

Manipulating molecules with quantum light

 Markus Kowalewski^{a,b} and Shaul Mukamel^{a,b,1}

It was first realized by Purcell (1) that the spontaneous emission rate of a quantum system can be enhanced or suppressed by placing it in a resonant radiofrequency cavity. Spontaneous emission as it was first theoretically described by Einstein (2) is not a pure property of matter. It is described by matter coupled to quantized radiation field modes, which can be manipulated in an artificial structure such as a cavity. Cavity quantum electrodynamics (QED) is used to describe such effects that intimately depend on the fact that light is made of photons. Cavity QED has been extensively studied in atoms and the experi-

mental proof was awarded with the Nobel Prize in 2012 (3). It has been applied to cooling of single atoms and for the detection of single atoms and creating and studying states with few photons and few atoms (4). In more recent developments these ideas have been extended to manipulate electronic states (5) and vibrations in molecules (6, 7). In PNAS, Flick et al. (8) introduce recent theoretical developments for the application of cavity QED to molecules and suggest possible novel applications to photochemistry. These include nonadiabatic dynamics of molecules in cavities, the modification of molecular properties, and the integration of QED with density functional theory.

A quantized electromagnetic field mode can be described as a harmonic oscillator whose coordinate is the electric field displacement (Fig. 1A). The zero point energy translates into a nonvanishing field intensity $\langle \epsilon^2 \rangle$ in the ground state $|0\rangle$ (vacuum fluctuations). The electric vacuum field increases for a small cavity volume

$$\epsilon_c = \sqrt{\frac{\hbar\omega_c}{V\epsilon_0}}, \quad [1]$$

where V is the cavity mode volume and ω_c its frequency. Cavity QED is based on the Jaynes–Cummings (JC) model (9), which describes the interaction of a two-level atom with a single quantized field mode:

$$\hat{H}_{JC} = \frac{\hbar\omega_0}{2}(2\hat{\sigma}^\dagger\hat{\sigma} - 1) + \hbar\omega_c\hat{a}^\dagger\hat{a} + \hbar g(\hat{a}^\dagger\hat{\sigma} + \hat{a}\hat{\sigma}^\dagger), \quad [2]$$

where a and σ are the annihilation operators of the field mode and the molecular excitation, respectively, and $\hbar\omega_0$ is the excitation energy of the molecule. The atom–cavity coupling $g = \mu\epsilon_c/2\hbar$ represents the interaction of the cavity field with the molecular dipole μ . The combined states of matter and field obtained from Eq. 2, known as dressed states (3) [or polaritons (10)], are shown in Fig. 1B. The new eigenvalues are split up by $2g\sqrt{n+1}$, where n in the number of photons initially in the cavity and the corresponding eigenfunctions may not be solely attributed to atomic or photonic degrees of freedom

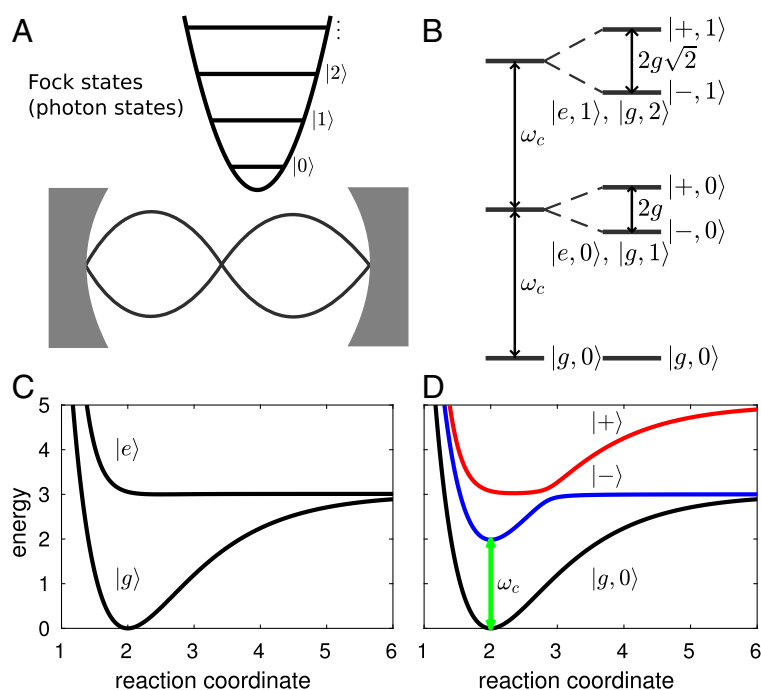


Fig. 1. (A) Illustration of the standing wave cavity mode and the resulting field quantization (Fock states). (B) Combined matter–field states (dressed states, $|\pm, n\rangle$) of the atomic JC model. (C) Bare potential energy surfaces of the ground and excited states. (D) Coupling with the vacuum state of a cavity mode (green arrow) leads to the molecular dressed states $|\pm\rangle$.

^aDepartment of Chemistry, University of California, Irvine, CA 92697-2015; and ^bDepartment of Physics and Astronomy, University of California, Irvine, CA 92697-2015

Author contributions: M.K. and S.M. wrote the paper.

The authors declare no conflict of interest.

See companion article on page 3026 in issue 12 of volume 114.

¹To whom correspondence should be addressed. Email: smukamel@uci.edu.

but are a mixture of both. In most spectroscopic measurements light can be treated as a classical field. In the quantum case the effective field intensity does not vanish even if there are no photons $n = 0$ (i.e., the field is in the vacuum state $|0\rangle$).

Cavity coupling can be classified into three parameter regimes. In the weak coupling regime the combined eigenstates can be written as product field/matter states (left side of Fig. 1B) and exchange of photons between cavity and the atom can be described perturbatively. In the strong coupling regime (9) the coupling of the atom with the vacuum field overcomes dissipative processes. Coherent oscillations and quantum effects associated with the vacuum field can be observed (right side of Fig. 1B). Ultrastrong coupling strengths g exceed the molecular excitation energy. In this regime the ground state $|g, 0\rangle$ of the coupled system will also be modified. Fast, off-resonant oscillations caused by the carrier frequency of the cavity mode (which have been neglected in Eq. 2) must be taken into account. The block diagonal structure of the JC Hamiltonian Eq. 2 (Fig. 1B) is lost, requiring many photon states for a proper description (11).

Strong coupling can be alternatively realized by subjecting the molecule to a classical strong laser field without a cavity. The major difference between a cavity and a strong classical field is that a molecule interacting with a strong laser field can absorb multiple photons opening a variety of reaction channels. In contrast, no photons can be absorbed from the vacuum state $|0\rangle$ of the cavity and the back action of the atoms on the field mode becomes relevant. The response to a classical light is causal; matter responds to the light field only at earlier times—light affects matter but matter does not affect the light. When molecules couple to quantum light the signals are not causal because both affect each other, which results in richer outcomes.

In PNAS, Flick et al. (8) theoretically investigate extensions of the proven concepts of cavity QED in atoms to molecules. This requires the inclusion of nuclear degrees of freedom that undergo a rich dynamics. Strong coupling to a photon mode can severely affect the shape of the potential energy surfaces and the subsequent molecular dynamics. New theoretical tools for quantum chemistry and molecular dynamics are thus called for.

In a molecule the cavity mode can either be resonant to a vibrational transition or an electronic transition. Taking a diatomic molecular model as a test case the authors study the effects of the cavity on its vibrational transitions with increasing coupling strength. The simulated infrared spectra of the coupled cavity–molecule system clearly show a vacuum Rabi splitting, as expected (Fig. 1B). For higher coupling strengths the molecular potential energy surfaces are sufficiently modified such that the equilibrium bond length changes up to 5% compared with the field free molecule. Studying the properties of the coupled system shows that the first electronic state, which is a flat dissociative state, becomes weakly bound. At higher coupling strengths the new dissociation coordinate also acquires a photonic character and becomes a polaritonic molecular coordinate.

The effect of coupling the cavity mode to the electronic states is illustrated in Fig. 1D: The two bare states $|g\rangle$ and $|e\rangle$ (Fig. 1C) result in an unmodified ground state $|g, 0\rangle$ and two dressed states $|\pm, 0\rangle$ (strong coupling regime). Out of resonance both states will mostly resemble the shape of the bare states. At the specific point where the cavity is in resonance with the bare states an avoided crossing is created. At this point all three degrees of freedom, photons, electrons, and vibrations, strongly mix and the Born–Oppenheimer (adiabatic) approximation, which allows for the separation of nuclear and electronic degrees of freedom,

breaks down. A transition between surfaces at the crossing can be viewed as stimulated emission or absorption of a cavity photon. Flick et al. (8) extended the model to a triatomic model, which allows for the formation of conical intersections (CIs) (12) rather than avoided crossings. A CI is formed when two or more potential energy surfaces with at least two vibrational coordinates cross and become degenerate. CIs provide ultrafast non-radiative relaxation pathways, which control product yields and rates of virtually all photochemical processes. In naturally occurring CIs the timescale of the electrons slows down and becomes comparable to that of the nuclei and their timescale separation (Born–Oppenheimer approximation) no longer holds. Introducing the quantized field of the cavity allows one to create CIs between two polariton states in a similar fashion as outlined in Fig. 1C and D. The electronic, nuclear, and photonic degrees are now strongly mixed and create a degenerate point (CI)

In summary, the study by Flick et al. shows that strong coupling to a cavity may alter the chemical properties of molecules, thereby significantly influencing the outcome of coherent control experiments and photochemical reactions.

between two polariton states. The authors show how the shape and location of the degenerate point can be controlled. Creating such single-photon-induced CIs artificially allows one to study and manipulate them in greater detail. This may give access for the measurement of geometric (Berry) phase effects as predicted by theory (12) that so far has eluded experimental detection in molecules.

In summary, the study by Flick et al. (8) shows that strong coupling to a cavity may alter the chemical properties of molecules, thereby significantly influencing the outcome of coherent control experiments and photochemical reactions. This could allow one to modify photochemistry (11, 13) by means photonic catalysts in microcavities. Potential applications include sunlight-assisted decomposition of pollutants, photostabilization of light-sensitive substances, and electron transfer in photovoltaics. To obtain sufficiently strong coupling for the modification of the molecular potential energy surfaces a small cavity mode volume V (Eq. 1) is required. This can be achieved with nanostructures (14). Further enhancement can result from the cooperative response of an ensemble of N molecules interacting coherently with the same cavity mode. The coupling strength and the vacuum Rabi splitting then scale as \sqrt{N} and spontaneous emission rates scale as N . This is known as superradiance (3, 15, 16). The recently reported giant 800-meV Rabi splitting in organic molecules (5) is related to the combined cooperative and cavity enhancement $\sqrt{N/V}$. However, in molecular processes, decoherence caused by the nuclear degrees of freedom (and coupling to the environment) can be expected to partially or completely erode the \sqrt{N} scaling behavior (17). Nevertheless, strong coupling has been reported even for a single molecule (18). The influence of cooperativity and the challenge of decoherence on various molecular properties is an active area of research. Future challenges also include the adaptation of theoretical methods from quantum optics and atomic systems to molecules and quantum chemistry methods. Quantum electrodynamic density functional theory (8) is an example of how both fields of research can be connected.

Cavities offer a powerful means for coupling quantum light to molecules. However, the quantum nature of light may be used for the manipulation and spectroscopic studies of molecules in many other ways that not necessarily involve cavities (19). Conventional nonlinear spectroscopy uses classical light to detect matter properties through the variation of its response with frequencies or time delays. Quantum states of light have been prepared and used in technological applications such as all-optical transistors, quantum cryptography (secure communication), and quantum computing. Importing quantum-state engineering of light to spectroscopic studies is an exciting open frontier. Entangled-photon pairs constitute an invaluable tool in fundamental tests of quantum mechanics—most famously in the violation of Bell's inequalities. One notable advantage for spectroscopy applications is that entangled-photon pairs are not subjected to the classical Fourier limitations on the joint temporal and spectral resolution. Different optical signals and photon counting setups are possible.

Two-photon absorption with classical light scales quadratically with the light intensity and therefore requires a high intensity to be visible against lower-order linear-scaling processes of classical light. With entangled photons, such signals scale linearly. This allows one to carry out microscopy and lithography applications at much lower photon fluxes, eliminating damage to, for example, biological samples. The quantum nature of light manifests in collective effects in many-body systems by its ability to project entanglement back and forth between field and matter. Higher excited states in molecular aggregates may then be prepared and controlled by placing a sample into the beam line of one of the two entangled photons and recording the change of the coincidence count rate (19) with the other photon. It is possible to achieve higher spectral and temporal resolutions and improve spatial resolution by ghost imaging of X-ray photons.

Acknowledgments

This work was supported by National Science Foundation Grant CHE-1361516 and the Alexander von Humboldt Foundation through the Feodor Lynen program (to M.K.).

- 1 Purcell EM (1946) Spontaneous emission probabilities at radio frequencies. *Phys Rev* 69:674.
- 2 Einstein A (1917) Zur Quantentheorie der Strahlung. *Physik Z* 18:121–128.
- 3 Haroche S, Raimond JM (2006) *Exploring the Quantum: Atoms, Cavities, and Photons*, Oxford Graduate Texts (Oxford Univ Press, Oxford), 1st Ed.
- 4 Hood CJ, Chapman MS, Lynn TW, Kimble HJ (1998) Real-Time cavity QED with single atoms. *Phys Rev Lett* 80(19):4157–4160.
- 5 Hutchison JA, Schwartz T, Genet C, Devaux E, Ebbesen TW (2012) Modifying chemical landscapes by coupling to vacuum fields. *Angew Chem Int Ed Engl* 51(7):1592–1596.
- 6 Shalabney A, et al. (2015) Enhanced Raman scattering from vibro-polariton hybrid states. *Angew Chem Int Ed Engl* 54(27):7971–7975.
- 7 Simpkins BS, et al. (2015) Spanning strong to weak normal mode coupling between vibrational and Fabry–Pérot cavity modes through tuning of vibrational absorption strength. *ACS Photonics* 2(10):1460–1467.
- 8 Flick J, Ruggenthaler M, Appel H, Rubio A (2017) Atoms and molecules in cavities, from weak to strong coupling in quantum-electrodynamics (QED) chemistry. *Proc Natl Acad Sci USA* 114(12):3026–3034.
- 9 Jaynes ET, Cummings FW (1963) Comparison of quantum and semiclassical radiation theories with application to the beam maser. *Proc IEEE* 51(1):89–109.
- 10 Hopfield JJ (1958) Theory of the contribution of excitons to the complex dielectric constant of crystals. *Phys Rev* 112(5):1555–1567.
- 11 Kowalewski M, Bennett K, Mukamel S (2016) Cavity femtochemistry: Manipulating nonadiabatic dynamics at avoided crossings. *J Phys Chem Lett* 7:2050–2054.
- 12 Domcke W, Yarkony DR, Köppel H (2011) *Conical Intersections* (World Scientific, Singapore), Vol 17.
- 13 Galego J, Garcia-Vidal FJ, Feist J (2016) Suppressing photochemical reactions with quantized light fields. *Nat Commun* 7:13841.
- 14 Tomljenovic-Hanic S, Steel MJ, de Sterke CM, Salzman J (2006) Diamond based photonic crystal microcavities. *Opt Express* 14(8):3556–3562.
- 15 Dicke RH (1954) Coherence in spontaneous radiation processes. *Phys Rev* 93(1):99–110.
- 16 Scully MO, Svidzinsky AA (2009) The super of superradiance. *Science* 325(5947):1510–1511.
- 17 Spano FC (2015) Optical microcavities enhance the exciton coherence length and eliminate vibronic coupling in J-aggregates. *J Chem Phys* 142(18):184707.
- 18 Faez S, Türschmann P, Haakh HR, Götzinger S, Sandoghdar V (2014) Coherent interaction of light and single molecules in a dielectric nanoguide. *Phys Rev Lett* 113(21):213601.
- 19 Dorfman KE, Schlavin F, Mukamel S (2016) Nonlinear optical signals and spectroscopy with quantum light. *Rev Mod Phys* 88:045008.