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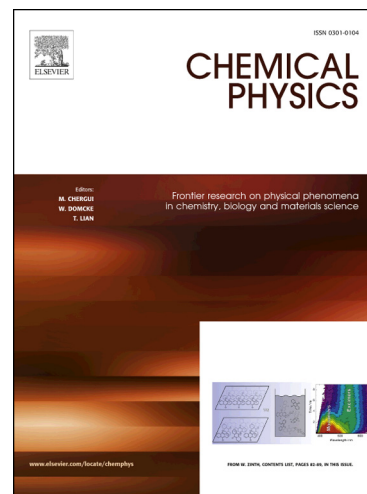
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Coherent dynamics in cavity femtochemistry: application of the multi-configuration time-dependent Hartree method.

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Abstract

The photochemistry of a molecular ensemble coupled to a resonance cavity and triggered by a femtosecond laser pulse is investigated from a real-time, quantum dynamics perspective with the multi-configuration time-dependent Hartree method. Coherent excitation of a superposition of electronic states in the ensemble leads to superradiant energy transfer to the cavity characterized by quadratic scaling with the number of molecules. Electronic decoherence associated with loss of nuclear wave packet overlap among those states destroys superradiant energy transfer, returning to a linear regime. For equal pump laser conditions, the photoexcitation probability per molecule decreases with increase of the number of molecules inside the cavity. This is caused by a loss of resonance condition of the laser with the bright electronic-photonic states of the coupled cavity-ensemble system. Increase of the laser bandwidth restores the energy transferred per molecule and the trigger probability remains independent of the number of molecules in the cavity.

Keywords: cavity electrodynamics, femtochemistry, superradiance, quantum dynamics

1. Introduction

The interaction of atoms [1–5] and ions [6] with quantized light has long been well known and investigated in depth. In recent years, interest for the fundamental properties and technological applications of hybrid light-matter systems of molecular nature is quickly raising, which is motivated to a large extent by the high tunability and relative ease of preparation of such systems [7–12]. From a *chemical* perspective, hybrid systems composed of a molecular ensemble coupled to a resonance cavity can lead to novel strategies to steer [8, 10, 12–17] and spectroscopically probe [18] the molecular properties and response of their individual members by exploiting their collective coupling to the cavity.

Recent theoretical investigations have elucidated cavity effects on the non-adiabatic molecular dynamics of a single coupled molecule [16, 19]. The effect on bonding and electronic structure parameters of molecules in a cavity has been as well the subject of recent investigations [14, 20–23]. As expected, such investigations confirm that structural properties such as bond length or orientation are, to a large extent, related to the individual coupling strength of each molecule to the cavity.

Specially interesting are theoretical proposals to exploit collective coupling effects as a way to alter the chemical evolution of the molecules in the cavity. These may involve either quenching [17] or enhancing [24] photochemical reactions in excited electronic states, in which the presence

of a molecular ensemble becomes important. In Ref. [17], for example, it was proposed that a photochemical reaction can be suppressed by the admixture of ground state character, which features a potential energy barrier, to some of the excited polaritonic (i.e. involving coupled electronic and photonic degrees of freedom) potential energy surfaces (PES), whereby an initial wavepacket was assumed to evolve on the lowest polaritonic PES after an instantaneous trigger process. In this respect, there is experimental evidence that, at least for reaction rates, the alteration of chemically relevant properties by a cavity is possible [10].

The quick increase in dimensionality of the Hilbert space when describing molecular-cavity problems involving a molecular ensemble has lead to the application of different kinds of theory approaches. On the one hand, an adiabatic separation of nuclear and electronic and photonic degrees of freedom can be invoked, which leads to the construction of polaritonic PES. To obtain those, the polaritonic Hamiltonian parametrized by the nuclear positions is diagonalized, very often in the single molecular electronic excitation space, such that the rank of the Hamiltonian matrix grows linearly with the number of molecules N [17, 24, 25]. Therefore, such treatments have been able to account for situations with a low excitation density – i.e. a low number of cavity photons per molecule.

On the other hand, full quantum dynamics studies based on the standard method, meaning a product-grid representation of the wavefunction for all degrees of freedom, have been reported [14, 16, 19, 23]. These approaches naturally account for quantum evolution of nuclear, electronic and

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