

SUPPLEMENTARY INFORMATION

for the paper

Broadband infrared and Raman probes of excited-state vibrational molecular dynamics; Simulation protocols based on loop diagrams

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(Dated: June 10, 2013)

Appendix A: Time-gated signals

Below we present the time gated signals corresponding to the frequency gated expressions given in the main text. We first read off the FDIR signal from the diagrams similar to Eqs. (9) - (10) and introduce the τ - dispersed signal in time domain analogues to Eq. (8)

$$S_{IR}(t, T) = \mathcal{I} \int_{-\infty}^t d\tau \mathcal{E}_2^*(t - T) \mathcal{E}_2(\tau - T) \tilde{S}_{IR}(t, T; \tau), \quad (\text{S1})$$

where $\tilde{S}_{IR}(t, T; \tau) = \tilde{S}_{IR}^{(i)}(t, T; \tau) + \tilde{S}_{IR}^{(ii)}(t, T; \tau)$ where

$$\begin{aligned} \tilde{S}_{IR}^{(i)}(t, T; \tau) &= \frac{2}{\hbar} \int_{-\infty}^t d\tau_1 \int_{-\infty}^{\tau_1} d\tau_5 \mathcal{E}_1^*(\tau_5) \mathcal{E}_1(\tau_1) \\ &\times \langle V_e G^\dagger(\tau, \tau_5) V_n^\dagger G^\dagger(t, \tau) V_n G(t, \tau_1) V_e^\dagger \rangle, \end{aligned} \quad (\text{S2})$$

$$\begin{aligned} \tilde{S}_{IR}^{(ii)}(t, T; \tau) &= \frac{2}{\hbar} \int_{-\infty}^t d\tau_1 \int_{-\infty}^{\tau_1} d\tau_5 \mathcal{E}_1(\tau_5) \mathcal{E}_1^*(\tau_1) \\ &\times \langle V_e G^\dagger(t, \tau_1) V_n G(t, \tau) V_n^\dagger G(\tau, \tau_5) V_e^\dagger \rangle. \end{aligned} \quad (\text{S3})$$

$\tilde{S}(t, T; \tau)$ is the signal at time t resulting from interaction with \mathcal{E}_2 at time $\tau - T$. The signal is obtained by integration over τ . The corresponding SRS signal reads

$$\begin{aligned} \tilde{S}_{SRS}^{(i)}(t, T; \tau) &= \frac{2}{\hbar} \int_{-\infty}^t d\tau_1 \int_{-\infty}^{\tau_1} d\tau_5 \mathcal{E}_1^*(\tau_5) \mathcal{E}_1(\tau_1) \times \\ &\mathcal{E}_3(t - T) \mathcal{E}_3^*(\tau - T) \langle V_e G^\dagger(\tau, \tau_5) \alpha_n G^\dagger(t, \tau) \alpha_n G(t, \tau_1) V_e^\dagger \rangle, \end{aligned} \quad (\text{S4})$$

$$\begin{aligned} \tilde{S}_{SRS}^{(ii)}(t, T; \tau) &= \frac{2}{\hbar} \int_{-\infty}^t d\tau_1 \int_{-\infty}^{\tau_1} d\tau_5 \mathcal{E}_1(\tau_5) \mathcal{E}_1^*(\tau_1) \times \\ &\mathcal{E}_3(t - T) \mathcal{E}_3^*(\tau - T) \langle V_e G^\dagger(t, \tau_1) \alpha_n G(t, \tau) \alpha_n G(\tau, \tau_5) V_e^\dagger \rangle. \end{aligned} \quad (\text{S5})$$

Eqs. (S4) - (S5) are analogue of (17) - (18).

The time-domain FDIR signals Eqs. (S2) - (S3) can be recast using SOS expansion

$$\begin{aligned} \tilde{S}_{IR}^{(i)}(t, T; \tau) &= \frac{2}{\hbar} \theta(\tau) \theta(t) \sum_{a, a', d} \mu_{ga'} \mu_{ag}^* \mu_{a'd}^* \mu_{ad} \times \\ &\mathcal{E}_1^*(\omega_{a'} + i\gamma_{a'}) \mathcal{E}_1(\omega_a - i\gamma_a) e^{-(i\omega_{ad} + \gamma_{ad})t + (i\omega_{a'd} + \gamma_{d - \gamma_{a'}})\tau}. \end{aligned} \quad (\text{S6})$$

$$\begin{aligned} \tilde{S}_{IR}^{(ii)}(t, T; \tau) &= -\frac{2}{\hbar} \theta(\tau) \theta(t) \sum_{a, a', c} \mu_{ga'} \mu_{ag}^* \mu_{a'c}^* \mu_{ca} \times \\ &\mathcal{E}_1^*(\omega_{a'} + i\gamma_{a'}) \mathcal{E}_1(\omega_a - i\gamma_a) e^{-(i\omega_{a'c} + \gamma_{a'c})t + (i\omega_{ac} + \gamma_c - \gamma_a)\tau}, \end{aligned} \quad (\text{S7})$$

that are analogues to Eqs. (23) - (24). The corresponding SRS signal reads

$$\begin{aligned} S_{SRS}^{(i)}(t, T) &= \mathcal{I} \frac{2i}{\hbar^4} \theta(\tau) \theta(t) \sum_{a, a', d} \mu_{ga'} \mu_{ag}^* \alpha_{a'd} \alpha_{ad} \\ &\times \mathcal{E}_1^*(\omega_{a'} + i\gamma_{a'}) \mathcal{E}_1(\omega_a - i\gamma_a) |\mathcal{E}_3|^2 \\ &\times e^{-i\omega_3(t - \tau) - (i\omega_{ad} + \gamma_{ad})t + (i\omega_{a'd} + \gamma_{d - \gamma_{a'}})\tau}, \end{aligned} \quad (\text{S8})$$

$$\begin{aligned} S_{SRS}^{(ii)}(t, T) &= -\mathcal{I} \frac{2i}{\hbar^4} \theta(\tau) \theta(t) \sum_{a, a', c} \mu_{ga'} \mu_{ag}^* \alpha_{a'c} \alpha_{ca} \\ &\times \mathcal{E}_1^*(\omega_{a'} + i\gamma_{a'}) \mathcal{E}_1(\omega_a - i\gamma_a) |\mathcal{E}_3|^2 \\ &\times e^{-i\omega_3(t - \tau) - (i\omega_{a'c} + \gamma_{a'c})t + (i\omega_{ac} + \gamma_c - \gamma_a)\tau}, \end{aligned} \quad (\text{S9})$$

For the ultrafast probe $\mathcal{E}_2(t - T) = \mathcal{E}_2 \delta(t - T)$ the τ - dispersed signal Eq. (S6) - (S7) then results in the full signal (S1)

$$\begin{aligned} S_{IR}(t, T) &= \mathcal{I} \frac{2i}{\hbar^4} \theta(t) \delta(t - T) \sum_{a, a'} \mu_{ga'} \mu_{ag}^* |\mathcal{E}_1|^2 |\mathcal{E}_2|^2 \\ &\times \left[\sum_d \mu_{a'd}^* \mu_{ad} e^{(i\omega_{a'a} - \gamma_{a'a})T} - \sum_c \mu_{a'c}^* \mu_{ca} e^{(i\omega_{aa'} - \gamma_{aa'})T} \right]. \end{aligned} \quad (\text{S10})$$

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The corresponding SRS signal reads

$$S_{SRS}(t, T) = \mathcal{I} \frac{2i}{\hbar^4} \theta(t) \delta(t - T) \sum_{a, a'} \mu_{ga'} \mu_{ag}^* |\mathcal{E}_1|^2 |\mathcal{E}_2|^2 |\mathcal{E}_3|^2 \times \left[\sum_d \alpha_{a'd} \alpha_{ad} e^{(i\omega_{a'a} - \gamma_{a'a})T} - \sum_c \alpha_{a'c} \alpha_{ca} e^{(i\omega_{aa'} - \gamma_{aa'})T} \right]. \quad (\text{S11})$$

Appendix B: Coupling to a classical bath

We assume that the system is coupled to a harmonic bath. The molecule is represented by the Hamiltonian

$$H = \sum_{\alpha=g,b} |\alpha\rangle H_\alpha \langle \alpha| + |a\rangle H_a(\mathbf{q}) \langle a| + |c\rangle H_c(\mathbf{q}) \langle c|, \quad (\text{S1})$$

where $H_\beta(\mathbf{q})$, $\beta = a, c$ is an operator in the nuclear Hilbert space, that is given by

$$H_a(\mathbf{q}) = \sum_j \left[\frac{\tilde{p}_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 (\tilde{q}_j) \tilde{q}_j^2 \right], \quad (\text{S2})$$

$$H_c(\mathbf{q}) = \hbar \omega_{ac}^{(0)} + \sum_j \left[\frac{\tilde{p}_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 (\tilde{q}_j) (\tilde{q}_j + \tilde{d}_j)^2 \right], \quad (\text{S3})$$

where $\omega_j(\tilde{q}_j)$ represents the time dependent frequency profile of the isomerization process. Introducing the dimensionless coordinate $q_j = (m_j \omega_j / \hbar)^{1/2} \tilde{q}_j$, displacement $d_j = (m_j \omega_j / \hbar)^{1/2} \tilde{d}_j$ and momentum $p_j = (m_j \omega_j \hbar)^{1/2} \tilde{p}_j$, Eqs. (S2) - (S3) read

$$H_a(\mathbf{q}) = \frac{1}{2} \sum_j \hbar \omega_j [p_j^2 + q_j^2], \quad (\text{S4})$$

$$H_c(\mathbf{q}) = \hbar \omega_{ac}^{(0)} + \frac{1}{2} \sum_j \hbar \omega_j [p_j^2 + (q_j + d_j)^2]. \quad (\text{S5})$$

We next define the vibrational frequency $\hbar \omega_{ac} = \hbar \omega_{ac}^{(0)} + \frac{1}{2} \sum_j d_j^2 \omega_j(q_j)$ and potential energy

$$U_{ac} = H_c - H_a - \hbar \omega_{ac} = \hbar \sum_j \omega_j(q_j) d_j q_j. \quad (\text{S6})$$

The dipole operator is given by

$$V = \sum_{\alpha, \alpha'} \mu_{\alpha\alpha'} |\alpha\rangle \langle \alpha'|, \quad (\text{S7})$$

where the summation runs over $\alpha, \alpha' = g, a, c, b$, and $\alpha \neq \alpha'$. Note that at this point we neglect any nuclear of the dipole operators $\mu_{\alpha\alpha'}$ (Condon approximation).

Following the definition of the frequency dispersed signal (6) we note that the angular brackets $\langle \dots \rangle$ in (6) now

represent the average over the bath degrees of freedom. Nuclear dynamics can be approximated by a combination of classical dynamics and additional phases. Introducing the reference Hamiltonian [S1]

$$H_{ref}(\tau) = \begin{cases} H_g, & \text{if } \tau < \tau_1, \tau_5, \\ H_a, & \text{if } \tau \geq \tau_1, \tau_5 \end{cases} \quad (\text{S8})$$

The Green's function can then be recast with respect to the reference Hamiltonian

$$G_\alpha(t_1, t_2) = \theta(t_1 - t_2) \exp_+ \left[-\frac{i}{\hbar} \int_{t_2}^{t_1} d\tau H_{ref}(\tau) \right] \times \exp_+ \left[-\frac{i}{\hbar} \int_{t_2}^{t_1} d\tau U_\alpha(\tau) \right], \quad (\text{S9})$$

where the “+” subscript correspond to the positive time ordering. We assume in Eq. (S1) the nuclear dynamics occurs only in the singly excited manifold (states a and c). Therefore for $\alpha = a, b$

$$G_\alpha(t_1, t_2) = \theta(t_1 - t_2) e^{-(i\omega_\alpha + \gamma_\alpha)(t_1 - t_2)}, \quad (\text{S10})$$

while

$$G_c^\dagger(t, \tau_3) = \theta(t - \tau_3) e^{i\omega_a(t - \tau_3)} \exp_- \left[\frac{i}{\hbar} \int_{\tau_3}^t d\tau U_{ac}(\tau) \right], \quad (\text{S11})$$

where

$$U_{ac}(\tau) = e^{\frac{i}{\hbar} H_a \tau} [H_c - H_a - \hbar \omega_{ac}] e^{-\frac{i}{\hbar} H_a \tau}. \quad (\text{S12})$$

Substituting this in Eqs. (S2) - (S3) and (S4) - (S5) we then get Eqs. (36) and (37), respectively.

In the reduced description when we treat bath degrees of freedom separately signals (9) - (10) and (17) - (18) contain in principle two averaging operations. First is averaging over statistical ensemble of classical trajectories $\langle \dots \rangle_e$. For a fixed trajectory one has to evaluate the average over the bath degrees of freedom $\langle \dots \rangle_b$. In order to evaluate the correlation function one has to consider the microscopic stochastic dynamics of the nuclei. For a fixed trajectory we evaluate the bath averaging $\langle U_{\nu\nu'}(\tau) \rangle_b = \hbar \omega_{\nu\nu'}(\tau)$ and obtain Eqs. (36) - (37). We then note that the frequency averaging over trajectories $\langle \omega_{\nu\nu'}(\tau) \rangle_e = \bar{\omega}_{\nu\nu'}$. One can further add a harmonic fluctuations around the mean value $\bar{\omega}_{\nu\nu'}$ via cumulant expansion. Note that for gaussian fluctuations this expansion is same for all trajectories. We thus obtain

$$\left\langle \left\langle \exp_- \left(\frac{i}{\hbar} \int_T^t d\tau U_{ac}(\tau) \right) \rho_g \right\rangle_b \right\rangle_e = e^{i \int_T^t \bar{\omega}_{ac}(\tau) d\tau} \times \left[1 + \mathcal{T}_- \left(\frac{i}{\hbar} \right)^2 \int_T^t d\tau_1 \int_T^{\tau_1} d\tau_2 \langle U_{ac}(\tau_1) U_{ac}(\tau_2) \rho_g \rangle_b + \dots \right] \quad (\text{S13})$$

Note that the linear term in expansion (S13) does not depend on time $\langle U_{ac}(\tau) \rho_g \rangle = \langle U_{ac} \rho_g(\tau) \rangle = \langle U_{ac} \rho_g(0) \rangle$.

We further obtain the cumulant expansion by postulating that expansion (S13) can be written as exponentiated in terms of power of U_{ac} . Introducing the two-time linewidth function

$$g_{ac}(t_1, t_2) = \int_{t_1}^{t_2} d\tau_1 \int_{t_1}^{\tau_1} d\tau_2 C_{ac}(\tau_2), \quad (\text{S14})$$

where $C_{ac}(\tau_2) = \hbar^{-2} \langle U_{ac}(\tau_2) U_{ac}(0) \rho_g \rangle$ represents the spectral density that contains all the microscopic information necessary for calculating the optical response functions within the second order cumulant approximation. We first note that $C(-t) = C^*(t)$. We next separate it into real and imaginary part $C(t) = C'(t) + C''(t)$. Using the fluctuation-dissipation and detailed balance

theorem one may show that

$$\tilde{C}(\omega) = [1 + \coth(\beta\hbar\omega/2)] \tilde{C}''(\omega), \quad (\text{S15})$$

where $\tilde{C}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} C(t)$ and $\beta = 1/k_B T_a$ with the ambient temperature T_a and Boltzmann constant k_B . For the continuous spectrum of harmonic fluctuations one can use the overdamped Brownian oscillator model, i.e.

$$\tilde{C}''(\omega) = 2\lambda \frac{\omega\Lambda}{\omega^2 + \Lambda^2}, \quad (\text{S16})$$

where λ represents the reorganization energy and Λ corresponds to the fluctuation time scale. In this case the linewidth function is given by Eq. (40).

[S1] S. Rahav and S. Mukamel, Phys. Rev. A **81**, 063810 (Jun 2010), [http://link.aps.org/doi/10.1103/PhysRevA.](http://link.aps.org/doi/10.1103/PhysRevA.81.063810)