Supporting Information: Manipulating nonadiabatic conical intersection dynamics by optical cavities

Bing Gu*,† and Shaul Mukamel*,†

†*Department of Chemistry, University of California, Irvine, CA 92697, USA*

‡*Department of Physics and Astronomy, University of California, Irvine, CA 92697, USA*

E-mail: bingg@uci.edu; smukamel@uci.edu

Contents

1 Theory of transient absorption spectroscopy for polaritonic chemistry

The theory for nonlinear molecular spectroscopy in optical cavities is conceptually similar to the ones for bare molecules but with the composite quantum light-molecule system playing the roles of bare molecules. The total Hamiltonian consists of the molecular Hamiltonian H_{M}, the cavity photon Hamiltonian H_{C}, and the cavity-matter interaction H_{CM}, and the external laser field-matter interaction $H_{\mathrm{LM}}(t)$,

$$H = H_{\mathrm{M}} + H_{\mathrm{C}} + H_{\mathrm{CM}} + H_{\mathrm{LM}}(t) \tag{1}$$

The laser field-matter interaction under the rotating-wave approximation (RWA) is given by

$$H_{\mathrm{LM}}(t) = \mathbf{X} \cdot \mathbf{E}^{(-)}(t) + \mathbf{X}^{\dagger} \cdot \mathbf{E}^{(+)}(t) \tag{2}$$

where $\mathbf{E}^{(+)}(t)$ is the positive frequency component of the electric field operator, $\mathbf{X}$ ($\mathbf{X}^{\dagger}$) is the deexcitation (excitation) component in the dipole operator, i.e., $-\boldsymbol{\mu} = \mathbf{X} + \mathbf{X}^{\dagger}$.

The optical signal can be defined as the time-averaged photon flux in the signal mode

$$S = -\int_{-\infty}^{+\infty} \frac{d}{dt} \langle N_{\mathrm{s}}(t) \rangle \, dt \tag{3}$$

where the expectation value is taken in the joint polariton-external photon space, and $N_{\mathrm{s}} = a_{\mathrm{s}}^{\dagger} a_{\mathrm{s}}$ is the photon number operator with a_{s} ($a_{\mathrm{s}}^{\dagger}$) the annihilation (creation) operator associated with the signal mode. Using the Heisenberg equation of motion $i\frac{d}{dt} \langle N_{\mathrm{s}}(t) \rangle = [N_{\mathrm{s}}(t), H]$ and the commutation relations for the photon operators $[a_{\mathbf{k}}, a_{\mathbf{k}'}^{\dagger}] = \delta_{\mathbf{k}\mathbf{k}'}$ in Eq. (3) yields

$$
\begin{aligned}
S &= -2\,\mathrm{Im}\int_{-\infty}^{+\infty}\left\langle \mathbf{X}(t)\cdot\hat{\mathbf{E}}_{\mathrm{s}}^{(-)}(t)\right\rangle dt \\
&= -2\,\mathrm{Im}\int_{-\infty}^{+\infty}\left\langle \mathbf{X}(\omega)\cdot\hat{\mathbf{E}}_{\mathrm{s}}^{(-)}(\omega)\right\rangle \frac{\mathrm{d}\omega}{2\pi}
\end{aligned}
\tag{4}
$$

where the Fourier transform is defined as $f(\omega) = \int_{-\infty}^{+\infty} \mathrm{d}t f(t)e^{i\omega t}$. The frequency-resolved signal can be identified as

$$
S(\omega) = -2\,\mathrm{Im}\left\langle \mathbf{X}(\omega)\cdot\hat{\mathbf{E}}_{\mathrm{s}}^{(-)}(\omega)\right\rangle \tag{5}
$$

In the semi-classical limit, the electric field operator can be taken as a complex number

$$
S(\omega) = -2\,\mathrm{Im}\left\langle \mathbf{X}(\omega)\right\rangle \mathbf{E}_{\mathrm{s}}^{(-)}(\omega) \tag{6}
$$

1.1 Transient absorption spectroscopy

In transient absorption spectroscopy, the laser pulses consist of the pump pulse $\mathbf{E}_1(t)$ and the probe pulse $\mathbf{E}_2(t)$ such that the total electric field is given by

$$
\mathbf{E}(t) = \mathbf{E}_1(t+T)e^{i(\mathbf{k}_1\cdot\mathbf{r}-\omega_1 t)} + \mathbf{E}_2(t)e^{i(\mathbf{k}_2\cdot\mathbf{r}-\omega_2 t)} + \mathrm{c.c.} \tag{7}
$$

where $\mathbf{E}_n(t) = \hat{\mathbf{e}}_n E_n(t)$ denotes the positive frequency component of n-th laser pulse in the total electric field corresponding to the photon annihilation operator, and $\hat{\mathbf{e}}_n$ is the associated polarization vector. The signal mode in this case is the probe mode and using Eq. (6) yields

$$
S_{\mathrm{TAS}}(\omega) = -2\,\mathrm{Im}\left\langle \mathbf{X}(\omega)\right\rangle \cdot \mathbf{E}_{\mathrm{s}}^{(-)}(\omega) \tag{8}
$$

The polarization can be obtained by directly propagating the composite polaritonic wavefunction according to the time-dependent Schrödinger equation.

Additional physical insights can be gained for the TAS by using the time-dependent perturbation theory for the polarization. For a molecule under an impulsive excitation, this treatment leads to[S1]

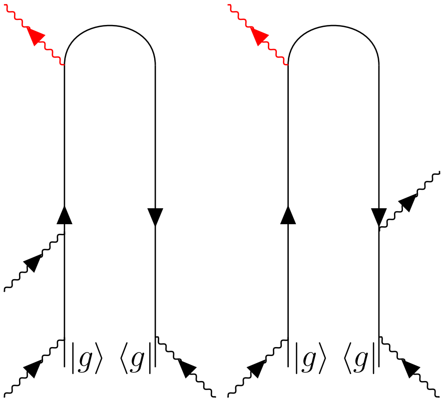

Figure S1: Time-loop diagrams for transient absorption signals: excited state absorption (left) and stimulated emission (right). The red arrow represents the light-matter interaction at time t that gives rise to the optical signal. The rules to translate the time-loop diagrams into analytical expressions can be found in.[S1]

$$\begin{aligned} S(t) &= -2\,\mathrm{Im}\int_{-\infty}^{+\infty}\mathrm{d}t\int_{-\infty}^{t}\mathrm{d}\tau E_2^*(t-T)E_2(\tau-T)\left(\chi^{\mathrm{SE}}(t,\tau)+\chi^{\mathrm{ESA}}(t,\tau)\right) \\ \chi^{\mathrm{ESA}}(t,\tau) &= -\left\langle \Psi_0 \,\middle|\, X_I(t)X_I^\dagger(\tau) \,\middle|\, \Psi_0 \right\rangle \\ \chi^{\mathrm{SE}}(t,\tau) &= \left\langle \Psi_0 \,\middle|\, X_I^\dagger(\tau)X_I(t) \,\middle|\, \Psi_0 \right\rangle \end{aligned} \quad , \qquad (9)$$

where $X = \mathbf{X}\cdot\hat{\mathbf{e}}_2$, $A_I(t) = U_0^\dagger(t)AU_0(t)$ with $U_0(t) = e^{-iH_0t}$ the propagator for polaritonic dynamics in the absence of external laser pulses. Here $|\Psi_0\rangle$ is the state immediately after the actinic pulse, which is the Frank-Condon state for impulsive excitation. Note that the excitation process is considered as a separate step here, hence Eq. (10) does not contain explicitly the pump pulse. The two contributions, excited state absorption χ^{ESA} and stimulated emission χ^{ES}, correspond to two different Liouville space pathways in the perturbation theory, and can be conveniently represented by the loop diagrams shown in Fig. S1. Using the Fourier transform of the field $E_2(t-T)$ in Eq. (9) leads to the frequency-resolved transient absorption signal

$$S_{\mathrm{TAS}}(\omega;T) = -2\,\mathrm{Im}\,E_2^*(\omega)\int_{-\infty}^{+\infty}\mathrm{d}t\,e^{i\omega(t-T)}\int_{-\infty}^{t}\mathrm{d}\tau E_2(\tau-T)(\chi^{\mathrm{ESA}}(t,\tau)+\chi^{\mathrm{SE}}(t,\tau)) \tag{10}$$

1.2 Real-time laser-driven dynamics for optical signals

There are two main approaches to simulate the TAS as well as other optical signals. One is to represent the molecule operators in the perturbative expression for the signal Eq. (9) in terms of the system eigenstates such that $X(t) = \sum_{\alpha\beta} X_{\alpha\beta}e^{i\omega_{\alpha\beta}t}$ with $\omega_{\alpha\beta} = \omega_\alpha - \omega_\beta$. This will lead to a sum-over-states formula. An alternative approach, that is employed here, is to explicitly solve the quantum dynamics with the presence of laser pulses.

As the TAS is determined by the polarization induced by the probe pulse, the real-time approach amounts to computing the differential polarization with the presence of both pump and probe pulses $P(\omega;T)$ and with only the pump pulse $P_0(\omega)$, i.e.,

$$S_{\mathrm{TAS}}(\omega;T) = 2\,\mathrm{Im}\left\{(P(\omega;T) - P_0(\omega))E_2(\omega)\right\}. \tag{11}$$

In general, the signal simulated from laser-driven dynamics consists of contributions associated with multiple Liouville-space pathways. To isolate the contribution from a particular pathway, one can use the phase-cycling technique.[S2]

1.3 Computational details

The time-dependent Schrödinger equation for the joint light-molecule system is integrated by the Runge-Kutta fourth-order method with time step $\delta t = 0.2$ fs. The size of basis set in all the simulations is set as $n_{\mathrm{cav}} = 2$, $n_{\mathrm{t}} = n_{\mathrm{c}} = 20$ such that the full polaritonic space consists of $3 \times 2 \times 20 \times 20 = 2400$ basis functions.

The transition dipole moments are obtained by quantum chemistry calculations with PYSCF program.[S3] In particular, the transition dipoles are computed using CASSCF(10,6)/6-

311G** (complete active space self-consistent field method with 10 orbitals and 6 electrons with basis set 6-311G**) at the ground-state equilibrium geometry optimized using density-functional theory with B3LYP functional[S4] and basis set 6-31G**.

For the TAS computations, we use a probe pulse with a Gaussian envelop,

$$E_2(t) = A_0 \sin(\omega_2 t + \phi_2) \exp\left(-\frac{t^2}{2\sigma^2}\right) \tag{12}$$

where $A_0 = 0.001$ a.u. is the electric field amplitude, $\omega_2 = 3$ eV the central frequency, $\phi_2 = 0$ the carrier envelop phase and $\sigma = 1$ fs the duration of the pulse.

2 Hierarchical equation of motion for dissipative polaritonic dynamics

Consider a polaritonic system interacting with a harmonic environment consisting of a set of harmonic oscillators. For the simplicity of presentation, we assume that the interaction Hamiltonian can be written as

$$H_{\mathrm{SB}} = S \otimes B, \tag{13}$$

where S (B) represents an system (bath) operator. It is straightforward to generalize the derivation below to more general interactions $H_{\mathrm{SB}} = \sum_\alpha S_\alpha \otimes B_\alpha$. If the system operator S is purely electronic, it can be straightforwardly extended to the full polaritonic space by $S \otimes I_{\mathrm{v}} \otimes I_{\mathrm{cav}}$, where $I_{\mathrm{v/cav}}$ is the identity operator in the vibrational/cavity space.

The dynamical map for the vibronic density matrix in the interaction picture of $H_0 = H_{\mathrm{S}} + H_{\mathrm{B}}$ is given by[S5]

$$\rho_I^{\mathrm{S}}(t) = \mathcal{M}(t)\rho^{\mathrm{S}}(0) \tag{14}$$

where

$$\mathcal{M}(t) = \mathcal{T} \exp\left(-\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \mathcal{S}^- \left(\operatorname{Re} D(t_1 - t_2)\mathcal{S}^- + i \operatorname{Im} D(t_1 - t_2)\mathcal{S}^+\right)\right), \qquad (15)$$

where $D(\tau) = \langle B_I(\tau)B \rangle$ is the environment correlation function with $B_I(t) = U_\mathrm{B}^\dagger(t) B U_\mathrm{B}(t)$, and $\mathcal{S}^\pm \rho = [S, \rho]_\pm$. To solve Eq. (14), we introduce the so-called auxiliary density matrices $(n = 0, 1, \cdots)$

$$\rho_n(t) = U_\mathrm{S}(t)\mathcal{T}\left\{\left(-i\int_0^t \mathrm{d}t_1 \left(\operatorname{Re} D(t - t_1)\mathcal{S}^- + i \operatorname{Im} D(t - t_1)\mathcal{S}^+\right)\right)^n \mathcal{M}(t)\right\}\rho^\mathrm{S}(0), \qquad (16)$$

where $\rho_0(t) \equiv \rho^\mathrm{S}(t)$.

If the environment correlation function is a decayed exponential $D(t) = D(0)e^{-\gamma t}$ as for the Drude spectral density at the high-temperature limit, the hierarchical equations of motion (HEOM) can be obtained by differentiating Eq. (16) w.r.t. time which leads to

$$\frac{\partial}{\partial t}\rho_0(t) = -i\mathcal{L}_\mathrm{S}\rho_0(t) - i\mathcal{S}^-\rho_1(t) \qquad (17)$$

and for $n \geq 1$

$$\frac{\partial}{\partial t}\rho_n(t) = (-i\mathcal{L}_\mathrm{S} - n\gamma)\rho_n(t) - i\mathcal{S}^-\rho_{n+1}(t) - in\big(\operatorname{Re} D(0)\mathcal{S}^- + i \operatorname{Im} D(0)\mathcal{S}^+\big)\rho_{n-1}(t). \qquad (18)$$

The infinity hierarchy of equations can be closed by e.g. setting a cutoff N where $\rho_{n>N} = 0$.

2.1 Relation between the environment correlation function and spectral density

From the Heisenberg equations of motion for the annihilation and creation operators, one can obtain $a_{k,I}(t) = e^{-i\omega_k t}a_k$ and $a^\dagger_{k,I}(t) = e^{i\omega_k t}a^\dagger_k$, respectively. Thus, the time-correlation function $D(t)$ can be calculated as

$$\begin{aligned} D(t) &= \sum_k |g_k|^2 \left(\left\langle a_{k,I}(t)a^\dagger_k \right\rangle + \left\langle a^\dagger_{k,I}(t)a_k \right\rangle \right) \\ &= \sum_k |g_k|^2 \left((1-\bar{n}_k)e^{-i\omega_k t} + \bar{n}_k e^{i\omega_k t} \right) \end{aligned} \tag{19}$$

where $\bar{n}_k = \langle a^\dagger_k a_k \rangle$ is the distribution function. At thermal equilibrium, $\bar{n}_k = 1/(e^{\beta\omega_k} - 1)$ corresponding to the Bose-Einstein distribution and Eq. (19) yields

$$D(t) = \int_0^\infty \frac{\mathrm{d}\omega}{\pi} J(\omega)[\coth(\beta\omega/2)\cos(\omega t) - i\sin(\omega t)] \tag{20}$$

References

(S1) Kowalewski, M.; Fingerhut, B. P.; Dorfman, K. E.; Bennett, K.; Mukamel, S. Simulating Coherent Multidimensional Spectroscopy of Nonadiabatic Molecular Processes: From the Infrared to the X-Ray Regime. *Chem. Rev.* **2017**, *117*, 12165–12226.

(S2) Cho, D.; Rouxel, J. R.; Kowalewski, M.; Saurabh, P.; Lee, J. Y.; Mukamel, S. Phase Cycling RT-TDDFT Simulation Protocol for Nonlinear XUV and X-Ray Molecular Spectroscopy. *J. Phys. Chem. Lett.* **2018**, *9*, 1072–1078.

(S3) Sun, Q.; Berkelbach, T. C.; Blunt, N. S.; Booth, G. H.; Guo, S.; Li, Z.; Liu, J.; McClain, J. D.; Sayfutyarova, E. R.; Sharma, S.; Wouters, S.; Chan, G. K.-L. PySCF: The

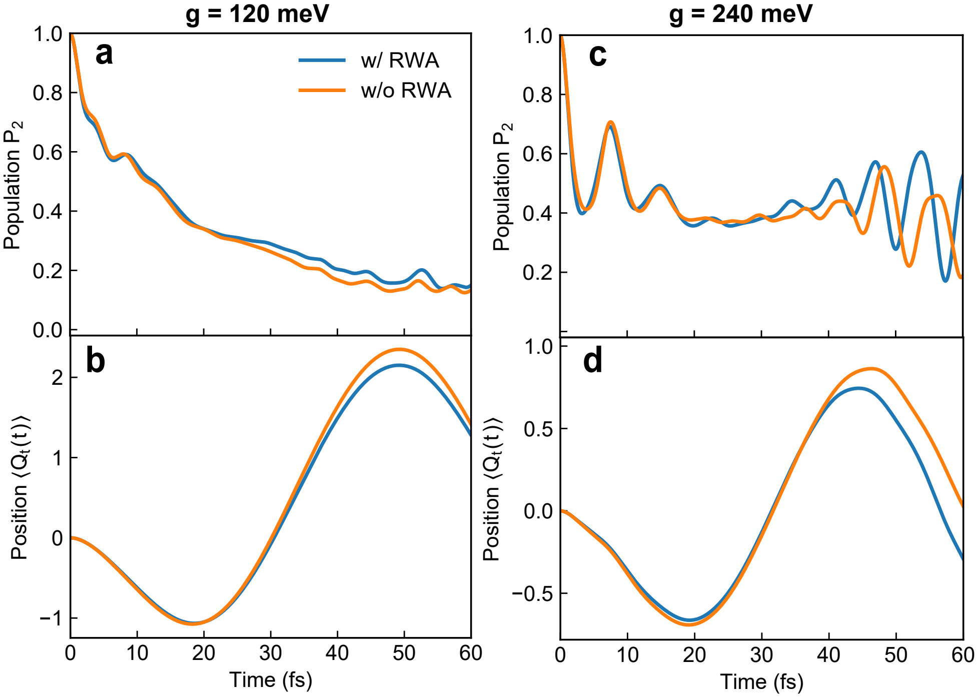

Figure S2: Effects of counter-rotating terms in polaritonic dynamics for case II at $g = 120, 240$ meV. (a,c) Population dynamics of state S_2 and (b,d) expectation values of the tuning mode with and without the rotating-wave approximation (RWA).

Python-Based Simulations of Chemistry Framework. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2018**, *8*, e1340.

(S4) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785–789.

(S5) Tang, Z.; Ouyang, X.; Gong, Z.; Wang, H.; Wu, J. Extended Hierarchy Equation of Motion for the Spin-Boson Model. *J. Chem. Phys.* **2015**, *143*, 224112.