## The "sequential order" rules in mechanical perturbation-based 2D infrared spectroscopy

For the completeness of discussion, the "sequential order" rules in mechanical perturbation-based 2D infrared spectroscopy ${ }^{29}$ are cited below:

Rule 1. If the asynchronous cross peak is located at the upper left section of the spectrum $\left(v_{1}>v_{2}\right)$, and the sign of the peak is positive, i.e., $\Psi\left(v_{1}, v_{2}\right)>0$, the dipole-transition moment associated with the band at the higher wavenumber $v_{1}$ reorients before the transition moment at $v_{2}$.

Rule 2. If the positive asynchronous cross peak is located at the lower right section of the spectrum $\left(v_{1}<v_{2}\right)$, the dipole-transition moment at lower wavenumber $v_{1}$ reorients before the transition moment at $v_{2}$.

Rule 3. For a negative cross peak, i.e., $\Psi\left(v_{1}, v_{2}\right)<0$, the temporal relationships described in Rules 1 and 2 are reversed.

Rule 4. If the corresponding synchronous correlation intensity at the same coordinate is negative, i.e., $\Phi\left(v_{1}, v_{2}\right)<0$, the temporal relationships described in Rules 1,2 , and 3 are reversed.

Rule 5. If the asynchronous correlation intensity at the coordinate vanishes, i.e.,
$\Psi\left(v_{1}, v_{2}\right)=0$, the reorientations of the two dipole-transition moments occur simultaneously.

Rule 6. If the synchronous correlation intensity at the same coordinate vanishes, i.e., $\Phi\left(v_{1}, v_{2}\right)=0$, the temporal relationship between the reorientations of dipole-transition moments cannot be determined.

It is well-known that in mechanical perturbation-based 2D infrared spectroscopy, the time-dependent behavior (i.e., waveform) of dynamic spectral intensity variations must be a simple sinusoid, i.e., a periodic change. Based on the dynamic IR linear dichroism (DIRLD) experimental set-up, the dynamic dichroic difference signal generated by the system is expected to take the form:

$$
\begin{equation*}
\Delta \tilde{A}(v, t)=\Delta \hat{A}(v) \sin [\omega t+\beta(v)] \tag{1}
\end{equation*}
$$

, which may also be expressed in terms of the sum of two orthogonal components:

$$
\begin{equation*}
\Delta \tilde{A}(v, t)=\Delta A^{\prime}(v) \sin \omega t+\Delta A^{\prime \prime}(v) \cos \omega t \tag{2}
\end{equation*}
$$

$\Delta A^{\prime}(v)$ and $\Delta A^{\prime \prime}(v)$ are respectively the in-phase spectrum and quadrature spectrum of the dynamic dichroism.

For a pair of dynamic IR dichroism signals measured at two different wavenumbers, $\Delta \tilde{A}\left(v_{1}, t\right)$ and $\Delta \tilde{A}\left(v_{2}, t\right)$, the dynamic IR cross-correlation function $X(\tau)$ is defined as:

$$
\begin{equation*}
X(\tau)=\lim _{T \rightarrow \infty} \frac{1}{T} \int_{-T / 2}^{T / 2} \Delta \tilde{A}\left(v_{1}, t\right) \cdot \Delta \tilde{A}\left(v_{2}, t+\tau\right) \mathrm{d} t \tag{3}
\end{equation*}
$$

For two periodic signals with an identical angular frequency $\omega$, the cross correlation function reduces to a very simple form:

$$
\begin{equation*}
X(\tau)=\Phi\left(v_{1}, v_{2}\right) \cos \omega \tau+\Psi\left(v_{1}, v_{2}\right) \sin \omega \tau \tag{4}
\end{equation*}
$$

The synchronous and asynchronous (quadrature) correlation intensities, $\Phi\left(v_{1}, v_{2}\right)$ and $\Psi\left(v_{1}, v_{2}\right)$, of the dynamic spectrum are given by:

$$
\begin{align*}
\Phi\left(v_{1}, v_{2}\right) & =1 / 2 \Delta \hat{A}\left(v_{1}\right) \cdot \Delta \hat{A}\left(v_{2}\right) \cos \left[\beta\left(v_{1}\right)-\beta\left(v_{2}\right)\right]  \tag{5}\\
& =1 / 2\left[\Delta A^{\prime}\left(v_{1}\right) \cdot \Delta A^{\prime}\left(v_{2}\right)+\Delta A^{\prime \prime}\left(v_{1}\right) \cdot \Delta A^{\prime \prime}\left(v_{2}\right)\right]
\end{align*}
$$

and

$$
\begin{align*}
\Psi\left(v_{1}, v_{2}\right) & =1 / 2 \Delta \hat{A}\left(v_{1}\right) \cdot \Delta \hat{A}\left(v_{2}\right) \sin \left[\beta\left(v_{1}\right)-\beta\left(v_{2}\right)\right] \\
& =1 / 2\left[\Delta A^{\prime \prime}\left(v_{1}\right) \cdot \Delta A^{\prime}\left(v_{2}\right)-\Delta A^{\prime}\left(v_{1}\right) \cdot \Delta A^{\prime \prime}\left(v_{2}\right)\right] \tag{6}
\end{align*}
$$

It is believed that the signs of the cross peaks of an asynchronous 2D correlation spectrum reveal the relative temporal relationship or order of the actual sequence of reorientation processes for various dipole-transition moments ${ }^{29}$, and the abovementioned set of rules was developed to determine the temporal sequence of reorientation processes based on above equations.

## A simulation study on the sequential order in mechanical perturbation-based 2D IR spectroscopy

From the sequential order rules, three cases may be summarized in mechanical perturbation-based 2D IR spectroscopy and the sequential order of two sinusoidal changes may be demonstrated using simulation data:
(1) $\Phi\left(v_{1}, v_{2}\right) \neq 0, \Psi\left(v_{1}, v_{2}\right) \neq 0$; (rules 1-4 )
(2) $\Phi\left(v_{1}, v_{2}\right) \neq 0, \Psi\left(v_{1}, v_{2}\right)=0$; (rule 5 )
(3) $\Phi\left(v_{1}, v_{2}\right)=0, \Psi\left(v_{1}, v_{2}\right) \neq 0 ;($ rule 6$)$

Case 1, Both $\Phi\left(v_{1}, v_{2}\right)$ and $\Psi\left(v_{1}, v_{2}\right)$ are nonzero in case 1 . One such example is demonstrated in figure 1, where the band intensity change at $1650 \mathrm{~cm}^{-1}$ takes the form of $y=5[\sin (0.4 x)+1]$ and that at $1720 \mathrm{~cm}^{-1}$ takes the form of $y=5[\sin (0.4 x+\pi / 4)+1]$, i.e., the function at $1720 \mathrm{~cm}^{-1}$ is $\pi / 4$ ahead of that at $1650 \mathrm{~cm}^{-1}$. The 2D results are shown in figure $1(\mathrm{C}$ and D$)$.


Figure 1, The band intensity change at $1650 \mathrm{~cm}^{-1}$ and $1720 \mathrm{~cm}^{-1}$ takes the form of

$$
y=5[\sin (0.4 x)+1] \text { and } y=5[\sin (0.4 x+\pi / 4)+1] \text {, respectively. }
$$

From the signs of the two cross peaks $(\Psi(1720,1650)>0, \Psi(1720,1650)>0)$ in the 2D plots, it is easy to judge using the above rules (1 and 3) that the band intensity change at $1720 \mathrm{~cm}^{-1}$ occurs before that at $1650 \mathrm{~cm}^{-1}$. This is consistent with the function forms they take, i.e., the $1720 \mathrm{~cm}^{-1}$ function is $\pi / 4$ ahead.

Figure 2 shows the result of two similar functions as in figure 1. The only difference is the phase difference of two functions, thereby the signs of the two cross peaks in the asynchronous plot.


Figure 2, The band intensity changes at $1650 \mathrm{~cm}^{-1}$ and $1720 \mathrm{~cm}^{-1}$ takes the form of

$$
1650 \mathrm{~cm}^{-1} \quad y=5[\sin (0.4 x)+1] \text { and } \quad y=5[\sin (0.4 x-\pi / 4)+1] \text { respectively. }
$$

Now, from the signs of the two cross peaks $(\Psi(1720,1650)>0, \Psi(1720,1650)<0)$ in the 2D plots, it is easy to judge using the above rules (2 and 3) that the band intensity change at $1720 \mathrm{~cm}^{-1}$ occurs after that at $1650 \mathrm{~cm}^{-1}$. This is also consistent with the function forms they take, i.e., the function at $1720 \mathrm{~cm}^{-1}$ is $\pi / 4 \mathrm{lag}$ behind.

It should be kept in mind that "the band intensity change at $1720 \mathrm{~cm}^{-1}$ occurs before/after that at $1650 \mathrm{~cm}^{-1 "}$ in the above examples means that the phase of the $1720 \mathrm{~cm}^{-1}$ signal is larger (earlier)/smaller (later) than that of the $1650 \mathrm{~cm}^{-1}$ signal.

Case 2, In this case, $\Phi\left(v_{1}, v_{2}\right) \neq 0, \Psi\left(v_{1}, v_{2}\right)=0$. This means that the two functions are completely in phase. This case can be straightforwardly demonstrated by assuming that the band intensity changes at $1650 \mathrm{~cm}^{-1}$ and $1720 \mathrm{~cm}^{-1}$ take the same
function form with only difference in magnitude. Figure 3A shows the band intensity changes with time (step). The 2D result is plotted in figure 3 (C and D). No asynchronous signal was observed, indicating that the two band intensity changes at $1650 \mathrm{~cm}^{-1}$ and $1720 \mathrm{~cm}^{-1}$ occur simultaneously, in terms of no phase difference.


Figure 3, The band intensity changes at $1650 \mathrm{~cm}^{-1}$ and $1720 \mathrm{~cm}^{-1}$ takes the form of

$$
y=7.5[\sin (0.4 x)+1] \text { and } y=5[\sin (0.4 x)+1] \text {, respectively. }
$$

Case 3. $\Phi\left(v_{1}, v_{2}\right)=0, \Psi\left(v_{1}, v_{2}\right) \neq 0$. This means that two functions must be 90 degree out of phase. This can be easily demonstrated in figure 4, where the band intensity change at $1650 \mathrm{~cm}^{-1}$ takes the form of $y=5[\sin (0.4 x)+1]$, and that at $1720 \mathrm{~cm}^{-1} \quad y=5[\sin (0.4 x+\pi / 2)+1]$. There is a phase difference of $\pi / 2$.


Figure 4, The band intensity change at $1650 \mathrm{~cm}^{-1}$ and $1720 \mathrm{~cm}^{-1}$ takes the form of

$$
y=5[\sin (0.4 x)+1] \text { and } y=5[\sin (0.4 x+\pi / 2)+1] \text {, respectively. }
$$

For two functions with a phase difference of $\pi / 2$, they may also take the forms of $y=5[\sin (0.4 x)+1]\left(1650 \mathrm{~cm}^{-1}\right)$ and $y=5[\sin (0.4 x-\pi / 2)+1]\left(1720 \mathrm{~cm}^{-1}\right)$, i.e., the function at $1720 \mathrm{~cm}^{-1}$ is $\pi / 2$ lag behind. The corresponding 2 D result is shown in figure $5(\mathrm{C}$ and D$)$.

## "Sequential order" rules in generalized 2D correlation spectroscopy

The synchronous and asynchronous 2D correlation intensities of two dynamic spectra $\tilde{y}_{j}\left(v_{1}\right), \widetilde{y}_{j}\left(v_{2}\right)$ in generalized 2D correlation spectroscopy are calculated in a different way from that in mechanical-perturabation based 2D IR correlation spectrsocopy:

$$
\begin{align*}
& \Phi\left(v_{1}, v_{2}\right)=\frac{1}{m-1} \sum_{j=1}^{m} \widetilde{y}_{j}\left(v_{1}\right) \bullet \tilde{y}_{j}\left(v_{2}\right)  \tag{7}\\
& \Psi\left(v_{1}, v_{2}\right)=\frac{1}{m-1} \sum_{j=1}^{m} \widetilde{y}_{j}\left(v_{1}\right) \cdot \widetilde{z}_{j}\left(v_{2}\right) \tag{8}
\end{align*}
$$

, and the discrete orthogonal spectra $\widetilde{z}_{j}\left(v_{2}\right)$ can be obtained from the dynamic spectra $\tilde{y}_{k}\left(v_{2}\right)$ by using a simple linear transformation operation

$$
\begin{equation*}
\widetilde{z}_{j}\left(v_{2}\right)=\sum_{k=1}^{m} N_{j k} \cdot \widetilde{y}_{k}\left(v_{2}\right) \tag{9}
\end{equation*}
$$

where,

$$
N_{j k}= \begin{cases}0 & \text { if } j=k  \tag{10}\\ \frac{1}{\pi(k-j)} & \text { otherwise }\end{cases}
$$

Because the dynamic spectrum vector $\widetilde{z}_{j}\left(v_{2}\right)$ is orthogonal to $\widetilde{y}_{k}\left(v_{2}\right)$, this transformation is taken as shifting the phase of each Fourier component of a function forward or backward by $\pi / 2$, which resulted in the automatic transfer with a simplified statement of the "sequential order" rules of the mechanical perturbation-based 2D IR spectroscopy to the generalized methodology, as cited below:
"The sign of an asynchronous cross peak becomes positive if the intensity change at $v_{1}$ occurs predominantly before $v_{2}$. On the other hand, the peak sign becomes negative if the change at $v_{1}$ occurs predominantly after $v_{2}$. However, this sign rule is reversed if the synchronous correlation intensity at the same coordinate becomes negative, i.e., $\Phi\left(v_{1}, v_{2}\right)<0$. Furthermore, if the intensity of the synchronous cross peak is zero, the sequential order cannot be determined."

