Impact of light-induced geometric phase on ultrafast radiative emission

Csaba Fábi, Gábor J. Halász, Lorenz S. Cederbaum, and Ágnes Vibók

1) ELKH-ELTE Complex Chemical Systems Research Group, P.O. Box 32, H-1518 Budapest 112, Hungary
2) Department of Theoretical Physics, University of Debrecen, PO Box 400, H-4002 Debrecen, Hungary
3) Department of Information Technology, University of Debrecen, P.O. Box 400, H-4002 Debrecen, Hungary
4) Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany
5) ELI-ALPS, ELI-HU Non-Profit Ltd, H-6720 Szeged, Dugonics tér 13, Hungary

It is known that light-induced conical intersections can be formed between polaritonic potential energy surfaces due to the interaction of a molecule with the quantized radiation field of an optical or plasmonic nanocavity. Here we discuss the geometric phase (GP) effect of light-induced conical intersections by investigating the radiative emission of the cavity as an experimentally measurable physical quantity. It is shown that in certain situations the numerically exact ultrafast radiative emission signal from the lower polaritonic surface can be well approximated by extending the single-surface adiabatic model with the GP term. This can be seen as a clear fingerprint of the GP associated with the light-induced conical intersection.
Conical intersections (CIs) are degeneracies between close-lying electronic states in molecular systems. Conical intersections (CIs) are ubiquitous in polyatomic molecules which possess a dense manifold of electronic states and several nuclear degrees of freedom. CIs enable radiationless transitions which take place between electronic states in the vicinity of nuclear configurations where the relevant potential energy surfaces (PESs) intersect. In order to properly describe these ultrafast processes one needs to invoke the coupled-electronic-state nonadiabatic approach instead of the so-called single-surface Born–Oppenheimer (BO) scheme which fails in the presence of CIs.

CIs can also emerge when the molecule is exposed to classical laser light or to the quantized radiation field of an optical or plasmonic nanocavity. These CIs are termed light-induced conical intersections (LICIs). In case of quantized light, the confined photonic mode of the cavity can resonantly couple the electronic states of the molecule, which gives rise to polaritonic states carrying both photonic and excitonic characters. Similarly to natural CIs, LICIs can also be harnessed to modify and control different topological, spectroscopic and dynamical properties of molecules.

We have recently shown for a realistic quantum-dynamical model of a four-atomic molecule (H$_2$CO, formaldehyde) that the time-resolved ultrafast radiative emission of the cavity enables to follow nonadiabatic population transfer between polaritonic surfaces, which can be seen as an unambiguous (and in principle experimentally accessible) dynamical fingerprint of the LICI. Here, we investigate the LICI-affected ultrafast radiative emission from the lower polaritonic state and demonstrate the role of the geometric phase (GP) associated with the LICI. From now on, the nomenclature developed for the description of natural nonadiabatic phenomena will be followed.

Nonadiabatic dynamics near a CI can be treated either in the adiabatic or diabatic representation which are related by a unitary transformation. The description of dynamics in the vicinity of a CI in the adiabatic representation reflects GP as a clear consequence that each real-valued adiabatic electronic wave function changes sign when transported continuously along a closed loop enclosing the CI. As the total molecular wave function has to be single valued, we choose to make the adiabatic electronic wave function complex by multiplying it with a position-dependent phase factor ensuring that the total wave function remains single valued. This modification of the electronic wave function has a direct effect on nuclear dynamics even when a single PES is considered. One way to include the GP ex-
plicitly in the single-state adiabatic representation is the vector potential approach\textsuperscript{34} which is referred to as the molecular Aharonov–Bohm effect.\textsuperscript{35,36} In several situations GP plays an important role in obtaining qualitatively correct results when problems are considered in the single-state adiabatic representation.\textsuperscript{37–41} Here we demonstrate that the adiabatic approximation can lead to significant overestimation of the ultrafast radiative emission from the lower polaritonic state, which can be ascribed to neglecting the GP.

A molecule coupled to a single cavity mode is described by the Hamiltonian\textsuperscript{42}

\[
\hat{H}_{cm} = \hat{H}_0 + \hbar \omega_c \hat{a}^\dagger \hat{a} - g \hat{\mu} \hat{e}(\hat{a}^\dagger + \hat{a}).
\] (1)

In Eq. (1) \( \hat{H}_0 \) refers to the Hamiltonian of the isolated molecule, \( \omega_c \) is the cavity angular frequency, \( \hat{a}^\dagger \) and \( \hat{a} \) denote creation and annihilation operators, \( g \) is the coupling strength parameter, \( \hat{\mu} \) corresponds to the molecular electric dipole moment operator and \( \hat{e} \) is the polarization vector of the cavity field. We choose to omit the quadratic dipole self-energy term\textsuperscript{43–47} 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 \( n = 0, 1, 2, \ldots \)) as

\[
\hat{H}_{cm} = \begin{bmatrix}
\hat{T} + V_X & 0 & 0 & W_1 & 0 & 0 & \ldots \\
0 & \hat{T} + V_A & W_1 & 0 & 0 & 0 & \ldots \\
0 & W_1 & \hat{T} + V_X + \hbar \omega_c & 0 & 0 & W_2 & \ldots \\
W_1 & 0 & 0 & \hat{T} + V_A + \hbar \omega_c & W_2 & 0 & \ldots \\
0 & 0 & 0 & W_2 & \hat{T} + V_X + 2\hbar \omega_c & 0 & \ldots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots
\end{bmatrix}
\] (2)

where \( \hat{T} \) denotes the kinetic energy operator, while \( V_X \) and \( V_A \) are the ground-state and excited-state PESs. The cavity-molecule coupling is described by the operator \( W_n = -g \sqrt{n} \vec{d} \hat{e} \) 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).

In many cases, effects associated with finite photon lifetime cannot be neglected, therefore, we employ the time-dependent Schrödinger equation

\[
\frac{i}{\hbar} \frac{\partial \psi}{\partial t} = \left( \hat{H} - \frac{\gamma_c}{2} \hat{N} \right) \psi
\] (3)
with a non-Hermitian Hamiltonian and the Lindblad equation\textsuperscript{27,48,49}

\[
\frac{\partial \hat{\rho}}{\partial t} = -i[\hat{H}, \hat{\rho}] + \gamma_c \hat{a} \hat{a}^\dagger - \frac{\gamma_c}{2} (\hat{\rho} \hat{N} + \hat{N} \hat{\rho})
\]  

(4)

to describe the quantum dynamics of the coupled cavity-molecule system and account for finite lifetime of the cavity mode. Note that $\hbar = 1$ is assumed for both equations, $\hat{\rho}$ is the density operator, $\hat{N} = \hat{a}^\dagger \hat{a}$ denotes the photon number operator and $\gamma_c$ is the cavity decay rate. Throughout this work we have applied the value $\gamma_c = 10^{-4}$ au which translates to a lifetime of $1/\gamma_c = 241.9$ fs.

The last two terms of Eq. (4) describe the incoherent decay of the cavity mode. As explained in Ref. 19, effects induced by the term $-\frac{\gamma_c}{2} (\hat{\rho} \hat{N} + \hat{N} \hat{\rho})$ can be incorporated in the Schrödinger equation by employing the non-Hermitian Hamiltonian $\hat{H} - i\frac{\gamma_c}{2} \hat{N}$. On the contrary, the term $\gamma_c \hat{a} \hat{a}^\dagger$ describes incoherent transitions $|n+1\rangle \rightarrow |n\rangle$ which cannot be accounted for by the Schrödinger equation of Eq. (3).

Following the computational framework reported in Ref. 27, the cavity mode is pumped with a laser pulse, which can be described by the Hamiltonian

\[
\hat{H} = \hat{H}_{cm} + \hat{H}_L \quad \text{with} \quad \hat{H}_L = -\mu_c E(t)(\hat{a}^\dagger + \hat{a}).
\]  

(5)

In Eq. (5) the effective dipole moment of the cavity mode is set to $\mu_c = 1.0$ au and the laser field has the form $E(t) = E_0 \sin^2(\pi t/T) \cos(\omega_L t)$ for $0 \leq t \leq T$, and $E(t) = 0$ for $t < 0$ and $t > T$, where $E_0$, $T$ and $\omega_L$ refer to the amplitude, length and carrier angular frequency of the laser pulse, respectively. Following Ref. 27, the radiative emission rate is expressed as $E_R \sim N(t)$ where $N(t)$ is the expectation value of the photon number operator $\hat{N}$. $N(t)$ can be evaluated as $N(t) = \langle \psi | \hat{N} | \psi \rangle$ (Schrödinger equation) or $N(t) = \text{tr}(\hat{\rho} \hat{N})$ (Lindblad equation).

Next, the diabatic Hamiltonian (see Eq. (5)) which includes both nonadiabatic and GP effects is transformed to the adiabatic Hamiltonian

\[
\hat{H}^{\text{ad}} = U^T \hat{H} U = U^T \hat{T} U + V^{\text{ad}} + U^T \hat{H}_L U
\]  

(6)

by diagonalizing the potential energy matrix of Eq. (2), that is, $V = UV^{\text{ad}} U^T$. $V^{\text{ad}}$ is a diagonal matrix containing the polaritonic PESs on its diagonal. This way, one can define the approximate adiabatic or BO Hamiltonian

\[
\hat{H}^{\text{BO}} = \hat{T} + V^{\text{ad}} + U^T \hat{H}_L U
\]  

(7)
by removing the nonadiabatic coupling terms from the kinetic energy operator \((U^T \hat{T} U \approx \hat{T})\). Note that \(\hat{H}^{\text{BO}}\) excludes both nonadiabatic and GP effects. The latter can be taken into account by the Mead and Truhlar approach\(^{34}\) which involves the multiplication of the nuclear wave function with a position-dependent phase factor \(\exp(-i\theta)\). This phase factor introduces a sign change of the nuclear wave function along closed loops encircling the CI. The current work focuses on pumping the system to the singly-excited subspace (molecule in ground electronic state with one photon and molecule in excited electronic state with zero photon) which accommodates the lower (LP) and upper (UP) polaritonic states. Therefore, in our case \(\theta\) corresponds to the transformation angle which parameterizes the two-by-two diabatic-to-adiabatic transformation in the singly-excited subspace,

\[
\theta = \frac{1}{2} \arctan \left( \frac{2W_1}{V_X + \hbar \omega_c - V_A} \right).
\]

These considerations lead to the Hamiltonian

\[
\hat{H}_{\text{GP}}^{\text{BO}} = \hat{H}^{\text{BO}} + \frac{i}{2} ((\nabla \theta) \nabla + \nabla (\nabla \theta)) + \frac{1}{2} (\nabla \theta)^2
\]

where \(\hat{H}^{\text{BO}}\) is supplemented by terms describing GP effects.\(^{29-32,34}\) We stress that \(\hat{H}^{\text{BO}}\) in Eq. (9) corresponds to either the LP or the UP states. Obviously, \(\hat{H}_{\text{GP}}^{\text{BO}}\) includes GP effects, but excludes the possibility of nonadiabatic transitions. Further details on \(\hat{H}_{\text{GP}}^{\text{BO}}\) are provided in the Supporting Information.

We utilize a two-dimensional vibrational model of the four-atomic \(\text{H}_2\text{CO}\) molecule, called the 2D(\(\nu_2,\nu_4\)) model which has been applied successfully in earlier work.\(^{18,23,28}\) The 2D(\(\nu_2,\nu_4\)) model treats the two singlet electronic states \(S_0\) (\(\tilde{X} 1A_1\)) and \(S_1\) (\(\tilde{A} 1A_2\)). In addition, the \(\nu_2\) (C=O stretch) and \(\nu_4\) (out-of-plane bend) vibrational modes of \(\text{H}_2\text{CO}\) are taken into account. As concluded by earlier studies,\(^{18,23,28}\) the 2D(\(\nu_2,\nu_4\)) model provides a physically correct description of the quantum dynamics of \(\text{H}_2\text{CO}\). Moreover, as two vibrational degrees of freedom are considered, the 2D(\(\nu_2,\nu_4\)) model, in contrast to one-dimensional descriptions, allows for the formation of LICIs between polaritonic PESs.\(^{18,20,21,23}\) We refer to the Supporting Information for further details concerning the 2D(\(\nu_2,\nu_4\)) model and technical aspects of the computations.

If the cavity wavenumber and coupling strength are chosen as \(\omega_c = 30245.5\ \text{cm}^{-1}\) and \(g = 0.1\ \text{au}\), respectively, the LICI is located at \(Q_2 = 10.05\) and \(Q_4 = 0\) (\(Q_2\) and \(Q_4\) are dimensionless normal coordinates of the modes \(\nu_2\) and \(\nu_4\)) at an energy corresponding to
FIG. 1. (a) Diabatic potentials ($V_X$, $V_A$ and $V_X + \hbar \omega_c$) as a function of the $Q_2$ (C=O stretch) normal coordinate (the out-of-plane normal coordinate is set to $Q_4 = 0$). The cavity wavenumber equals $\omega_c = 30245.5$ cm$^{-1}$. (b) Two-dimensional lower (LP) and upper (UP) polaritonic surfaces as a function of the $Q_2$ and $Q_4$ normal coordinates. The cavity wavenumber and coupling strength are $\omega_c = 30245.5$ cm$^{-1}$ and $g = 0.1$ au, respectively. The character of the polaritonic surfaces is indicated by a purple-orange colormap (purple: photonic, orange: excitonic).

30897.6 cm$^{-1}$ above the minimum of the ground-state polaritonic PES (or 29390.5 cm$^{-1}$ referenced to the lowest energy level). The corresponding diabatic and adiabatic LP and UP PESs are shown in Figure 1. Figure 2 shows absolute values of the transition dipole moments between the lowest-energy eigenstate (initial state) and selected eigenstates for the three models investigated (exact, approximate adiabatic (BO) and approximate adiabatic with GP (BOGP)) and Fourier transforms (absolute value) of the pump pulses that are used to transfer population to the LP state from the initially populated lowest-energy eigenstate. In addition, selected energy levels together with eigenstate labels shown in Figure 2 are provided in Table I. The corresponding eigenstates can be assigned to the LP PES either exactly (BO and BOGP models) or dominantly (exact model). Photonic part population values, defined as the integral of the LP probability density over the photonic region of the
FIG. 2. Absolute values of transition dipole moments between selected eigenstates and the lowest-energy eigenstate for the three different models investigated (exact, approximate adiabatic (BO) and approximate adiabatic with geometric phase (BOGP)). Fourier transforms (absolute value) of the 200 fs laser pulses applied in this study are also shown (carrier wavenumbers: $\omega_L = 29400$ cm$^{-1}$ (left curve) and $\omega_L = 30400$ cm$^{-1}$ (right curve)). Energy levels of selected eigenstates are referenced to the lowest energy level ($E - E_{\text{lowest}}$). The energetic position of the light-induced conical intersection (LICI), explicitly marked in the figure, is 29390.5 cm$^{-1}$ referenced to $E_{\text{lowest}}$. Energy levels corresponding to eigenstate labels indicated in the figure are provided in Table I. Exact eigenstates with vanishing transition dipole moments are indicated by black dots on the energy axis. The cavity wavenumber and coupling strength are $\omega_c = 30245.5$ cm$^{-1}$ and $g = 0.1$ au, respectively.

LP PES, are also specified in Table I.

In Figure 3 population of the LP state (panels a and b) and the ultrafast emission signal (panels c and d) for the exact, BO and BOGP models are presented. In this case the cavity mode is pumped with a laser pulse of $\omega_L = 29400$ cm$^{-1}$, $T = 200$ fs and $E_0 = 0.001$ au (corresponding to a field intensity of $I = 3.51 \cdot 10^{10}$ W/cm$^2$), which leads to population transfer from the initially populated lowest-energy eigenstate to the LP PES with high selectivity. The value $\omega_L = 29400$ cm$^{-1}$ essentially coincides with the LICI energy of 29390.5 cm$^{-1}$ (referenced to the lowest energy level). Results obtained with the time-dependent Schrödinger
TABLE I. Selected energy levels ($E$ in units of cm$^{-1}$), eigenstate labels and photonic part populations for the three models investigated (exact: labels 0 – 3, approximate adiabatic (BO): labels 1A/B, 3A/B and 4B, approximate adiabatic with geometric phase (BOGP): labels 0b, 1a/b, 2a/b and 3a/b, see also Figure 2). Each energy level is referenced to the lowest energy level of the given model (exact: $E_{\text{lowest}} = 1507.4$ cm$^{-1}$, BO and BOGP: $E_{\text{lowest}} = 1507.1$ cm$^{-1}$). The energy of the light-induced conical intersection (LICI) is 29390.5 cm$^{-1}$ referenced to $E_{\text{lowest}}$. The cavity wavenumber and coupling strength are $\omega_c = 30245.5$ cm$^{-1}$ and $g = 0.1$ au, respectively.

| Eigenstate label | $E - E_{\text{lowest}}$ / 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                     |

and Lindblad equations show good agreement with each other, as can be seen in Figure 3 (panels a and b: LP population, panels c and d: emission). It is conspicuous in Figure 3 that the maximal LP population for the BO model is approximately five times as large as the corresponding exact and BOGP values. In each model the ultrafast emission signal (proportional to the expectation value of the photon number operator $\hat{N}$) follows the shape of the corresponding LP population curve. Moreover, while the exact LP population and
FIG. 3. (a-b) Population of the lower polaritonic (LP) state for the three different models investigated (exact, approximate adiabatic (BO) and approximate adiabatic with geometric phase (BOGP)) during and after excitation with a 200 fs laser pulse (carrier wavenumber: $\omega_L = 29400$ cm$^{-1}$). The cavity wavenumber and coupling strength are $\omega_c = 30245.5$ cm$^{-1}$ and $g = 0.1$ au. Populations of polaritonic states higher than LP are negligible (see dashed lines with empty markers). (c-d) Ultrafast emission signals for the three different models. The emission is proportional to the expectation value of the photon number operator $\hat{N}$. The cavity and laser parameters are the same as for panels a and b. Results obtained with the time-dependent Schrödinger (TDSE) and Lindblad equations are explicitly labeled in each panel. Note that the exact emission is significantly overestimated by the BO model, while the BOGP model shows an excellent agreement with the exact results.

emission values are significantly overestimated by the BO model, the exact results agree well with their BOGP counterparts. In order to understand these observations populations and probability densities of the relevant eigenstates are analyzed for the three different models, depicted in the left column of Figure 5. Since exact eigenstates are computed using the
diabatic representation, the relevant exact eigenstates are first transformed to the adiabatic representation and the LP densities of the resulting states are then evaluated. One can notice that for the BO model a single eigenstate (denoted by 1A) is populated dominantly with a maximal population of 0.23 (see panel b in Figure 5) which is roughly five times as large as the maximal population of the dominant exact (1, panel a in Figure 5) and BOGP (1a and 1b, panel c in Figure 5) eigenstates. In addition, maximal populations of the dominant eigenstates for the exact and BOGP models sum up to a nearly identical value (about 0.04). In all models, the dominantly-populated eigenstates lie around the energetic position of the LICI (see Table I for the energy level values). Of course, in each case several other eigenstates are also populated to some extent, but the dominant populations can be attributed to the few eigenstates mentioned. The previous analysis of populations together with the fact that the photonic part populations of the dominant eigenstates (see Table I) do not differ significantly from each other explain the origin of both the overestimation of the BO model and the good agreement between the exact and BOGP results. The conclusions drawn about eigenstate populations are also supported by Figure 2 where transition dipole moments and energetic positions of relevant eigenstates are highlighted. One can observe in Figure 2 that the energy of the BO eigenstate labeled 1A lies closer to the center of the Fourier transform of the pulse with $\omega_L = 29400 \text{ cm}^{-1}$ than the dominant BOGP (1a and 1b) and exact (1) eigenstates, which explains why the BO eigenstate 1A can acquire substantially higher maximal population than the dominant exact and BOGP eigenstates. Another interesting observation is that while eigenstates 1, 1a and 1b tend to avoid the LICI, eigenstate 1A has its maximal amplitude in the vicinity of the LICI (see the Supporting Information for probability density figures). This finding justifies why the BO results are qualitatively different from the exact and BOGP ones and further supports the excellent agreement between the exact and BOGP models in this particular case.

A significantly different situation is presented in Figure 4. In this case the cavity mode is pumped with a laser pulse of $\omega_L = 30400 \text{ cm}^{-1}$, $T = 200 \text{ fs}$ and $E_0 = 0.001 \text{ au}$ ($I = 3.51 \cdot 10^{10} \text{ W/cm}^2$) and the dominantly-populated eigenstates are well above the LICI energy for all the three models (see Table I for energy level values). It can be seen in Figure 4 that the exact model gives rise to the largest LP population and emission values. The Schrödinger and Lindblad equations lead to essentially identical results again. Since the GP correction slightly reduces the BO LP population and emission values, the BOGP results get even
FIG. 4. (a-b) Population of the lower polaritonic (LP) state for the three different models investigated (exact, approximate adiabatic (BO) and approximate adiabatic with geometric phase (BOGP)) during and after excitation with a 200 fs laser pulse (carrier wavenumber: \(\omega_L = 30400 \text{ cm}^{-1}\)). The cavity wavenumber and coupling strength are \(\omega_c = 30245.5 \text{ cm}^{-1}\) and \(g = 0.1 \text{ au}\). Populations of polaritonic states higher than LP are negligible (see dashed lines with empty markers). (c-d) Ultrafast emission signals for the three different models. The emission is proportional to the expectation value of the photon number operator \(\hat{N}\). The cavity and laser parameters are the same as for panels a and b. Results obtained with the time-dependent Schrödinger (TDSE) and Lindblad equations are explicitly labeled in each panel. Note that in this case the exact emission is underestimated by the BO model and inclusion of the geometric phase does not improve the BO model.

Further from their exact counterparts. As a consequence, the BOGP model is not able to approximate the exact description in this case. Careful analysis of the populations and photonic part populations of the relevant eigenstates (see the right column of Figure 5 and Table I) serves as an unequivocal explanation for the ultrafast emission results obtained
FIG. 5. (a–c) Populations of relevant eigenstates for the three different models investigated (exact, approximate adiabatic (BO) and approximate adiabatic with geometric phase (BOGP)). Populations are shown during excitation with a 200 fs laser pulse (carrier wavenumber: $\omega_L = 29400 \text{ cm}^{-1}$). (d–f) Same as for panels a–c with $\omega_L = 30400 \text{ cm}^{-1}$. Probability densities for selected eigenstates are shown in the insets. Eigenstate labels indicated in the panels and the corresponding energy level values are provided in Table I. All data shown in this figure were obtained with the time-dependent Schrödinger equation.
with the three different models. Here, the dominantly-populated eigenstates are 3 (exact), 3B (BO) and 3b (BOGP) (see the Supporting Information for probability density figures) which reach maximal population of 0.09, 0.04 and 0.03, respectively, while possessing almost identical photonic part populations. The maximal population values can be rationalized by comparing the energetic positions of the eigenstates 3, 3B and 3b to the Fourier transform of the laser pulse with $\omega_L = 30400 \text{ cm}^{-1}$ (see Figure 2). This finding helps interpret the shape of the LP population and emission curves. Obviously, the impact of the LICI is very strong in both cases presented.

We note that similar effects can be observed for other cavity setups. Another example is presented in the Supporting Information. Here the cavity wavenumber and coupling strength equal $\omega_c = 29957.2 \text{ cm}^{-1}$ and $g = 0.1 \text{ au}$, respectively, while the LICI is located at $Q_2 = 8.84$ and $Q_4 = 0$ at an energy corresponding to 30776.1 cm$^{-1}$ above the minimum of the ground-state polaritonic PES (or 29269.0 cm$^{-1}$ referenced to the lowest energy level). The cavity mode is pumped with two different laser pulses of $\omega_L = 29200 \text{ cm}^{-1}$ and $\omega_L = 30300 \text{ cm}^{-1}$, both with $T = 200 \text{ fs}$ and $E_0 = 0.001 \text{ au}$ ($I = 3.51 \cdot 10^{10} \text{ W/cm}^2$). In the first case the GP terms are able to correct the BO model. As a consequence, the BOGP results agree with the exact ones well, while in the second case the GP fails to improve upon the BO model. We believe that a remarkable role is played by the energetic position of the LICI and those of the eigenstates which are dominantly populated by the pump pulse. If the relevant energy levels are well above the LICI, we can expect breakdown of the BOGP model which, in turn, provides very good results around the LICI.

By means of accurate quantum-dynamical calculations, we have simulated the ultrafast radiative emission signal from the lower polaritonic (LP) surface of a polyatomic molecule (H$_2$CO, formaldehyde) placed in a plasmonic nanocavity. It has been shown that in the presence of a light-induced conical intersection, which is a common situation if the cavity mode resonantly couples two electronic states of a polyatomic molecule, the adiabatic approximation (BO model) breaks down. However, if the LP surface is populated around the LICI, the BO approximation extended with geometric-phase (GP) terms (BOGP model) can accurately reproduce the exact emission signal. In other words, the multistate diabatic representation can be well approximated by the BOGP model which excludes nonadiabatic transitions. However, this is not always the case as highlighted in this work. Well above the position of the LICI in energy, the BOGP model fails to provide appropriate results. The
current study clearly demonstrates that a remarkable role is played by the energetic position of the LICI and those of the eigenstates which are dominantly populated by the pump pulse. We stress that if the relevant energy levels are significantly above the energetic position of the LICI, the BOGP model no longer works and cannot offer an acceptable alternative of the exact diabatic representation.

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Supporting Information

I. THEORETICAL CONSIDERATIONS

As discussed in the manuscript, the Hamiltonian of a molecule coupled to a single cavity mode has the form

\[ \hat{H}_{cm} = \hat{H}_0 + \hbar \omega_c \hat{a} \hat{a}^\dagger - g \hat{\mu} \hat{e} (\hat{a} \hat{a}^\dagger + \hat{a}^\dagger \hat{a}) \]  

(10)

which, assuming two electronic states, can be recast as

\[
\hat{H}_{cm} = \begin{bmatrix}
\hat{T} + V_X & 0 & 0 & W_1 & 0 & 0 & \cdots \\
0 & \hat{T} + V_A & W_1 & 0 & 0 & 0 & \cdots \\
0 & W_1 & \hat{T} + V_X + \hbar \omega_c & 0 & 0 & W_2 & \cdots \\
W_1 & 0 & 0 & \hat{T} + V_A + \hbar \omega_c & W_2 & 0 & \cdots \\
0 & 0 & 0 & W_2 & \hat{T} + V_X + 2 \hbar \omega_c & 0 & \cdots \\
0 & 0 & W_2 & 0 & 0 & \hat{T} + V_A + 2 \hbar \omega_c & \cdots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots
\end{bmatrix} 
\]  

(11)

We refer to the manuscript regarding the notations used in Eqs. (10) and (11). The interaction of the cavity mode with a laser pulse is described by the Hamiltonian

\[ \hat{H}_L = -\mu_c E(t) (\hat{a} \hat{a}^\dagger + \hat{a}^\dagger \hat{a}) \]  

(12)

which gives rise to the total Hamiltonian

\[ \hat{H} = \hat{H}_{cm} + \hat{H}_L. \]  

(13)

All previous equations correspond to the diabatic representation. The adiabatic representation is defined by diagonalizing the potential energy part \( V \) of the Hamiltonian in Eq. (11),

\[ V^{ad} = U^T V U \]  

(14)

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

\[ \hat{H}^{ad} = U^T \hat{H} U = U^T \hat{T} U + V^{ad} + U^T \hat{H}_L U. \]  

(15)

The adiabatic 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,

\[ \hat{H}^{BO} = \hat{T} + V^{ad} + U^T \hat{H}_L U. \]  

(16)
As a next step, geometric phase (GP) effects are incorporated by taking the similarity-transformed Hamiltonian

\[ \hat{H}_{\text{BO}}^{\text{GP}} = \exp(i\theta) \hat{H}_{\text{BO}} \exp(-i\theta) \]  

(17)

where \( \exp(-i\theta) \) is a position-dependent phase factor which will enable us to work with single-valued nuclear wave functions. As discussed in the manuscript, the coupled cavity-molecule system is pumped to the singly-excited subspace by a laser pulse. Therefore, in our particular case, \( \theta \) is chosen as the angle which parameterizes the two-by-two orthogonal transformation matrix

\[ U = \begin{bmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{bmatrix} \]  

(18)

which diagonalizes the potential energy matrix corresponding to the singly-excited subspace. Thus, the matrix

\[ U^T \begin{bmatrix} V_A & W_1 \\ W_1 & V_X + \hbar \omega_c \end{bmatrix} \]  

(19)

is diagonal if

\[ \theta = \frac{1}{2} \arctan \left( \frac{2W_1}{V_X + \hbar \omega_c - V_A} \right) \]  

(20)

Eq. (17) can be rearranged by evaluating the action of the kinetic energy operator on \( \exp(-i\theta) \), which yields

\[ \hat{H}_{\text{BO}}^{\text{GP}} = \hat{H}_{\text{BO}} + \frac{i}{2}(\nabla \theta) \nabla + \frac{1}{2}(\nabla^2 \theta) + \frac{1}{2}(\nabla \theta)^2. \]  

(21)

In the 2D(\( \nu_2, \nu_4 \)) 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

\[ [\nabla, \nabla \theta] = \nabla(\nabla \theta) - (\nabla \theta) \nabla = \nabla^2 \theta \]  

(22)

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

\[ i(\nabla \theta) \nabla + \frac{i}{2}(\nabla^2 \theta) = \frac{i}{2}((\nabla \theta) \nabla + \nabla(\nabla \theta)). \]  

(23)

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

\[ \hat{H}_{\text{GP}}^{\text{BO}} = \hat{H}_{\text{BO}} + \frac{i}{2}((\nabla \theta) \nabla + \nabla(\nabla \theta)) + \frac{1}{2}(\nabla \theta)^2 \]  

(24)

which was employed in numerical computations carried out in this study.
II. COMPUTATIONAL MODEL AND TECHNICAL DETAILS

As already described in previous work,\textsuperscript{18,23,28} the four-atomic formaldehyde (H\textsubscript{2}CO) molecule has a planar equilibrium structure (\(C_{2v}\) point-group symmetry) in the ground electronic state (\(\tilde{X} \: ^1A_1\)) 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 (\(\tilde{A} \: ^1A_2\)). The ground-state equilibrium structure and definition of the body-fixed coordinate axes are depicted in Figure 6. Out of the six vibrational normal modes of H\textsubscript{2}CO the \(\nu_2\) (C=O stretch, \(A_1\) symmetry) and \(\nu_4\) (out-of-plane bend, \(B_1\) symmetry) vibrational modes are included in the computational model called the 2D(\(\nu_2,\nu_4\)) model. The corresponding anharmonic fundamentals in the ground electronic state (obtained by six-dimensional variational computations) are 1738.1 cm\(^{-1}\) (\(\nu_2\) mode) and 1147.0 cm\(^{-1}\) (\(\nu_4\) mode).

![Equilibrium structure of the H\textsubscript{2}CO molecule in the ground electronic state and definition of the body-fixed coordinate axes](image)

FIG. 6. Equilibrium structure of the H\textsubscript{2}CO 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) (\(V_X\) and \(V_A\)) and the transition dipole moment (TDM) surface were com-
puted 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 body-fixed $y$ axis in all computations. Since H$_2$CO does not have any first-order nonadiabatic coupling between the X and A electronic states around its equilibrium geometry, light-induced nonadiabatic effects can be unambiguously distinguished from natural ones.

The time-dependent Schrödinger and Lindblad equations were 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 the numerically-exact diabatic computations, approximate adiabatic 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 Schrödinger and Lindblad equations were 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 POPULATION, EMISSION AND PROBABILITY DENSITY FIGURES

Figures 7 and 8 show population and emission figures (exact, approximate adiabatic (BO) and approximate adiabatic with geometric phase (BOGP)) for the cavity parameters $\omega_c = 29957.2$ cm$^{-1}$ and $g = 0.1$ au. The cavity mode is pumped with the following laser pulses: $\omega_L = 29200$ cm$^{-1}$ (Figure 7) and $\omega_L = 30300$ cm$^{-1}$ (Figure 8), both with $T = 200$ fs and $E_0 = 0.001$ au (corresponding to a field intensity of $I = 3.51 \cdot 10^{10}$ W/cm$^2$). Figures 9 and 10 provide probability density figures for selected eigenstates with $\omega_c = 30245.5$ cm$^{-1}$ and $g = 0.1$ au (see the text and Table 1 of the manuscript for more information on eigenstate labels).
FIG. 7. (a-b) Population of the lower polaritonic (LP) state for the three different models investigated (exact, approximate adiabatic (BO) and approximate adiabatic with geometric phase (BOGP)) during and after excitation with a 200 fs laser pulse (carrier wavenumber: $\omega_L = 29200$ cm$^{-1}$). The cavity wavenumber and coupling strength are $\omega_c = 29957.2$ cm$^{-1}$ and $g = 0.1$ au. Populations of polaritonic states higher than LP are negligible (see dashed lines with empty markers). (c-d) Ultrafast emission signals for the three different models. The emission is proportional to the expectation value of the photon number operator $\hat{N}$. The cavity and laser parameters are the same as for panels a and b. Results obtained with the time-dependent Schrödinger (TDSE) and Lindblad equations are explicitly labeled in each panel. Note that the exact emission is significantly overestimated by the BO model, while the BOGP model shows an excellent agreement with the exact results.
FIG. 8. (a-b) Population of the lower polaritonic (LP) state for the three different models investigated (exact, approximate adiabatic (BO) and approximate adiabatic with geometric phase (BOGP)) during and after excitation with a 200 fs laser pulse (carrier wavenumber: $\omega_L = 30300$ cm$^{-1}$). The cavity wavenumber and coupling strength are $\omega_c = 29957.2$ cm$^{-1}$ and $g = 0.1$ au. Populations of polaritonic states higher than LP are negligible (see dashed lines with empty markers). (c-d) Ultrafast emission signals for the three different models. The emission is proportional to the expectation value of the photon number operator $\hat{N}$. The cavity and laser parameters are the same as for panels a and b. Results obtained with the time-dependent Schrödinger (TDSE) and Lindblad equations are explicitly labeled in each panel. Note that in this case the exact emission is underestimated by the BO model and inclusion of the geometric phase does not improve the BO model.
FIG. 9. Probability density figures for selected eigenstates (exact: 1, approximate adiabatic (BO): 1A, approximate adiabatic with geometric phase (BOGP): 1a and 1b, see the text and Table 1 of the manuscript for more information). $Q_2$ and $Q_4$ are dimensionless normal coordinates of the modes $\nu_2$ and $\nu_4$. 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. 10. Probability density figures for selected eigenstates (exact: 3, approximate adiabatic (BO): 3B, approximate adiabatic with geometric phase (BOGP): 3b, see the text and Table 1 of the manuscript for more information). $Q_2$ and $Q_4$ are dimensionless normal coordinates of the modes $\nu_2$ and $\nu_4$. 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 $Q_4 = 0$. 