Ultrafast Heterogeneous Electron Transfer in Nano-Hybrid Systems

Computational Studies on Perylene at Ti_2O Clusters

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The task:

- simulation of linear and transient absorbance
- calculation of 2PPE spectra

What becomes necessary ?

- inclusion of neutral and cationic dye states
- continuum of surface/conduction band states
- vibrational multi-mode description
- formation of electron-vibrational wavepackets
- ultrafast optical excitation and detection

Single electron model with reduced set of vibrational coordinates !

Content of the Talk

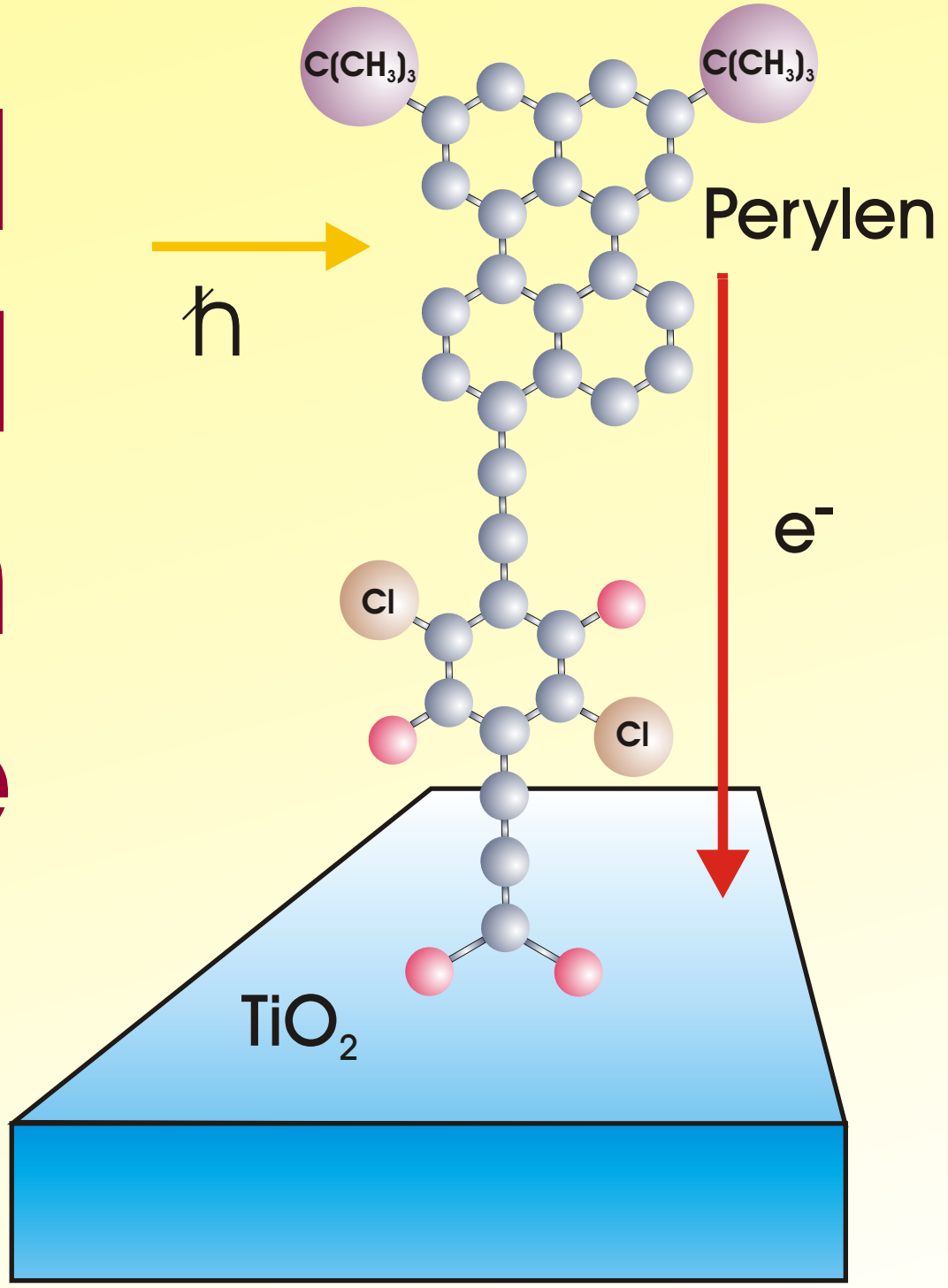
- the reduced dimensionality model

- determination of parameters via the fit of linear absorbance
- direct charge transfer contributions

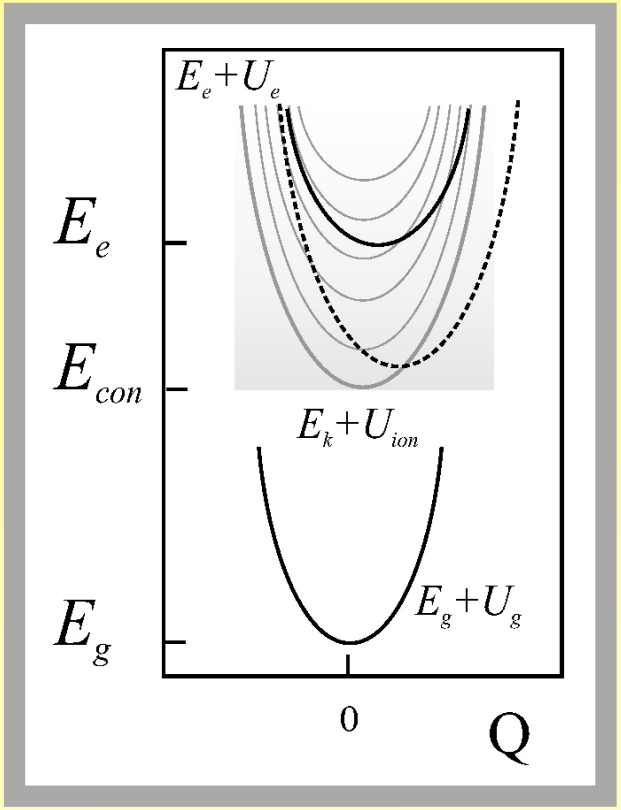
- ultrafast injection dynamics
- electronic wavepacket formation in the conduction band

- 2PPE spectra

Model and Simulation Technique



PES of the Model System



- molecular ground and excited state
- semiconductor band states

Hamiltonian

vibrational Hamiltonian of state a

$$H_{\mathrm{mol-sem}} = \sum_{a=g,e,\mathbf{k}} (\hbar\varepsilon_a + H_a(Q))|\varphi_a\rangle\langle\varphi_a| + \sum_{\mathbf{k}} (V_{\mathbf{k}e}\,|\varphi_{\mathbf{k}}\rangle\langle\varphi_e| + \mathrm{h.c.})$$

transfer coupling between the dye and the semiconductor

$$H_{\mathrm{field}}(t) = -\mathbf{E}(t)\hat{\mu}$$

coupling to the radiation field

Simulation Technique - solution of the time-dependent Schroedinger equation

$$|\Psi(t)\rangle = \sum_{a,M} C_{aM}(t)\,\chi_{aM}(Q)\,|\varphi_a\rangle$$

expansion of the state vector with respect to the electron-vibrational states

Important quantities

broadening function (semiconductor band state induced)

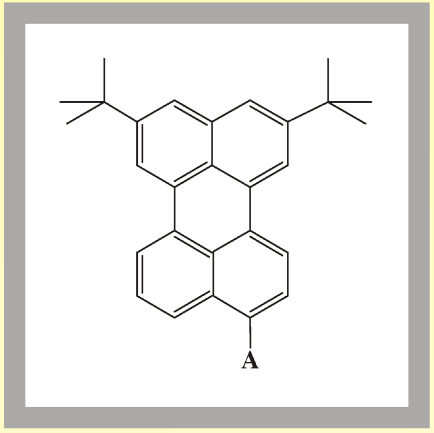
$$\Gamma(\Omega) = \frac{\pi}{\hbar^2}\mathcal{N}(\Omega)|V_e(\Omega)|^2$$

density of states

$$\mathcal{N}(\Omega) = \sum_{\mathbf{k}} \delta(\Omega - \varepsilon_{\mathbf{k}})$$

Ramakrishna, Willig, May, PRB 62, R16330 (2000)
Ramakrishna, Willig, May, CPL 351,242 (2002)
Wang, Willig, May, JCP 124, 014712 (2006)
Wang, Willig, May, Mol. Sim. (in press)

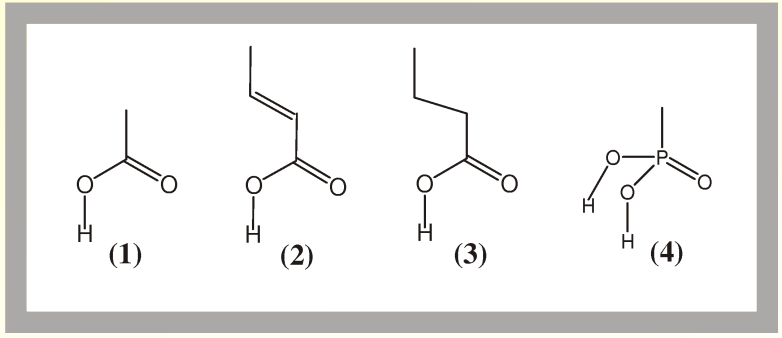
Linear Absorption Spectra



Perylene in Solution and at the TiO_2-Surface

Four different anchor groups

(1) carboxylic acid
(2) acrylic acid
(3) propionic acid
(4) phosphonic acid



Computation of the linear absorption via excited-state wavepacket propagation

$$\alpha(\omega) = \frac{4\pi\omega n_{\mathrm{mol}} |\mathbf{d}_{eg}|^2}{3\hbar c} \mathrm{Re} \int_0^\infty dt\, e^{i(\omega+\varepsilon_g)t} \langle \chi_{g0}\varphi_e | e^{-iH_{\mathrm{mol-sem}}t/\hbar} | \varphi_e \chi_{g0} \rangle$$

Hamiltonian, including the coupling to the band continuum

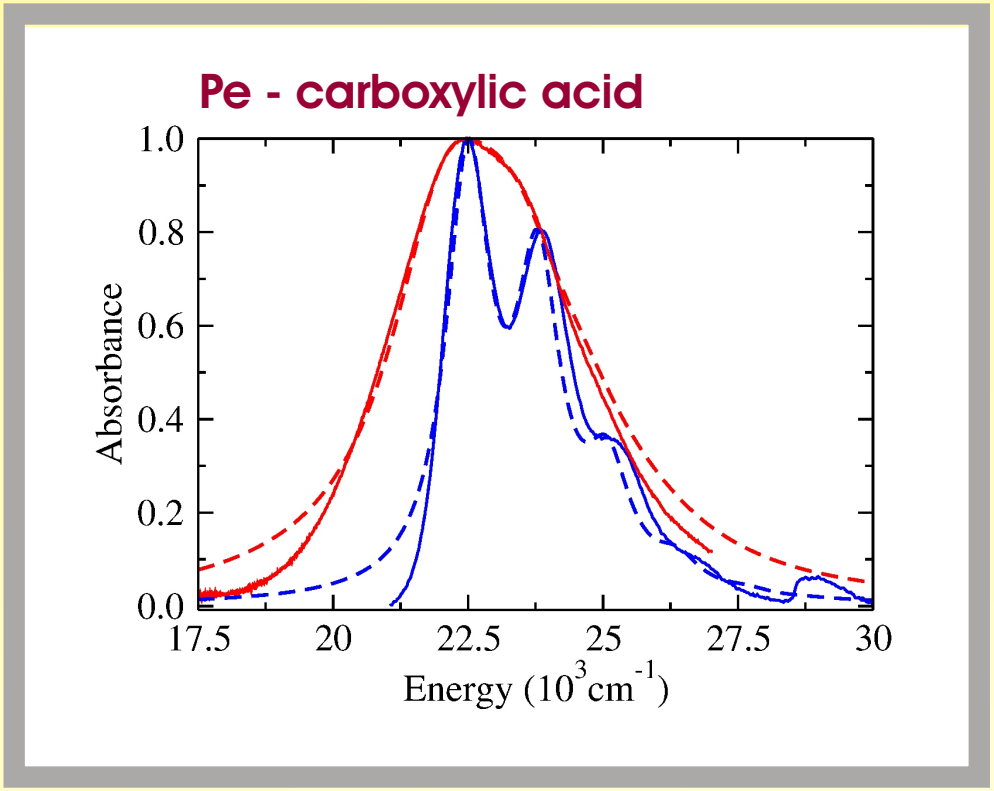
Absorption spectrum in wide-band limit

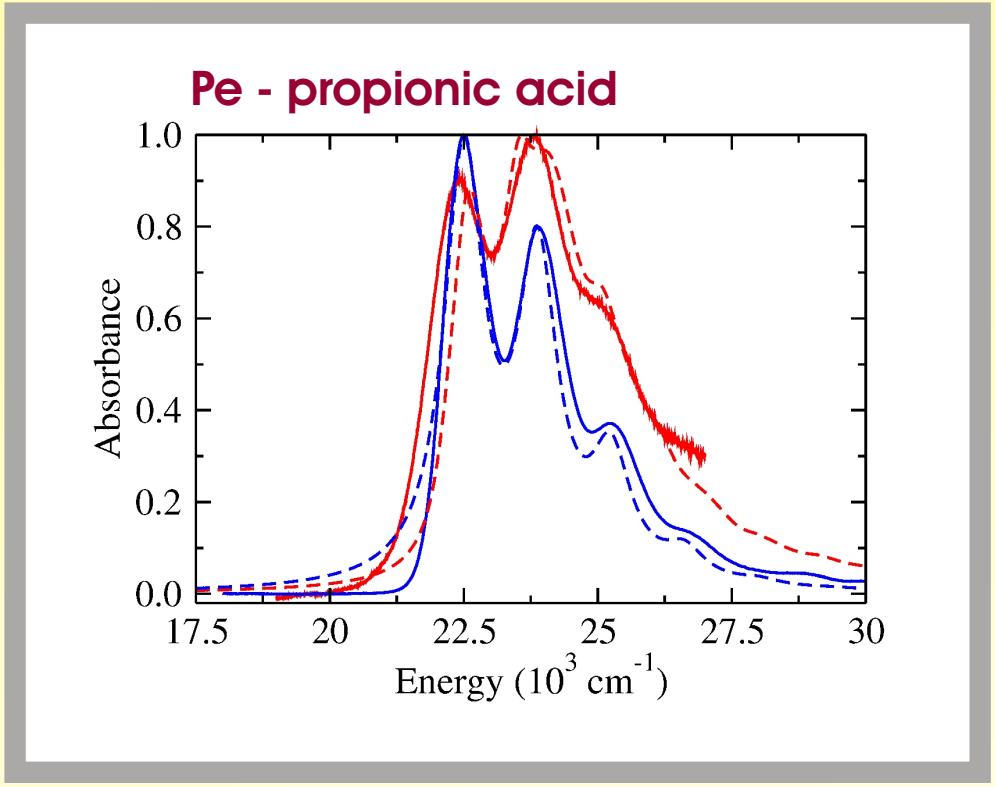
$$\alpha(\omega) = \frac{4\pi\omega n_{\mathrm{mol}} \mid \mathbf{d}_{eg} \mid^2}{3\hbar c} \sum_{M,N} \frac{f(\hbar\omega_{gM}) |\langle \chi_{gM} | \chi_{eN} \rangle|^2 \mid \mathrm{Im}\bar{\Sigma} \mid}{(\omega - \varepsilon_{eg} - \omega_{eN,gM} - \mathrm{Re}\bar{\Sigma})^2 + (\mathrm{Im}\bar{\Sigma})^2}$$

line-shift and line-broadening

Solvent versus Surface Attached Case

(full lines: experiment, dashed lines: theory)





$h\Gamma$=0.094 eV

$h\Gamma$=0.021 eV

Wang, Ernstorfer, Willig, and May, JPCB 109, 9589 (2005)
Wang, Willig, and May, JCP 124, 014712 (2006)

Contribution of Charge Transfer Excitations

intra-molecular contribution

charge transfer contribution

$$\alpha(\omega) = \frac{4\pi\omega n_{\mathrm{mol}}}{3c\hbar}\,\mathrm{Re}\int_0^\infty dt\, e^{i(\omega+\varepsilon_g)t}$$

$$\langle\chi_{g0}|\,\{\,\mathbf{d}^*_{eg}\mathbf{d}_{eg}\langle\varphi_e|e^{-iH_{\mathrm{mol-sem}}t/\hbar}|\varphi_e\rangle + \sum_{\mathbf{k},\mathbf{q}}\mathbf{d}^*_{\mathbf{k}g}\mathbf{d}_{\mathbf{q}g}\langle\varphi_{\mathbf{k}}|e^{-iH_{\mathrm{mol-sem}}t/\hbar}|\varphi_{\mathbf{q}}\rangle$$

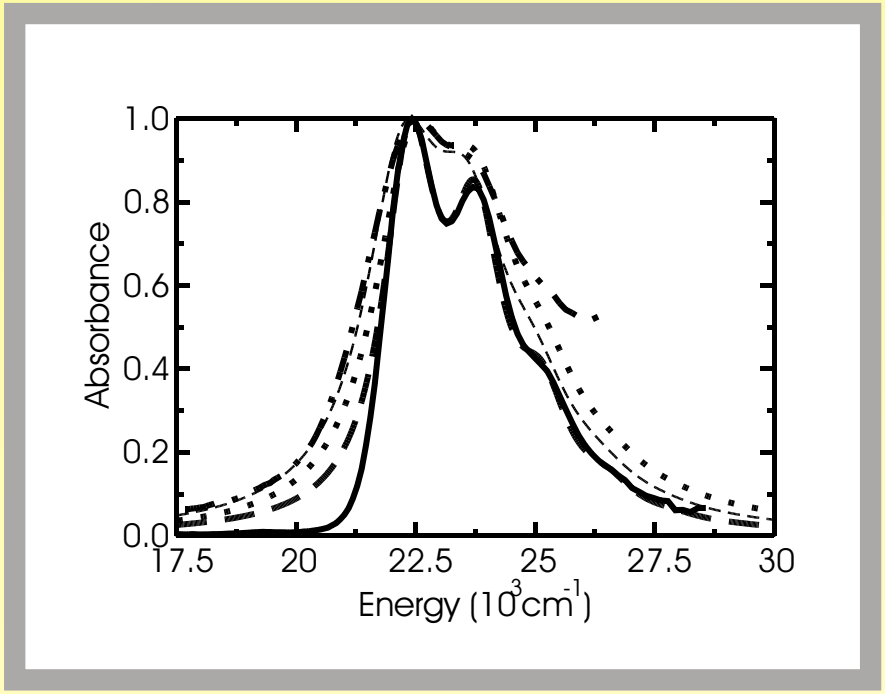
$$+\sum_{\mathbf{k}}\mathbf{d}^*_{\mathbf{k}g}\mathbf{d}_{eg}\langle\varphi_{\mathbf{k}}|e^{-iH_{\mathrm{mol-sem}}t/\hbar}|\varphi_e\rangle + \sum_{\mathbf{q}}\mathbf{d}^*_{eg}\mathbf{d}_{\mathbf{q}g}\langle\varphi_e|e^{-iH_{\mathrm{mol-sem}}t/\hbar}|\varphi_{\mathbf{q}}\rangle\,\}\,|\chi_{g0}\rangle$$

mixed contribution

mixed contribution

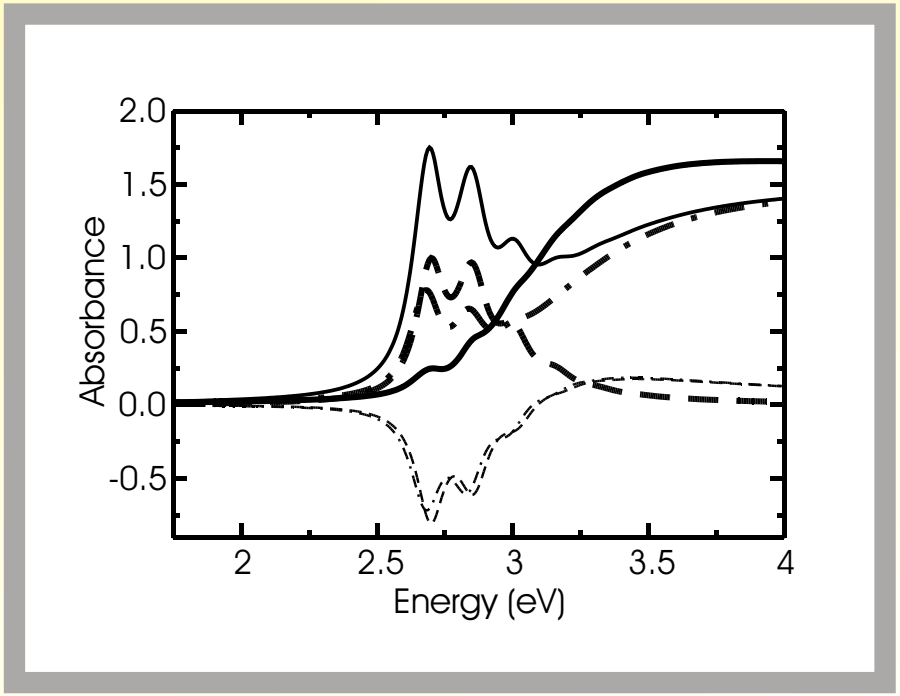
Wang, Willig, May, Mol. Sim. (in press)

Pe-catechol on Ti_2O ($d_{CT}=0.05d_{eg}$)



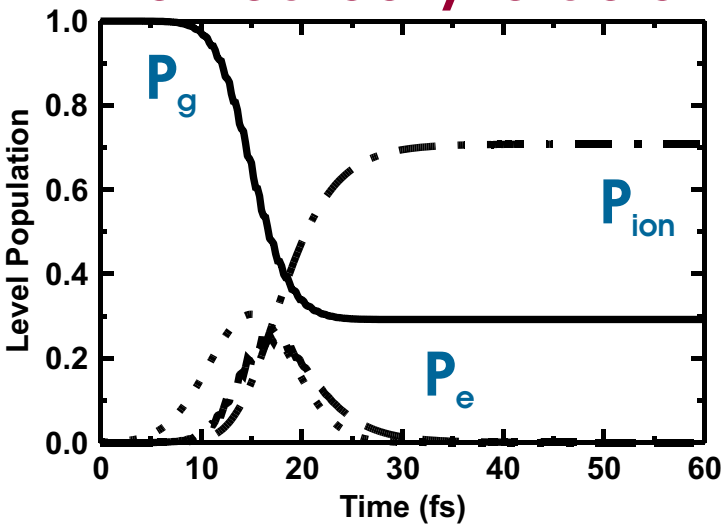
experimental curves
solid - solvent case
dashed-dotted - surface adsorbed
dotted curve - calculations
(thin curve - intramolecular contribution)

Pe-catechol on Ti_2O in a fictitious near band edge position ($d_{CT}=d_{eg}$)



solid curve - total absorption
dashed - intramolecular contribution
dashed-dotted - charge transfer contribution
thin dotted - mixed contributions
thin full curve - intramolecular plus charge transfer contribution

Charge Injection Dynamics



Charge Injection Dynamics after 10 fs Laser Pulse Excitation (dotted curve)

Electronic state population

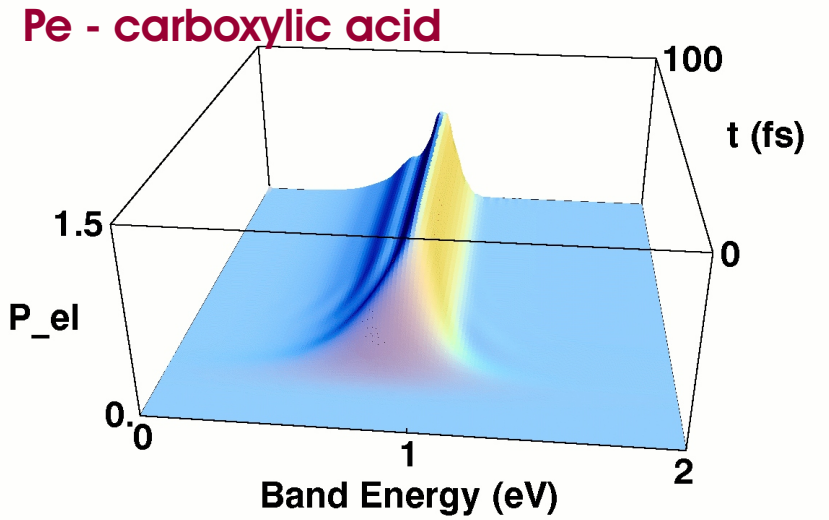
$$P_a(t) = \sum_M |C_{aM}(t)|^2$$

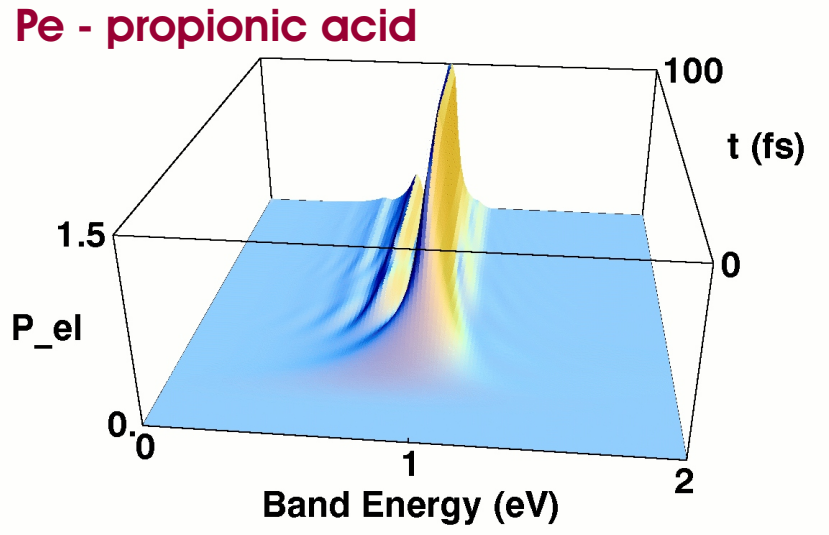
Injection rate

$$k_{\mathrm{HET}} = 2\bar{\Gamma} = \frac{2\pi}{\hbar^2}\bar{\mathcal{N}}|\bar{V}_e|^2$$

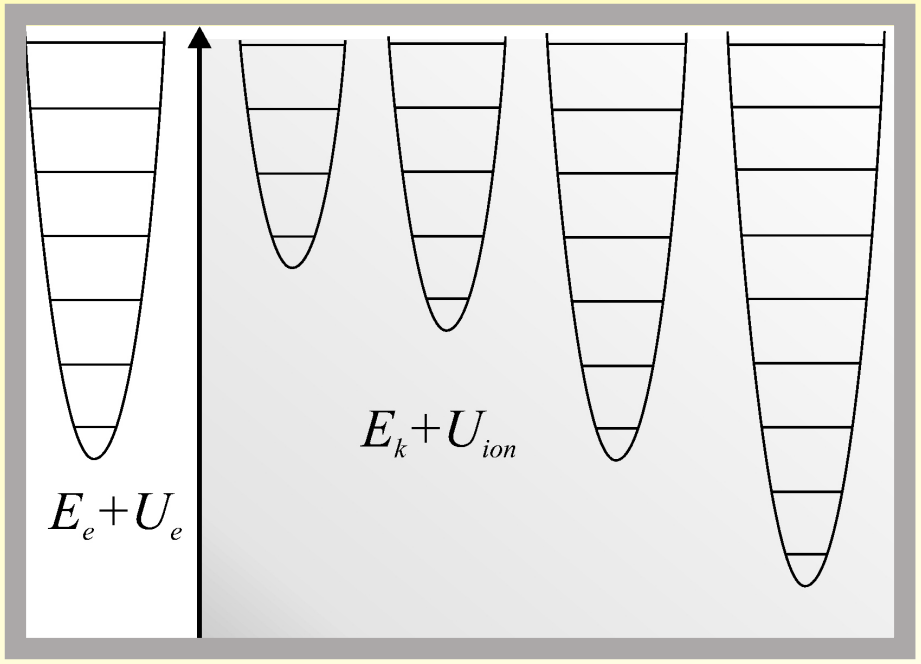
Wang, Willig, and May, JCP 124, 014712 (2006)

Electron Distribution in the Conduction Band





$$P_{\mathrm{el}}(\Omega;t) = \sum_{M} |C_M(\Omega;t)|^2$$

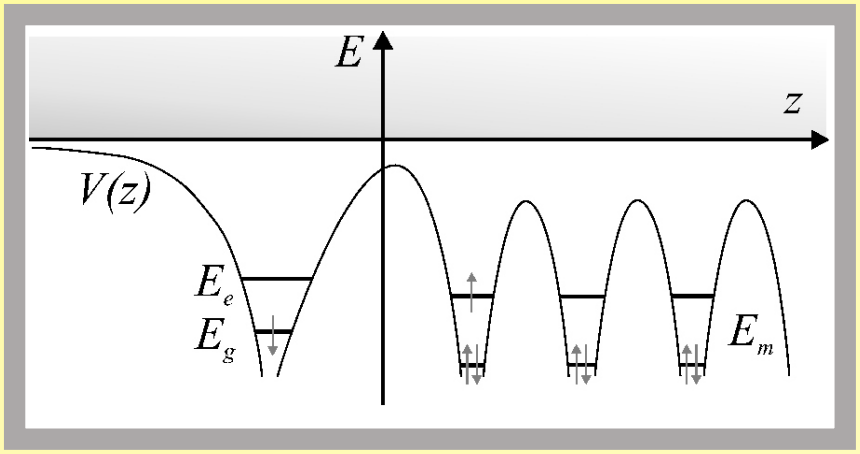


PES scheme for charge injection

$$P_{\mathrm{ion}}(t) = \sum_{\mathbf{k},M} |C_{\mathbf{k}M}(t)|^2 \equiv \int d\Omega\, \mathcal{N}(\Omega) P_{\mathrm{el}}(\Omega;t)$$

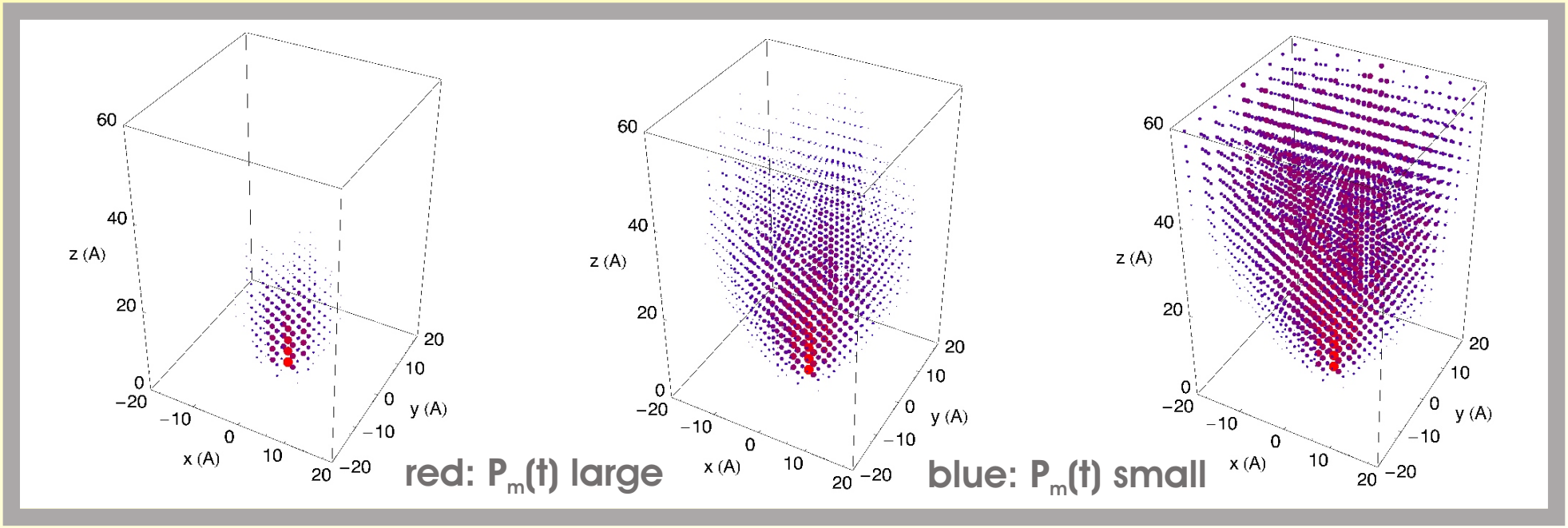
overall cationic (band state) population

2PPE Spectra



tight-binding model for Pe-carboxylic acid on Ti_2O (concentration on Ti-atoms)

electron distribution after injection in the Ti_2O cluster (10 fs laser pulse excitation,localized at 15 fs)



t=10 fs t=20 fs t=50 fs

Electron distribution after photoemission (in vacuum)

$$P_{\mathbf{k}}^{(\mathrm{vac})}(t) = \langle \chi_\kappa(t) | \chi_\kappa(t) \rangle$$

Electron-vibrational state after impulsive probe pulse action (in linear response regime)

field-strength

wavefunction of electronic continuum

$$\chi_\kappa(Q,t) = \frac{i}{\hbar}\Theta(t-t_2)e^{i\varepsilon_\kappa(t-t_2)}\mathbf{E}_2(t_2)\tau_2 \sum_{mM} \langle \phi_\kappa^{(-)} | \hat{\mu} | \varphi_m \rangle \, C_{mM}(t_2) \, \chi_{\mathrm{ion}M}(Q)$$

tight-binding state at site m

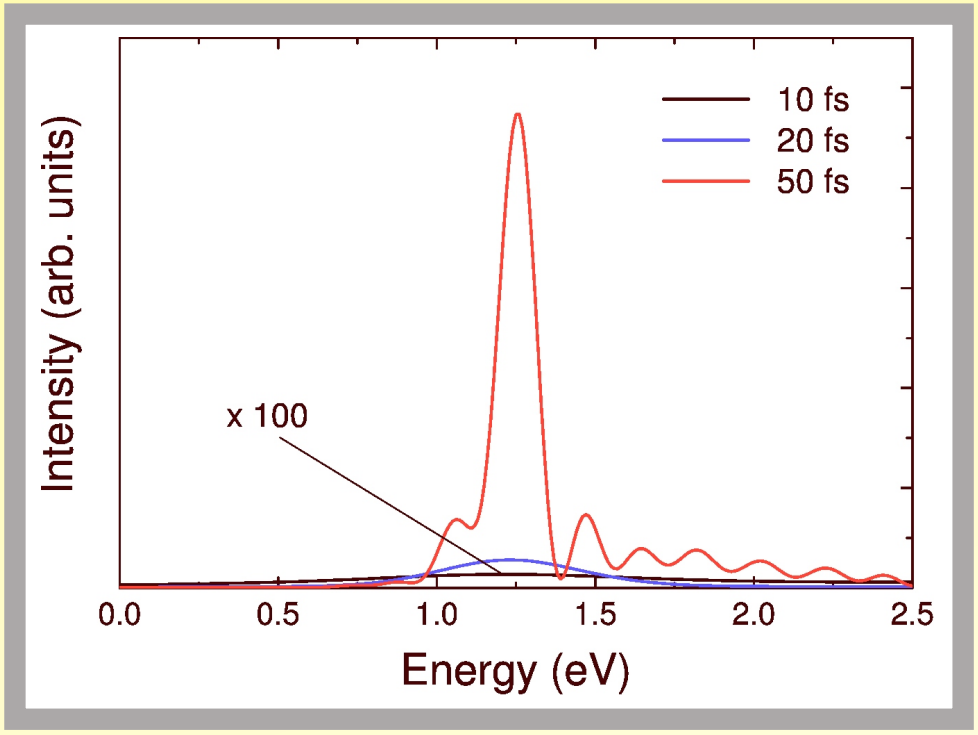
expansion coefficients of the overall wavefunction

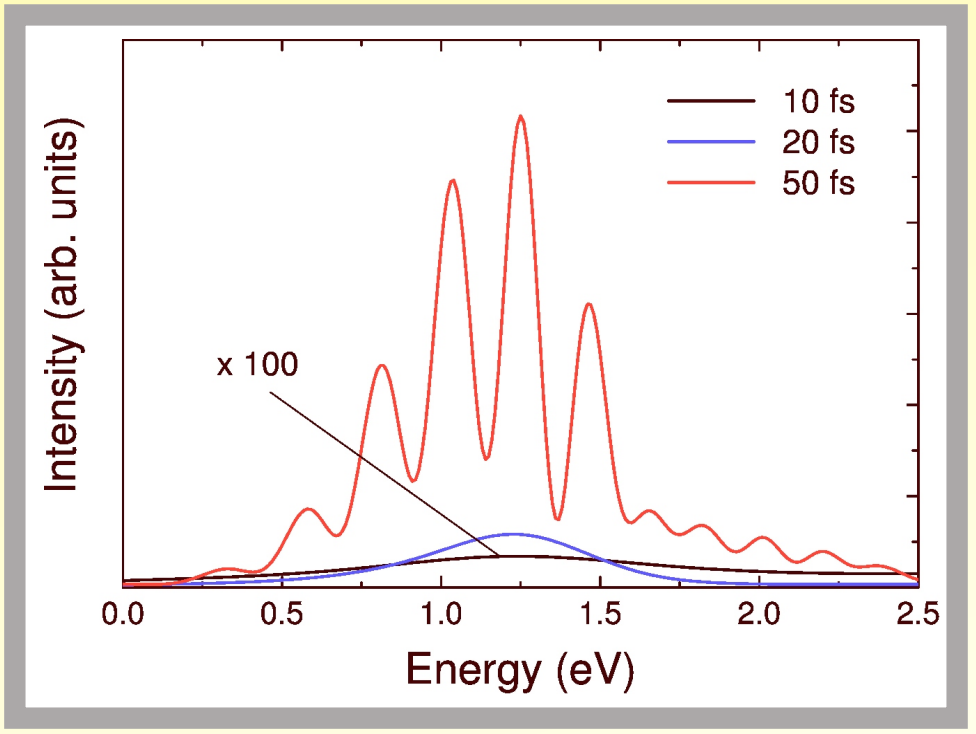
vibrational wavefunction of molecular anion

electronic continuum state at Ti-position m

$$P_{\mathbf{k}}^{(\mathrm{vac})}(t) \sim \sum_M \Big| \sum_m \phi_{\mathbf{k}}^{(-)*}(\mathbf{r}_m) C_{mM}(t) \Big|^2$$

Idealized 2PPE Spectra of Pe-carboxylic Acid
- 10 fs pump pulse (localized at 15 fs)
- impulsive probe pulse action





excited-state cationic-state reorganization energy: 0.014 eV

excited-state cationic-state reorganization energy: 0.140 eV

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