

Cavity Control of Molecular Spectroscopy and Photophysics

Bing Gu,* Yonghao Gu, Vladimir Y. Chernyak, and Shaul Mukamel*



Cite This: <https://doi.org/10.1021/acs.accounts.3c00280>



Read Online

ACCESS |

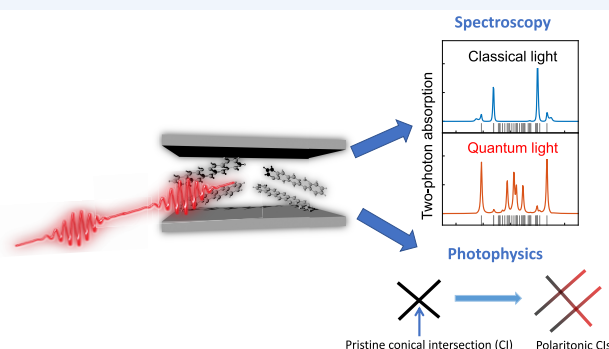
Metrics & More

Article Recommendations

CONSPECTUS: Optical cavities have been established as a powerful platform for manipulating the spectroscopy and photophysics of molecules. Molecules placed inside an optical cavity will interact with the cavity field, even if the cavity is in the vacuum state with no photons. When the coupling strength between matter excitations, either electronic or vibrational, and a cavity photon mode surpasses all decay rates in the system, hybrid light–matter excitations known as cavity polaritons emerge. Originally studied in atomic systems, there has been growing interest in studying polaritons in molecules. Numerous studies, both experimental and theoretical, have demonstrated that the formation of molecular polaritons can significantly alter the optical, electronic, and chemical properties of molecules in a noninvasive manner.

This Account focuses on novel studies that reveal how optical cavities can be employed to control electronic excitations, both valence and core, in molecules and the spectroscopic signatures of molecular polaritons. We first discuss the capacity of optical cavities to manipulate and control the intrinsic conical intersection dynamics in polyatomic molecules. Since conical intersections are responsible for a wide range of photochemical and photophysical processes such as internal conversion, photoisomerization, and singlet fission, this provides a practical strategy to control molecular photodynamics. Two examples are given for the internal conversion in pyrazine and singlet fission in a pentacene dimer. We further show how X-ray cavities can be exploited to control the core-level excitations of molecules. Core polaritons can be created from inequivalent core orbitals by exchanging X-ray cavity photons. The core polaritons can also alter the selection rules in nonlinear spectroscopy.

Polaritonic states and dynamics can be monitored by nonlinear spectroscopy. Quantum light spectroscopy is a frontier in nonlinear spectroscopy that exploits the quantum-mechanical properties of light, such as entanglement and squeezing, to extract matter information inaccessible by classical light. We discuss how quantum spectroscopic techniques can be employed for probing polaritonic systems. In multimolecule polaritonic systems, there exist two-polariton states that are dark in the two-photon absorption spectrum due to destructive interference between transition pathways. We show that a time–frequency entangled photon pair can manipulate the interference between transition pathways in the two-photon absorption signal and thus capture classically dark two-polariton states. Finally, we discuss cooperative effects among molecules in spectroscopy and possibly in chemistry. When many molecules are involved in forming the polaritons, while the cooperative effects clearly manifest in the dependence of the Rabi splitting on the number of molecules, whether they can show up in chemical reactivity, which is intrinsically local, is an open question. We explore the cooperative nature of the charge migration process in a cavity and show that, unlike spectroscopy, polaritonic charge dynamics is intrinsically local and does not show collective many-molecule effects.



KEY REFERENCES

- Gu, B.; Nenov, A.; Segatta, F.; Garavelli, M.; Mukamel, S. Manipulating Core Excitations in Molecules by X-ray Cavities. *Phys. Rev. Lett.* **2021**, *126*, 053201.¹ Strong coupling with an X-ray cavity mode leads to hybrid novel core polaritonic excitations.
- Gu, B.; Mukamel, S. Optical-Cavity Manipulation of Conical Intersections and Singlet Fission in Pentacene Dimers. *J. Phys. Chem. Lett.* **2021**, *12*, 2052–2056.² Pushing the conical intersection away from the Franck–Condon region by cavities lowers the probability to reach it and hence the singlet fission rate.

- Gu, B.; Mukamel, S. Manipulating Two-Photon-Absorption of Cavity Polaritons by Entangled Light. *J. Phys. Chem. Lett.* **2020**, *11*, 8177–8182.³ The entangled two-photon absorption was, for the first time, applied to polaritonic systems, and it was found that classically dark

Received: May 12, 2023

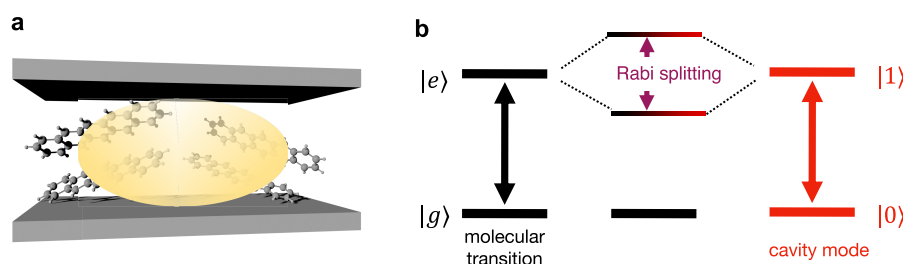


Figure 1. (a) Schematic of molecules embedded in an optical cavity. (b) Vacuum Rabi splitting of a two-level system coupled to a single cavity mode.

two-polariton states become bright under entangled photon illumination.

- Gu, B.; Mukamel, S. Manipulating nonadiabatic conical intersection dynamics by optical cavities. *Chem. Sci.* **2020**, *11*, 1290–1298.⁴ Strong coupling can be employed to tune the pristine conical intersections in the molecule, and thus control photophysics.

INTRODUCTION

Exploiting vacuum fluctuations to influence the physical properties of matter dates back to the Purcell effect,⁵ where the spontaneous emission rate of an atom is enhanced by inserting it in a resonant cavity. The energy in this case is irreversibly dissipated from the atom to the field; this is known as the weak coupling regime. If the coupling strength can be made strong enough to surpass the decay rates of both the molecules and the cavity, the system enters the strong coupling regime, whereby the light and matter can exchange energy coherently. In this regime, the matter and photon degrees of freedom combine to form hybrid excitations, known as polaritons. A polariton is a quantum quasiparticle that is formed as a superposition of a matter excitation (e.g., a plasmon, exciton, or phonon) with a photon, an elementary excitation of the quantum electromagnetic field. The polariton concept was first introduced in the 1950s⁶ for phonon and exciton polaritons in crystals.

Advances in technology had led to the creation of a new field of cavity polariton physics and chemistry, allowing control over the photon modes, confining them to optical cavities,⁷ as schematically shown in Figure 1a. Microcavities enhance the light–matter coupling strength by confining light into a small volume at the scale of the wavelength or even subwavelength. An optical cavity can be realized in a plethora of devices; one that is commonly used is the Fabry–Perot (FP) microcavity, consisting of two parallel mirrors with high reflectivity. A photon can be confined inside the cavity for a sufficiently long time to interact with embedded molecules, i.e., with a small cavity mode decay rate κ . The quality factor, defined as $Q = \frac{\omega_c}{2\kappa}$, where ω_c is the resonance frequency, is widely used to characterize how well an optical cavity stores light. The effective light–matter coupling strength is given by

$$g = \sqrt{N}\mu\mathcal{E} = \sqrt{N}\mu\sqrt{\frac{\hbar\omega_c}{2\epsilon_0 V}} \quad (1)$$

where $\mathcal{E}$ represents the vacuum electric field fluctuations, N is the number of molecules in the active cavity mode volume, ϵ_0 is the dielectric constant of the vacuum, V is the mode volume, and μ is the transition dipole moment. The $\sqrt{N}$ factor represents the cooperativity of molecules interacting with the same photon mode and indicates that the effective coupling strength is enhanced by the molecular density. The price to be paid is that

this introduces a manifold of dark states, which complicates the analysis. The light–matter coupling strength can be alternatively enhanced by reducing the mode volume V . It is difficult to achieve subwavelength confinement with FP cavities, since reducing the mirror distance also increases the cavity resonance frequency, with nanometer separation corresponding to resonance in the X-ray regime. Subwavelength confinement is possible with plasmonic cavities, where the mode volume can be reduced to the nanoscale with the resonance frequency kept in the optical regime, making it possible to realize single-molecule strong coupling.⁸ While the cavity field is purely transversal ($\nabla \cdot \mathbf{E} = 0$) in FP-type cavities, the plasmonic field also contains a longitudinal component from the free electron motion in the metal nanostructures. This has an important consequence in electromagnetic field quantization.

Originally studied in atoms,^{9,10} there is growing interest in investigating strong coupling in molecular systems. Molecular polaritons, either vibrational or electronic, can have a significant influence on the optical, electronic, and chemical properties of molecules.¹¹ The dynamical phenomena observed in optical cavities, mostly with the Fabry–Perot geometries, include demonstration of molecular exciton cavity polaritons,¹² polariton lasing using a molecular material,¹³ polariton-mediated energy transfer between conventional^{14–16} and vibrational¹⁷ donors and acceptors, cavity polaritons formed from molecules located in different regions of a multilayer Fabry–Perot resonator,¹⁸ and collective strong light–matter coupling effects in the ultrafast nonradiative relaxation processes in polariton states.¹⁹ Examples involving chemical reactions include modified photoisomerization rates and reversing the branching ratio in ground-state chemical reactions.^{20–22} An intensive theoretical effort has been made toward understanding the mechanism behind polariton-mediated processes and their experimental signatures.^{23,24} Very recent theoretical studies include two-photon absorption of entangled photon pairs by cavity polaritons³ and X-ray spectroscopy in a cavity where different core electrons couple via polariton formation.¹

For a dielectric medium, polaritons can be studied macroscopically through the solutions of Maxwell's equations, with the information about matter excitations contained in the resonances of the position- and frequency-dependent dielectric constant.²⁵ This is a first-principles rather than phenomenological approach, provided that we view the dielectric constant as a polarization operator, which is well-defined in quantum electrodynamics. Treating the dielectric constant as the polarization operator can be viewed as a bridge between the quantum picture proposed in ref 26 and the classical approach of ref 6, where all information on quantum dynamics of matter excitations and resonant properties is contained in its dielectric constant. From the viewpoint of many-body physics, there is no substantial difference between computing the Green/correla-

tion functions of the electromagnetic field and the material variables since they are directly related. The approach based on field correlation functions has been applied to various problems associated with multiscale modeling (e.g., computation of the fluctuation forces) since 1950s.²⁷ The technical advantage of such an approach in its application to cavity polariton systems is its universality in being applicable to systems with a large number of molecules, where the latter can be treated on the level of modification of the material dielectric constant (which is asymptotically exact when the system has a large number of molecules on the wavelength scale), as well as considering systems with a small number of molecules; in the latter case, one needs to deal with the microscopic polarizability $\chi^{(1)}(\mathbf{r}, \mathbf{r}'; \omega)$, explicitly treated as the kernel of the polarization operator. In this Account, we focus on relatively simple cavity models. The above approach provides a bridge between the paradigmatic models considered in some detail below and more experimentally relevant settings that involve FP-type optical cavities. Such a link allows importing intuition gained by studying simple quantum models to treat polariton phenomena in cavities with more complicated geometries as well as developing a theoretical framework for accurate treatment of realistic cavity shapes, including accounting for finite polariton lifetimes.

Describing chemistry in optical cavities requires adequate theoretical tools that account for the nuclear motions. The Floquet framework that describes classical light-driven matter shares some similarities with the cavity polaritons, e.g., Autler–Townes effects versus Rabi splitting.²⁸ Understanding molecular polaritons requires going beyond the semiclassical light–matter interaction framework and employing cavity quantum electrodynamics with a quantized description of the confined electromagnetic field and a nonperturbative treatment of the light–matter interaction.^{29–31} In the semiclassical framework commonly adopted in molecular spectroscopy,³² the electromagnetic field is not treated as a dynamical variable but merely externally drives the molecules. Representing the electric field operator as a number is justified for laser pulses, where the number of photons is so large that field fluctuations can be neglected. This approximation clearly breaks down for the vacuum field because vacuum fluctuations, instead of the field itself, dominate the light–matter coupling.

■ PARADIGMATIC MODELS

The discrete Fabry–Perot photon modes arise from confinement by the cavity mirrors. Consider the vector potential $\mathbf{A}(\mathbf{z}, t) = \sum_k \hat{\mathbf{x}} [\alpha_k(t) u_k(z) + \alpha_k^*(t) u_k^*(z)]$, where $\alpha_k(t) = \alpha_k(0) e^{i\omega_k t}$ and the mode function $u(z)$ satisfies the Helmholtz equation inside the “box”, $\nabla^2 u_k(z) = -(\omega_k/c)^2 u_k(z)$. This implies, for perfect conductors where the electric fields vanish at the boundaries ($u(0) = u(L) = 0$), that $u_n(z) \propto \sin \frac{n\pi z}{L}$, $n = 1, 2, \dots$, where L is the cavity length. The boundary conditions thus result in a set of discrete modes. Quantization of these modes is made by replacing the coefficients α by boson operators $\alpha \rightarrow \sqrt{\frac{\hbar}{2\omega\epsilon_0}} a$. If the characteristic transition frequency of the embedded matter is close to one of the cavity modes, a single cavity mode suffices to describe the cavity field–molecule interaction, although spatial-dependent effects such as transport require multiple modes.³³

The elementary model describing the interaction between a cavity photon mode with resonance frequency ω_c and a two-level system with transition frequency ω_0 is the quantum Rabi model, $H = \omega_c a^\dagger a + \omega_0 \sigma^\dagger \sigma + g(a + a^\dagger) \sigma_x$, where $\sigma = |g\rangle\langle e|$ is the

lowering operator of the molecular system and a ($a^\dagger$) is the annihilation (creation) operator of the photon mode satisfying the bosonic commutation relations $[a, a^\dagger] = 1$. This Hamiltonian can be derived by starting with the nonrelativistic minimal coupling Hamiltonian in the long-wavelength approximation $\mathbf{A}(\mathbf{r}) \approx \mathbf{A}(\mathbf{r}_0)$, truncation of the matter space, and neglect of the diamagnetic term $\mathbf{A}^2$. If the rotating-wave approximation is made by neglecting the counterrotating terms, $\sigma^\dagger a^\dagger + a\sigma$, then the Rabi model reduces to the Jaynes–Cummings model H_{JC} . This model has $U(1)$ continuous symmetry, $\sigma \rightarrow \sigma e^{-i\varphi}$, $a \rightarrow a e^{i\varphi}$, that leads to the conservation of the number of excitations, i.e., $[\hat{N}, H] = 0$, where $\hat{N} = a^\dagger a + \sigma^\dagger \sigma$. The counterrotating terms couple states with excitation number differing by 2, e.g., $|g0\rangle$ and $|e1\rangle$, and thus break the continuous symmetry. Nevertheless, the parity of the excitation $\mathcal{P} = e^{i\pi\hat{N}}$ is still conserved. When the light–matter coupling strength is a significant fraction of the transition frequency, the neglected counterrotating terms become important and introduce state mixing and level shifts.^{34,35} The Jaynes–Cummings model can be exactly solved with the single-polariton eigenstates given by $|P_\pm\rangle = \frac{1}{\sqrt{2}}(|g1\rangle \pm |e0\rangle)$, and eigenenergies $E_\pm = \frac{1}{2}(\omega_0 + \omega_c \pm \sqrt{\Omega^2 + \Delta^2})$, where $\Delta = \omega_c - \omega_0$ and $\Omega = 2g$ is the Rabi frequency (Figure 1b). The Rabi splitting can be measured through the absorption spectrum or the cavity transmission (or reflection) spectrum.

Moving from atoms to molecules, the polaritonic dynamics becomes significantly more complex due to the nuclear degrees of freedom (i.e., vibrations, rotations, and conformations) which couple to the electronic motion.³⁶ The transition energy now depends parametrically on the molecular configuration $\mathbf{R}$. We focus on regions in configuration space where the energy gap $E_g(\mathbf{q}) = E_e(\mathbf{R}) - E_g(\mathbf{R})$ is close to the cavity frequency; this is where the potential energy surfaces are significantly modulated by tuning the cavity parameters, which results in modifying a specific region of the excited-state PES (e.g., Franck–Condon region and conical intersection region), thereby altering the photochemistry and photophysics. In addition to the excited-state PES, the ground-state PES can also be modified by the counterrotating terms at ultrastrong coupling, which may lead to control of ground-state chemistry. Furthermore, the high density of electronic states can be very dense for molecules, as is typical for transition metal complexes,³⁷ and the simple picture of Rabi splitting for a two-level system may not apply.

■ CAVITY PHOTOCHEMISTRY

Most photochemical and photophysical processes, such as photoisomerization in vision³⁸ and photostability of DNA molecules under UV radiation,³⁹ are controlled by conical intersections (CIs). These are degenerate points (or seams) in the nuclear configuration space between the adiabatic potential energy surfaces. The common Born–Oppenheimer approximation relies on energy (or equivalently time) scale separation between the electronic and nuclear motions. However, this breaks down in the vicinity of CIs, where the electronic energy gap becomes small and comparable to the energy scale of nuclear motion. The non-adiabatic couplings between the two electronic states, neglected in the BO approximation, become important and are responsible for nonradiative electronic transitions.

By placing molecules in a high-Q optical cavity, the potential energy landscape can be manipulated by strong light–matter

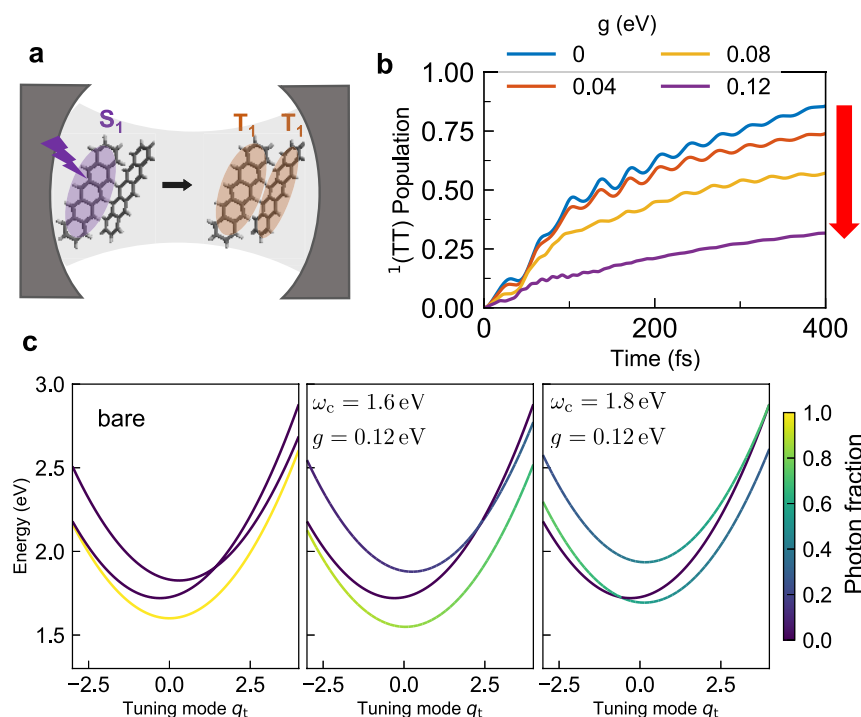


Figure 2. Cavity modification of singlet fission rate. (a) Schematic of the singlet fission process in an optical cavity. (b) SF rate suppression at $\omega_c = 1.8$ eV for various coupling strengths. (c) Cut of the (left) bare $|S_0\rangle\otimes|1\rangle$, S_1 , and S_2 and (middle and right panels) polaritonic potential energy surfaces along the tuning mode at $g = 0.12$ eV and $\omega_c = 1.6$ and 1.8 eV. The conical intersection is being pushed away from the Franck–Condon region. Adapted from ref 2. Copyright 2021 American Chemical Society.

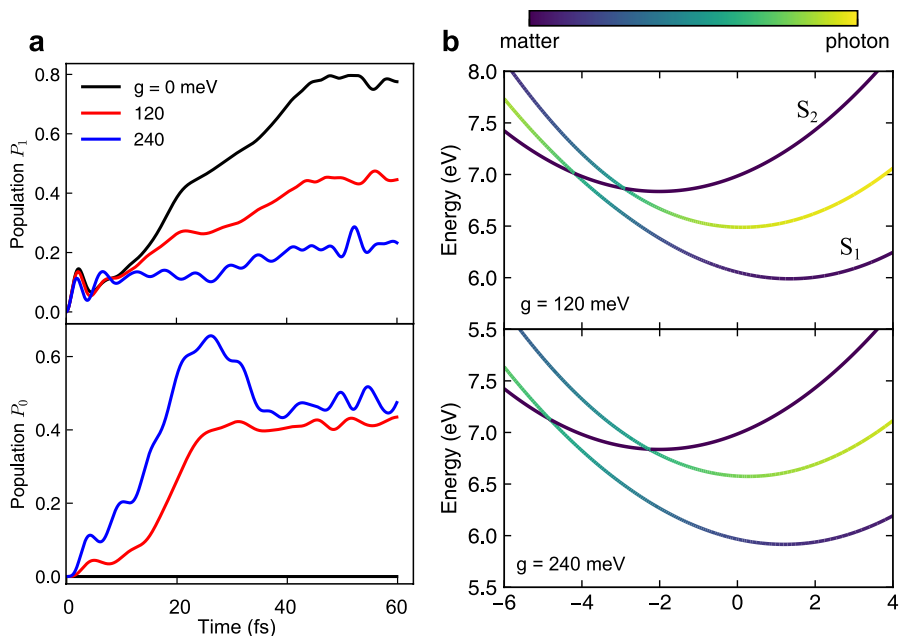


Figure 3. Cavity-modified internal conversion in pyrazine. The cavity mode is assumed to couple to the S_0 – S_1 transition. (a) Population dynamics of the (upper) S_1 and (lower) S_0 states at various coupling strengths g . (b) Cuts of the polaritonic potential energy surfaces along the tuning mode at different coupling strengths. The ground state is not shown. From ref 45. CC BY-NC 3.0.

coupling. Electronic strong coupling with few molecules has been achieved in plasmonic cavities;⁸ FP-type cavities require many molecules to reach the strong coupling regime. When the cavity mode lifetime is longer than the dynamics, a Born–Oppenheimer-like picture can be developed by expanding the polaritonic wave function as $\Psi(\mathbf{q}, \mathbf{r}, \mathbf{R}, t) = \sum_n \Phi_n(\mathbf{q}, \mathbf{r}; \mathbf{R}) \chi_n(\mathbf{R}, t)$, analogous to the Born–Huang expansion for the bare

molecule. The adiabatic polaritonic states $\Phi_n(\mathbf{q}, \mathbf{r}; \mathbf{R})$ are defined as the eigenstates of the polariton Hamiltonian $H_p(\mathbf{R}) = H - \hat{T}_N$, i.e., the total Hamiltonian without the nuclear kinetic energy operator. They play the same role as the adiabatic electronic states in bare molecules. The coupled photon–electron–nuclear polariton dynamics is then determined by the polaritonic potential energy surfaces $\mathcal{E}_n(\mathbf{R})$ rather than the

adiabatic potential energy surfaces. The polaritonic PESs can show rich features such as light-induced CIs for diatomic molecules, polaritonic CIs by a splitting of the pristine CIs, and dark states^{40,41} not present in the bare PESs.

Below we give two examples where the polaritonic photo-dynamics under single-molecule strong coupling differs significantly from that of its bare counterpart.

We start with singlet fission in pentacene molecules. Singlet fission is an exciton multiplication process whereby a singlet high-energy exciton splits into two lower-energy triplet excitons. The two triplet excitons are correlated, forming an overall singlet; thus, the process is spin-allowed and can occur on a picosecond to femtosecond time scale. It has been proposed that singlet fission materials can boost the efficiency of photovoltaic devices,⁴² and the intriguing possibility that optical cavities may be employed to modify singlet fission rates has attracted much attention.^{2,43,44}

We have shown that for a CI-mediated singlet fission in pentacene dimer, the cavity can suppress the singlet fission rate (Figure 2b) by pushing the CI away from the Franck–Condon region.² This is clearly seen in the cut of the polaritonic PESs along the tuning mode. The location of the polaritonic conical intersections depends sensitively on the coupling strength and cavity resonance frequency (Figure 2c). Upon vertical excitation to the singlet state, the molecule must cross a barrier to reach the CI and trigger singlet fission. The barrier is shallow in the bare molecule and can be overcome by thermal fluctuations but becomes significantly higher when the cavity–molecule coupling is switched on. The probability to reach the polaritonic CI and the singlet fission rate are thus suppressed.

Another example is the ultrafast internal conversion rate in pyrazine. Upon absorption of an optical photon, pyrazine is vertically excited to the S_2 state. The molecule then undergoes a 60 fs nonradiative decay process mediated by a CI to the S_1 state. By placing this molecule in an optical cavity with resonance frequency close to the $S_0 \rightarrow S_1$ transition energy at the CI, it was theoretically demonstrated that the internal conversion process is accelerated by strong light–matter coupling (Figure 3a). In the bare molecule, the electronic excitation relaxes to the S_1 state, whereas in a cavity, the molecule relaxes to both the S_0 and S_1 states. This is rationalized by the fact that on the polaritonic PESs (Figure 3b), a pristine CI splits into two polaritonic CIs. The electronic relaxation is then dictated by the one closer to the Franck–Condon region. The locations of the two polaritonic CIs can be controlled by varying the cavity parameters.

These two examples demonstrated that an optical cavity provides a general platform for manipulating the conical intersection dynamics of molecules. Many other chemical processes mediated by the CIs should be subjected to cavity control.

■ MODIFYING CORE EXCITATIONS BY X-RAY CAVITIES

X-ray cavities have been employed in the study of X-ray quantum optics.⁴⁶ Such thin-film cavities are only a few nanometers apart. X-ray cavities can be exploited to manipulate core-level excitations. This is shown by theoretical demonstrations for 1,1-difluoroethylene and a transition metal complex, ferricyanide.

Core excitations in molecules involve core orbitals localized on specific atoms. For 1,1-difluoroethylene, the molecular structure displayed in Figure 4a, contains two inequivalent carbon atoms with different chemical environments that result in

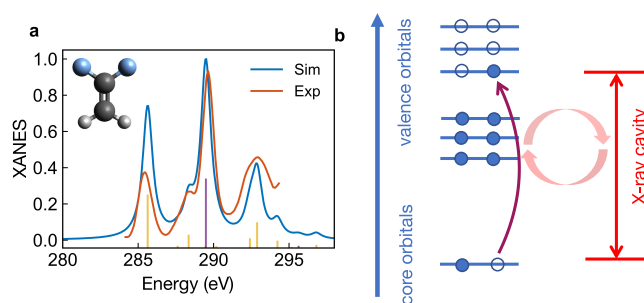


Figure 4. (a) XANES spectra of 1,1-difluoroethylene: simulations versus experiments. (b) Schematic of core excitations in a molecule coupled to an X-ray cavity photon mode. Adapted with permission from ref 1. Copyright 2021 American Physical Society.

different core excitation energies. As shown in the XANES spectrum (Figure 5), the two main transitions arising from the C K-edge (1s orbital) of CH_2 and CF_2 are separated by the ~ 3 eV chemical shift. By placing the molecules into an X-ray cavity, the cavity photon mode, coupled to both core transitions, mediates an effective coupling between the cores, thus creating hybrid states consisting of both cores and the cavity photon. Figure 5 shows modifications of the XANES spectra at various coupling strengths. The lower panel shows the decomposition of each peak into three components.

Another example of X-ray-cavity-altered core-level excitation is demonstrated by simulating the iron K-edge in a transition metal complex, ferricyanide ($[\text{Fe}(\text{III})(\text{CN})_6]^{3-}$), in an aqueous environment.³⁷ Core polariton states are observed in a resonant X-ray cavity, and the correlations between valence excitations and core polaritons can be revealed by the stimulated X-ray Raman signal.

UV–vis cavities can be exploited to control valence excitations, thus enabling many interesting phenomena associated with exciton polaritons. Similarly, X-ray cavities provide a platform for controlling core excitations.

From the theory side, an accurate description of the core polaritons requires further developments. On the nanometer length scale, the electric dipole approximation may not be valid. This can be addressed by adopting the minimal-coupling Hamiltonian, which uses the charge and current densities rather than multipoles.⁴⁷

■ QUANTUM LIGHT SPECTROSCOPY OF MOLECULAR POLARITONS

Nonlinear spectroscopic techniques can monitor the polaritonic dynamics in real time. Time-resolved techniques, including transient absorption and two-dimensional infrared and optical spectroscopy, have been applied to probe the nonlinear response functions of polaritonic systems.^{48,49} Theories and simulation techniques^{24,50} have been extended to polaritons. Quantum light spectroscopy is a frontier branch of nonlinear spectroscopy that exploits the quantum-mechanical properties of light to extract matter information not accessible by classical light.⁵¹ A widely used technique is entangled two-photon absorption.^{52,53} In classical two-photon absorption, a molecule is promoted from the ground state to an excited state by simultaneously absorbing two single-color or two color photons. In the quantum version, the classical light is replaced by an entangled photon pair.

Applications of this technique to a polariton model with N nonidentical two-level molecules interacting with a single cavity mode have shown that entangled photons can access classically

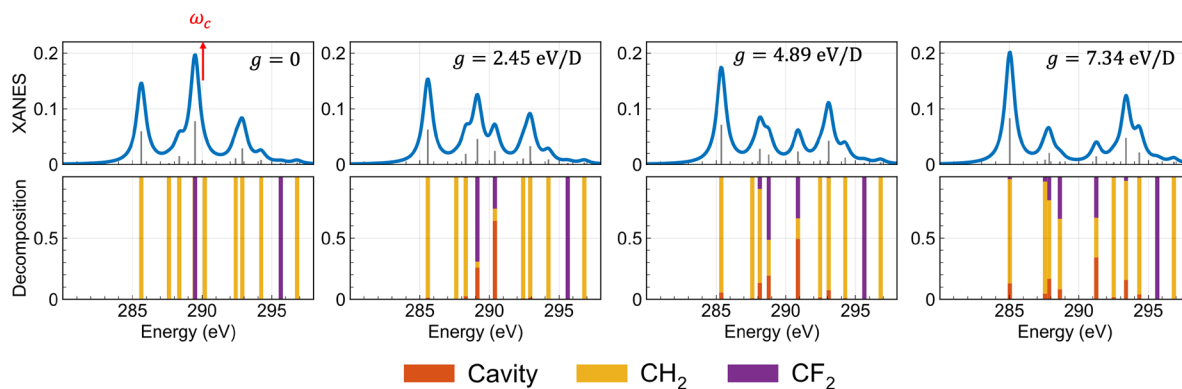


Figure 5. (top) XANES of 1,1-difluoroethylene in an X-ray cavity at various coupling strengths. (bottom) Decomposition of each transition into two inequivalent carbon cores and an X-ray cavity photon. Adapted with permission from ref 1. Copyright 2021 American Physical Society.

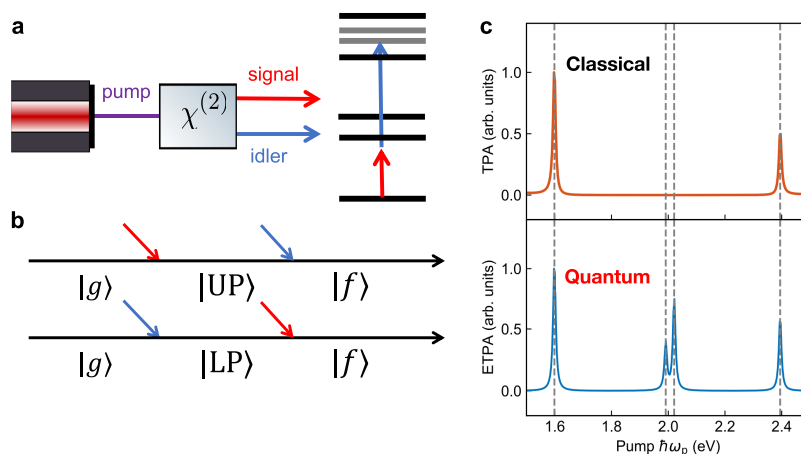


Figure 6. Quantum light spectroscopy of cavity polaritons. (a) Schematic of entangled two-photon absorption of a polaritonic system. (b) Two transition pathways that destructively interfere and result in a dark two-polariton state. (c) Classical versus entangled two-photon absorption for a polaritonic system with two two-level systems and a single cavity mode. Adapted from ref 3. Copyright 2020 American Chemical Society.

dark two-polariton states.³ The bipolariton states $\{|f\rangle\}$ are dark not because of the dipole selection rule but due to destructive quantum interference between different transition pathways. The two-photon entangled beams are commonly labeled as the signal and the idler. For classical light, the transition amplitude to reach a final state $|f\rangle$ through an intermediate state $|e\rangle$, $|g\rangle \xrightarrow{\omega_s} |e\rangle \xrightarrow{\omega_i} |f\rangle$ (pathway 1), calculated by using time-dependent perturbation theory to second-order in the light–matter interaction,³ is given by

$$T_{is}^{(e)}[g \rightarrow f] = \frac{D_{fg}^{(e)}}{\omega_{eg} - \omega_s} \delta(\omega_{fg} - \omega_s - \omega_i) \quad (2)$$

where $D_{fg}^{(e)} = \langle f|\boldsymbol{\mu} \cdot \mathbf{e}_i|e\rangle \langle e|\boldsymbol{\mu} \cdot \mathbf{e}_s|g\rangle$ and $\mathbf{e}_{s/i}$ is the polarization vector of the signal/idler beam. The subscripts of T label the photon sequence interacting with the molecule, i.e., signal photon first and idler later, or vice versa. The denominator represents the detuning between the transition frequency, $\omega_{eg} = \omega_e - \omega_g$, and the frequency of the first photon interacting with the molecule, ω_s . Reversing this sequence of photon interactions leads to another set of two-photon transition pathways, $|g\rangle \xrightarrow{\omega_i} |e\rangle \xrightarrow{\omega_s} |f\rangle$, with transition amplitude $T_{si}^{(e)} = \frac{\mu_{fe}\mu_{gs}}{\omega_{eg} - \omega_i}$. For a polariton system, the intermediate states are the upper (UP) and lower (LP) polaritons, $e, e' \in \{\text{UP}, \text{LP}\}$. For two-polariton states with eigenenergies close to the sum of the UP and LP energies, we

have $\omega_{fg} = \omega_{UP} + \omega_{LP} = \omega_s + \omega_i$, where the second equality reflects energy conservation. If the final state further satisfies $D_{fg}^{(\text{UP})} = D_{fg}^{(\text{LP})}$, this leads to vanishing of the sum of two transition amplitudes $T_{is}^{(\text{UP})} + T_{si}^{(\text{LP})} = 0$. It follows that two-polariton states close to $\omega_{UP} + \omega_{LP}$ will undergo destructive interference, rendering them dark in classical two-photon absorption.

By using time–frequency entangled light generated by spontaneous parametric downconversion, the above interference can be controlled by tuning the entanglement time. Classically dark two-polariton states can then become bright in entangled two-photon absorption (Figure 6c). Using entangled light, the transition amplitude for pathway 1 is given by³

$$\mathcal{T}_{is} \propto \frac{D_{fg}^{(e)}}{\Delta_e^{(s)}} \frac{1 - e^{-i\Delta_e^{(s)}T_e/2}}{\sqrt{T_e}} \delta(\omega_{fg} - \omega_s - \omega_i) \quad (3)$$

where T_e is the entanglement time, the maximum arrival time difference between the photon pair. The transition amplitude for an entangled photon pair can thus be modulated by varying the entanglement time.

Quantum light provides a new means to manipulate and control the interference among excitation pathways in polaritonic systems. This can be utilized in spectroscopy, microscopy, interferometry, and coherent control schemes.^{51,52,54}

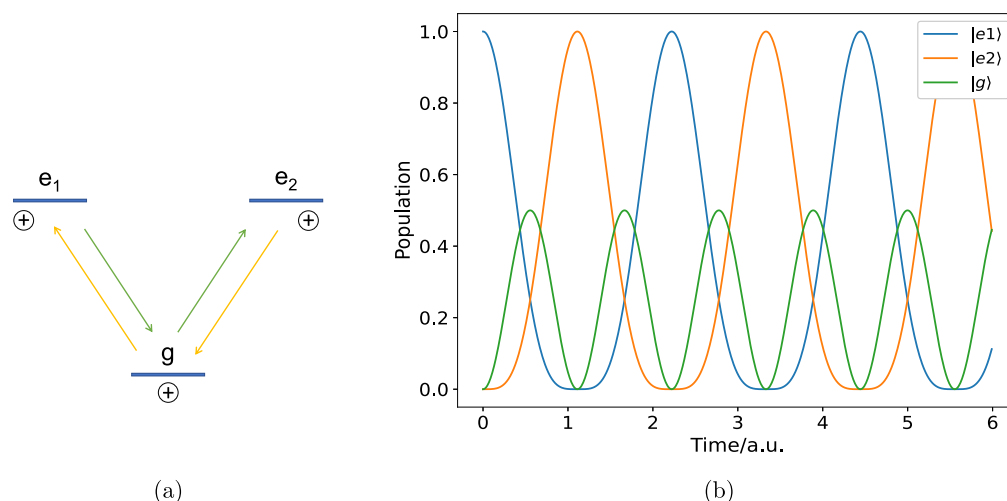


Figure 7. (a). Diagrammatic sketch of the three-level ionized molecule system employed in the collective effects study of polaritonic charge dynamics. (b) State population dynamics calculated from the collective states of N identical three-level molecules. The coupling constant is $g_0 = 1$. Numerical calculations for N from 1 to 50 show virtually the same results, which implies lack of cooperativity population dynamics. Adapted from ref 58. Copyright 2023 American Chemical Society.

MOLECULAR COOPERATIVITY

The cooperative nature of molecular polaritons is an important open issue in the understanding of polariton-mediated chemistry. The $\sqrt{N}$ factor in the effective cavity coupling strength suggests that the light–matter coupling is collectively enhanced in the molecular response. It has been theoretically and experimentally demonstrated that the Rabi splitting scales with the $\sqrt{N}$ factor.⁵⁵ However, whether this molecular cooperativity can survive in the electronic dynamics, photo-physical processes, and chemical reactions is under debate. The details of local and collective effects in cavity-altered chemistry are an open issue. Strong coupling with few molecules has been reported.⁸ However, all experiments related to chemistry were carried out in the many-molecule regime.^{56,57}

We next explore the role of cooperativity in the charge migration process,⁵⁸ i.e., the ultrafast electronic charge motion upon photoionization before the nuclei have time to move. This is the primary step in many chemical and biochemical reactions.⁵⁹ We explore this issue by using the Tavis–Cummings model, which represents an ensemble of many three-level molecules coupled to a single optical cavity mode. In our model, the photoionized molecule has a ground state $|g\rangle$ and two degenerate excited states $|e_1\rangle$ and $|e_2\rangle$ which represent cations with a localized charge hole at different locations (Figure 7a). The ionized molecules are initially prepared in the $|e_1\rangle$ state, and the charge migration process can be described by the transition from $|e_1\rangle$ to $|e_2\rangle$ with frozen nuclei. Placing N identical photoionized molecules in the optical cavity, the excitation space consists of all combinations of k molecules at e_1 , l molecules at e_2 , and $N - k - l$ molecules at g with the same number of cavity photons. These combinations create an $(N + 1)(N + 2)/2$ -dimensional symmetric basis set of collective states. We further assume that the sum of the transition dipole moments from the ground state to the two excited states is parallel to the cavity polarization: $\mu_{e_1g} + \mu_{e_2g} \parallel \mathbf{e}_c$. The nonzero interaction Hamiltonian elements depends on the number of molecules N : $H_{kl,k-l} = \sqrt{k(N - k - l + 1)}g_0$ and $H_{kl,kl-1} = \sqrt{l(N - k - l + 1)}g_0$, where g_0 is the single-molecule coupling constant.

The charge migration process is followed by a population oscillation between $|e_1\rangle$ and $|e_2\rangle$. We assume that initially all molecules are at $|e_1\rangle$ and numerically calculate the population dynamics of $|g\rangle$, $|e_1\rangle$, and $|e_2\rangle$ for the molecule number N varying from 1 to 50. In contrast with the $\sqrt{N}$ dependence of the Rabi splitting, the charge oscillation pattern shown in Figure 7b is virtually independent of N . The collective factors such as $\sqrt{k(N - k - l + 1)}$, explicitly included in our interaction Hamiltonian matrix elements, cancel out and reduce to the single-molecule result once a local observable such as molecular charge migration is monitored.

Molecular cooperativity provides a convenient realization of the strong coupling regime. However, whether it can affect an observable depends on the local nature of specific chemical processes. Figure 7 demonstrates that unlike spectroscopy, molecular charge dynamics in cavity-altered chemistry is local and shows no many-molecule collective effect. The same conclusion should apply to any local observable such as photophysical processes and chemical reactions.

CONCLUSIONS AND PERSPECTIVES

Substantial efforts have been made on the first-principles modeling of polaritonic systems by generalizing the rich quantum chemistry toolbox such as density functional theory and coupled cluster to strongly coupled molecule–photon systems.⁶⁰ Quantum dynamical methods such as matrix product states and multiconfigurational time-dependent Hartree that can alleviate the exponential scaling of computational cost have been developed and applied to study polaritonic chemistry.^{61,62}

While most current studies employ linearly polarized cavity modes, it is possible to incorporate optical chirality into the cavity field. This can be achieved by, e.g., using Faraday mirrors instead of regular mirrors⁶³ and offers novel opportunities to explore chiral light–matter interactions.⁶⁴ Another interesting direction is to employ several coupled cavities. Coupled cavity arrays can be fabricated with waveguides and photonic crystals and have been suggested as a platform for quantum simulation and quantum networks.⁶⁵

AUTHOR INFORMATION

Corresponding Authors

Bing Gu – Department of Chemistry and Department of Physics, School of Science, Westlake University, Hangzhou, Zhejiang 310030, China; Institute of Natural Sciences, Westlake Institute for Advanced Study, Hangzhou, Zhejiang 310024, China; orcid.org/0000-0002-5787-3334; Email: gubing@westlake.edu.cn

Shaul Mukamel – Department of Chemistry and Department of Physics and Astronomy, University of California, Irvine, California 92697, United States; orcid.org/0000-0002-6015-3135; Email: smukamel@uci.edu

Authors

Yonghao Gu – Department of Chemistry and Department of Physics and Astronomy, University of California, Irvine, California 92697, United States; orcid.org/0000-0002-0868-6620

Vladimir Y. Chernyak – Department of Chemistry and Department of Mathematics, Wayne State University, Detroit, Michigan 48202, United States

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.accounts.3c00280>

Author Contributions

CRedit: **Bing Gu** conceptualization, data curation, investigation, methodology, software, visualization, writing-original draft; **Yonghao Gu** data curation, investigation, software, visualization, writing-original draft; **Vladimir Y. Chernyak** conceptualization, data curation, investigation, writing-original draft; **Shaul Mukamel** conceptualization, funding acquisition, methodology, writing-review & editing.

Notes

The authors declare no competing financial interest.

Biographies

Bing Gu is an Assistant Professor of Chemistry and Physics at Westlake University in China. He received his Ph.D. from the University of South Carolina, Columbia in 2016. He then worked at the University of Rochester and later the University of California, Irvine, as a postdoctoral fellow before joining Westlake University in 2023. His research interests include nonlinear spectroscopy with quantum light, nonadiabatic quantum molecular dynamics, polaritonic chemistry, and quantum hydrodynamics.

Yonghao Gu received his Ph.D. in Physical Chemistry from Fudan University, Shanghai, in 2016 and is currently a postdoctoral research fellow in Prof. Shaul Mukamel's group at the University of California, Irvine. His research interests include method development of quantum chemistry and theoretical study of nonlinear spectroscopy and polariton chemistry.

Vladimir Y. Chernyak is Professor of Chemistry and Professor of Mathematics at Wayne State University. He received his Ph.D. from the USSR Academy of Sciences in 1983. Before joining Wayne State University in 2004, he worked in several Research Institutions of the USSR State Bureau of Standards and USSR Academy of Sciences, the University of Rochester, and Corning Incorporated. His research interests are in the areas of chemical physics, optical spectroscopy, statistical and quantum physics, mathematical physics, computer science, electrical engineering, applied topology, and applied geometry. He is a Fellow of the American Physical Society.

Shaul Mukamel, currently Distinguished Professor of Chemistry and Physics & Astronomy at the University of California, Irvine, received his Ph.D. in 1976 from Tel Aviv University. Following postdoctoral appointments at MIT and the University of California, Berkeley, he held faculty positions at Rice University, the Weizmann Institute, and the University of Rochester before joining UCI in 2003. His research interests broadly span the areas of ultrafast multidimensional spectroscopy of molecules from the infrared to the X-ray regimes, excitons in chromophore aggregates and photosynthetic complexes, non-adiabatic conical intersection dynamics, polaritons in cavities, and molecular electrodynamics.

ACKNOWLEDGMENTS

V.Y.C. and S.M. gratefully acknowledge the support of the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences Award DESC0022134, which primarily funded this work. S.M. gratefully acknowledges the support of the National Science Foundation (Grant CHE-2246379).

REFERENCES

- (1) Gu, B.; Nenov, A.; Segatta, F.; Garavelli, M.; Mukamel, S. Manipulating Core Excitations in Molecules by X-ray Cavities. *Phys. Rev. Lett.* **2021**, 126, No. 053201.
- (2) Gu, B.; Mukamel, S. Optical-Cavity Manipulation of Conical Intersections and Singlet Fission in Pentacene Dimers. *J. Phys. Chem. Lett.* **2021**, 12, 2052–2056.
- (3) Gu, B.; Mukamel, S. Manipulating Two-Photon-Absorption of Cavity Polaritons by Entangled Light. *J. Phys. Chem. Lett.* **2020**, 11, 8177–8182.
- (4) Gu, B.; Mukamel, S. Manipulating Nonadiabatic Conical Intersection Dynamics by Optical Cavities. *Chem. Sci.* **2020**, 11, 1290–1298.
- (5) Purcell, E. M. Spontaneous Emission Probabilities at Radio Frequencies. *Phys. Rev.* **1946**, 69, 681.
- (6) Hopfield, J. J. Theory of the Contribution of Excitons to the Complex Dielectric Constant of Crystals. *Phys. Rev.* **1958**, 112, 1555–1567.
- (7) Vahala, K. J. Optical Microcavities. *Nature* **2003**, 424, 839–846.
- (8) Chikkaraddy, R.; de Nijs, B.; Benz, F.; Barrow, S. J.; Scherman, O. A.; Rosta, E.; Demetriadou, A.; Fox, P.; Hess, O.; Baumberg, J. J. Single-Molecule Strong Coupling at Room Temperature in Plasmonic Nanocavities. *Nature* **2016**, 535, 127–130.
- (9) Boca, A.; Miller, R.; Birnbaum, K. M.; Boozer, A. D.; McKeever, J.; Kimble, H. J. Observation of the Vacuum Rabi Spectrum for One Trapped Atom. *Phys. Rev. Lett.* **2004**, 93, 233603.
- (10) Raizen, M. G.; Thompson, R. J.; Brecha, R. J.; Kimble, H. J.; Carmichael, H. J. Normal-Mode Splitting and Linewidth Averaging for Two-State Atoms in an Optical Cavity. *Phys. Rev. Lett.* **1989**, 63, 240–243.
- (11) Ahn, W.; Triana, J. F.; Recabal, F.; Herrera, F.; Simpkins, B. S. Modification of Ground-State Chemical Reactivity via Light–Matter Coherence in Infrared Cavities. *Science* **2023**, 380, 1165–1168.
- (12) Lidzey, D.; Bradley, D.; Skolnick, M.; Virgili, T.; Walker, S.; Whittaker, D. Strong Exciton–Photon Coupling in an Organic Semiconductor Microcavity. *Nature* **1998**, 395, 53–55.
- (13) Kéna-Cohen, S.; Forrest, S. R. Room-Temperature Polariton Lasing in an Organic Single-Crystal Microcavity. *Nat. Photonics* **2010**, 4, 371–375.
- (14) Coles, D. M.; Yang, Y.; Wang, Y.; Grant, R. T.; Taylor, R. A.; Saikin, S. K.; Aspuru-Guzik, A.; Lidzey, D. G.; Tang, J. K.-H.; Smith, J. M. Strong Coupling between Chlorosomes of Photosynthetic Bacteria and a Confined Optical Cavity Mode. *Nat. Commun.* **2014**, 5, 5561.
- (15) Plumhof, J. D.; Stöferle, T.; Mai, L.; Scherf, U.; Mahrt, R. F. Room-Temperature Bose–Einstein Condensation of Cavity Exciton–Polaritons in a Polymer. *Nat. Mater.* **2014**, 13, 247–252.
- (16) Zhong, X.; Chervy, T.; Wang, S.; George, J.; Thomas, A.; Hutchison, J. A.; Devaux, E.; Genet, C.; Ebbesen, T. W. Non-Radiative

Energy Transfer Mediated by Hybrid Light–Matter States. *Angew. Chem.* **2016**, *128*, 6310–6314.

(17) Xiang, B.; Ribeiro, R. F.; Du, M.; Chen, L.; Yang, Z.; Wang, J.; Yuen-Zhou, J.; Xiong, W. Intermolecular Vibrational Energy Transfer Enabled by Microcavity Strong Light–Matter Coupling. *Science* **2020**, *368*, 665–667.

(18) Avramenko, A. G.; Rury, A. S. Cavity Polaritons Formed from Spatially Separated Quasi-degenerate Porphyrin Excitons: Structural Modulations of Bright and Dark State Energies and Compositions. *J. Phys. Chem. C* **2020**, *126*, 15776–15787.

(19) Avramenko, A. G.; Rury, A. S. Quantum Control of Ultrafast Internal Conversion Using Nanoconfined Virtual Photons. *J. Phys. Chem. Lett.* **2020**, *11*, 1013–1021.

(20) Ebbesen, T. W. Hybrid Light–Matter States in a Molecular and Material Science Perspective. *Acc. Chem. Res.* **2016**, *49*, 2403–2412.

(21) Hirai, K.; Hutchison, J. A.; Uji-i, H. Recent Progress in Vibropolaritonic Chemistry. *ChemPlusChem* **2020**, *85*, 1981–1988.

(22) Polak, D.; Jayaprakash, R.; Lyons, T. P.; Martínez-Martínez, L. Á.; Leventis, A.; Fallon, K. J.; Coulthard, H.; Bossanyi, D. G.; Georgiou, K.; Petty, A. J., II; Anthony, J.; Bronstein, H.; Yuen-Zhou, J.; Tartakovskii, A. I.; Clark, J.; Musser, A. J. Manipulating Molecules with Strong Coupling: Harvesting Triplet Excitons in Organic Exciton Microcavities. *Chem. Sci.* **2020**, *11*, 343–354.

(23) Garcia-Vidal, F. J.; Ciuti, C.; Ebbesen, T. W. Manipulating Matter by Strong Coupling to Vacuum Fields. *Science* **2021**, *373*, eabd0336.

(24) Ribeiro, R. F.; Dunkelberger, A. D.; Xiang, B.; Xiong, W.; Simpkins, B. S.; Owrutsky, J. C.; Yuen-Zhou, J. Theory for Nonlinear Spectroscopy of Vibrational Polaritons. *J. Phys. Chem. Lett.* **2018**, *9*, 3766–3771.

(25) Agranovich, V. M.; Ginzburg, V. In *Crystal Optics with Spatial Dispersion, and Excitons*; Cardona, M., Fulde, P., Queisser, H.-J., Eds.; Springer Series in Solid-State Sciences, Vol. 42; Springer: Berlin, 1984.

(26) Agranovich, V. M. Dispersion of Electromagnetic Waves in Crystals. *Sov. Phys. JETP* **1960**, *37*, 307–313.

(27) Abrikosov, A. A.; Gor'kov, L. P.; Dzyaloshinski, I. E. *Methods of Quantum Field Theory in Statistical Physics*; Prentice-Hall, 1963.

(28) Chu, S.-I.; Telnov, D. A. Beyond the Floquet Theorem: Generalized Floquet Formalisms and Quasienergy Methods for Atomic and Molecular Multiphoton Processes in Intense Laser Fields. *Phys. Rep.* **2004**, *390*, 1–131.

(29) Haroche, S.; Raimond, J.-M. *Exploring the Quantum: Atoms, Cavities, and Photons*; Oxford University Press, 2006.

(30) Cohen-Tannoudji, C.; Dupont-Roc, J.; Grynberg, G. *Photons and Atoms: Introduction to Quantum Electrodynamics*; Wiley, 1989.

(31) Craig, D. P.; Thirunamachandran, T. *Molecular Quantum Electrodynamics: An Introduction to Radiation–Molecule Interactions*; Courier Corporation, 1998.

(32) Mukamel, S. *Principles of Nonlinear Optical Spectroscopy*; Oxford University Press, 1995.

(33) Engelhardt, G.; Cao, J. Polariton Localization and Dispersion Properties of Disordered Quantum Emitters in Multimode Microcavities. *Phys. Rev. Lett.* **2023**, *130*, 213602.

(34) Frisk Kockum, A.; Miranowicz, A.; De Liberato, S.; Savasta, S.; Nori, F. Ultrastrong Coupling between Light and Matter. *Nat. Rev. Phys.* **2019**, *1*, 19–40.

(35) Mandal, A.; Krauss, T. D.; Huo, P. Polariton-Mediated Electron Transfer via Cavity Quantum Electrodynamics. *J. Phys. Chem. B* **2020**, *124*, 6321–6340.

(36) Szidarovszky, T.; Halász, G. J.; Császár, A. G.; Cederbaum, L. S.; Vibók, Á. Conical Intersections Induced by Quantum Light: Field-Dressed Spectra from the Weak to the Ultrastrong Coupling Regimes. *J. Phys. Chem. Lett.* **2018**, *9*, 6215–6223.

(37) Gu, B.; Cavaletto, S. M.; Nascimento, D. R.; Khalil, M.; Govind, N.; Mukamel, S. Manipulating Valence and Core Electronic Excitations of a Transition-Metal Complex Using UV/Vis and X-ray Cavities. *Chem. Sci.* **2021**, *12*, 8088–8095.

(38) Polli, D.; Altoè, P.; Weingart, O.; Spillane, K. M.; Manzoni, C.; Brida, D.; Tomasello, G.; Orlandi, G.; Kukura, P.; Mathies, R. A.;

Garavelli, M.; Cerullo, G. Conical Intersection Dynamics of the Primary Photoisomerization Event in Vision. *Nature* **2010**, *467*, 440–443.

(39) Kang, H.; Lee, K. T.; Jung, B.; Ko, Y. J.; Kim, S. K. Intrinsic Lifetimes of the Excited State of DNA and RNA Bases. *J. Am. Chem. Soc.* **2002**, *124*, 12958–12959.

(40) Kowalewski, M.; Bennett, K.; Rouxel, J. R.; Mukamel, S. Monitoring Nonadiabatic Electron–Nuclear Dynamics in Molecules by Attosecond Streaking of Photoelectrons. *Phys. Rev. Lett.* **2016**, *117*, No. 043201.

(41) Vendrell, O. Coherent Dynamics in Cavity Femtochemistry: Application of the Multi-Configuration Time-Dependent Hartree Method. *Chem. Phys.* **2018**, *509*, 55–65.

(42) Smith, M. B.; Michl, J. Singlet Fission. *Chem. Rev.* **2010**, *110*, 6891–6936.

(43) Martínez-Martínez, L. A.; Du, M.; Ribeiro, R. F.; Kéna-Cohen, S.; Yuen-Zhou, J. Polariton-Assisted Singlet Fission in Acene Aggregates. *J. Phys. Chem. Lett.* **2018**, *9*, 1951–1957.

(44) Climent, C.; Casanova, D.; Feist, J.; García-Vidal, F. J. Not Dark Yet: Strong Light–Matter Coupling Can Accelerate Singlet Fission Dynamics. *arXiv (Physics.Chemical Physics)*, October 5, 2021, 2110.02173, ver. 1. <https://arxiv.org/abs/2110.02173> (accessed 2023-05-12).

(45) Gu, B.; Mukamel, S. Manipulating Nonadiabatic Conical Intersection Dynamics by Optical Cavities. *Chem. Sci.* **2020**, *11*, 1290–1298.

(46) Adams, B. W.; Buth, C.; Cavaletto, S. M.; Evers, J.; Harman, Z.; Keitel, C. H.; Pálffy, A.; Picón, A.; Röhlberger, R.; Rostovtsev, Y.; Tamasaku, K. X-ray Quantum Optics. *J. Mod. Opt.* **2013**, *60*, 2–21.

(47) Tanaka, S.; Chernyak, V.; Mukamel, S. Time-Resolved x-Ray Spectroscopies: Nonlinear Response Functions and Liouville-space Pathways. *Phys. Rev. A* **2001**, *63*, No. 063405.

(48) Grafton, A. B.; Dunkelberger, A. D.; Simpkins, B. S.; Triana, J. F.; Hernández, F. J.; Herrera, F.; Owrutsky, J. C. Excited-State Vibration–Polariton Transitions and Dynamics in Nitroprusside. *Nat. Commun.* **2021**, *12*, 214.

(49) Xiang, B.; Ribeiro, R. F.; Dunkelberger, A. D.; Wang, J.; Li, Y.; Simpkins, B. S.; Owrutsky, J. C.; Yuen-Zhou, J.; Xiong, W. Two-Dimensional Infrared Spectroscopy of Vibrational Polaritons. *Proc. Natl. Acad. Sci. U.S.A.* **2018**, *115*, 4845–4850.

(50) Cho, D.; Gu, B.; Mukamel, S. Optical Cavity Manipulation and Nonlinear UV Molecular Spectroscopy of Conical Intersections in Pyrazine. *J. Am. Chem. Soc.* **2022**, *144*, 7758–7767.

(51) Dorfman, K. E.; Schlawin, F.; Mukamel, S. Nonlinear Optical Signals and Spectroscopy with Quantum Light. *Rev. Mod. Phys.* **2016**, *88*, No. 045008.

(52) Schlawin, F.; Dorfman, K. E.; Mukamel, S. Entangled Two-Photon Absorption Spectroscopy. *Acc. Chem. Res.* **2018**, *51*, 2207–2214.

(53) Raymer, M. G.; Landes, T.; Marcus, A. H. Entangled Two-Photon Absorption by Atoms and Molecules: A Quantum Optics Tutorial. *J. Chem. Phys.* **2021**, *155*, No. 081501.

(54) Gu, B.; Keefer, D.; Aleotti, F.; Nenov, A.; Garavelli, M.; Mukamel, S. Photoisomerization Transition State Manipulation by Entangled Two-Photon Absorption. *Proc. Natl. Acad. Sci. U. S. A.* **2021**, *118*, No. e2116868118.

(55) Wright, A. D.; Nelson, J. C.; Weichman, M. L. Rovibrational Polaritons in Gas-Phase Methane. *J. Am. Chem. Soc.* **2023**, *145*, 5982–5987.

(56) Schwartz, T.; Hutchison, J. A.; Léonard, J.; Genet, C.; Haacke, S.; Ebbesen, T. W. Polariton Dynamics under Strong Light–Molecule Coupling. *ChemPhysChem* **2013**, *14*, 125–131.

(57) Suzuki, M.; Nishiyama, K.; Kani, N.; Yu, X.; Uzumi, K.; Funahashi, M.; Shimokawa, F.; Nakanishi, S.; Tsurumachi, N. Observation of Ultrastrong-Coupling Regime in the Fabry–Pérot Microcavities Made of Metal Mirrors Containing Lemke Dye. *Appl. Phys. Lett.* **2019**, *114*, 191108.

(58) Gu, Y.; Gu, B.; Sun, S.; Yong, H.; Chernyak, V. Y.; Mukamel, S. Manipulating Attosecond Charge Migration in Molecules by Optical Cavities. *J. Am. Chem. Soc.* **2023**, *145*, 14856–14864.

(59) Wörner, H. J.; Arrell, C. A.; Banerji, N.; Cannizzo, A.; Chergui, M.; Das, A. K.; Hamm, P.; Keller, U.; Kraus, P. M.; Liberatore, E.; Lopez-Tarifa, P.; Lucchini, M.; Meuwly, M.; Milne, C.; Moser, J.-E.; Rothlisberger, U.; Smolentsev, G.; Teuscher, J. L.; van Bokhoven, J. A.; Wenger, O. Charge migration and charge transfer in molecular systems. *Struct. Dyn.* **2017**, *4*, No. 061508.

(60) Haugland, T. S.; Ronca, E.; Kjønsstad, E. F.; Rubio, A.; Koch, H. Coupled Cluster Theory for Molecular Polaritons: Changing Ground and Excited States. *Phys. Rev. X* **2020**, *10*, No. 041043.

(61) del Pino, J.; Schröder, F. A. Y. N.; Chin, A. W.; Feist, J.; Garcia-Vidal, F. J. Tensor Network Simulation of Non-Markovian Dynamics in Organic Polaritons. *Phys. Rev. Lett.* **2018**, *121*, 227401.

(62) Vendrell, O. Coherent Dynamics in Cavity Femtochemistry: Application of the Multi-Configuration Time-Dependent Hartree Method. *Chem. Phys.* **2018**, *509*, 55.

(63) Sun, S.; Gu, B.; Mukamel, S. Polariton Ring Currents and Circular Dichroism of Mgporphyrin in a Chiral Cavity. *Chem. Sci.* **2022**, *13*, 1037–1048.

(64) Yoo, S.; Park, Q.-H. Chiral Light-Matter Interaction in Optical Resonators. *Phys. Rev. Lett.* **2015**, *114*, 203003.

(65) Xiang, B.; Wang, J.; Yang, Z.; Xiong, W. Nonlinear Infrared Polaritonic Interaction between Cavities Mediated by Molecular Vibrations at Ultrafast Time Scale. *Sci. Adv.* **2021**, *7*, No. eabf6397.