Electronic Supplementary Information for:

Radiative emission of polaritons controlled by light-induced geometric phase

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I. THEORETICAL CONSIDERATIONS

The Hamiltonian of a molecule coupled to a single cavity mode has the form

$$\hat{H}_{\rm cm} = \hat{H}_0 + \hbar\omega_{\rm c}\hat{a}^{\dagger}\hat{a} - g\hat{\vec{\mu}}\vec{e}(\hat{a}^{\dagger} + \hat{a}).$$
(1)

We refer to the manuscript regarding the notations used in Eq. (1). Note that the quadratic dipole self-energy term¹⁻⁵ is omitted in Eq. (1) as it is expected to have negligible effects for the cases investigated in this work. If two molecular electronic states (X and A) are considered, the Hamiltonian of Eq. (1) can be recast in the direct product basis of the electronic states ($|X\rangle$ and $|A\rangle$) and Fock states of the cavity mode ($|n\rangle$ with n = 0, 1, 2, ...) as

$$\hat{H}_{\rm cm} = \begin{bmatrix} \hat{T} + V_{\rm X} & 0 & 0 & W_1 & 0 & 0 & \dots \\ 0 & \hat{T} + V_{\rm A} & W_1 & 0 & 0 & 0 & \dots \\ 0 & W_1 & \hat{T} + V_{\rm X} + \hbar\omega_{\rm c} & 0 & 0 & W_2 & \dots \\ W_1 & 0 & 0 & \hat{T} + V_{\rm A} + \hbar\omega_{\rm c} & W_2 & 0 & \dots \\ 0 & 0 & W_2 & \hat{T} + V_{\rm X} + 2\hbar\omega_{\rm c} & 0 & \dots \\ 0 & 0 & W_2 & 0 & 0 & \hat{T} + V_{\rm A} + 2\hbar\omega_{\rm c} & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix}$$
(2)

where \hat{T} denotes the kinetic energy operator, while $V_{\rm X}$ and $V_{\rm A}$ are the ground-state and excited-state potential energy surfaces (PESs). The cavity-molecule coupling is described by the operator $W_n = -g\sqrt{n}\vec{de}$ where \vec{d} is the molecular transition dipole moment vector. It is important to note that terms pertaining to the X and A permanent dipole moments are neglected in Eq. (2).

The interaction of the cavity mode with a laser pulse is described by the Hamiltonian

$$\hat{H}_{\rm L} = -\mu_{\rm c} E(t)(\hat{a}^{\dagger} + \hat{a}) \tag{3}$$

which gives rise to the total Hamiltonian

$$\hat{H} = \hat{H}_{\rm cm} + \hat{H}_{\rm L}.\tag{4}$$

All previous equations correspond to the diabatic representation.^{6–8} The adiabatic representation is defined by diagonalizing the potential energy part (V) of the Hamiltonian in Eq. (2),

$$V^{\rm ad} = U^{\rm T} V U \tag{5}$$

where $V^{\rm ad}$ contains the polaritonic PESs on its diagonal. Accordingly, the Hamiltonian in the adiabatic representation equals

$$\hat{H}^{\mathrm{ad}} = U^{\mathrm{T}}\hat{H}U = U^{\mathrm{T}}\hat{T}U + V^{\mathrm{ad}} + U^{\mathrm{T}}\hat{H}_{\mathrm{L}}U.$$
(6)

The Born–Oppenheimer (BO) approximation is defined by neglecting the kinetic coupling terms in \hat{H}^{ad} (in other words, the approximation $U^{T}\hat{T}U \approx \hat{T}$ is made), that is,

$$\hat{H}^{\rm BO} = \hat{T} + V^{\rm ad} + U^{\rm T} \hat{H}_{\rm L} U. \tag{7}$$

We stress that here the terms diabatic and adiabatic refer to the coupled cavity-molecule system. Of course, in the field-free case, the electronic states $|X\rangle$ and $|A\rangle$ are adiabatic electronic states. However, for a molecule coupled to the cavity mode, the light-matter interaction terms appear in the potential energy part of Eq. (2). Therefore, $\hat{H}_{\rm cm}$ corresponds to the diabatic representation and one can move to the adiabatic representation by diagonalizing the potential energy part of $\hat{H}_{\rm cm}$.

As a next step, geometric phase (GP) effects are incorporated by taking the similaritytransformed Hamiltonian

$$\hat{H}_{\rm GP}^{\rm BO} = \exp(\mathrm{i}\theta)\hat{H}^{\rm BO}\exp(-\mathrm{i}\theta) \tag{8}$$

where $\exp(-i\theta)$ is a position-dependent phase factor which will enable us to work with single-valued nuclear wave functions.^{9–13} As discussed in the manuscript, the coupled cavitymolecule system is pumped to the singly-excited subspace (ground electronic state with one photon and excited electronic state with zero photon) by a laser pulse. If the cavity frequency is in near-resonance with the X \rightarrow A electronic transition, it is a good approximation to separate matrix elements of the potential energy matrix (V) of Eq. (2) corresponding to the singly-excited subspace ($V_{\rm A}$ and $V_{\rm X} + \hbar\omega_c$)^{14,15} and work with a two-dimensional block of V defined as

$$V_{\rm S} = \begin{bmatrix} V_{\rm A} & W_1 \\ W_1 & V_{\rm X} + \hbar\omega_{\rm c} \end{bmatrix}.$$
 (9)

Therefore, in our particular case, θ is chosen as the angle which parameterizes the two-by-two orthogonal transformation matrix

$$U = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}$$
(10)

which diagonalizes $V_{\rm S}$. Thus, the matrix

$$U^{\mathrm{T}}V_{\mathrm{S}}U = \begin{bmatrix} \cos\theta & -\sin\theta\\ \sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} V_{\mathrm{A}} & W_{\mathrm{1}}\\ W_{\mathrm{1}} & V_{\mathrm{X}} + \hbar\omega_{\mathrm{c}} \end{bmatrix} \begin{bmatrix} \cos\theta & \sin\theta\\ -\sin\theta & \cos\theta \end{bmatrix}$$
(11)

is diagonal if

$$\theta = \frac{1}{2} \arctan\left(\frac{2W_1}{V_{\rm X} + \hbar\omega_{\rm c} - V_{\rm A}}\right). \tag{12}$$

This procedure is clearly an approximation which will be further investigated in future work. An alternative way of evaluating the transformation angle θ would be the block diagonalization idea proposed in Refs. 16 and 17. Finally, we stress that the Lindblad equation is solved using the full cavity-molecule Hamiltonian \hat{H} with $n = 0, \ldots, n_{\text{max}}$ (see the next section for more information) and only the calculation of the angle θ involves the two-by-two approximation used in Eqs. (9), (10), (11) and (12).

Eq. (8) can be rearranged by evaluating the action of the kinetic energy operator on $\exp(-i\theta)$, which yields

$$\hat{H}_{\rm GP}^{\rm BO} = \hat{H}^{\rm BO} + i(\nabla\theta)\nabla + \frac{i}{2}(\nabla^2\theta) + \frac{1}{2}(\nabla\theta)^2.$$
(13)

In the 2D(ν_2, ν_4) model (see the next section for further discussion) used in numerical computations, $\hat{T} = -\frac{1}{2} \left(\frac{\partial^2}{\partial Q_2^2} + \frac{\partial^2}{\partial Q_4^2} \right)$ and $\nabla = \left(\frac{\partial}{\partial Q_2}, \frac{\partial}{\partial Q_4} \right)$. By substituting the commutator

$$[\nabla, \nabla\theta] = \nabla(\nabla\theta) - (\nabla\theta)\nabla = \nabla^2\theta \tag{14}$$

into the second GP term $(\frac{i}{2}(\nabla^2\theta))$ one can show that the sum of the first two GP terms becomes

$$i(\nabla\theta)\nabla + \frac{i}{2}(\nabla^2\theta) = \frac{i}{2}((\nabla\theta)\nabla + \nabla(\nabla\theta)).$$
(15)

This way, $\hat{H}_{\rm GP}^{\rm BO}$ can be transformed to a more symmetric form

$$\hat{H}_{\rm GP}^{\rm BO} = \hat{H}^{\rm BO} + \frac{i}{2}((\nabla\theta)\nabla + \nabla(\nabla\theta)) + \frac{1}{2}(\nabla\theta)^2$$
(16)

which was employed in numerical computations carried out in this study.

II. COMPUTATIONAL MODEL AND TECHNICAL DETAILS

As already described in previous work,^{18–20} the four-atomic formaldehyde (H₂CO) molecule has a planar equilibrium structure (C_{2v} point-group symmetry) in the ground electronic state (\tilde{X} ¹A₁) and two symmetry-equivalent nonplanar equilibrium structures (C_s point-group symmetry) which are connected by a planar transition state structure (C_{2v} point-group symmetry) in the excited electronic state (\tilde{A} ¹A₂). The ground-state equilibrium structure and definition of the body-fixed coordinate axes are depicted in Figure S1. Out of the six vibrational normal modes of H₂CO the ν_2 (C=O stretch, A₁ symmetry) and ν_4 (out-of-plane bend, B₁ symmetry) vibrational modes are included in the computational model called the 2D(ν_2, ν_4) model. The corresponding anharmonic fundamentals in the ground electronic state (obtained by six-dimensional variational computations) are 1738.1 cm⁻¹ (ν_2 mode) and 1147.0 cm⁻¹ (ν_4 mode).



FIG. S1. Equilibrium structure of the H_2CO molecule in the ground electronic state and definition of the body-fixed coordinate axes (the equilibrium structure is placed in the yz plane).

In order to set up the $2D(\nu_2,\nu_4)$ model normal coordinates corresponding to the planar transition state structure of the excited electronic state were evaluated and the four inactive normal coordinates (Q_1, Q_3, Q_5, Q_6) were set to zero. Then, the $2D(\nu_2,\nu_4)$ potential energy surfaces (PESs) $(V_X \text{ and } V_A)$ and the transition dipole moment (TDM) surface were computed as a function of the Q_2 and Q_4 normal coordinates at the CAM-B3LYP/6-31G^{*} level of theory. Finally, two-dimensional PES and TDM functions were generated by interpolating the ab initio PES and TDM points.

Due to symmetry, the TDM vanishes at any geometry of C_{2v} symmetry. Moreover, in the $2D(\nu_2,\nu_4)$ model, only the body-fixed y component of the TDM can be nonzero and the TDM is always perpendicular to the permanent dipole moment of both electronic states. This observation motivates the choice that the cavity field is polarized along the bodyfixed y axis in all computations. Since H₂CO does not have any first-order nonadiabatic coupling between the X and A electronic states around its equilibrium geometry, lightinduced nonadiabatic effects can be unambiguously distinguished from natural ones.

The Lindblad equation was solved numerically in the diabatic representation using the direct product of two-dimensional discrete variable representation basis functions and Fock states of the cavity mode $|n\rangle$ with n = 0, 1, 2. In addition to numerically-exact diabatic computations, Born–Oppenheimer (BO) computations were carried out without (BO model) or with the GP terms (BOGP model). In both cases the potential energy part of the diabatic Hamiltonian was diagonalized at each two-dimensional grid point to obtain polaritonic PESs. The Lindblad equation was then transformed to the adiabatic representation, nonadiabatic coupling terms were omitted and the resulting equations were solved numerically using the same two-dimensional discrete variable representation basis for each polaritonic PES.

III. SUPPLEMENTAL DATA AND FIGURES

Table S1 provides relevant energy levels of the coupled cavity-molecule system together with eigenstate labels and photonic part populations used in the manuscript (cavity parameters are $\omega_{\rm c} = 30245.5 \,{\rm cm}^{-1}$ and $g = 0.1 \,{\rm au}$). Figure S2 shows absolute values of the transition dipole moments between the lowest-energy eigenstate (initial state) and selected eigenstates of the cavity-molecule system for the three models investigated (exact, Born–Oppenheimer (BO) and BO with geometric phase (BOGP)). Fourier transforms of the laser pulses that are used to transfer population to the LP state are also given in Fig. S2. Selected energy levels together with eigenstate labels shown in Fig. S2 are provided in Table S1. Figure S3 depicts populations of relevant eigenstates (exact, Born–Oppenheimer (BO) and BO with geometric phase (BOGP) models) for the following cavity and laser parameters: $\omega_c = 30245.5 \text{ cm}^{-1}$ and g = 0.1 au, and $\omega_{\rm L} = 29400$ cm⁻¹ or $\omega_{\rm L} = 30400$ cm⁻¹, both with T = 200 fs and $E_0 = 0.001$ au (corresponding to a field intensity of $I = 3.51 \cdot 10^{10} \text{ W/cm}^2$). Figures S4 and S5 provide probability density figures for selected eigenstates with $\omega_c = 30245.5 \text{ cm}^{-1}$ and g = 0.1 au (see Table S1 for more information on eigenstate labels). As exact eigenstates are computed using the diabatic representation, exact eigenstates are first transformed to the adiabatic representation and LP densities of the resulting states are then evaluated. Figure S6 shows population and emission figures (exact, BO and BOGP models) for the cavity parameters $\omega_c = 29957.2 \text{ cm}^{-1}$ and g = 0.1 au. In this case the cavity mode is pumped with the following laser pulses: $\omega_{\rm L} = 29200 \text{ cm}^{-1}$ (panels a-b) and $\omega_{\rm L} = 30300 \text{ cm}^{-1}$ (panels c-d), both with T = 200 fs and $E_0 = 0.001$ au.

TABLE S1. Selected energy levels of the coupled cavity-molecule system (E in units of cm⁻¹), eigenstate labels and photonic part populations for the three models investigated (exact: labels 0-3, Born–Oppenheimer (BO): labels 1A/B, 3A/B and 4B, BO with geometric phase (BOGP): labels 0b, 1a/b, 2a/b and 3a/b). Each energy level is referenced to the lowest energy level of the given model (exact: $E_{\text{lowest}} = 1507.4 \text{ cm}^{-1}$, BO and BOGP: $E_{\text{lowest}} = 1507.1 \text{ cm}^{-1}$). The energy of the light-induced conical intersection (LICI) is 29390.5 cm⁻¹ referenced to E_{lowest} . The cavity wavenumber and coupling strength are $\omega_c = 30245.5 \text{ cm}^{-1}$ and g = 0.1 au, respectively.

Eigenstate label	$(E - E_{\text{lowest}}) / \text{cm}^{-1}$	Photonic part population
0	28863.7	0.11
1	29805.9	0.46
2	30039.7	0.12
3	30620.1	0.37
1A	29523.7	0.24
1B	29924.0	0.33
3A	30599.5	0.07
3B	30669.0	0.33
4B	31200.7	0.30
0b	28819.7	0.12
1a	29699.1	0.15
1b	29766.2	0.31
2a	30039.3	0.14
2b	30063.7	0.32
3a	30627.2	0.05
3b	30713.2	0.37



FIG. S2. Absolute values of transition dipoles between selected cavity-molecule eigenstates and the lowest-energy eigenstate for three different models (exact, Born–Oppenheimer (BO) and BO with geometric phase (BOGP)). Fourier transforms (absolute value) of the 200 fs laser pulses used to initiate the dynamics are also shown (carrier wavenumbers: $\omega_{\rm L} = 29400 \text{ cm}^{-1}$ (left curve, dashed line) and $\omega_{\rm L} = 30400 \text{ cm}^{-1}$ (right curve, dash-dotted line)). Energy levels of selected eigenstates are referenced to the lowest energy level ($E - E_{\rm lowest}$). The energetic position of the light-induced conical intersection (LICI), explicitly marked in the figure, is 29390.5 cm⁻¹ referenced to $E_{\rm lowest}$. The cavity wavenumber and coupling strength are $\omega_{\rm c} = 30245.5 \text{ cm}^{-1}$ and g = 0.1 au, respectively.



FIG. S3. (a-c) Populations of relevant eigenstates of the coupled cavity-molecule system for the three different models investigated (exact, Born-Oppenheimer (BO) and BO with geometric phase (BOGP)). Populations are shown during excitation with a 200 fs laser pulse (carrier wavenumber: $\omega_{\rm L} = 29400 \text{ cm}^{-1}$). (d-f) Same as for panels a-c with $\omega_{\rm L} = 30400 \text{ cm}^{-1}$. Eigenstate labels indicated in the panels are defined in Table S1. The cavity parameters are $\omega_c = 30245.5 \text{ cm}^{-1}$ and g = 0.1 au for all panels.



FIG. S4. Probability density figures for selected eigenstates of the coupled cavity-molecule system (exact: 1, Born–Oppenheimer (BO): 1A, BO with geometric phase (BOGP): 1a and 1b, see Table S1 for more information). Q_2 and Q_4 are dimensionless normal coordinates of the modes ν_2 and ν_4 . The cavity wavenumber and coupling strength are $\omega_c = 30245.5 \text{ cm}^{-1}$ and g = 0.1 au, respectively. The red dot indicates the position of the LICI at $Q_2 = 10.05$ and $Q_4 = 0$.



FIG. S5. Probability density figures for selected eigenstates of the coupled cavity-molecule system (exact: 3, Born–Oppenheimer (BO): 3B, BO with geometric phase (BOGP): 3b, see Table S1 for more information). Q_2 and Q_4 are dimensionless normal coordinates of the modes ν_2 and ν_4 . The cavity wavenumber and coupling strength are $\omega_c = 30245.5$ cm⁻¹ and g = 0.1 au, respectively. The red dot indicates the position of the LICI at $Q_2 = 10.05$ and $Q_4 = 0$.



FIG. S6. (a) Population of the lower polaritonic (LP) state for the three different models investigated (exact, Born–Oppenheimer (BO) and BO with geometric phase (BOGP)) during and after excitation with a 200 fs laser pulse (carrier wavenumber: $\omega_{\rm L} = 29200 \text{ cm}^{-1}$). The cavity wavenumber and coupling strength are $\omega_{\rm c} = 29957.2 \text{ cm}^{-1}$ and g = 0.1 au. Populations of polaritonic states higher than LP are negligible (see dashed lines with empty markers). (b) Ultrafast emission signals for the three different models with the parameters of panel a. The emission is proportional to the expectation value of the photon number operator \hat{N} . The exact emission is significantly overestimated by the BO model, while the BOGP model shows an excellent agreement with the exact results. (c-d) Same as for panels a-b with $\omega_{\rm L} = 30300 \text{ cm}^{-1}$. In contrast to panels a-b, the exact emission is underestimated by the BO model and inclusion of the GP does not improve the BO model.

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