# Collective rovibronic dynamics of a diatomic gas coupled by cavity

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We consider an ensemble of homonuclear diatomic molecules coupled to the two polarization directions of a Fabry-Pérot cavity via fully quantum simulations. Accompanied by analytical results, we identify a coupling mechanism mediated simultaneously by the two perpendicular polarizations, and inducing polaritonic relaxation towards molecular rotations. This mechanism is related to the concept of light-induced conical intersections (LICIs). However, unlike LICIs, these nonadiabatic pathways are of a collective nature, since they depend on the *relative* intermolecular orientation of all electronic transition dipoles in the polarization plane. Notably, this rotational mechanism directly couples the bright upper and lower polaritonic states, and it stays in direct competition with the collective relaxation towards dark states.

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#### I. INTRODUCTION

Strong coupling between matter excitations and quantized electromagnetic modes leads to the formation of hybrid lightmatter states, polaritons [1,2]. Due to their hybrid nature, polaritons possess new properties differing from the bare material system [3], which has stimulated research across the natural sciences [4], including ultracold physics [5,6], material sciences [7,8], molecular physics [9,10], and chemistry [11]. However, important questions remain elusive in the field of polaritonic chemistry, including the role of collective and local effects, molecular decoherence pathways, and cavity losses [12,13]. This significant difficulty originates from the contrast between theoretically simulated scenarios, which navigate a compromise between small isolated systems and model approximations in fundamental theories, and the majority of experiments conducted in solution and condensed phases.

The recent advent of an experimental platform for the formation of gas-phase molecular polaritons in Fabry-Pérot (FP) cavities enables studying molecules under strong-coupling conditions with a high level of control, and over wide temperature ranges [14,15]. These platforms can provide much sought-after experimental insight into fundamental mechanisms through which molecules and quantized electromagnetic modes interact, and the basis for comparisons to accurate quantum-dynamics simulations of molecular ensembles. In light of these developments, we study the full-dimensional quantum dynamics of prototypical gas-phase diatomic molecules inside a FP cavity by efficient numerical propagation of the time-dependent Schrödinger equation for

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the cavity-ensemble system with the multilayer multiconfiguration time-dependent Hartree (ML-MCTDH) method [16–19]. Our simulations highlight the competition between nonradiative relaxation pathways involving rotational, vibrational, and electronic degrees of freedom (DOF) of the ensemble. Most importantly, we characterize a rotational collective coupling mechanism associated with the relative orientation of the transition dipole moments in the ensemble. This channel couples the upper and lower polaritons via conical intersections, and it stays in direct competition with the decay to the dark-state manifold via vibrational collective conical intersections (CCIs) [20]. Using a non-Hermitian formalism for cavity losses, we establish that this mechanism is robust toward photon leakage and operates for much longer times than the bare cavity lifetime. The experimental verification of these competing mechanisms would constitute a leap forward in our microscopic understanding of polaritonic photochemistry.

So far, theoretical studies have mainly focused on the role of the angle between the molecular transition dipole moment (TDM) vector and the cavity polarization direction of a onedimensional FP cavity model [21-26]. This rotational DOF has been shown to give rise to light-induced conical intersections (LICIs) in molecules which are coupled to quantized electromagnetic modes [23,27]. Originally, LICIs were proposed for diatomic molecules exposed to strong classical laser fields where degeneracies between dressed potential energy surfaces are lifted along the polarization angle (with respect to the molecular axis), and the interatomic separation [28,29]. Their rich nonadiabatic effects have been studied theoretically and experimentally, including topological phase effects [30], intensity borrowing and highly mixed rovibrational levels in absorption spectra [23,31] as well as quantum interference in laser-induced photodissociation [32].

## **II. THEORY**

A single angle is sufficient to characterize the orientation of a diatom with respect to a linearly polarized laser field. In a realistic FP cavity, on the other hand, doubly degenerate cavity

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FIG. 1. (a) Schematic of a gas of homonuclear diatomic molecules inside a FP cavity with polarization directions  $\vec{\epsilon}_x$  and  $\vec{\epsilon}_y$ . Space-fixed axes x, y, z are parallel to  $\vec{\epsilon}_x, \vec{\epsilon}_y, \vec{k}$ . The orientation of molecular dipoles with respect to the space-fixed frame is parametrized by spherical coordinates  $\theta$  and  $\varphi$ . (b) Polaritonic potential energy curves for two molecules,  $\varepsilon_{N=2}^{\pm}$ , along a relative angle  $\varphi_1 - \varphi_2$  (upper panel). Nonadiabatic couplings  $\vec{F}_{ij}$  (lower panel) among the two LP or UP states (gray), and between LP and UP (black) diverge at respective degeneracies of pPECs (gray and black triangles). Parameters  $\omega_C = \Delta^{(1)} = \Delta^{(2)} = 4.71$  eV and  $\lambda = 0.1/\sqrt{2}$  eV were used.

modes with orthogonal polarization directions are intrinsically present [33]. Hence, two rotational DOFs must be included in order to account for molecular orientations with respect to the *x*- and *y*-polarized cavity modes: the out-of-plane rotation along the polar angle  $\theta_i$ , and the in-plane rotation along the azimuthal angle  $\varphi_i$  (where "plane" refers to the cavity polarization plane), as depicted in Fig. 1(a). While  $\theta_i$  modulates the overall individual coupling strength of each molecule to the cavity, the in-plane rotation  $\varphi_i$  tunes the mixing between *x*-polarized and *y*-polarized cavity-mode contributions to the molecule-cavity interaction.

Crucially, the in-plane rotations  $\varphi_i$  determine the collective dynamics of the ensemble in a way that the out-of-plane angles  $\theta_i$  do not. We examine and explain this collective mechanism on the basis of analytical considerations and numerical simulations. This leads to an extension of the notion of LICI to azimuthal angles, where the ensemble dynamics is determined by collective in-plane rotations of the transition dipole moments inside the FP cavity. In particular, conical intersections (CIs) among polaritons, whose branching spaces are spanned by molecular vibrations and rotations (both inand out-of-plane planes), lead to ultrafast and nonresonant electronic-energy transfer to rotations. We note that the resonant scenario, in which a microcavity is directly coupled to a rotational transition, has been studied recently on the single molecule level [21].

We consider an ensemble of *N* noninteracting, homonuclear diatomic molecules strongly coupled to two quantized electromagnetic modes with polarization directions  $\vec{\epsilon}_x$  and  $\vec{\epsilon}_y$  inside a FP cavity. The cavity-ensemble Hamiltonian for this systems reads [19,34]

$$\hat{H} = \sum_{i=1}^{N} \hat{H}_{\text{mol}}^{(i)} + \hat{H}_{\text{cav}},$$
(1)

where  $\hat{H}_{cav}$  describes the cavity and cavity-ensemble interaction,

$$\hat{H}_{cav} = \hbar \omega_c (\hat{a}_x^{\dagger} \hat{a}_x + \hat{a}_y^{\dagger} \hat{a}_y) + g \sum_{i=1}^N \hat{\vec{\mu}}^{(i)} \vec{\epsilon}_x (\hat{a}_x^{\dagger} + \hat{a}_x) + \hat{\vec{\mu}}^{(i)} \vec{\epsilon}_y (\hat{a}_y^{\dagger} + \hat{a}_y),$$
(2)

with cavity frequency  $\omega_c$ , the coupling strength *g* between the molecules and cavity modes, and the total dipole operator of the molecular ensemble  $\sum_{i=1}^{N} \hat{\mu}^{(i)}$ . The quadratic dipole self-energy term is neglected as it is only relevant for very strong-coupling strengths which are not considered here [35]. The validity of this approximation is examined and confirmed in the Supplemental Material [36].

For the simulations we consider a molecular Hamiltonian with interatomic distance  $R_i$  and two electronic states, a ground and an excited electronic state with potential energy curves (PECs)  $V_0$  and  $V_1$  without intrinsic molecular nonadiabatic couplings. To investigate the impact of vibrational motion, PECs are expanded around the Franck-Condon (FC) geometry  $R_i^{(0)}$  up to second order in terms of nuclear displacements  $Q_i = R_i - R_i^{(0)}$ ,  $V_0(Q_i) = E_0 + \frac{1}{2}\omega_v^2 Q_i^2$ , and  $V_1(Q_i) = E_1 + \kappa Q_i + \frac{1}{2}\omega_v^2 Q_i^2$ ,

$$\hat{H}_{\text{mol}}^{(i)} = [\hat{T}_{\text{rot}}(\varphi_i, \theta_i) + \hat{T}_n(Q_i)] \mathbf{1}_{2 \times 2} + \begin{pmatrix} V_0(Q_i) & 0\\ 0 & V_1(Q_i) \end{pmatrix},$$
(3)

where  $\mathbf{1}_{2\times 2}$  denotes the two-dimensional identity matrix,  $\hat{T}_n(Q_i)$  is the vibrational kinetic energy operator, and  $\hat{T}_{rot}(\varphi_i, \theta_i) = \hat{L}^2_{\varphi_i\theta_i}/2\mathcal{I}$  is the rotational kinetic energy operator with moment of inertia  $\mathcal{I}$  and rotational angular momentum  $\hat{L}_{\varphi_i\theta_i}$ . We assume constant moment of inertia  $\mathcal{I}$  throughout this paper, effectively neglecting centrifugal coupling between rotations and vibrations. We note that this coupling is very small compared to other mechanisms, and that it could be easily reintroduced if needed. This approximation simplifies the analysis of the energy transfer from the cavity and electronic excitations to the rotational degrees of freedom. For analytical investigations, we perform an adiabatic separation between the "fast" electronic as well as cavity mode DOFs and the "slow" molecular vibrational and rotational DOFs [37]. The representation of this adiabatic Hamiltonian,  $\hat{H}_{ad} = \hat{H} - \sum_{i=1}^{N} [\hat{T}_{rot}(\varphi_i, \theta_i) + \hat{T}_n(Q_i)]$ , in the basis of noninteracting cavity-ensemble states and in the single-excitation subspace, gives rise to a molecular Tavis-Cummings Hamiltonian [20,38]

$$\hat{H}_{\text{MTC}} = \begin{pmatrix} \hbar\omega_c & 0 & \gamma_x^{(1)} & \gamma_x^{(2)} & \cdots \\ 0 & \hbar\omega_c & \gamma_y^{(1)} & \gamma_y^{(2)} & \cdots \\ \gamma_x^{(1)} & \gamma_y^{(1)} & \Delta^{(1)} & 0 & \cdots \\ \gamma_x^{(2)} & \gamma_y^{(2)} & 0 & \Delta^{(2)} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \quad (4)$$

which has been extended to a two-dimensional FP cavity model. Its eigenvalues and associated eigenvectors correspond to the polaritonic (as well as dark) states and polaritonic potential energy surfaces (pPES), respectively [11]. Here,  $\Delta^{(i)}(Q_i) = V_1(Q_i) - V_0(Q_i)$  is the energy gap of the *i*th molecule. The cavity photon energy  $\hbar\omega_c$ is tuned resonant to the energy gap at the FC point  $(Q_i = 0)$ .  $\gamma_x^{(i)}(\varphi_i, \theta_i) = g|\vec{\mu}_{01}^{(i)}(Q_i)| \cos \varphi_i \sin \theta_i \ \gamma_y^{(i)}(\varphi_i, \theta_i) =$  $g|\vec{\mu}_{01}^{(i)}(Q_i)|\sin\varphi_i\sin\theta_i$  are the orientation-dependent dipole couplings of the *i*th molecule with the x- and y-polarized cavity mode, respectively. We assume a constant TDM  $|\vec{\mu}_{01}^{(i)}(Q_i)| = \mu_{01}$  and introduce  $\lambda = g\mu_{01}$ . The common assumption of fully aligned TDMs would result in an upper polaritonic (UP) and lower polaritonic (LP) branch which are separated by the collective Rabi splitting  $\hbar\Omega_R = 2\lambda\sqrt{N}$ at  $Q_1 = \cdots = Q_N = 0$ . We stress that pPESs are exclusively used to illustrate the key points of our analysis. All numerical simulations are performed with ML-MCTDH, employing the full Hamiltonian (1).

## **III. RESULTS AND DISCUSSION**

The analytical treatment of  $\hat{H}_{\text{MTC}}$  for arbitrary *N* and including all rotational DOFs can be found in the Supplemental Material [36]. Here, we limit the analytical considerations to the collective effects emerging from molecular rotations inside the polarization plane by fixing the polar angles to  $\theta_1 = \cdots = \theta_N = \pi/2$  and the vibrational DOFs to the FC point. For a single molecule rotating in the polarization plane,  $\hat{H}_{\text{MTC}}$  is rotationally invariant as any  $\varphi_1$  dependence can be removed by a rotation around  $\varphi_1$  in the basis of *x*- and *y*-polarized cavity modes: A single molecule feels the same cavity field strength for all orientations in the cavity polarization plane. Consequently, the single-molecule pPESs are independent of the in-plane rotation angle,  $\varepsilon_{N=1}^{\pm} = \hbar \omega_c \pm \lambda$ .

The situation drastically changes with one more molecule inside the cavity. A strong dependence of the polaritonic energy landscape on the intermolecular alignment,  $\cos^2(\varphi_1 - \varphi_2)$ , is found. Two pairs of UP and LP states are obtained analytically,

$$\varepsilon_{N=2}^{\pm,1} = \hbar\omega_c \pm \lambda \sqrt{1 - \sqrt{\cos^2(\varphi_1 - \varphi_2)}},\tag{5}$$

$$\varepsilon_{N=2}^{\pm,2} = \hbar\omega_c \pm \lambda \sqrt{1 + \sqrt{\cos^2(\varphi_1 - \varphi_2)}}.$$
 (6)

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In this case, LP and UP states separated by the collective Rabi splitting  $\hbar\Omega_R = 2\lambda\sqrt{2}$  are only found if the molecular TDMs are fully aligned, i.e., if  $\cos^2(\varphi_1 - \varphi_2) = 1$ . In the full rotational subspace this configuration corresponds to a line of degeneracy where the two remaining polaritonic states (with pPES given by  $\varepsilon_{N=2}^{\pm,1}$ ) cross. The cooperative molecular rotation along  $\varphi_1 - \varphi_2$ , which breaks the alignment, will lift this degeneracy [see Fig. 1(b), upper panel]. If vibrational DOFs are included, they can serve as a second branching coordinate, resulting in a conical intersection (CI) between a UP and LP surface [36].

This topology shares great similarity with LICIs and intrinsic molecular CIs including a divergent nonadiabatic coupling vector [39]  $\vec{F}_{ii} = \langle \psi_i | \vec{\nabla}_{\varphi} \psi_i \rangle$  among the adiabatic eigenstates  $|\psi_i\rangle$  of  $\hat{H}_{MTC}$  near the intersection [see Fig. 1(b), lower panel]. We stress, however, that they are of a collective nature: Each molecule, individually coupled, displays rotationally invariant pPESs along  $\varphi_i$ , and the CI locations depend on the relative in-plane orientations of the molecular ensemble. Collective CIs (CCIs) have been reported for fully aligned molecular ensembles, where collective nuclear displacements lead to (pseudo-)Jahn-Teller interactions among bright and dark polaritonic states [20]. We refer to the latter as vibrational-type CCI to distinguish them from the rotational-type CCIs introduced in this paper. The topology of the rotational-type CCI for two molecules is further analyzed in the Supplemental Material [36], where it is shown how all polaritonic bright and dark states are connected by CCIs involving collective rotations of the molecular ensemble.

In the following, prototypical diatomic molecules with vibrational frequency  $\omega_v = 0.074 \text{ eV}$ , tuning parameter  $\kappa =$ 0.1194 eV, an energy difference of 4.72 eV between the ground and excited electronic state at the FC point, and a rotational constant of  $B = 0.2 \text{ cm}^{-1}$  are considered. These model parameters reflect a typical UV excitation of a medium weight diatomic molecule, e.g., Na<sub>2</sub> ( $B \approx 0.15 \text{ cm}^{-1}$ ) or Li<sub>2</sub>  $(B \approx 0.67 \text{ cm}^{-1})$  [40]. The cavity photon energy is tuned resonant to the molecular electronic transition,  $\hbar\omega_c = 4.72 \text{ eV}$ , with a Rabi splitting of  $\hbar\Omega_R = 0.3$  eV for fully aligned ensembles. While this collective coupling strength is typical for condensed-phase cavities [41], state-of-the-art gas-phase experiments cannot yet achieve this value [14]. For a better comparison of the collective phenomena, the Rabi splitting is kept constant among different ensemble sizes by scaling the coupling strength by  $1/\sqrt{N}$ . Simulations without scaling of the coupling strength are shown in Fig. S3 of the Supplemental Material [36]. A one-photon excitation of the cavity defines the initial state in all numerical propagations, while keeping the molecules in their respective rovibronic ground states at t = 0. This is akin to a short, impulsive excitation that creates a coherent superposition of UP and LP states in the electronic and cavity subspaces.

For a single molecule, the presence of a LICI between the UP and LP states strongly mixes rovibrational and electronic-photonic DOFs. As seen in Fig. 2(c), this enables nonresonant energy transfer from the initial cavity excitation to the



FIG. 2. Molecular rotational dynamics after excitation of x-polarized cavity mode for various ensemble sizes. (a), (b) Total kinetic rotational energy  $\langle \hat{T}_{\theta\varphi} \rangle(t)$  and in-plane rotational energy  $\langle \hat{T}_{\varphi} \rangle(t)$ . Energies are given in units of the rotational constant  $B = 0.2 \text{ cm}^{-1}$ . (c)–(f) Populations of rotational states with quantum number j and magnetic quantum number m for N = 1 and N = 2 at t = 200 fs. (g) Time-dependent population of molecular electronic excited states  $P_{\text{exc}}^{\text{mol}}(t)$ .

molecular out-of-plane rotation [42], whereas in-plane rotation remains unaffected. This situation breaks down, however, when adding more molecules to the cavity, as can be seen from Fig. 2(b). Now, *collective* CIs, as introduced around Eqs. (5) and (6), are present along with *individual* LICIs. This opens an additional channel for collective nonresonant rotational energy transfer to the molecular in-plane rotations. As a result, a fast increase of both  $\langle \hat{T}_{\theta\varphi} \rangle(t)$  and  $\langle \hat{T}_{\varphi} \rangle(t)$  is observed for N > 1. Not only rotational states with large *j* but also with a large z component (up to  $m = \pm 10$  for N = 2) are populated, as shown in Figs. 2(e) and 2(f). Inspecting the rotational dynamics serves as a proxy to assess the contributions of collective and individual CI dynamics involving in-plane and out-of-plane rotations: The fraction  $\langle \hat{T}_{\varphi} \rangle(t) / \langle \hat{T}_{\theta\varphi} \rangle(t)$  at 200 fs increases with an increasing number of molecules, reaching from 29% (N = 2) to 49% (N = 10). Thus, ultrafast dynamics along the in-plane and out-of-plane rotational angles are virtually coexistent in molecular ensembles strongly coupled to a two-dimensional FP cavity. In the picture of pPESs, as presented in Fig. 1(b), the initially prepared coherent polaritonic wave packet will quickly dephase due to such collective rotational dynamics around CIs among polaritonic surfaces.

The vibrational degree of freedom of diatomic molecules in FP cavities supports an additional source of nonadiabaticity, namely vibrational-type CCIs which contribute to the ultrafast nonradiative decay from the UP branch for N > 2, and nonadiabatic nuclear dynamics inside the dark-state manifold [20]. This mechanism has been shown to coexist with LICIs in Ref. [27], where LICIs facilitate the access to the dark-state manifold. This argument can be extended to rotational-type CCIs which also connect the UP and the dark-state manifold (cf. Fig. 1 and Fig. S1 in Supplemental Material [36]). With an increasing number of molecules, the rotational energy transfer rate decreases as more energy is diverted toward molecular vibrations [Figs. 2(a) and 2(b)]. Simultaneously, the Rabicycling dynamics (oscillations with period  $\tau_R \approx 13.8$  fs, best visible for N = 1) is quenched, and the overall population of bare molecular excited states  $P_{\rm exc}^{\rm mol}(t)$  within the dark-state manifold increases [Fig. 2(g)].

In realistic experimental setups, cavities are subject to radiative losses, leading to finite cavity photon lifetimes of typically a few tens of femtoseconds. This sparks the question of how robust to losses is the cavity-enabled relaxation mechanism. We include cavity photon losses in Hamiltonian (1) through damping non-Hermitian terms  $-i\frac{\Gamma}{2}\hat{a}^{\dagger}_{\alpha}\hat{a}_{\alpha}$  for  $\alpha = x, y$ [43]. Since the dynamics is restricted to the single excitation subspace, this approach is equivalent to propagating the density matrix according to a Lindblad master equation [44,45]. Figures 3(a) and 3(b) demonstrate remarkable robustness of the nonadiabatic rotational energy transfer mechanisms over 200 fs against cavity photon decay, even for very short lifetimes of  $1/\Gamma_f = 10$  fs. This can be explained by the rapid involvement of the dark-state manifold, such that dynamics occurs within predominantly molecular states after the first 20 fs [cf. Fig. 2(g)]. Since the cavity emission rate is proportional to the photon number  $\langle \hat{N}_{cav} \rangle = \langle \hat{a}_{x}^{\dagger} \hat{a}_{x} + \hat{a}_{y}^{\dagger} \hat{a}_{y} \rangle$ , the lifetime of the coupled cavity-molecule system is significantly increased compared to the bare cavity lifetime, as shown in Fig. 3(c). By coupling dark and bright polaritonic manifolds, rovibrational motion then provides the necessary interaction channels among molecules and photonic modes, without which any cavity-induced effects would be absent. Our results of gas-phase quantum dynamics simulations thus are in line with recent reports on dark states protecting polariton



FIG. 3. Impact of cavity photon decay for an ensemble of five molecules from slow to fast decay. Three decay constants (in atomic units) are considered,  $\Gamma_f = 0.00243$ ,  $\Gamma_m = 0.00122$ ,  $\Gamma_s = 0.00081$ , corresponding to lifetimes 10, 20, and 30 fs. (a), (b) Total kinetic rotational energy  $\langle \hat{T}_{\theta\varphi} \rangle(t)$  and in-plane rotational energy  $\langle \hat{T}_{\varphi} \rangle(t)$ . (c) Time-dependent expectation value of photon number operator  $\hat{N}_{cav}$ . (d), (e) Same as (a), (b) with a varying gradient  $\kappa$  of the molecular energy gap at the FC point.

transport from cavity losses [46], and dark-state participation in cavity-modified chemical reactivity and energy transport [12,47–49]. Hence, due to the robustness against radiative decay, the nonradiative polariton relaxation involving collective rotations and vibrations is preserved in lossy cavities. Both an increase in the number of coupled molecules, which increases the number of dark states, and an increase in vibronic coupling, as demonstrated in Figs. 3(d) and 3(e) for an increasing gradient of the molecular energy gap at the FC point, increase the nonradiative relaxation rate through vibrational-type

#### **IV. CONCLUSION**

CCIs [20].

In summary, examining the rotational quantum dynamics of electronically coupled gas-phase polaritonic ensembles of up to ten molecules for fixed Rabi splitting offers direct PHYSICAL REVIEW RESEARCH 6, 033134 (2024)

insights into competing cavity-enabled nonradiative relaxation pathways upon cavity excitation. Real-time wave-packet propagations unveil pronounced patterns in the distribution of molecular rotational levels and the competition between rotational and vibrational energy transfer. Moreover, the mechanisms are robust toward cavity losses, thus providing a potential experimental proxy for probing polaritonic decay dynamics in pump-probe measurements.

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