

Manipulating Ultrafast Nondiabatic Dynamics of Molecules in Optical Cavities

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Abstract: Strong coupling of molecules to the vacuum field of a cavity can modify the potential energy surfaces, opening new photochemical reaction pathways. We theoretically investigate the ultrafast dynamics of molecules confined in optical micro cavities.

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1. Introduction

Cavity quantum electrodynamics is a well established field of research, which has successfully demonstrated the field quantization of resonator modes experimentally and theoretically. The experiments are usually done with atoms and associated with slow or moderate time scales (ns-ms). However, novel experiments with molecules in micro cavities show collective enhanced strong coupling on the order of several hundreds meV [1]. This sets the timescale for the interaction into the ultrafast (fs) regime and opens new possibilities for the ultrafast dynamics and spectroscopy of molecular systems. The strong coupling to the radiation field can alter the molecular levels, profoundly affecting the dynamics of basic photophysical and photochemical processes. In contrast to strong laser fields [2] the cavity can even be in the vacuum state, preventing competing multiphoton absorption processes. Specially tailored nano materials may then serve as a photonic catalyst that can be used in instead of a chemical catalyst.

In this contribution we present approach for the nonadiabatic dynamics arising from the introduction of the nuclear degrees of freedom into the Jaynes-Cummings (JC) model along with simulations for different typical scenarios of ultrafast reactions. We examine the regime beyond the JC model and investigate the possibility to modify existing nonadiabatic processes in a molecular system.

2. Nonadiabatic Dynamics in the Strong Coupling Regime

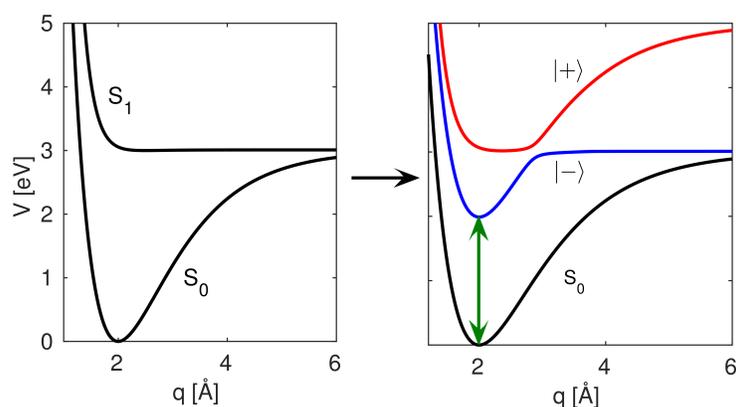


Fig. 1. Schematic illustration of molecular potential energy surfaces $|g\rangle \equiv S_0$ and $|e\rangle \equiv S_1$ (left panel). The right panel displays the dressed states $|-\rangle$ and $|+\rangle$ resulting from the cavity coupling. The cavity mode with frequency ω_c is indicated by the green arrow.

Our approach is based on the JC model [3], which includes the nuclear degrees of freedom and puts the formalism on equal footing with the description of conical intersections (CoIns). The JC-Hamiltonian includes the electric field

in its quantized form:

$$H_{JC} = \frac{\hbar}{2} \omega_0 (\sigma^\dagger \sigma - \sigma \sigma^\dagger) + \hbar \omega_c \left(a^\dagger a + \frac{1}{2} \right) + \hbar g (a^\dagger \sigma + a \sigma^\dagger) \quad (1)$$

where a and a^\dagger are annihilation and creation operators of the cavity mode, σ and σ^\dagger are the annihilation and creation operators of the electronic excitation, and $\omega_0 = (V_e - V_g)/\hbar$. All parameters of the JC model, such as the cavity coupling $g = \mu_{eg} \mathcal{E}_{vac}$, and the cavity detuning $\delta_c = \omega_0 - \omega_c$ now depend on the nuclear coordinates q_i [4]. This results in a break down of the Born-Oppenheimer approximation.

The interaction due to the cavity coupling can then be expressed in terms of nonadiabatic coupling matrix elements [5] and be described by derivative couplings:

$$f_{-,+}^{(i)} = \frac{\Delta G_i}{4g} \left(1 - \frac{\delta_c^2}{4g^2 + \delta_c^2} \right) - \frac{\delta_c}{4g^2 + \delta_c^2} \frac{\partial g}{\partial q_i} \quad (2)$$

From Eq. 2 it becomes clear that the derivative coupling term $f_{-,+}$, connecting $|-\rangle$ and $|+\rangle$, depends on the gradient difference ΔG_i of the molecular potential energy surfaces and the derivative of the transition dipole moment (via $\partial_{q_i} g$). Eq. 2 is valid within the rotating wave approximation (RWA). We particularly chose the dressed representation instead of the bare states since this yields a more intuitive potential energy surfaces (see Fig. 1).

For a two level atom the strong coupling regime is defined as $g \gg \kappa, \Gamma$, i.e. the cavity coupling g has to be larger than the dissipation rate of the cavity mode κ or the rate of spontaneous emission Γ . However, in the case of ultrafast excited dynamics, this definition of strong coupling is of limited use. Instead the time scale of the nuclear wave packet motion has to be related to the coupling strength, as this determines the interaction on the ultrafast time scale.

3. Vacuum Field Manipulation of Photochemistry

The quantized field of the cavity allows for a direct modification of the molecular states. An avoided crossing is introduced when the cavity mode is resonance with the molecular states. This provides a variety of possibilities to directly modify their photochemistry. The example shown in the schematics in Fig. 1 allows for stabilization of the dissociative state (S_1), extending its lifetime [5]. However, the situation can also be reversed by coupling a bound

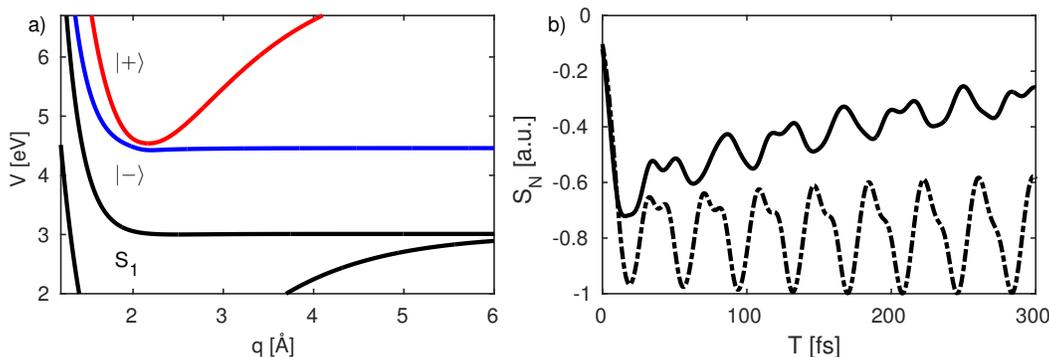


Fig. 2. (a) Dressed state potential energy curves of the photonic catalyst model ($|+\rangle \approx S_2$). (b) Transient absorption signal (10 fs FWHM probe) of the bare system (dashed line) and the dressed states (solid line), revealing the potential energy surface manipulation.

state to a dissociative state, decreasing the lifetime of a molecule. This situation is shown in Fig. 2(a). We assume that a bound state S_2 is accessible by a dipole transition from the ground state S_0 . The dissociative state S_1 does not have a transition dipole moment with the ground state, but is accessible from S_2 . Figure 2(b) shows the comparison of the simulated transient absorption signals after excitation with a UV pulse. The signal for the bare state system is modulated by the wave packet motion in the S_2 state and only affected by the anharmonicity of the potential, while signal for the dressed state system decays on a time scale of ≈ 300 fs. The coupling to the dissociative state can be interpreted as stimulated emission caused by the vacuum field of the cavity mode.

4. Cavity Induced Modification of Electronic Curve Crossings

CoIns are present in a wide range of molecules and affect the photochemistry of many important processes. Instead of using the cavity coupling in the optical regime and coupling two well-separated states, the frequency of the cavity can also be chosen to couple in the vicinity of an already existing curve crossing. The goal here is to interfere with nonadiabatic coupling between the electronic states and influence the branching ratio. The RWA is no longer valid in this regime as the cavity coupling is on the same order of magnitude as the transition frequency between the electronic states. The non-RWA terms ($\sigma^\dagger a^\dagger$, σa), which have been neglected in Eq. 1, now have to be taken into account. This can be either achieved by using coherent added photon states [6], or by transforming the annihilation and creation operators of the cavity into a quadrature space representation [7] (i.e. $a = \sqrt{\omega_c/\hbar}(\hat{X} + i\hat{P}/\omega_c)$), which yields the new Hamiltonian for the coupled molecule-cavity system:

$$H_{MC} = \frac{\hbar}{2}\omega_0(\sigma^\dagger\sigma - \sigma\sigma^\dagger) - \frac{\hbar}{2}\frac{\partial^2}{\partial X^2} + \frac{1}{2}\omega_c^2\hat{X}^2 + g\sqrt{2\hbar\omega_c}\hat{X}(\sigma^\dagger + \sigma) \quad (3)$$

This results in a scheme which can easily be combined with the wave packet simulation of the nuclear degrees of freedom on a numerical grid, greatly simplifying the calculation.

We theoretically demonstrate the control possibilities on the excited state dynamics of sodium iodide [7], which has been a benchmark for femtochemistry [8]. The NaI molecule is excited by a laser pulse, which launches the nuclear dynamics. The avoided crossing between the covalent and ionic states is at 8 Å. The cavity is set to be in resonance at the avoided crossing. The nuclear wave packet dynamics is then calculated for different coupling strengths g and initial excitations of the cavity mode using Eq. 3. The resulting branching ratios are shown in Fig. 3(b). With the cavity

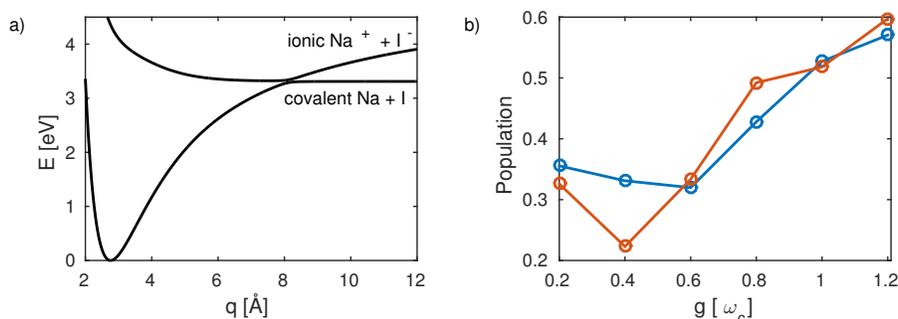


Fig. 3. (a) Potential energy surfaces of NaI. (b) Population of the covalent decay channel vs. the coupling strength g for different initial states of the cavity mode (blue $|e, 0\rangle$, red $|e, 1\rangle$).

initially in the vacuum state (Fig.3(b), blue line), the population in the covalent channel is mainly increased by the stimulated emission into the cavity mode. Setting the cavity initially in the one-photon Fock state (Fig.3(b), red line) partial absorption also becomes possible leading to depletion of the covalent channel at $g \approx 0.4\omega_c$. The simulation shows that the population transfer at the avoided crossing can be influenced by the cavity coupling over a wide range. This control mechanism principle can in principle also be extended to CoIns.

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