

# **A Novel Method of Constructing Two-dimensional Correlation Spectroscopy without Subtracting a Reference Spectrum**

## **Supporting Information**

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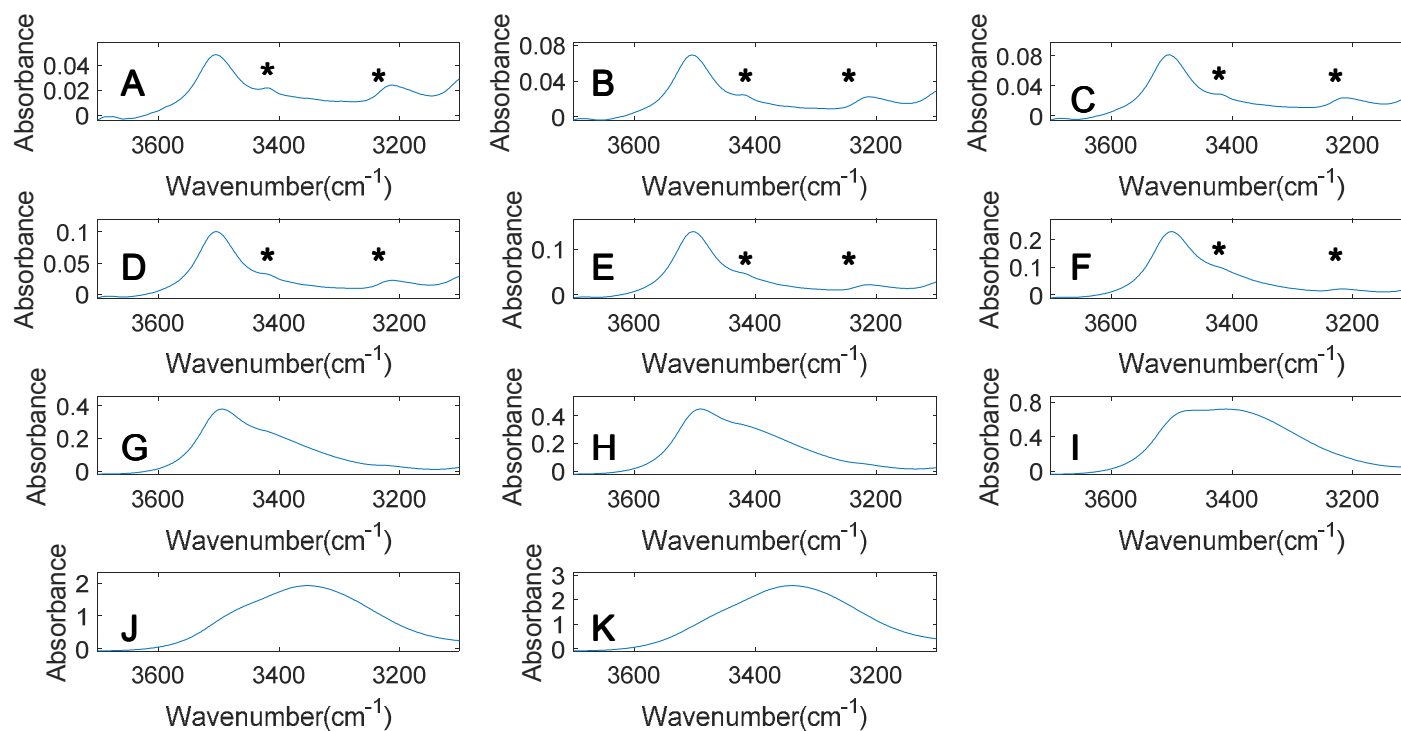
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**Part 1 FTIR spectra of diethyl ether solution containing different amounts of methanol**

**Table S1 The relationship between molar ratio of methanol and OH stretching band**

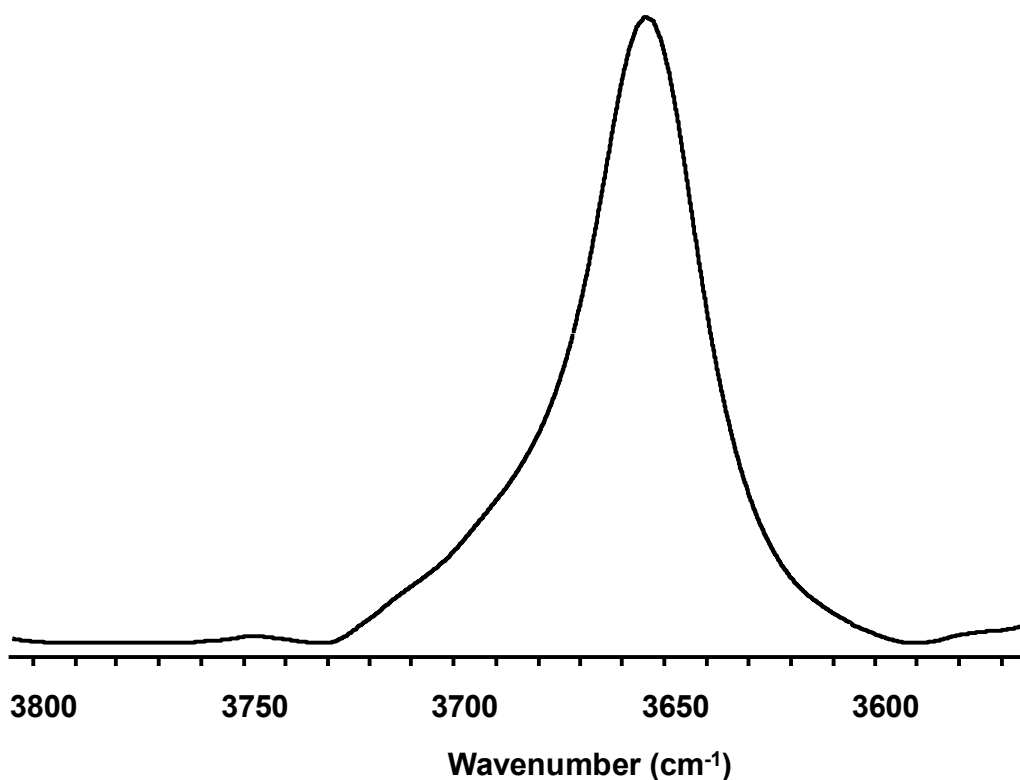
<b>Index</b>	<b><math>n_{\text{methanol}}:n_{\text{diethyl ether}}</math></b>
<b>A</b>	0.014
<b>B</b>	0.021
<b>C</b>	0.026
<b>D</b>	0.034
<b>E</b>	0.0489
<b>F</b>	0.0973
<b>G</b>	0.204
<b>H</b>	0.259
<b>I</b>	0.5770
<b>J</b>	2.321
<b>K</b>	5.109



**Figure S1 FTIR spectra of diethyl ether solutions containing different amounts of methanol. The molar ratios between methanol and diethyl ether are listed in Table S1.**

\* The peaks marked by \* are from the overtone bands of diethyl ether.

**Figure S2** shows an FTIR spectrum of hexane solution containing methanol (less than  $1 \times 10^{-4}$  mol/ml). The OH stretching band of methanol appears as a sharp single peak around  $3654 \text{ cm}^{-1}$ . In this case, the concentration of methanol is quite low, and thus methanol exists in a free state and no hydrogen bond is formed among methanol molecules.

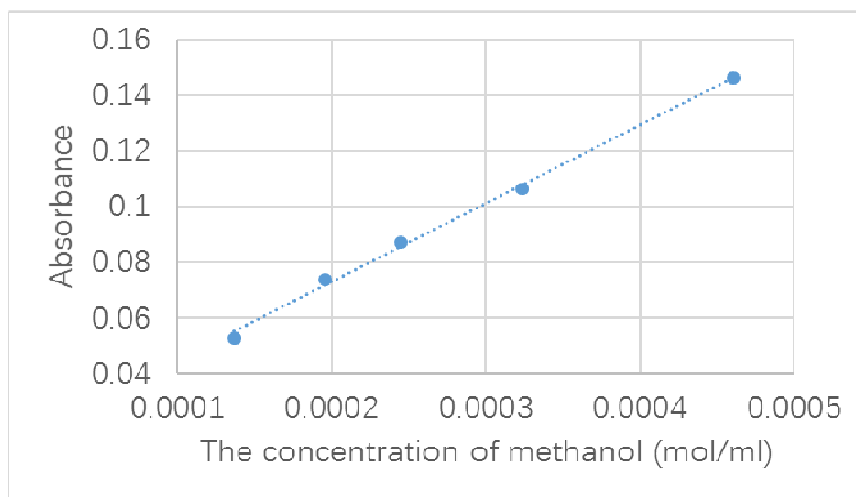


**Figure S2** An FTIR spectrum of methanol in a hexane solution (The concentration of methanol is less than  $1 \times 10^{-4}$  mol/ml).

From **Figure S1**, we learn that: As the concentration of methanol is below  $4.61 \times 10^{-4}$  mol/ml, a single narrow OH stretching peak appear at  $3504 \text{ cm}^{-1}$ . In comparison with **Figure S2**, the OH stretching band of methanol dissolved in diethyl ether (the concentration is below  $4.61 \times 10^{-4}$

mol/ml) undergoes a red shift. That is to say, a hydrogen bond forms on the methanol molecules. Since the concentration of methanol is quite low and the content of diethyl ether is overwhelmingly larger than that of methanol, the OH stretching band around  $3504\text{ cm}^{-1}$  can be assigned to the methanol whose OH group acts as a hydrogen bonding donor and form a single hydrogen bond with the oxygen atom so that a methanol-diethyl ether complex is formed (**Scheme 1** in the main text).

When the concentration of methanol is below  $4.61 \times 10^{-4}\text{ mol/ml}$ , increasing the concentration does not bring about changes in the band shape of the OH stretching band. However, the intensities of the OH stretching band at  $3504\text{ cm}^{-1}$  increases linearly with the increment of the concentration of methanol (**Figure S3**). This phenomenon demonstrates that the concentration of the aforementioned methanol-diethyl ether increases with the concentration of methanol. Moreover, methanol molecules do not form other form of hydrogen bonding structure.



**Figure S3** Linear relationship between the concentrations of methanol and the absorbance of the 3504 cm<sup>-1</sup> band in the FTIR spectra.

As the concentration of methanol increases further, the OH stretching band becomes broad and exhibits a red shift. In addition, the intensity of the OH stretching band increases significantly. The reason for this phenomenon is that methanol molecules form dimer, trimer, tetramer and/or multimer via methanol-methanol hydrogen bond shown in **Scheme 2** in the main text. The formation of the above complex aggregation via hydrogen bonding among methanol molecules is out of the scope of this work.

In this paper, we kept the concentration of methanol below 4.61×10<sup>-4</sup> mol/ml. Under this condition, whether interconversion between methanol-diethyl ether complex (**Scheme 2** in the main text) and methanol-THF complex (**Scheme 3** in the main text) occur or not is investigated using 2D asynchronous spectra.

**Part 2 Discussion on the intensity factor is**  $(\vec{C}_p^{(init)})^T N \vec{C}_U^{(eq)}$

N is the M order Hilbert-Noda matrix as follows

$$\mathbf{N} = \begin{bmatrix} 0 & 1 & \frac{1}{2} & \frac{1}{3} & \dots & \frac{1}{j-i} \\ -1 & 0 & 1 & \frac{1}{2} & \dots & \dots \\ -\frac{1}{2} & -1 & 0 & 1 & \dots & \dots \\ -\frac{1}{3} & \dots & -1 & 0 & 1 & \frac{1}{2} \\ \dots & \dots & -\frac{1}{2} & -1 & 0 & 1 \\ -\frac{1}{j-i} & \dots & \dots & \dots & -1 & 0 \end{bmatrix}_{\text{M}} \quad (\text{S1})$$

where  $i, j \leq M$

The M order N matrix can be regarded as a summation of  $M(M-1)/2$  sub-matrices ( $\mathbf{N}_{i,j}$ ).

$$\mathbf{N} = \sum_{j=i+1}^M \sum_{i=1}^{M-1} \mathbf{N}_{i,j} \quad (\text{S2})$$

The sub-matrices can be defined as:

$$\mathbf{N}_{i,j}(x,y) = \begin{bmatrix} 0 & \dots & 0 & \dots & 0 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & 0 & \dots & \frac{1}{j-i} & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & -\frac{1}{j-i} & \dots & 0 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & 0 & \dots & 0 & \dots & 0 \end{bmatrix} \quad (\text{S3})$$

Intensity factor can be expressed as:

$$(\bar{\mathbf{C}}_{\mathbf{P}}^{(init)})^T \mathbf{N} \bar{\mathbf{C}}_{\mathbf{U}}^{(eq)} = \sum_{j=i+1}^M \sum_{i=1}^{M-1} V_{i,j} \quad (\text{S4})$$

where:

$$\begin{aligned}
 V_{i,j} &= (\vec{C}_p^{(init)})^T \mathbf{N}_{i,j} \vec{C}_U^{(eq)} \\
 &= \begin{bmatrix} C_p^{1(init)} & \dots & C_p^{i(init)} & \dots & C_p^{j(init)} & \dots & C_p^{M(init)} \end{bmatrix} \begin{bmatrix} 0 & \dots & 0 & \dots & 0 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & 0 & \dots & \frac{1}{j-i} & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & -\frac{1}{j-i} & \dots & 0 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & 0 & \dots & 0 & \dots & 0 \end{bmatrix} \begin{bmatrix} C_U^{1(eq)} \\ \dots \\ C_U^{K(eq)} \\ \dots \\ C_U^{j(eq)} \\ \dots \\ C_U^{M(eq)} \end{bmatrix} \\
 &= \frac{1}{j-i} (C_p^i C_U^j - C_U^i C_p^j)
 \end{aligned} \tag{S5}$$



As shown in **Table 5** in the main text, the initial concentration of P is constant. Thus, Eq. S5 can be simplified as

$$V_{i,j} = \frac{C_P}{j-i} (C_U^{j(eq)} - C_U^{i(eq)}) \quad (S6)$$

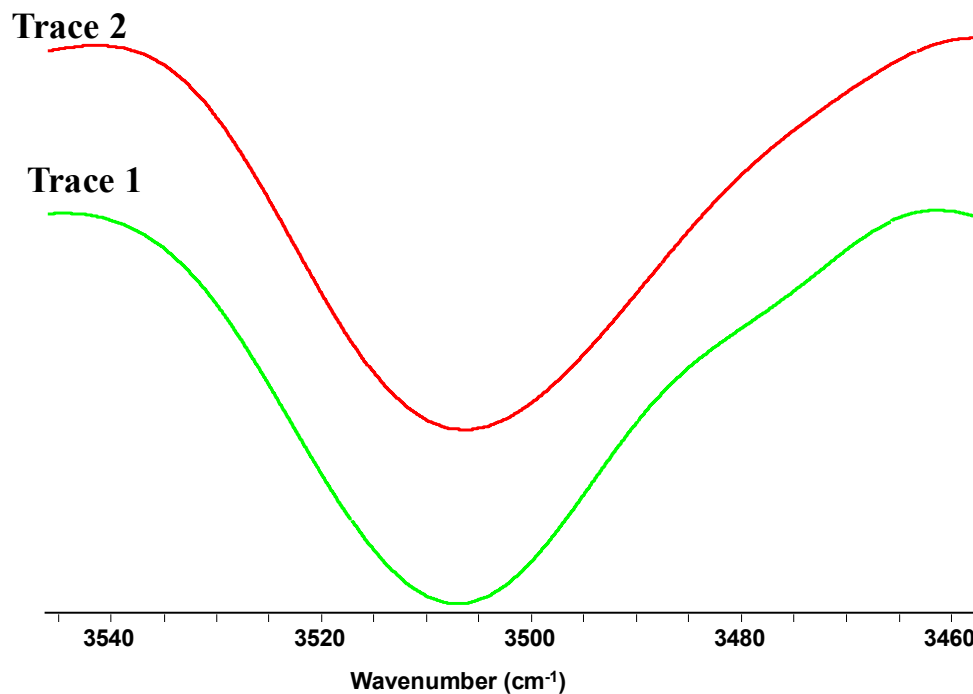
In addition, the initial concentration of Q decreases with the increment of i.

Namely,  $C_Q^{i(init)} > C_Q^{j(init)}$ , when  $i < j$ .

Moreover, the initial concentration of P is constant. For the equilibrium reaction shown in eq. 1 in the main text, we have:  $C_U^i > C_U^j$ , when  $i < j$ .

Thus, we have  $V_{i,j} < 0$ . Since every  $V_{i,j}$  is negative, the summation of all the  $V_{i,j}$  terms are negative. Therefore, we come to the following conclusion: Although we do not know the exact values of equilibrium concentration of U, the sign of the intensity factor  $(\vec{C}_P^{(init)})^T \mathbf{N} \vec{C}_U^{(eq)}$  is always positive when the initial concentrations of P and Q are adopted as in **Table 5** in the main text.

**Part 3 Second derivative spectra of the OH stretching bands of a diethyl solution contain methanol and a THF solution containing methanol.**



**Figure S4** Second derivative spectrum of

Trace 1: The OH stretching band of diethyl ether solution containing methanol ( $2.47 \times 10^{-4}$  mol/ml)

Trace 2: The OH stretching band of diethyl ether solution containing methanol ( $2.47 \times 10^{-4}$  mol/ml) and THF ( $7.40 \times 10^{-4}$  mol/ml)

**Part 4 The relationship between the patterns of cross peak in 2D asynchronous spectrum and possible changes of the peak parameters of the characteristic peak of U.**

To explore what happens on the OH stretching band when the methanol-THF complexes is formed. We performed a computer simulate on a model system. Herein P stands for the OH stretching band of

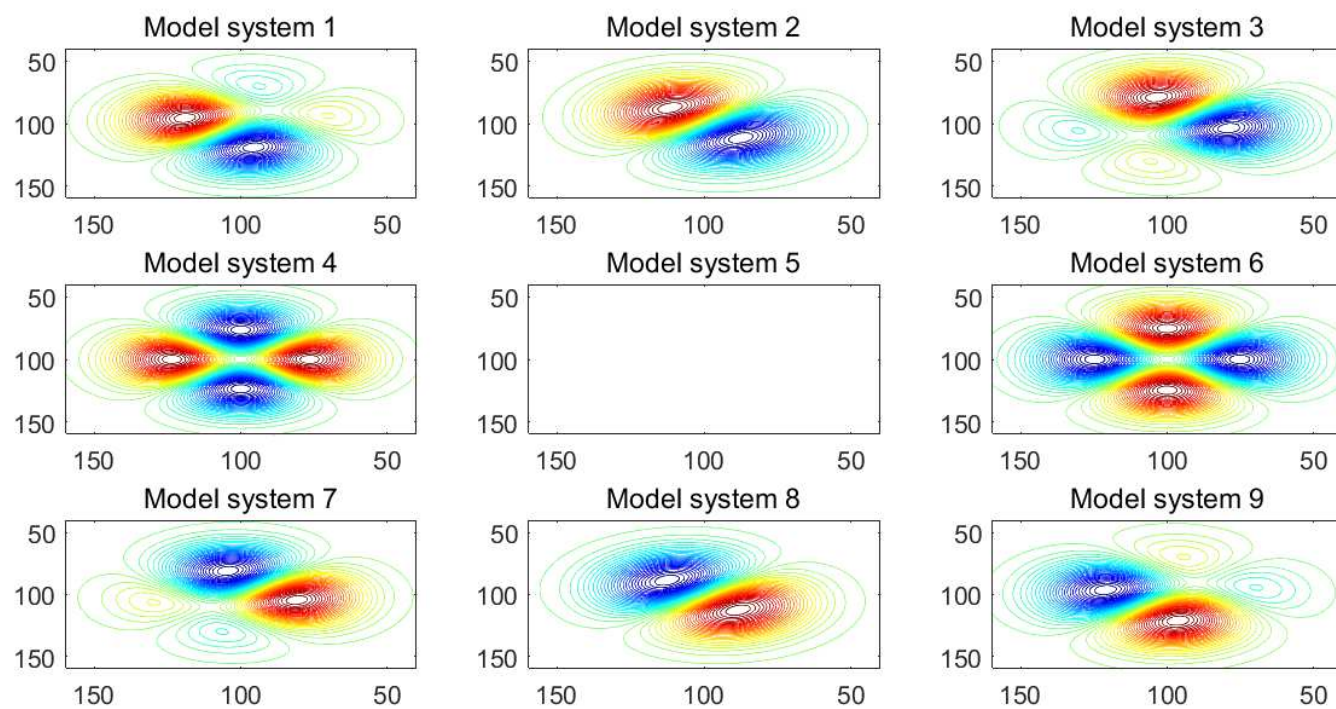
methanol-diethyl ether complex and U stands for the OH stretching band of the methanol-THF complex. Since the pattern of cross peaks around cannot be used to reflect the changes on the changes of the absorptivity of the band, the absorptivity of the peak of band U are all set the same as P. The qualitative difference on peak position, bandwidth can be classified into nine situations shown in **Table S2**.

**Table S2 Nine possible situations concerning the changes on peak position and bandwidth of the 100 cm<sup>-1</sup> band. The peak position and bandwidth of P are 100 cm<sup>-1</sup> and 20 cm<sup>-1</sup>, respectively.**

Model systems	Peak position (cm <sup>-1</sup> )	Bandwidth (cm <sup>-1</sup> )
1	99	19
2	99	20
3	99	21
4	100	19
5	100	20
6	100	21
7	101	19
8	101	20
9	101	21

The corresponding cross peak of pattern factor is shown in **Figure S3**. The pattern of **Figure 3B** in the main text is the same as **Situation**

**System 2** in **Figure S5**. That is to say, the bandwidth of the OH stretching band of the methanol-THF complex is almost the same as that of the methanol-diethyl ether. Moreover, the OH stretching band of the methanol-THF complex exhibits a red shift in comparison with that of the methanol-diethyl complex.



**Figure S5** Cross peaks around (100, 100) in  $\Psi(x, y)$  of the nine model systems, the peak parameter of U can be found in

**Table S2.**