Two-dimensional Asynchronous spectrum with auxiliary cross peaks in probing intermolecular interactions

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Appendix

1. The expression of the asynchronous correlation spectrum in the ASAP approach.

$$\Psi(\nu_1,\nu_2)=\frac{1}{n-1}\sum_{i=1}^{25}\mathrm{R}_i(\nu_1,\nu_2) \tag{A1}$$

$$\begin{aligned}
\mathrm{R}_1(\nu_1,\nu_2)&=\mathrm{f}_\mathrm{P}(\nu_1)\,\mathrm{f}_\mathrm{P}(\nu_2)[\vec{\tilde{C}}_\mathrm{P}^{\mathrm{init}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{P}^{\mathrm{init}}]\\
\mathrm{R}_2(\nu_1,\nu_2)&=\mathrm{f}_\mathrm{P}(\nu_1)\,\mathrm{f}_\mathrm{Q}(\nu_2)[\vec{\tilde{C}}_\mathrm{P}^{\mathrm{init}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{Q}^{\mathrm{init}}]\\
\mathrm{R}_3(\nu_1,\nu_2)&=\mathrm{f}_\mathrm{P}(\nu_1)[\mathrm{f}_\mathrm{U}(\nu_2)-\mathrm{f}_\mathrm{P}(\nu_2)][\vec{\tilde{C}}_\mathrm{P}^{\mathrm{init}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{U}^{\mathrm{seq}}]\\
\mathrm{R}_4(\nu_1,\nu_2)&=\mathrm{f}_\mathrm{P}(\nu_1)[\mathrm{f}_\mathrm{V}(\nu_2)-\mathrm{f}_\mathrm{Q}(\nu_2)][\vec{\tilde{C}}_\mathrm{P}^{\mathrm{init}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{V}^{\mathrm{seq}}]\\
\mathrm{R}_5(\nu_1,\nu_2)&=\mathrm{f}_\mathrm{P}(\nu_1)\,\mathrm{f}_\mathrm{S}(\nu_2)[\vec{\tilde{C}}_\mathrm{P}^{\mathrm{init}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{S}^{\mathrm{init}}]\\
\mathrm{R}_6(\nu_1,\nu_2)&=\mathrm{f}_\mathrm{Q}(\nu_1)\,\mathrm{f}_\mathrm{P}(\nu_2)[\vec{\tilde{C}}_\mathrm{Q}^{\mathrm{init}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{P}^{\mathrm{init}}]\\
\mathrm{R}_7(\nu_1,\nu_2)&=\mathrm{f}_\mathrm{Q}(\nu_1)\,\mathrm{f}_\mathrm{Q}(\nu_2)[\vec{\tilde{C}}_\mathrm{Q}^{\mathrm{init}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{Q}^{\mathrm{init}}]\\
\mathrm{R}_8(\nu_1,\nu_2)&=\mathrm{f}_\mathrm{Q}(\nu_1)[\mathrm{f}_\mathrm{U}(\nu_2)-\mathrm{f}_\mathrm{P}(\nu_2)][\vec{\tilde{C}}_\mathrm{Q}^{\mathrm{init}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{U}^{\mathrm{seq}}]\\
\mathrm{R}_9(\nu_1,\nu_2)&=\mathrm{f}_\mathrm{Q}(\nu_1)[\mathrm{f}_\mathrm{V}(\nu_2)-\mathrm{f}_\mathrm{Q}(\nu_2)][\vec{\tilde{C}}_\mathrm{Q}^{\mathrm{init}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{V}^{\mathrm{seq}}]\\
\mathrm{R}_{10}(\nu_1,\nu_2)&=\mathrm{f}_\mathrm{Q}(\nu_1)\,\mathrm{f}_\mathrm{S}(\nu_2)[\vec{\tilde{C}}_\mathrm{Q}^{\mathrm{init}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{S}^{\mathrm{init}}]\\
\mathrm{R}_{11}(\nu_1,\nu_2)&=[\mathrm{f}_\mathrm{U}(\nu_1)-\mathrm{f}_\mathrm{P}(\nu_1)]\,\mathrm{f}_\mathrm{P}(\nu_2)[\vec{\tilde{C}}_\mathrm{U}^{\mathrm{seq}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{P}^{\mathrm{init}}]\\
\mathrm{R}_{12}(\nu_1,\nu_2)&=[\mathrm{f}_\mathrm{U}(\nu_1)-\mathrm{f}_\mathrm{P}(\nu_1)]\,\mathrm{f}_\mathrm{Q}(\nu_2)[\vec{\tilde{C}}_\mathrm{U}^{\mathrm{seq}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{Q}^{\mathrm{init}}]\\
\mathrm{R}_{13}(\nu_1,\nu_2)&=[\mathrm{f}_\mathrm{U}(\nu_1)-\mathrm{f}_\mathrm{P}(\nu_1)][\mathrm{f}_\mathrm{U}(\nu_2)-\mathrm{f}_\mathrm{P}(\nu_2)][\vec{\tilde{C}}_\mathrm{U}^{\mathrm{seq}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{U}^{\mathrm{seq}}]\\
\mathrm{R}_{14}(\nu_1,\nu_2)&=[\mathrm{f}_\mathrm{U}(\nu_1)-\mathrm{f}_\mathrm{P}(\nu_1)][\mathrm{f}_\mathrm{V}(\nu_2)-\mathrm{f}_\mathrm{Q}(\nu_2)][\vec{\tilde{C}}_\mathrm{U}^{\mathrm{seq}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{V}^{\mathrm{seq}}]\\
\mathrm{R}_{15}(\nu_1,\nu_2)&=[\mathrm{f}_\mathrm{U}(\nu_1)-\mathrm{f}_\mathrm{P}(\nu_1)]\,\mathrm{f}_\mathrm{S}(\nu_2)[\vec{\tilde{C}}_\mathrm{U}^{\mathrm{seq}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{S}^{\mathrm{init}}]\\
\mathrm{R}_{16}(\nu_1,\nu_2)&=[\mathrm{f}_\mathrm{V}(\nu_1)-\mathrm{f}_\mathrm{Q}(\nu_1)]\,\mathrm{f}_\mathrm{P}(\nu_2)[\vec{\tilde{C}}_\mathrm{V}^{\mathrm{seq}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{P}^{\mathrm{init}}]\\
\mathrm{R}_{17}(\nu_1,\nu_2)&=[\mathrm{f}_\mathrm{V}(\nu_1)-\mathrm{f}_\mathrm{Q}(\nu_1)]\,\mathrm{f}_\mathrm{Q}(\nu_2)[\vec{\tilde{C}}_\mathrm{V}^{\mathrm{seq}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{Q}^{\mathrm{init}}]\\
\mathrm{R}_{18}(\nu_1,\nu_2)&=[\mathrm{f}_\mathrm{V}(\nu_1)-\mathrm{f}_\mathrm{Q}(\nu_1)][\mathrm{f}_\mathrm{U}(\nu_2)-\mathrm{f}_\mathrm{P}(\nu_2)][\vec{\tilde{C}}_\mathrm{V}^{\mathrm{seq}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{U}^{\mathrm{seq}}]\\
\mathrm{R}_{19}(\nu_1,\nu_2)&=[\mathrm{f}_\mathrm{V}(\nu_1)-\mathrm{f}_\mathrm{Q}(\nu_1)][\mathrm{f}_\mathrm{V}(\nu_2)-\mathrm{f}_\mathrm{Q}(\nu_2)][\vec{\tilde{C}}_\mathrm{V}^{\mathrm{seq}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{V}^{\mathrm{seq}}]\\
\mathrm{R}_{20}(\nu_1,\nu_2)&=[\mathrm{f}_\mathrm{V}(\nu_1)-\mathrm{f}_\mathrm{Q}(\nu_1)]\,\mathrm{f}_\mathrm{S}(\nu_2)[\vec{\tilde{C}}_\mathrm{V}^{\mathrm{seq}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{S}^{\mathrm{init}}]\\
\mathrm{R}_{21}(\nu_1,\nu_2)&=\mathrm{f}_\mathrm{S}(\nu_1)\,\mathrm{f}_\mathrm{P}(\nu_2)[\vec{\tilde{C}}_\mathrm{S}^{\mathrm{init}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{P}^{\mathrm{init}}]\\
\mathrm{R}_{22}(\nu_1,\nu_2)&=\mathrm{f}_\mathrm{S}(\nu_1)\,\mathrm{f}_\mathrm{Q}(\nu_2)[\vec{\tilde{C}}_\mathrm{S}^{\mathrm{init}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{Q}^{\mathrm{init}}]\\
\mathrm{R}_{23}(\nu_1,\nu_2)&=\mathrm{f}_\mathrm{S}(\nu_1)[\mathrm{f}_\mathrm{U}(\nu_2)-\mathrm{f}_\mathrm{P}(\nu_2)][\vec{\tilde{C}}_\mathrm{S}^{\mathrm{init}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{U}^{\mathrm{seq}}]\\
\mathrm{R}_{24}(\nu_1,\nu_2)&=\mathrm{f}_\mathrm{S}(\nu_1)[\mathrm{f}_\mathrm{V}(\nu_2)-\mathrm{f}_\mathrm{Q}(\nu_2)][\vec{\tilde{C}}_\mathrm{S}^{\mathrm{init}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{V}^{\mathrm{seq}}]\\
\mathrm{R}_{25}(\nu_1,\nu_2)&=\mathrm{f}_\mathrm{S}(\nu_1)\,\mathrm{f}_\mathrm{S}(\nu_2)[\vec{\tilde{C}}_\mathrm{S}^{\mathrm{init}}]^\mathrm{T}\mathbf{N}[\vec{\tilde{C}}_\mathrm{S}^{\mathrm{init}}]
\end{aligned}$$

2. In the main text, we pointed out $\mathrm{R}_{21}(\nu_1,\nu_2)$ and $\mathrm{R}_{22}(\nu_1,\nu_2)$ in the ASAP

approach can be removed when the concentration series of S is in a linear relationship with the initial concentration of P and Q simultaneously.

$$a\,\mathrm{C}_{\mathrm{S}}^{i(\mathrm{init})} + b\,\mathrm{C}_{\mathrm{Q}}^{i(\mathrm{init})} = c \tag{A2a}$$

$$m\,\mathrm{C}_{\mathrm{S}}^{i(\mathrm{init})} + h\,\mathrm{C}_{\mathrm{P}}^{i(\mathrm{init})} = d \tag{A2b}$$

where a , b , c, m, h and d are preset constants.

Eq. A2 also can be expressed by Eq. A3.

$$\mathrm{C}_{\mathrm{Q}}^{i(\mathrm{init})} = \frac{c}{b} - \frac{a\,\mathrm{C}_{\mathrm{S}}^{i(\mathrm{init})}}{b} \tag{A3a}$$

$$\mathrm{C}_{\mathrm{P}}^{i(\mathrm{init})} = \frac{d}{h} - \frac{m\,\mathrm{C}_{\mathrm{S}}^{i(\mathrm{init})}}{h} \tag{A3b}$$

The expression of dynamic concentration of P, Q and S are given in Eq. A4.

$$\tilde{\mathrm{C}}_{\mathrm{Q}}^{i(\mathrm{init})} = \mathrm{C}_{\mathrm{Q}}^{i(\mathrm{init})} - \mathrm{C}_{\mathrm{Q}}^{\mathrm{init(av)}} = \frac{c}{b} - \frac{a\,\mathrm{C}_{\mathrm{S}}^{i(\mathrm{init})}}{b} - \mathrm{C}_{\mathrm{Q}}^{\mathrm{init(av)}} \tag{A4a}$$

$$\tilde{\mathrm{C}}_{\mathrm{P}}^{i(\mathrm{init})} = \mathrm{C}_{\mathrm{P}}^{i(\mathrm{init})} - \mathrm{C}_{\mathrm{P}}^{\mathrm{init(av)}} = \frac{d}{h} - \frac{m\,\mathrm{C}_{\mathrm{S}}^{i(\mathrm{init})}}{h} - \mathrm{C}_{\mathrm{P}}^{\mathrm{init(av)}} \tag{A4b}$$

$$\tilde{\mathrm{C}}_{\mathrm{S}}^{i(\mathrm{init})} = \mathrm{C}_{\mathrm{S}}^{i(\mathrm{init})} - \mathrm{C}_{\mathrm{S}}^{\mathrm{init(av)}} \tag{A4c}$$

where $\mathrm{C}_{\mathrm{Q}}^{\mathrm{init(av)}}$, $\mathrm{C}_{\mathrm{P}}^{\mathrm{init(av)}}$ and $\mathrm{C}_{\mathrm{S}}^{\mathrm{init(av)}}$ are the average concentration of Q, P and S over n solutions.

$$\mathrm{C}_{\mathrm{Q}}^{\mathrm{init(av)}} = \frac{1}{n}\sum_{n}^{i=1} \mathrm{C}_{\mathrm{Q}}^{i(\mathrm{init})} \tag{A5a}$$

$$\mathrm{C}_{\mathrm{P}}^{\mathrm{init(av)}} = \frac{1}{n}\sum_{n}^{i=1} \mathrm{C}_{\mathrm{P}}^{i(\mathrm{init})} \tag{A5b}$$

$$C_{\mathrm{S}}^{\mathrm{init(av)}} = \frac{1}{n}\sum_{n}^{i=1} C_{\mathrm{S}}^{i(\mathrm{init})} \tag{A5c}$$

After combining Eq. A3 to Eq. A5, Eq. A4 changes into the following expressions.

$$\tilde{C}_{\mathrm{Q}}^{i(\mathrm{init})} = C_{\mathrm{Q}}^{i(\mathrm{init})} - C_{\mathrm{Q}}^{\mathrm{init(av)}} = \frac{c}{b} - \frac{a\,C_{\mathrm{S}}^{i(\mathrm{init})}}{b} - C_{\mathrm{Q}}^{\mathrm{init(av)}} = \frac{c}{b} - \frac{a\,C_{\mathrm{S}}^{i(\mathrm{init})}}{b} - \frac{c}{b} - \frac{a C_{\mathrm{S}}^{\mathrm{init(av)}}}{b} = -\frac{a\tilde{C}_{\mathrm{S}}^{i(\mathrm{init})}}{b} \tag{A6a}$$

$$\tilde{C}_{\mathrm{P}}^{i(\mathrm{init})} = C_{\mathrm{P}}^{i(\mathrm{init})} - C_{\mathrm{P}}^{\mathrm{init(av)}} = \frac{d}{h} - \frac{m\,C_{\mathrm{S}}^{i(\mathrm{init})}}{h} - C_{\mathrm{P}}^{\mathrm{init(av)}} = \frac{d}{h} - \frac{m\,C_{\mathrm{S}}^{i(\mathrm{init})}}{h} - \frac{d}{h} - \frac{m C_{\mathrm{S}}^{\mathrm{init(av)}}}{h} = -\frac{m\tilde{C}_{\mathrm{S}}^{i(\mathrm{init})}}{h} \tag{A6b}$$

Thus:

$$\vec{\tilde{C}}_{\mathrm{Q}}^{\mathrm{init}} = -\frac{a}{b}\vec{\tilde{C}}_{\mathrm{S}}^{\mathrm{init}} \tag{A7a}$$

$$\vec{\tilde{C}}_{\mathrm{P}}^{\mathrm{init}} = -\frac{m}{h}\vec{\tilde{C}}_{\mathrm{S}}^{\mathrm{init}} \tag{A7b}$$

Therefore:

$$\mathrm{R}_{21}(\nu_1,\nu_2) = \mathrm{f}_{\mathrm{P}}(\nu_1)\mathrm{f}_{\mathrm{S}}(\nu_2)[\vec{\tilde{C}}_{\mathrm{P}}^{\mathrm{init}}]^{\mathrm{T}}\mathbf{N}[\vec{\tilde{C}}_{\mathrm{S}}^{\mathrm{init}}] = \mathrm{f}_{\mathrm{P}}(\nu_1)\mathrm{f}_{\mathrm{S}}(\nu_2)[-\frac{m}{h}\vec{\tilde{C}}_{\mathrm{S}}^{\mathrm{init}}]^{\mathrm{T}}\mathbf{N}[\vec{\tilde{C}}_{\mathrm{S}}^{\mathrm{init}}] = -\frac{m}{h}\mathrm{f}_{\mathrm{P}}(\nu_1)\mathrm{f}_{\mathrm{S}}(\nu_2)[\vec{\tilde{C}}_{\mathrm{S}}^{\mathrm{init}}]^{\mathrm{T}}\mathbf{N}[\vec{\tilde{C}}_{\mathrm{S}}^{\mathrm{init}}] \tag{A8a}$$

$$\mathrm{R}_{22}(\nu_1,\nu_2) = \mathrm{f}_{\mathrm{Q}}(\nu_1)\mathrm{f}_{\mathrm{S}}(\nu_2)[\vec{\tilde{C}}_{\mathrm{Q}}^{\mathrm{init}}]^{\mathrm{T}}\mathbf{N}[\vec{\tilde{C}}_{\mathrm{S}}^{\mathrm{init}}] = \mathrm{f}_{\mathrm{Q}}(\nu_1)\mathrm{f}_{\mathrm{S}}(\nu_2)[-\frac{a}{b}\vec{\tilde{C}}_{\mathrm{S}}^{\mathrm{init}}]^{\mathrm{T}}\mathbf{N}[\vec{\tilde{C}}_{\mathrm{S}}^{\mathrm{init}}] = -\frac{a}{b}\mathrm{f}_{\mathrm{Q}}(\nu_1)\mathrm{f}_{\mathrm{S}}(\nu_2)[\vec{\tilde{C}}_{\mathrm{S}}^{\mathrm{init}}]^{\mathrm{T}}\mathbf{N}[\vec{\tilde{C}}_{\mathrm{S}}^{\mathrm{init}}] \tag{A8b}$$

Based on the property of Hilbert-Noda transformation matrix **N** listed in Eq. A9, the value of R_{21} and R_{22} is zero.

$$\vec{\mathbf{B}}^{\mathrm{T}}\mathbf{N}\vec{\mathbf{B}} = 0 \tag{A9}$$

$$\mathrm{R}_{21}(\nu_1,\nu_2) = 0 \tag{A10a}$$

$$\mathrm{R}_{22}(\nu_1,\nu_2) = 0 \tag{A10b}$$