Cavity-Modulated Quantum Control of Chemical Reactions

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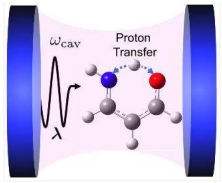
Chemical Reactions in Cavity

- Chemical processes are all around us. They take place in atomic scales driven by complicated mechanisms. As the movements of molecules are fast and tiny, they are difficult to control.
- Optical cavities can generate strong and well-defined light field, tuned at specific energies. When the chemicals are strongly-coupled to cavity, the potential energy surfaces or reactant are altered correspondingly.
- This cavity quantum electrodynamics (QED) chemistry opens new possibilities for guiding reactions along desired pathways. Yet a detailed understanding of how electronic degrees of freedom strongly couple with light requires theoretical model.[1]

Proton Transfer Reaction

- Proton transfer (PT) is an essential process in many fundamental chemical and biological reactions and has application in fuel cells, stable white light generation, and solar energy harvesting devices.
- Excited-state intramolecular proton transfer (ESIPT) has also gained a lot of interest in recent years. Ultrafast ESIPT occurs in sub-picosecond timescale and has high efficiency.



Modelling Hamiltonian

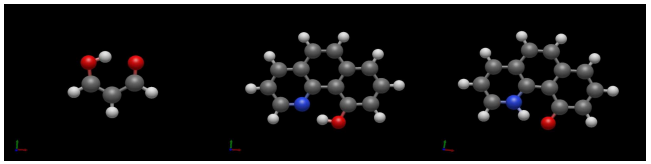
- The interaction between the molecule and photons can be described by the Pauli-Fierz Hamiltonian.

$$\hat{H} = \hat{H}^e + \omega_{cav} b^\dagger b - \sqrt{\frac{\omega_{cav}}{2}}(\lambda \cdot \Delta d)(b^\dagger + b) + \frac{1}{2}(\lambda \cdot \Delta d)^2$$

- The first term is the electronic Hamiltonian within the Born–Oppenheimer approximation.
- The second term denotes the photonic Hamiltonian for a single cavity mode.
- The third term describes the dipolar coupling between the electronic and the photonic degrees of freedom.
- The last term describes the dipole self-energy, which is independent of the cavity mode.
- Since the last term is always positive, the ground state is thus bounded from below, allowing us to perform self-consistent field calculations.

Systems of Interest

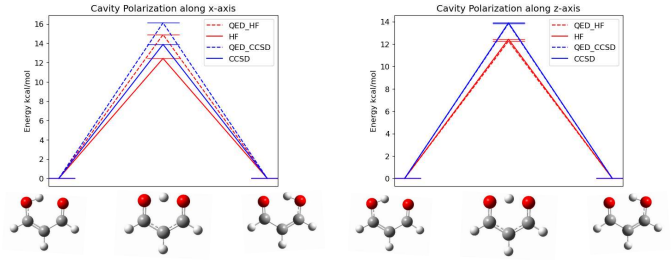
- We studied two systems that undergo proton transfer reaction: malonaldehyde (left) and10-hydroxybenzo[h]quinoline (denoted as HBQ) (middle, right). The second complex tautomerize its structure from enol form in ground state (middle) to keto form (right) under ESIPT.



Computational Methods

- The calculation script was initially retrieved from work by Pavosevic et al. [2] and adjusted. The results for malonaldehyde are consistent with literature. All calculations performed with Psi4Numpy package in python.
- The QED calculations were performed in an optical cavity with frequency ω= 3 eV and coupling strength λ= 0.1 au, which both are within the range of current experimental setups. The x-direction of polarized light is set as the direction of proton transfer, while z-direction is perpendicular to molecular planes.
- To demonstrate the impact of including photonic Hamiltonian in the calculations, we first compute single point energies of optimized structure using traditional Hartree-Fock (HF) and Coupled-Cluster Single-Double (CCSD). While the former gives an approximation of the energy of many-body system, and the latter accounts for electron correlations and further improves accuracy. The results are compared to electrodynamics results (QED-HF and QED-CCSD), whose Hamiltonians described in previous section.

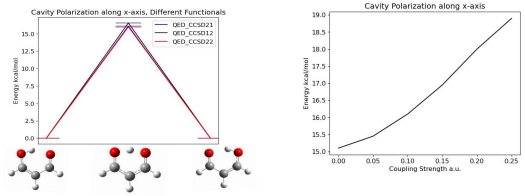
Results



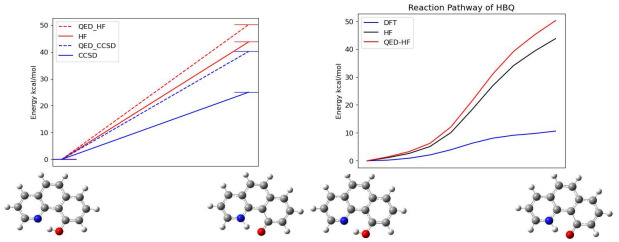
- The energy barrier of transition state is higher when coupled to cavity polarized to the proton transfer direction and remains almost the same when polarized perpendicular to the plane.

Results Continued

- As we modify the QED-CCSD-mn parameters, which denote the highest degree of interactions involving m electrons and n photons, there is a corresponding alteration in the energy of the transition state. QED-CCSD-21 effectively balances computational cost with accuracy.
- The energy barrier increases with growing coupling strength between the system and cavity.



- Moving on to the HBQ study, the energy barrier between enol and keto states significantly increase when coupled to cavity (~15 kcal/mol in the case of CCSD).
- Reaction pathway of the proton transferred process shows that the contribution of photonic coupling is small near enol ground state by grows rapidly as approaching to the keto form.
- Comparisons with literature [3] DFT results suggest an overestimation of the energy barrier. This discrepancy may be attributed to the inadequacy of the basis set size..



Future Work and References

- Improve the accuracy in calculations by using larger basis-sets.
- Apply the methodology to other chemical reactions.
- Adjust the model Hamiltonian to make it applicable to excited state manifold.

[1 Ebbesen. T. W. Hybrid light–matter states in a molecular and material science perspective. Accounts of chemical research 2016, 49, 2403–2412.
[2] Pavosevic, F.; Hammes-Schiffer, S.; Rubio, A.; Flick, J. Cavity-Modulated Proton Transfer Reactions. Journal of the American Chemical Society 2022, 144, 4995–5002.
[3] Loe, C. M.; Liekhus-Schmaltz, C.; Govind, N.; Khalil, M. Spectral signatures of ultrafast excited-state intramolecular proton transfer from computational multi-edge transient x-ray absorption spectroscopy. The Journal of Physical Chemistry Letters 2021, 12, 9840–9847.

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