Collective Jahn-Teller Interactions through Light-Matter Coupling in a Cavity

Oriol Vendrell[*]

Department of Physics and Astronomy, Aarhus University, Ny Munkegade 120, 8000 Aarhus C, Denmark
and Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, INF 229, 69120 Heidelberg, Germany

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The ultrafast nonradiative relaxation of a molecular ensemble coupled to a cavity mode is considered theoretically and by real-time quantum dynamics. For equal coupling strength of single molecules to the cavity mode, the nonradiative relaxation rate from the upper to the lower polariton states is found to strongly depend on the number of coupled molecules. The coupling of both bright and dark polaritonic states among each other constitutes a special case of (pseudo-)Jahn-Teller interactions involving collective displacements the internal coordinates of the molecules in the ensemble, and the strength of the first order vibronic coupling depends exclusively on the gradient of the energy gaps between molecular electronic states. For $N > 2$ molecules, the $N - 1$ dark light-matter states between the two optically active polaritons feature true collective conical intersection crossings, whose location depends on the internal atomic coordinates of each molecule in the ensemble, and which contribute to the ultrafast nonradiative decay from the upper polariton.

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The interaction of atoms and molecules with quantized light has the potential to open new routes towards manipulating their physical and chemical properties, and towards the development of hybrid matter-light systems with new attributes [1–6]. Over the past few years, ground breaking experiments that realize the aforementioned scenario using, e.g., microcavities [7–11] have demonstrated the effective tuning of reaction rates and probabilities [9], and energy transfer rates among different molecular species [12] and of molecular vibrations [13,14]. A growing body of theoretical results [13,15–30] has lead, among others, to propose mechanisms to suppress [20] and catalyze chemical processes [25] through a cavity mode, or modify the nonadiabatic dynamics of a single molecule strongly coupled to an electromagnetic mode [22].

Experimentally, it has been observed that photoexcitation of the upper polariton branch (UPB) in a coupled cavity-matter system is followed by population transfer to the lower polariton branch (LPB) before light emission from the UPB can take place [7,10]. Time-resolved measurements in hybrid organic dye-molecule systems indicate that population transfer from the UPB to the LPB occurs within a timescale of tens to hundreds of femtoseconds [10] orders of magnitude shorter than the radiative lifetime of the molecular excited states in isolation. However, an increasing relaxation rate with the number (or density) of coupled molecules, which would be caused by collective enhancement mechanisms, has not yet been reported from experiment. Similarly, theoretical models of the relaxation process based on perturbative rates in the context of Fermi's golden rule and coupling to quantized vibrational modes predict fast relaxation rates of the order of tens to hundreds of femtoseconds, but most crucially not an increase of those rates with the size of the molecular ensemble [30–34].

In this Letter, the quantum dynamics of a molecular ensemble coupled a quantized electromagnetic mode is considered theoretically and it is found that the decay rate from the upper to the lower polariton branch is strongly enhanced by the number of molecules in the ensemble. It is demonstrated that the vibronic origin of the ultrafast relaxation involving both bright and dark polaritons is of a *collective* nature, as opposed to being driven by local intramolecular vibrations. In particular, it is shown that dark polaritonic states are connected by collective conical intersections (CCI), whose degeneracy is lifted along collective displacements of the molecules in the ensemble. The topological properties of the coupling among bright and dark polaritons, and in particular of CCI, are discussed and a direct link between the molecular Tavis-Cummings (MTCH) and Jahn-Teller Hamiltonians (JTH) is established. The considered model is not constrained to describe molecules coupled to a cavity mode and the decay mechanisms considered in this Letter may apply as well to other physical situations in which otherwise uncoupled or weakly coupled subsystems interact via a single link.

The starting point is an ensemble of noninteracting diatomic molecules aligned with the polarization axis of the quantized light mode (also referred to throughout the Letter as cavity mode). The Hamiltonian for this system reads

$$\hat{H} = \hat{T}_n + \hat{H}_{\mathsf{el}} + \hat{H}_{\mathsf{cav}} + \hat{H}_{\mathsf{las}}, \tag{1}$$

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where $\hat{T} = \sum_{\kappa}^{N} \hat{t}_{n}^{(\kappa)}$ is the sum of nuclear kinetic energy operators for each κth molecule, $\hat{H}_{\mathrm{el}} = \sum_{\kappa}^{N} \hat{h}_{\mathrm{el}}^{(\kappa)}$ is the sum of all other intramolecular Hamiltonian terms for each molecule

$$\hat{h}_{\mathrm{el}}^{(\kappa)} = \hat{t}_{e}^{(\kappa)} + \hat{v}_{ee}^{(\kappa)} + \hat{v}_{en}^{(\kappa)} + \hat{v}_{nn}^{(\kappa)}, \tag{2}$$

$\hat{H}_{\mathrm{cav}}$ is the cavity and cavity-ensemble Hamiltonian, and $\hat{H}_{\mathrm{las}}$ describes the eventual coupling to an external laser field. The terms in Eq. (2) correspond to the κth electronic kinetic energy and the Coulombic terms represent the electron-electron repulsion, electron-nuclei attraction, and nuclei-nuclei repulsion, respectively. The cavity Hamiltonian is given by [17,24,28,35]

$$\hat{H}_{\mathrm{cav}} = \hbar\omega_c \left(\frac{1}{2} + \hat{a}^{\dagger}\hat{a} \right) + g\vec{\epsilon}_c\,\vec{\hat{D}}\,(\hat{a}^{\dagger} + \hat{a}), \tag{3}$$

where ω_c is the angular frequency of the cavity mode, $\vec{\epsilon}_c$ is its polarization direction, and $g = \sqrt{\hbar\omega_c/2V\epsilon_0}$ is the coupling strength between the cavity and the molecules where V is the quantization volume. $\vec{\hat{D}} = \sum_{\kappa}^{N} \vec{\mu}^{(\kappa)}$ is total dipole operator of the ensemble. In Eq. (3), the quadratic dipole self-energy term is being neglected, which is only relevant at much higher coupling strengths than considered here. For further details see, e.g., Refs. [24,35]. The coupling to an external laser field is introduced semiclassically in the length gauge and dipole approximation as $\hat{H}_{\mathrm{las}} = -\vec{E}(t)\vec{\hat{D}}$, where the electric field takes the form $\vec{E}(t) = \vec{\epsilon}_L A(t)\cos(\omega_L t)$. It is assumed for simplicity that external laser fields couple to the molecules and do not pump the cavity mode directly. In general this is not necessarily the case and direct coupling to the cavity mode can be easily introduced [30]. However, since strong coupling is assumed (cf. discussion below), this model choice has only observable consequences at times below the Rabi cycling period of the hybrid system, in the order of a few tens of femtoseconds, and is not of relevance for our discussion. For illustrative purposes we consider sodium iodide (NaI), whose ultrafast photodissociation dynamics in the first excited electronic state ^1A coupled to the ground state ^1X has been the subject of extensive experimental and theoretical investigations (see, e.g., Ref. [36]), also in the context of cavity-induced chemistry [22,28]. Details on the potential energy and transition dipole curves of NaI [28] and a detailed account of the quantum dynamics numerical techniques employed in this work can be found elsewhere [28,37,38]. Throughout this Letter the effective cavity-matter coupling is taken as $g/\omega_c = 0.01$, where g was defined around Eq. (3) and can be seen as the rms vacuum electric field amplitude of the cavity mode [3]. This coupling strength is small compared to the single-molecule ultrastrong coupling regime, characterized by a Rabi splitting of the polaritonic energy levels (at zero detuning) $\hbar\omega_R = 2g\mu_{01}$ comparable to the transition energy. The cavity mode has a photon energy $\hbar\omega_c = 3.81$ eV, which is resonant with the energy difference between ground and excited electronic states of the molecules at the Franck-Condon (FC) geometry. The collective Rabi splitting is given by $\hbar\Omega_R = 2g\mu_{01}\sqrt{N}$ [39], where N is the number of coupled molecules and μ_{01} the transition dipole matrix element. The Rabi splitting at the FC geometry is given in Table I for various numbers of molecules. Rabi splittings of the order indicated in Table I have been observed experimentally in microcavities with coupled organic dye molecules [10,12].

TABLE I. Number of molecules N in the ensemble, collective Rabi splitting $\hbar\Omega_R$ at the FC geometry of the molecules (eV), total excitation probability of the system $P_{\mathrm{ex}}^{\mathrm{tot}}$, single-molecule excitation probability $P_{\mathrm{ex}}^{\mathrm{sm}}$, relaxation rate Γ_N (fs^{-1}), and lifetime of the upper polariton τ_N (fs), where $\tau_N = 1/\Gamma_N$.

N	$\hbar\Omega_R$	$\hbar\omega_L$	$P_{\mathrm{ex}}^{\mathrm{tot}}$	$P_{\mathrm{ex}}^{\mathrm{sm}}$	$\Gamma_N \times 10^3$	τ_N
1	0.11	3.92	0.089	0.089	0.344	2903
2	0.16	3.94	0.19	0.10	0.643	1555
3	0.20	3.96	0.25	0.091	0.964	1037
4	0.22	3.97	0.35	0.10	1.136	880
5	0.26	3.99	0.42	0.10	1.310	763
7	0.30	4.01	0.56	0.11	1.414	707

We note here that, for an ensemble of molecules featuring a dissociative excited state and coupled to a cavity mode, photodissociation can only occur in the LPB. This is because, as one of the molecules dissociates, it ceases to be resonant with the cavity mode, the lower polariton turns into a pure electronic excitation of such molecule, and the excitation energy is not available anymore for neither the cavity nor the other molecules, which subsequently remain in their respective ground states (cf. Fig. 2). For this reason, the rate of photodissociation directly maps the rate of relaxation from the UPB to the LPB, which will be used below.

The relaxation dynamics of the UPB in real time is accessed by pumping the system with an external laser of pulse of duration 15 fs (fwhm) photon energy tuned to the upper polariton region and a peak field amplitude of 10^{-3} au. This field strength together with the short pulse duration ensure that light absorption takes place largely in the single photon regime. The photon energy of the laser pulse is tuned in each case to be resonant with the UPB such that the single-molecule excitation probability $P_{\mathrm{ex}}^{\mathrm{sm}}$ remains constant (cf. Table I) [40]. The single-molecule dissociation probability is defined as $P_{\mathrm{dis}}(t) = \langle\Psi(t)|\hat{\Theta}(R_1 - R_d)|\Psi(t)\rangle$, where $\Theta(x)$ is the Heaviside step function and $R_d = 15$ au. As was mentioned above, the relaxation dynamics from the upper to the lower polariton branches can be traced through the probability of photodissociation, which can only occur in the LPB.

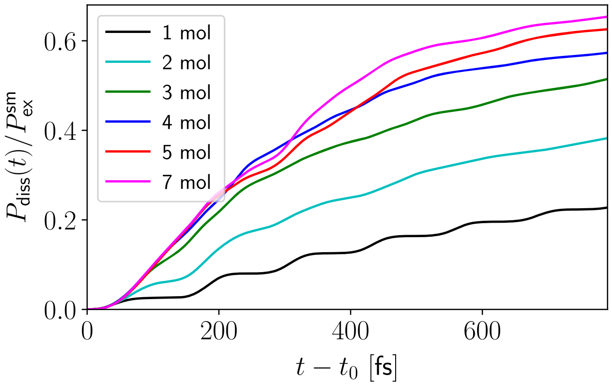

FIG. 1. Single-molecule photodissociation probability $P_{\text{dis}}(t) = \langle\Psi(t)|\Theta(R_1 - R_b)|\Psi(t)\rangle$ as a function of time for an ensemble of different size interacting with a laser pulse of photon energy $\hbar\omega_L = 3.9$ eV. $R_b = 15$ au. The dashed curves correspond to fitted first order rate expressions.

Inspection of $P_{\text{dis}}(t)/P_{\text{ex}}^{\text{sm}}$ in Fig. 1 for different ensemble sizes pumped to the UPB indicates a strong dependence of the single-molecule dissociation kinetics on the number of coupled molecules. It is important to note that this dependence is exclusively caused by the cavity and not by the increase of the total excitation probability with the number of molecules, which is clear from the fact that the compared quantities $P_{\text{dis}}(t)$ and $P_{\text{ex}}^{\text{sm}}$ are marginal probabilities for a single molecule [40]. This is the main effect discussed in this Letter.

The dissociation probability curves in Fig. 1 are used, for the sake of comparison, to compute relaxation rates Γ_N (cf. Table I) under the assumption of first order kinetics [40]. For $N = 1$, $1/\Gamma_1 \approx 2900$ fs, whereas $1/\Gamma_7$ drops to about 700 fs. As discussed, Γ_N describes the whole relaxation dynamics, from the upper to the lower polariton, where molecular dissociation is possible, and it increases linearly to sublinearly with the number of molecules in the ensemble.

Conversely, descriptions based on Fermi's golden rule rates find an inverse dependence of those rates with $1/N$ [30,31,34]. This fact hints at a possible breakdown of the perturbative description of those rates, at least for small numbers of molecules, and to the possible involvement of *cooperative* decay pathways of nonadiabatic nature coupling the polaritonic bright and dark states. The rate increase becomes less pronounced as the number of molecules increases, which may be due to trapping in the dark states region caused by its large density of states [29], but also by the fact that the nuclei have a finite mass and hence the rate of decay driven by vibronic interactions cannot simply increase indefinitely.

The matrix representation of the $\hat{H}_{\text{el}} + \hat{H}_{\text{cav}}$ operator in the basis of noninteracting cavity-ensemble states and in the single-excitation space (SES) results in the MTCH [40]

$$\mathcal{H}_{\text{el-cav}}^{[1]} = \begin{bmatrix} \hbar\omega_c & \gamma^{(1)}(R_1) & \gamma^{(2)}(R_2) & \gamma^{(3)}(R_3) & \cdots \\ \gamma^{(1)}(R_1) & \Delta^{(1)}(R_1) & 0 & 0 & \cdots \\ \gamma^{(2)}(R_2) & 0 & \Delta^{(2)}(R_2) & 0 & \cdots \\ \gamma^{(3)}(R_3) & 0 & 0 & \Delta^{(3)}(R_3) & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix}, \tag{4}$$

where $\Delta^{(\kappa)}(R_\kappa) = V_1^{(\kappa)}(R_\kappa) - V_0^{(\kappa)}(R_\kappa)$ is the energy gap of the κth molecule and $\gamma^{(\kappa)}(R_\kappa) = g\mu_{01}^{(\kappa)}(R_\kappa)$ is the dipole coupling of the κth molecule to the cavity mode. Inspection of the MTCH already reveals some important aspects of the role of molecular vibrations in coupling the bright and dark polaritonic states. In the simpler case of an ensemble of two-level atoms coupled to a cavity, and in the zero-detuning case [i.e., all diagonal entries in Eq. (4) set to the same value and no nuclear position dependency], all dark states are degenerate, appear at the average energy of the two bright polaritons and feature no dipole coupling to the ground state of the hybrid system [2]. When nuclear motion is present, the degeneracy of the dark states is lifted through the nuclear displacements that modulate the energy gap of the corresponding molecule. This leads to regions of conical intersection among the dark polaritonic states, whose existence has been discussed recently as well by Feist and collaborators [27].

We note here that the Hamiltonian [Eq. (4)] has the form of an arrowhead matrix, whose properties have been investigated in the contexts of applied mathematics [41,42] and molecular physics [43]. The most important property of arrowhead matrices for our purposes is the fact that for every m molecules with the same energy gap Δ, there is an eigenvalue $\lambda_j = \Delta$ of multiplicity $m - 1$ [42]. Hence, for $m = 2$ molecules with the same energy gap, there is one eigenstate of $\mathcal{H}_{\text{el-cav}}^{[1]}$ at the corresponding energy value. In case $m = 3$ molecules have the same energy gap, e.g., molecules 1 to 3, there are two degenerate eigenstates at that energy. For the case of identical molecules, this degeneracy is found in the one-dimensional space $R_1 = R_2 = R_3$ and it is lifted by displacements in the two-dimensional branching space that removes this equality [40]. Such CCI are referred here as *collective* to emphasize the fact that their location in coordinate space depends on the internal coordinates of more than one molecule in the ensemble.

As an example, a cut through the potential energy surfaces obtained by diagonalization of the MTCH the SES and for $N = 5$ is shown in Fig. 2. For five molecules, six polaritonic states are present in the SES, two of which are the bright polaritons and four of them are nominally dark. In the cut shown, $R_2 = R_3 = 5.35$ au, $R_4 = R_5 = 5.5$ au, and R_1 is scanned between 4 and 7.5 au. Two CCI are seen along this PES cut at precisely $R_1 = 5.35$ and

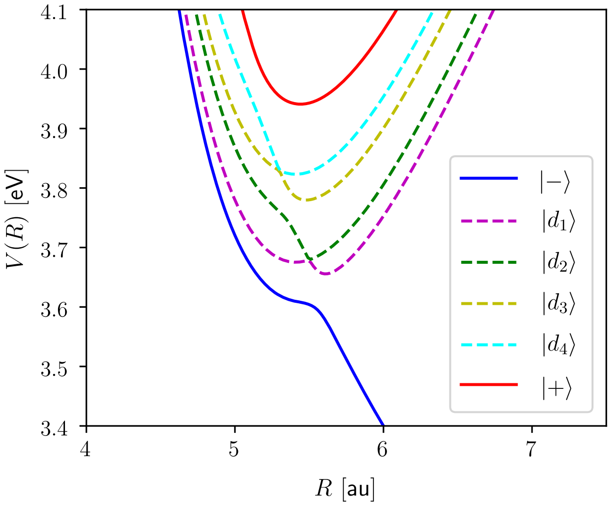

FIG. 2. Polaritonic PES obtained by the diagonalization of Hamiltonian [Eq. (4)] for the case of $N = 5$ molecules. Upper and lower solid curves correspond to the nominally bright polaritons whereas the dashed curves correspond to the nominally dark states.

$R_1 = 5.5$, i.e., at points with three equal intermolecular distances.

The local permutation symmetry of three identical molecules giving rise to a CCI of two polaritonic states can be described within the permutation symmetry group S_3 [44], which among others is isomorphic with the D_3 point group of an equilateral triangle [45]. As is well known, molecules of D_3 and related symmetry point groups, e.g., C_{3v}, are Jahn-Teller active [45,46], where the degeneracy among electronic states is lifted linearly for displacements out of the highly symmetric atomic arrangement, resulting in conically intersecting potential energy surfaces.

The explicit connection between the MTCH and JTH for the case $m = 3$ has been worked out in detail [40]. Polaritonic states, both bright and dark are coupled to each other by collective molecular displacements, which in the case of identical molecules can be classified according to the symmetry representations of the corresponding permutation symmetry group.

Assuming identical molecules, such that the molecular indices of the $\Delta^{(j)}$ and $\gamma^{(j)}$ in Eq. (4) disappear, the two bright polaritons are separated by an energy gap $2\gamma\sqrt{N}$ at the fully symmetric configuration $(R_1^0, \ldots, R_N^0)$ for which all molecular gaps are resonant with the cavity mode. These two polaritonic states are coupled in the first order through displacements of the symmetry adapted coordinate (SAC) belonging to the fully symmetric representation $\rho = N^{-1/2} \sum_j^N d_j$, where $d_j = R_j - R_j^0$. The linear coupling constant is $\beta/2\sqrt{N}$, where $\beta = \partial\Delta/\partial R_j$ is the gradient of the molecular energy gap at the resonant geometry [40]. The bright and dark polaritonic states are separated by an energy gap $\gamma\sqrt{N}$ and are linearly coupled by pseudo-Jahn-Teller interactions through displacements of SACs belonging to degenerate representations of the corresponding symmetry group. The coupling constant for such interactions is in this case $\beta/\sqrt{2N}$. The dark polaritonic states are also coupled in the first order through displacements of the degenerate SACs. The coupling constant is also of the form $\beta/\sqrt{2N}$. However, these states present no energy gap at the fully symmetric configuration, giving rise to the CCIs, and hence the vibronic coupling within this space is the strongest.

Therefore, cavity-induced CCI are, from a mathematical standpoint, analogous to the commonly encountered [47] intramolecular conical intersection case [45,46,48–50], which is demonstrated by the direct link among the MTCH and JTH. This includes their divergent nonadiabatic coupling matrix elements $\langle\psi_i|\vec{\nabla}_R|\psi_j\rangle$ at the regions of intersection [40], where $|\psi_j\rangle$ are the eigenstates of $\mathcal{H}^{[1]}_{\text{el-cav}}$.

Although we see that the vibronic coupling constants decrease with the size of the system, the number of possible decay pathways increases faster. Moreover, Fig. 2 demonstrates how small displacements of the molecules around the equilibrium position of their respective ground states R_j^0 can lead to energy shifts of CCI of the same order as the Rabi splitting, thus bringing the nominally dark states much closer to the bright polaritonic PES. These effects are missed in rate-theory descriptions.

In summary, real-time wave packet simulations of a molecular ensemble coupled to a cavity mode reveal that the nonradiative relaxation rate from the upper to the lower polaritonic states increases with the number of coupled molecules. As a consequence, by pumping the system to the upper polariton, the cavity coupling strongly influences the kinetics of, in this example, chemical bond breaking in the excited state as a function of the number of coupled molecules. This effect is not predicted by models based on perturbative rates. The molecular Tavis-Cummings Hamiltonian can be casted by a suitable transformation in the form of a Jahn-Teller Hamiltonian, which sheds light on the collective nature of the molecular vibrations coupling both bright and dark polaritons among each other, and relates all vibronic interactions to a single parameter, the gradient of the molecular energy gap.

In the context of polariton relaxation, the CCI may be an important ingredient for fast localization and loss of coherence once the dark state manifold is reached. Since only the value of $\Delta(R_j)$ is determinant for the existence of the CCI [42], these are expected to be robust against molecular rotations or other external perturbations that modulate the off-diagonal coupling strength of individual molecules to the cavity mode, as well as to local interactions with an environment, which will lead only to displacements of the locus of intersection. The dependence of the relaxation rates on the number (or density) of coupled molecules may open application possibilities in the design of polaritonic devices and these kinds of dynamics, specially for larger ensembles and more complex molecules, remain to be further investigated.

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[*] oriol.vendrell@pci.uni-heidelberg.de

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