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Creating Molecular Entanglement in Functionalized Semiconductor Nanostructures

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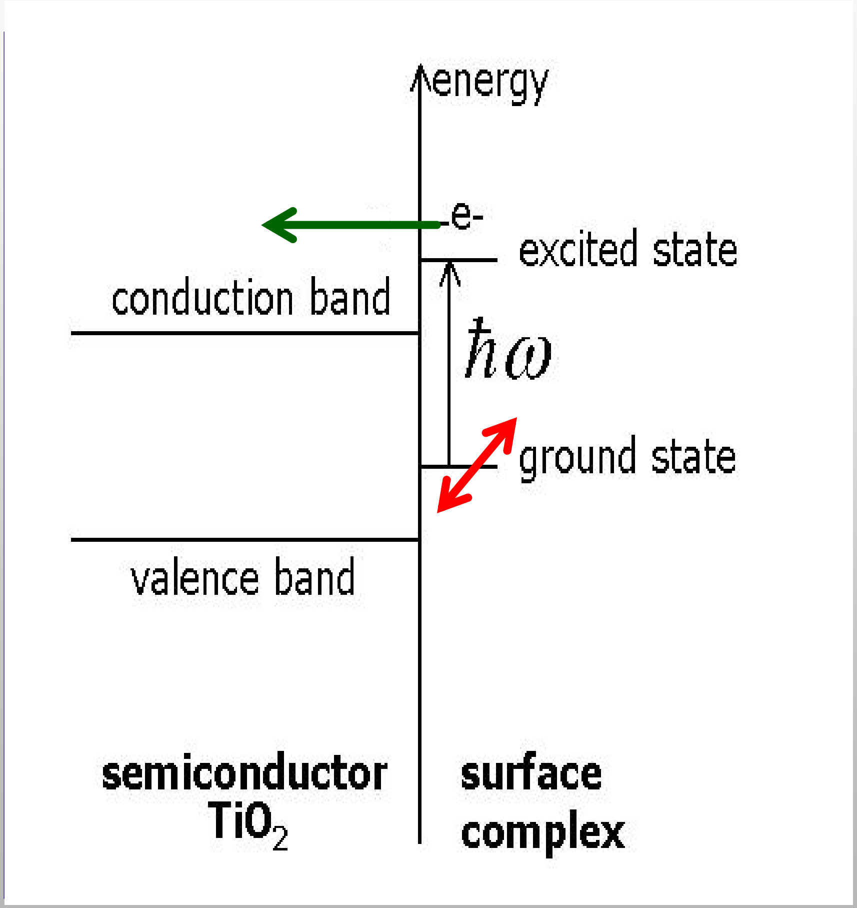
Photo-Excitation and Relaxation Processes



Interfacial electron transfer

Hole relaxation dynamics

Aspects of Study

- Interfacial Electron Transfer Dynamics
  - Relevant timescales and mechanisms
  - Total photo-induced current
  - Dependence of electronic dynamics on the crystal symmetry and dynamics
- Hole Relaxation Dynamics
  - Decoherence timescale.
  - Effect of nuclear dynamics on quantum coherences, coherent-control and entanglement.

Luis G.C. Rego and Victor S. Batista, *J. Am. Chem. Soc.* **125**, 7989 (2003);

Victor S. Batista and Paul Brumer, *Phys. Rev. Lett.* **89**, 5889 (2003), *ibid*. **89**, 28089 (2003);

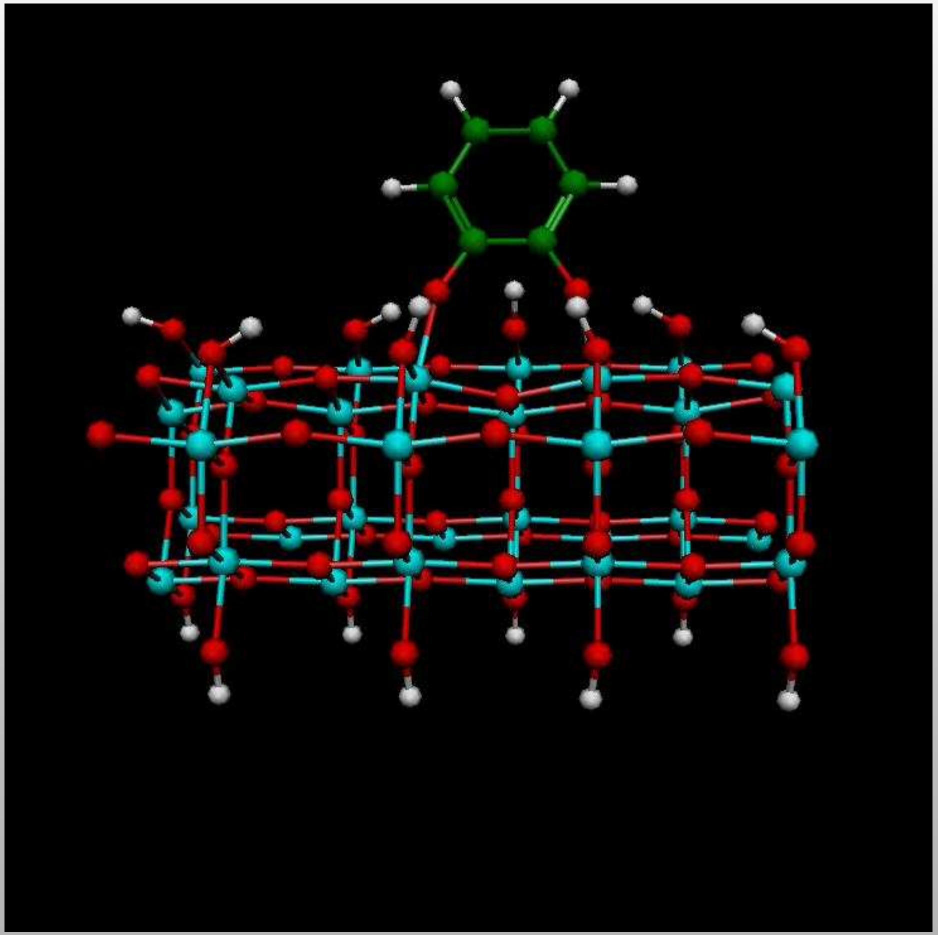
Samuel Flores and Victor S. Batista, *J. Phys. Chem. B*, **108**, 6745 (2003).

Model System – Unit Cell

TiO_2-anatase nanostructure functionalized by an adsorbed catechol molecule

124 atoms:

32 [TiO_2] units = 96
catechol [$C_6H_{6-2}0_2$] unit = 12
16 capping H atoms = 16



Mixed Quantum-Classical Dynamics Propagation Scheme

$\left|\Psi(t)\right\rangle = \hat{U}(t)\left|\Psi(0)\right\rangle$, where $\hat{U}(t) = e^{-\frac{i}{\hbar}\hat{H}t}$

and $\left|\Psi(t)\right\rangle = \sum_q B_q(t) \left|\phi_q(t)\right\rangle$ with

Short-Time Propagation Scheme

$$\boxed{B_q(t+\tau) = \sum_p B_p(t) \quad e^{-\frac{i}{\hbar}[E_p(t)+E_q(t+\tau)]\frac{\tau}{2}} \left\langle \phi_q(t+\tau) \middle| \phi_p(t) \right\rangle}$$

Time-Dependent Molecular Orbitals

$$\left|\phi_q(t)\right\rangle = \sum_i C_{i,q}(t)\left|K_i(t)\right\rangle$$

which are obtained by solving the Extended-Hückel generalized eigenvalue equation :

$$\boxed{H(t)C(t) = S(t)C(t)E(t)}$$

where **H** is the Extended Hückel Hamiltonian in the basis of Slater type atomic orbitals (AO's), $\left|K_i(t)\right\rangle$ including 4*s*, 3*p* and 3*d* AO's of Ti^{4+} ions, 2*s* and 2*p* AO's of O^{2-} ions, 2*s* and 2*p* AO's of C atoms and 1*s* AO's of *H* atoms (*i.e.,* 596 basis functions per unit cell). **S** is the overlap matrix in the AO's basis set.

Time-Dependent Propagation Scheme cont’d

For a sufficiently small integration time step τ,

$$U(t+{}^{\tau}\!/_{2})\left|\Psi(t)\right\rangle = \sum_q B_q(t)\,e^{-\frac{i}{\hbar}E_q(t)\frac{\tau}{2}}\left|q(t)\right\rangle$$

$$U(t-{}^{\tau}\!/_{2},t+\tau)\left|\Psi(t+\tau)\right\rangle = \sum_q B_q(t+\tau)\,e^{\frac{i}{\hbar}E_q(t+\tau)\frac{\tau}{2}}\left|q(t+\tau)\right\rangle$$

Time-Dependent Propagation Scheme cont’d

Setting 🟧 equal to 🟦 and multiplying by a MO at the iterated time gives the expression

$$B_q(t+\tau)=\sum_p B_p(t)e^{-\frac{i}{\hbar}(E_p(t)+E_q(t+\tau))\frac{\tau}{2}}\left\langle q(t+\tau)\middle| p(t)\right\rangle$$

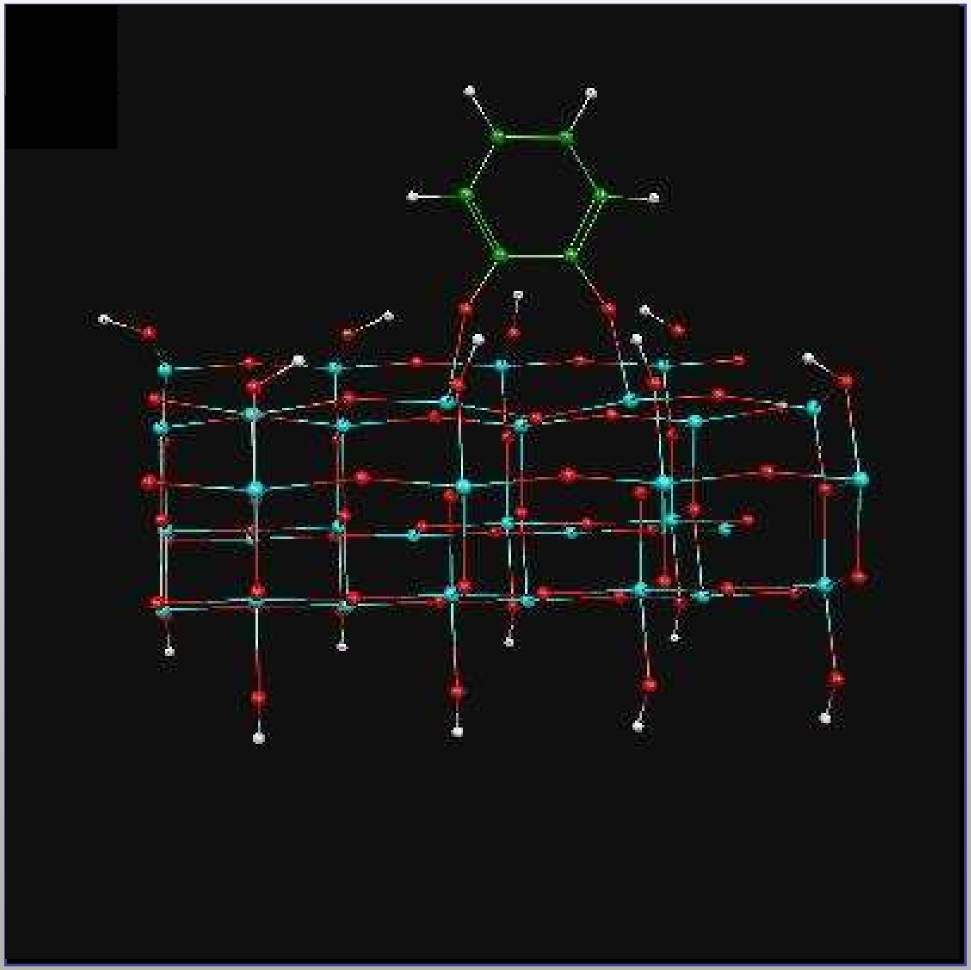
when $\tau \longrightarrow 0$,

$$\boxed{B_q(t+\tau)\approx B_q(t)e^{-\frac{i}{\hbar}(E_p(t)+E_q(t+\tau))\frac{\tau}{2}}}$$

Ab Initio DFT-Molecular Dynamics Simulations

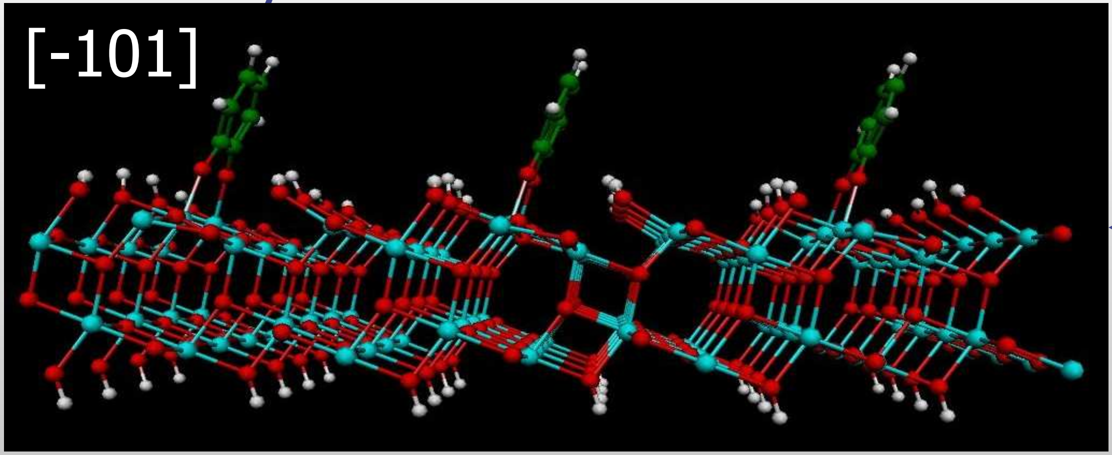
VASP/VAMP simulation package

Hartree and Exchange Correlation Interactions: Perdew-Wang functional
Ion-Ion interactions: ultrasoft Vanderbilt pseudopotentials



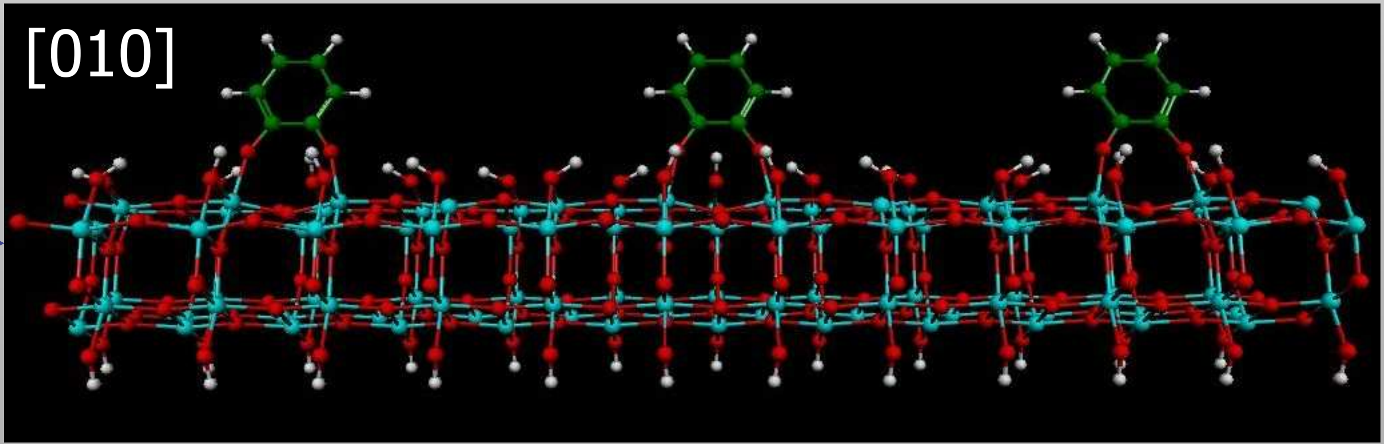
Model System – Mixed Quantum-Classical Simulations

Three unit cells along one planar directions with periodic boundary conditions in the other.

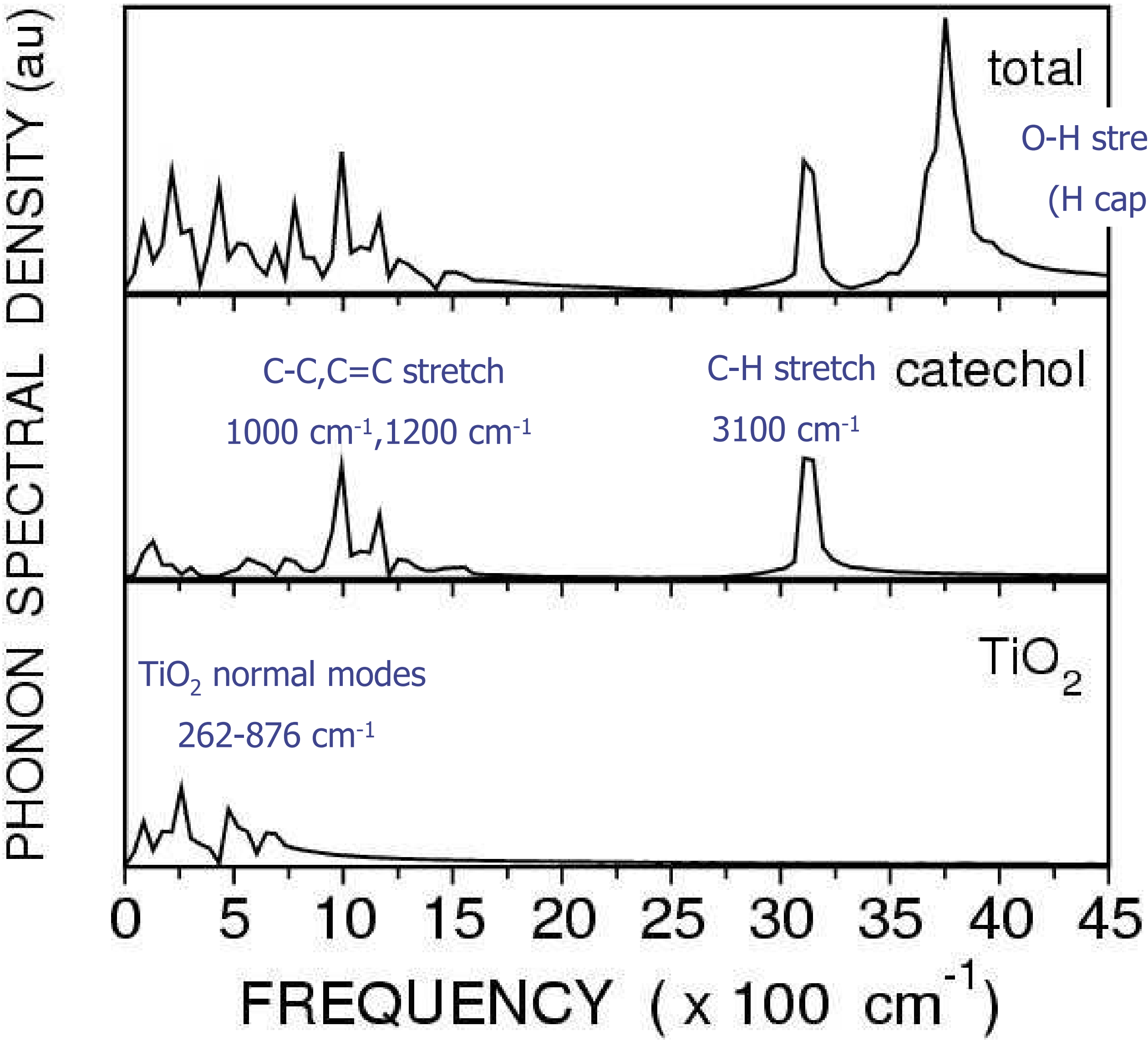


Three unit cells extending the system in [-101] direction

System extened in the [010] direction



Phonon Spectral Density



O-H stretch, 3700 cm^{-1}

(H capping atoms)

C-C,C=C stretch

1000 cm^{-1},1200 cm^{-1}

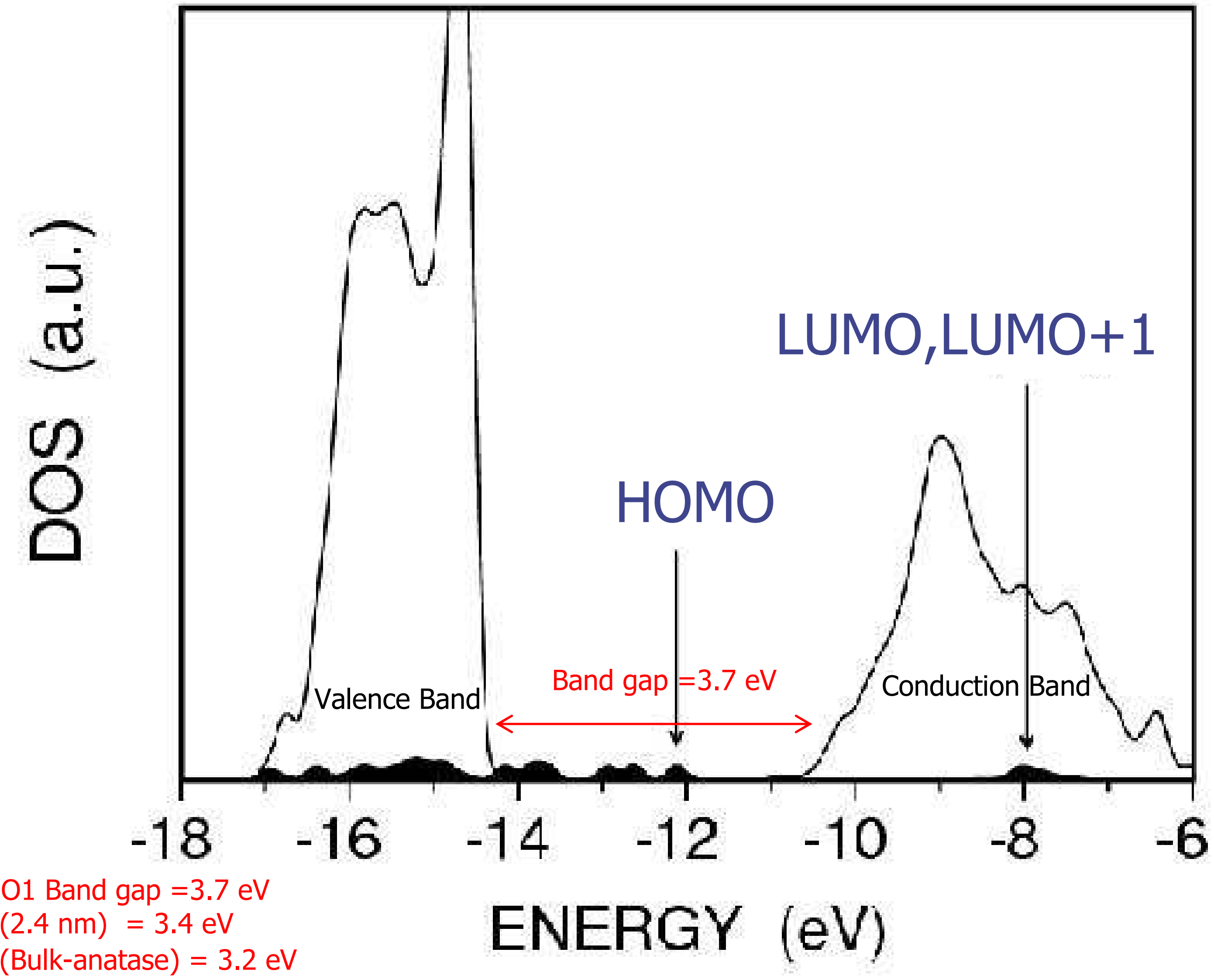
C-H stretch

3100 cm^{-1}

TiO_2 normal modes

262-876 cm^{-1}

Electronic Density of States (1.2 nm particles)



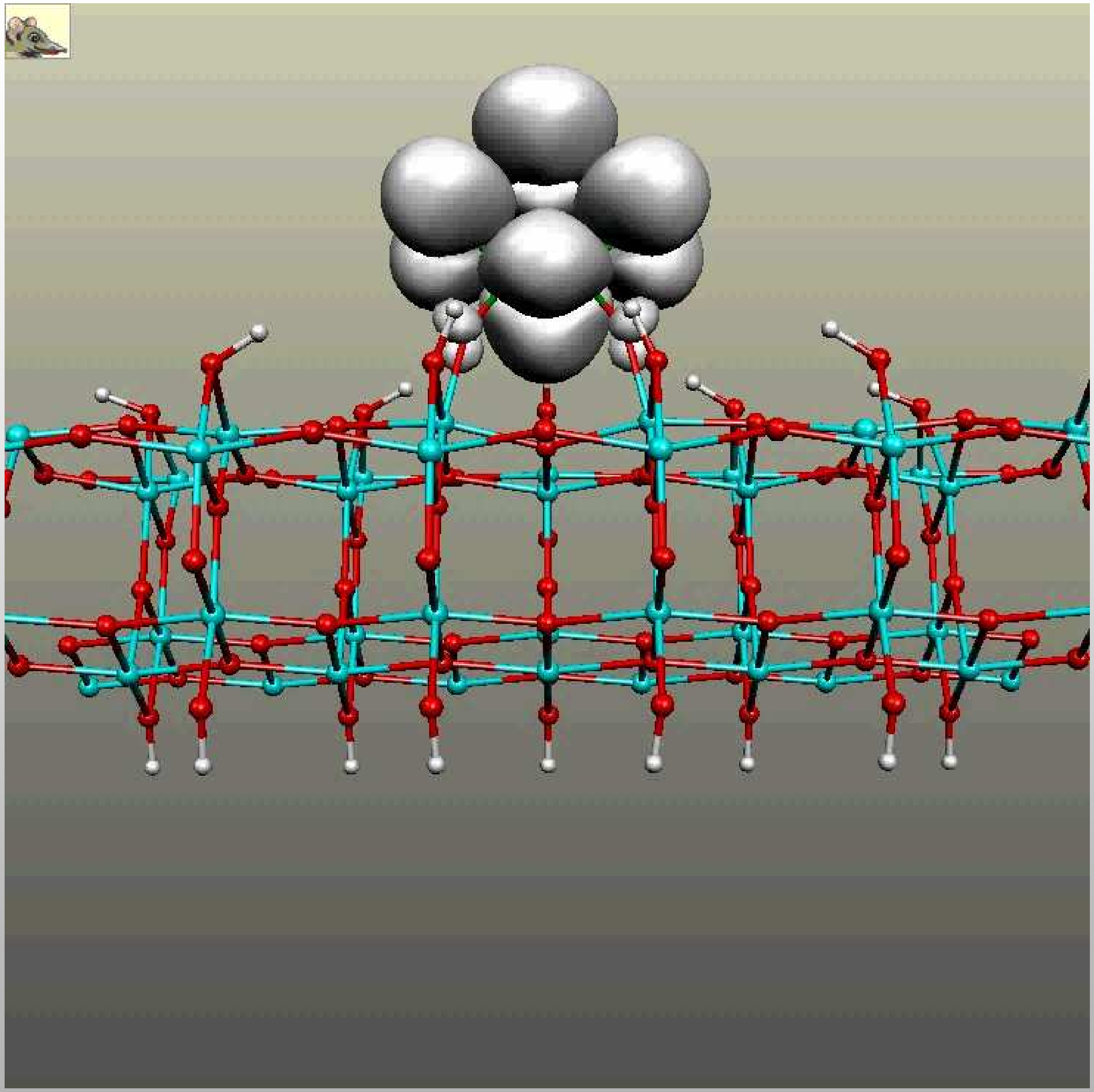
ZINDO1 Band gap =3.7 eV
Exp. (2.4 nm) = 3.4 eV
Exp. (Bulk-anatase) = 3.2 eV

Propagation Scheme cont'd

Therefore, we can calculate the wavefunction and electronic density for all t>0 and we can also define the survival probability for the electron to be found on the initially populated adsorbate molecule

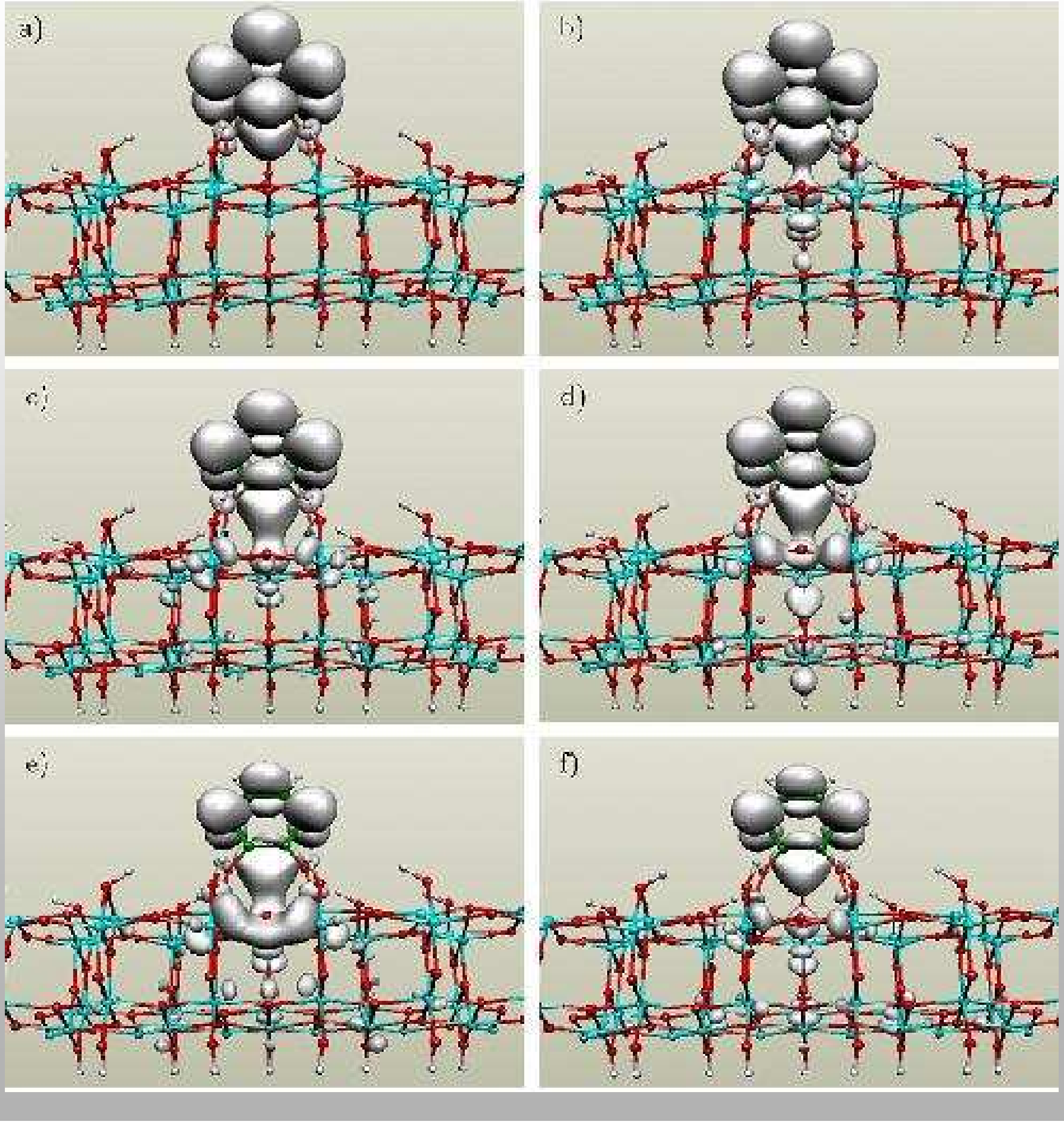
$$P_{MOL}(t) = \left| \sum_{j,\beta}^{SYS} \sum_{i,\alpha}^{MOL} C_{i,\alpha}^{*}(t) C_{j,\beta}(t) S_{\alpha,\beta}^{i,j} \right|$$

Injection from LUMO

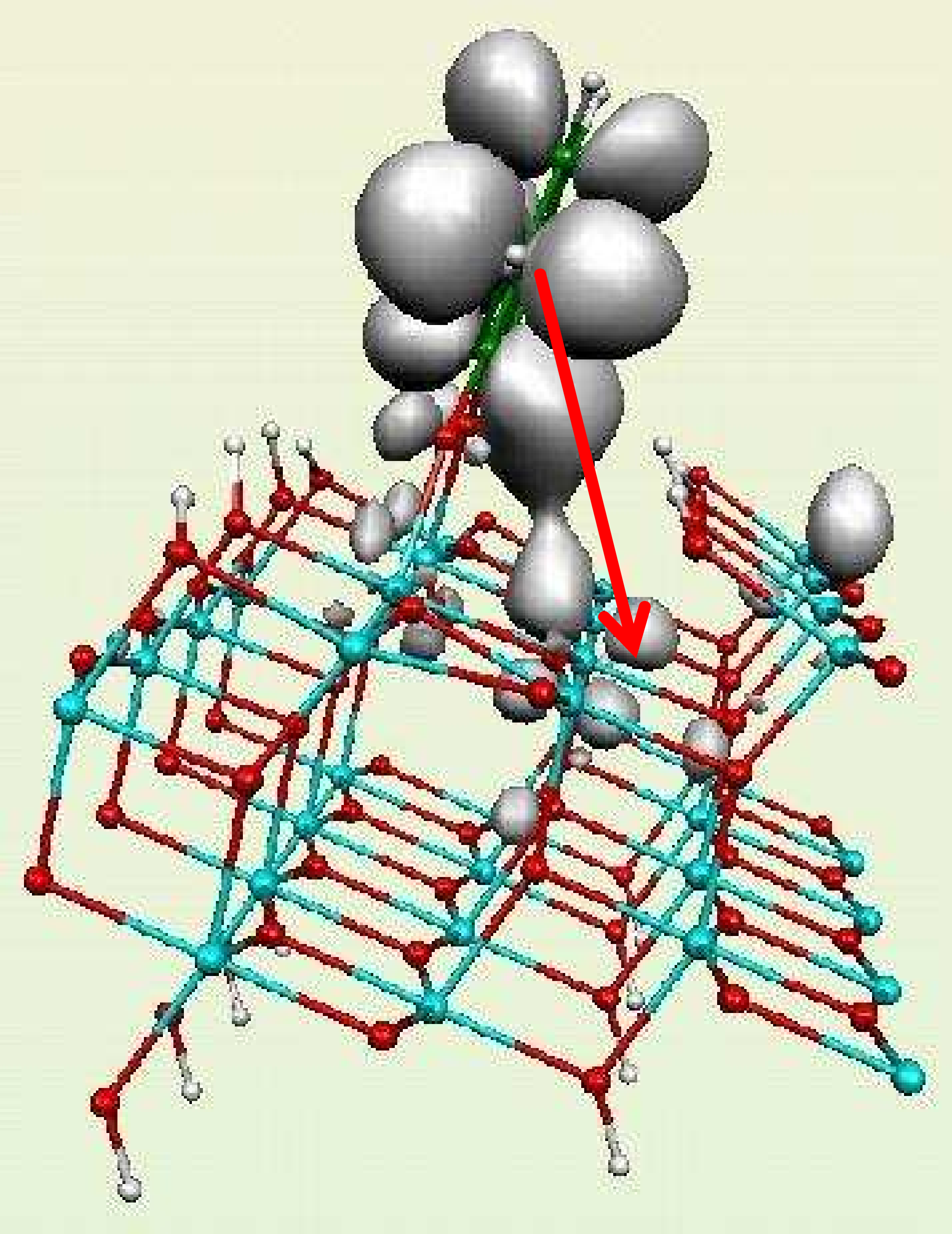


TiO2 system extended in [-101] direction with PBC in [010] direction

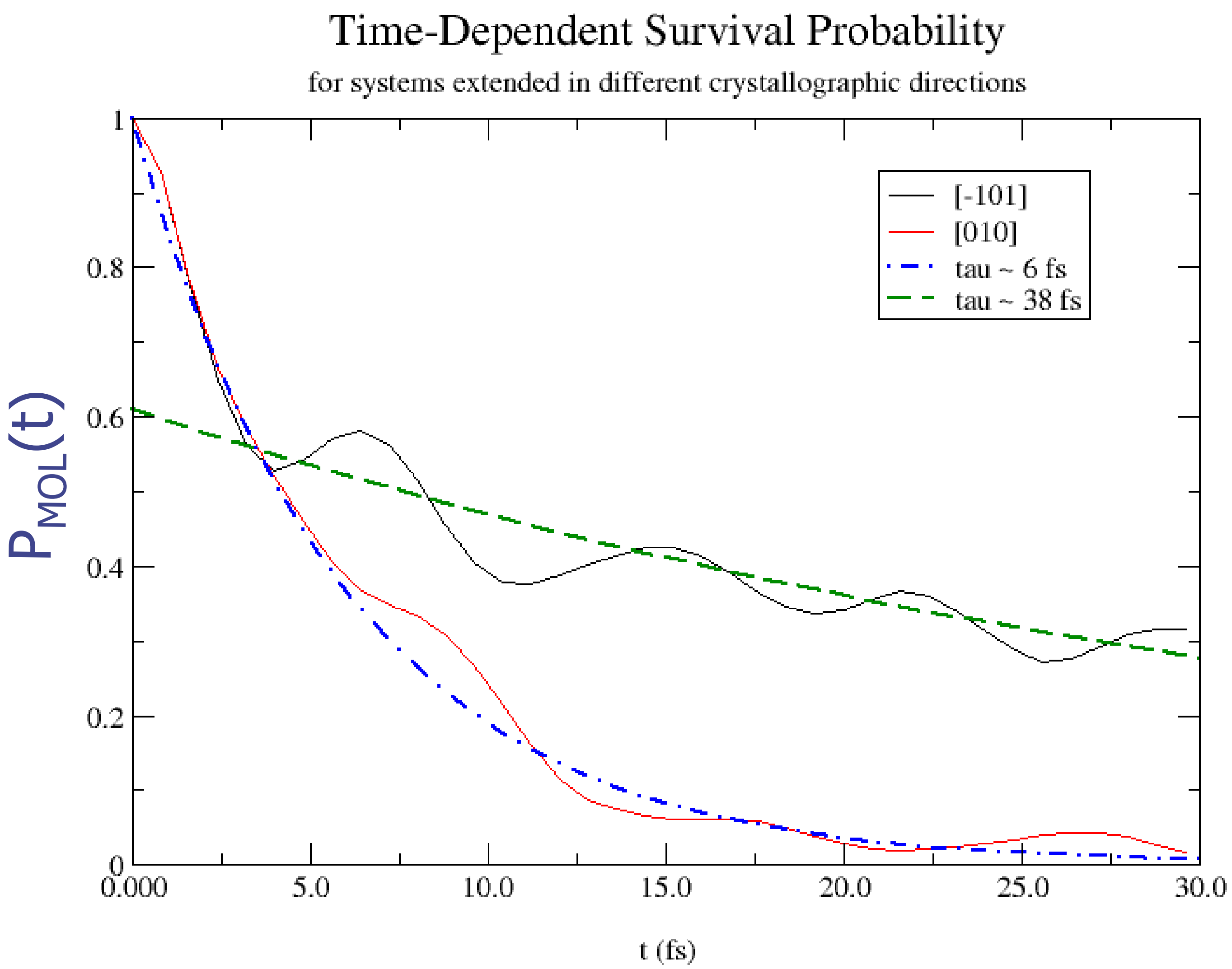
Injection from LUMO (frozen lattice, 0 K)



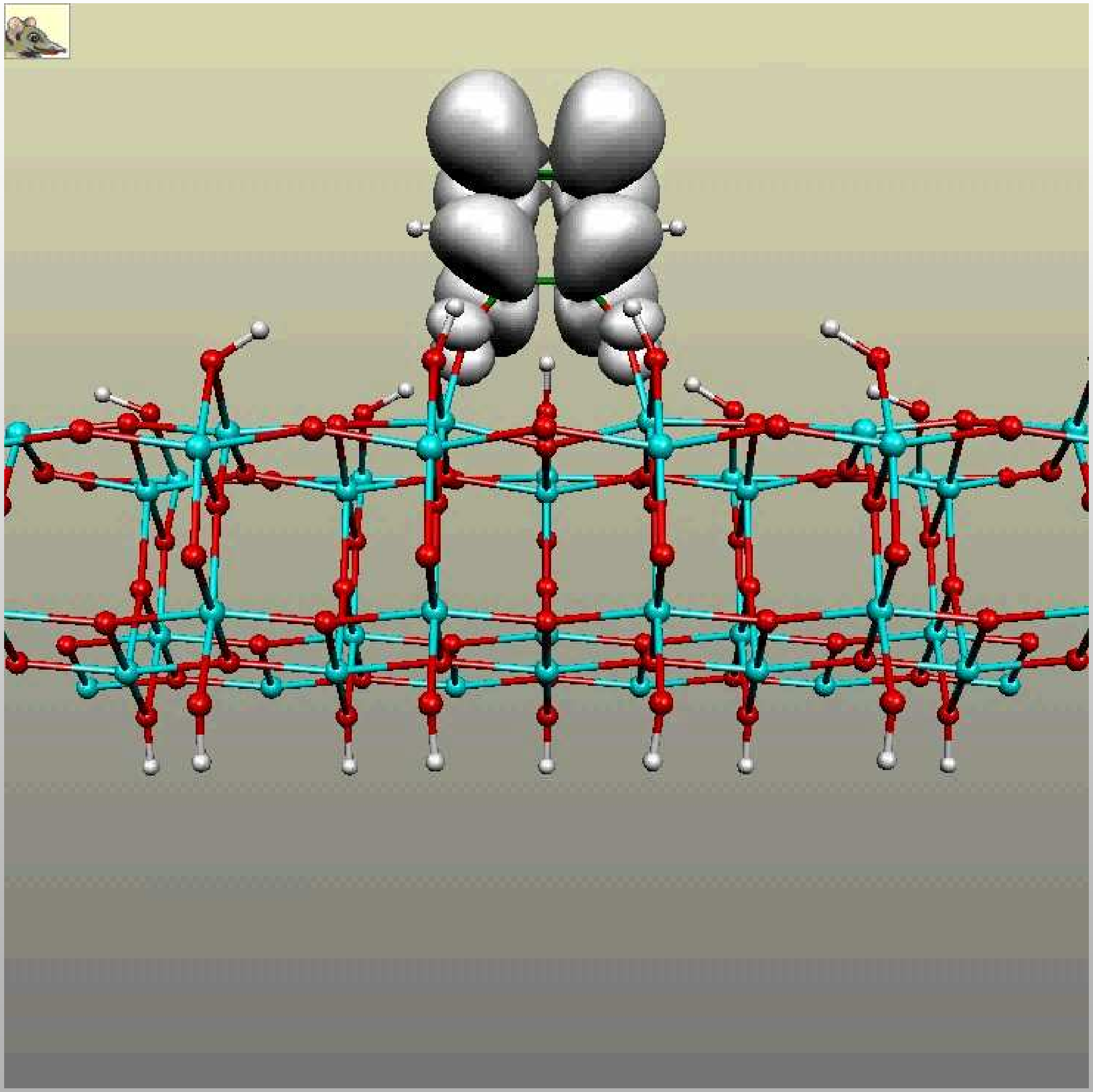
LUMO Injection cont'd



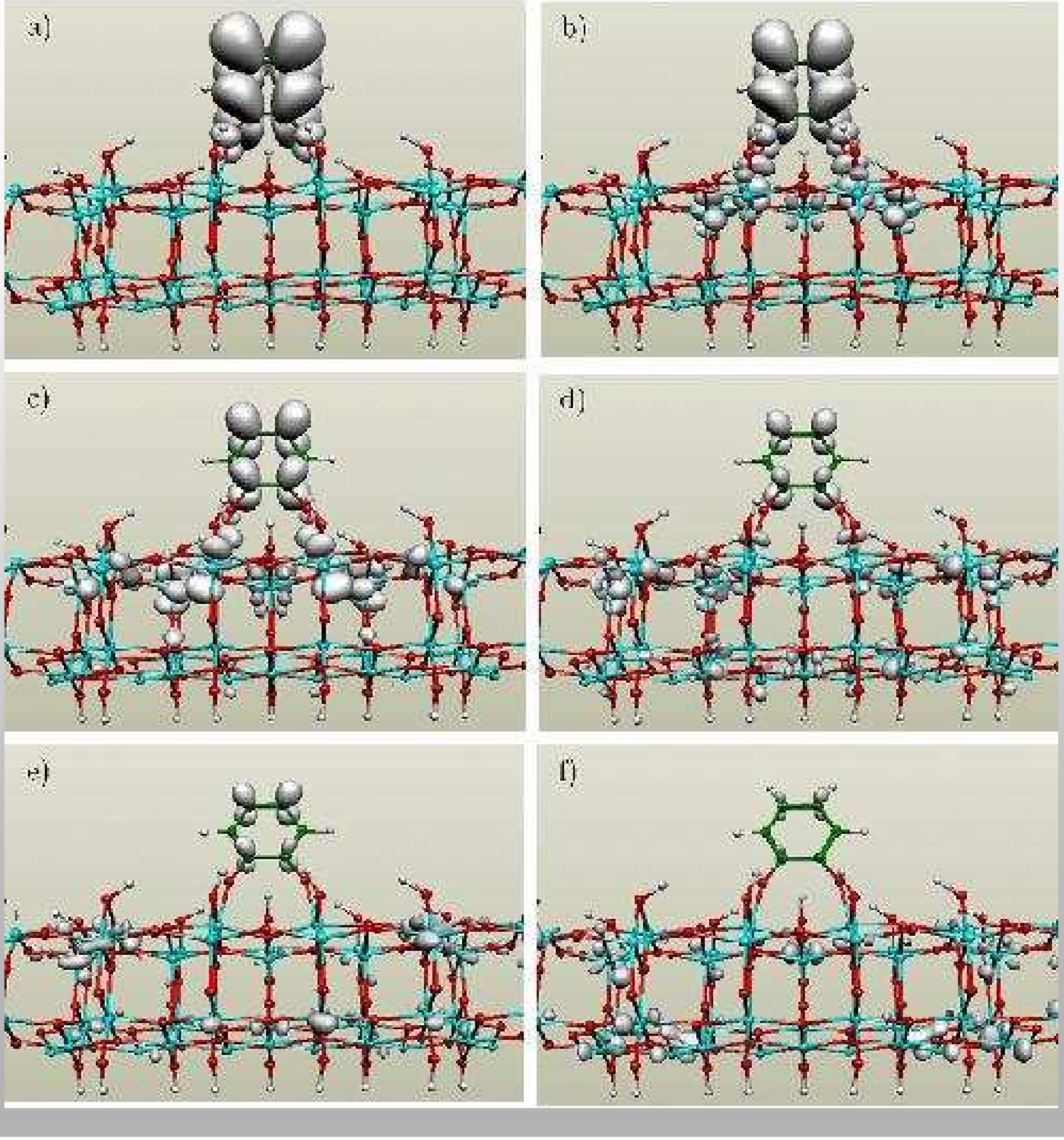
LUMO Injection (frozen lattice) cont'd



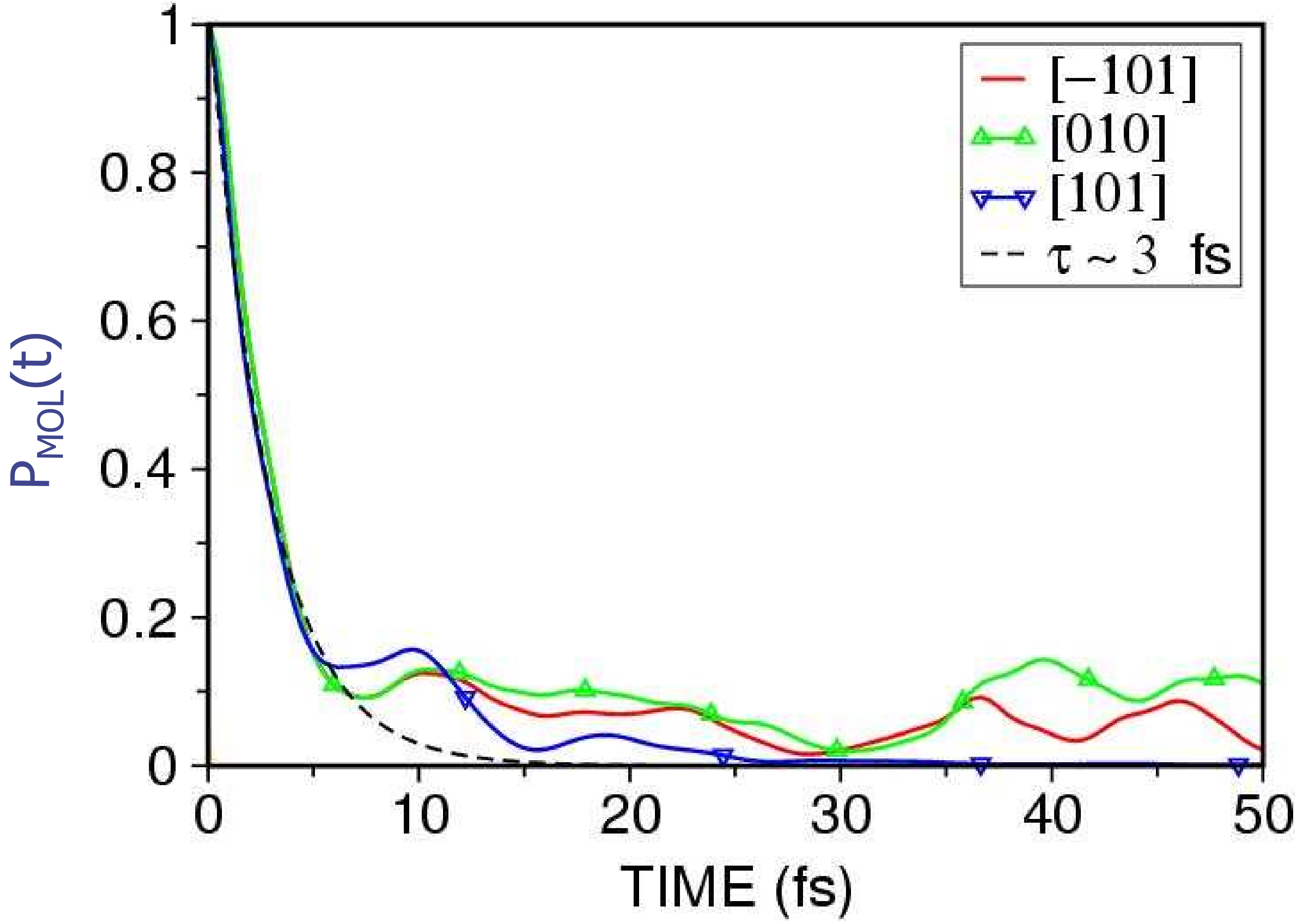
Injection from LUMO+1



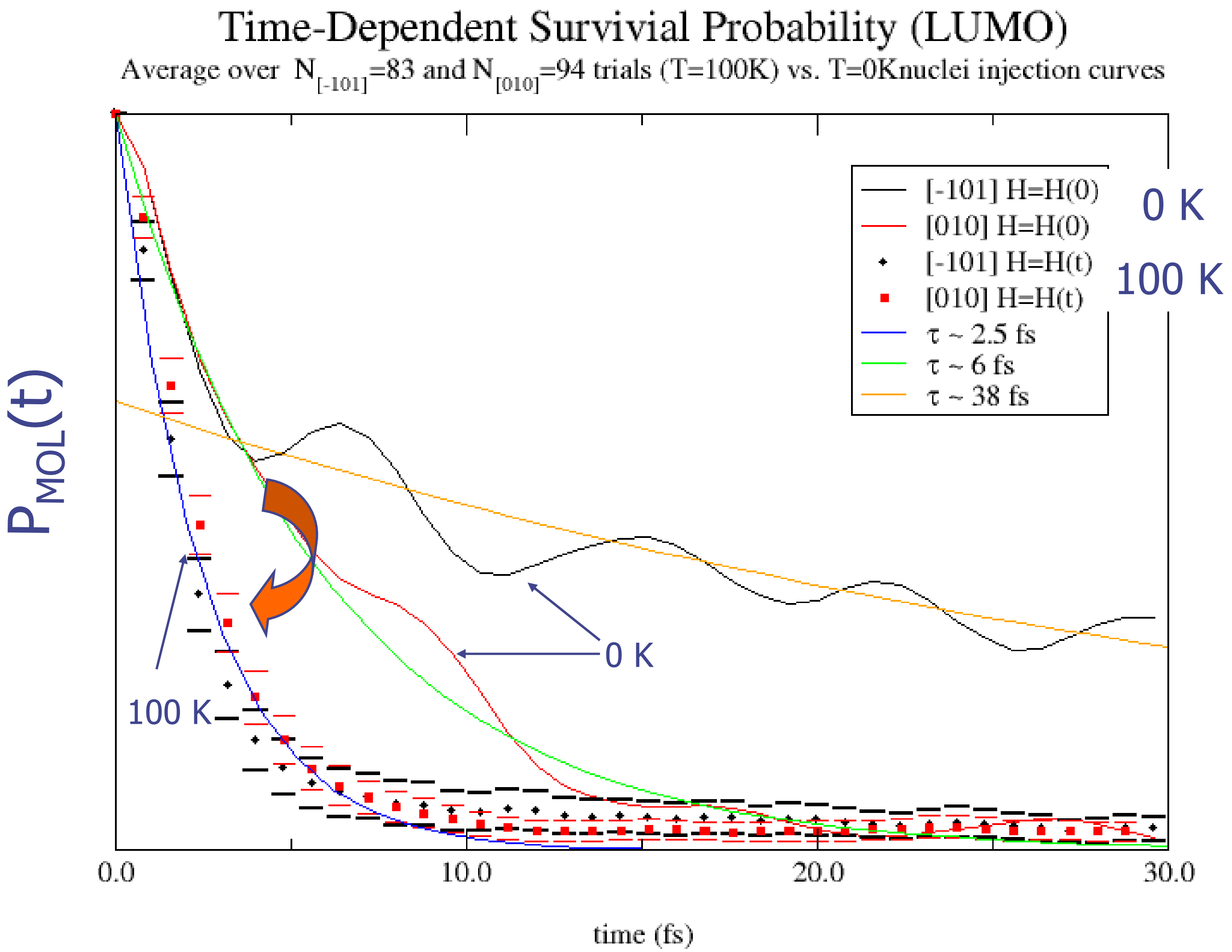
Injection from LUMO+1 (frozen lattice, 0 K)



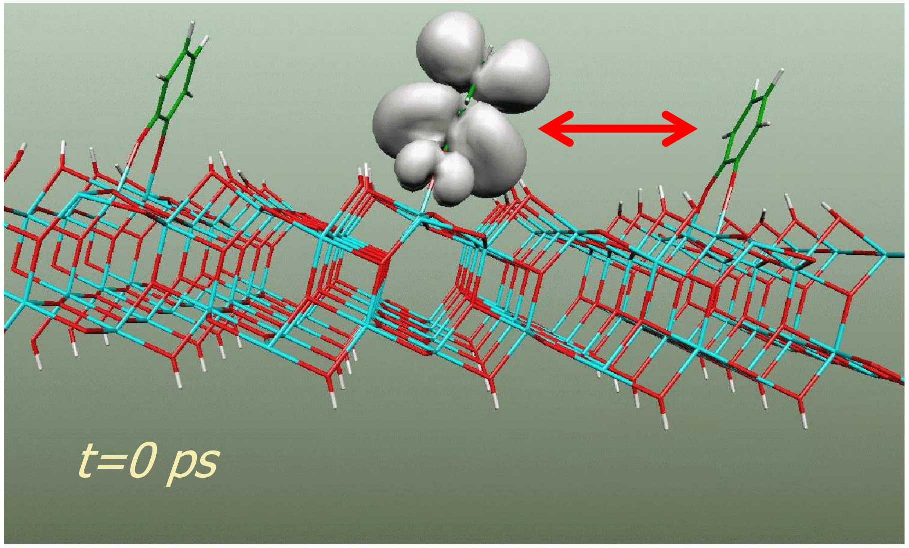
LUMO+1 Injection (frozen lattice) cont'd

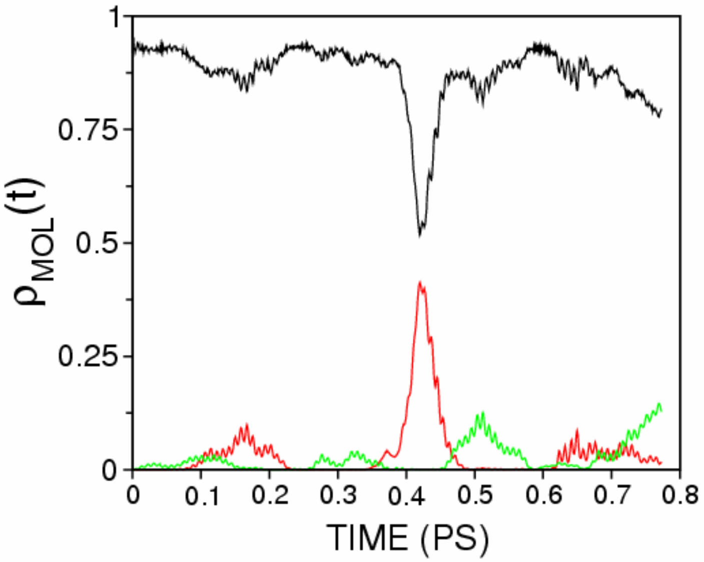


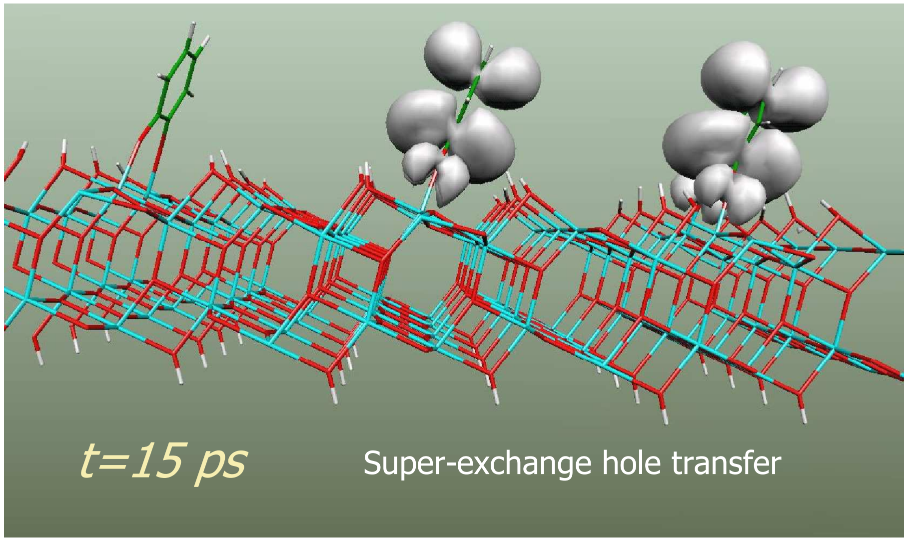
LUMO Injection at Finite Temperature (100 K)

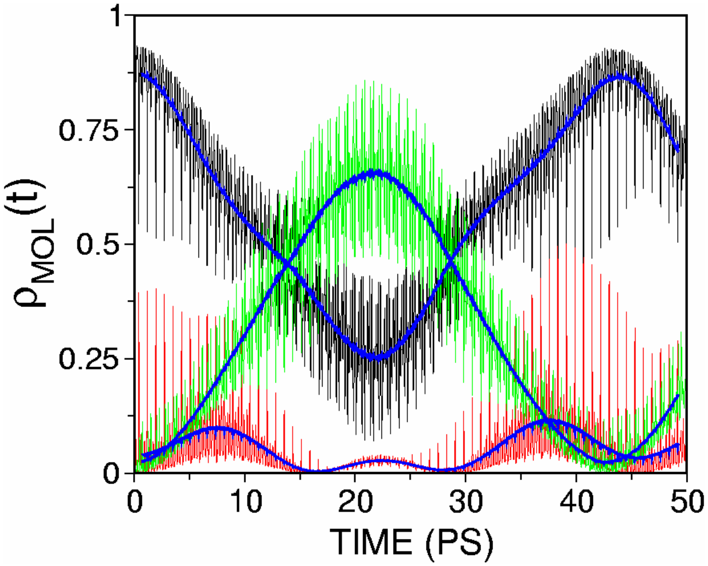


Hole-Relaxation Dynamics in the Semiconductor Band Gap

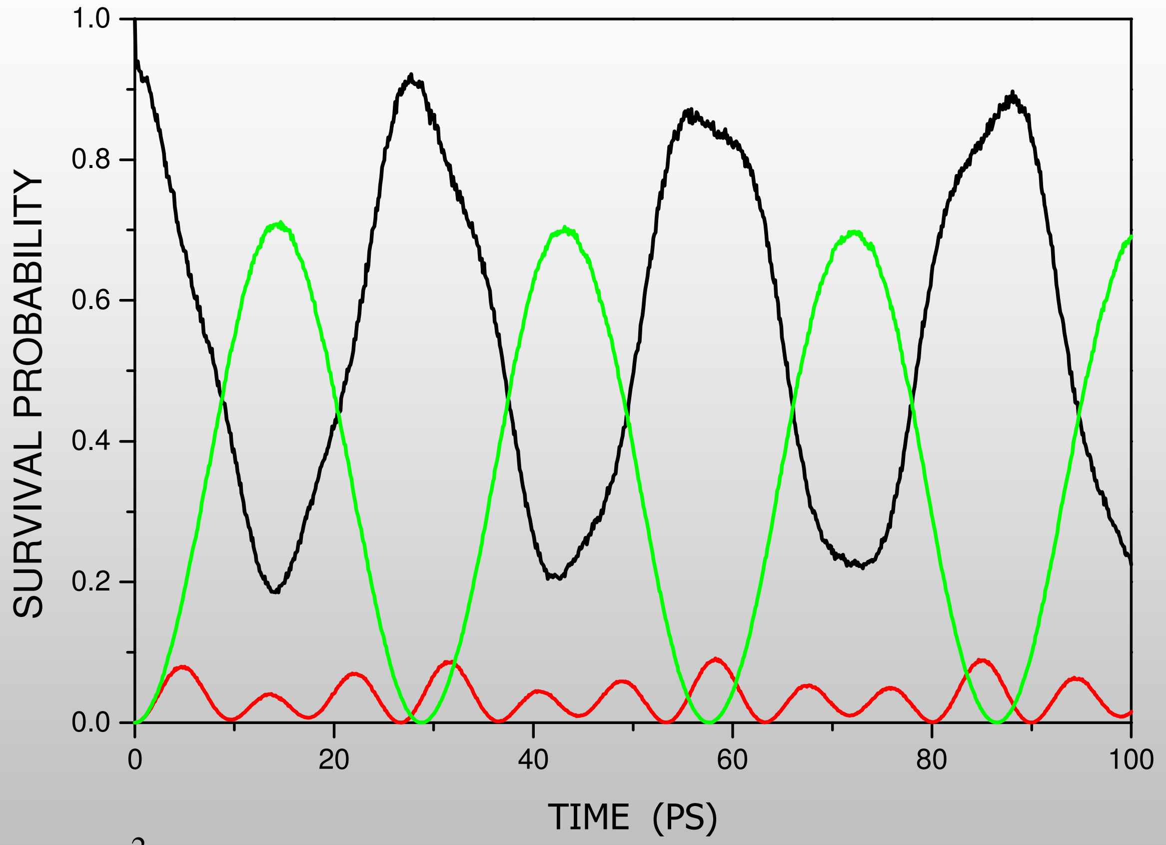








Coherent Hole-Tunneling Dynamics



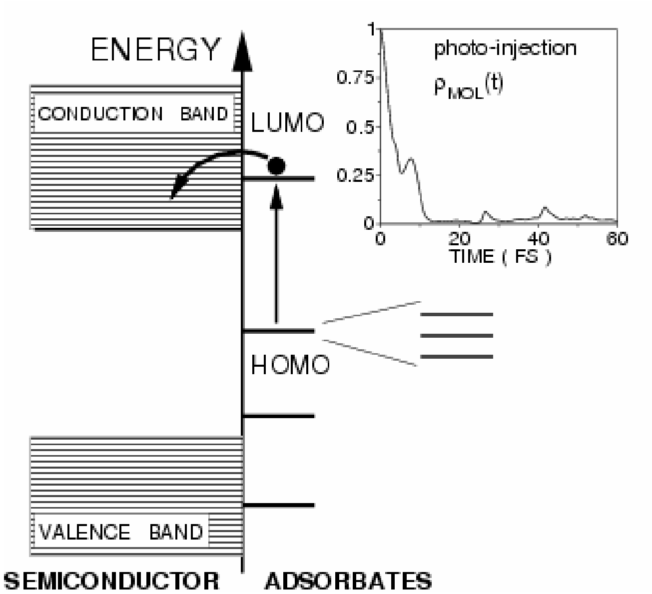
$$P_j(t) = \frac{\gamma_{jk}^2/\hbar^2}{\Gamma_{jk}^2}\sin^2(\Gamma_{jk} t); \qquad \Gamma_{jk} = \sqrt{(\gamma_{jk}/\hbar)^2 + (\omega_{jk}/2)^2}$$

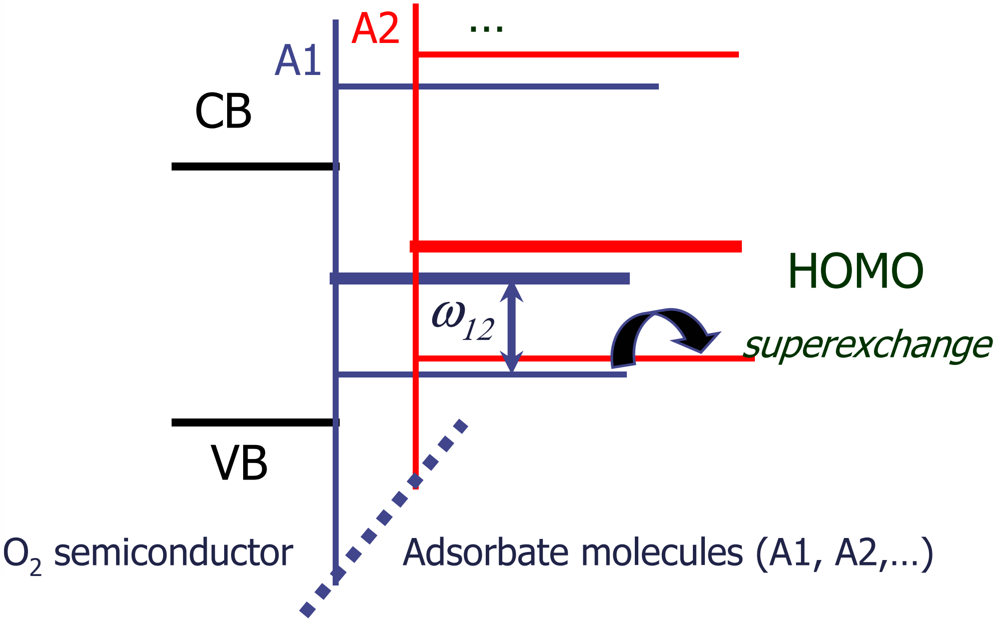
$$\gamma_{RC} = 1.2*\gamma_{LC} \qquad \omega_{LC} = 4.5*\omega_{RC}$$

Investigation of Coherent-Control

$$\left|\Psi(t)\right\rangle \xrightarrow[t=k^{*}\tau]{\tau\,=\,200\text{ fs},\ \omega_{12}} \left|\Psi(t)\right\rangle - 2\frac{\left\langle\Psi(0)\middle|\Psi(t)\right\rangle}{\left\langle\Psi(0)\middle|\Psi(0)\right\rangle}\left|\Psi(0)\right\rangle$$

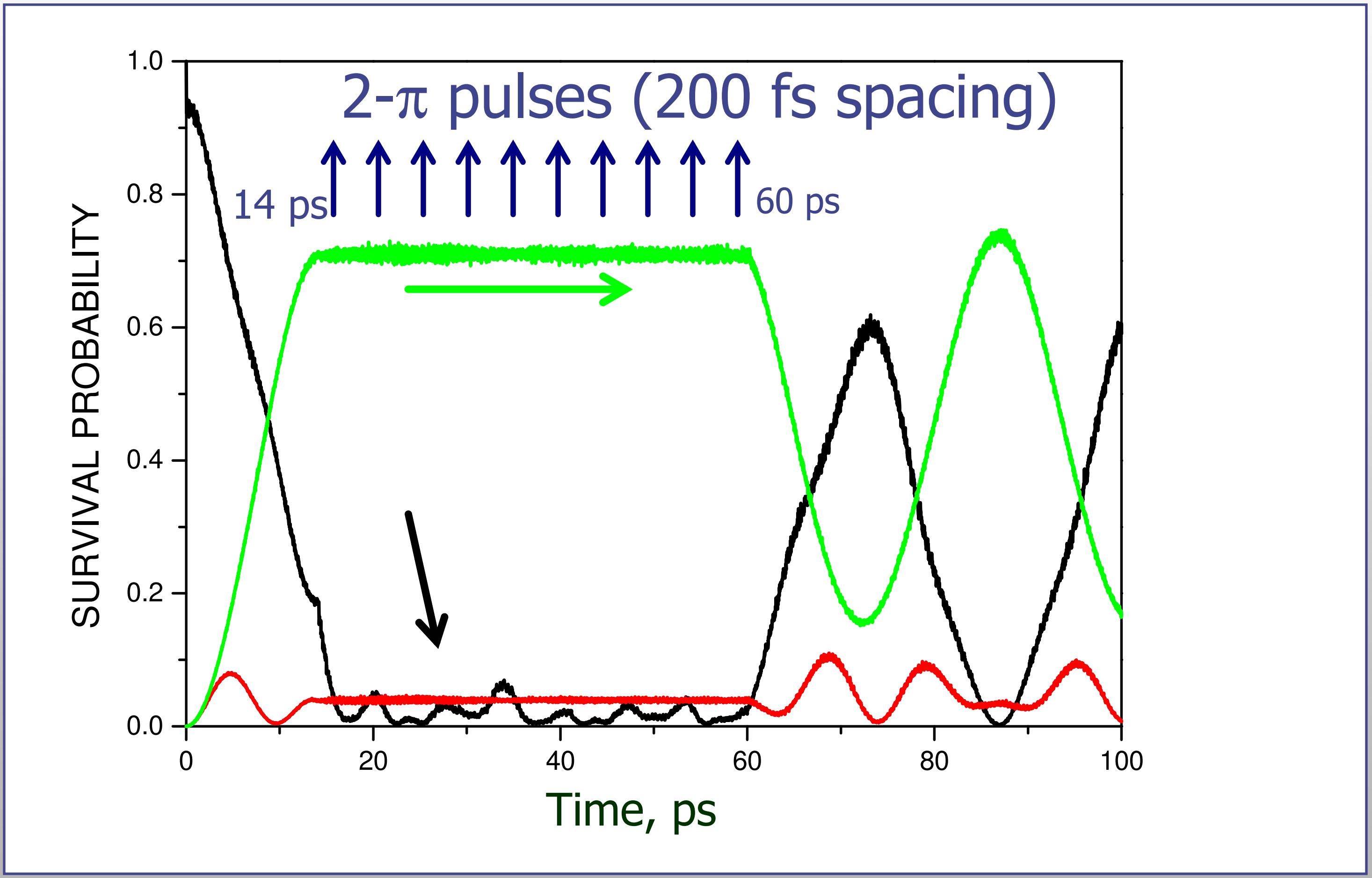
2-π pulses



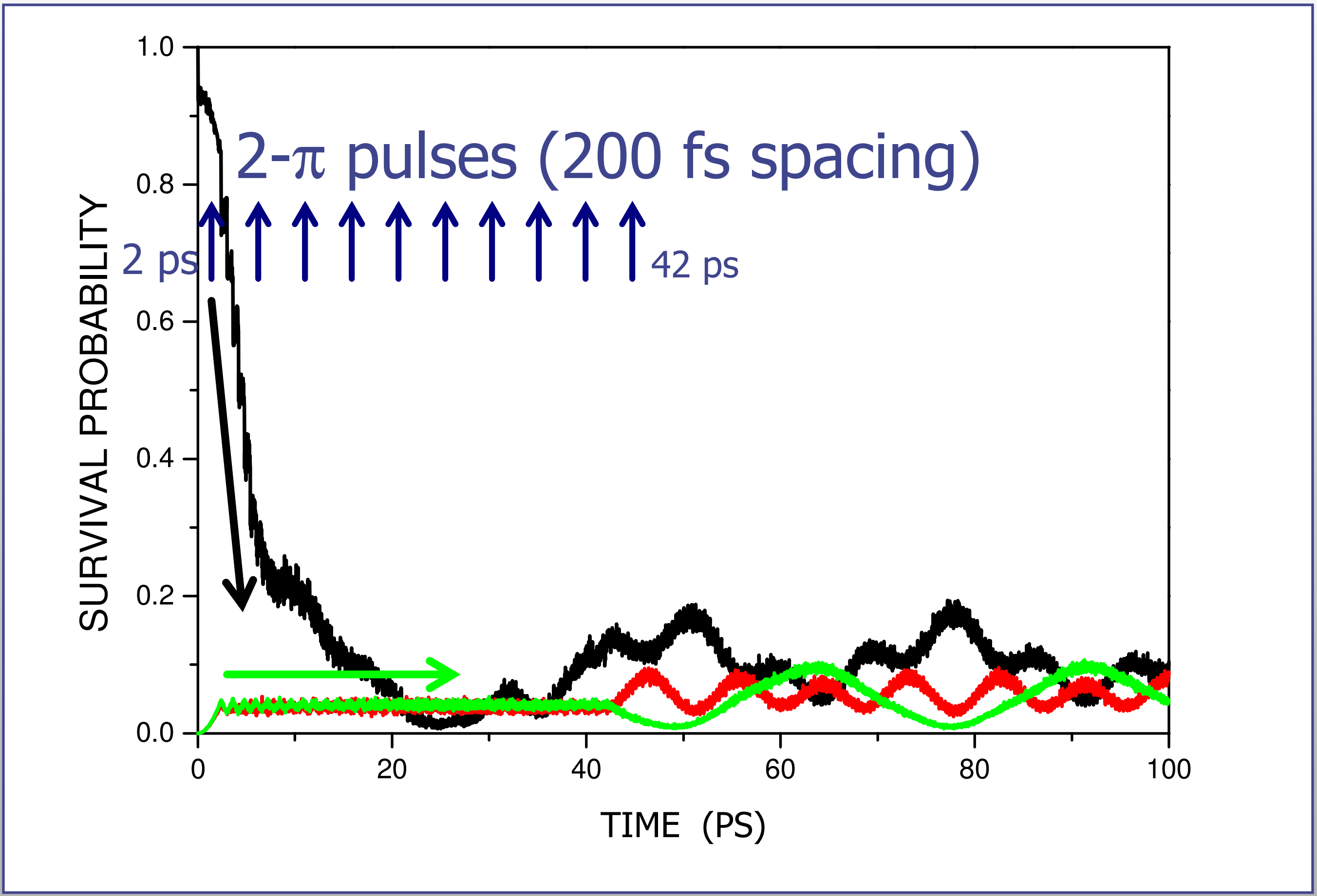


Train of 2-π pulses : Agarwal et. al. *Phys. Rev. Lett.* **86**, 4271 (2001)

Investigation of Coherent-Control cont'd



Investigation of Coherent-Control



Reduced Density Matrix: Hole-States

$$\rho_t = \sum_{\xi} p_{\xi} \left|\Psi_t^{\xi}\right\rangle\left\langle\Psi_t^{\xi}\right|$$

$$= \left(\begin{array}{c:c} \text{Adsorbates} & \text{Coupling} \\ \hdashline \text{Coupling} & \text{Semiconductor} \end{array}\right)$$

Index ξ indicates a particular initial nuclear configuration

Occupancy Notation

$$\left| HOMO_L \right\rangle \Rightarrow \left| 100 \right\rangle$$

$$\left| HOMO_C \right\rangle \Rightarrow \left| 010 \right\rangle$$

$$\left| HOMO_R \right\rangle \Rightarrow \left| 001 \right\rangle$$

Thus these kets describe the state of *all three* adsorbates -- at once, *i.e.*, the state of the hole as distributed among all three adsorbates.

Investigation of Entanglement cont'd

Example: In the occupancy representation,

$$\left|\Psi_t^{\xi}\right\rangle \approx C_{100}^{\xi}\left|100\right\rangle + C_{010}^{\xi}\left|010\right\rangle + C_{001}^{\xi}\left|001\right\rangle + \sum_{k\in TiO_2} C_{100}^{\xi}\left|k\right\rangle$$

a state $\left|\Psi_0\right\rangle$ defined by only two nonzero expansion coefficients represents a physical state of *maximal entanglement* , e.g.,

$$C_{010}^{0} = C_{001}^{0} = \frac{1}{\sqrt{2}}$$

between the **center** and **right** adsorbates.

Investigation of Coherences cont'd

Compute the *subspace* density matrix explicitly

$$\rho_t^{Ads} = \sum_{\xi} p_{\xi} \left| \Psi_t^{\xi} \right\rangle^{Ads} \left\langle \Psi_t^{\xi} \right|^{Ads}$$

$$= \left\langle \begin{pmatrix} \left|C_{100}\right|^2 & C_{100} C_{010}^* & C_{100} C_{001}^* \\ C_{010} C_{100}^* & \left|C_{010}\right|^2 & C_{010} C_{001}^* \\ C_{001} C_{100}^* & C_{001} C_{010}^* & \left|C_{001}\right|^2 \end{pmatrix} \right\rangle_{\xi}$$

Investigation of Coherences cont'd

Off-diagonal elements are indicative of decoherence

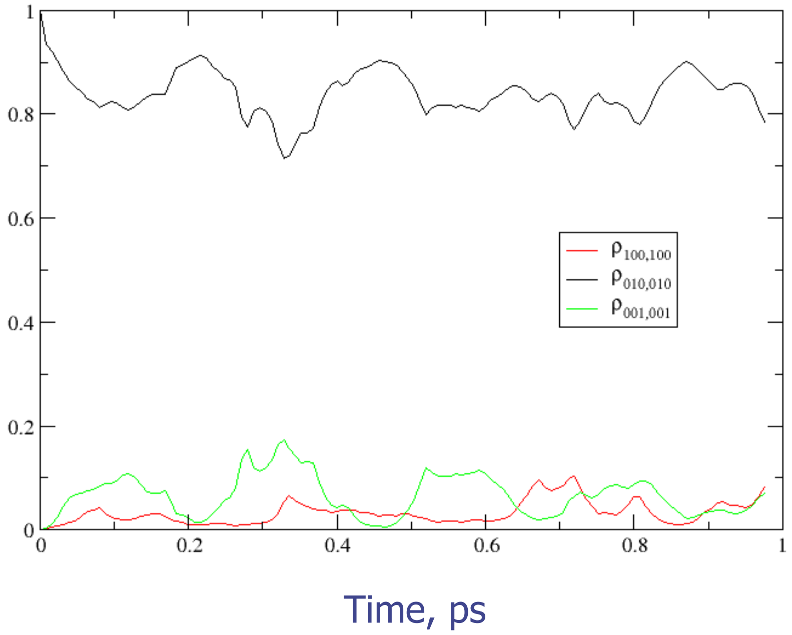
$$\boxed{\rho^{Ads}_{\alpha,\alpha'}(t) = \left\langle R_\alpha R_{\alpha'} e^{i(\phi_\alpha - \phi_{\alpha'})} \right\rangle}$$

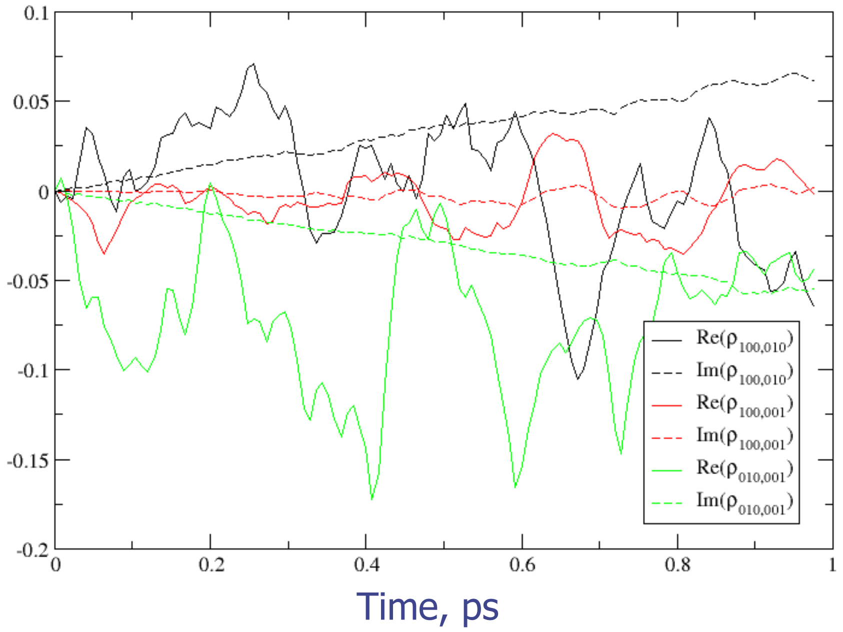
if nuclear motion randomizes the phases, i.e, $\boxed{(\phi_\alpha - \phi_{\alpha'})}$ becomes a random quantity and the average

$$\boxed{\left\langle R_\alpha R_{\alpha'} e^{i(\phi_\alpha - \phi_{\alpha'})} \right\rangle \to 0}$$

The system will no longer be in a coherent superposition of adsorbate states.

Investigation of Coherences cont'd

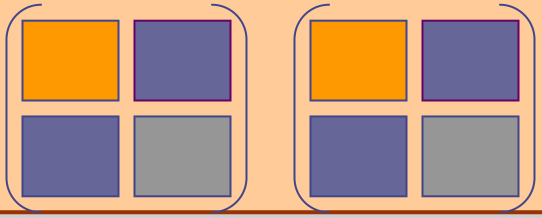

Diagonal Elements of the Reduced Density Matrix
T=100 K

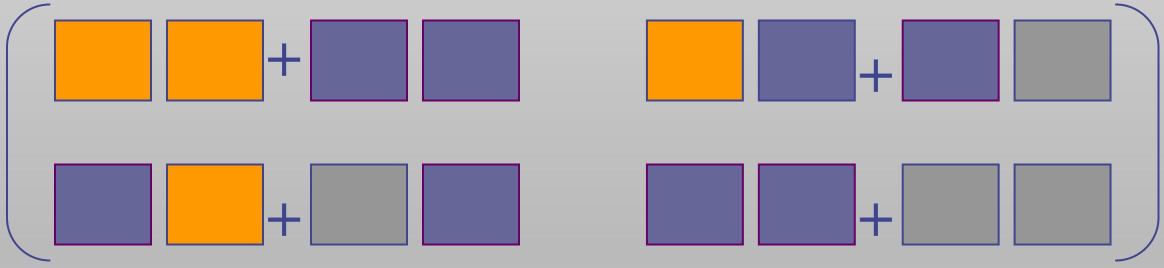

Off-Diagonal Elements of the Reduced Density Matrix
T=100 K

Investigation of Coherences cont’d

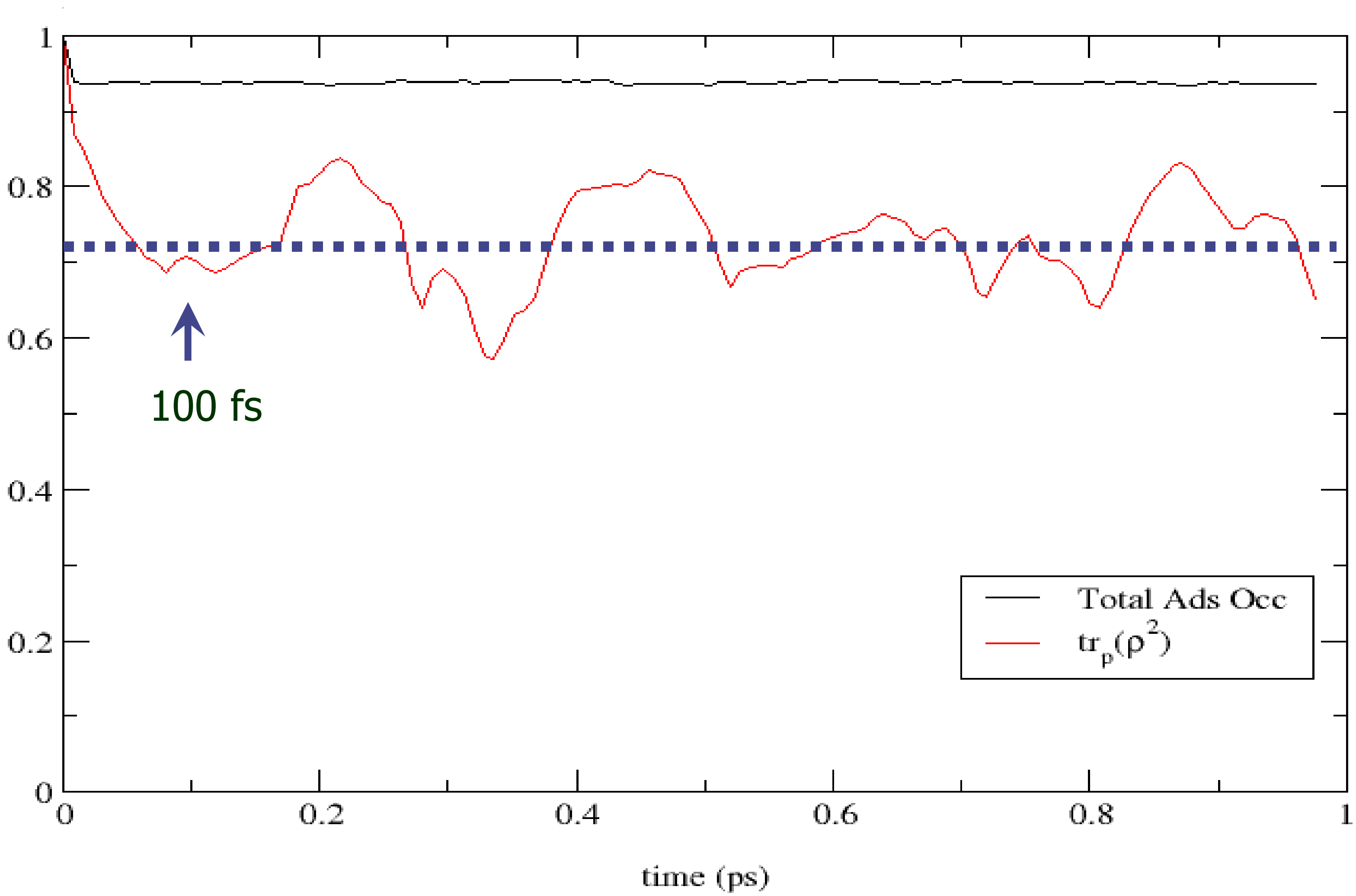
Measure of decoherence: $Tr\left[\rho_t^2\right]$

$\rho^2 =$





Decoherence Dynamics cont'd



Conclusions

- We have investigated interfacial electron transfer and hole tunneling relaxation dynamics according to a mixed quantum-classical approach that combines *ab-initio* DFT molecular dynamics simulations of nuclear motion with coherent quantum dynamics simulations of electronic relaxation.

- We have investigated the feasibility of creating entangled hole-states localized deep in the semiconductor band gap. These states are generated by electron-hole pair separation after photo-excitation of molecular surface complexes under cryogenic and vacuum conditions.

- We have shown that it should be possible to coherently control superexchange hole-tunneling dynamics under cryogenic and vacuum conditions by simply applying a sequence of ultrashort 2π-pulses with a frequency that is resonant to an auxiliary transition in the initially populated adsorbate molecule.

- We conclude that large scale simulations of quantum dynamics in complex molecular systems can provide valuable insight (into the behavior of the quantum coherences in exisiting materials), which might be essential to bridge the gap between the quantum information and quantum control communities.

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