Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Extracting Molecular Responses from Ultrafast Charge Dynamics at Material Interfaces

Chenglai Wang†[2], Yingmin Li†[2], Wei Xiong*[1,2]

Email: w2xiong@ucsd.edu

[1] Department of Chemistry and Biochemistry, University of California - San Diego, La Jolla, CA

[2] Materials Science and Engineering Program, University of California – San Diego, La Jolla, CA

Supplementary Materials

S1. A detailed procedure of data analysis method

The essential part of model input is described by equation 2, consisting of three components, two Lorentzian functions L_i served as molecular responses, and one constant served as non-resonant responses, NR; the corresponding dynamics are modeled by several single exponentials, T_i; Lastly, the IR spectra are modeled by a Gaussian profile, G.

$$R(\omega,t) = \{[L_1(\omega) + NR_1(\omega)] * T_1(t) + [L_2(\omega)] * T_2(t) + [NR_2(\omega)] * T_3(t)\} * G(\omega) \quad L_i(\omega) = \frac{\Delta a_i * e^{i*\varphi_i}}{\omega - b_i + i * c_i},$$

$$T_i(t) = e^{-t/\tau_i}, \quad NR_i(\omega) = \Delta a_{NRi} * e^{i\varphi_{NRi}}, \quad G(w) = g * e^{-(\frac{\omega-\omega 0}{\delta})^2}$$

Table 1. Parameters of the model input

	Molecular Resonance L_1	**Molecular Resonance L_2**	
Amplitude (Δa_i)	-2	-3	
Center wavelength (b_i, cm^{-1})	2830	2900	
Linewidth (c_i,cm^{-1})	5	9.5	
Phase (φ_i, Radian)	0	0	
	Dynamics T_1	**Dynamics T_2**	**Dynamics T_3**
Lifetime (τ_i, fs)	500	1000	2000
	Nonresonance NR_1	**Nonresonance NR_2**	
Amplitude (Δa_{NRi})	1	1.5	
Phase (φ_{NRi})	0.3	2	

Parameters of G: g=20, $\omega 0 = 2870$, $\delta = 80$

To perform global analysis, we used Glotaran to decompose both the real and imaginary spectral dynamics into multiple spectral and dynamic components (parameters in Table 2). In the main article, we only showed the imaginary part of the model input (Fig.1c). The components of the real parts are included in the supplemental materials (Figure S1a). The retrieved dynamics was good as-is and require no additional data analysis (Figure S1b).

Table 2. parameters used in Glotaran

	Kinetic Model	**Instructment Reaction Function (IRF)**

Model Input	K1=0.5 K2=0.05 K3=0.02	Irf1=50 Irf2=0.2
P3HT/gold	K1=0.45836 K2=0.108032 K3=0.00274973	Irf1=28.0094 Irf2=0.00599425

For the spectral components, only S1 had a mixture of molecular and NR features, which required extra data processing. We first combined the real and imaginary parts together to generate the complex spectra of S1 and then plot S1 phase (Fig.1d). We averaged the flat region of the phase, which generate -2.43. Then we multiplied $e^{-i*-2.43}$ to the spectral component S1 to get S1' (a phase rotated S1). The imaginary spectrum should only contain molecular resonant signal (Fig.1e). The corresponding Matlab codes are

```
%Phase and phase rotation
Recon1=Realcom1(:,2)+Imagcom1(:,2)*i;                %Spectral component from Glotaran
Ph_com1=angle(Recon1);                                    %calculate the phase
Plot(Ph_com1)                                %plot the phase of component 1
Ph=mean(Ph_com1(a:b))%manually identify the flat phase region (a:b) and take average
PhR_Recon1=Recon1*exp(-i*Ph)                                        %phase rotation
```

Then we applied Fourier transform only to imaginary spectrum (molecular spectral responses) to convert it into time-domain. To apply causality (no signals before laser pulse interact with the samples (e.g. t<0)), we multiplied the time-domain function by the Heaviside function (Fig.1f). We then divided the value at t=0 by 2, to remove an artifacts due to fast Fourier transform.

```
%Apply causality to simulate dynamics
spec_off_rebuild=zeros(length(PhR_Recon1),1);
spec_off_1=fft(imag(PhR_Recon1)*i);                                  %Fourier transform
spec_off_rebuild(1:401)=spec_off_1(1:401);                                  %Heaviside
spec_off_rebuild(1)=spec_off_rebuild(1)/2;                        %Remove an artifact
```

The time-domain dynamics were inversely Fourier transformed back. Because of causality, the real part of the molecular responses are restored now. We note the causality implementation is a numerical way to apply the Kronig-Kramer relationship. We then restored S1 original phase by multiplying S1' $e^{i*-2.3}$. The retrieved spectrum restored both real and imaginary parts of spectra, free of NR (Fig.1g).

```
spec_off_retrieve=ifft(spec_off_rebuild);                  %inversely Fourier transform
spec_off_retrieve=spec_off_retrieve*exp(i*Ph);             %restore the original phase
```

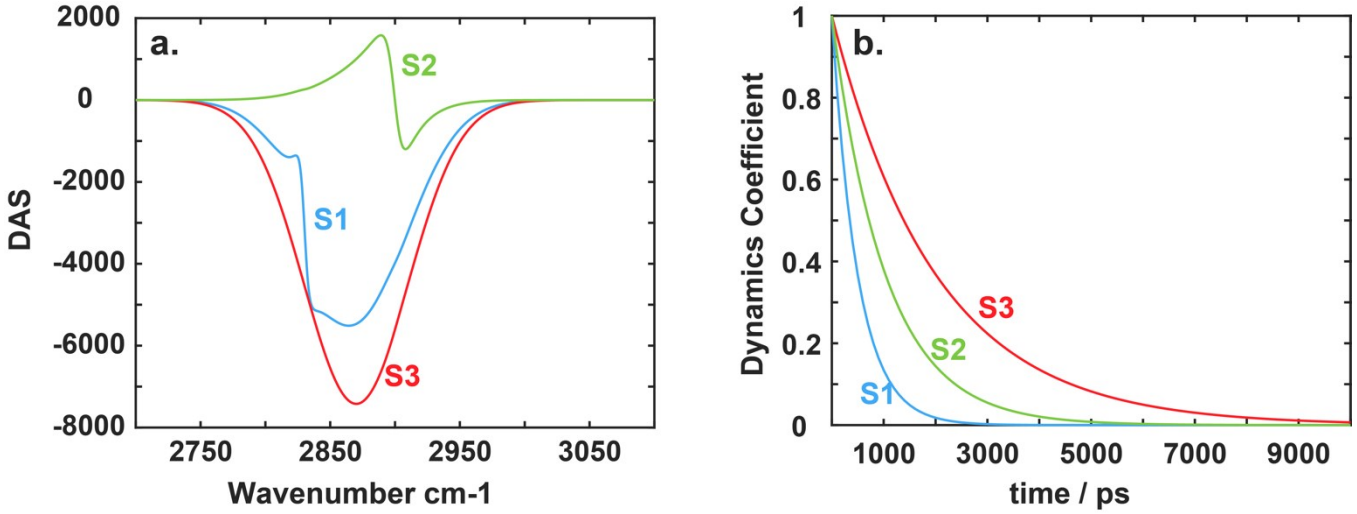

Figure S1. Spectral and dynamic component of real part

S2. Reliability Test

To test the reliability of our method against noise, we introduced random white noise to the model input. We changed the noise level, to make the signal to noise ratio (SNR) as 30, 24, 17 and 10. We then performed the global analysis and then determined the phase of NR signal.

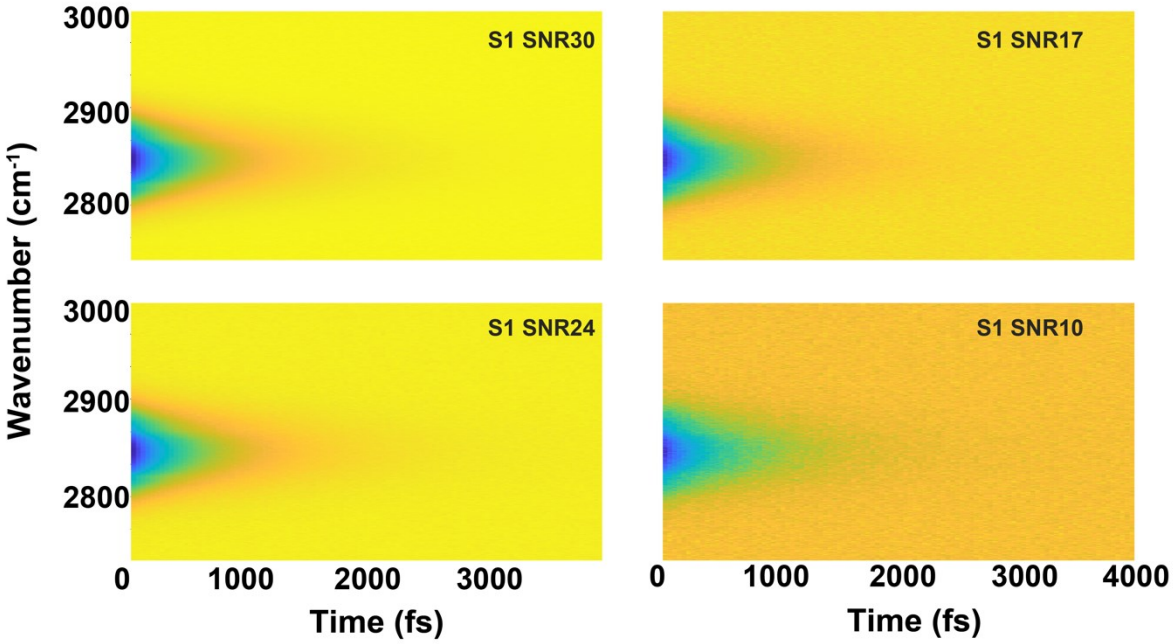

Figure S2. Model with different white noise input

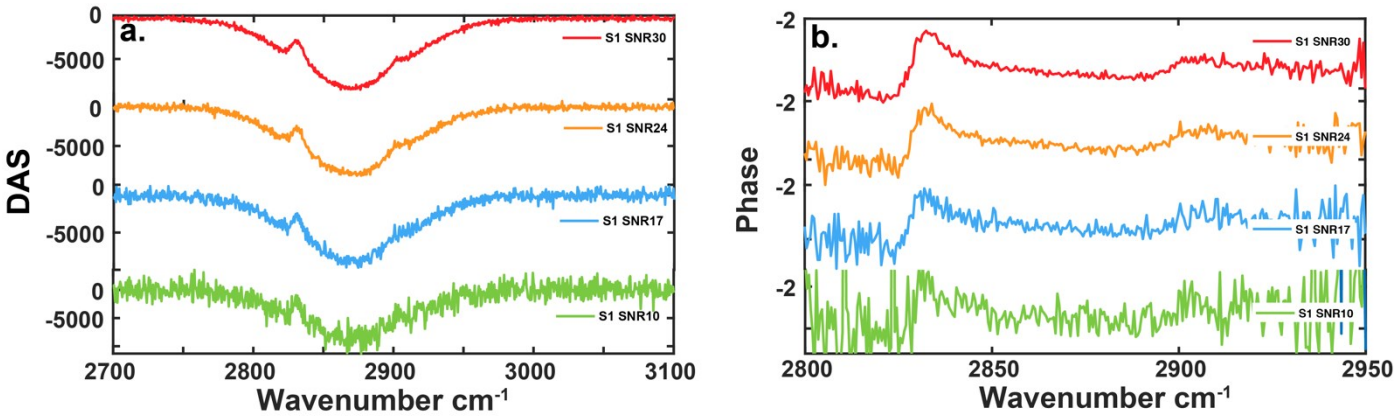

Figure S3. a) Spectral component S1, b) Phase plot of S1

From the figure S2 and S3, the quality of data would become worse with increaing white noise. However, the molecular feature and the dynamics remain the same, regardless of the noise level. For example, from SNR 30 to 10, the position of molecular feature is always constant at 2830 cm-1, which agrees with input parameter (Fig.S3a). The NR phase from the flat region also remain simialr, but with larger fluctuations as the white noise becomes large (Figure S3.b). The flutuation is alleviated by taking an average in the flat region from 2850 cm^{-1} to 2900 cm^{-1}, reporting a NR phase of -2.43 ± 0.2. This result suggests that the retraival of phase is quite reliable.