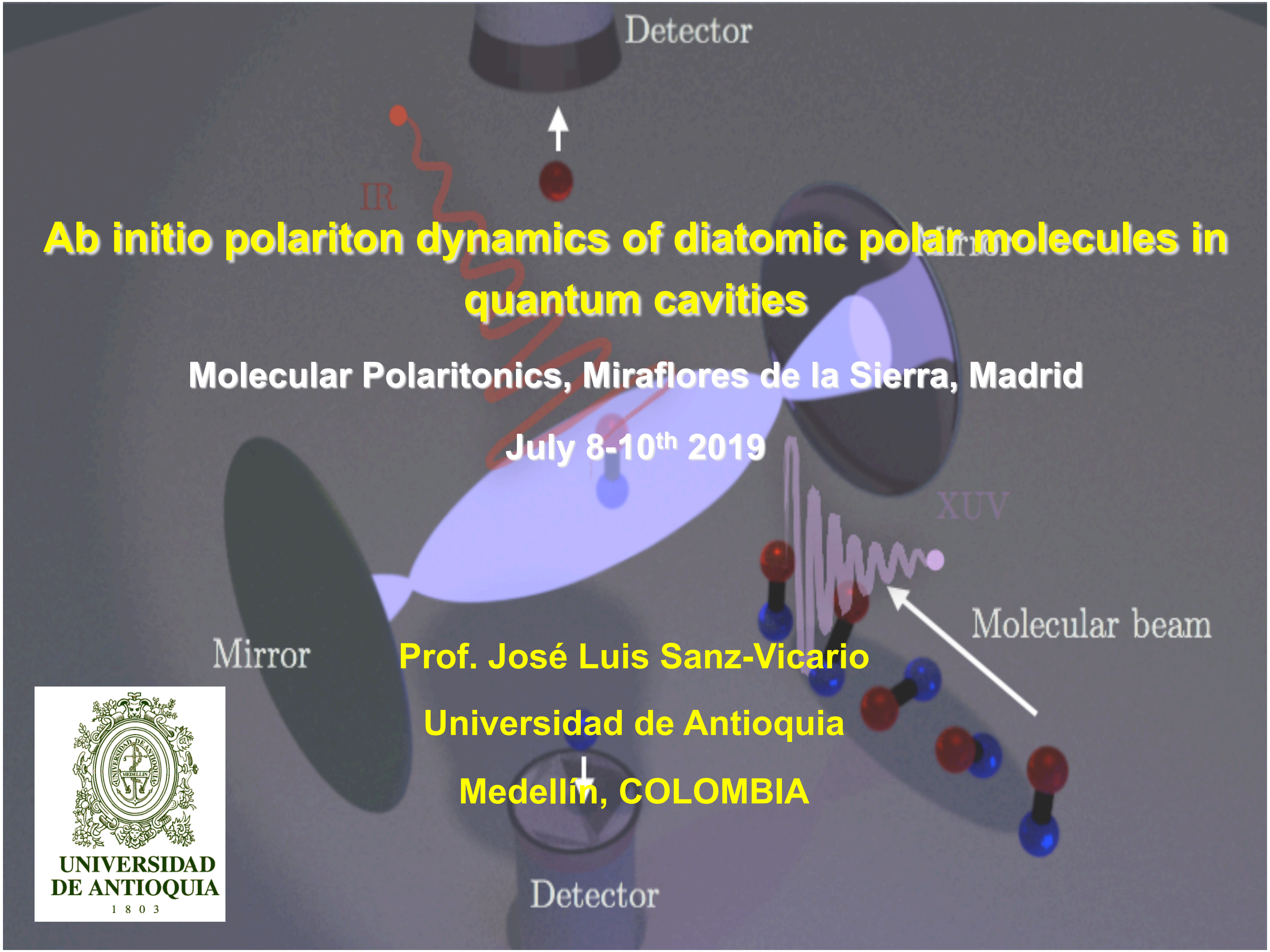
Ab initio polariton dynamics of diatomic polar molecules in quantum cavities

Molecular Polaritonics, Miraflores de la Sierra, Madrid

July 8-10th 2019



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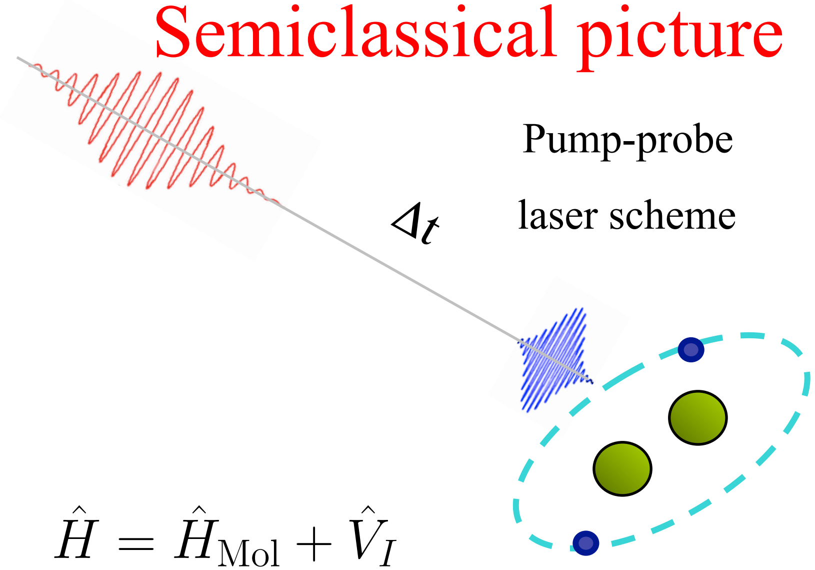
Radiation-matter interaction

Semiclassical picture



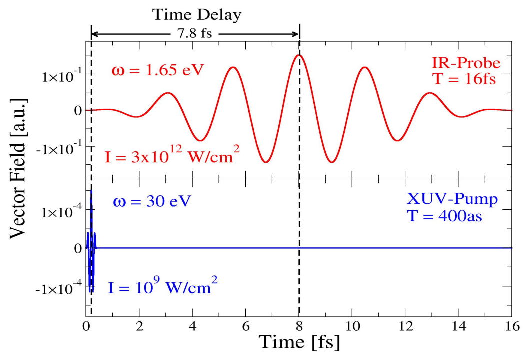
Pump-probe

laser scheme

$$\hat{H} = \hat{H}_{\mathrm{Mol}} + \hat{V}_I$$

$$\hat{V}_I(t) = -\hat{\boldsymbol{\mu}} \cdot \mathbf{E}(t)$$

$$\mathbf{E}(t) = E_0 \cdot f(t) \cdot \sin[\omega t + \varphi] \cdot \mathbf{e}_p$$



Radiation-matter interaction

Quantum picture

$$\hat{H}_{Mol-rad} = \hat{H}_{Mol} + \hat{H}_{cav}$$

$$\hat{H}_{cav} = \frac{1}{2}\hat{p}^2 + \frac{1}{2}\omega_c^2\left(\hat{x} + \frac{\lambda}{\omega_c}\hat{\mu}(R)\right)^2$$

$$= \frac{1}{2}\left(\hat{p}^2 + \omega_c^2\hat{x}^2\right) + \lambda\omega_c\hat{x}\hat{\mu}(R) + \frac{1}{2}\lambda^2\hat{\mu}^2(R)$$

- Radiation HO
- Radiation-molecule interaction
- Dipole self-energy term: correction to the molecular structure

Quantum Optics

Quantum radiation as a set of harmonic oscillators for each quantized mode

$$\hat{H}_{field} = \hbar\omega_c\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)$$

The electric field is an operator

$$\hat{E}_z(q) = E_0\left(\hat{a} + \hat{a}^\dagger\right)\hat{e}_z$$

$$E_0 = \sqrt{\frac{\hbar\omega_c}{V\varepsilon_0}}$$

Jaynes-Cummings Hamiltonian

$$\hat{H} = \hat{H}_{\text{Mol}} + \hat{H}_{\text{Field}} + \hat{H}^I_{\text{Mol-Field}}$$

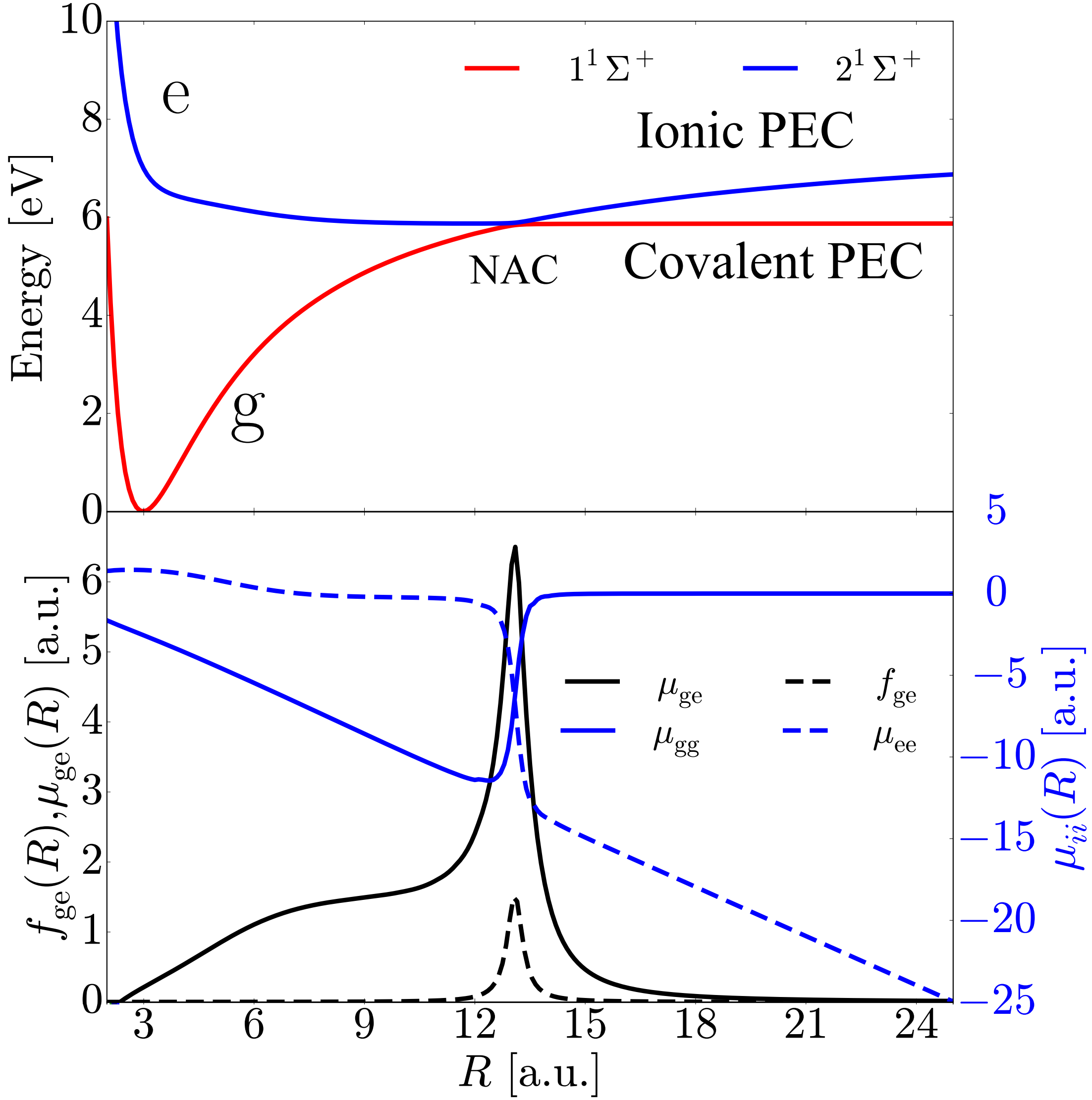
$$\hat{H}_{\text{Mol}} = \frac{1}{2}\hbar\omega_0\hat{\sigma}_3$$

$$\hat{H}_{\text{Field}} = \hbar\omega_c\left(\hat{a}^\dagger\hat{a} + 1/2\right)$$

$$\hat{H}^I_{\text{Mol-Field}} = \hbar\lambda_0\left(\hat{a} + \hat{a}^\dagger\right)\left(\hat{\sigma}_+ + \hat{\sigma}_-\right)$$

$$\lambda_0 = \mu_{ge;z}E_0/\hbar$$

Diatomic polar molecules



LiF

- LiF is a polar molecule: it has diagonal dipole moments
- The two lowest Σ states are coupled radiatively and with a non-adiabatic coupling.
- One can use an adiabatic picture or a diabatic one

Computed with MOLPRO

(MCSCF + MRCI)

Basis Set: Aug-cc-pVQZ

Molecular Polaritonic States

$$V_I = \hbar\lambda_0(\hat{a} + \hat{a}^\dagger)(\hat{\sigma}_+ + \hat{\sigma}_-)$$

$$\lambda_0 = \mu_{ge;z} E_0/\hbar$$

Representation of the cavity radiation in coordinate space

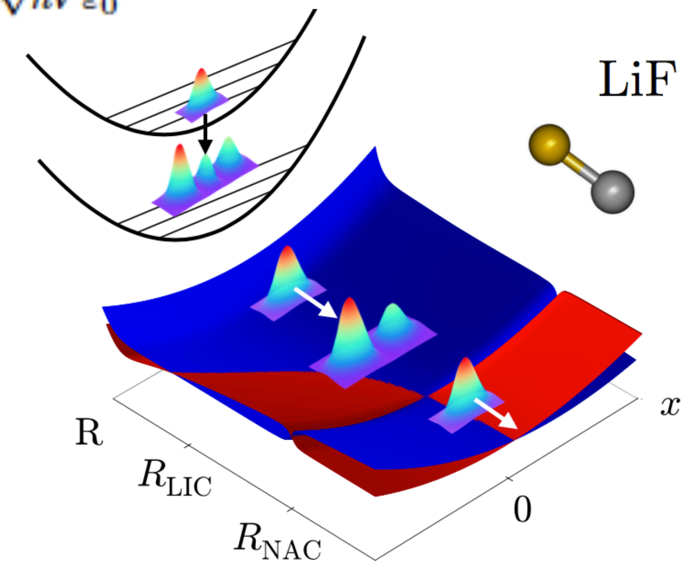
$$(\hat{a} + \hat{a}^\dagger) = \sqrt{\frac{2\omega_c}{\hbar}}\,\hat{x}$$

$$V_I = \chi\omega_c\sqrt{2\hbar}\,\hat{x}\,\hat{\mu}(R)(\hat{\sigma}_+ + \hat{\sigma}_-)$$

$$\chi = \frac{\lambda}{\sqrt{2\hbar}} = \frac{1}{\sqrt{\hbar V \varepsilon_0}}$$

2 degrees of freedom for propagation

- Internuclear distance R
- Harmonic oscillator coordinate x



Entangled polaritonic state!!!

$$\langle R, x|\Psi(t)\rangle = \varphi_g(R,x,t)|g\rangle + \varphi_e(R,x,t)|e\rangle$$

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J. Phys. Chem. A 2018, **122**, 2266

Polaritonic photodynamics in cavities

Solving the Time-dependent Schrödinger equation:

$$i\hbar\frac{d}{dt}\begin{bmatrix}\varphi_g(R,x,t)\\ \varphi_e(R,x,t)\end{bmatrix} = \left\{\begin{pmatrix} -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + E_g(R) - \frac{\hbar^2}{2}\frac{\partial^2}{\partial x^2} + \frac{1}{2}\omega_c^2 x^2 & 0 \\ 0 & -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + E_e(R) - \frac{\hbar^2}{2}\frac{\partial^2}{\partial x^2} + \frac{1}{2}\omega_c^2 x^2 \end{pmatrix} + \begin{pmatrix} \chi\omega_c\sqrt{2\hbar}\,\mu_{gg}(R)x & \chi\omega_c\sqrt{2\hbar}\,\mu_{ge}(R)x \\ \chi\omega_c\sqrt{2\hbar}\,\mu_{eg}(R)x & \chi\omega_c\sqrt{2\hbar}\,\mu_{ee}(R)x \end{pmatrix} + \mathbf{C}(R)\right\}\begin{bmatrix}\varphi_g(R,x,t)\\ \varphi_e(R,x,t)\end{bmatrix}$$

Including non-adiabatic couplings (NAC)

$$C_{ij}(R) = -\frac{\hbar^2}{2\mu}\left[2\langle i|\frac{\partial}{\partial R}|j\rangle(R)\frac{\partial}{\partial R} + \langle i|\frac{\partial^2}{\partial R^2}|j\rangle(R)\right]$$

$$= -\frac{\hbar^2}{2\mu}\left[2f_{ij}(R)\frac{\partial}{\partial R} + h_{ij}(R)\right]$$

All dynamic calculations performed with Ab Initio MCTDH method

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Light induced crossings

QUANTUM PICTURE

Light Induced potentials by the cavity

$$E_{\pm} = \frac{E_g(R) + E_e(R)}{2} \pm \frac{\hbar}{2}\Omega_{n_c}(R) \qquad \Omega_{n_c}(R) = \sqrt{4[\lambda(R)]^2(n_c + 1) + \Delta_c(R)}$$

The crossing appears when the detuning is zero (for $\lambda(R)$ and n_c small enough)

$$\Delta_c = [E_e(R) - E_g(R)] - \hbar\omega_c = 0$$

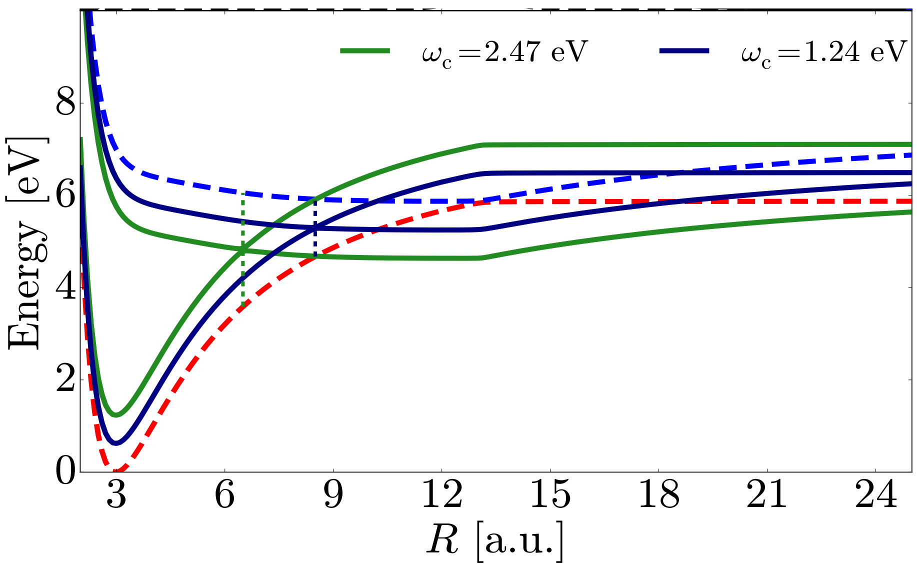

Table 1. Set of Cavity Mode Wavelengths λ_c and Frequencies ω_c Used in This Work[a]

λ_c [nm]	400	500	600	700	1000	2250
ω_c [eV]	3.01	2.47	2.09	1.76	1.24	0.54
R_{LIC} [au]	5.8	6.5	7.0	7.5	8.5	10.5

[a]The cavity frequency determines the position of the light-induced crossing (LIC) at the internuclear distance R_{LIC}, where the detuning $\Delta_c = [E_e(R) - E_g(R)]/\hbar - \omega_c$ is zero.

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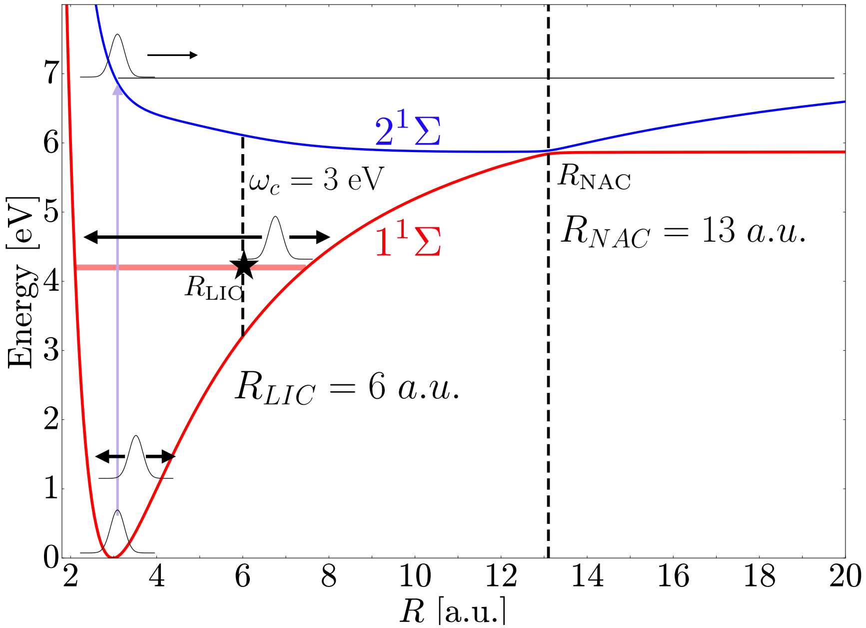
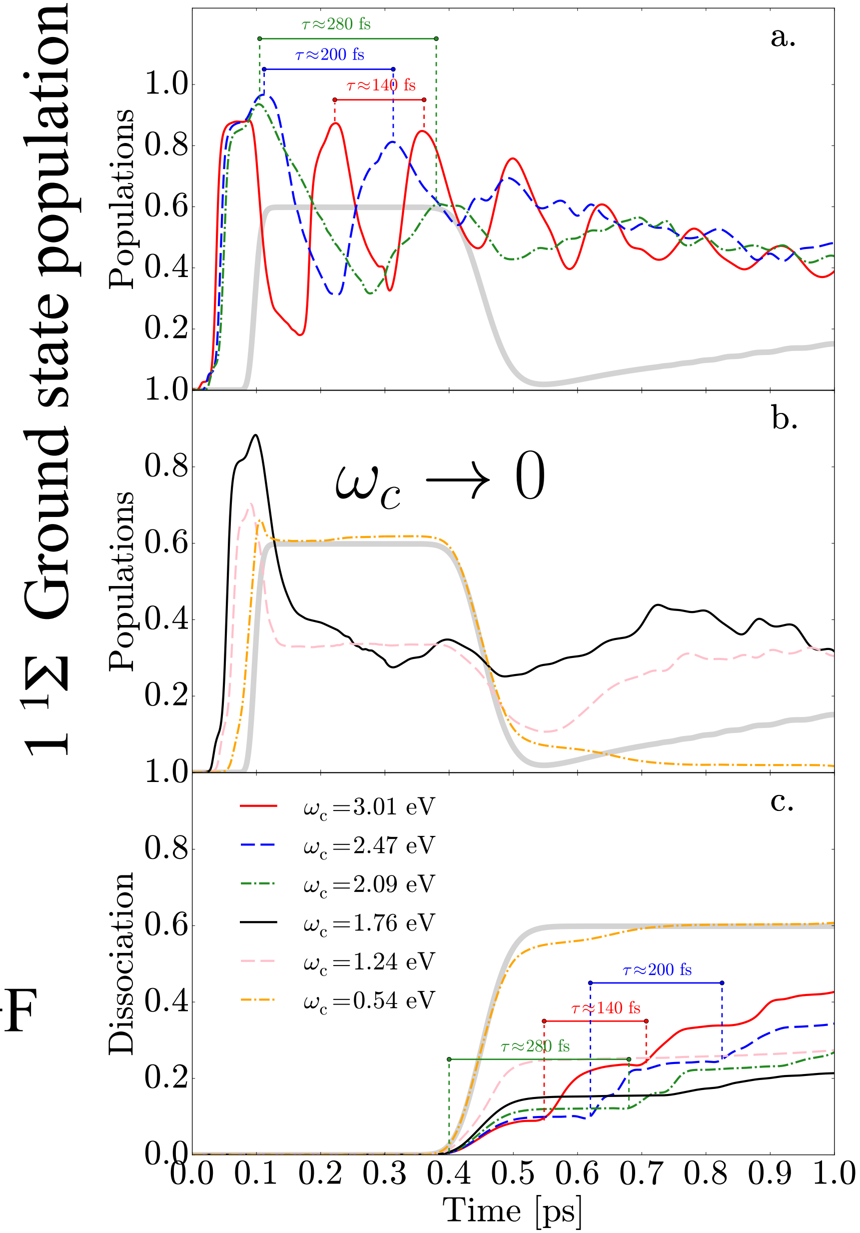
The position of LIC depends on the cavity mode frequency ω_c

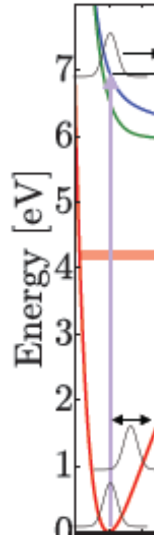


$$V_{\rm I} = \hat{\mu}_{\rm ge}\chi\omega_{\rm c}\sqrt{2\hbar}\hat{x}(\hat{\sigma}_+ + \hat{\sigma}_-)$$

Dissociation yield LiF -> Li+F

Polaritonic dynamics





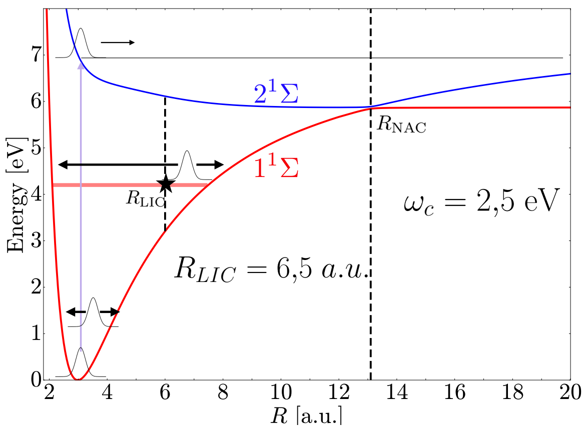
Polaritonic wavepacket dynamics

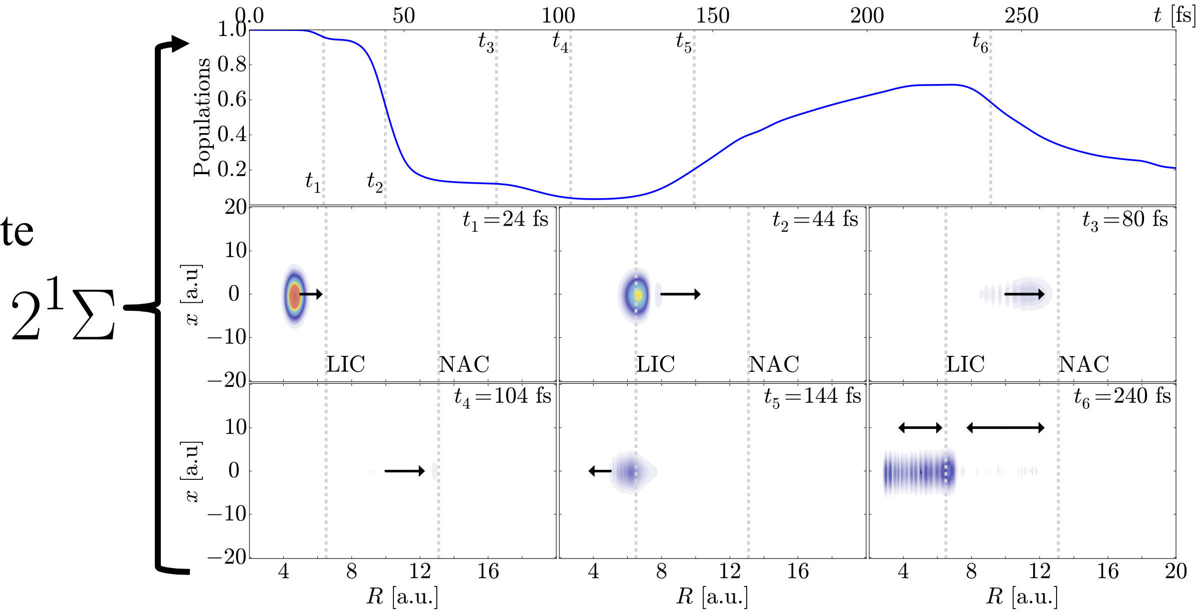
Initial state $|\Psi(t=0)\rangle$

$$= |\chi_{v=0}\rangle \cdot |0\rangle$$

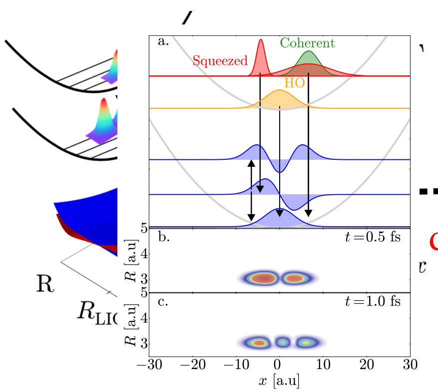
FC vibrational ground state

Vacuum state

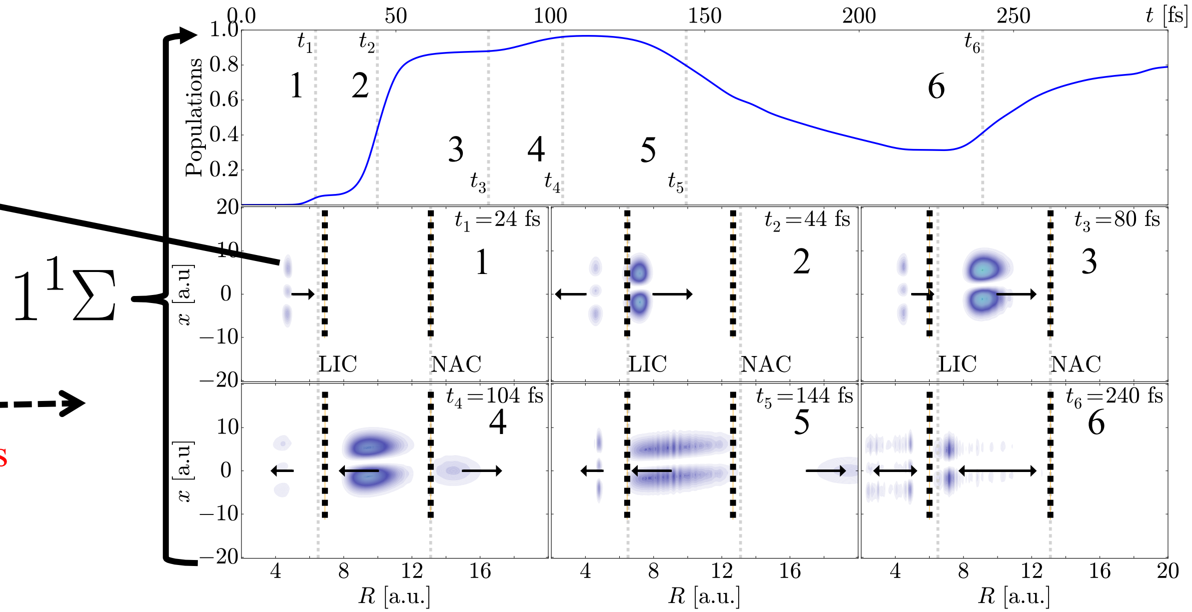




Dynamic Casimir effect



2D dynamics



Polaritons with coherent states of radiation

Initial state $|\Psi(t=0)\rangle = |\chi_{v=0}\rangle \cdot |\alpha\rangle$

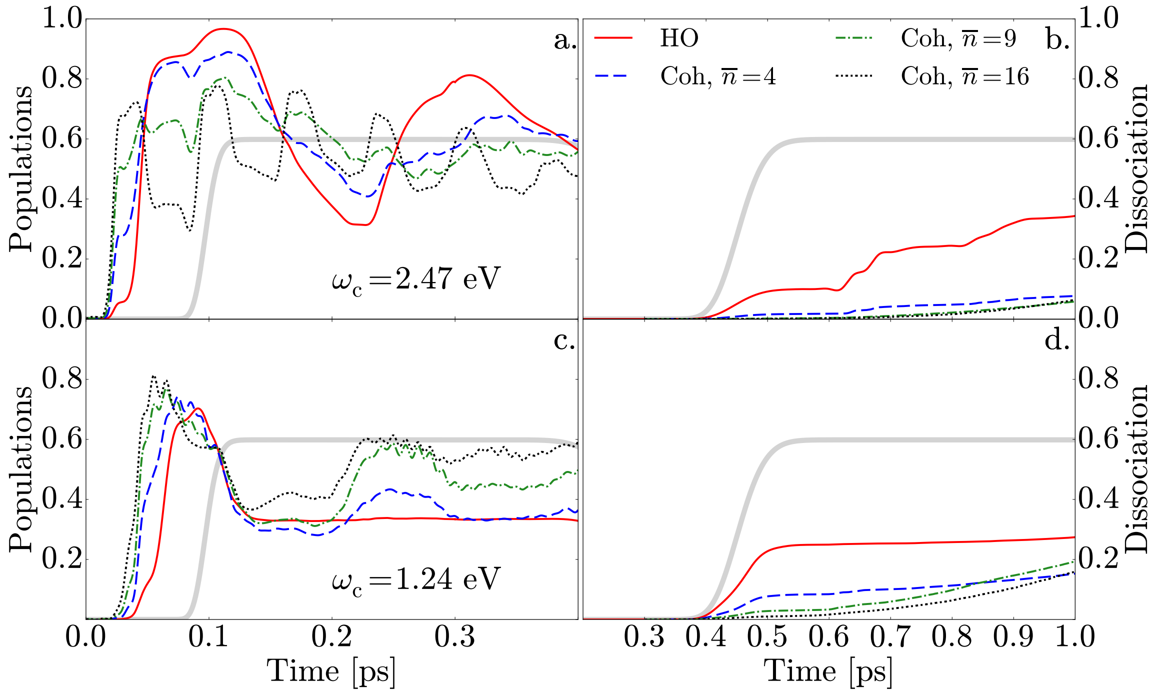
$$\psi_\alpha(x) = \left(\frac{1}{2\pi[\Delta x_\alpha]^2}\right)^{1/4} e^{-1/4(x-\langle x\rangle_\alpha/\Delta x_\alpha)^2} e^{i\langle p\rangle_\alpha x}$$

$$\Delta x_\alpha = \sqrt{\frac{\hbar}{2\omega_c}}$$

$$\langle x\rangle_\alpha = \sqrt{\frac{\hbar}{2\omega_c}}(\alpha + \alpha^*)$$

$$\langle p\rangle_\alpha = -i\sqrt{\frac{\hbar\omega_c}{2}}(\alpha - \alpha^*)$$

Polaritonic dynamics



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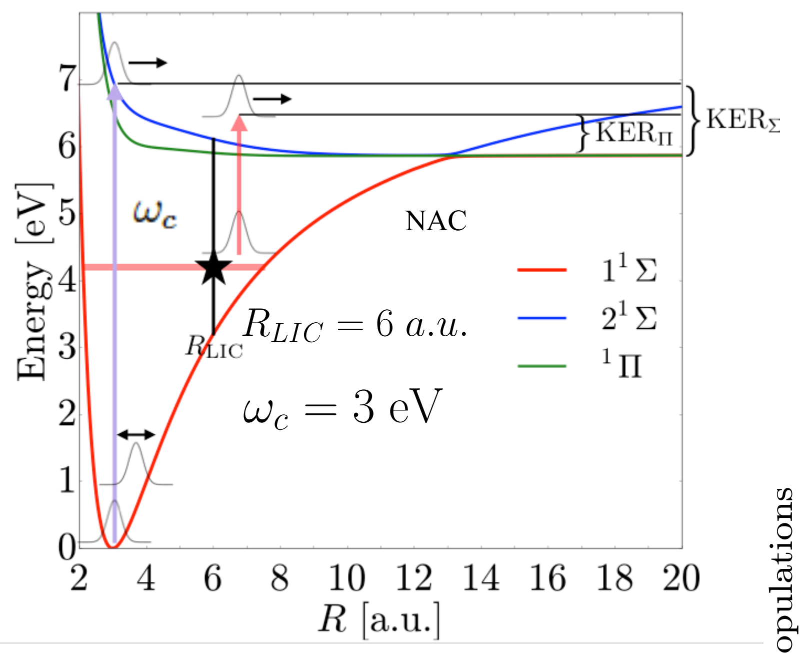
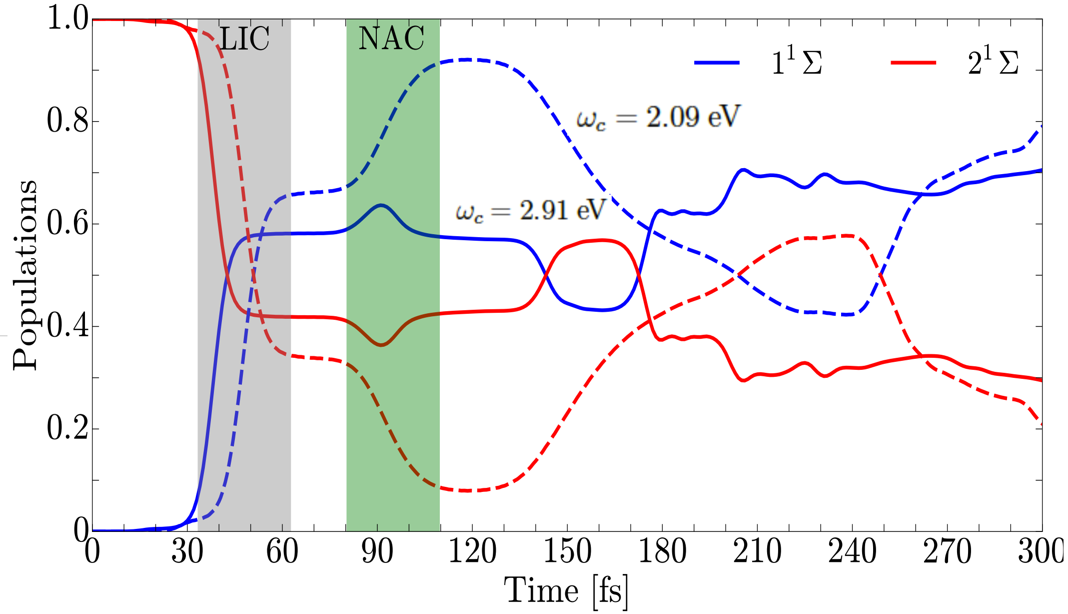
Revealing the fingerprints of cavity LIC

Pump-Probe Scheme



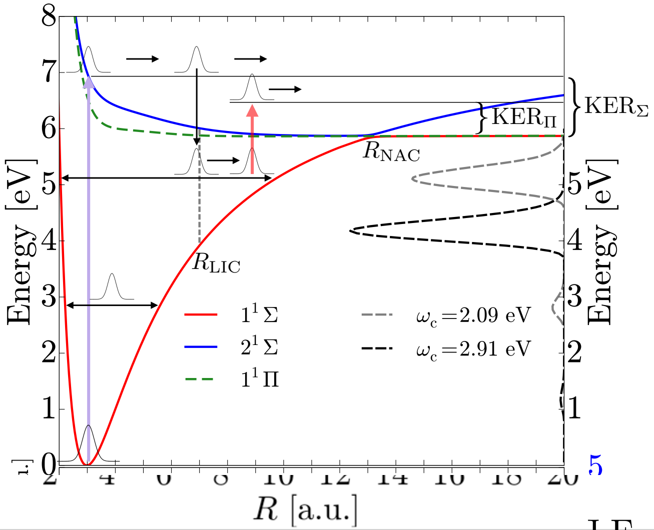
Population dynamics in Σ states



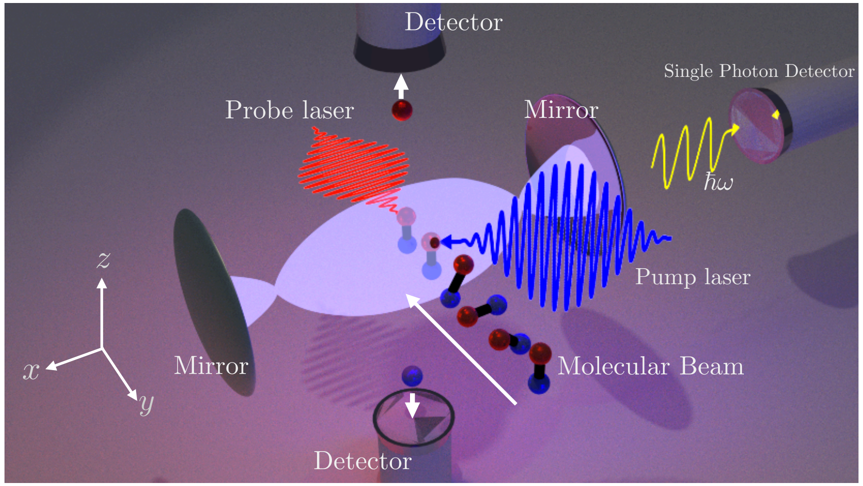
J.F. Triana and J.L. Sanz-Vicario, Physical Review Letters **122**, 063603 (2019)

Revealing the fingerprints of cavity LIC

Pump-Probe Scheme



Experimental setup



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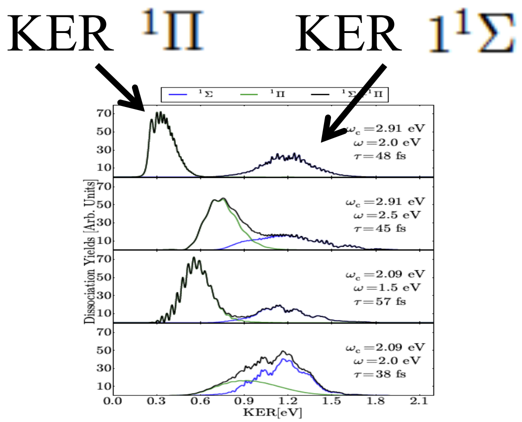
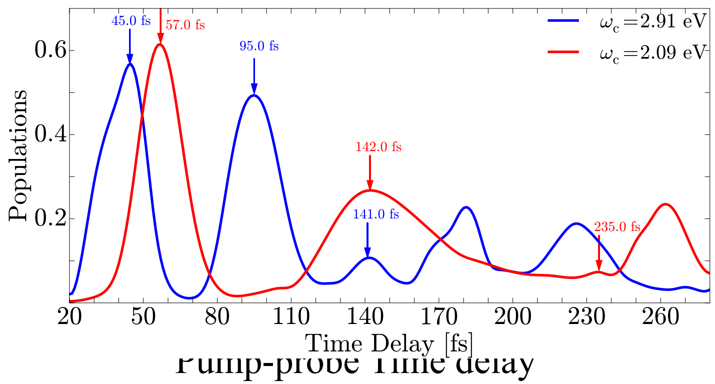
Two-channel KER spectrum



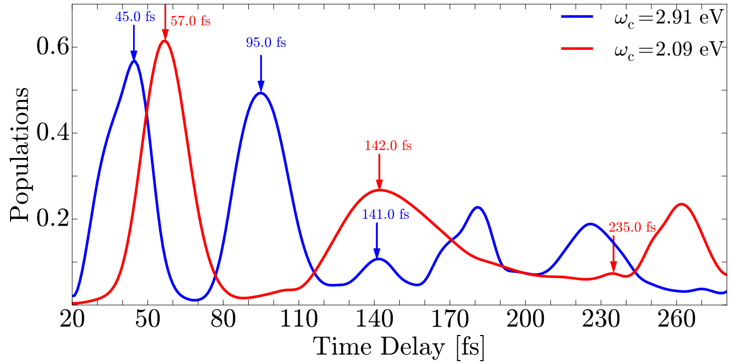
Dissociation via $^1\Pi$ state against Pump-probe time delay



Fragment yield Li+F enhancement at maxima are related to the passage across the LIC!!!

Revealing the fingerprints of cavity LIC

$^1\Pi$ population to Li+F dissociation



Cavity mode

$\omega_c = 2.91$ eV, $R_{LIC} = 6\ a.u.$

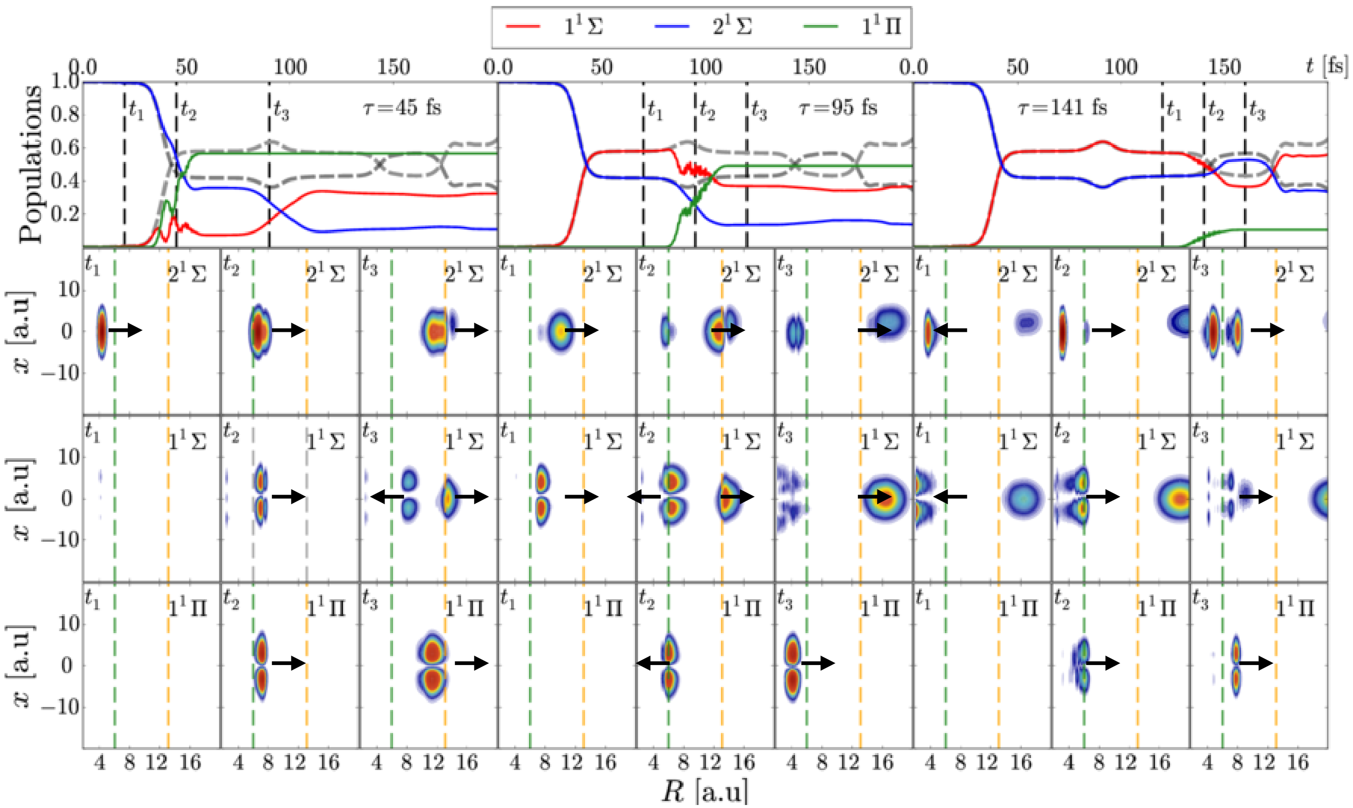
Probe Laser $R_{NAC} = 13\ a.u.$

$\omega_L = 2.5\ eV$

$2^1\Sigma$

$1^1\Sigma$

$^1\Pi$



J.F. Triana and J.L. Sanz-Vicario, Physical Review Letters **122**, 063603 (2019)

Conclusions:

•New effects in the photodynamics of molecules in quantum optical cavities to be explored.

•Quantum effects of radiation cannot be modelled with semiclassical methods (different photodynamics for different quantum states: Fock, coherent or squeezed states).

•A proposal ot unveil the presence and location of cavity LICs is outlined, to bring together theory and experiment.

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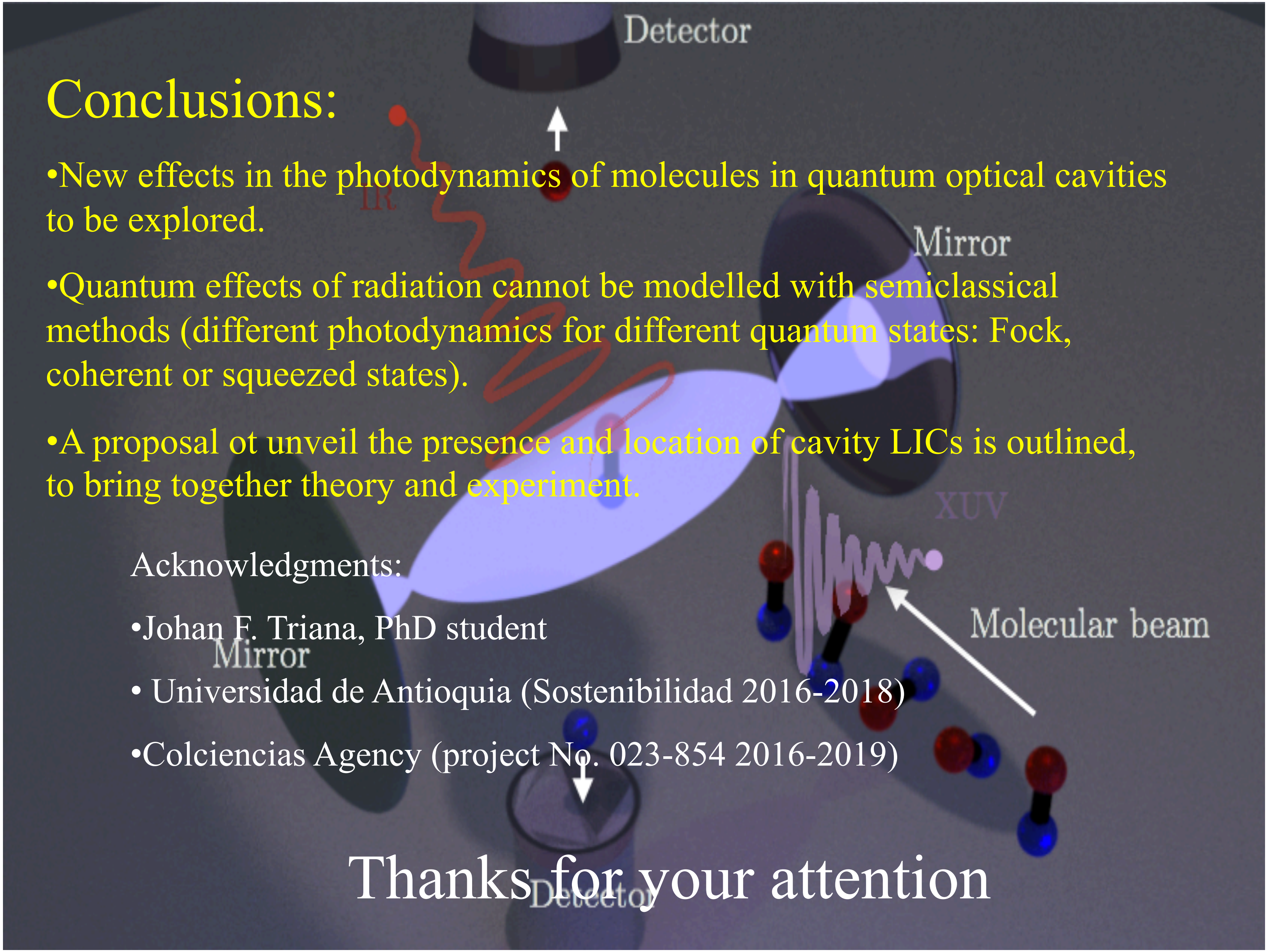
Thanks for your attention



DFG - Universidad de Antioquia: Kolumbianisch-deutsche Forschungskooperation

January-2019

Colombian-German Collaboration in Research: Universidad de Antioquia and DFG offer joint funding opportunities for bilateral research projects

On the basis of the Letter of Intent signed in January 2019 between the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) and the Universidad de Antioquia (UdeA) in Colombia, researchers from Germany and UdeA can submit proposals for joint research projects in any field of research. Submission of research proposals is possible at any time within the Research Grants Programme at DFG as well as the corresponding CODI-programme at UdeA. The proposals for German-Colombian research projects have to be submitted simultaneously to the DFG and UdeA.