Max-Planck-Institut für Physik komplexer Systeme

Wavepacket dynamics at conical intersection and its spectroscopic manifestation

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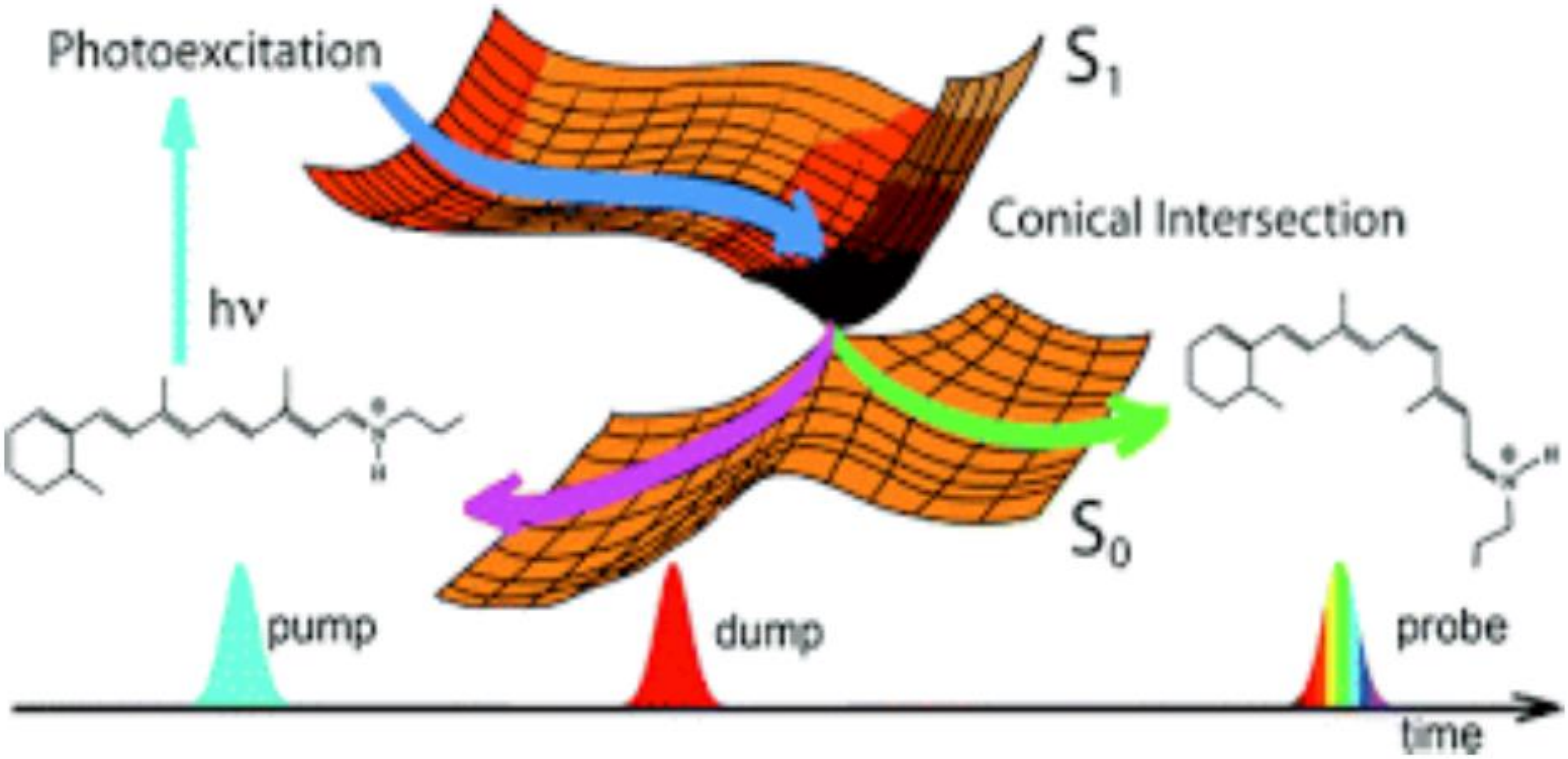
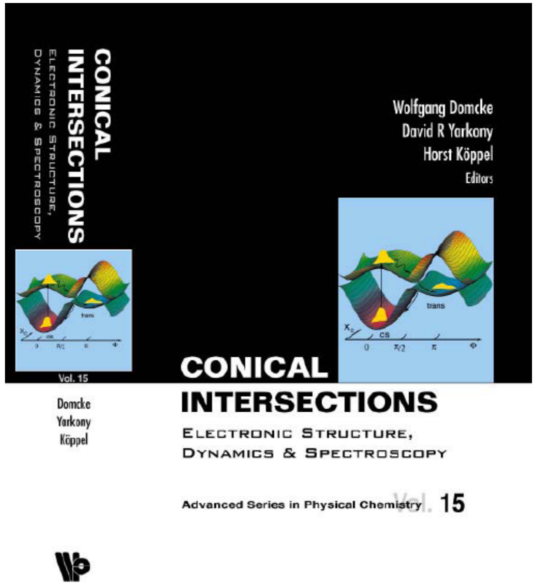
Dec 9, 2021, VISTA Seminar

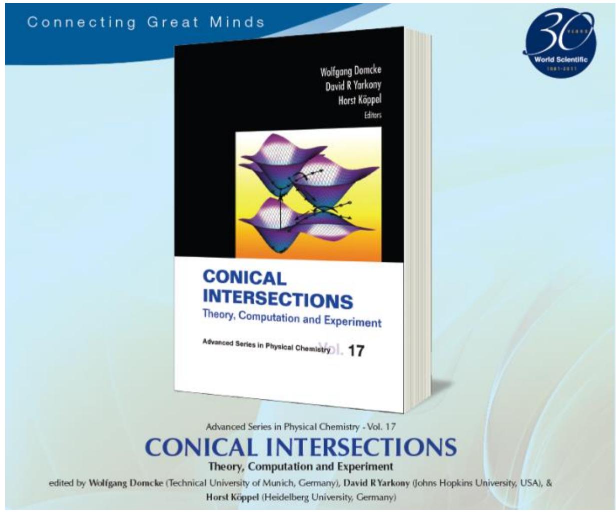
Conical intersections



• Dynamics at conical intersections in dissipative environment

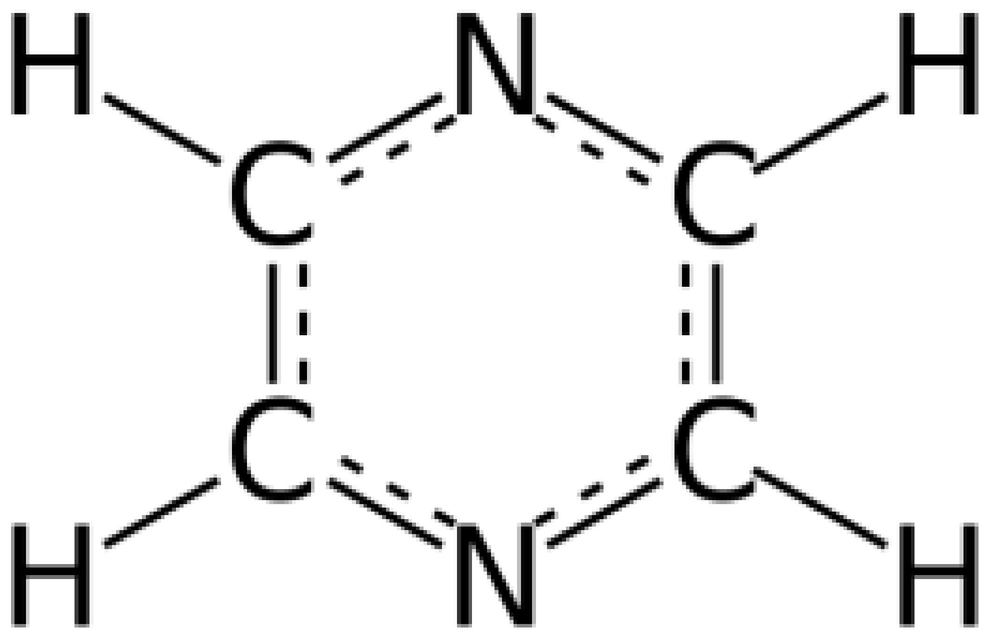
• Spectroscopic characterization of conical intersections: Recent suggestions

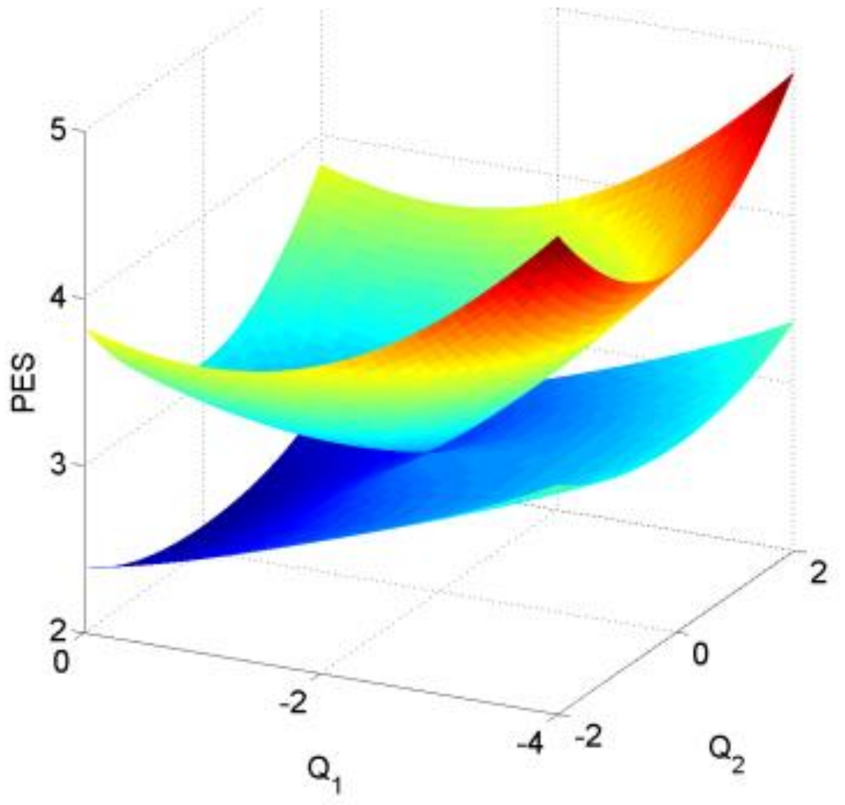




24-mode conical intersection model of pyrazine

- Multimode quantum dynamics with a multiple Davydov D2 trial states: Application to a 24-dimensional conical intersection model





Model Hamiltonian

$$H = H_S + H_B + H_{SB}.$$

$$H_S = \sum_{l=10a,6a,1,9a} \frac{\omega_l}{2}\left(-\frac{\partial^2}{\partial Q_l^2} + Q_l^2\right)\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} -\Delta & 0 \\ 0 & \Delta \end{pmatrix} + \begin{pmatrix} 0 & \lambda \\ \lambda & 0 \end{pmatrix} Q_{10a} + \sum_{m=6a,1,9a} \begin{pmatrix} \kappa_m^{(1)} & 0 \\ 0 & \kappa_m^{(2)} \end{pmatrix} Q_m.$$

$$H_B = \sum_{n=1}^{N_{\mathrm{bath}}} \frac{\omega_n}{2}\left(-\frac{\partial^2}{\partial Q_n^2} + Q_n^2\right)\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$H_{SB} = \sum_{n=1}^{N_{\mathrm{bath}}} \begin{pmatrix} \kappa_n^{(1)} & 0 \\ 0 & \kappa_n^{(2)} \end{pmatrix} Q_n$$

Multiple Davydov ansatz

Multiple Davydov D2 ansatz

state amplitude   phonon displacement

$$|\mathrm{D}_2^{\mathrm{M}}(t)\rangle = |S_1\rangle \sum_{u=1}^{\mathrm{M}} A_u(t) \exp\left(\sum_l f_{ul}(t) b_l^\dagger - \mathrm{H.c.}\right)|0\rangle_v + |S_2\rangle \sum_{u=1}^{\mathrm{M}} B_u(t) \exp\left(\sum_l f_{ul}(t) b_l^\dagger - \mathrm{H.c.}\right)|0\rangle_v$$

Dirac-Frenkel time-dependent variational method

$$L = \langle \Phi(t)| \frac{i\hbar}{2} \frac{\overleftrightarrow{\partial}}{\partial t} - \hat{H} |\Phi(t)\rangle$$

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\alpha}_m^*}\right) - \frac{\partial L}{\partial \alpha_m^*} = 0$$

Observables

diabatic state population

$$P_k^{\mathrm{di}}(t) = \langle \mathrm{D}_2^M(t)|(|\mathrm{S}_k\rangle\langle \mathrm{S}_k|)|\mathrm{D}_2^M(t)\rangle.$$

adiabatic state population

$$|\tilde{\mathrm{S}}_k\rangle = \sum_{k'=1,2} \mathbf{M}(Q_{10a}, \mathbf{Q}_t)_{kk'}|\mathrm{S}_{k'}\rangle, \qquad k = 1, 2$$

$$\begin{aligned}\hat{P}_1^{\mathrm{ad}} &= \mathbf{M}^\dagger \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \mathbf{M} \\ &= \frac{1}{2} - \frac{1}{2(\Omega^2 + \lambda^2 Q_{10a}^2)^{1/2}} \begin{pmatrix} -\Omega & \lambda Q_{10a} \\ \lambda Q_{10a} & \Omega \end{pmatrix}\end{aligned}$$

$$\hat{P}_1^{\mathrm{ad}} = \frac{1}{2} - \frac{1}{2\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-(\Omega^2 + \lambda^2 Q_{10a}^2)x^2} dx \begin{pmatrix} -\Omega & \lambda Q_{10a} \\ \lambda Q_{10a} & \Omega \end{pmatrix}$$

$$\hat{\mathrm{P}}_2^{ad} = 1 - \hat{\mathrm{P}}_1^{\mathrm{ad}}$$

$$\mathrm{P}_k^{\mathrm{ad}} = \langle \mathrm{D}_2^{\mathrm{M}}(\mathrm{t})|\hat{\mathrm{P}}_k^{\mathrm{ad}}|\mathrm{D}_2^{\mathrm{M}}(\mathrm{t})\rangle$$

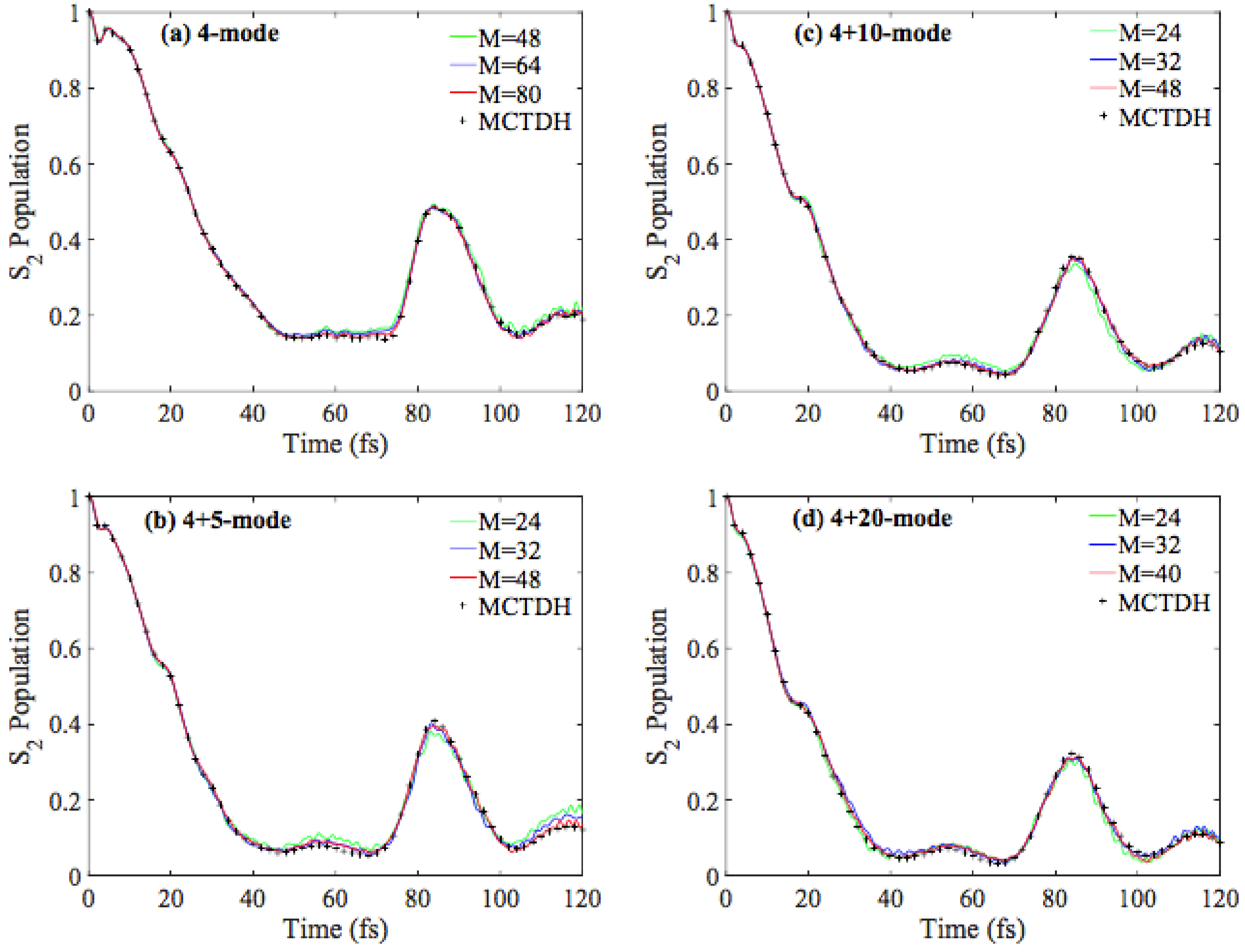
Observables

adiabatic wave packets

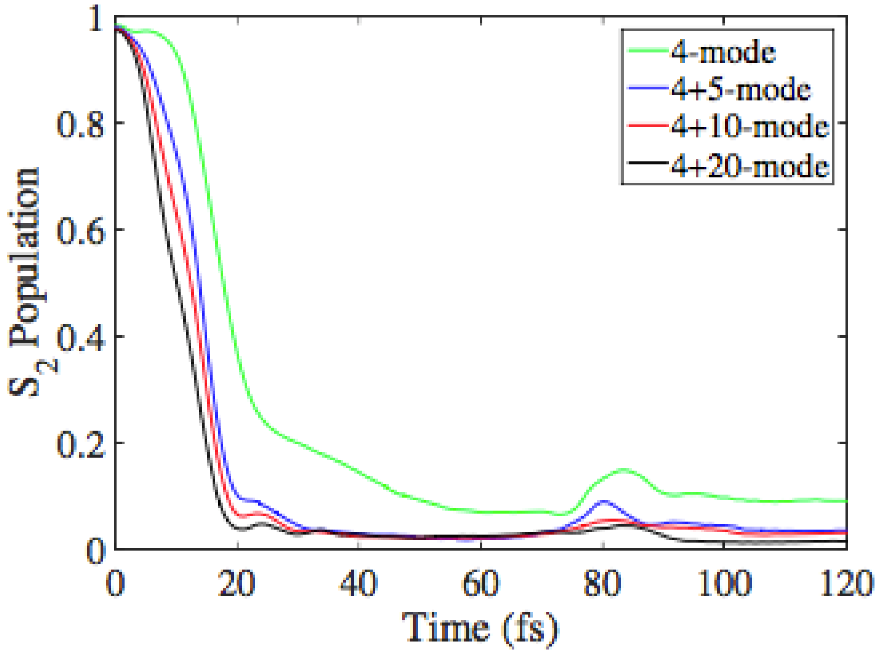
$$
\begin{aligned}
&P_k^{\mathrm{ad}}(Q_i,t) \\
&= \int dQ_1 \cdots \int dQ_{i-1} \int dQ_{i+1} \cdots \int dQ_{\mathrm{N}_l} \langle Q_1| \cdots \langle Q_{\mathrm{N}_l}| \langle \tilde{S}_k | \mathrm{D}_2^{\mathrm{M}}(t) \rangle \langle \mathrm{D}_2^{\mathrm{M}}(t) | \tilde{S}_k \rangle |Q_1\rangle \cdots |Q_{\mathrm{N}_l}\rangle
\end{aligned}
$$

Diabatic and adiabatic population

Diabatic population

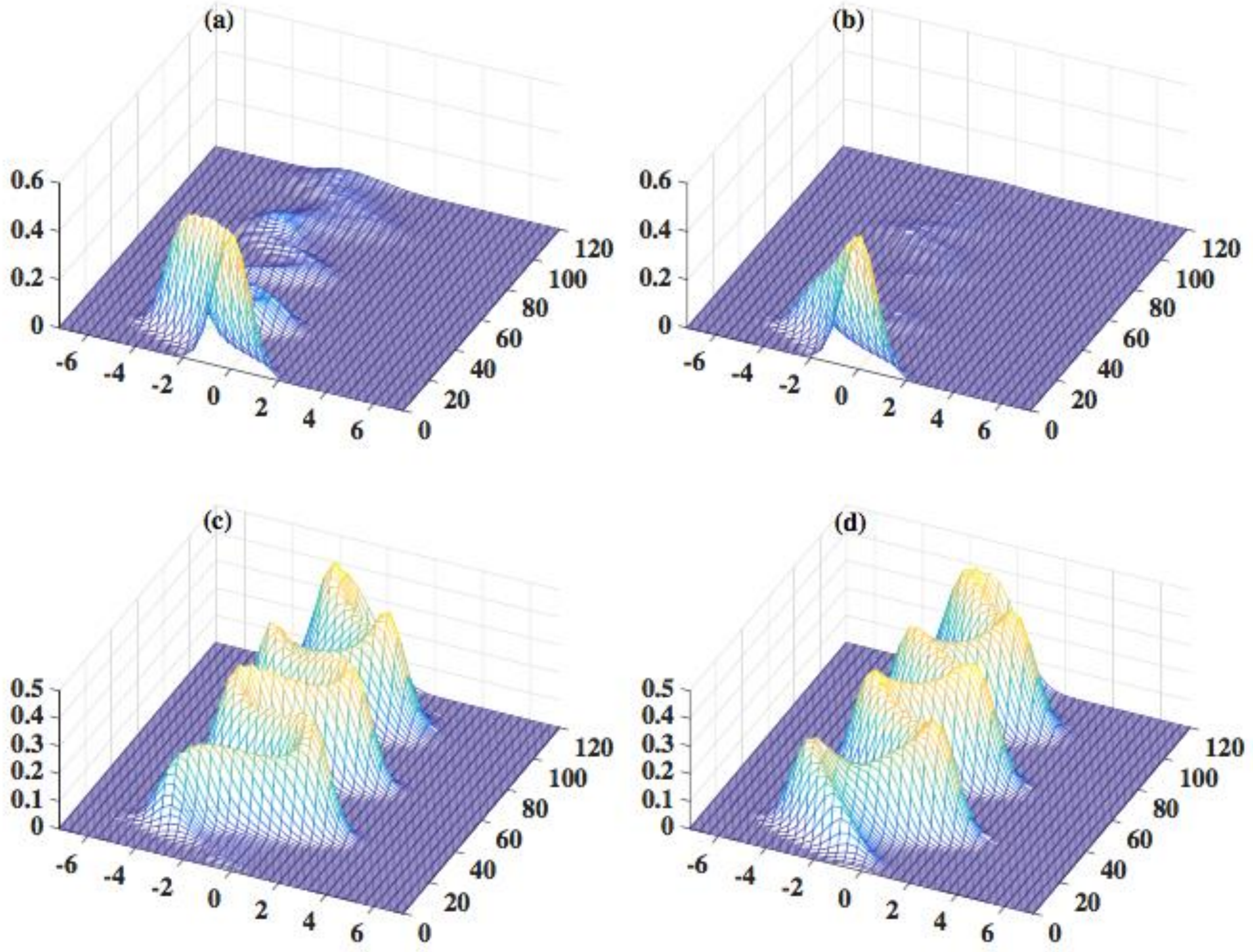


Adiabatic population



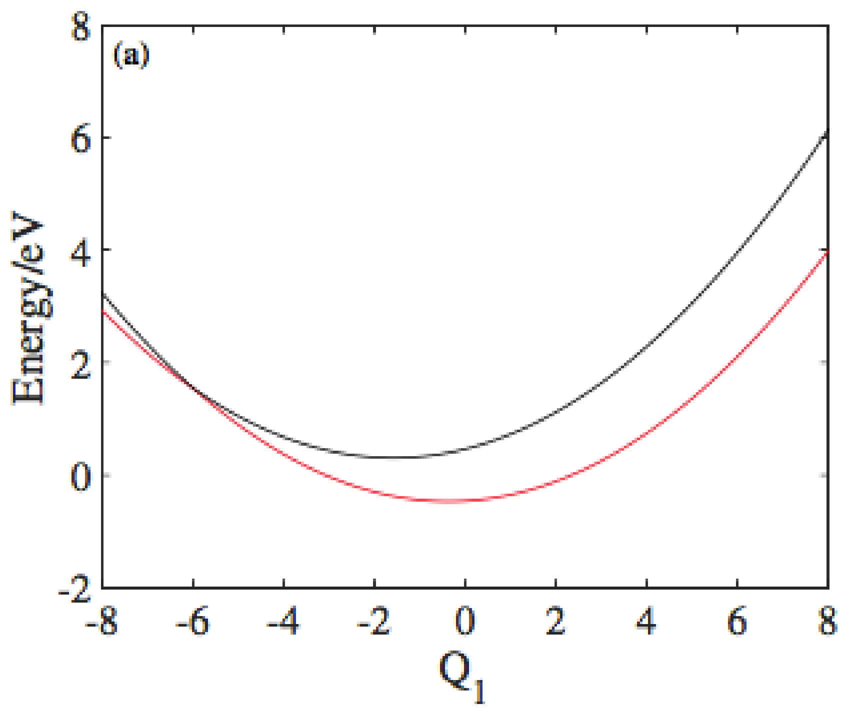
J. Chem. Phys, **150**, 024101, 2019

Wavepacket dynamics



4mode

4+20 mode



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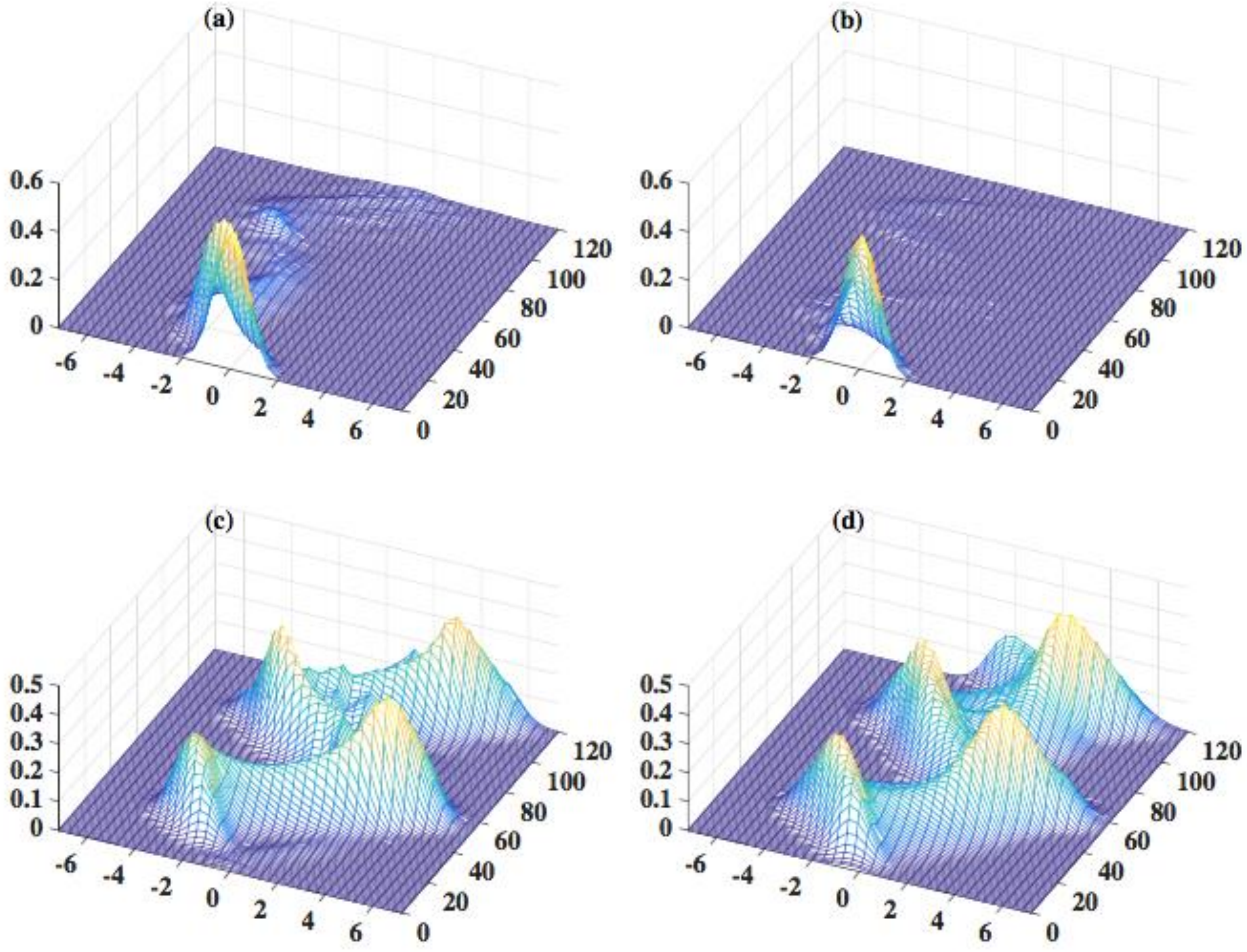
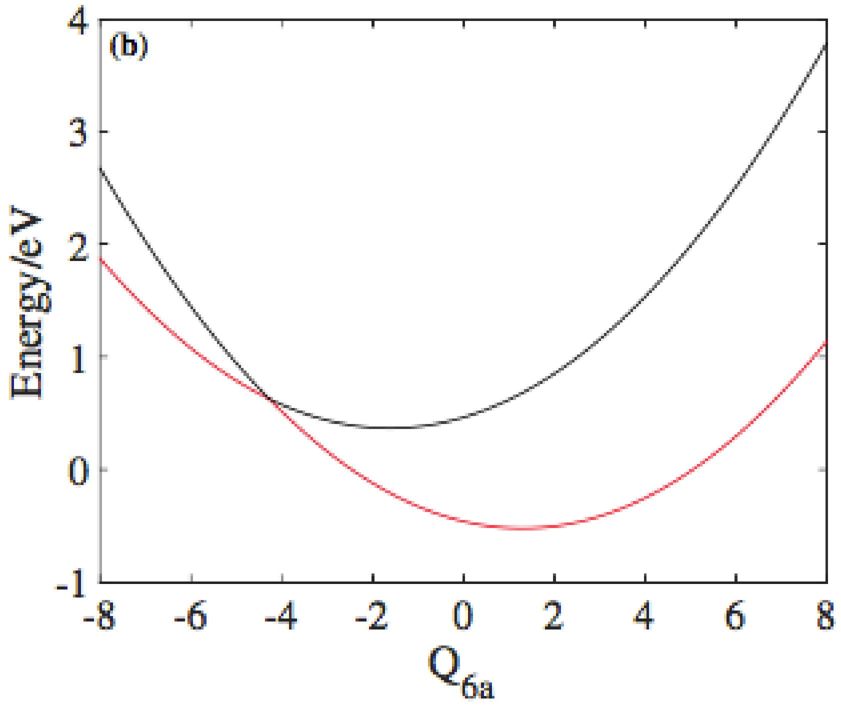
Wavepacket dynamics



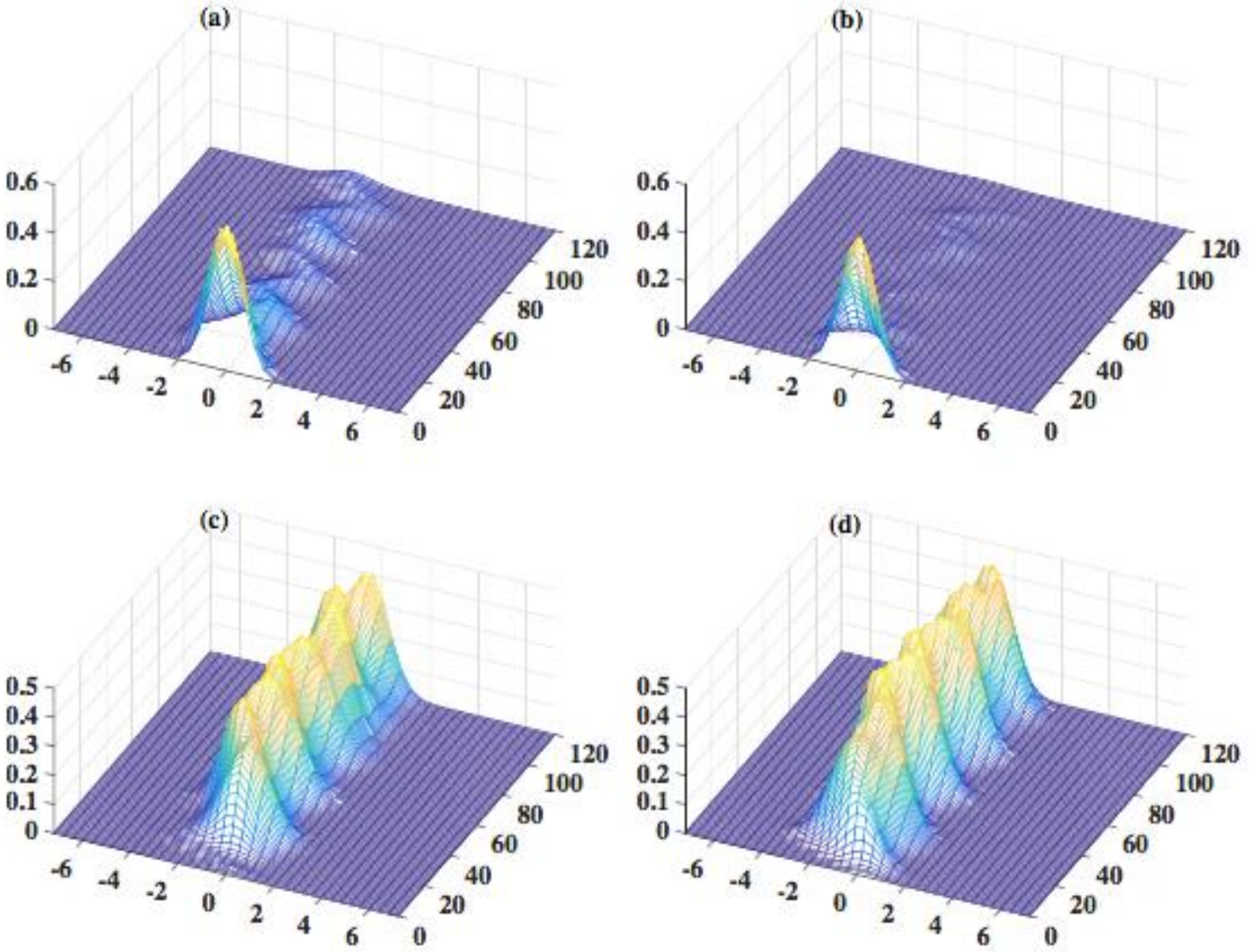
4mode

4+20 mode



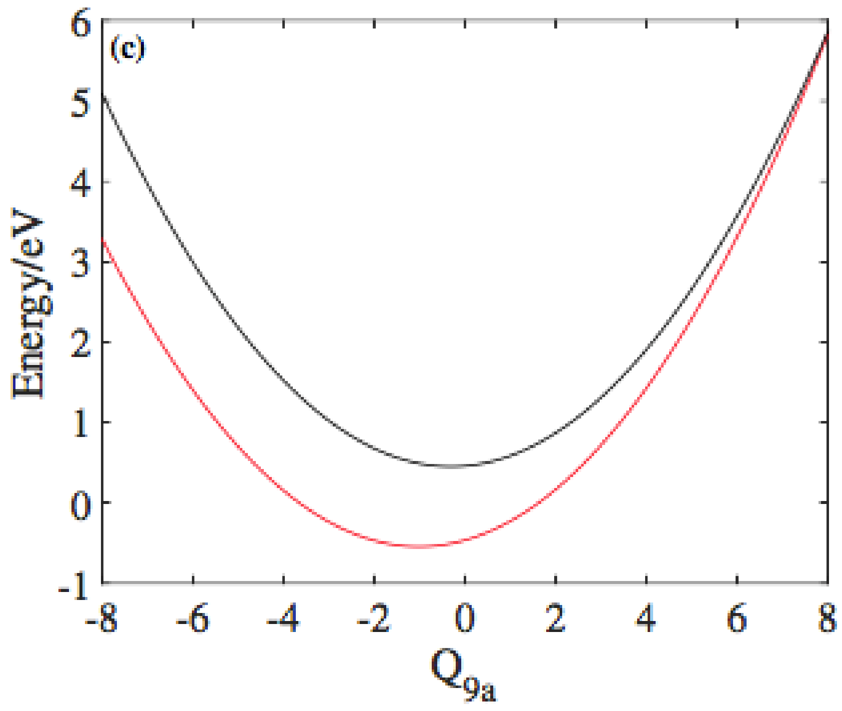
J. Chem. Phys, **150**, 024101, 2019

Wavepacket dynamics



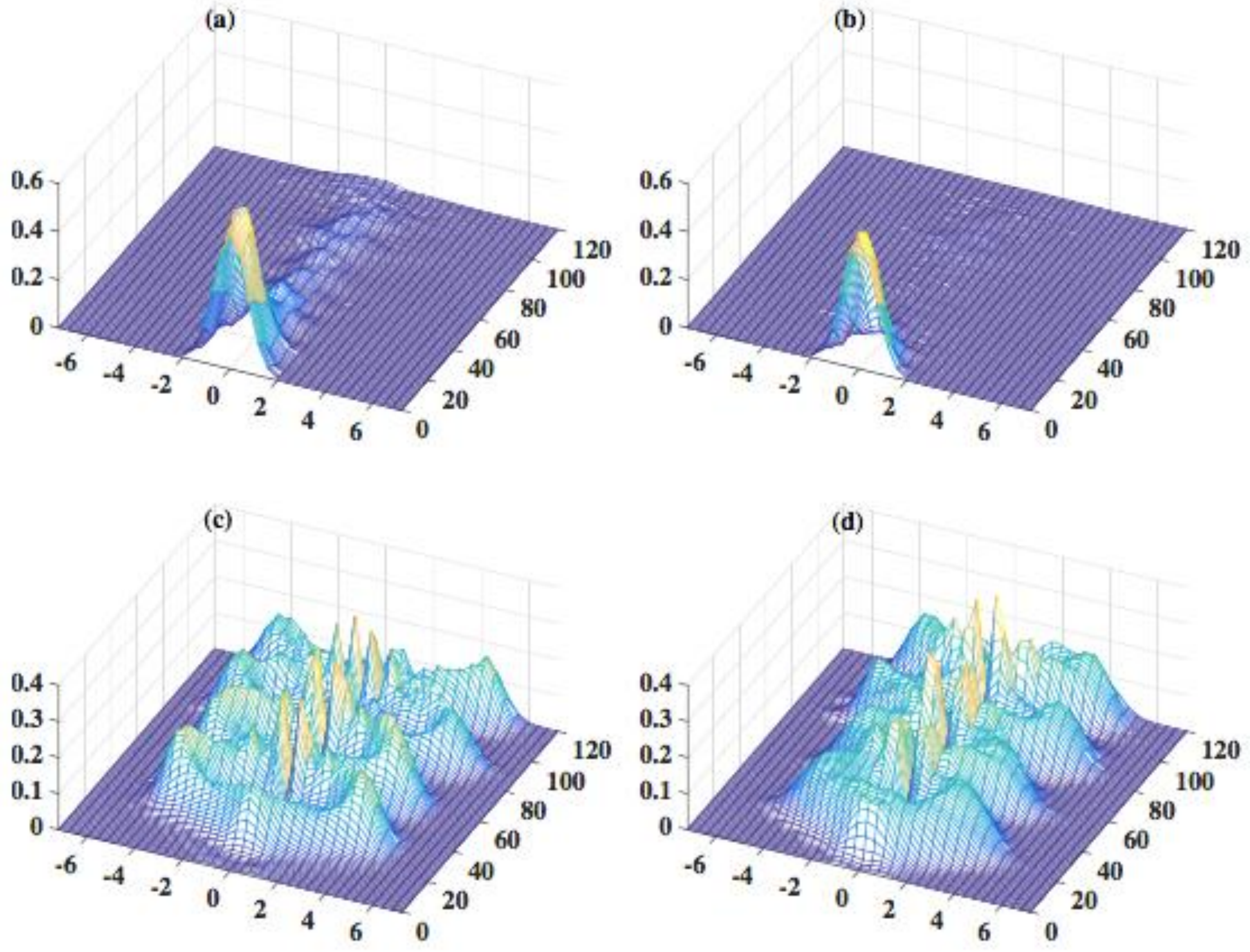
4mode

4+20 mode



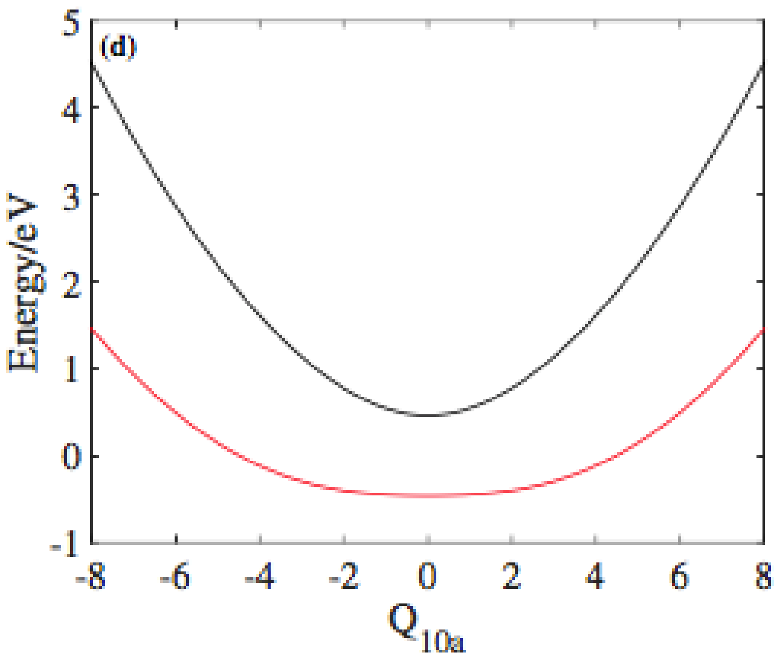
J. Chem. Phys, **150**, 024101, 2019

Wavepacket dynamics



4mode

4+20 mode

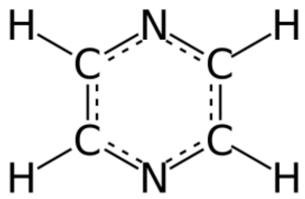


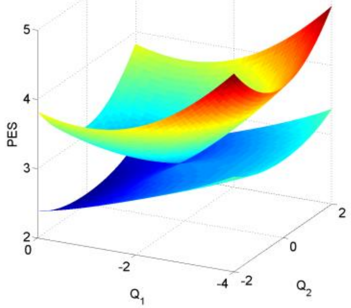
J. Chem. Phys, **150**, 024101, 2019

How to detect & characterize dynamics at conical intersections via Multidimensional spectroscopy

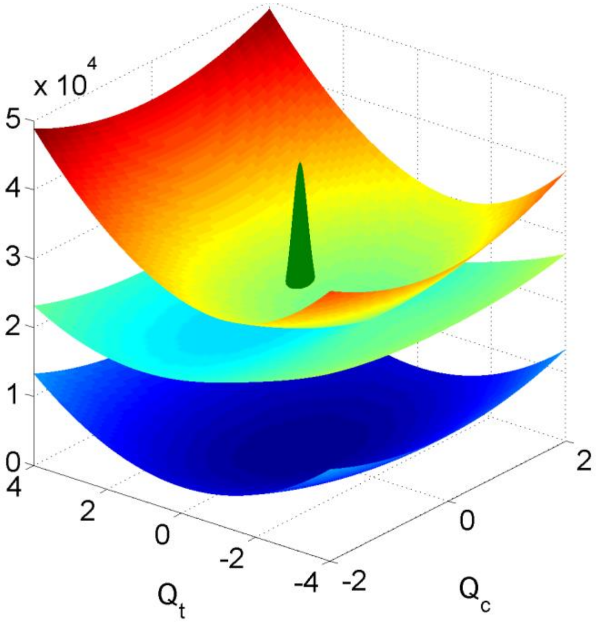
Time &frequency resolved fluorescence

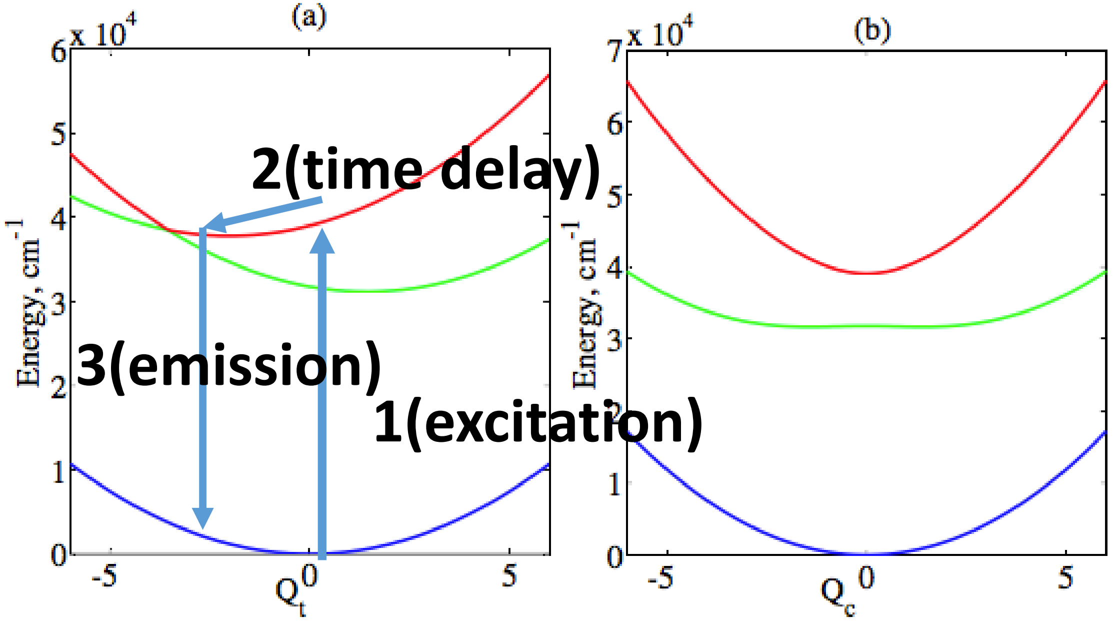
- Take a minimal two-electronic-states two-vibrational-modes model of conical intersection ($S_1(n\pi^*)$-$S_2(\pi^*\pi^*)$ conical intersection in pyrazine)





- Couple the conical intersection to the **dissipative** environment





Hierarchy Equation of Motion (HEOM)

$$H^{(\mathrm{S})} = \sum_{k=0,1,2} |k\rangle(h_k + \epsilon_k)\langle k| + (|1\rangle\langle 2| + |2\rangle\langle 1|)\lambda Q_{\mathrm{c}}$$

$$h_k = \frac{1}{2}\sum_{j=\mathrm{c,t}} \hbar\Omega_j\{P_j^{\,2} + Q_j^{\,2}\} + \kappa_k Q_{\mathrm{t}}$$

$$H^{(\mathrm{B})} = \{|0\rangle\langle 0| + |1\rangle\langle 1| + |2\rangle\langle 2|\} \sum_{j=\mathrm{c,t}}\sum_{\alpha} \frac{1}{2}\hbar\omega_{\alpha,j}\{p_{\alpha,j}^{\;\;2} + q_{\alpha,j}^{\;\;2}\}$$

$$H^{(\mathrm{SB})} = \{|1\rangle\langle 1| + |2\rangle\langle 2|\} \sum_{j=\mathrm{c,t}}\sum_{\alpha} \{c_{\alpha,j} q_{\alpha,j} Q_j\}$$

$$J_j(\omega) = \sum\nolimits_\alpha c_{\alpha,j}^{\;\;2}\delta(\omega - \omega_{\alpha,j}) \quad (j = \mathrm{c,\ t})$$

$$J_j(\omega) = 2\lambda_j\gamma_j\omega/(\omega^2 + \gamma_j^2), \qquad j = c, t$$

$$\partial_t \boldsymbol{\rho}(t) = -\frac{\mathrm{i}}{\hbar}[H^{(\mathrm{S})}, \boldsymbol{\rho}(t)] - \mathcal{R}\boldsymbol{\rho}(t)$$

HEOM (Tanimura, Kubo)

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{l_c,l_t}(t) \quad &= -(i\mathscr{L}^{(s)} + l_c\gamma_c + l_t\gamma_t)\rho_{l_c,l_t}(t) \\ &+\Phi_c\rho_{l_c+1,l_t}(t) + \Phi_t\rho_{l_c,l_t+1}(t) \\ &+l_c\gamma_c\Theta_c\rho_{l_c-1,l_t}(t) \\ &+l_t\gamma_t\Theta_t\rho_{l_c,l_t-1}(t)\end{aligned}$$

$$\begin{aligned}\Phi_j \;&=\; iV_j^{\times} \\ \Theta_j \;&=\; i\left(\frac{2\lambda_j}{\beta\hbar^2}V_j^{\times} - i\frac{\lambda_j}{\hbar}\gamma_j V_j^{\circ}\right)\end{aligned}$$

ARRAYFIRE A Tensor Library for GPUs

Equation of Motion Phase matching approach (EOM-PMA)

System-field interaction Hamiltonian

$$H_\alpha(t) = -\eta_\alpha E_\alpha(t - t_\alpha)\{\mathrm{e}^{\mathrm{i}\omega_\alpha t}X + \mathrm{e}^{-\mathrm{i}\omega_\alpha t}X^\dagger\}$$

$$X = |0\rangle\langle 2| \qquad X^\dagger = |2\rangle\langle 0|$$

Equation of motion phase-matching approach (EOM-PMA) [Maxim Gelin and Wolfgang Domcke]

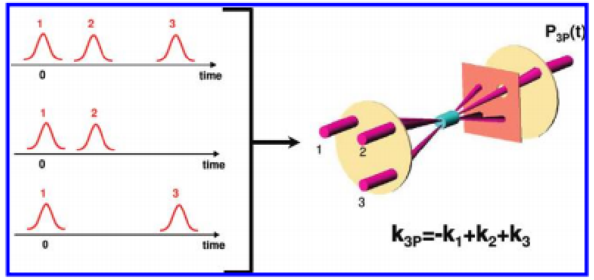
ACCOUNTS of chemical research

Efficient Calculation of Time- and Frequency-Resolved Four-Wave-Mixing Signals

MAXIM F. GELIN, DASSIA EGOROVA, AND WOLFGANG DOMCKE*
Department of Chemistry, Technical University of Munich, D-85747 Garching, Germany

RECEIVED ON FEBRUARY 9, 2009

CONSPECTUS



Ideal spontaneous emission spectrum

$$S(t, \omega_\mathrm{f}) = \mathrm{Im}\{A(t, \omega_\mathrm{f})\}$$

$$A(t, \omega_\mathrm{f}) = \mathrm{Tr}\{\mathrm{e}^{-\mathrm{i}\omega_\mathrm{f}t}X^\dagger[\bar{\rho}_{00}(t) - \rho_{00}(t)]\} + O({\eta_\mathrm{f}}^3)$$

$$\partial_t\boldsymbol{\rho}(t) = -\frac{\mathrm{i}}{\hbar}[H^{(\mathrm{S})} - H_\mathrm{p}(t), \boldsymbol{\rho}(t)] - (\mathcal{R} + \mathcal{D})\boldsymbol{\rho}(t)$$

$$\partial_t\bar{\boldsymbol{\rho}}(t) = -\frac{\mathrm{i}}{\hbar}[H^{(\mathrm{S})} - H_\mathrm{p}(t), \bar{\boldsymbol{\rho}}(t)] + \frac{\mathrm{i}}{\hbar}\mathrm{e}^{\mathrm{i}\omega_\mathrm{f}t}X\bar{\boldsymbol{\rho}}(t) - (\mathcal{R} + \mathcal{D})\bar{\boldsymbol{\rho}}(t)$$

pump pulse

gate pulse fluorescence

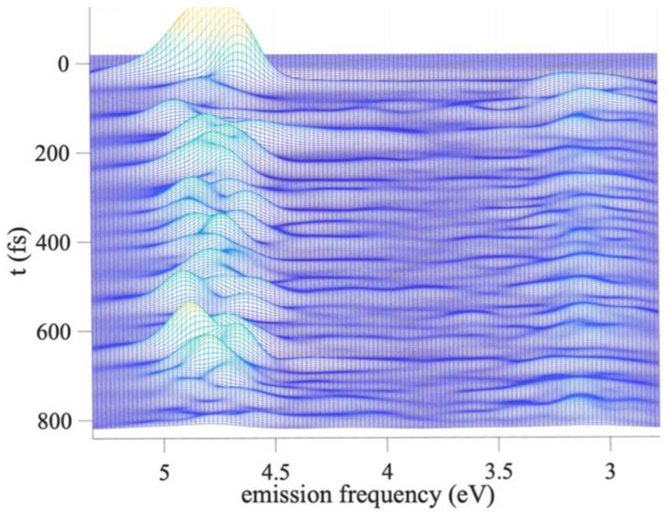
Measurable time- and frequency-gated (TFG) SE spectrum

$$S_\mathrm{TFG}(t, \omega_\mathrm{f}) \sim \mathrm{Im}\int_{-\infty}^{\infty}\mathrm{d}\omega' \int_{-\infty}^{\infty}\mathrm{d}t'\ \Phi(t - t', \omega_\mathrm{f} - \omega')A(t', \omega')$$

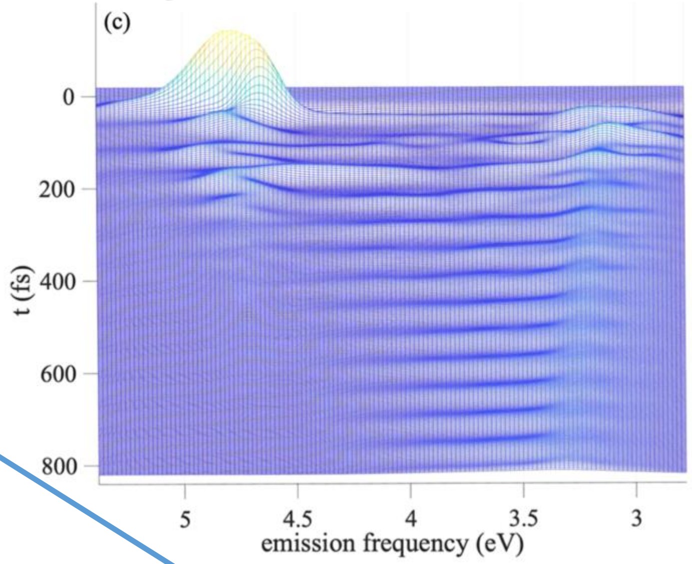
Time- and Frequency-Resolved Fluorescence Spectra

$$J_j(\omega) = 2\lambda_j\gamma_j\omega/(\omega^2+\gamma_j^2), \qquad j = c, t$$

$\gamma_j^{-1} = 50$ fs

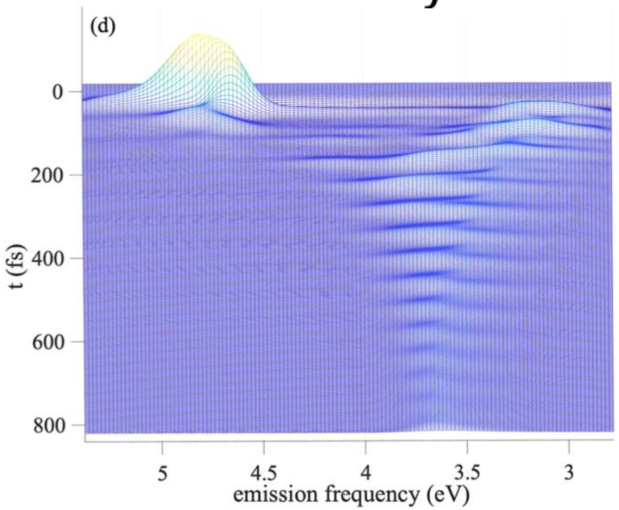


Zero system-bath coupling $\lambda_j = 0$



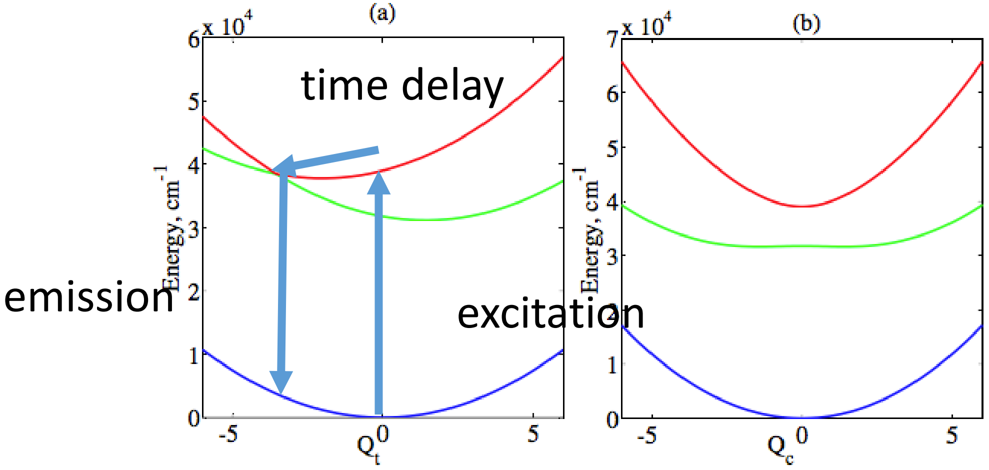
Weak system-bath coupling

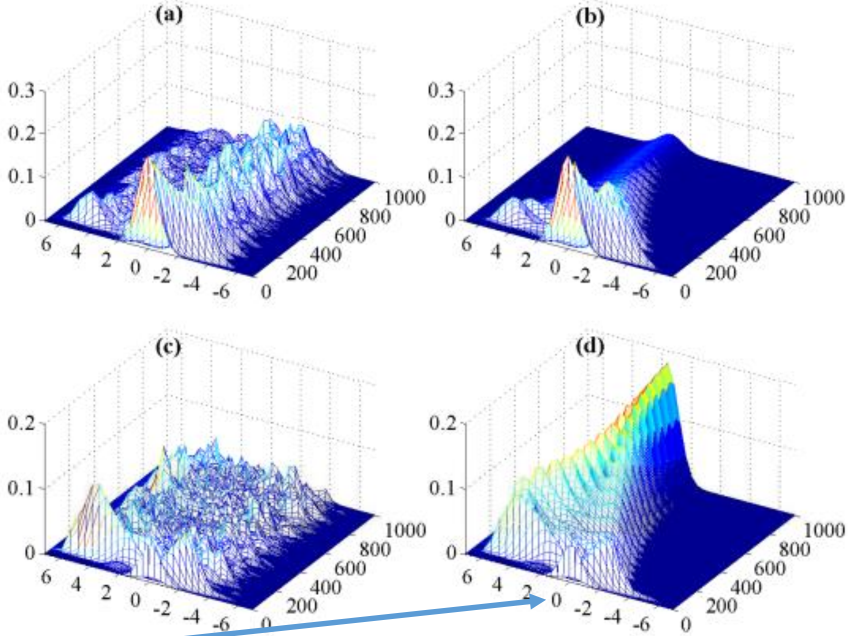
$\lambda_j = 10$ cm^{-1}



intermediate system-bath coupling

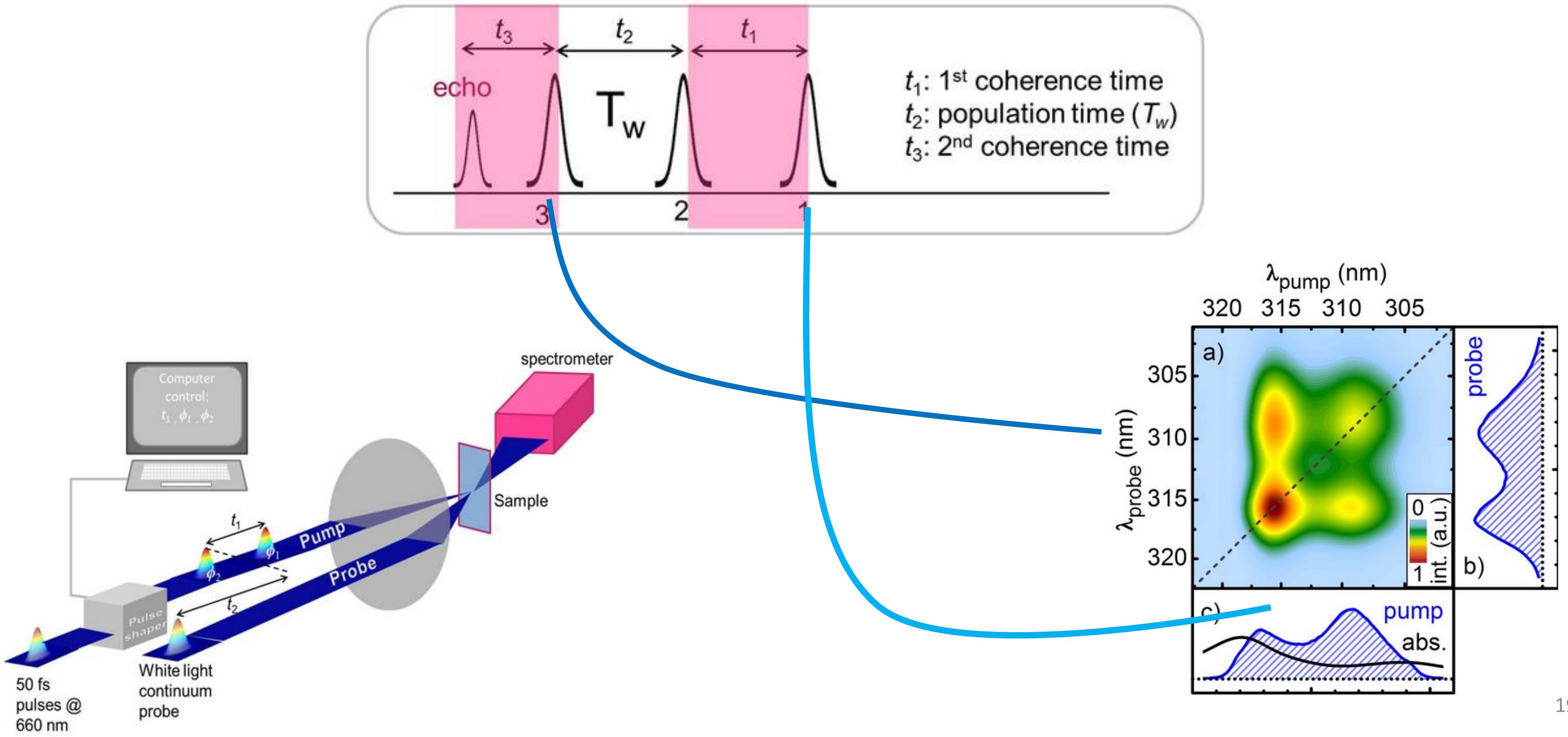
$\lambda_j = 60$ cm^{-1}





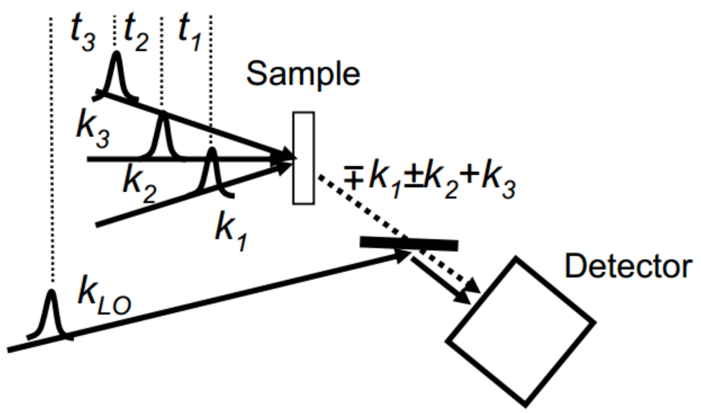
J. Phys. Chem. Lett, **10**, 5873-5880, 2019

Electronic 2D spectroscopy

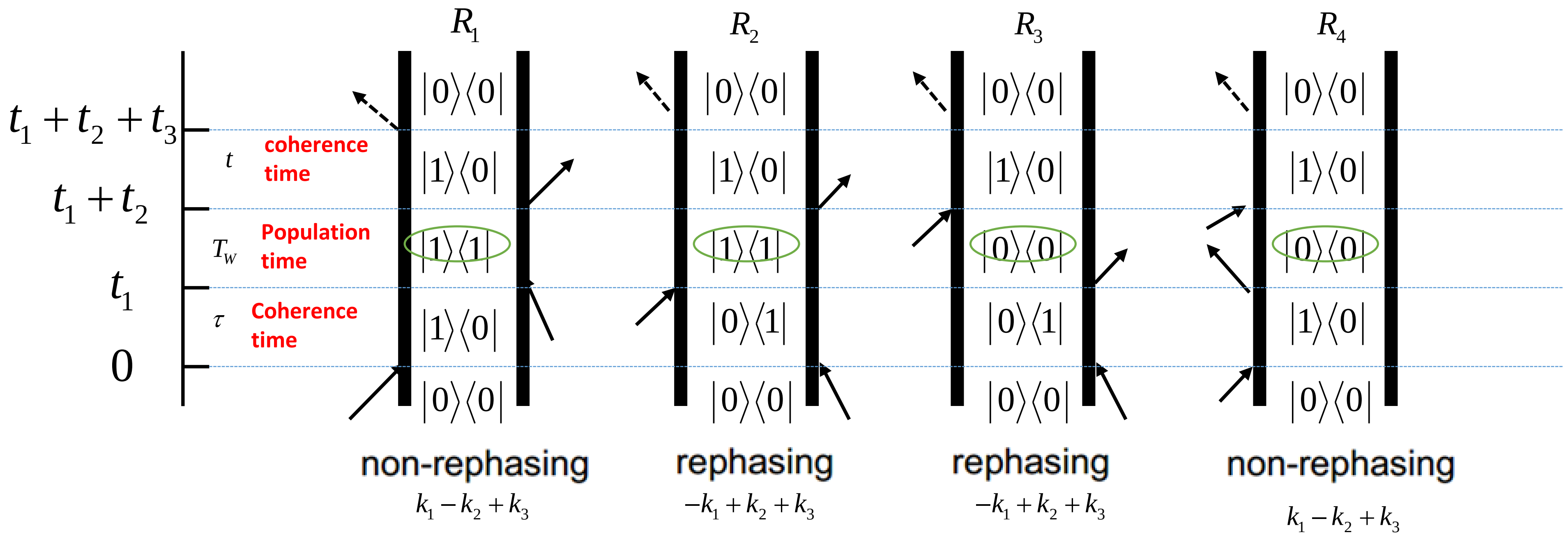


Double-Sided Feynman Diagrams

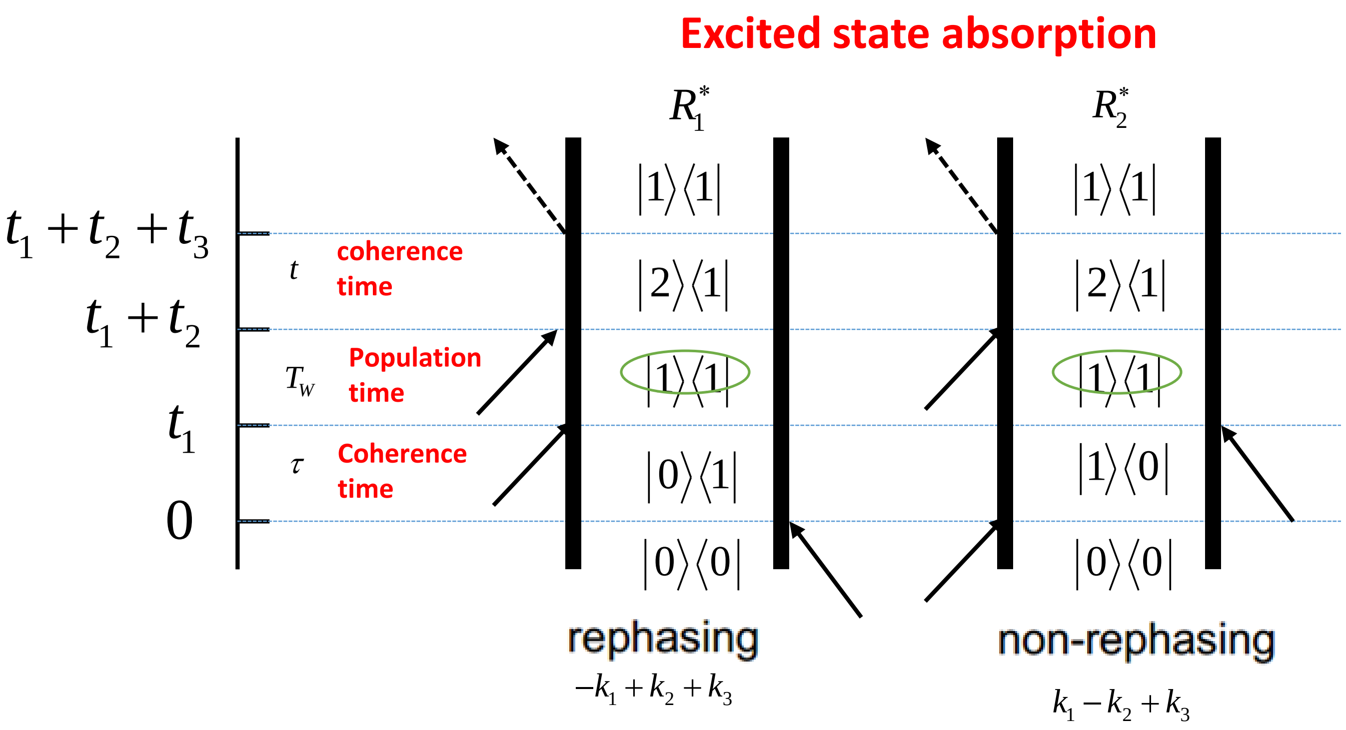
$$R_1(t_3,t_2,t_1) = \Phi(t_1, t_1+t_2, t_1+t_2+t_3, 0).$$
$$R_2(t_3,t_2,t_1) = \Phi(0, t_1+t_2, t_1+t_2+t_3, t_1).$$
$$R_3(t_3,t_2,t_1) = \Phi(0, t_1, t_1+t_2+t_3, t_1+t_2).$$
$$R_4(t_3,t_2,t_1) = \Phi(t_1+t_2+t_3, t_1+t_2, t_1, 0).$$



Stimulated Emission **Ground state bleaching**



Double-Sided Feynman Diagrams



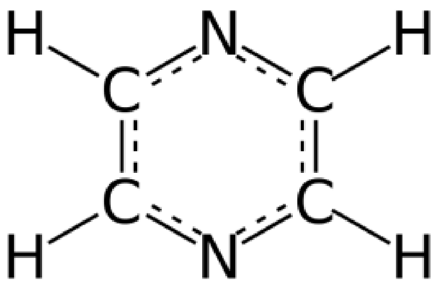
$$P_R^{(3)}(t,T_w,\tau)=-i\left[R_2(t,T_w,\tau)+R_3(t,T_w,\tau)-R_1^*(t,T_w,\tau)\right]$$

$$P_{NR}^{(3)}(t,T_w,\tau)=-i\left[R_1(t,T_w,\tau)+R_4(t,T_w,\tau)-R_2^*(t,T_w,\tau)\right]$$

$$S_R(\omega_t,T_w,\omega_\tau)=\mathrm{Re}\int_0^\infty\int_0^\infty dtd\tau iP_R^{(3)}(t,T_w,\tau)e^{-i\omega_\tau\tau+i\omega_t t}$$

$$S_{NR}(\omega_t,T_w,\omega_\tau)=\mathrm{Re}\int_0^\infty\int_0^\infty dtd\tau iP_{NR}^{(3)}(t,T_w,\tau)e^{i\omega_\tau\tau+i\omega_t t}$$

Simulation of four-wave-mixing signals with multiconfigurational Ehrenfest dynamics



Hamiltonian

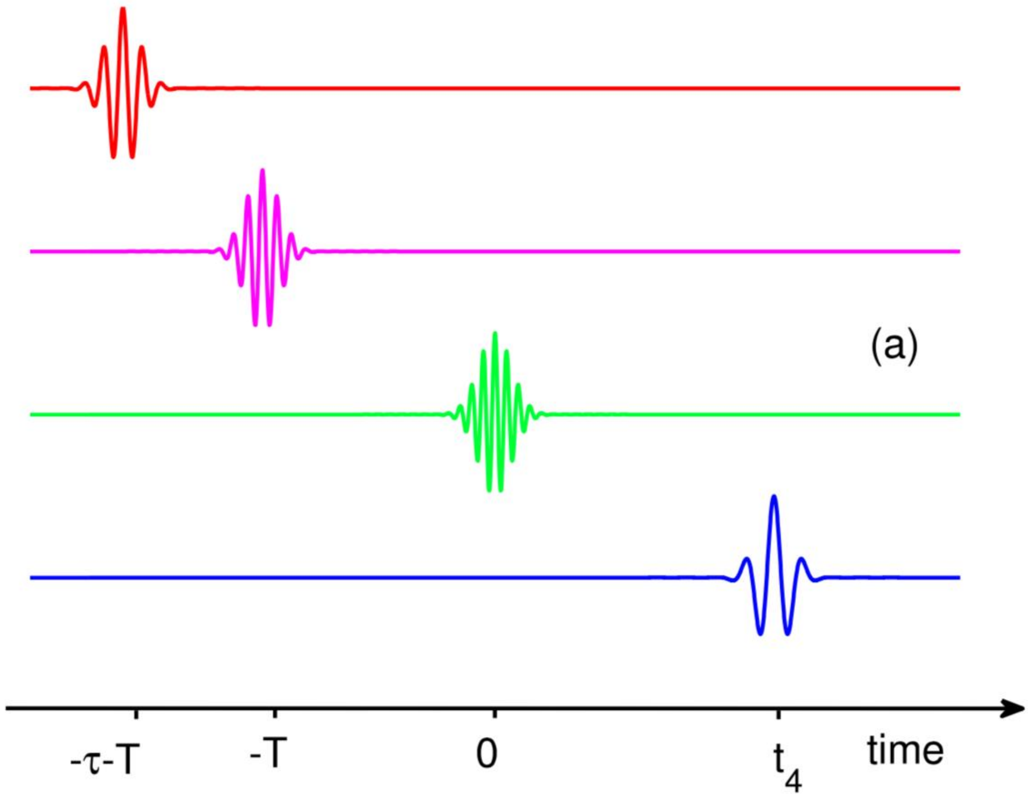
$$H = \sum_{k=\mathrm{S}_1,\mathrm{S}_2} \epsilon_k |k\rangle\langle k| + \sum_q \omega_q b_q^\dagger b_q + \frac{1}{\sqrt{2}} \sum_{k\neq k'}^{\mathrm{S}_1,\mathrm{S}_2} \lambda |k\rangle\langle k'| \left(b_{10a}^\dagger + b_{10a}\right) + \frac{1}{\sqrt{2}} \sum_{k=\mathrm{S}_1,\mathrm{S}_2} \sum_{q\neq 10a} \kappa_q^k |k\rangle\langle k| \left(b_q^\dagger + b_q\right)$$

System-field interaction Hamiltonian

$$H_L = -\sum_{\alpha=1}^{3} \left(\mathbf{E}_\alpha(\mathbf{r},t)\cdot\boldsymbol{\mu}_+ + \mathbf{E}_\alpha^*(\mathbf{r},t)\cdot\boldsymbol{\mu}_-\right)$$

$$\mathbf{E}_\alpha(\mathbf{r},t) = \mathbf{e}_\alpha E_\alpha(t-\tau_\alpha) e^{i\mathbf{k}_\alpha\cdot\mathbf{r} - i\omega_\alpha t}$$

$$\tau_1 = -T_{\mathrm{w}} - \tau, \quad \tau_2 = -T_{\mathrm{w}}, \quad \tau_3 = 0$$



Four time correlation functions

$$R_1(t_3,t_2,t_1) = \Phi(t_1, t_1+t_2, t_1+t_2+t_3, 0),$$

$$R_2(t_3,t_2,t_1) = \Phi(0, t_1+t_2, t_1+t_2+t_3, t_1),$$

$$R_3(t_3,t_2,t_1) = \Phi(0, t_1, t_1+t_2+t_3, t_1+t_2),$$

$$R_4(t_3,t_2,t_1) = \Phi(t_1+t_2+t_3, t_1+t_2, t_1, 0)$$

$$\Phi(\tau_4,\tau_3,\tau_2,\tau_1) = \langle \Phi_0 | \mu_- e^{-\frac{i}{\hbar}H(\tau_4-\tau_3)} \mu_+ e^{-\frac{i}{\hbar}H_{\mathrm{ph}}(\tau_3-\tau_2)} \mu_- e^{-\frac{i}{\hbar}H(\tau_2-\tau_1)} \mu_+ |\Psi_0\rangle$$

$$\begin{aligned} |\Psi(t)\rangle =& \sum_{u=1}^{M} \left(\sum_{k}^{\mathrm{S}_1,\mathrm{S}_2} A_{uk}(t)|k\rangle \right) |\mathbf{z}_u(t)\rangle \\ =& \sum_{u=1}^{M} \left(\sum_{k}^{\mathrm{S}_1,\mathrm{S}_2} A_{uk}(t)|k\rangle \right) \exp\left[\sum_q \left(z_{uq} b_q^\dagger - z_{uq}^* b_q \right) \right] |0\rangle_{\mathrm{ph}} \end{aligned}$$

Multiconfigurational Enrenfest Dynamics (MCE, Dmitry Shalashilin)

Simulation of 4WM signals with MCE

Stimulated emisssion (SE)

$$S_{\rm SE}(\omega_\tau, T_w, \omega_t) = {\rm Re}\int_0^\infty \int_0^\infty d\tau dt[R_1(\tau, T_w, t)e^{i\omega_\tau t + i\omega_t t} + R_2(\tau, T_w, t)e^{-i\omega_\tau \tau + i\omega_t t}]$$

ground state bleach (GSB)

$$S_{\rm GSB}(\omega_\tau, T_w, \omega_t) = {\rm Re}\int_0^\infty \int_0^\infty d\tau dt[R_4(\tau, T_w, t)e^{i\omega_\tau t + i\omega_t t} + R_3(\tau, T_w, t)e^{-i\omega_\tau \tau + i\omega_t t}]$$

2D spectra

$$S_{\rm tot}(\omega_\tau, T_w, \omega_t) = S_{\rm GSB}(\omega_\tau, T_w, \omega_t) + S_{\rm SE}(\omega_\tau, T_w, \omega_t)$$

Transient absorption (TA) spectroscopy

$$P_{\rm TA}({\rm T_w}, t) \sim -i\left[R_1(0, {\rm T_w}, t) + R_2(0, {\rm T_w}, t) + R_3(0, {\rm T_w}, t) + R_4(0, {\rm T_w}, t)\right]$$

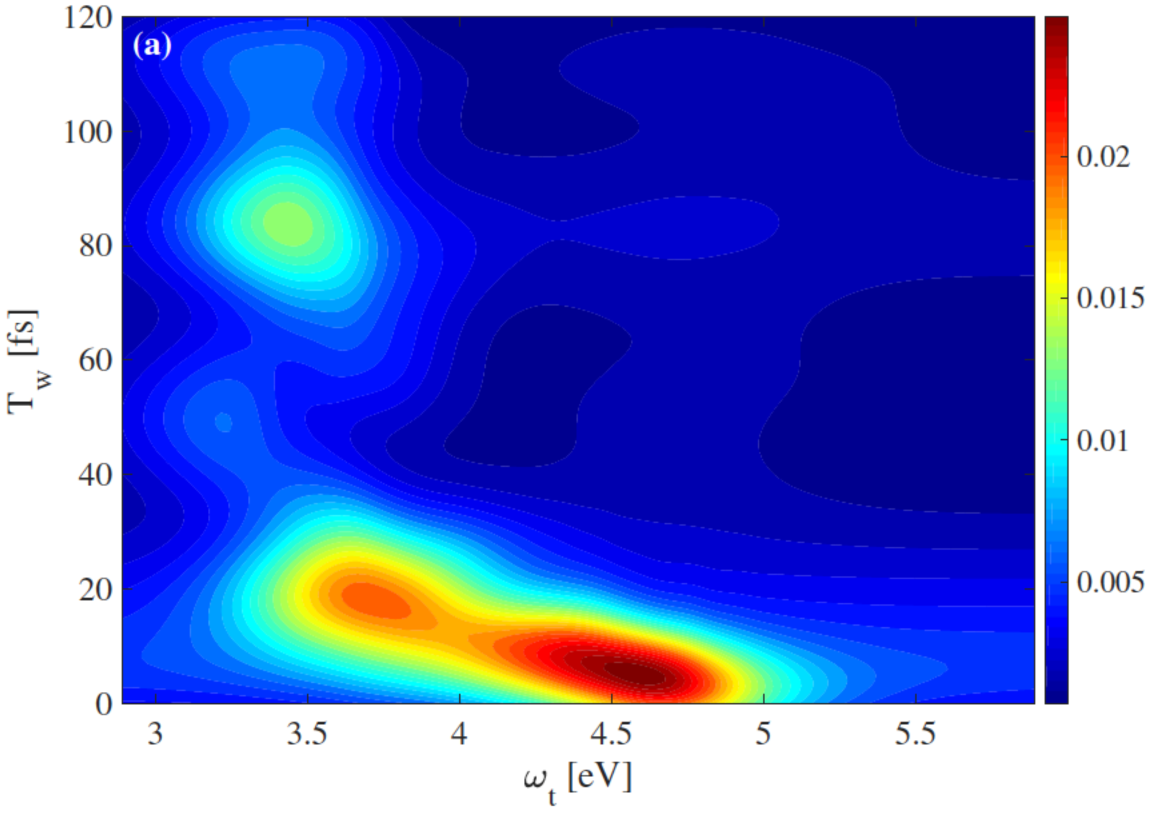
$$S_{\rm TA}({\rm T_w}, \omega_t) = {\rm Re}\int_0^\infty dt i P_{\rm TA}({\rm T_w}, t)e^{i\omega_t t}$$

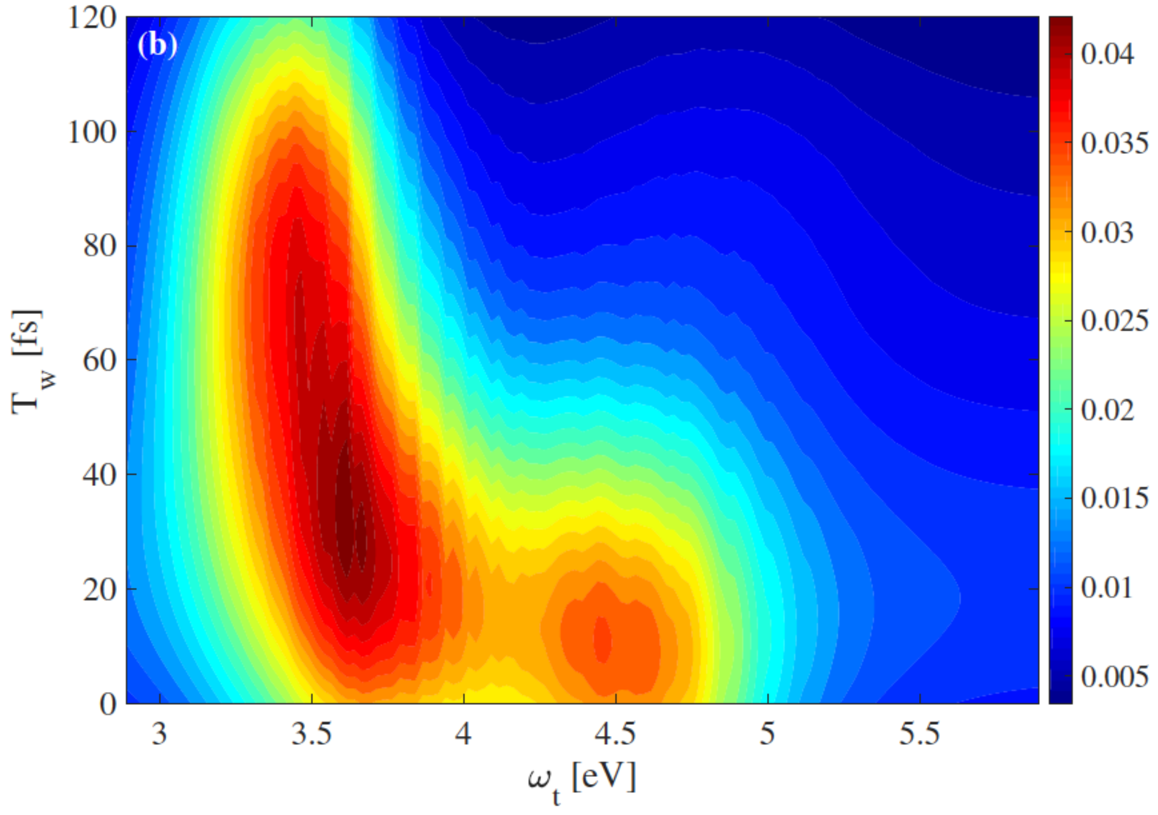
Time-resolved fluorescence spectroscopy

$$S_{\rm TFG}({\rm T_w}, \omega_t) \sim {\rm Re}\int_0^\infty dt_2 dt R_2(0, t_2, t)e^{i\omega_t t}E_f(t + t_2 - {\rm T_w})E_f(t_2 - {\rm T_w})$$

$$E_f(t) = \exp\{-(t/\tau_f)^2\}$$

TFG fluorescence spectra $S_{\mathrm{TFG}}(\mathrm{T_w}, \omega_t)$



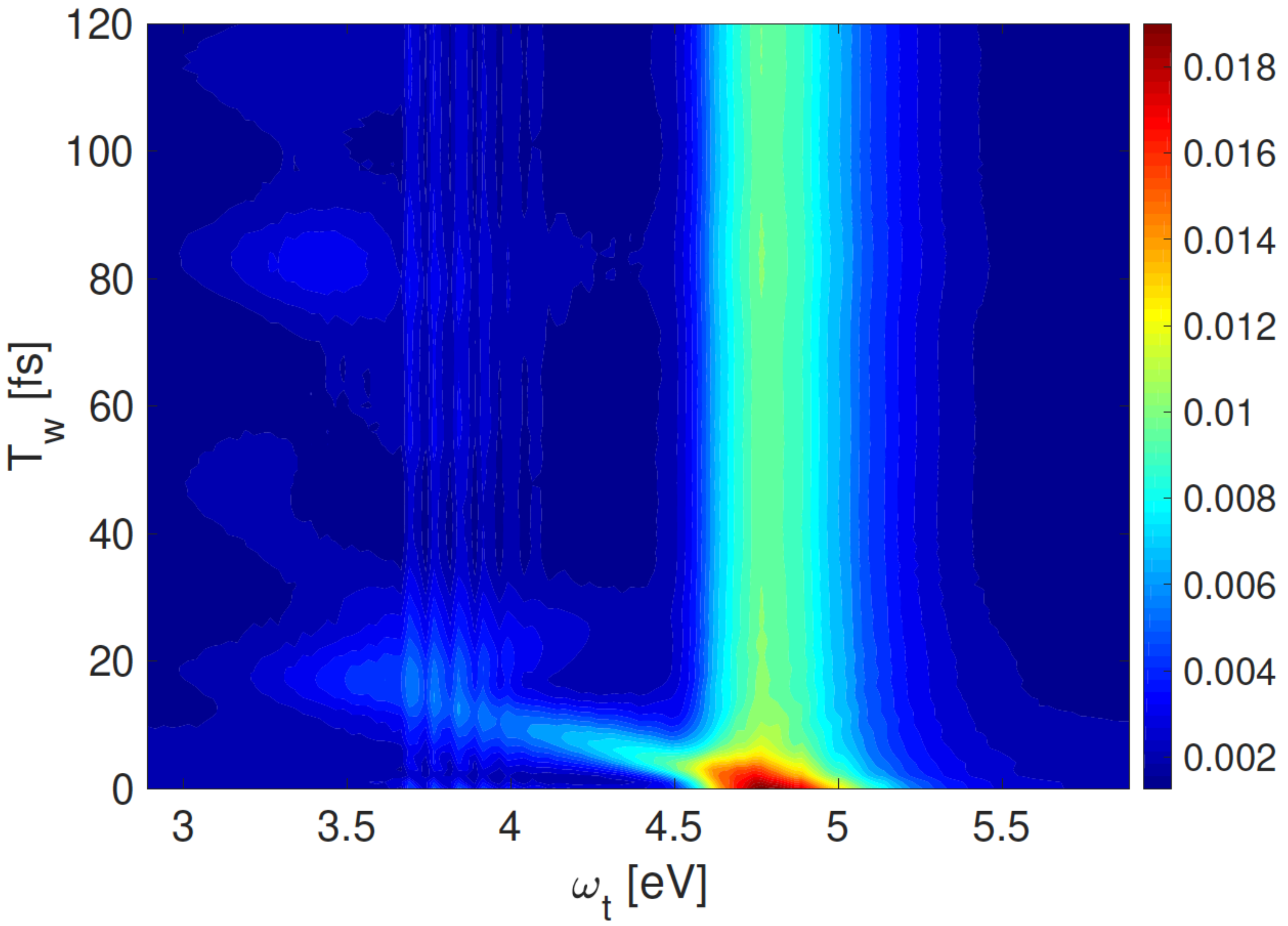


good time resolution $\tau_f = 12$ fs

good frequency resolution $\tau_f = 60$ fs

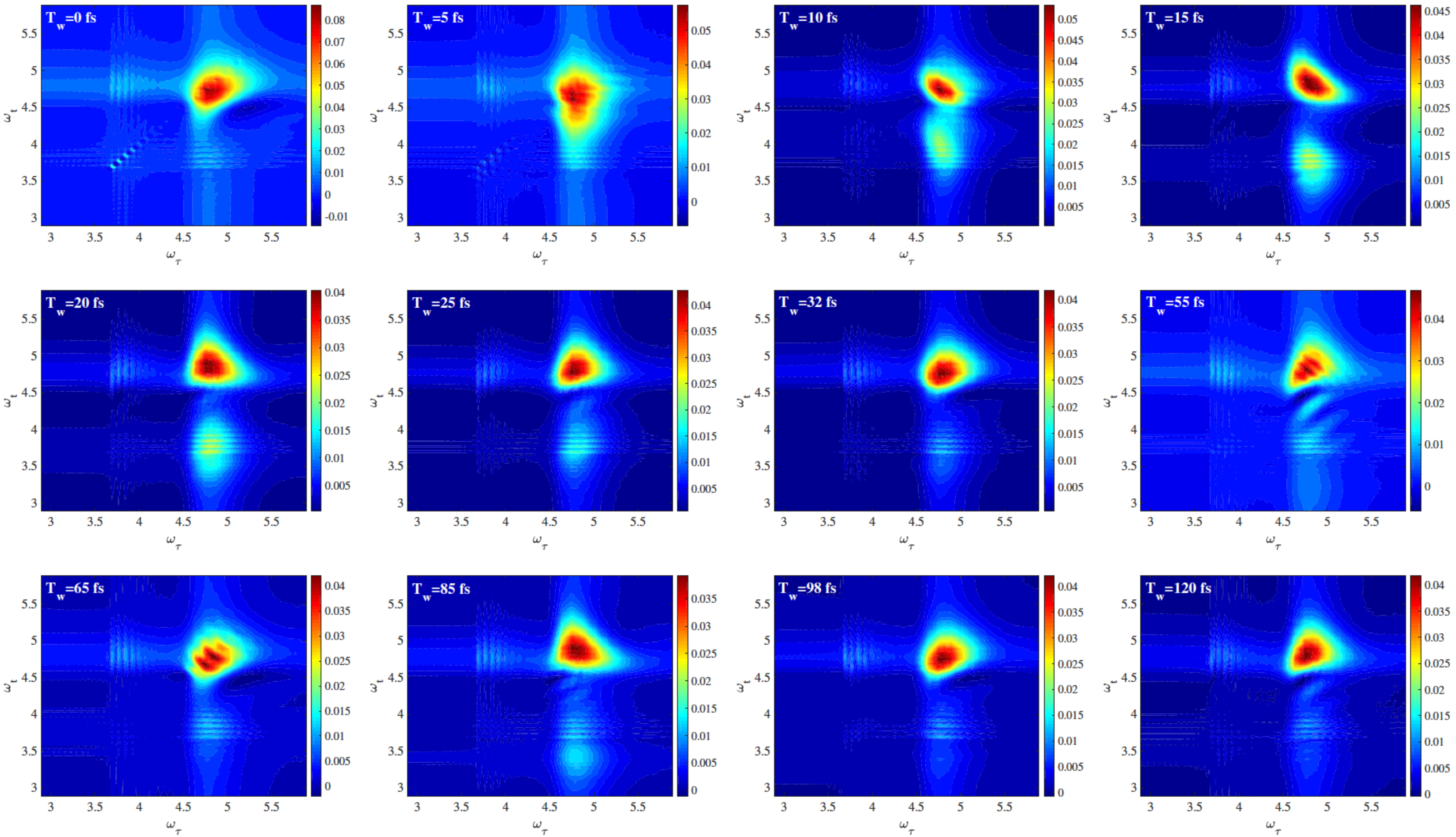
J. Chem. Phys, **154**, 054105, 2021

Transient absorption signal $S_{\mathrm{TA}}(\mathrm{T_w}, \omega_t)$



J. Chem. Phys, **154**, 054105, 2021

2D electronic spectra $S(\omega_\tau, \mathrm{T_w}, \omega_t)$



J. Chem. Phys, **154**, 054105, 2021

Efficient simulation of time and frequency resolved four wave mixing signals at finite temperature: The thermo-field dynamics approach

Zero temperature four-time correlation function

$$\Phi^e(\tau_4,\tau_3,\tau_2,\tau_1) = \langle \Phi_0 | \boldsymbol{\mu}_- e^{-iH_e(\tau_4-\tau_3)} \boldsymbol{\mu}_+ e^{-ih_g(\tau_3-\tau_2)} \boldsymbol{\mu}_- e^{-iH_e(\tau_2-\tau_1)} \boldsymbol{\mu}_+ |\Psi_0\rangle \;, \; |\Psi_0\rangle = |g\rangle|0\rangle_g$$

Finite temperature four-time correlation function

$$\Phi^e(\tau_4,\tau_3,\tau_2,\tau_1) = \mathrm{Tr}\left(\rho_g \langle g| e^{ih_g\tau_4} \boldsymbol{\mu}_- e^{-iH_e(\tau_4-\tau_3)} \boldsymbol{\mu}_+ e^{-ih_g(\tau_3-\tau_2)} \boldsymbol{\mu}_- e^{-iH_e(\tau_2-\tau_1)} \boldsymbol{\mu}_+ e^{-ih_g\tau_1} |g\rangle\right)$$

$$\rho_g = Z_g^{-1} \exp\{-\beta h_g\}$$

Thermo-field dynamics (TFD)

$$|\mathbf{0}(\beta)\rangle = Z_g^{-1/2} \sum_l e^{-\beta\hbar\omega_l/2} |l, \tilde{l}\rangle$$

$$= Z_g^{-1/2} e^{-\frac{1}{2}\beta h_g} |\boldsymbol{I}\rangle; \quad |\boldsymbol{I}\rangle = \sum |l, \tilde{l}\rangle$$

$$\langle Q\rangle = \mathrm{Tr}\{\rho_g Q\} = \langle \mathbf{0}(\beta)|Q|\mathbf{0}(\beta)\rangle$$

$$h_g = \sum_l \omega_l b_l^\dagger b_l; \quad \tilde{h}_g = \sum_l \omega_l \tilde{b}_l^\dagger \tilde{b}_l$$

$$|\mathbf{0}(\beta)\rangle = \mathrm{e}^{-\mathrm{i}\hat{G}} |\mathbf{0}\rangle_g \qquad \hat{G} = \hat{G}^\dagger = -\mathrm{i} \sum_l \theta_l (\hat{b}_l \hat{\tilde{b}}_l - \hat{b}_l^\dagger \hat{\tilde{b}}_l^\dagger)$$

Efficient simulation of time and frequency resolved four wave mixing signals at finite temperature: The thermo-field dynamics approach

Thermo-field dynamics (TFD)

$$\boxed{\Phi^e(\tau_4,\tau_3,\tau_2,\tau_1) = \langle g|\langle \mathbf{0}|\boldsymbol{\mu}_- e^{-i\bar{H}_{e\theta}(\tau_4-\tau_3)}\boldsymbol{\mu}_+ e^{-i\bar{h}_{g\theta}(\tau_3-\tau_2)}\boldsymbol{\mu}_- e^{-i\bar{H}_{e\theta}(\tau_2-\tau_1)}\boldsymbol{\mu}_+|\mathbf{0}\rangle|g\rangle}$$

$$\bar{h}_{g\theta} = e^{iG}\left(h_g - \tilde{h}_g\right)e^{-iG}$$

$$\bar{H}_{e\theta} = e^{iG}\left(H_e - \tilde{h}_g\right)e^{-iG}$$

$$e^{iG}b_l e^{-iG} = b_l\cosh(\theta_l) + \tilde{b}_l^\dagger\sinh(\theta_l),$$

$$e^{iG}\tilde{b}_l e^{-iG} = \tilde{b}_l\cosh(\theta_l) + b_l^\dagger\sinh(\theta_l),$$

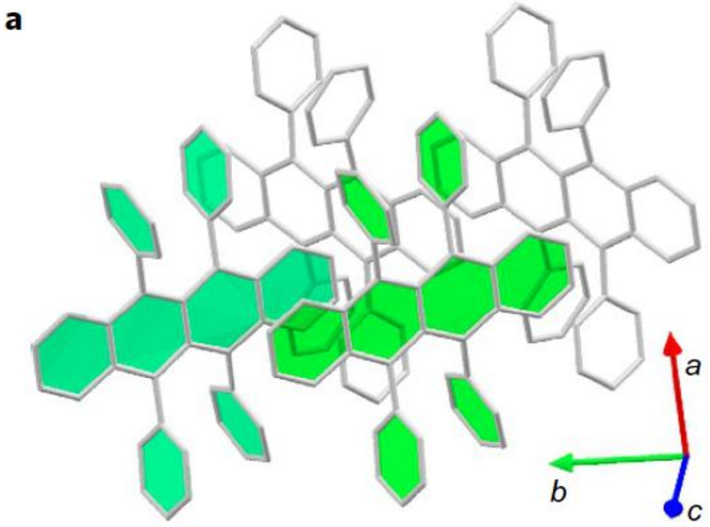
$$e^{iG}\left(b_l^\dagger b_l - \tilde{b}_l^\dagger\tilde{b}_l\right)e^{-iG} = b_l^\dagger b_l - \tilde{b}_l^\dagger\tilde{b}_l.$$

Zero temperature four time correlation function

$$\boxed{\Phi^e(\tau_4,\tau_3,\tau_2,\tau_1) = \langle\Phi_0|\boldsymbol{\mu}_- e^{-iH_e(\tau_4-\tau_3)}\boldsymbol{\mu}_+ e^{-ih_g(\tau_3-\tau_2)}\boldsymbol{\mu}_- e^{-iH_e(\tau_2-\tau_1)}\boldsymbol{\mu}_+|\Psi_0\rangle}\ , \quad |\Psi_0\rangle = |g\rangle|0\rangle_g.$$

Model Hamiltonian of CI mediated singlet fission in rubrene

Two states singlet fission model Singlet state S_1 Triplet pair state TT



$$\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{SB}$$

$$\hat{H}_S = |g\rangle \hat{h}_g \langle g| + \sum_{e=\mathrm{S}_1,\mathrm{TT}} |e\rangle(\epsilon_e + \hat{h}_e)\langle e| + (|\mathrm{S}_1\rangle\langle \mathrm{TT}| + |\mathrm{TT}\rangle\langle \mathrm{S}_1|)\lambda \hat{Q}_c$$

$$\hat{h}_e = \hat{h}_g + \sum_{m=t} \kappa_m^{(e)} \hat{Q}_m$$

$$\hat{h}_g = \frac{1}{2}\sum_{j=c,t} \hbar\Omega_j \left\{\hat{P}_j^2 + \hat{Q}_j^2\right\}$$

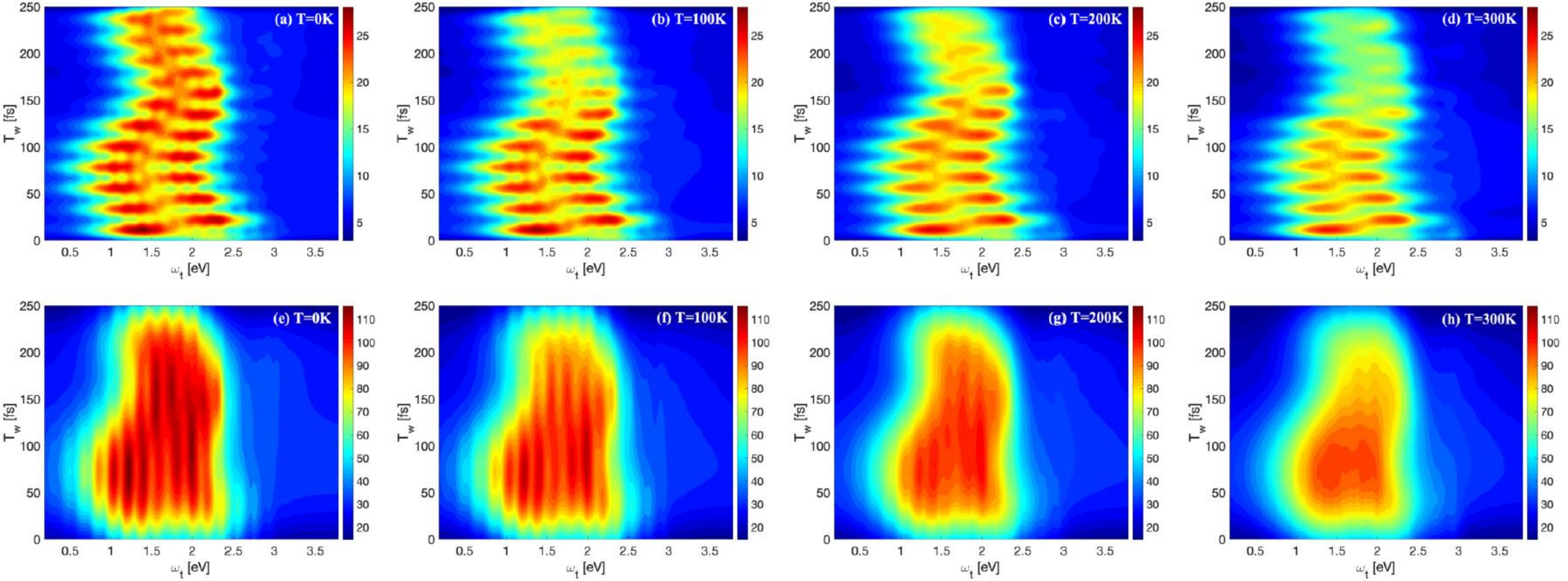
$$\hat{H}_B = \sum_n \frac{1}{2}\hbar\omega_n \left\{\hat{p}_n^2 + \hat{q}_n^2\right\}$$

$$\hat{H}_{SB} = \sum_{e=\mathrm{S}_1,\mathrm{TT}} |e\rangle(\sum_n \kappa_n^{(e)} \hat{q}_n)\langle e|$$

$$J(\omega) = \sum_n \kappa_n^2 \delta(\omega - \omega_n) = 2\eta \frac{\omega_c \omega}{\omega^2 + \omega_c^2}$$

	S_1	TT	Ω	$\tau = 2\pi/\Omega$
ϵ_e	2.58	2.5812		
κ_{t_1}	0.3720	-0.3720	0.1860	22.2
κ_{t_2}	0.0745	-0.0745	0.0260	159.1
κ_c	0	0	0.0154	268.6
		$\lambda = 0.05$		

TFG fluorescence spectra

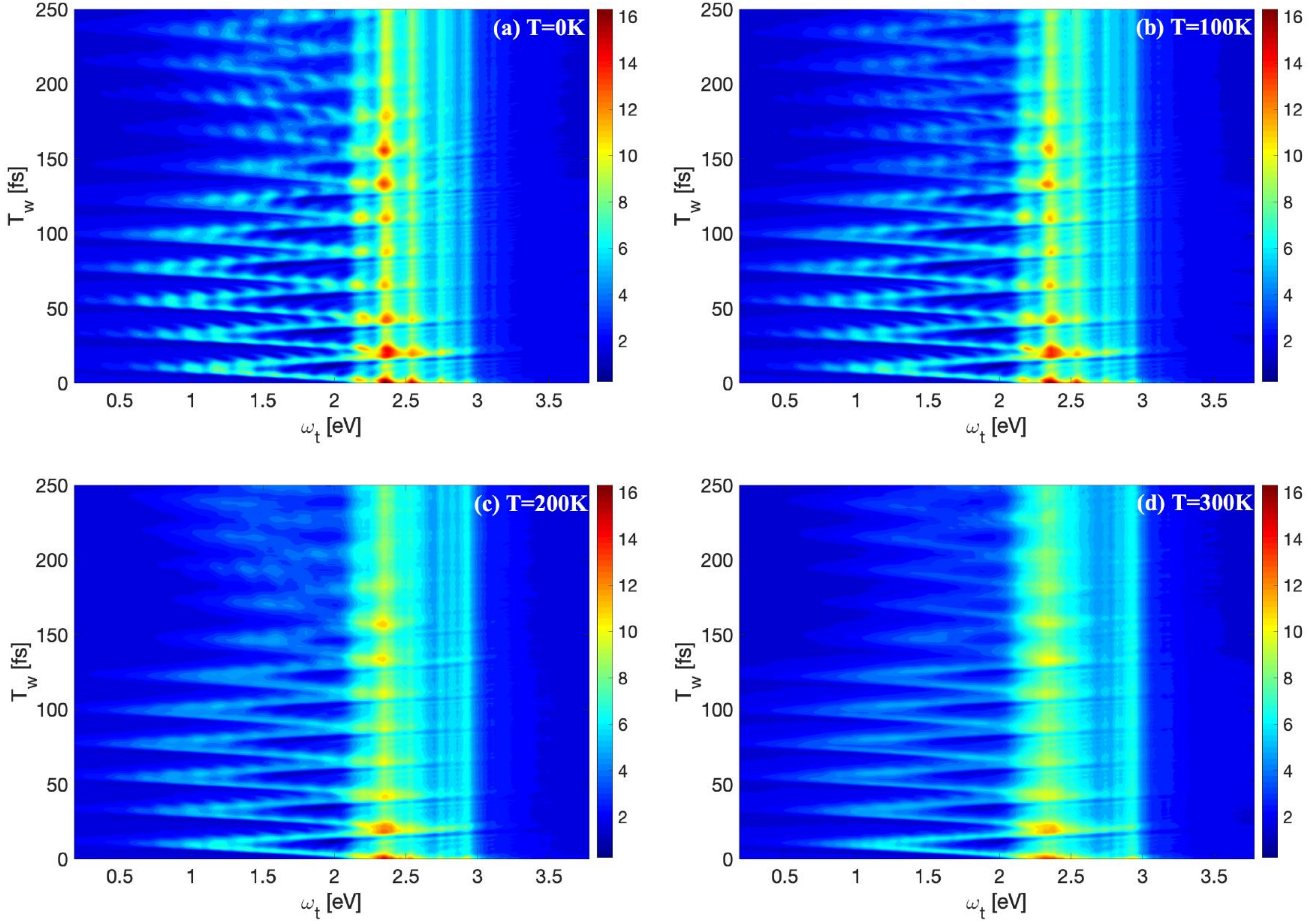


Upper panels: good time resolution $\tau_f = 12$ fs

Lower panels: good frequency resolution $\tau_f = 60$ fs

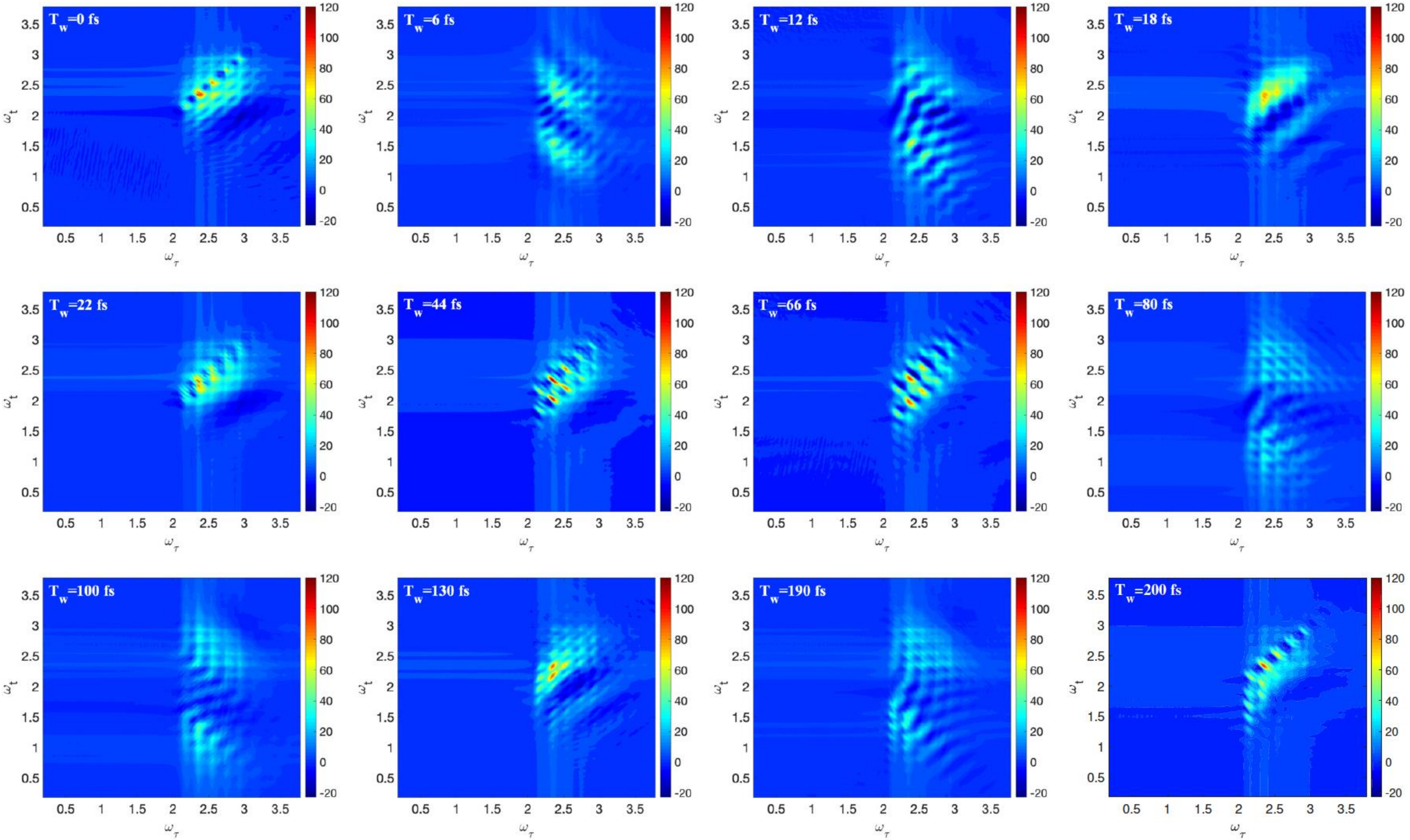
J. Chem. Theory. Comput, 17, 4359-4373 (2021)

Transient absorption spectra



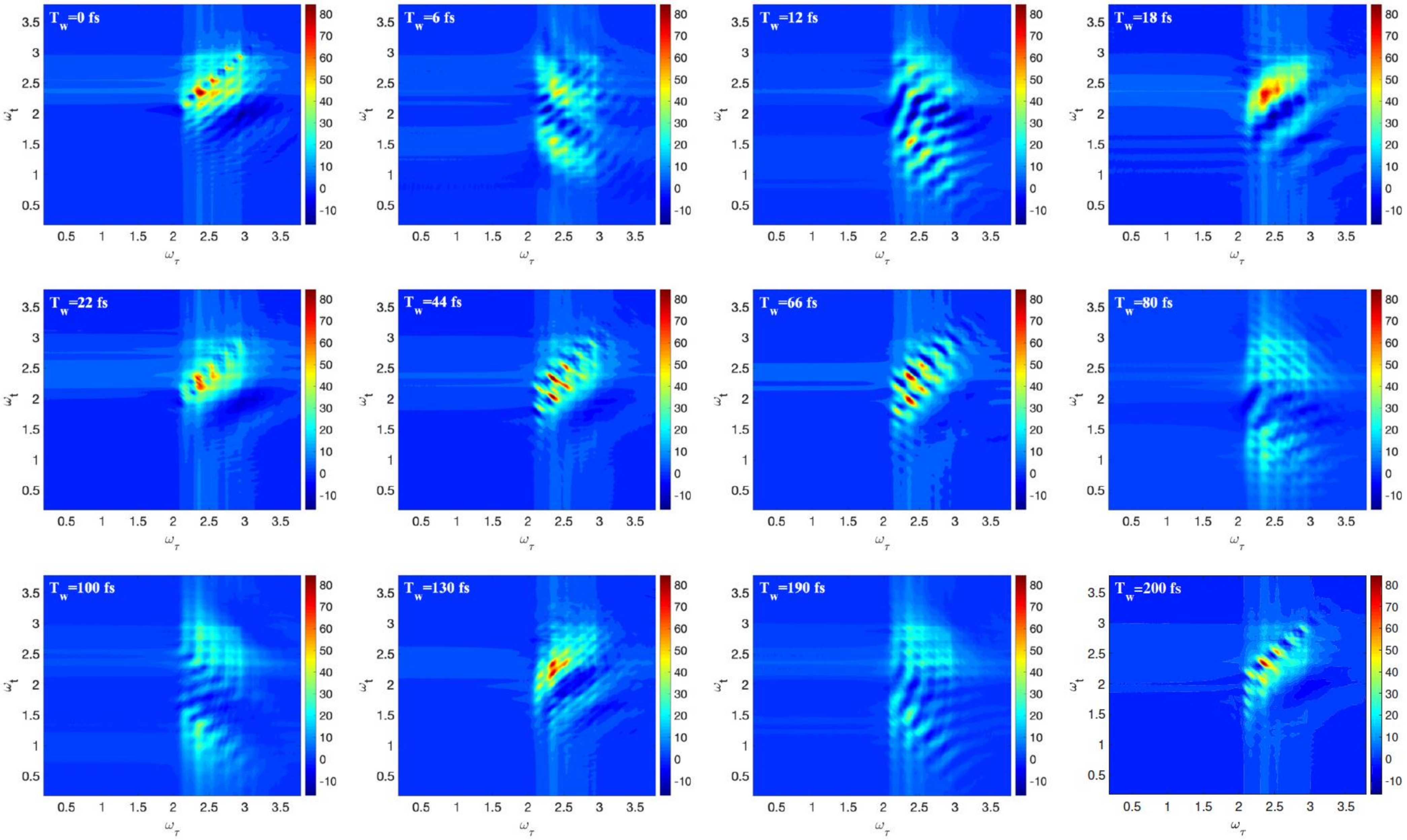
J. Chem. Theory. Comput, 17, 4359-4373 (2021)

2D electronic spectra at T=0K



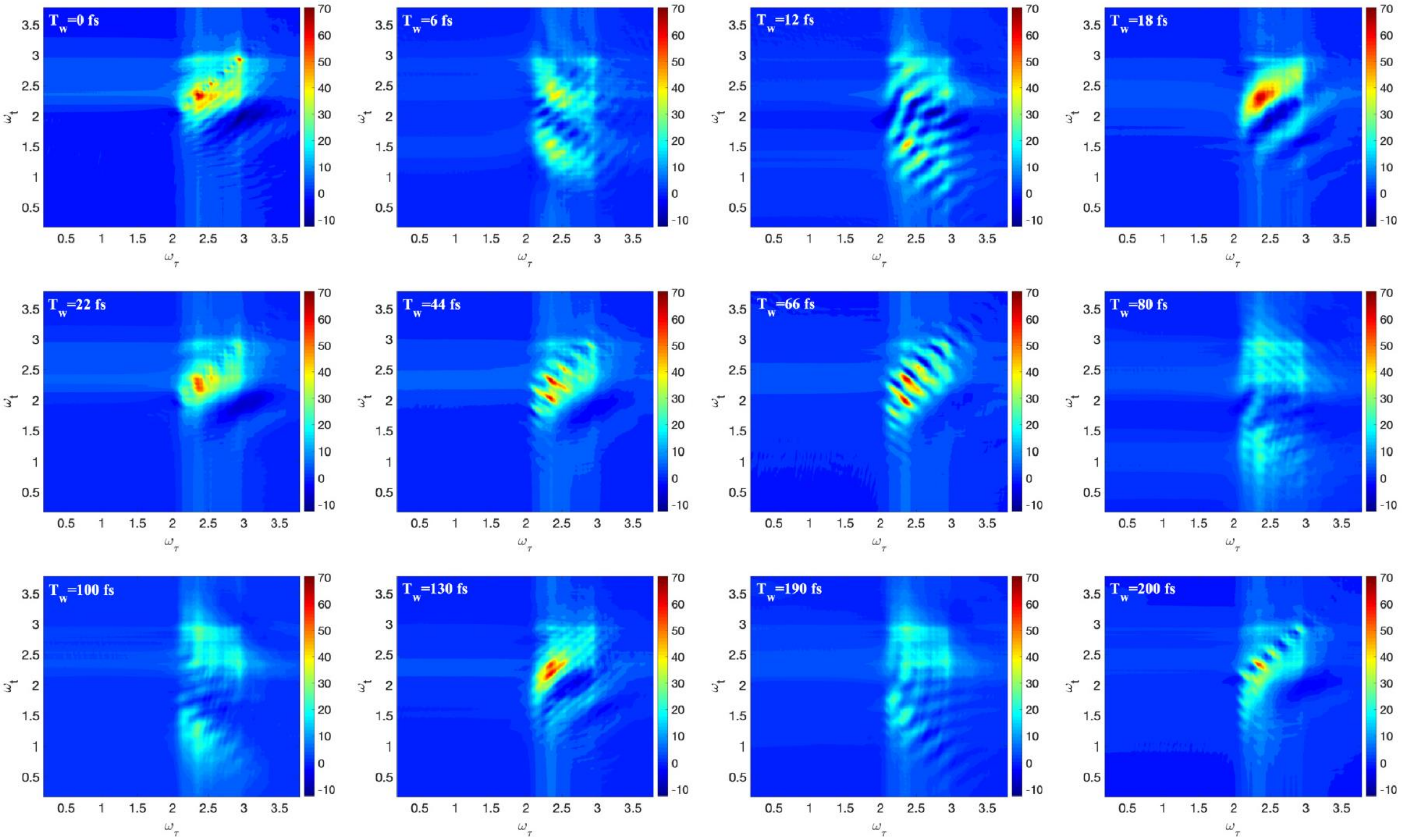
J. Chem. Theory. Comput, 17, 4359-4373 (2021)

2D electronic spectra at T=100K



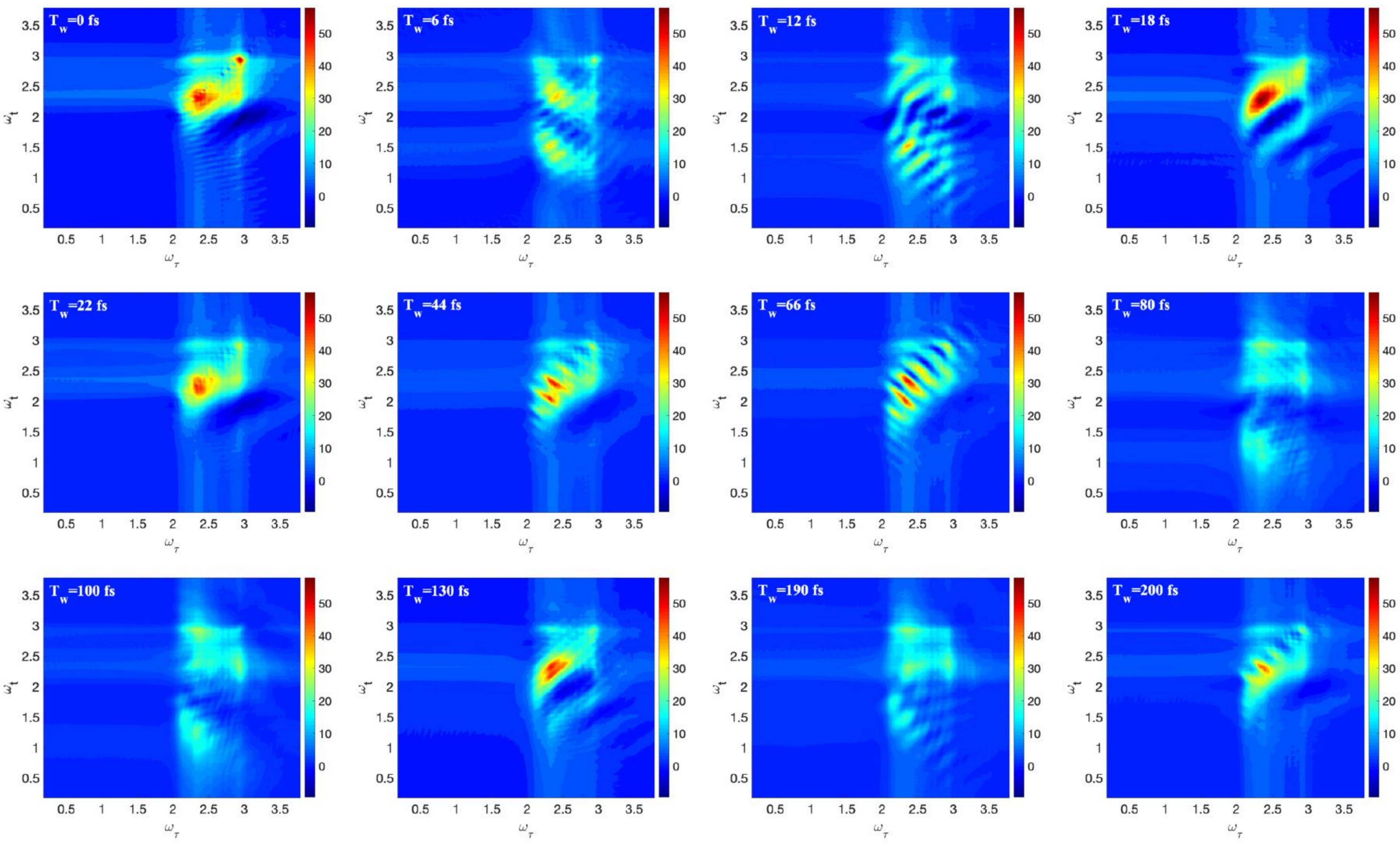
J. Chem. Theory. Comput, 17, 4359-4373 (2021)

2D electronic spectra at T=200K



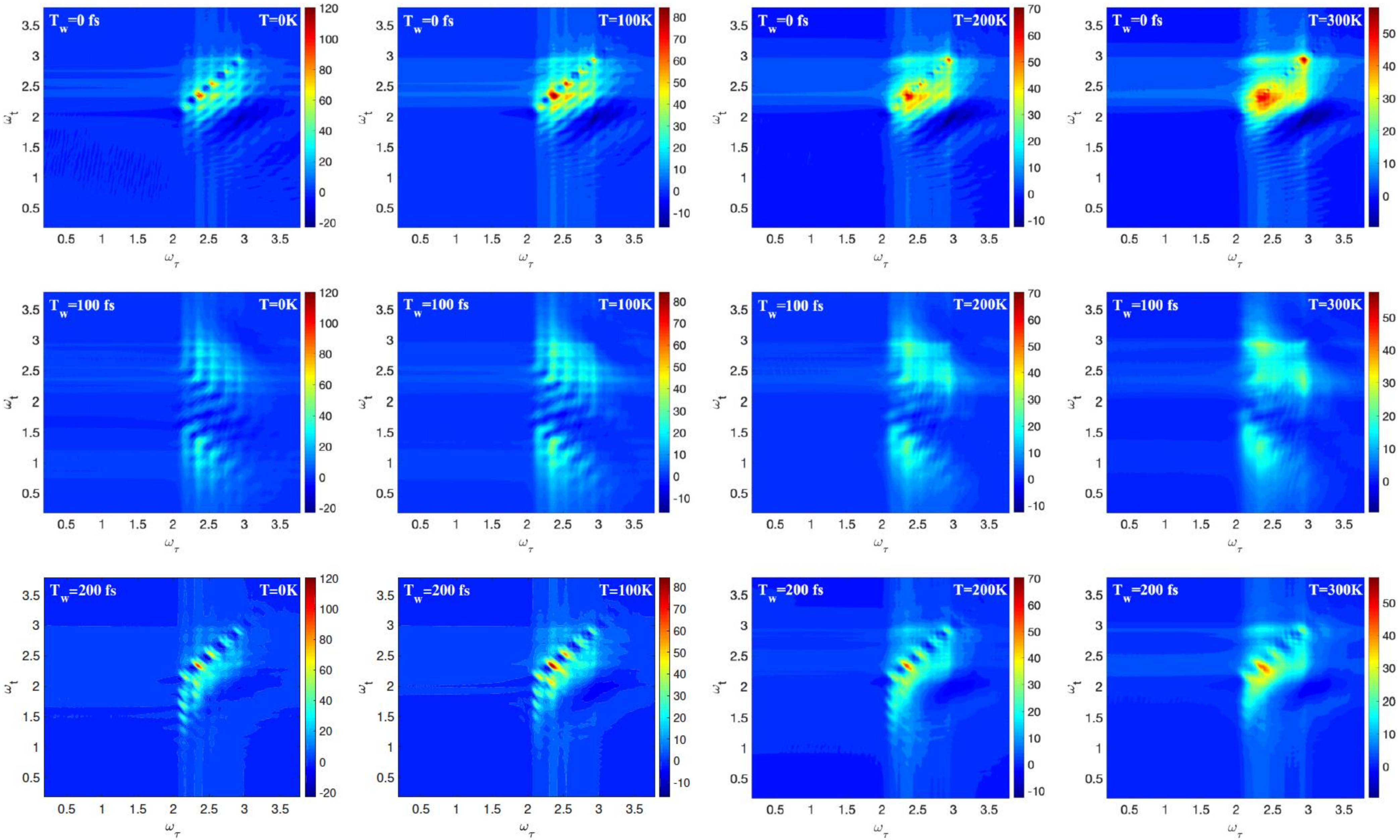
J. Chem. Theory. Comput, 17, 4359-4373 (2021)

2D electronic spectra at T=300K



J. Chem. Theory. Comput, 17, 4359-4373 (2021)

2D electronic spectra at T=0K,100K,200K,300K



J. Chem. Theory. Comput, 17, 4359-4373 (2021)

On the fly Ab initio surface hopping simulations of four-wave-mixing signals of Nonadiabatic Excited-State Dynamics Using the Doorway-Window representation

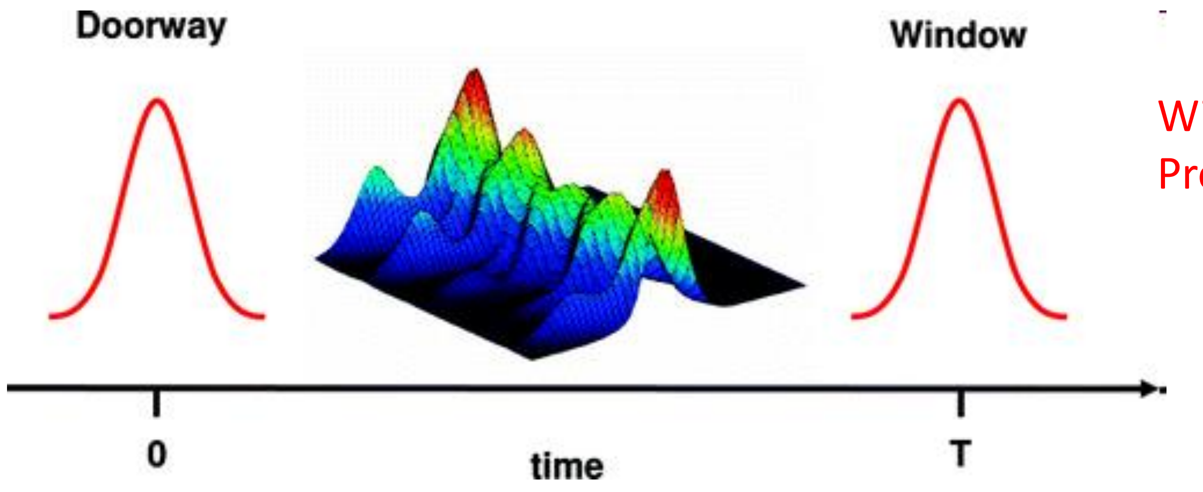
On-the-fly Ab initio direct dynamics:

1. Only local information of adiabatic PES needed, computed “on-the-fly” with ab initio electronic structure theory, avoid the tedious construction of global PES.
2. Cost of classical trajectory scales linearly with DOFs, avoids the curse of dimensionality

Nonadiabatic transition between adiabatic PES→ surface hopping

Doorway-window representation of the signals

Create doorway wave packet via pump pulse



Window wavepacket created by Probe pulse

Time evolution of doorway wave packet is projected into the window wave packet.

Hamiltonian

$$H = \begin{pmatrix} H_0 & 0 & 0 \\ 0 & H_1 & 0 \\ 0 & 0 & H_2 \end{pmatrix}$$

$\longrightarrow$ Electronic ground state

$\longrightarrow$ $E_j \sim \omega_{pu},\ \omega_{pr}$

$\longrightarrow$ $E_j \sim 2\omega_{pu},\ 2\omega_{pr}$

$$\mu^{\uparrow} = \begin{pmatrix} 0 & \mu_{01} & 0 \\ 0 & 0 & \mu_{12} \\ 0 & 0 & 0 \end{pmatrix}, \quad \mu^{\downarrow} = \begin{pmatrix} 0 & 0 & 0 \\ \mu_{10} & 0 & 0 \\ 0 & \mu_{21} & 0 \end{pmatrix}$$

$$\frac{d}{dt}\rho(t) = -i[H - \mu^{\uparrow}\mathcal{E}(t) - \mu^{\downarrow}\mathcal{E}^*(t), \rho(t)]. \qquad \rho(t = -t_0) = \begin{pmatrix} \rho_B & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Nonlinear response functions

$$\mathcal{P}(t) \sim -i \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \mathcal{E}_{pu}(t+T-t_3-t_2-t_1)\mathcal{E}_{pu}(t+T-t_3-t_2)\mathcal{E}_{pr}(t-t_3)\times$$

$$\left\{e^{-i\omega_{pu}t_1} e^{i\omega_{pr}(t_3-t)} R_R(t_3,t_2,t_1) + e^{i\omega_{pu}t_1} e^{i\omega_{pr}(t_3-t)} R_{NR}(t_3,t_2,t_1)\right\}.$$

$$R_R(t_3,t_2,t_1) = R_{\mathrm{II}}(t_3,t_2,t_1) + R_{\mathrm{III}}(t_3,t_2,t_1) - R_{\mathrm{VI}}(t_3,t_2,t_1),$$

$$R_{NR}(t_3,t_2,t_1) = R_{\mathrm{I}}(t_3,t_2,t_1) + R_{\mathrm{IV}}(t_3,t_2,t_1) - R_{\mathrm{V}}(t_3,t_2,t_1).$$

Pump-probe signals

$$S_{\mathrm{int}}(T,\, \omega_{\mathrm{pr}}) \sim \int \mathrm{d}t \mathcal{P}(T,\, t)\mathcal{E}_{\mathrm{pr}}(t)\mathrm{e}^{i\omega_{\mathrm{pr}}t}$$

Time delay between the pump and probe pulses

envelope of the probe pulse

J. Chem. Theory. Comput, **17**, 2394-2408 (2021)

Doorway-window representation of the pump-probe specra

$$S(\omega_{pu},T,\omega_{pr},\tau_t) \sim \mathrm{ReTr}\left[e^{i\widetilde{H}_0T}\widetilde{W}_0(\omega_{pr},\tau_t)e^{-i\widetilde{H}_0T}\widetilde{D}_0(\omega_{pu}) + e^{i\widetilde{H}_1T}\left\{\widetilde{W}_1(\omega_{pr},\tau_t) - \widetilde{W}_2(\omega_{pr},\tau_t)\right\}e^{-i\widetilde{H}_1T}\widetilde{D}_1(\omega_{pu})\right]$$

GSB

density loss in the ground state

SE

ESA

light-induced density in the manifold I

For changing to classical trajectories

1. Classical Condon approximation

$$\langle g|e^{i\widetilde{H}_0t_3}\mu_{01}e^{-i\widetilde{H}_1t_3}|e\rangle \to e^{\omega_{ge}t}\mu_{ge}, \qquad \langle f|e^{i\widetilde{H}_2t_3}\mu_{21}e^{-i\widetilde{H}_1t_3}|e\rangle \to e^{i\omega_{fe}t_3}\mu_{fe},$$

$\omega_{ge} = \varepsilon_e - \varepsilon_g$, $\omega_{fe} = \varepsilon_f - \varepsilon_g$, etc. are functions of nuclear coordinates

2. Classical Averaging

$$\rho_B \to \rho_g^{Wig}(\boldsymbol{R}_g, \boldsymbol{P}_g).$$

3. Classical population evolution

T-evolutions of

GSB

$$e^{i\widetilde{H}_0T}\widetilde{W}_0(\omega_{pr},\tau_t)e^{-i\widetilde{H}_0T}$$

SE ESA

$$e^{i\widetilde{H}_1T}\left\{\widetilde{W}_1(\omega_{pr},\tau_t) - \widetilde{W}_2(\omega_{pr},\tau_t)\right\}e^{-i\widetilde{H}_1T}$$

evolutions over trajectories in the electronic ground state and lower-lying excited electronic states

J. Chem. Theory. Comput, **17**, 2394-2408 (2021)

Transient absorption pump probe spectra for pyrazine

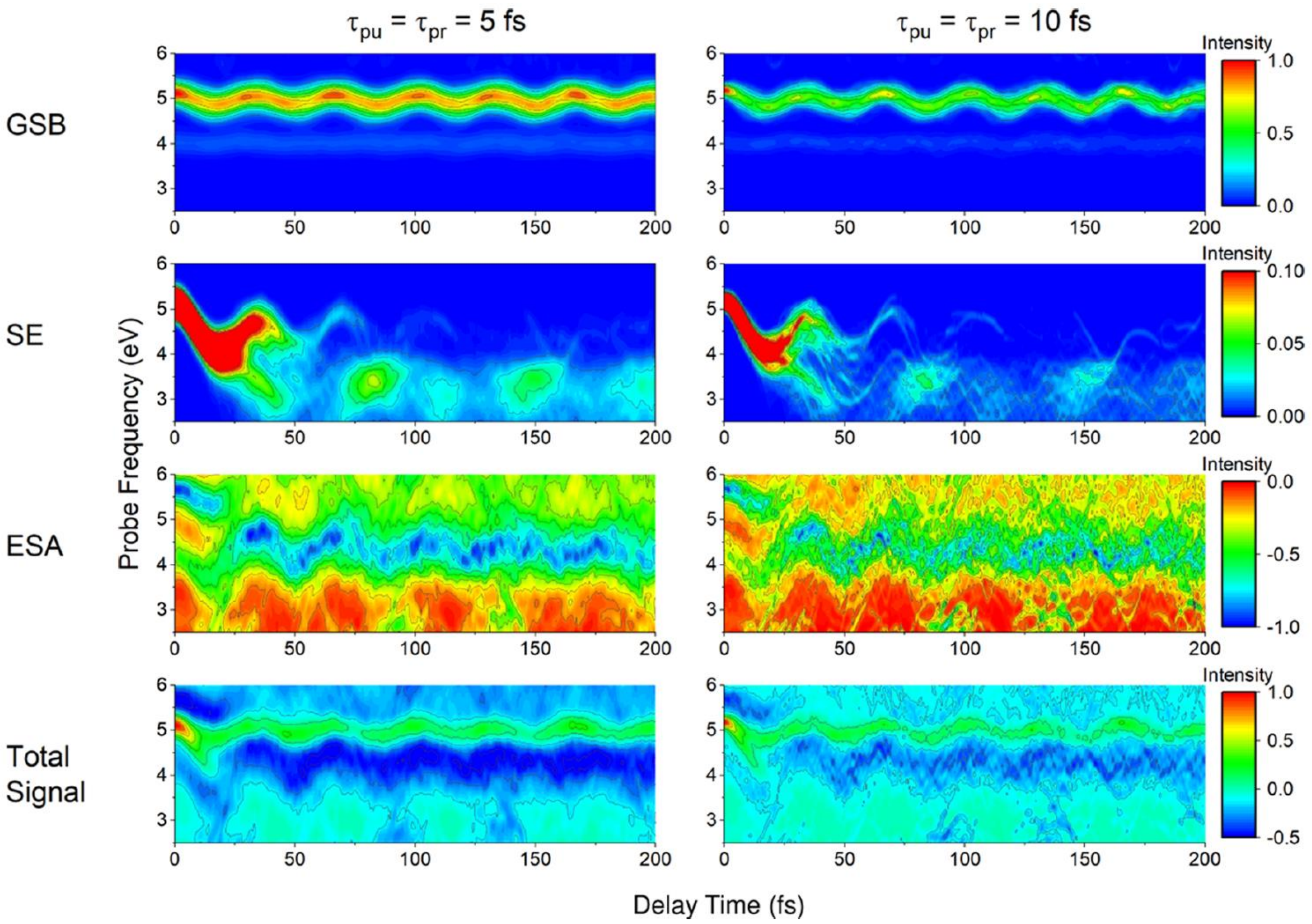
$B_{3u}(n\pi^*)$, $A_u(n\pi^*)$, $B_{2u}(\pi\pi^*)$, and $B_{2g}(n\pi^*)$

4.18, 4.83, 5.08, and 5.85 eV

low-lying excited states

The next 30 electronic states with vertical excitation energies up to 10eV

High-lying excited states



J. Chem. Theory. Comput, **17**, 2394-2408 (2021)

Outlook

• Use **cavity** to control the photochemistry and characterize its dynamics by multidimensional spectroscopy

• Simulate **time-resolved X-ray (electron) diffraction** of CI systems (the structural change associated with the electronic transitions)

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