

Controlling the dynamics in the vicinity of quantum light-induced conical intersections



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1 Introduction

Nonadiabatic effects appear due to avoided crossings or conical intersections that are either intrinsic properties in field-free space or induced by a classical laser field in a molecule. It was demonstrated that avoided crossings in diatomics can also be created in an optical cavity [1–3]. Here, the quantized radiation field mixes the nuclear and electronic degrees of freedom creating hybrid field-matter states called polaritons. In the present theoretical study we go further and create conical intersections in diatomics by means of a radiation field in the framework of cavity quantum electrodynamics (QED). By treating all degrees of freedom, that is the rotational, vibrational, electronic and photonic degrees of freedom on an equal footing we can control the nonadiabatic quantum light-induced dynamics by means of conical intersections [4].

First, we study the quantum light-induced nonadiabatic dynamics of the LiF molecule both in 1D and 2D frameworks to demonstrate the difference between the effects of the radiation field-induced AC and CI. The underlying dynamics is mainly governed by the interplay between one of the quantum light-induced phenomena (either LIAC or LICl) and of the natural avoided crossing which is present in the field-free molecule.

Second, the close similarity between the classical and the cavity radiation field description of the light is demonstrated. We discuss for both the LIAC and LICl situations to what extent the different physical scenarios, a molecule in a laser field and a molecule in a cavity, show the same results.

2 Methods and numerical details

The cavity Hamiltonian in the basis of the Σ_1 and Σ_2 surfaces of LiF is:

$$\hat{H}_{cavity} = \left(-\frac{1}{2M_r} \frac{\partial^2}{\partial R^2} + \frac{1}{2M_r R^2} L_\theta^2 \right) \mathbf{1} + \begin{pmatrix} V_{\Sigma_1} & K \\ -K & V_{\Sigma_2} \end{pmatrix} + \left(-\frac{1}{2} \frac{\partial^2}{\partial x^2} + \frac{1}{2} \omega_c^2 x^2 \right) \mathbf{1} + \begin{pmatrix} \chi \omega_c \sqrt{2} \cdot \mu_{\Sigma_1} \cos \theta \cdot x & \chi \omega_c \sqrt{2} \cdot \mu_{\Sigma_1 \Sigma_2} \cos \theta \cdot x \\ \chi \omega_c \sqrt{2} \cdot \mu_{\Sigma_1 \Sigma_2} \cos \theta \cdot x & \chi \omega_c \sqrt{2} \cdot \mu_{\Sigma_2} \cos \theta \cdot x \end{pmatrix}. \quad (1)$$

Electric dipole approximation is assumed and the molecule interacts with only a single mode of the cavity. In eq. 1, the first term represents the rovibrational kinetic energy of the LiF molecule with R and θ being the vibrational and rotational degrees of freedom, respectively. M_r is the reduced mass of the LiF molecule, L_θ is the angular momentum operator (with $m = 0$ fixed) and the $\mathbf{1}$ symbol represents the 2×2 unit matrix. The second term contains the field-free adiabatic potential curves V_{Σ_1} and V_{Σ_2} (see Fig. 1(a)). The K field-free nonadiabatic coupling operator operator is approximated as $K(R) \approx \frac{1}{2M_r} (2\tau(R) \frac{\partial}{\partial R} + \frac{\partial}{\partial R} \tau(R))$, where $\tau(R)$ is first order nonadiabatic coupling term, shown in Fig. 1(b). The third term in eq. 1 represents the harmonic oscillator description of the photon mode with the unit-less photon displacement coordinate x . Here ω_c is the cavity mode angular frequency. The last term of

eq. 1 describes the interaction between the molecule and the quantized field. Here χ is the cavity coupling strength, while μ_i and μ_{ij} ($i,j=\Sigma_1, \Sigma_2$) are the transition and permanent dipoles, respectively. In the actual calculations $\hbar\omega_c = 3.995$ eV is taken which corresponds to the resonant coupling of the Σ_1 and Σ_2 states around $R=5$ a.u. The coupling strength χ ranges from 0.0012 to 0.04 to simulate moderate and strong coupling strengths.

The initial wave packet at $t = 0$ is created from the product of the ro-vibrational ground state of Σ_1 located at $R=3$ a.u. and one of the Fock states and is placed on the upper adiabatic potential Σ_2 . The Fock states are considered eigenstates of the $\left(-\frac{1}{2} \frac{\partial^2}{\partial x^2} + \frac{1}{2} \omega_c^2 x^2 \right)$ Hamiltonian.

The time-dependent (TD) classical Hamiltonian in the basis of the adiabatic states Σ_1 and Σ_2 of LiF reads:

$$\hat{H}_{classical}(t) = \left(-\frac{1}{2M_r} \frac{\partial^2}{\partial R^2} + \frac{1}{2M_r R^2} L_\theta^2 \right) \mathbf{1} + \begin{pmatrix} V_{\Sigma_1} & K \\ -K & V_{\Sigma_2} \end{pmatrix} - \varepsilon_0 \cdot \cos(\omega_c t) \cdot f(t) \begin{pmatrix} \mu_{\Sigma_1} \cos \theta & \mu_{\Sigma_1 \Sigma_2} \cos \theta \\ \mu_{\Sigma_1 \Sigma_2} \cos \theta & \mu_{\Sigma_2} \cos \theta \end{pmatrix}. \quad (2)$$

In eq. 2, the first term represents the vibrational and rotational kinetic energy (the same as in eq. 1), while the second term contains the field-free V_{Σ_1} and V_{Σ_2} potential curves and the K nonadiabatic coupling operator. The third term of eq. 2 describes the laser-molecule interaction in the dipole approximation. Here ε_0 is the amplitude of the electric field, ω_c is the angular frequency of the laser, $f(t)$ is the envelope function which set to unity during the whole propagation ($t_{final}=1000$ fs). μ_i and μ_{ij} ($i,j=\Sigma_1, \Sigma_2$) are the permanent and transition dipoles, respectively. The actual value of the applied laser energy was set to $\hbar\omega_c = 3.995$ eV, which resonantly couples the electronic states at $R = 5$ a.u., and the peak laser intensities ranges from $I_0 = 3 \times 10^{11}$ W/cm² to 3×10^{13} W/cm². We note that during the calculations the permanent dipoles μ_{Σ_1} and μ_{Σ_2} are neglected in eqs. 1 and 2 as only the relative results provided by the and Hamiltonians eqs. 1 and 2 are the focus of our interest.

The MCTDH (multi configurational time-dependent Hartree) method [5] has been applied to solve the time-dependent Schrödinger-equation.

The total propagation time was set to $t_{final}=1000$ fs and the state populations and dissociation rates were calculated according to

$$P_i(t) = \langle \psi_i(R, \theta, x, t) | \psi_i(R, \theta, x, t) \rangle \quad i = \Sigma_1, \Sigma_2 \quad (3)$$

and

$$P_{diss}(t) = \langle \psi_{\Sigma_1}(t) | \Theta(R - R_D) | \psi_{\Sigma_1}(t) \rangle + 2 \int_0^t dt' \langle \psi(t') | W | \psi(t') \rangle. \quad (4)$$

In eq. 4, Θ is the Heaviside step function, $R_D=20$ a.u. is the starting point of the dissociation region, and $-iW$ is the CAP.

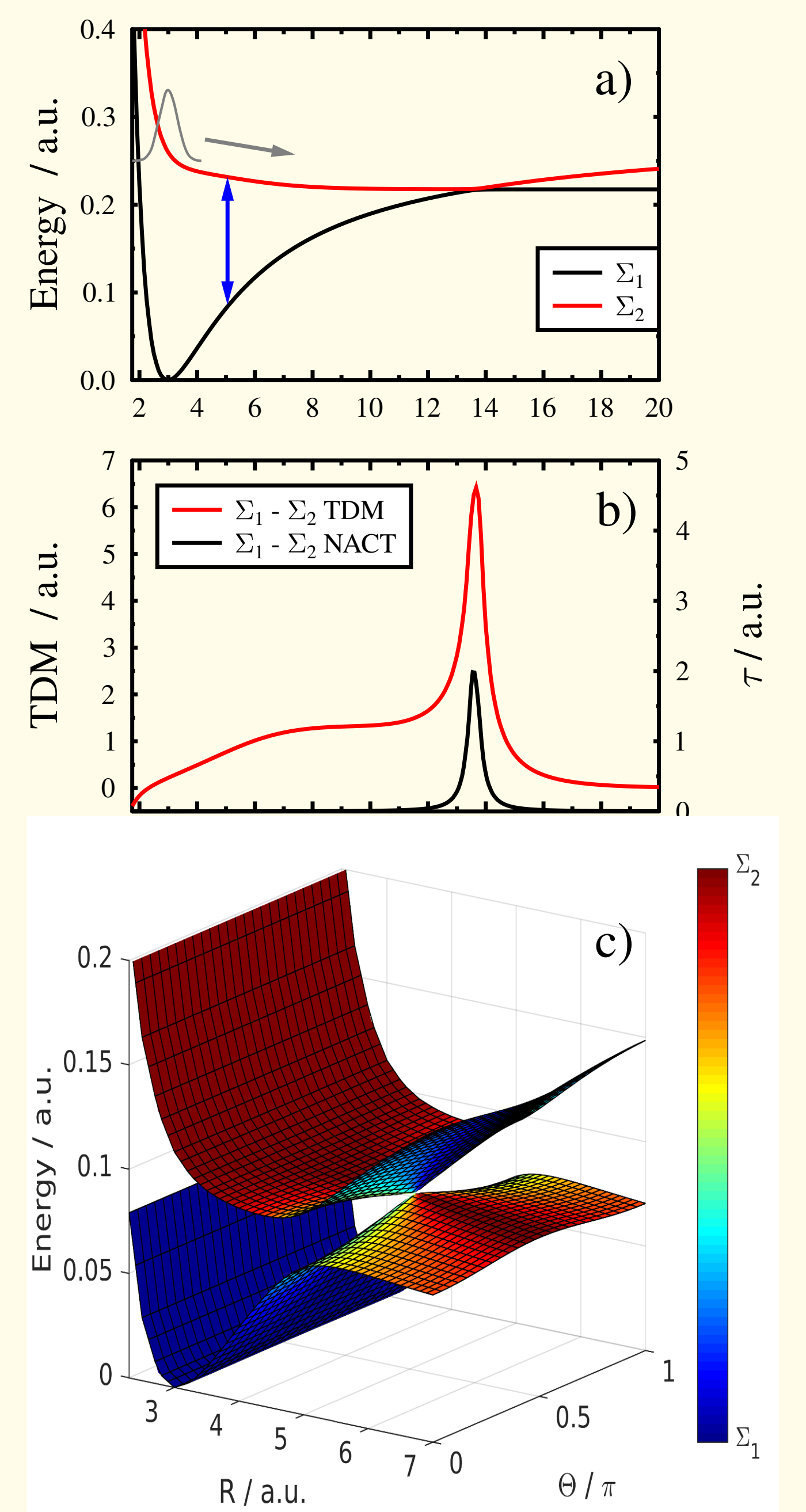


Figure 1: (a) Bare ground Σ_1 (black line) and excited Σ_2 (red line) electronic potential energy curves of the LiF molecule. The initial wave packet around $R = 3$ a.u. is indicated by the gray line while the resonant coupling of the electronic states at $R = 5$ a.u. is indicated by the vertical blue arrow. (b) Transition dipole moment (green line) and intrinsic nonadiabatic coupling (red line) functions of the Σ_1 and Σ_2 electronic states. (c) Dressed states potential energy surfaces of the LiF molecule representing the quantum light-induced CI for a cavity coupling $\chi = 0.02$ and a cavity resonance frequency $\omega_c = 0.1468$ a.u. The color code indicates the state character in the terms of the bare states $|\Sigma_1, n+1\rangle$ and $|\Sigma_2, n\rangle$ within a Jaynes-Cummings model. The LICl is located at $\theta=\pi/2$.

3 Results and discussions

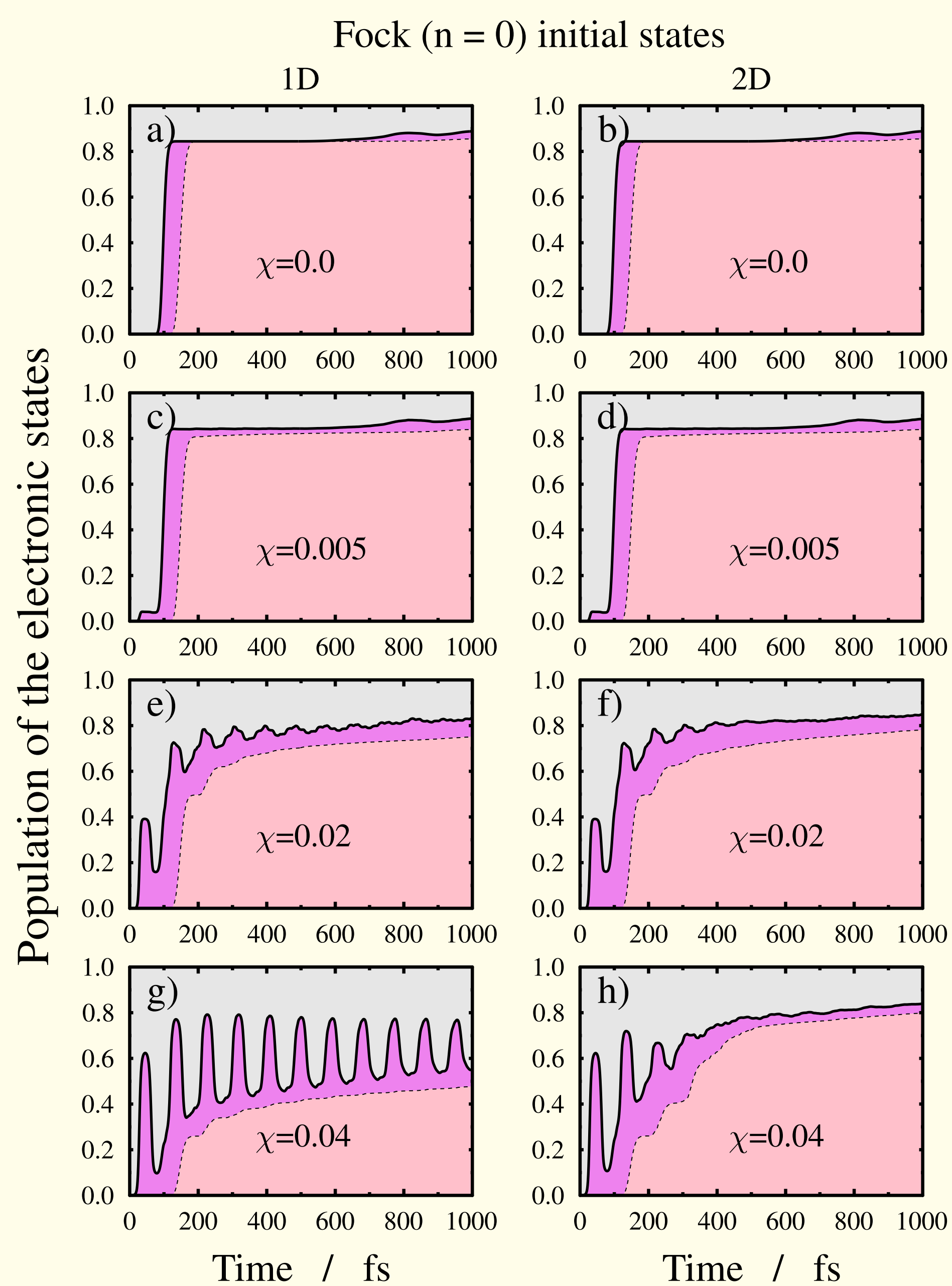


Figure 2: Population of the ground and excited electronic states as a function of time computed in 1D and 2D. Panels on the left-hand side (a-g)) show the 1D results, while those on the right-hand side (b-h)) depict the 2D results for a given cavity coupling strength; from top to bottom $\chi=0$, $\chi=0.005$, $\chi=0.02$ and $\chi=0.04$. The purple and gray areas correspond to the population of the Σ_1 and the Σ_2 states, respectively. The pink regions show the ground state population being in the dissociation region ($R > 20$ a.u.). In all the panels the Fock vacuum state ($n = 0$) is considered as an initial state along the cavity mode.

The dissociation is much less suppressed in the cavity LICl picture than that of the cavity LIAC. Similarly to the classical situation, the quantized radiation field couples to the molecular degrees of freedom, the ultrafast decay channel created by the LICl is much more efficient with respect to the fast population transfer than the AC. The time evolution of the QD is determined by the interplay between the radiation-field induced and intrinsic nonadiabaticity, but at sufficiently strong coupling region the quantum LICl dominates the process.

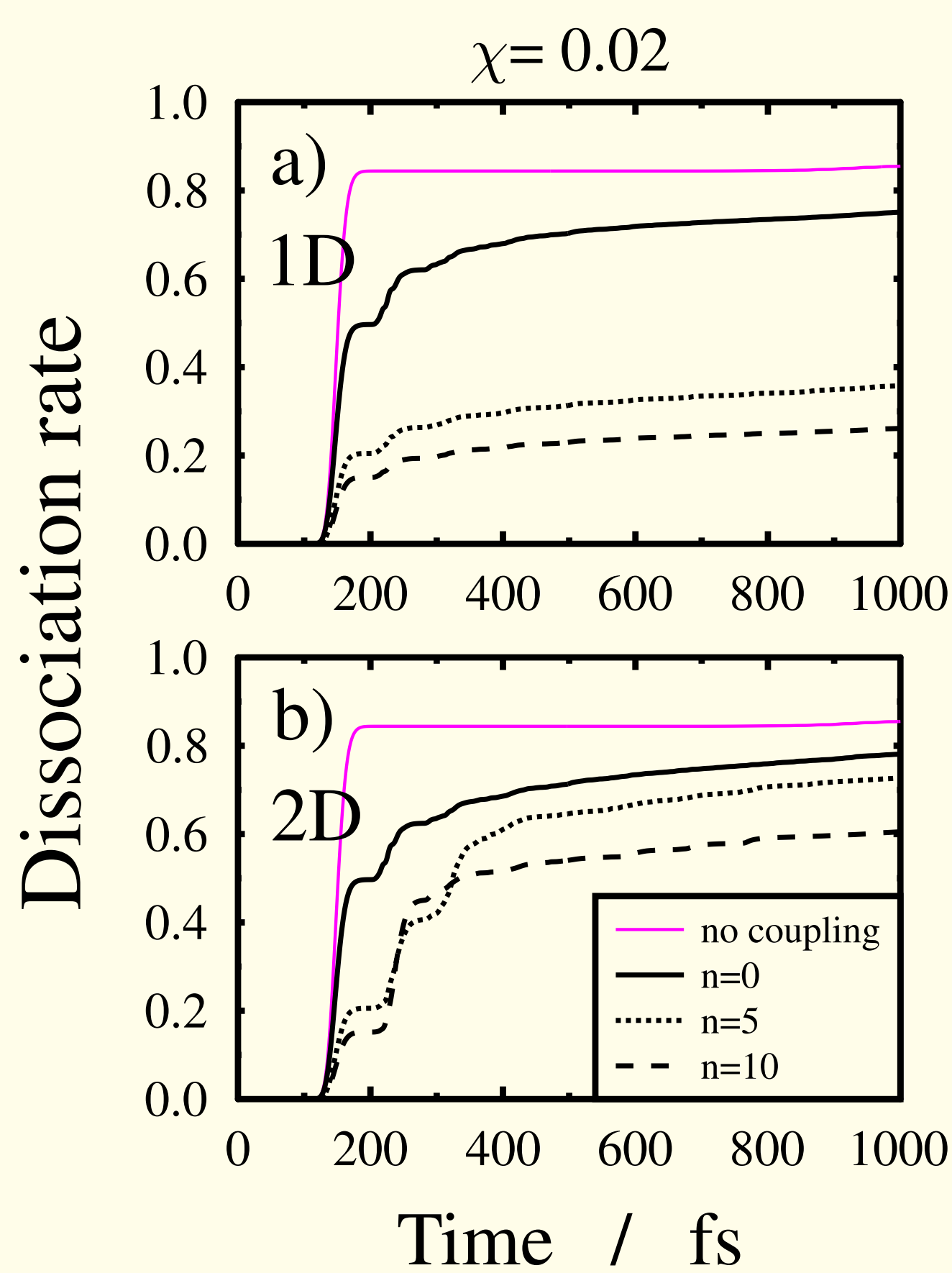


Figure 3: Time-evolution of the ground state dissociation rate for the LiF molecule considering different initial Fock states along the cavity mode. 1D and 2D results are compared in panels a) and b), respectively for a given cavity coupling strength of $\chi=0.02$. Besides the different photon number Fock states, the field-free results are shown by the magenta curves.

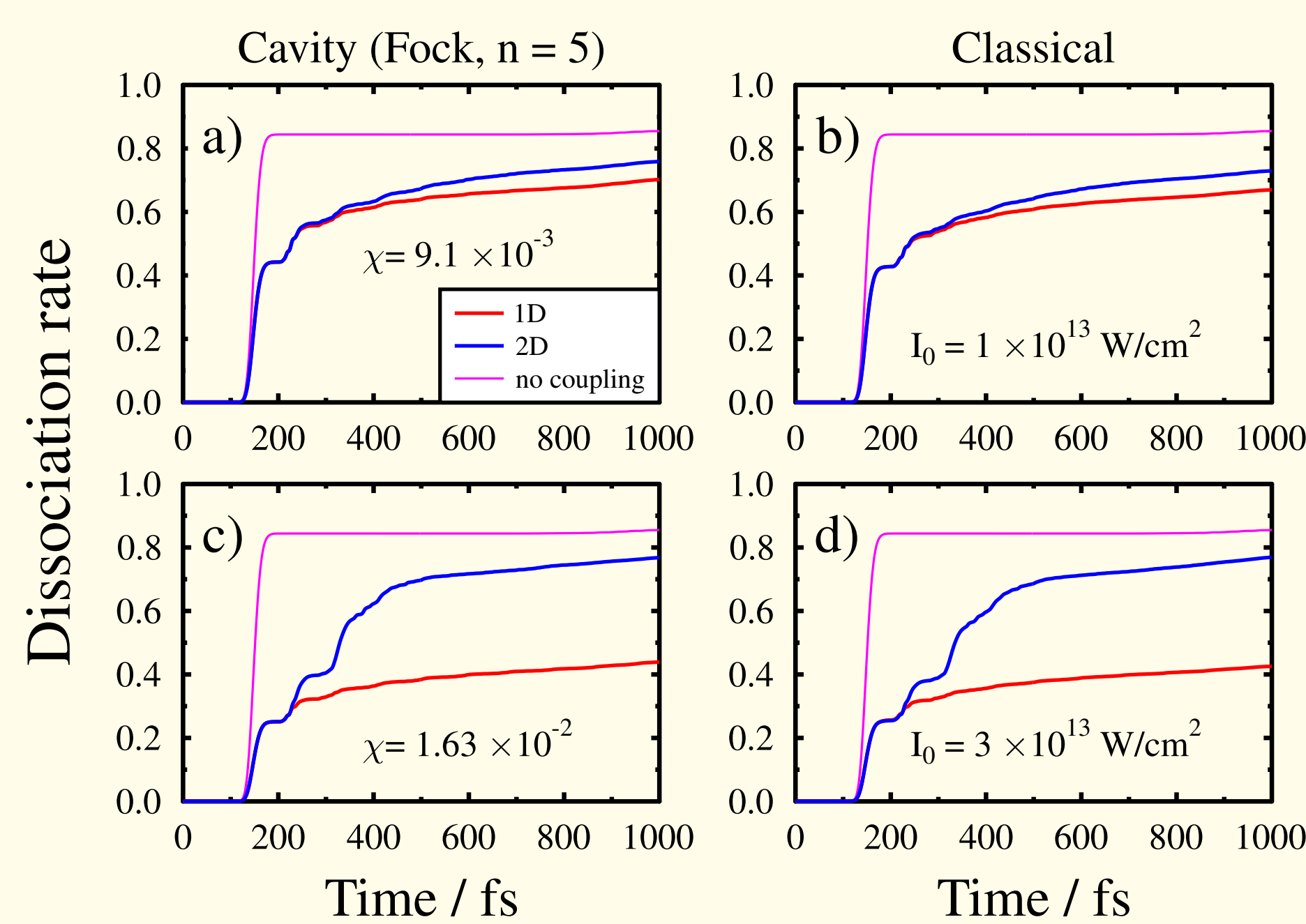


Figure 4: Comparison of the time-dependent ground-state dissociation rates of the LiF molecule modified by quantum and classical laser light. The correspondence between the quantum and classical light results is demonstrated for two different intensities and cavity coupling values. The 1D and 2D dissociation rates are shown by the red and blue lines, respectively. The magenta curves depict the bare results.

For ($n=0$ Fock state) the dissociation curves are similar but the effect, that the dissociation is more efficient in 2D, can already be seen. For ($n=5$ and $n=10$ Fock states) the efficiency of LICl is increasing compared to the 1D model. The decay channel provided by the quantum LICl is more efficient for transferring the population to the lower polaritonic state, which leads to significantly higher dissociation rates. The effect is similar to what we experience in the case of increasing coupling strengths. The increasing photon number provides an increasing coupling strength, which is enhanced by $\sqrt{n+1}$, leading to a more efficient LICl.

Practically there are no differences have been found between the classical and cavity results. Like in the 1D model [3] this agreement demonstrates again – at least in the studied time interval – the close similarity between the classical and the cavity radiation field description of the light.

4 Conclusion

The dynamical properties of diatomic molecules can be strongly modified by quantized light in an optical cavity. The LICl created by quantum light allows for a much more efficient population transfer than a LIAC. The stronger the cavity coupling, the more prominent the effect. This difference can be explained by the fact that the LICl retains a degeneracy between the dressed states even for large coupling strengths. In contrast the dressed state curves of the 1D model become increasingly separated for larger coupling strengths, which leads to a decreased mixing between the nuclear degrees of freedom and the electron+photon degrees of freedom. In addition, we found a close similarity between the classical and the cavity radiation field description of the light for the 2D calculations. The latter is fully consistent with our previous findings for a 1D model and classical light, which has been compared to a 1D model and quantum light [4].

References

- [1] Galego, J.; Garcia-Vidal, F. J.; Feist, J. Cavity-Induced Modifications of Molecular Structure in the Strong-Coupling Regime. *Phys. Rev. X* **2015**, *5*, 1-14.
- [2] Kowalewski, M.; Bennett, K.; Mukamel, S. Cavity Femtochemistry: Manipulating Nonadiabatic Dynamics at Avoided Crossings. *J. Phys. Chem. Lett.* **2016**, *7*, 2050-2054.
- [3] Csehi, A.; Halász, G. J.; Cederbaum, L. S.; Vibók, Á. Competition between Light-Induced and Intrinsic Nonadiabatic Phenomena in Diatomics. *J. Phys. Chem. Lett.* **2017**, *8*, 1624.
- [4] András Csehi; Markus Kowalewski; Gábor J. Halász; Ágnes Vibók; Ultrafast dynamics in the vicinity of quantum light-induced conical intersections; submitted to *New J. Phys.*
- [5] Worth, G. A. et. al. The MCTDH package, version 8.4, University of Heidelberg, Germany; <http://mctdh.uni-hd.de/> **2007**.