Ultrafast Heterogeneous Electron Transfer: The Perylene TiO_2 System

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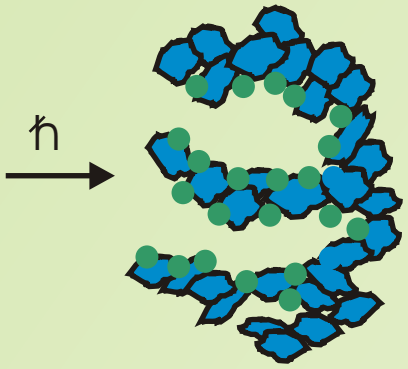
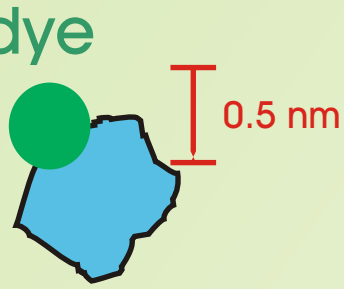
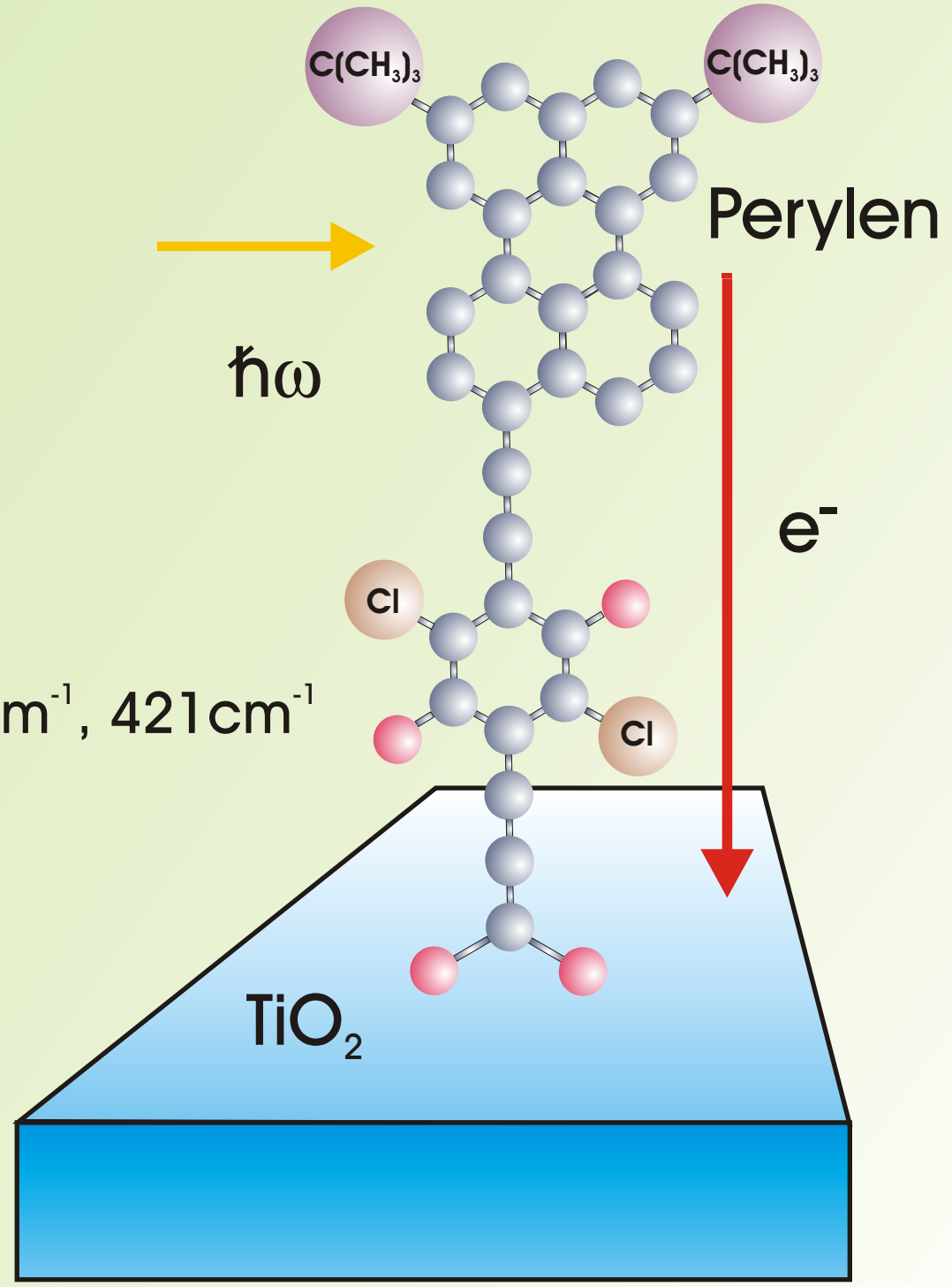
Perylene on TiO_2





$t_{ET} = 75fs$

$_{vib} = 357cm^{-1}, 421cm^{-1}$



- current interest in photoinduced heterogeneous ET
  - V. Sundström (Lund)
  - M. Grätzel (Laussanne)

- besides TiO_2 use of ZnO- and SnO_2-systems

- study of charge injection
  after internal conversion,
  from triplet states,
  from different conformations,

- transport and relaxation in the
  semiconductor conduction band

- back-reactions

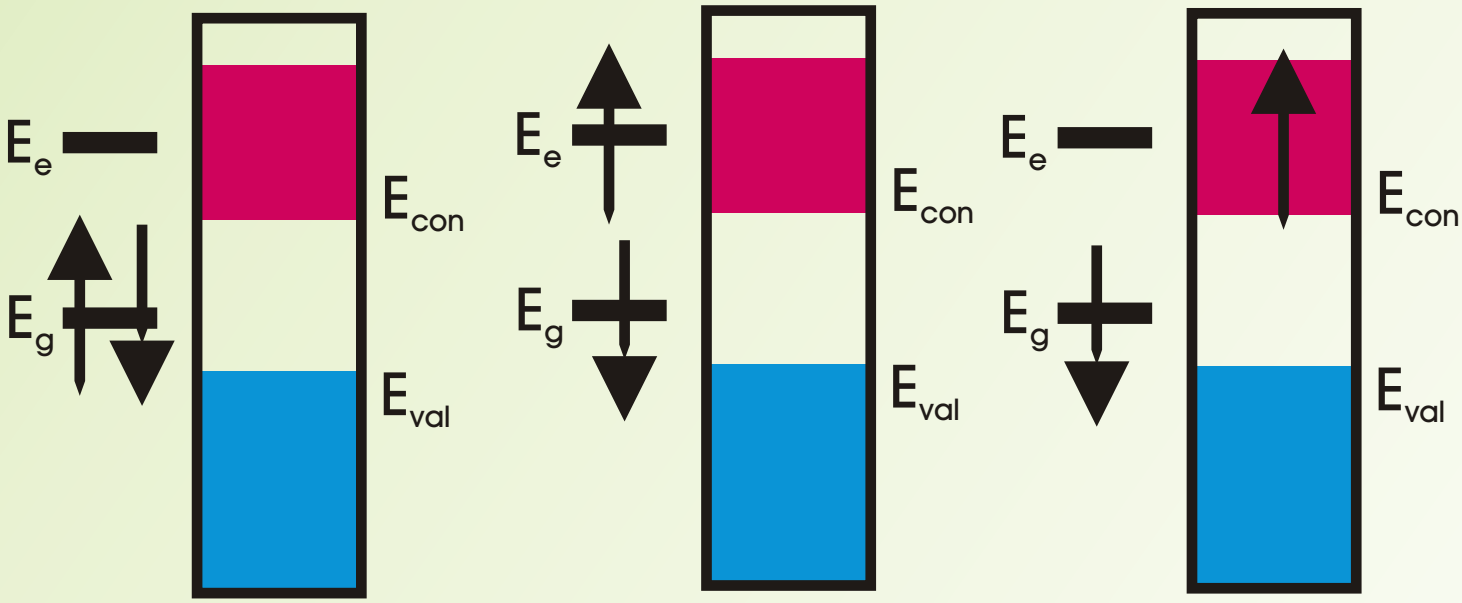
- charge injection time of 6 fs
  for the system alizarin / TiO_2

- theory of nonadiabatic ET well established (Marcus, Jortner)

- ultrafst ET transfer times below 1 ps
  since 15 eyars
  search for vibrational coherences

- hetrogeneous ET (perylene / TiO_2)
  outside a solvent (high vacuum)
  injection times below 100 fs

Energy level scheme and PES (perylene / TiO_2)



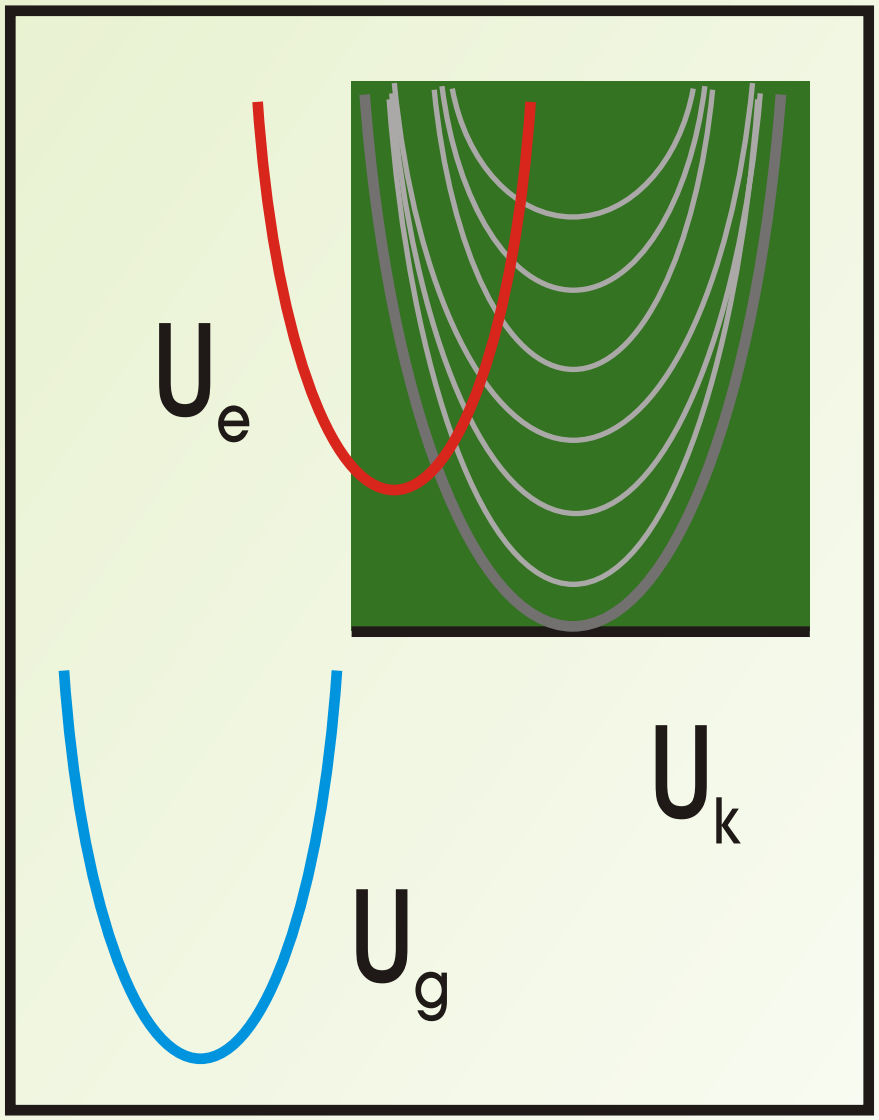
diabatic states

$|D>|A>$ $|D^*>|A>$ $|D^+>|A^->$

$\hbar\omega = 0.1\text{eV}$

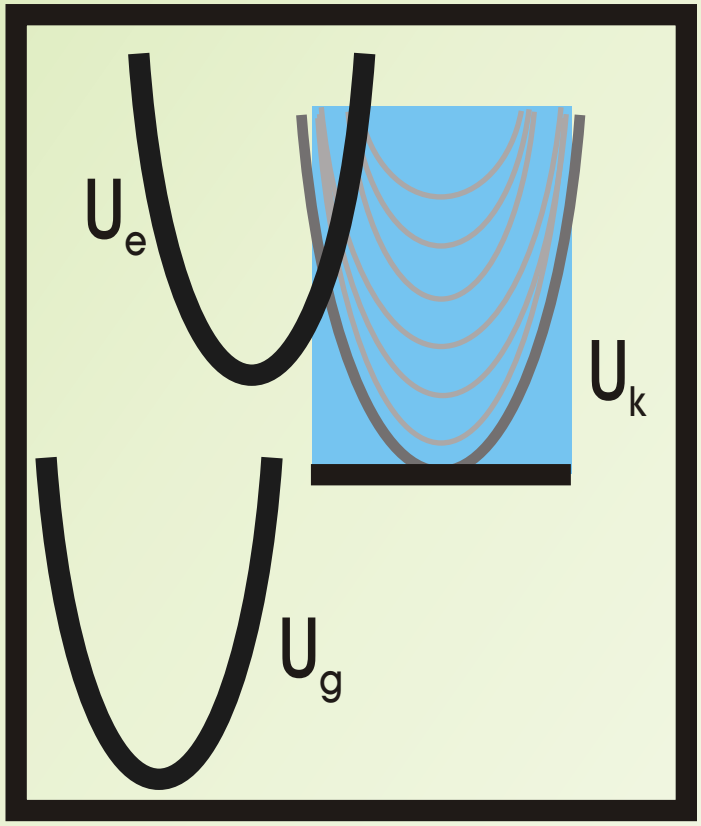
$\lambda = 0.1\text{-}0.3\text{eV}$

$\tau_{ET} = 75\text{fs}$

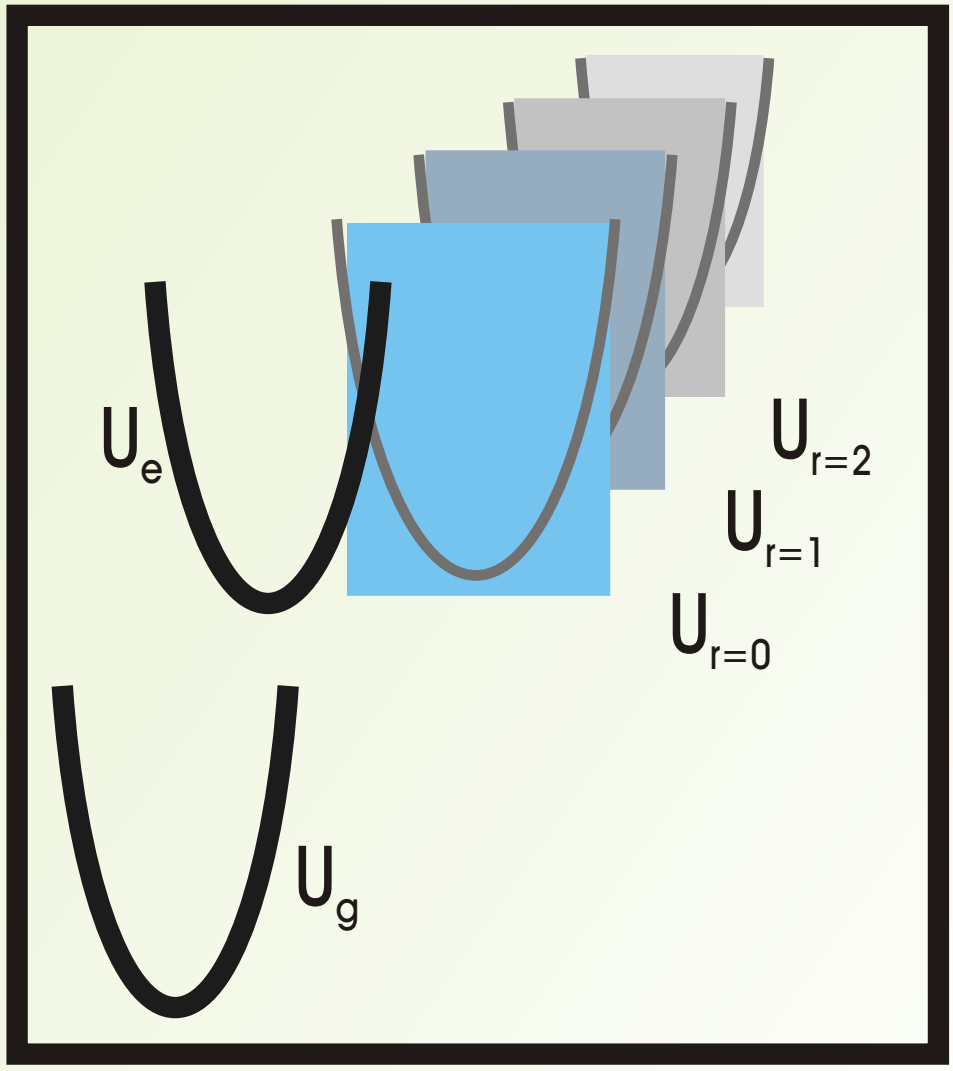


PES

with conduction band continuum

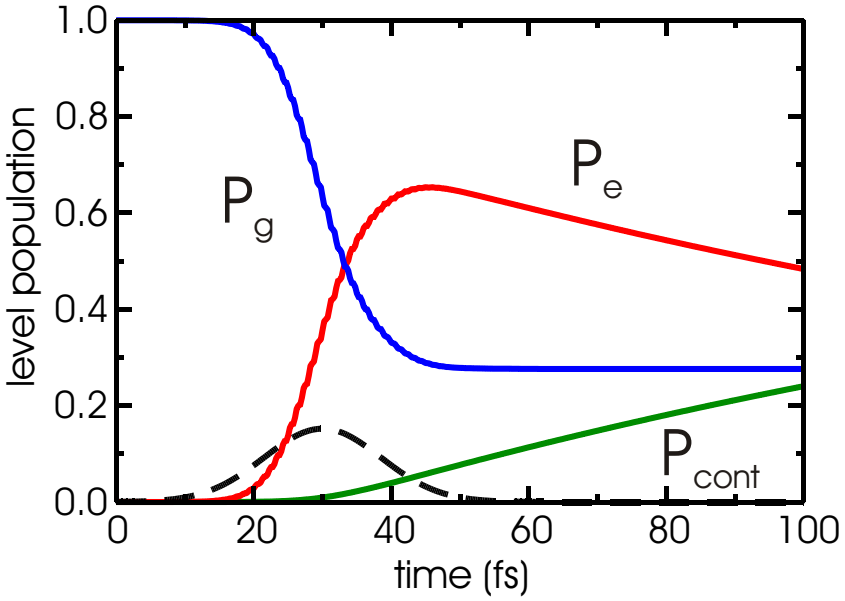


after polynomial expansion

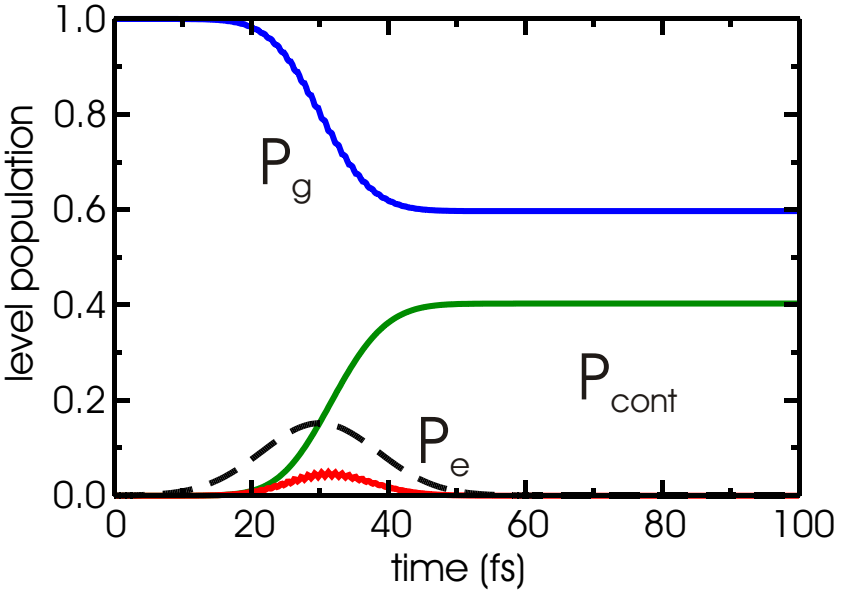


Change of the Injection Time

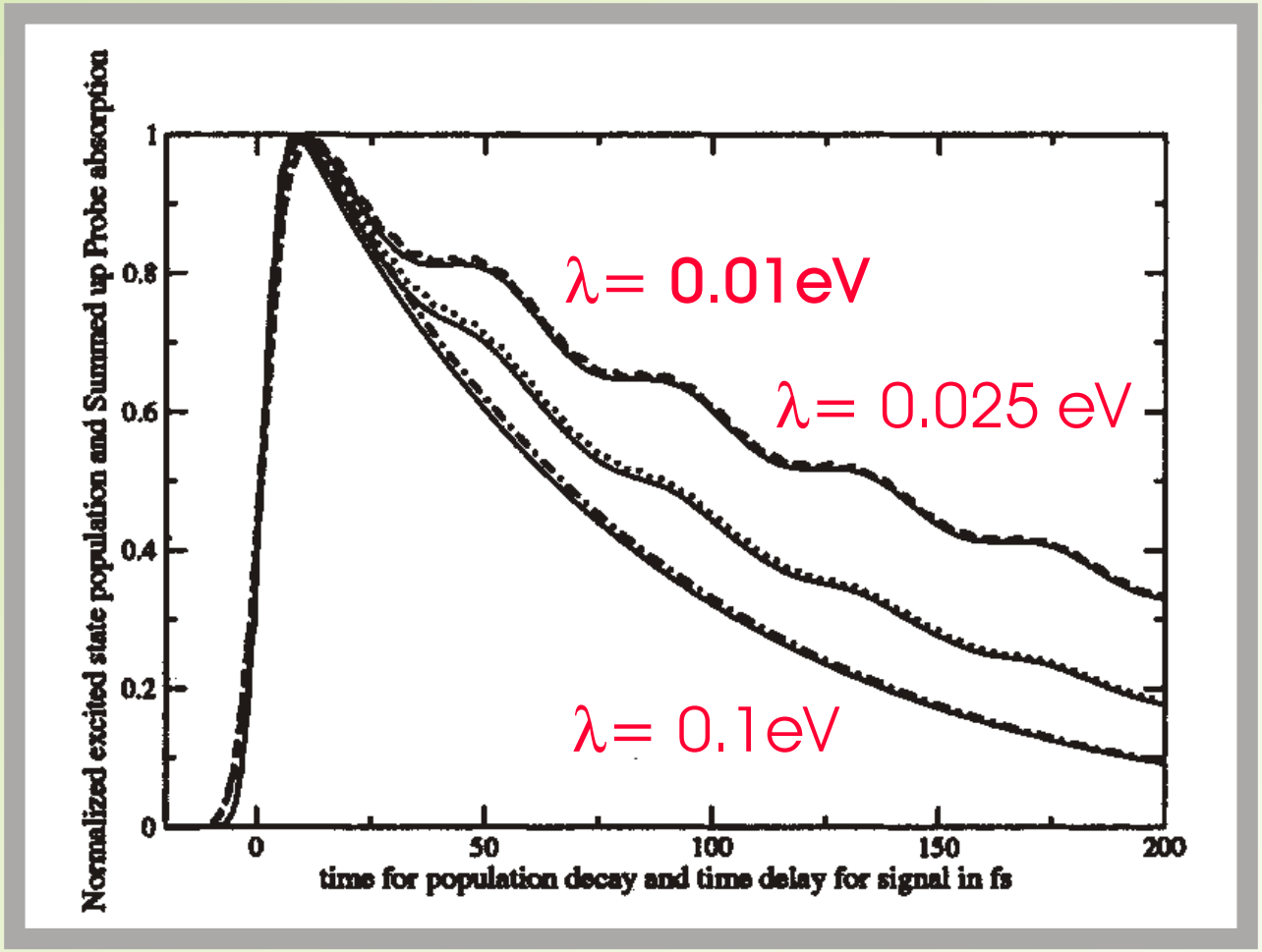
V = 0.02 eV

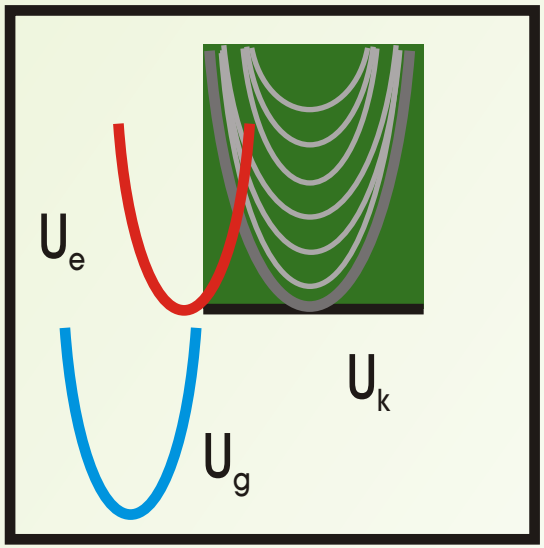


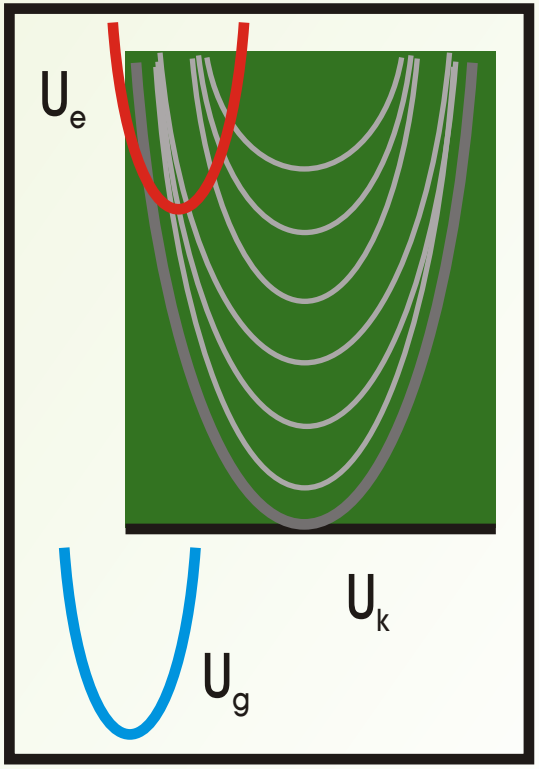
V = 0.2 eV



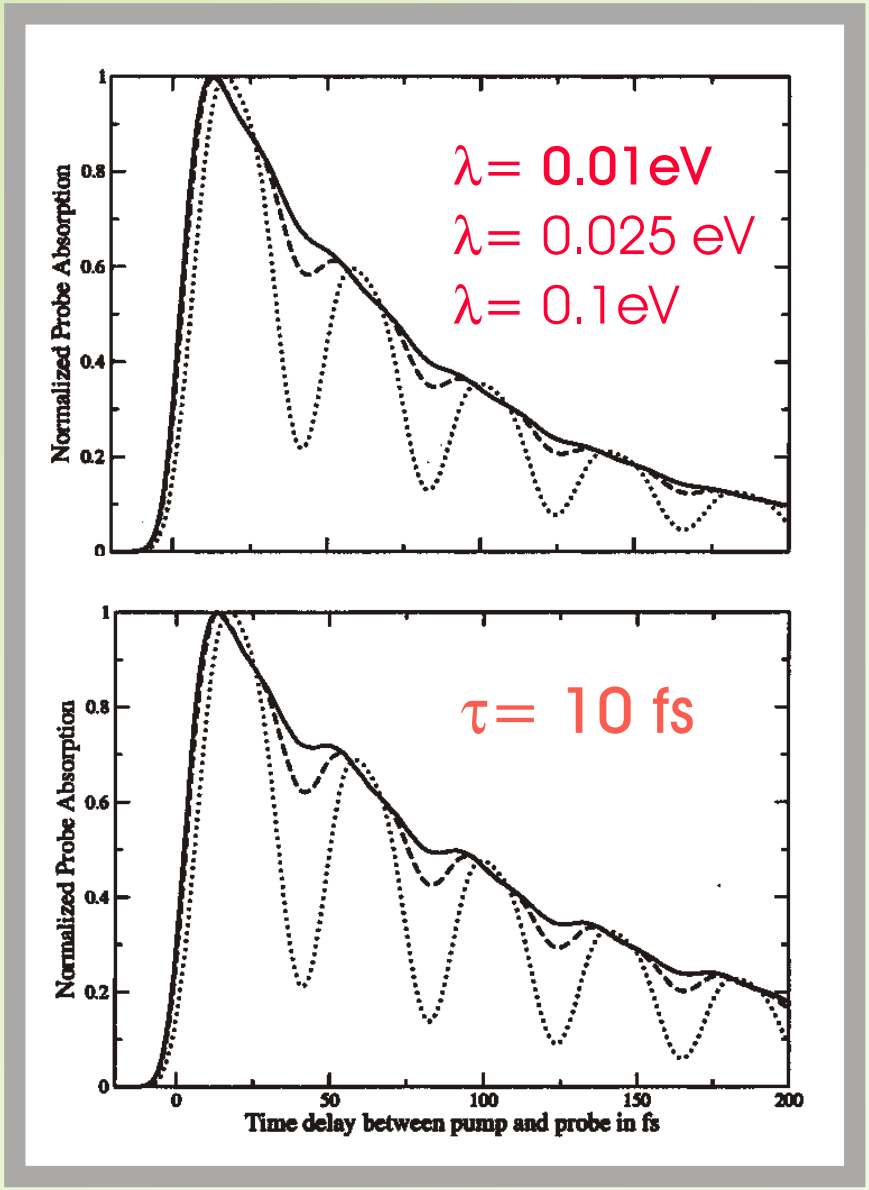
Charge injection into the band continuum

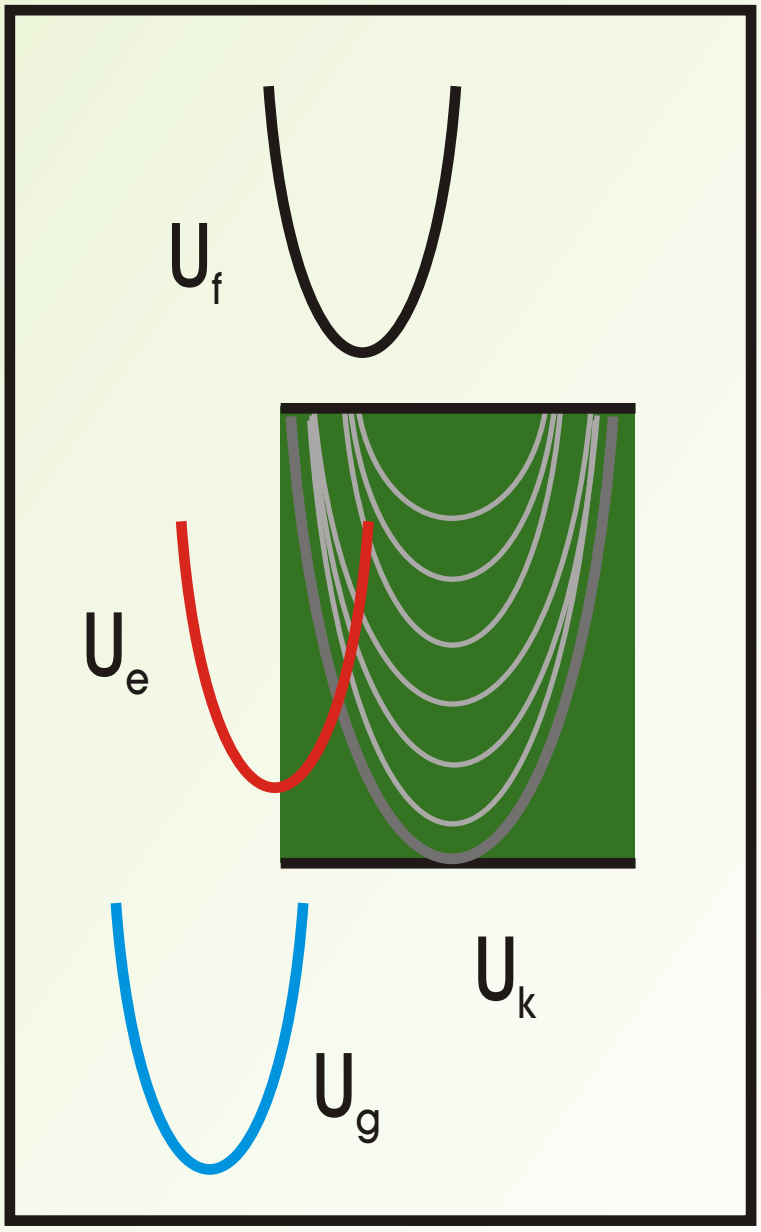




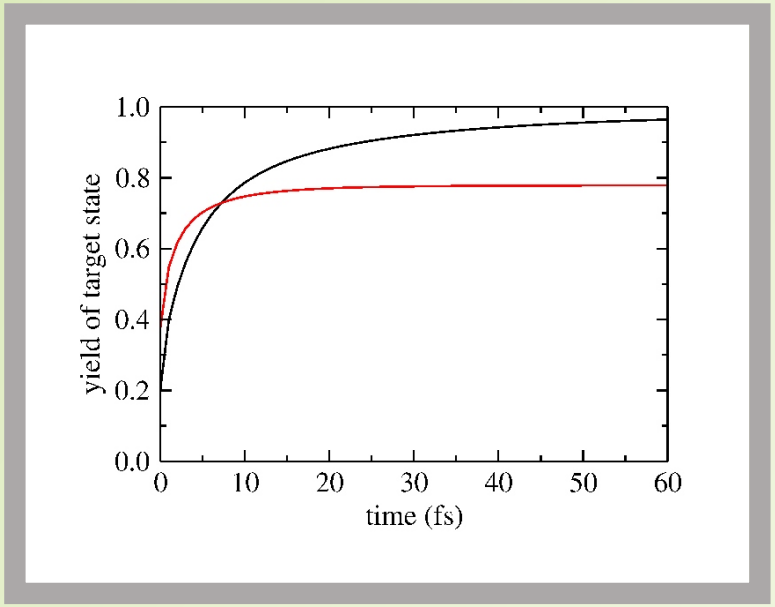


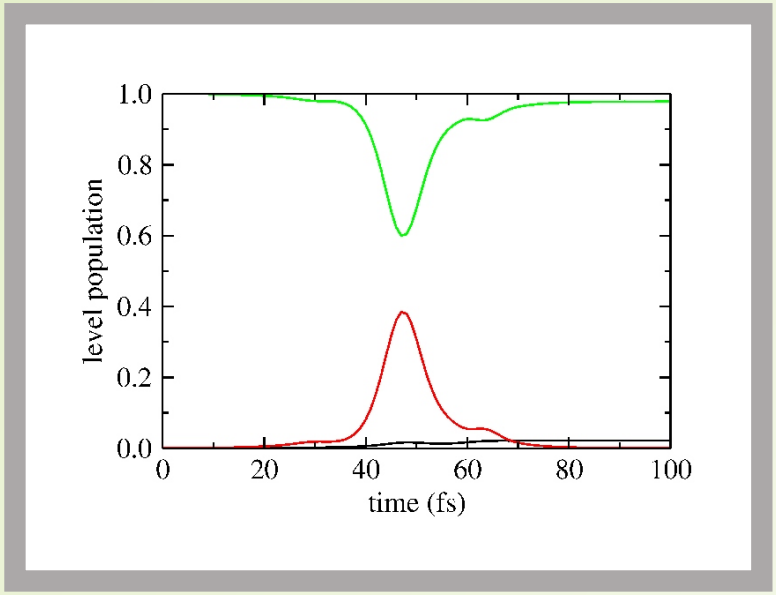
Transient Absorption Spectra





Laser pulse control of the charge injection process



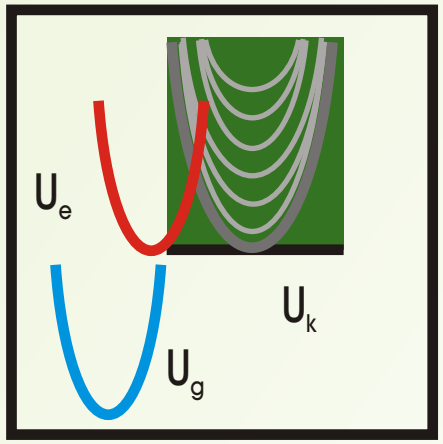


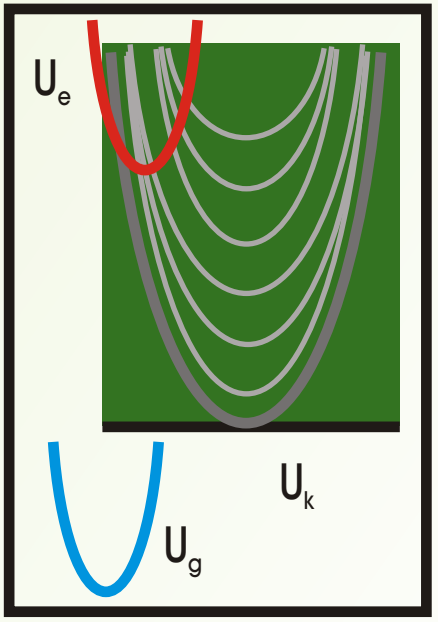
target state:

displaced vibrational ground-state in U_g

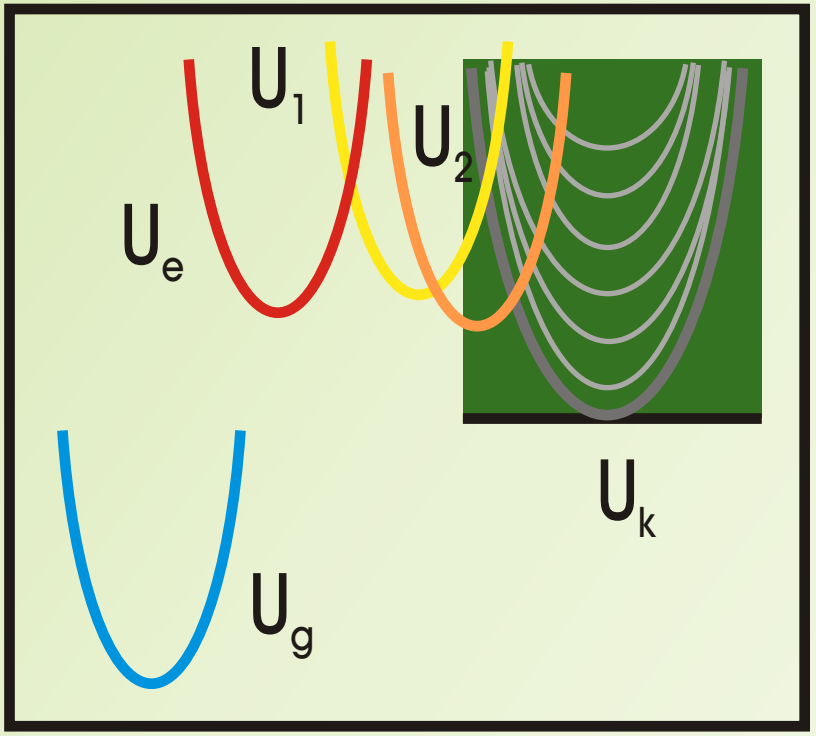
length of the control pulse:

100f





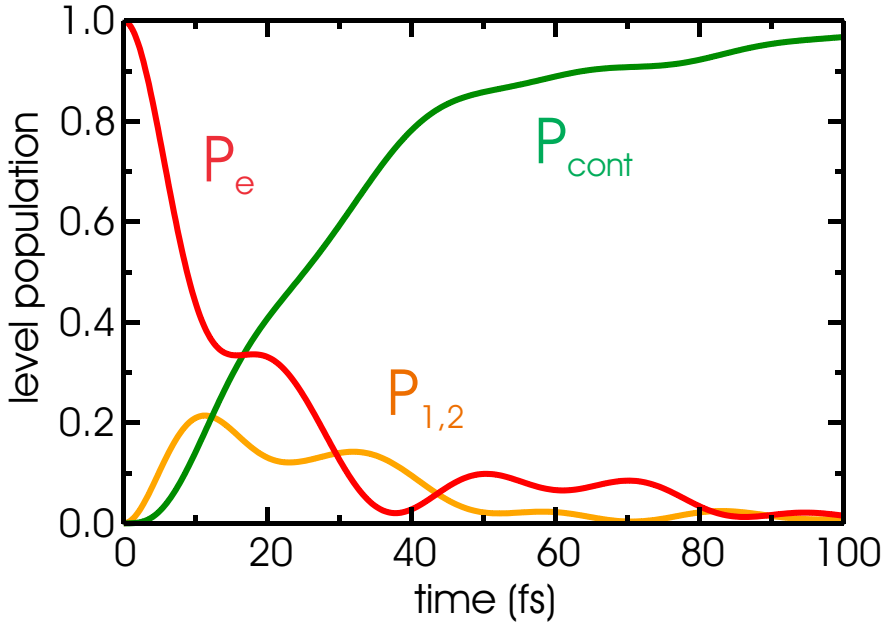
Bridge Mediated Heterogeneous Electron Transfer



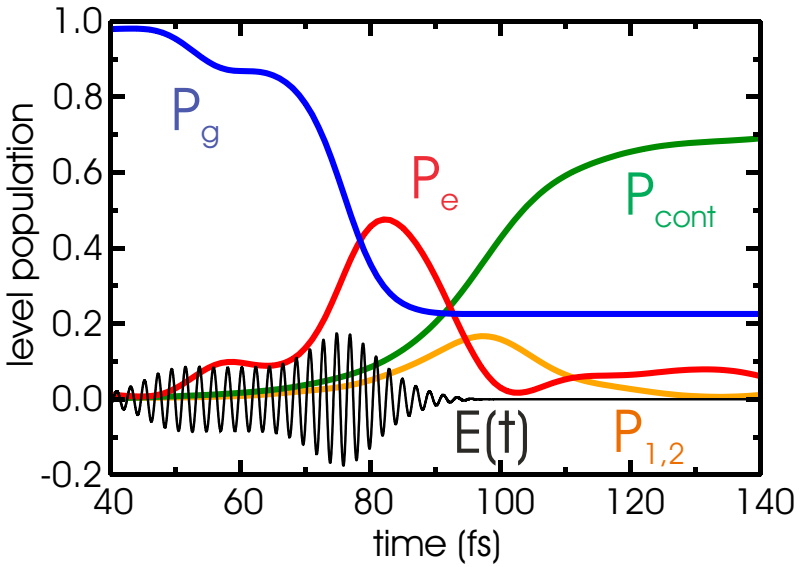
3eV

2eV

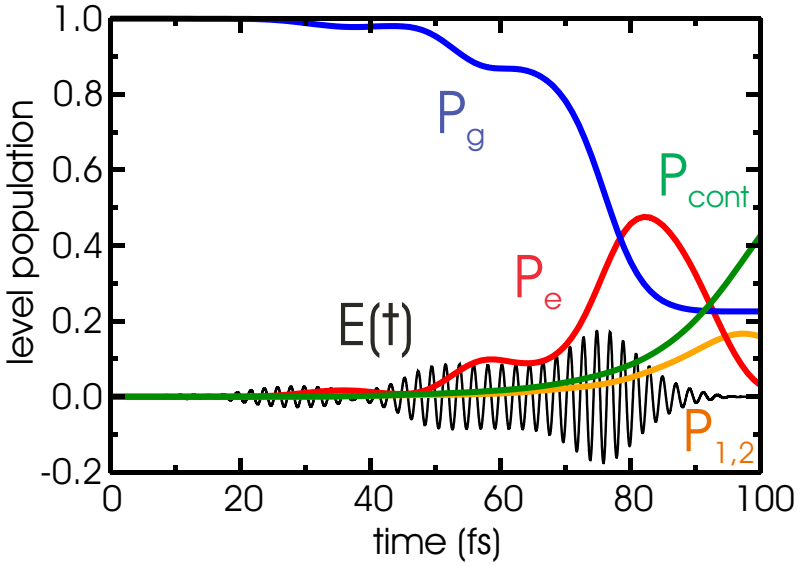
$\hbar\omega$=0.1eV, λ=0.1-0.3eV



Laser Pulse Control of Bridge Mediated Heterogeneous ET



$V_{e,1}=V_{1,cont}=V_{e,2}=V_{2,cont}=0.05$ eV



$V_{e,1}=V_{1,cont}=0.05$ eV

$V_{e,2}=V_{2,cont}=0.07$ eV