Many-molecule reaction triggered by a single photon in polaritonic chemistry

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The second law of photochemistry states that in most cases, no more than one molecule is activated for an excited-state reaction for each photon absorbed by a collection of molecules. In this work, we demonstrate that it is possible to trigger a many-molecule reaction using only one photon by strongly coupling the molecular ensemble to a confined light mode. The collective nature of the resulting hybrid states of the system (the so-called polaritons) leads to the formation of a polaritonic “supermolecule” involving the degrees of freedom of all molecules, opening a reaction path on which all involved molecules undergo a chemical transformation. We theoretically investigate the system conditions for this effect to take place and be enhanced.

Photochemical reactions underlie many essential biological functions, such as vision or photosynthesis. In this context, the second law of photochemistry (also known as Stark-Einstein law) states that “one quantum of light is absorbed per molecule of absorbing and reacting substance” [1]. This means that the quantum yield \( \phi = \frac{N_{\text{prod}}}{N_{\text{phot}}} \) of the reaction, which describes the percentage of molecules that end up in the desired reaction product per absorbed photon, has a maximum value of 1. This limit can be overcome in some specific cases, such as in photochemically induced chain reactions [2, 3], or in systems that support singlet fission to create multiple triplet excitons (and thus electron-hole pairs) in solar cells [4, 5]. In this work, we demonstrate a novel and general approach to circumvent the Stark-Einstein law by exploiting the collective nature of polaritonic (hybrid light-matter) states formed by bringing a collection of molecules into strong coupling with a confined light mode. We show that this can allow many molecules to undergo a photochemical reaction after excitation by just a single photon. Polaritonic chemistry, i.e., the potential to manipulate chemical structure and reactions through the formation of polaritons was experimentally demonstrated in 2012 [6], and has become the topic of intense experimental and theoretical research in the past few years [7–15]. However, existing applications and proposals have been limited to enhancing or suppressing the rates of single-molecule reactions. In contrast, we here show that polaritonic chemistry can open fundamentally new pathways that allow for reactions that are not present in the uncoupled system, and thus possess the potential to unlock a new class of collective reactions.

The mechanism we introduce relies on the delocalized character of the hybrid light-matter excitations (polaritons) formed under strong coupling, which conceptually leads to the formation of a single “supermolecule” involving all the molecules as well as the trapped photon. The photochemical reaction induced in this “supermolecule” can then lead to most or even all of its molecular constituents undergoing a structural change, corresponding to an effective quantum yield significantly larger than 1, although it can obviously not lead to a violation of energy conservation. We thus investigate a class of reactions that release energy, i.e., where the initial starting state after absorption of a photon has higher energy than the final state, in which all involved molecules have undergone a reaction. We focus on a class of model molecules with a structure as proposed for use in solar energy storage [16–18], described within a simplified model treating a single reaction coordinate, as shown in Fig. 1a. In our model molecule, the electronic ground state contains two local minima: a stable ground-state configuration (at \( q = q_g \approx 0.8 \text{ a.u.} \)) and a metastable configuration (at \( q = q_m \approx 0.7 \text{ a.u.} \)) which contains a stored energy of about 1 eV. The activation barrier for thermal relaxation from the metastable configuration to the global minimum has a height of more than 1 eV, leading to a lifetime on the order of days or even years for the metastable configuration [19], and thus making it interesting for solar energy storage. In addition, the molecule possesses an excited state with a relatively flat potential minimum close to the ground transition state. As indicated in Fig. 1a, vibrational relaxation on the excited-state surface and subsequent radiative decay gives a roughly equal quantum yield for reaching either the stable or the metastable configuration in the electronic ground state. As expected in a conventional photochemical reaction, the quantum yields in the bare molecule add up to one (indeed, the Stark-Einstein law can be reformulated as “the sum of quantum yields must be unity”).

We now assume that a collection of these molecules is placed inside a photonic structure supporting a single confined light mode. This could be physically realized using a variety of approaches, such as dielectric microcavities, photonic crystal cavities, or plasmonic nanocavities [20–26]. We analyze the system using the methods developed in our previous work [8, 9], which describe the collective structure of the coupled system of many-molecules and the photon mode through the use of polaritonic potential energy surfaces (PES) encompassing the nuclear degrees of freedom of all molecules. This picture immediately allows to take into account and understand the collective motion.
induced on the molecules through their mutual coupling to the photonic mode. For the specific case of five molecules, we show the coupled PES in Fig. 1b. Here, we take a cut of the five-dimensional PES where only the first molecule \( q_1 \) is allowed to move, while all others are fixed to the equilibrium position of the metastable ground-state configuration \( q_i = q_{\text{ms}} \) for \( i = 2, \ldots, 5 \).

Already for the motion of just a single molecule, our results show that the quantum yield for the energy-releasing back-reaction can be significantly enhanced under strong coupling. The lowest-energy excited PES (see Fig. 1b) is formed by hybridization of the uncoupled excited-state surfaces of the molecules with the surface representing a photon in the cavity and the molecule in the ground state (a copy of the ground-state surface shifted upwards by the photon energy of the confined light mode). The photon energy \( \omega_c = 2.55 \text{ eV} \) is close to resonant with the electronic excitation energy at the metastable configuration \( q = q_{\text{ms}} \), while most other molecular configurations (and specifically, the stable configuration \( q = q_s \)) are out of resonance with the cavity. This implies that the nature of the lowest excited-state PES changes depending on the molecular position \( q \), corresponding to a polariton in some cases, and corresponding to a bare molecular state in others (as indicated by the color scale in Fig. 1). In the polaritonic states, each molecule is in its electronic ground state most of the time (since the excitation is distributed over all the molecules and the photonic mode), such that the polaritonic parts of the lowest excited-state PES inherit their shape mostly from the ground-state PES [9]. This leads to the formation of a new minimum in the lowest excited PES at the same position as the fully relaxed ground-state minimum \( q_s \). However, in contrast to the ground-state PES, there is no significant activation barrier to vibrational relaxation within the lowest excited-state PES. Instead, a “bridge” is formed, with a shape closely resembling that of the bare-molecule excited-state PES due to the fact that the cavity is far-detuned from the excited state in that area of configuration space (around \( q_1 \approx 0 \)). In the absence of barriers, a molecular system will quickly relax to the lowest-energy vibrational state on the lowest excited-state PES, according to Kasha’s rule [27].

The vibrational relaxation in the lowest excited hybrid light-matter PES will thus lead to localization of the nuclear wave packet close to the ground-state minimum \( q_s \). If radiative decay happens at this point, this would give a quantum yield of essentially unity for the back-reaction from the metastable to the stable configuration. While this already presents a large cavity-induced change of the photochemical properties of such molecules, we next show that the collective nature of the polaritons can result in an even more dramatic qualitative change that allows the system to keep releasing energy, with all molecules relaxing from the metastable to the stable configuration one after the other.

To understand this, we have to take into account that the polaritonic PESs formed under strong coupling encompass the nuclear degrees of freedom of all involved molecules [8, 9]. This collective nature can in particular also allow nuclear motion on different molecules to become coupled, and in the current case creates a reaction path along which the system can release the energy stored in all molecules, while staying on a single adiabatic PES reached by single-photon absorption in the initial state. This is demonstrated for motion of two of the involved molecules in Fig. 2a, which shows a two-dimensional cut of the PES of the lowest-energy excited state (with all other molecules again frozen in the metastable position \( q = q_{\text{ms}} \)). We calculate the minimum energy path (MEP) connecting the initial configuration \( q_1 = q_2 = q_{\text{ms}} \) to the location where the first two molecules have released their stored energy \( (q_1 = q_2 = q_s) \) using the nudged elastic band method [28]. Along this path, indicated as a series of points in Fig. 2a, there are no significant reaction barriers, such that vibrational relaxation after absorption of a single photon indeed can lead to deactivation of both molecules. The MEP also demonstrates that, to a good approximation, the reaction proceeds in steps, with the molecules moving one after the other (i.e., in the first leg, only \( q_1 \) changes, while in the second leg, only \( q_2 \) changes). We note here that due to the indistinguishability of the molecules, there is an equivalent path where the order of motion of the molecules is reversed.

FIG. 1. Potential energy surfaces of a system with \( N = 5 \) molecules and one light mode under motion of one molecule (a) without light-matter coupling, and (b) in the strong coupling regime for \( \Omega_R = 0.3 \text{ eV} \) at the initial position \( q_1 = q_{\text{ms}} \approx -0.7 \text{ a.u.} \). The photon energy is \( \omega_c = 2.55 \text{ eV} \). The color scale represents the cavity mode fraction of the excited states, going from pure photon (purple) to pure exciton (orange).
In order to gain additional insight into the properties of the polariton states that enable this step-wise many-molecule reaction triggered by a single photon, we further analyze the lowest excited PES by showing its molecular participation ratio in Fig. 2b. Here, the molecular participation ratio is defined as [29]

\[ P_{\alpha}(\vec{q}) = \frac{\sum_{i} |\langle \epsilon_i | \Psi_{\alpha}(\vec{q}) \rangle|^2}{\sum_{i} |\langle \epsilon_i | \Psi_{\alpha}(\vec{q}) \rangle|^4}, \]

where \( |\epsilon_i\rangle \) denotes the excited state of molecule \( i \), and the sums are over all molecules. The participation ratio gives an estimate of the number of molecular states that possess a significant weight in a given state \( |\Psi_{\alpha}\rangle \), with possible values ranging from \( P_{\alpha} = 1 \) to \( P_{\alpha} = N \) (for \( N \) molecules). Analyzing it for the lowest-energy excited state PES (see Fig. 2b) demonstrates that the surface at the starting point corresponds to a collective polariton, with the excitation equally distributed over all molecules. Along the MEP, the excitation collapses onto a single molecule (the one that is moving), demonstrated by the participation ratio decreasing to 1 for \( q_1 \lesssim -0.5 \) a.u. and \( q_1 \lesssim 0.4 \) a.u.. As the molecule moves, it again enters into resonance with the cavity (and the other molecules) and the state changes character to a fully delocalized polariton with \( P_{LX} = N \) (at \( q_1 \approx 0.45 \) a.u.). However, as the first molecule keeps moving, it falls out of resonance again and effectively “drops out” of the polaritonic state, leaving the excitation in a polaritonic state distributed over the photonic mode and the remaining \( N - 1 \) molecules (\( P_{LX} = 4 \)), which then forms the starting point for the second molecule to undergo the reaction. Following the MEP along the second leg (where \( q_1 \approx q_5 \) and \( q_2 \) moves from \( q_{\text{ms}} \) to \( q_{\text{s}} \)), the same process repeats, but now involving one less molecule.

We now demonstrate that the same process can keep repeating for many molecules. To this end, we calculate the MEP for varying numbers of molecules from \( N = 2 \) to \( N = 50 \), with a collective Rabi splitting of \( \Omega_R = 0.3 \) eV in the initial molecular configuration (\( q_i = q_{\text{ms}} \) for all \( i \)) for all cases. As shown in Fig. 2c, the energy profile along the MEP is structurally similar for any number of molecules. The main change is that for larger values of \( N \), the collective protection effect demonstrated in [9] makes the PES resemble the shape of the uncoupled PES more strongly, leading to a less smooth MEP with slightly higher barriers, comparable to the average thermal kinetic energy at room temperature. In addition, the significant change of collective state when passing the barrier (with the excitation collapsing from all molecules onto a single one along the “bridge”) leads to narrow avoided crossings in the adiabatic picture. In a diabatic picture formed by the purely polaritonic PES and the single-molecule excited PES, their coupling can be shown to scale with \( N^{-1/2} \) [9] (for a fixed collective Rabi frequency), such that the transition rate to enter into and leave from the “bridge” part of the lowest excited-state PES scales with \( N^{-1} \). However, there are many equivalent paths in each step (as any of the remaining molecules could undergo the reaction), removing the overall scaling with \( N \) for the probability of passing over an arbitrary one of the multiple equivalent barriers and implies that using standard transition state theory provides a good approximation for the average time taken to pass the involved barriers. This gives \( \tau \approx \frac{A}{\kappa_{3T}} \exp \left( \frac{\Delta E}{k_B T} \right) \lesssim 1 \) ps at room temperature [19], even without taking into account that the wavepacket arrives at the second, higher, barrier with significant kinetic energy. This highlights the importance of the lifetime of the hybrid light-matter states to determine the feasibility of triggering multiple reactions with a single photon. In most current experiments, polariton lifetimes (which are an average of the lifetimes of their constituents) are very short, leading to highly energetic reactive states that can give rise to multiple reactions even without taking into account that the wavepacket arrives at the second, higher, barrier with significant kinetic energy. This highlights the importance of the lifetime of the hybrid light-matter states to determine the feasibility of triggering multiple reactions with a single photon.
mirrors. In contrast, the lifetime of the molecular excitations can be limited by their spontaneous radiative decay, which is on the order of nanoseconds for typical organic molecules. Consequently, if long-lived photonic modes as available in low-loss dielectric structures such as photonic crystals or microtoroidal cavities are used instead, there is no fundamental reason preventing polariton lifetimes that approach nanoseconds. This would thus give enough time for thousands of molecules to undergo a reaction before the excitation is lost due to radiative decay.

In conclusion, we have demonstrated that under strong coupling, a single photon could be used to trigger a photochemical reaction in many molecules. This corresponds to an effective quantum yield (number of reactant molecules per absorbed photon) of the reaction that is significantly larger than one, and thus provides a possible pathway to break the second (or Stark-Einstein) law of photochemistry. The basic physical effect responsible for this surprising feature is the delocalized nature of the polaritonic states obtained under collective strong coupling, which require a treatment of the whole collection of molecules as a single polaritonic “supermolecule”. For the specific model studied here, this strategy could resolve one of the main problems of solar energy storage: How to efficiently retrieve the stored energy from molecules that are designed for the opposite purpose, i.e., for storing energy very efficiently under normal conditions [17, 18]. By reversibly bringing the system into strong coupling (e.g., through a moving mirror that brings the cavity into and out of resonance), one could thus trigger the release the stored energy through absorption of a single ambient photon.

We thank G. Groenhof for helpful discussions. This work has been funded by the European Research Council under grant agreements ERC-2011-AdG-290981 and ERC-2016-STG-714870, by the European Union Seventh Framework Programme under grant agreement FP7-PEOPLE-2013-CIG-618229, and the Spanish MINECO under contract MAT2014-53432-C5-5-R and the “María de Maeztu” program for Units of Excellence in R&D (MDM-2014-0377).

Appendix: Theoretical model

We here describe the molecular model in more detail. The adiabatic PESs of the single bare molecule are both constructed independently from two coupled harmonic potentials as follows:

\[ V_i(q) = \frac{1}{2} \left( v_i(q) + w_i(q) - \sqrt{4h_i^2 + [v_i(q) - w_i(q)]^2} \right), \]  
(A.2)

where \( i \in \{ gs, es \} \) indicates either the ground state or excited state PES. The terms \( v_i(q) \) and \( w_i(q) \), coupled through \( h_i \), are harmonic (i.e., quadratic) potentials. For the case of \( V_{gs}(q) \) the harmonic potentials are exactly centered at \( q_i \) and \( q_{ms} \), respectively, while the ones for \( V_{es}(q) \) are slightly offset with respect to these configurations. Although there is a relatively large number of free parameters that control the molecular details, we have checked the robustness of our results against reasonable variations.

When introducing the quantized light mode to the system, its coupling to the molecules is accounted for through an additional term in the Hamiltonian, given by the scalar product of the molecular dipole moment \( \hat{\mu}(q) \) and the EM single-photon electric field strength \( E_{1ph} \). For simplicity, we use a dipole moment that is constant along the reaction coordinate and assume perfect alignment between the molecular dipoles and the electric field direction. We have checked that these assumptions do not significantly affect the results presented above. The electronic and photonic part of the full \( N \)-molecule system Hamiltonian (which determines the hybrid light-matter PES on which nuclear motion takes place) is then given by:

\[ \hat{H}_{SC}(q) = \omega_c \hat{a} \hat{a} + \sum_i \left( \hat{V}(q_i) + \hat{\mu}(q_i) \cdot \hat{E}_{1ph}(\hat{a} + \hat{a}^\dagger) \right), \]  
(A.3)

where \( \hat{V} \) is the diagonal electronic potential operator with the previously calculated PESs \( V_{gs}(q) \) and \( V_{es}(q) \), and \( \hat{a}^\dagger \) and \( \hat{a} \) are the bosonic creation and annihilation operators associated with the confined light mode of energy \( \omega_c \). Diagonalization of \( \hat{H}_{SC} \) within the single-excitation subspace yields the polaritonic PES. The collective coupling strength can then be parametrized through the collective Rabi frequency \( \Omega_R = 2\sqrt{N} \hat{\mu} \cdot \hat{E}_{1ph} \).

To understand the approximate classical trajectory that defines the reaction coordinate of the full “supermolecule” system, we calculate the minimum energy path between the initial and final configurations using the nudged elastic band method. For the initial position, we assume that all molecules are at \( q = q_{ms} \), corresponding to short-pulse excitation from the ground state in the metastable configuration, according to the Franck-Condon principle. For the final position, we use \( q_i = q_f \) for all \( i \), i.e., the position where all the molecules are in the stable configuration (corresponding to the global minimum of the PES). Due to the indistinguishability of our molecules, any of the available molecules can undergo the reaction in each step, and there are \( N! \) equivalent paths from the initial to the final position. In the results presented above, we thus show only one of these equivalent paths (the one in which the order of reactions corresponds to the numbering of the molecules).

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