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Modulating Molecular Motions with Exciton Polariton Based on Correlated Electron-Nuclear Dynamics

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Abstract

Light-driven rotary molecular motors (LDRMs)[1] can transform the energy of light to rotary motion of one part of the molecule with respect to another. The energy of the mechanical motion can be harnessed in various nanosized devices, which already find first applications in fields such as nanotechnology, optogenetics, synthetic biology, nanomedicine, and functional materials. For a long while, various stimuli orthogonal to the motor's source of energy were used to manipulate its operational characteristics; such as the speed of rotation. However, these stimuli employed predominantly chemical means and were difficult to apply *in situ* during the motor's operation.

Here, we investigate possibilities arising from strong light-matter interactions occurring in optical cavities to alter characteristics of the excited state decay in molecular motor molecule. By performing nonadiabatic dynamics (NAMD) simulations of motor's photodynamics in the presence of strong coupling with a cavity mode, we use the Jaynes-Cummings (JC) model to introduce a strong coupling between a lossless cavity mode with an LDRM described as a two-level molecular system. The electronic states of LDRM in the presence of the cavity mode will be described by the spin-restricted ensemble-referenced Kohn-Sham (REKS) method and its state-averaged (SA-REKS) and state-interaction (SI-SA-REKS, or SSR) variants modified to accommodate the JC model. The SSR/REKS method will be used in a simplified density functional tight-binding (DFTB) formulation, *i.e.* DFTB/SSR, which enables one to study very large molecular systems at a very low computational cost. [2] We employ surface hopping dynamics based on exact factorization [3] for NAMD simulation to account for electron-nuclear correlation in polariton states. As a result, it was found that the coupling with a mode detuned off resonance with the molecular optical transition offers a means to considerably increase the excited state decay lifetime and to either inhibit or slow down the motor's rotation.

References
[1] Nature **401** (1999) 152-155, J. Am. Chem. Soc. 124 (2002) 5037-5051
[2] J. Chem. Phys. **160** (2024) 154103
[3] J. Phys. Chem. Lett. **9** (2018) 1097-1104, J. Comp. Chem. **42** (2021) 1755-1766