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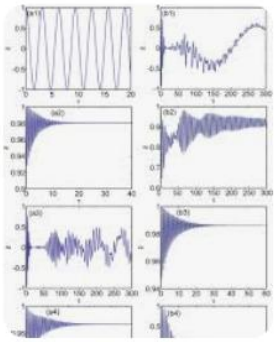
How to turn your on-the-fly dynamics code into a simulator of nonlinear spectroscopic signals via doorway-window method

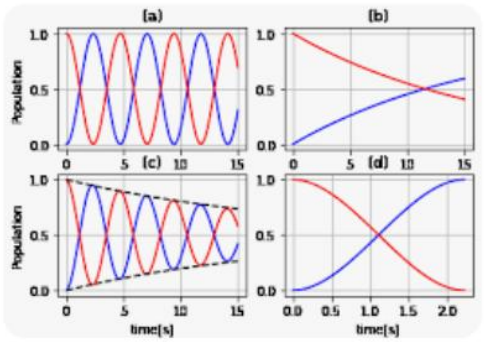
Maxim F. Gelin

We, theoreticians, like to calculate population dynamics ...



R⁶ ResearchGate

Time evolution of t...



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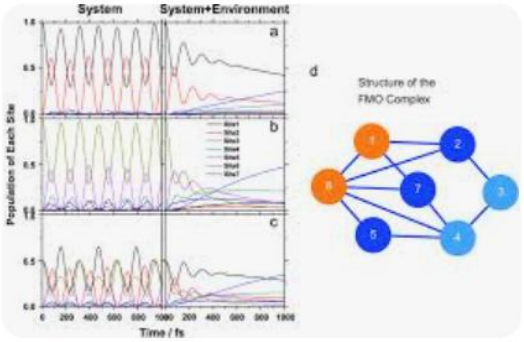
Population evolution under quantum ...



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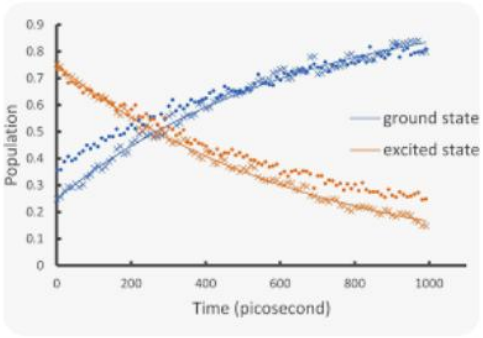
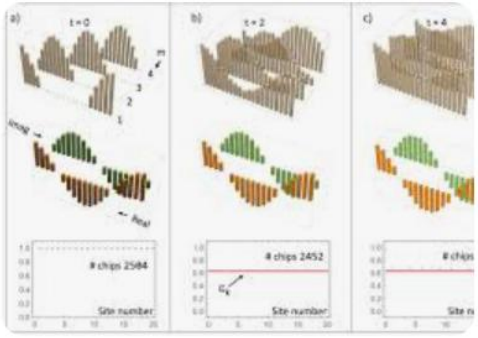
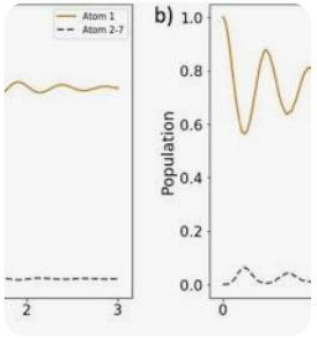
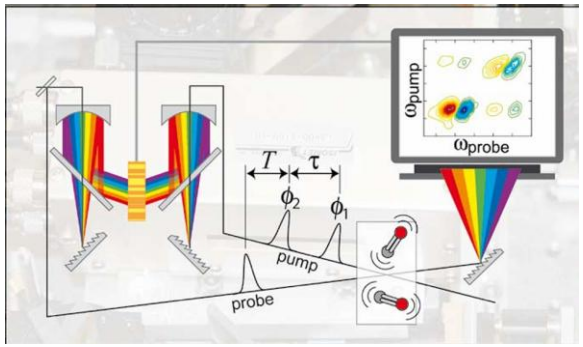
The quantum evolution for the site ...







What's about spectroscopic signals?



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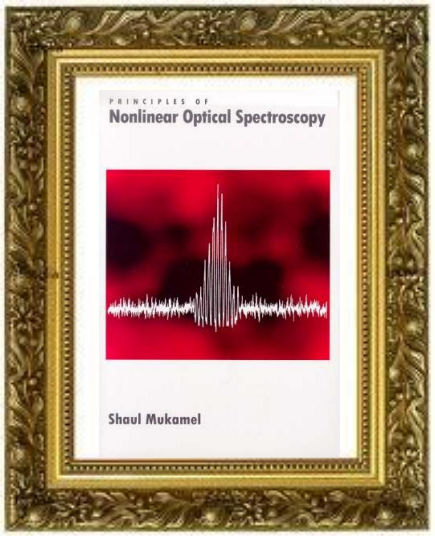
How to turn your pump–probe instrument into a multidimensional spectrometer: 2D IR and Vis spectroscopies *via* pulse shaping

Sang-Hee Shim and Martin T. Zanni*

Received 12th August 2008, Accepted 30th October 2008
First published as an Advance Article on the web 10th December 2008
DOI: 10.1039/b813817f

I decided to plagiarize/modify Zanni's title:

How to turn your on-the-fly dynamics code into a simulator of nonlinear spectroscopic signals via doorway-window method



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Fundamental notions and models (1995)

Computer revolution in theoretical spectroscopy

- AI & ML & Quantum Computers
- Ab initio parameterization of system Hamiltonians
- The use of more realistic (therefore complex and multidimensional) models of molecular systems (**HEOM and MCTDH are the game changers**)
- Simulation of spectroscopic signals on-the-fly

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Before:

*efficient **analytical** methods in many-body quantum dynamics*

- Memory function formalism, Mori formalism
- Projection operator formalism
- Variational methods
- Davydov Ansatz
- Thermo-Field Dynamic
- Doorway-Window representation

Now:

*efficient **numerical** methods in many-body quantum dynamics and theoretical spectroscopy*

The doorway–window representation

Developed by **Yan** & **Mukamel**;

Extended by
Tanimura, Domcke & **Stock, Novoderezkin**

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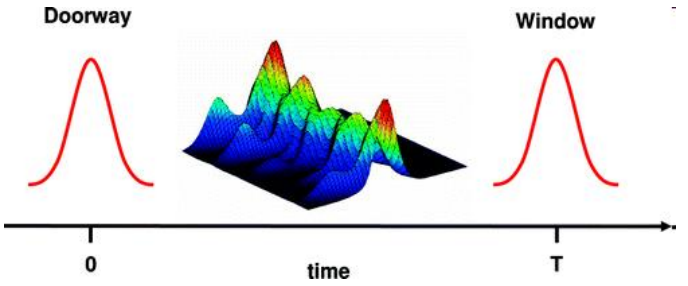
$T >>$ pump & probe duration



W is responsible for time–frequency resolution

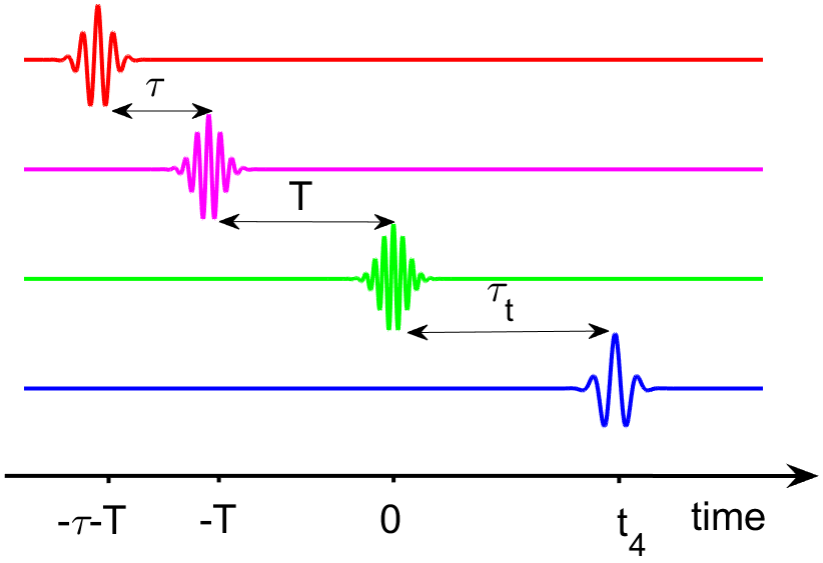
$$S_{\mathrm{pp}}(T,\omega_{probe}) = \left\langle W(\omega_{probe})G(T)D \right\rangle$$

D is responsible for wavepacket excitation

Frequency of the second (probe) pulse

Time delay between the pulses

Time evolution G(T) is not affected by optical dephasing:
We are seating in populations of the system density matrix



General 4-wave-mixing signal

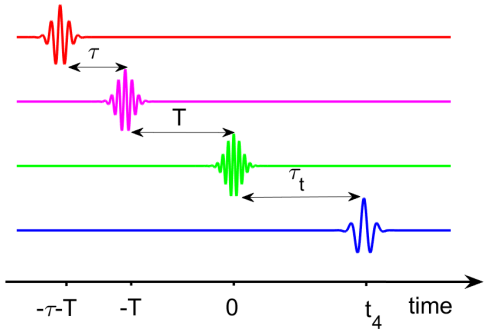
$$I_\alpha(\tau,T,\tau_t)\sim \mathrm{Re}\sum_{k=0,\mathrm{I},\mathrm{II}}\int_{-\infty}^{\infty}dt\int_0^{\infty}dt_3\int_0^{\infty}dt_2\int_0^{\infty}dt_1 E_1(t+\tau+T-t_3-t_2-t_1)\times$$

$$E_2(t+T-t_3-t_2)E_3(t-t_3)E_4(t-\tau_t)e^{i\xi_\alpha\omega_{pu}(t_1-\tau)}e^{i\omega_{pr}(t_3-\tau_t)}R_{\alpha k}(t_3,t_2,t_1).$$

Third-order response functions

DW change of integration variables

$$t=t'+t_3,\quad t_2=t'+T-t_2'$$



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DW representation of 4-wave-mixing signals

$$I_\alpha(\tau, T, \tau_t) \sim \mathrm{Re} \sum_{k=0,\mathrm{I},\mathrm{II}} a_k \mathrm{Tr}\left[W_k(\tau_t)\mathcal{L}(T)D_\alpha(\tau)\right],$$

$$D_\alpha(\tau) = \int_{-\infty}^{\infty} dt_2' \int_0^{\infty} dt_1 E_2(t_2') E_1(t_2' + \tau - t_1) e^{i\xi_\alpha \omega_{pu}(t_1-\tau)} \mathcal{D}_\alpha(t_1)$$

$$W_k(\tau_t) = \int_{-\infty}^{\infty} dt' \int_0^{\infty} dt_3 E_4(t' + t_3 - \tau_t) E_3(t') e^{i\omega_p(t_3-\tau_t)} \mathcal{W}_k(t_3).$$

DW representation vs exact calculation

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Pump-probe

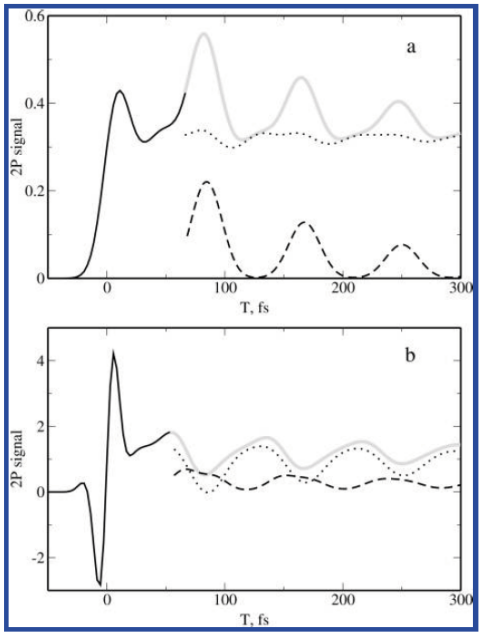
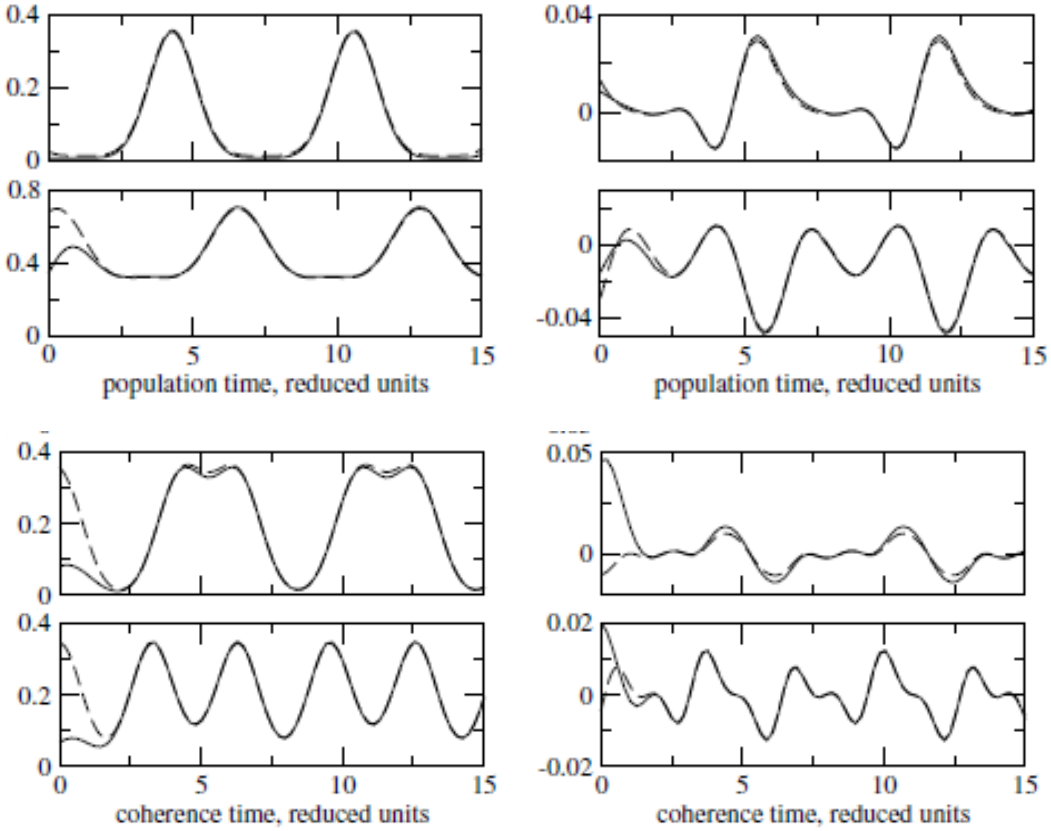
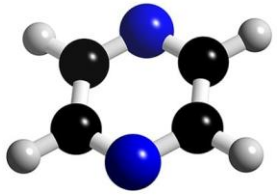


Figure 1. 2P signal $S_{2P}(T)$ induced by weak (λ_a = 0.01 eV, (a)) and strong (λ_a = 0.1 eV, (b)) short ($\Gamma_a = \Omega$) pulses. Full black lines, exact calculation; full gray lines, strong-pulse DW approximation. Dotted and dashed lines depict the ground-state and excited-state contributions to the strong-pulse DW signal.

Three-pulse photon echo





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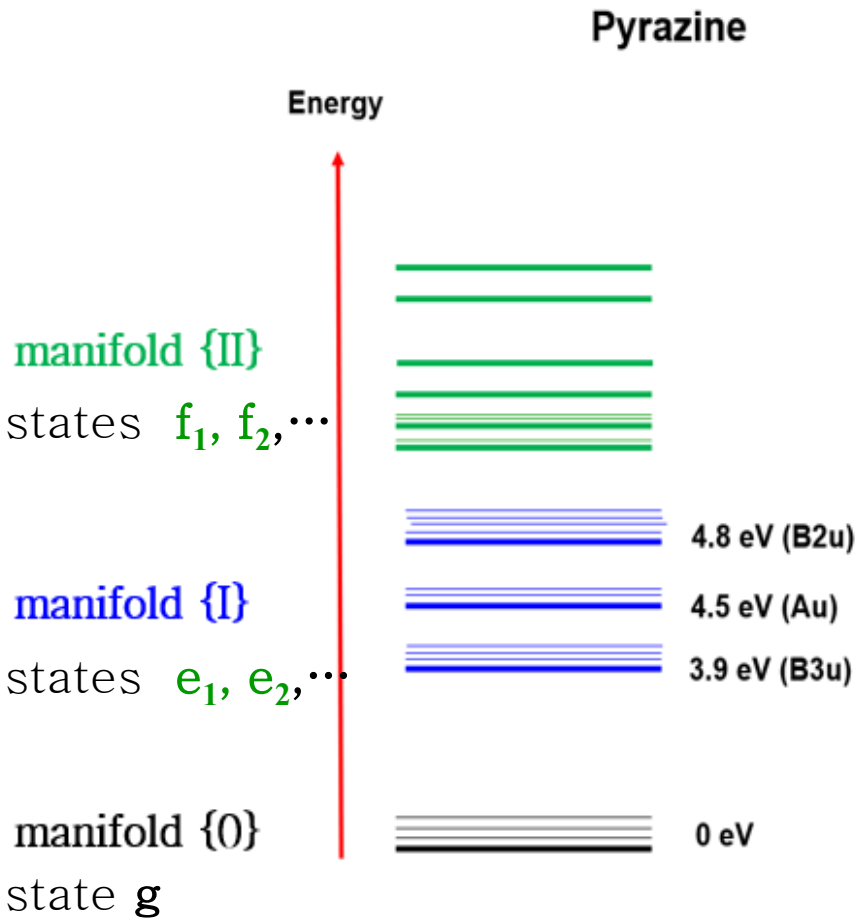
$$H = \begin{pmatrix} H_0 & 0 & 0 \\ 0 & H_{\mathrm{I}} & 0 \\ 0 & 0 & H_{\mathrm{II}} \end{pmatrix}$$

$$\mu^{\downarrow} = \begin{pmatrix} 0 & \mu_{0,\mathrm{I}} & 0 \\ 0 & 0 & \mu_{\mathrm{I,II}} \\ 0 & 0 & 0 \end{pmatrix}, \quad \mu^{\uparrow} = \begin{pmatrix} 0 & 0 & 0 \\ \mu_{\mathrm{I},0} & 0 & 0 \\ 0 & \mu_{\mathrm{II,I}} & 0 \end{pmatrix}$$



$$\boldsymbol{R}_e(T), \boldsymbol{P}_e(T)$$

$$\boldsymbol{R}_g(T), \boldsymbol{P}_g(T)$$

For changing to classical trajectories, make three approximations

I. Classical approximation for electronic coherences:

$$\langle g|e^{iH_0 t_3}\boldsymbol{\mu}_{0,\mathrm{I}}e^{-iH_\mathrm{I}t_3}|e\rangle \approx e^{iU_{ge}(\boldsymbol{R})t_3}\boldsymbol{\mu}_{ge}(\boldsymbol{R}) \qquad \langle f|e^{iH_\mathrm{II}t_3}\boldsymbol{\mu}_{\mathrm{II},\mathrm{I}}e^{-iH_\mathrm{I}t_3}|e\rangle \approx e^{iU_{fe}(\boldsymbol{R})t_3}\boldsymbol{\mu}_{fe}(\boldsymbol{R})$$

$$U_{eg}(\boldsymbol{R}) = V_e(\boldsymbol{R}) - V_g(\boldsymbol{R}) \qquad U_{fe}(\boldsymbol{R}) = V_f(\boldsymbol{R}) - V_e(\boldsymbol{R})$$

II. Classical averaging

Trace over nuclear degrees of freedom is replaced by the sampling of classical trajectories from the classical Wigner distribution

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

Trace over electronic degrees of freedom remains

III. Classical population evolution

T-evolutions of

$$W_0(\omega_{pr}, \tau_t, T) = e^{iH_0T}W_0(\omega_{pr}, \tau_t)e^{-iH_0T},$$

$$W_\mathrm{I}(\omega_{pr}, \tau_t, T) = e^{iH_\mathrm{I}T}W_\mathrm{I}(\omega_{pr}, \tau_t)e^{-iH_\mathrm{I}T}, \qquad W_\mathrm{II}(\omega_{pr}, \tau_t, T) = e^{iH_\mathrm{I}T}W_\mathrm{II}(\omega_{pr}, \tau_t)e^{-iH_\mathrm{I}T}.$$

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

Transient absorption pump-probe

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$$S_{int}(T,\omega_{pr}) \sim \langle D_0(\omega_{pu},\boldsymbol{R}_g,\boldsymbol{P}_g) W_0^{int}(\omega_{pr},\boldsymbol{R}_g(T),\boldsymbol{P}_g(T))\rangle +$$

$$\langle D_{\mathrm{I}}(\omega_{pu},\boldsymbol{R}_g,\boldsymbol{P}_g) W_{\mathrm{I}}^{int}(\omega_{pr},\boldsymbol{R}_e(T),\boldsymbol{P}_e(T))\rangle - \langle D_{\mathrm{I}}(\omega_{pu},\boldsymbol{R}_g,\boldsymbol{P}_g) W_{\mathrm{II}}^{int}(\omega_{pr},\boldsymbol{R}_e(T),\boldsymbol{P}_e(T))\rangle.$$

$$D_0(\omega_{pu},\boldsymbol{R}_g,\boldsymbol{P}_g) = \sum_e \mathcal{E}_{pu}^2(\omega_{pu} - U_{eg}(\boldsymbol{R}_g)) |\mu_{ge}(\boldsymbol{R}_g)|^2 \rho_g^{Wig}(\boldsymbol{R}_g,\boldsymbol{P}_g),$$

$$D_{\mathrm{I}}(\omega_{pu},\boldsymbol{R}_g,\boldsymbol{P}_g) = \mathcal{E}_{pu}^2(\omega_{pu} - U_{eg}(\boldsymbol{R}_g)) |\mu_{ge}(\boldsymbol{R}_g)|^2 \rho_g^{Wig}(\boldsymbol{R}_g,\boldsymbol{P}_g).$$

$$W_0^{int}(\omega_{pr},\boldsymbol{R}_g(T),\boldsymbol{P}_g(T)) = \sum_e \mathcal{E}_{pr}^2(\omega_{pr} - U_{eg}(\boldsymbol{R}_g(T))) |\mu_{ge}(\boldsymbol{R}_g(T))|^2,$$

$$W_{\mathrm{I}}^{int}(\omega_{pr},\boldsymbol{R}_e(T),\boldsymbol{P}_e(T)) = \mathcal{E}_{pr}^2(\omega_{pr} - U_{e(T)g}(\boldsymbol{R}_e(T))) |\mu_{ge(T)}(\boldsymbol{R}_e(T))|^2,$$

$$W_{\mathrm{II}}^{int}(\omega_{pr},\boldsymbol{R}_e(T),\boldsymbol{P}_e(T)) = \sum_f \mathcal{E}_{pr}^2(\omega_{pr} - U_{fe(T)}(\boldsymbol{R}_e(T))) |\mu_{e(T)f}(\boldsymbol{R}_e(T))|^2.$$

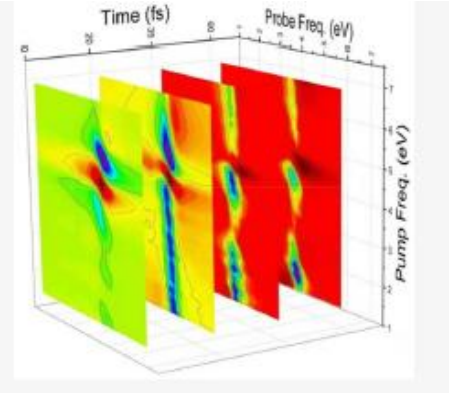
We need just electronic energies and transition dipole moments along trajectories to calculate any nonlinear spectroscopic signal

$$U_{eg}(\boldsymbol{R}_g(T)) \qquad |\mu_{ge}(\boldsymbol{R}_g(T))|^2$$

$$U_{e(T)g}(\boldsymbol{R}_e(T)) \qquad |\mu_{ge(T)}(\boldsymbol{R}_e(T))|^2$$

$$U_{fe(T)}(\boldsymbol{R}_e(T)) \qquad |\mu_{e(T)f}(\boldsymbol{R}_e(T))|^2$$

The numerical effort is comparable to that for the calculation of population evolutions



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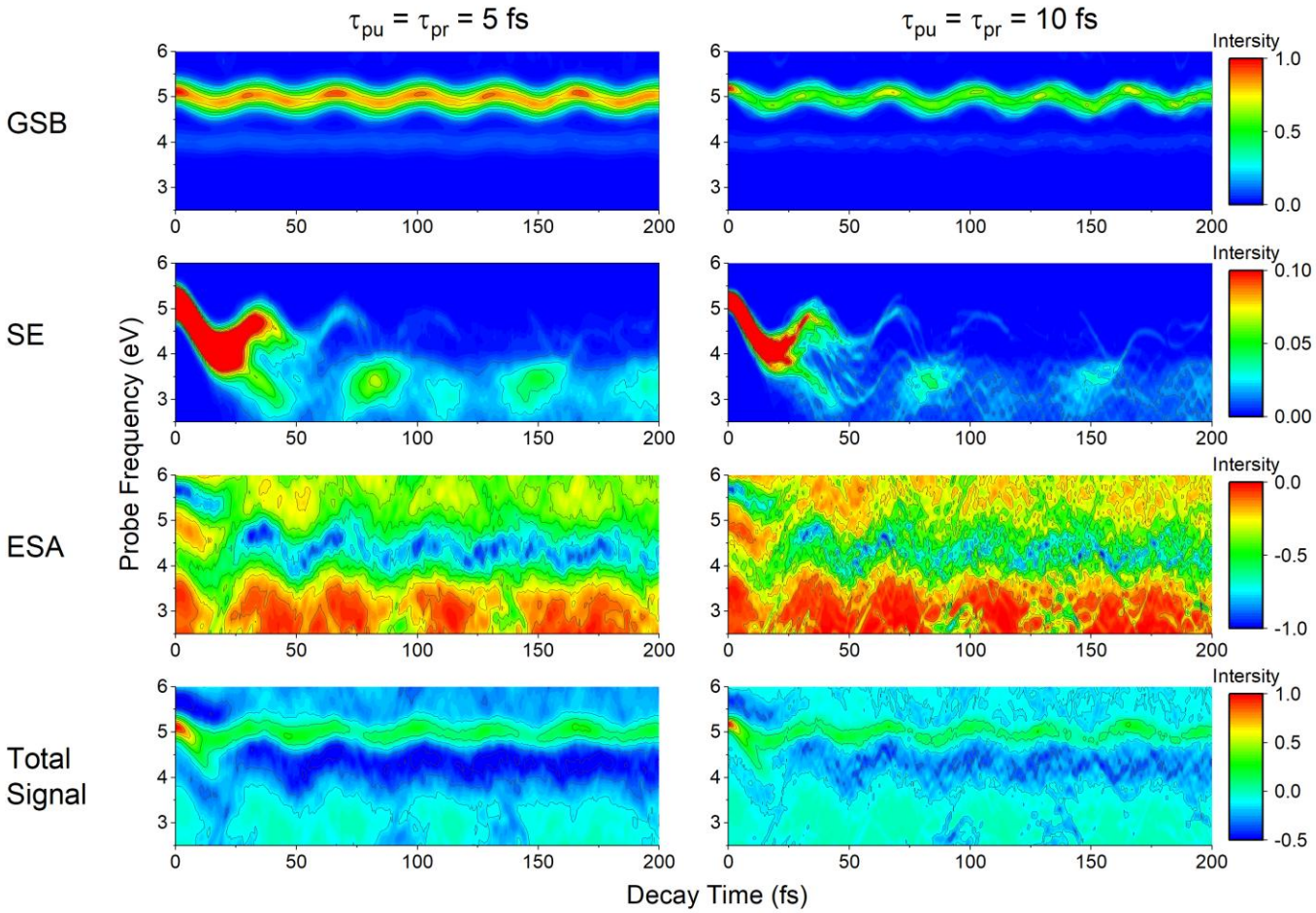
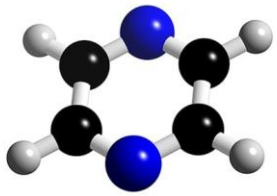
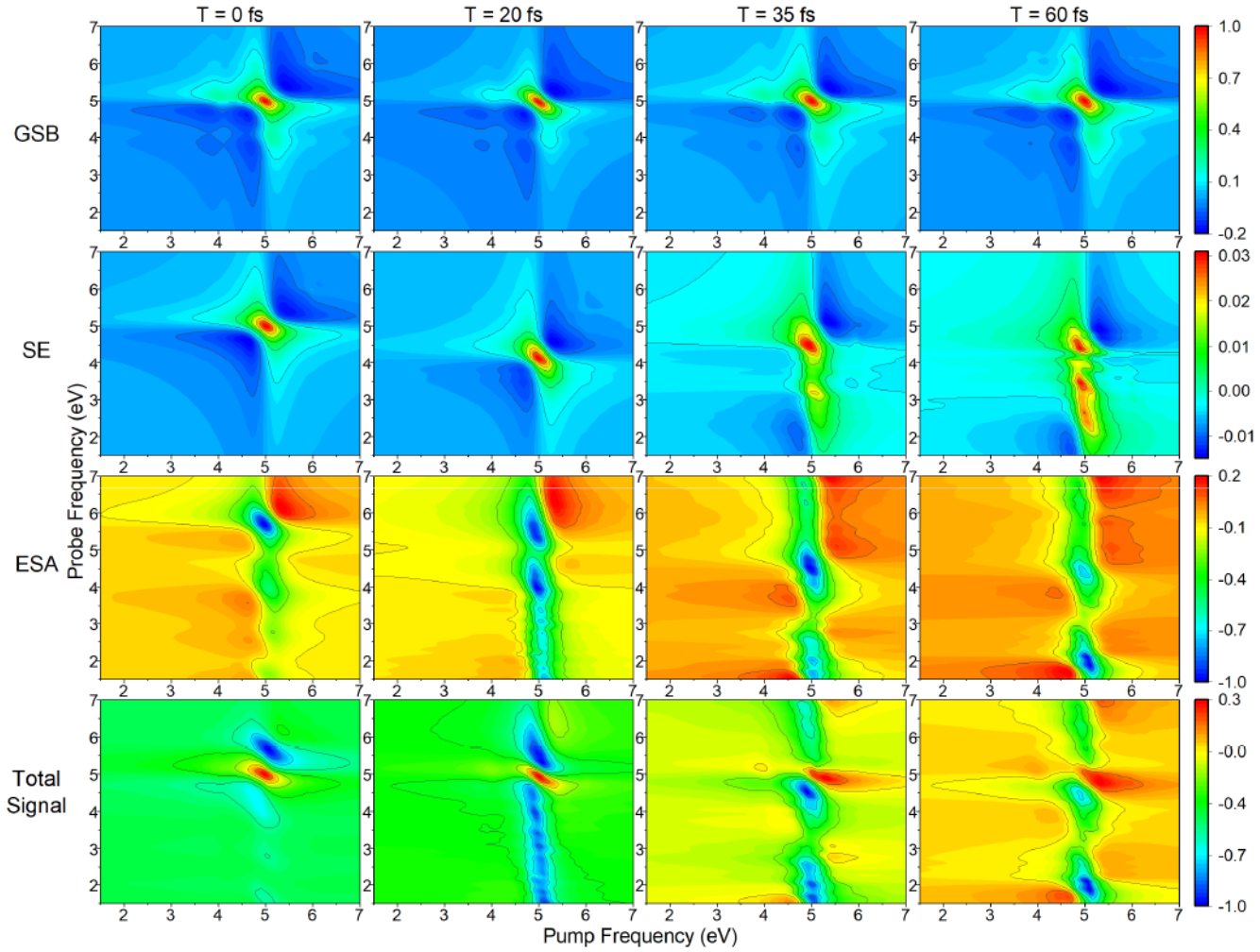
Signals for pyrazine: TA PP integral



State	E	f
S_1 (B_{3u})	4.17	0.006
S_2 (A_u)	4.83	0.000
S_3 (B_{2u})	5.07	0.099
S_4 (B_{2g})	5.85	0.000



Signals for pyrazine: photon-echo 2D



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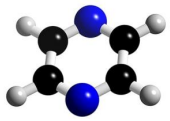

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What else?

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Combined Surface-Hopping, Dyson Orbital, and B-Spline Approach for the Computation of Time-Resolved Photoelectron Spectroscopy Signals: The Internal Conversion in Pyrazine

Tomislav Piteša, Marin Sapunar, Aurora Ponzi, Maxim F. Gelin, Nađa Došlić,* Wolfgang Domcke, and Piero Decleva*

Cite This: *J. Chem. Theory Comput.* 2021, 17, 5098–5109

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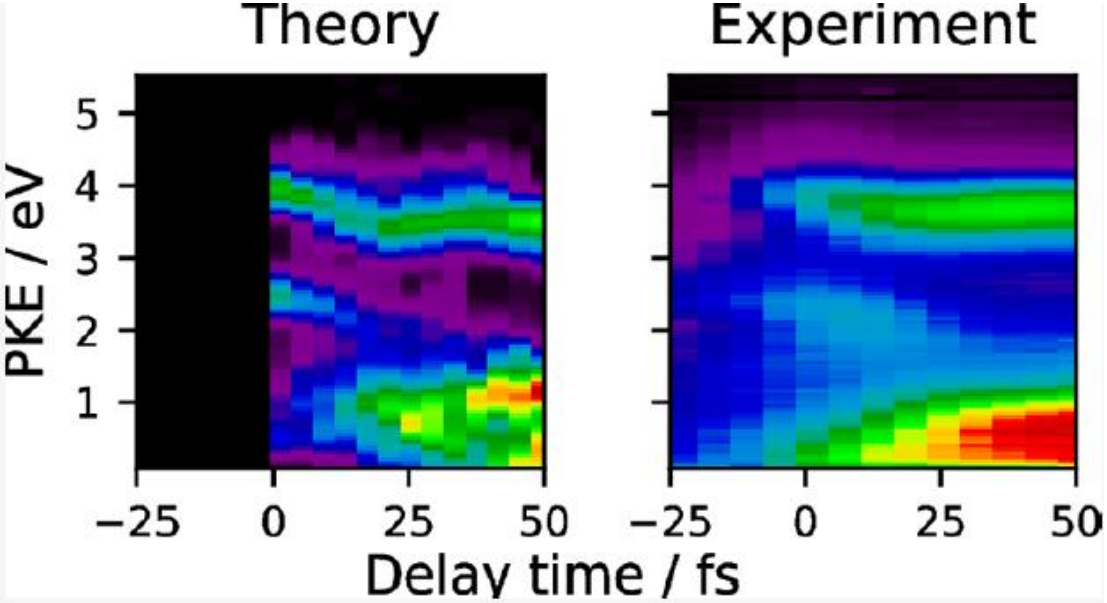

Coupled {0}−{I} manifolds

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$$H = \begin{pmatrix} H_0 & H_{0,\mathrm{I}} & 0 \\ H_{\mathrm{I},0} & H_{\mathrm{I}} & H_{\mathrm{I,II}} \\ 0 & H_{\mathrm{II,I}} & H_{\mathrm{II}} \end{pmatrix}$$

$$\hat{W}_0^{int} = W_0^{int},$$

$$\hat{W}_{\mathrm{I}}^{int} = \begin{cases} W_{\mathrm{I}}^{int}, & \text{if trajectory stays within } \{\mathrm{I}\} \\ -W_0^{int}, & \text{if trajectory jumps from } \{\mathrm{I}\} \text{ to } \{0\} \end{cases}$$

$$\hat{W}_{\mathrm{II}}^{int} = \begin{cases} W_{\mathrm{II}}^{int}, & \text{if trajectory stays within } \{\mathrm{I}\} \\ 0, & \text{if trajectory jumps from } \{\mathrm{I}\} \text{ to } \{0\} \end{cases}$$

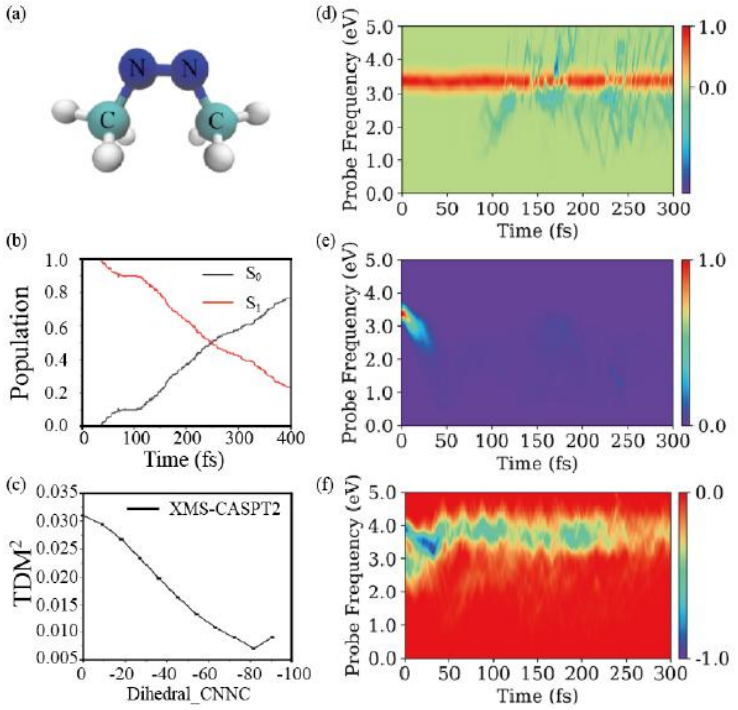

Figure 2: (a) Structure of azomethane. (b) Time-dependent fractional occupations of the S_0 and S_1 electronic states of azomethane in non-adiabatic dynamics staring from the S_1 state. (c) Dependence of the TMD of azomethane on the central torsional angle. Normalized (d) GSB, (e) SE, and (f) ESA contributions to the integral TA PP signal of azomethane as a function of the pump-probe delay time T and the probe-pulse carrier frequency ω_{pr}. Duration of both pump and probe pulses is 5 fs. The carrier frequency ω_{pu} of the pump pulse is tuned into resonance with the $S_1(n\pi^*)$ state. Adapted from[163]. Copyright American Chemical Society.

Polarization-sensitive signals

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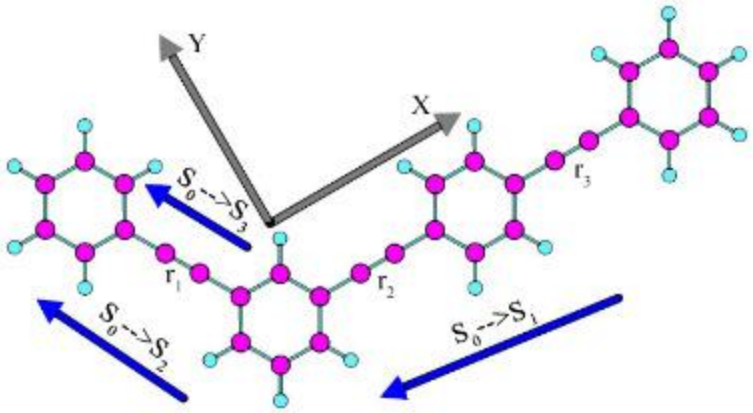
$$I_\alpha(\tau,T,\tau_t)=\sum_{a,b,c,d=x,y,z} s_p^{(a)}s_p^{(b)}s_u^{(c)}s_u^{(d)}\mathrm{Re}\sum_{k=0,\mathrm{I},\mathrm{II}} a_k\left\langle D_\alpha^{(ab)}(\boldsymbol{R},\boldsymbol{P};\tau)W_k^{(cd)}(\boldsymbol{R}(T),\boldsymbol{P}(T);\tau_t)\right\rangle$$



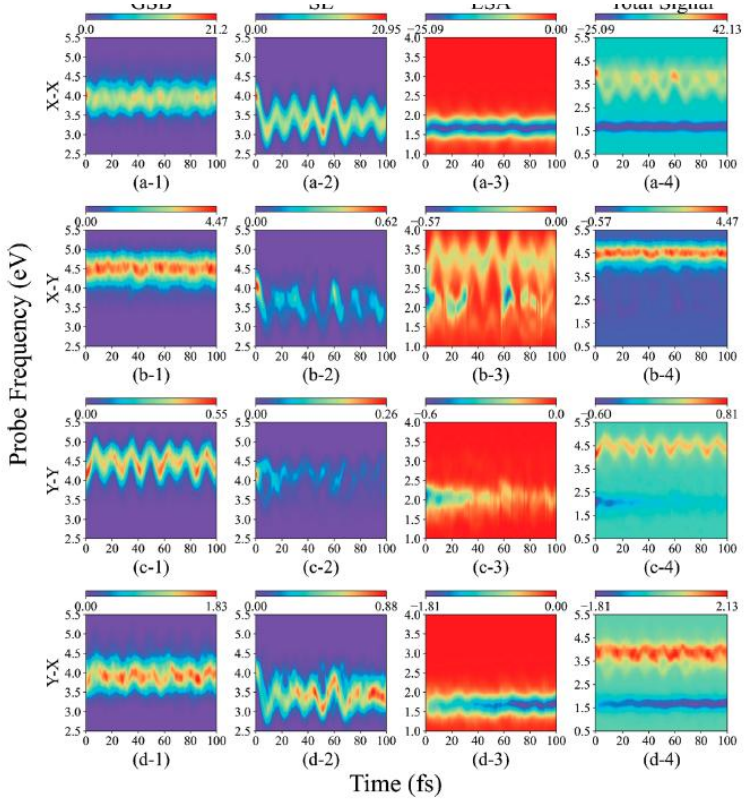


Figure 3. (1) GSB, (2) SE, and (3) ESA contributions and (4) total integral signal $I_{\mathrm{int}}(\tau,\omega_{\mathrm{pr}})$ as a function of τ and ω_{pr}. The notation α–β (α,β = X, Y) on the left side indicates that the pump pulse polarization (e_{pu}) is along the α-axis direction, while the probe pulse polarization (e_{pr}) is along the β-axis direction. The central frequency of the pump pulse is ω_{pu} = 4.03 eV, and the pulse durations are τ_{pu} = τ_{pr} = 5 fs.

Vis pump – Xray probe

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Letter

Tuning UV Pump X-ray Probe Spectroscopy on the Nitrogen K Edge Reveals the Radiationless Relaxation of Pyrazine: *Ab Initio* Simulations Using the Quasiclassical Doorway–Window Approximation

Tobias Kaczun,* Adrian L. Dempwolff,* Xiang Huang, Maxim F. Gelin, Wolfgang Domcke,* and Andreas Dreuw*

Cite This: *J. Phys. Chem. Lett.* 2023, 14, 5648–5656

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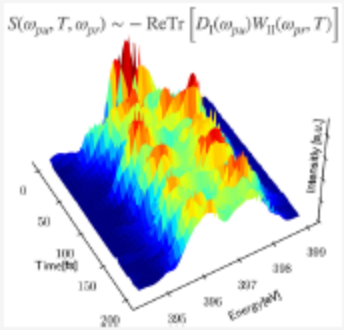
ABSTRACT: Transient absorption UV pump X-ray probe spectroscopy has been established as a versatile technique for the exploration of ultrafast photoinduced dynamics in valence-excited states. In this work, an *ab initio* theoretical framework for the simulation of time-resolved UV pump X-ray probe spectra is presented. The method is based on the description of the radiation–matter interaction in the classical doorway–window approximation and a surface-hopping algorithm for the nonadiabatic nuclear excited-state dynamics. Using the second-order algebraic–diagrammatic construction scheme for excited states, UV pump X-ray probe signals were simulated for the carbon and nitrogen K edges of pyrazine, assuming a duration of 5 fs of the UV pump and X-ray probe pulses. It is predicted that spectra measured at the nitrogen K edge carry much richer information about the ultrafast nonadiabatic dynamics in the valence-excited states of pyrazine than those measured at the carbon K edge.



On-the-fly ML-enhanced simulations

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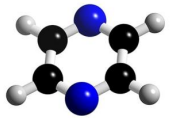

Artificial-Intelligence-Enhanced On-the-Fly Simulation of Nonlinear Time-Resolved Spectra

Sebastian V. Pios, Maxim F. Gelin, Arif Ullah, Pavlo O. Dral,* and Lipeng Chen*

Cite This: *J. Phys. Chem. Lett.* 2024, 15, 2325−2331
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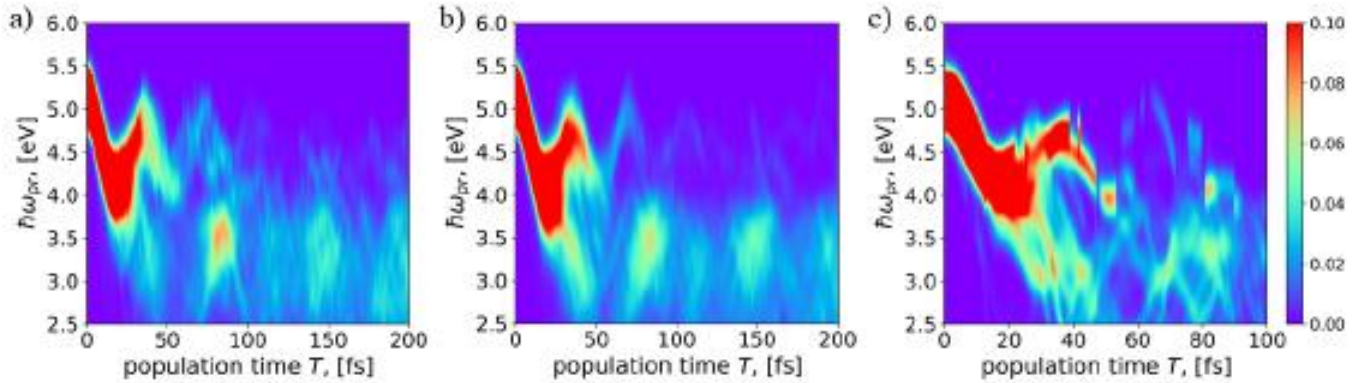

Figure 2: Integral time-resolved stimulated-emission spectrum $I(T, \omega_{pr})$ of pyrazine as a function of the population time T and the carrier frequency ω_{pr} of the probe pulse. (a). The converged spectrum calculated with 600 ML-accelerated trajectories. (b). Reference spectrum calculated with 600 pure ab-initio trajectories. (c). Spectrum calculated from 50 pure ab-initio trajectories (100 fs), which were used for the construction of the ML training set.

Strong-pump strong-probe

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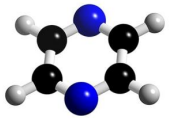
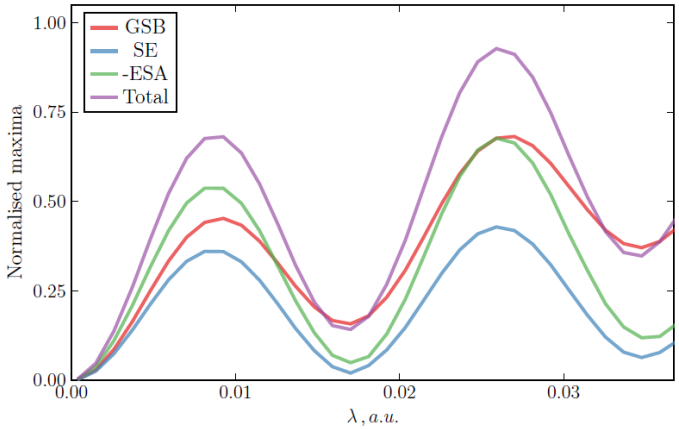
$$D_0(\omega_{pu}, \boldsymbol{R}_g, \boldsymbol{P}_g) = \sum_e \frac{\lambda_{pu}^2 |\mu_{ge}(\boldsymbol{R}_g)|^2}{\Omega_{eg}^2(\boldsymbol{R}_g)} (1 - \cos(\Omega_{eg}(\boldsymbol{R}_g)\tau_{pu})) \rho_g^{Wig}(\boldsymbol{R}_g, \boldsymbol{P}_g),$$

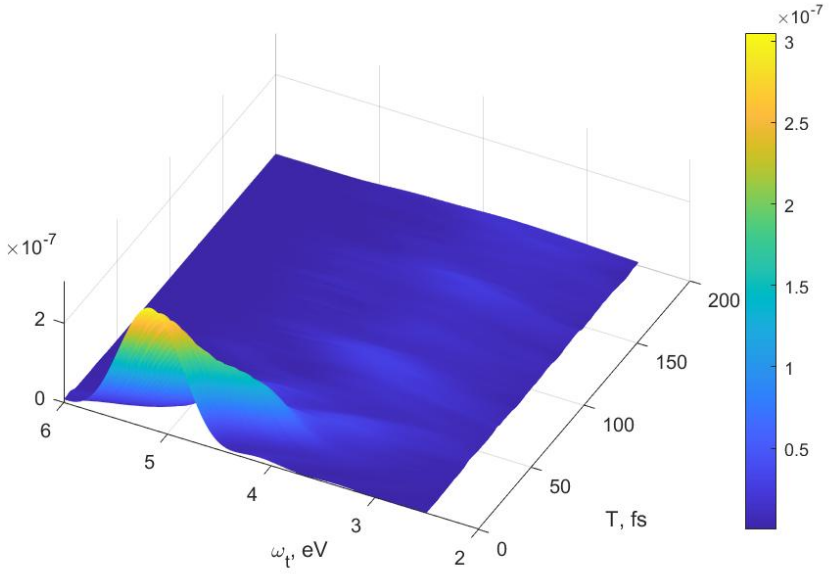
$$D_{\mathrm{I}}(\omega_{pu}, \boldsymbol{R}_g, \boldsymbol{P}_g) = \frac{\lambda_{pu}^2 |\mu_{ge}(\boldsymbol{R}_g)|^2}{\Omega_{eg}^2(\boldsymbol{R}_g)} (1 - \cos(\Omega_{eg}(\boldsymbol{R}_g)\tau_{pu})) \rho_g^{Wig}(\boldsymbol{R}_g, \boldsymbol{P}_g)$$

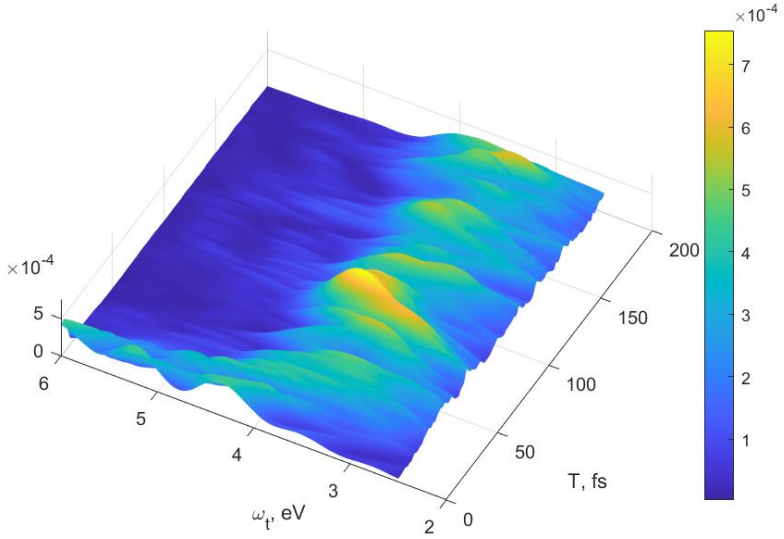
$$\Omega_{eg}(\boldsymbol{R}_g) = \sqrt{(U_{eg}(\boldsymbol{R}_g) - \omega_{pu})^2 + 4\lambda_{pu}^2 |\mu_{ge}(\boldsymbol{R}_g)|^2}$$

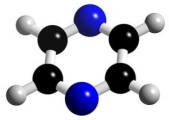




Strong-pump strong-probe







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DW combined with mapping approach

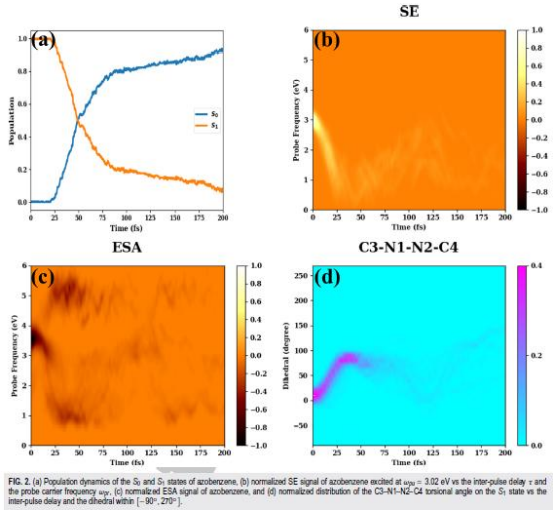
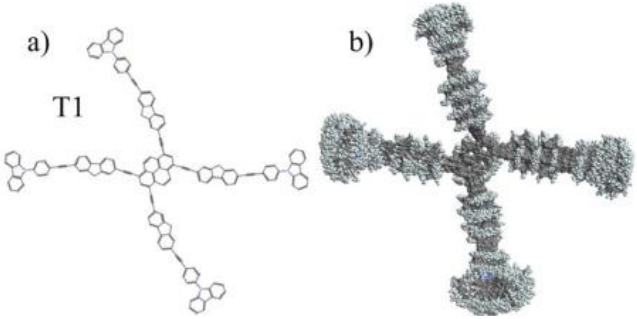
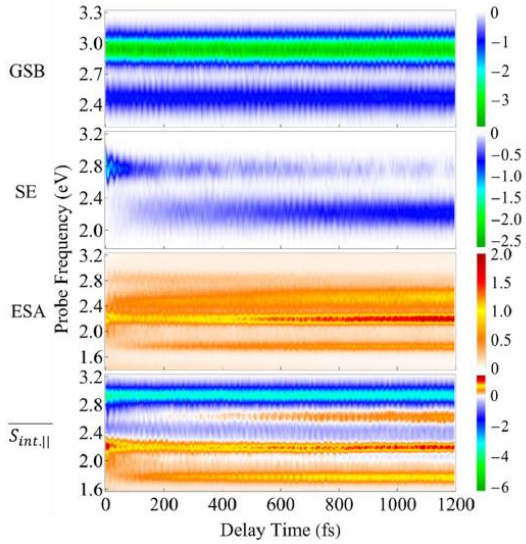


FIG. 2. (a) Population dynamics of the S_0 and S_1 states of azobenzene, (b) normalized SE signal of azobenzene excited at ω_{pu} = 3.02 eV vs the inter-pulse delay τ and the probe carrier frequency ω_{pr}, (c) normalized ESA signal of azobenzene, and (d) normalized distribution of the C3–N1–N2–C4 torsional angle on the S_1 state vs the inter-pulse delay and the dihedral within [−90°, 270°].

DW combined with Ehrenfest dynamics





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Plans for the future:

1. New signals
6-wave mixing,
UV/Vis pump – IR probe,
Odd-wave-mixing at interfaces

2. Better simulation methods
NAF (Jian Liu)
Account for **electronic coherences**

3. Comparison with numerically "exact" quantum simulations

Conclusions

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The developed simulation method and protocol

- Requires – as input -- **electronic energies and dipole moments** along classical trajectories in the electronic ground states and lower-laying excited electronic states
- Works for **any (quasi)classical trajectory method**: Tully's surface hopping, Ehrenfest, mapping approach, etc.
- Fully accounts for pulse effects (shapes, durations, chirps)
- Up to now, has been applied to the simulation of signals of femtosecond **UV/vis** spectroscopy, **photo-electron** spectroscopy. and visible pump **X-ray** probe spectroscopy
- Allows simulation of femtosecond spectroscopic signals of **realistic molecular systems** under **realistic experimental conditions** (strong pulses of any shape) by using **ab initio** methods

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Theory:

Wiley Interdisciplinary Reviews: Computational Molecular Science

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Computation of Time-Resolved Nonlinear Electronic Spectra From Classical Trajectories

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Soft: WaveMixings.jl

https:// doi.org/10.5281/zenodo.15598121

WaveMixings.jl: a Julia package for performing on-the-fly time-resolved nonlinear electronic spectra from quasi-classical trajectories

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Startup

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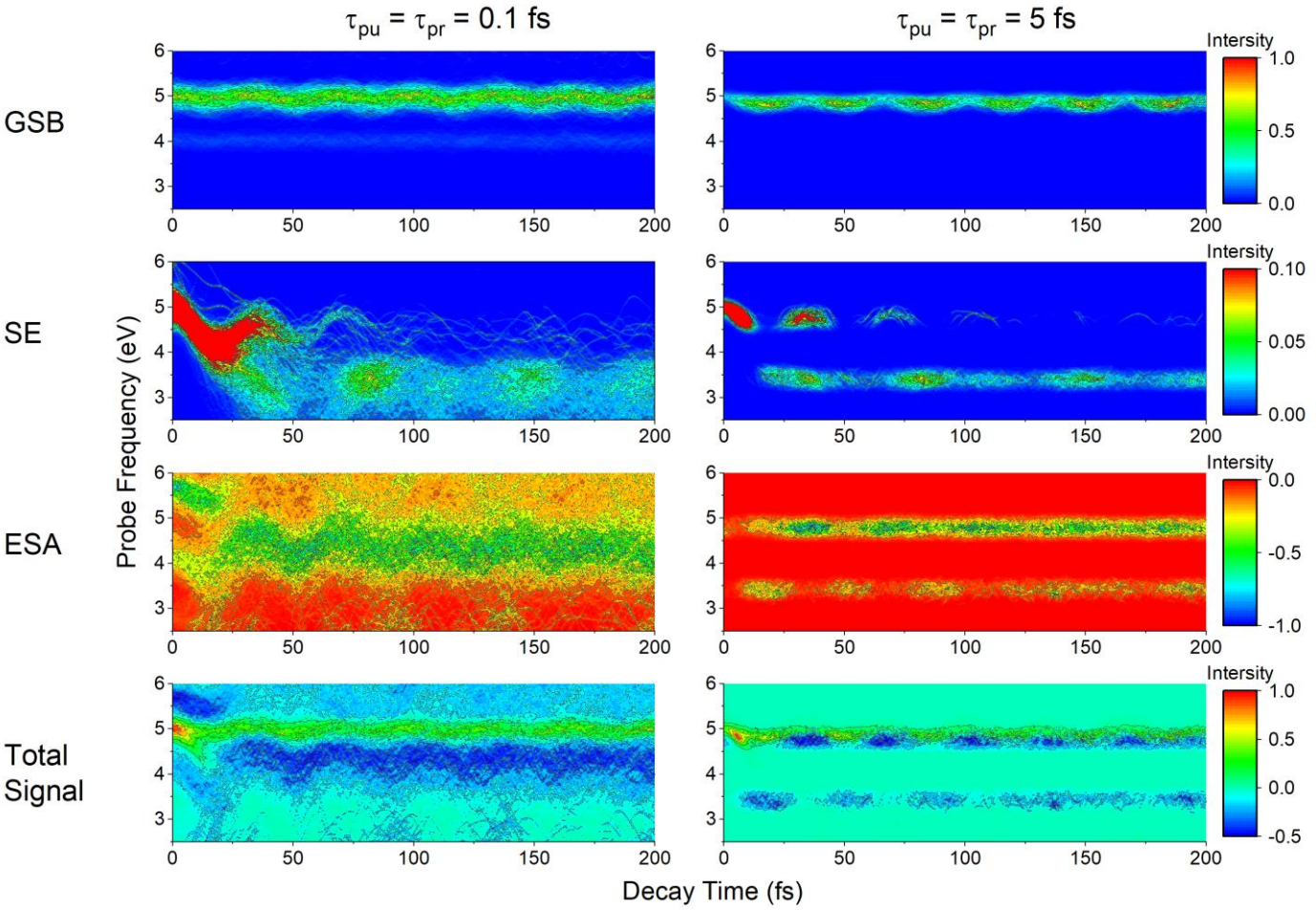
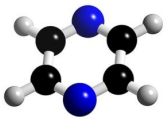
Signals for pyrazine: TA PP dispersed





2D signal

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$$S^{(\alpha)}(\omega_\tau, T, \omega_t) = S^{(\alpha)}_{GSB}(\omega_\tau, T, \omega_t) + S^{(\alpha)}_{SE}(\omega_\tau, T, \omega_t) + S^{(\alpha)}_{ESA}(\omega_\tau, T, \omega_t)$$

$$S^{(\alpha)}_{GSB}(\omega_\tau, T, \omega_t) \sim \mathrm{Re}\langle D^{(\alpha)}_0(\omega_\tau, \boldsymbol{R}_g, \boldsymbol{P}_g) W_0(\omega_t, \boldsymbol{R}_g(T), \boldsymbol{P}_g(T))\rangle$$

$$S^{(\alpha)}_{SE}(\omega_\tau, T, \omega_t) \sim \mathrm{Re}\langle D^{(\alpha)}_{\mathrm{I}}(\omega_\tau, \boldsymbol{R}_g, \boldsymbol{P}_g) W_{\mathrm{I}}(\omega_t, \boldsymbol{R}_{e(T)}(T), \boldsymbol{P}_{e(T)}(T))\rangle$$

$$S^{(\alpha)}_{ESA}(\omega_\tau, T, \omega_t) \sim -\mathrm{Re}\langle D^{(\alpha)}_{\mathrm{I}}(\omega_\tau, \boldsymbol{R}_g, \boldsymbol{P}_g) W_{\mathrm{II}}(\omega_t, \boldsymbol{R}_{e(T)}(T), \boldsymbol{P}_{e(T)}(T))\rangle.$$

$$D^{(R)}_0(\omega_\tau, \boldsymbol{R}_g, \boldsymbol{P}_g) = \rho^{Wig}_g(\boldsymbol{R}_g, \boldsymbol{P}_g) \sum_e \frac{\mathcal{E}^2_1(\omega_\tau - \omega_p)|\mu_{ge}(\boldsymbol{R}_g)|^2}{\nu - i(U_{eg}(\boldsymbol{R}_g) - \omega_\tau)},$$

$$D^{(NR)}_0(\omega_\tau, \boldsymbol{R}_g, \boldsymbol{P}_g) = \rho^{Wig}_g(\boldsymbol{R}_g, \boldsymbol{P}_g) \sum_e \frac{\mathcal{E}^2_1(\omega_\tau - \omega_p)|\mu_{ge}(\boldsymbol{R}_g)|^2}{\nu + i(U_{eg}(\boldsymbol{R}_g) - \omega_\tau)},$$

$$D^{(R)}_{\mathrm{I}}(\omega_\tau, \boldsymbol{R}_g, \boldsymbol{P}_g) = \rho^{Wig}_g(\boldsymbol{R}_g, \boldsymbol{P}_g) \frac{\mathcal{E}^2_1(\omega_\tau - \omega_p)|\mu_{ge}(\boldsymbol{R}_g)|^2}{\nu - i(U_{eg}(\boldsymbol{R}_g) - \omega_\tau)}$$

$$D^{(NR)}_{\mathrm{I}}(\omega_\tau, \boldsymbol{R}_g, \boldsymbol{P}_g) = \rho^{Wig}_g(\boldsymbol{R}_g, \boldsymbol{P}_g) \frac{\mathcal{E}^2_1(\omega_\tau - \omega_p)|\mu_{ge}(\boldsymbol{R}_g)|^2}{\nu + i(U_{eg}(\boldsymbol{R}_g) - \omega_\tau)}$$

$$W_0(\omega_t, \boldsymbol{R}_g(T), \boldsymbol{P}_g(T)) = \sum_e \frac{\mathcal{E}^2_4(\omega_t - \omega_p)|\mu_{ge}(\boldsymbol{R}_g(T))|^2}{\nu + i(U_{eg}(\boldsymbol{R}_g(T)) - \omega_t)},$$

$$W_{\mathrm{I}}(\omega_t, \boldsymbol{R}_{e(T)}(T), \boldsymbol{P}_{e(T)}(T)) = \frac{\mathcal{E}^2_4(\omega_t - \omega_p)|\mu_{ge(T)}(\boldsymbol{R}_{e(T)}(T))|^2}{\nu + i(U_{e(T)g}(\boldsymbol{R}_{e(T)}(T)) - \omega_t)},$$

$$W_{\mathrm{II}}(\omega_t, \boldsymbol{R}_{e(T)}(T), \boldsymbol{P}_{e(T)}(T)) = \sum_f \frac{\mathcal{E}^2_4(\omega_t - \omega_p)|\mu_{e(T)f}(\boldsymbol{R}_{e(T)}(T))|^2}{\nu + i(U_{fe(T)}(\boldsymbol{R}_{e(T)}(T)) - \omega_t)}$$

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(ii) **On-the-fly** simulations of nonlinear femtosecond spectroscopic signals

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Ab Initio Surface-Hopping Simulation of Femtosecond Transient-Absorption Pump–Probe Signals of Nonadiabatic Excited-State Dynamics Using the Doorway–Window Representation

Maxim F. Gelin, Xiang Huang, Weiwei Xie, Lipeng Chen, Nađa Došlić, and Wolfgang Domcke*

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Combined Surface-Hopping, Dyson Orbital, and B-Spline Approach for the Computation of Time-Resolved Photoelectron Spectroscopy Signals: The Internal Conversion in Pyrazine

Tomislav Piteša, Marin Sapunar, Aurora Ponzi, Maxim F. Gelin, Nađa Došlić,* Wolfgang Domcke, and Piero Decleva*

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