Mirrors and reaction rates: how 'quantum' is vibrational polariton chemistry?

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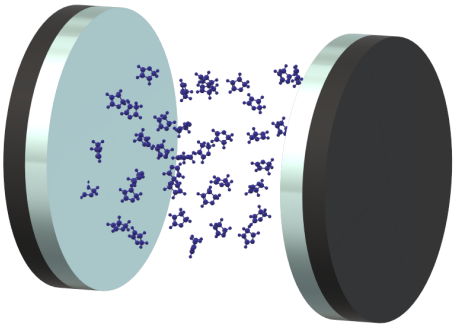
A recent series of experiments [1-4] has shown that certain chemical reactions can be sped up or slowed down just by placing the reaction mixture between a pair of mirrors (in a so-called 'optical cavity'). The origins of this surprising phenomenon are still poorly understood. Simple transition state theory maintains that an optical cavity cannot affect reaction rates. More advanced theories do predict a cavity effect, but fail to replicate the experimental finding that rates only change if the cavity is tuned ‘on resonance’, i.e. if one of the standing light waves inside the cavity closely matches a molecular vibrational frequency. It is only recently that this resonant effect emerged for the first time in a computational study [5], which involved a full quantum-dynamical simulation of a model system. To better understand the underlying mechanism, we studied the same model system using an approximate method (ring-polymer molecular dynamics, or RPMD) that captures quantum statistical effects, such as zero-point energy and tunneling, but treats dynamics classically. In general this approach accurately predicts rate constants for reactions in solution, while remaining computationally tractable for atomistic simulations. Whether or not RPMD can reproduce the resonance effects will help us understand how an optical cavity alters chemical reactivity. This has important practical implications for future work in the field, since many affordable but approximate methods would be disqualified if the cavity effect turned out to be fully quantum dynamical in nature.



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