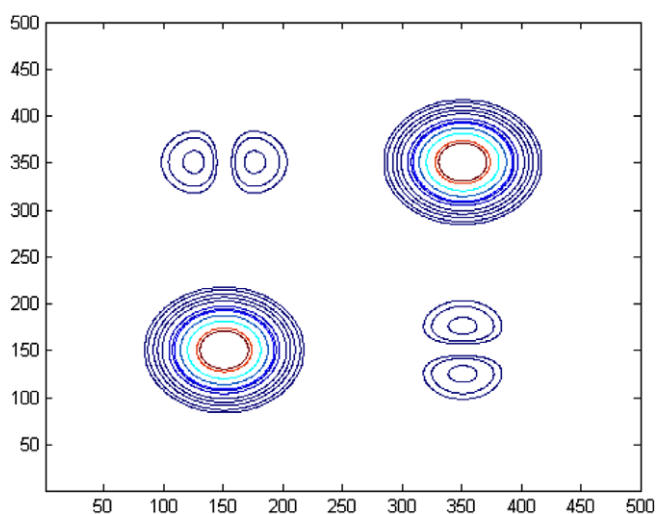


Fig. 12. 2D synchronous spectrum of the model system. Effect of variation of bandwidth of the characteristic band of P'.  $W_P$  is 20 cm<sup>-1</sup> and  $W_{P'}$  is 22 cm<sup>-1</sup>, other spectral parameters are listed in Table 5.

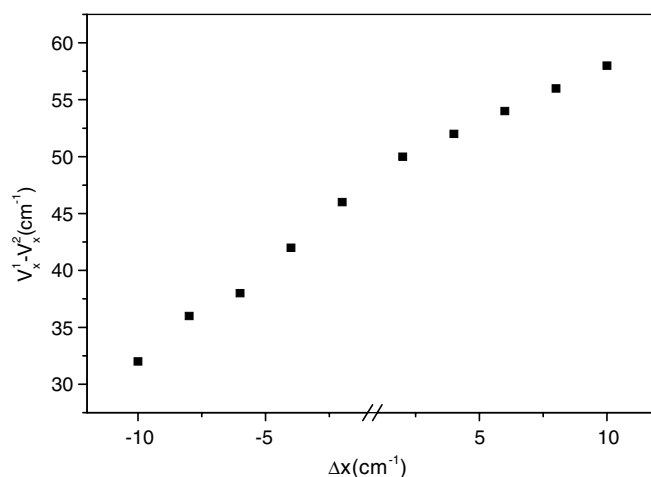


Fig. 13. Relationship between  $V_x^1$  and  $V_x^2$  of the cross peaks and  $\Delta x_P$  when the bandwidth of P' is changeable.

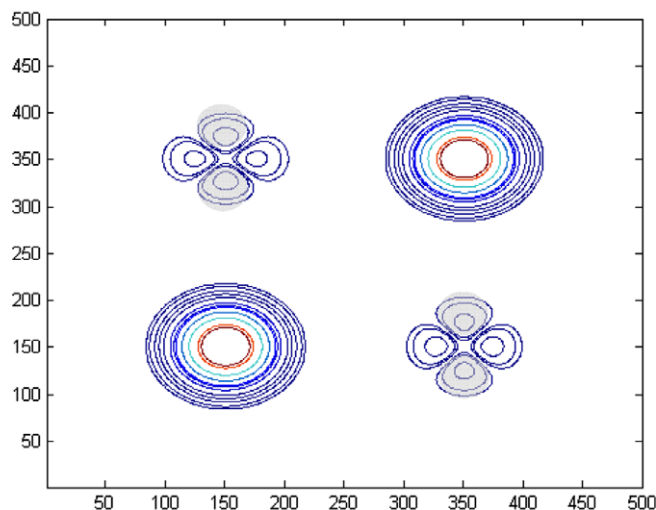


Fig. 14. 2D synchronous spectrum of the model system. Effect of variation of bandwidth of the characteristic band of P', Q'.  $W_P$  is 20 cm<sup>-1</sup> and  $W_{P'}$  is 22 cm<sup>-1</sup>.  $W_Q$  is 20 cm<sup>-1</sup> and  $W_{Q'}$  is 18 cm<sup>-1</sup> other spectral parameters are listed in Table 5. The cross peaks in the shaded areas mean that the signs of those peaks are negative.

Fig. 13 plots the variation in peak positions between the two cross peaks against  $\Delta W_P$ . It turns out that the larger  $\Delta W_P$  becomes, the farther apart the two peaks separate. Additionally, if  $\Delta W_P$  is smaller than zero, the two cross peaks changes into negative cross peaks.

When the bandwidths of the peaks for both P' and Q' are variable, a cluster of four cross peaks can be observed. The four cross peaks form a diamond whose two diagonals are parallel to the two spectral axes (Fig. 14). In addition, the center of the diamond is just at (150, 350).

#### 4. Conclusions

In this paper, we carry out a preliminary investigation on the spectral behavior on the cross peaks in 2D synchro-

nous spectrum generated by using OSD based on computer simulation. The results demonstrate that variation on different spectral parameters, such as peak position, bandwidth and absorptivity, caused by intermolecular interactions results in rich and complex behavior. It should be pointed out that many subtle spectral changes that is very difficult to be visualized in conventional 1D spectra can be magnified significantly and manifested in a pronounced manner in the 2D synchronous cross peaks. Consequently, the cross peaks in 2D synchronous spectrum generated by using orthogonal sample design scheme can be utilized as a potent resolution enhancement tool that can differentiate the highly overlapping bands, when even the second derivative spectral technique fails to resolve the bands.

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