Ultrafast Heterogeneous Electron Transfer: The Perylene TiO$_2$ System

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Perylene on TiO$_2$

$\hbar\omega$  

$T_iO_2$ colloids

$t_{ET} = 75$ fs  
$\omega_{vib} = 357$ cm$^{-1}$, 421 cm$^{-1}$

0.5 nm

dye

Perylene

$C(CH_3)_3$  
$C(CH_3)_3$  
$Cl$  
$Cl$
- 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)

- ultrafast ET transfer times below 1 ps since 15 years
  search for vibrational coherences

- heterogeneous ET (perylene / TiO₂)
  outside a solvent (high vacuum)
  injection times below 100 fs
Energy level scheme and PES (perylene / TiO$_2$)

diabatic states

$|D\rangle |A\rangle$  $|D^*\rangle |A\rangle$  $|D^+\rangle |A^-\rangle$
\[ \hbar \omega = 0.1 \text{eV} \]

\[ \lambda = 0.1 - 0.3 \text{eV} \]

\[ \tau_{\text{ET}} = 75 \text{fs} \]
PES

with conduction band continuum

after polynomial expansion
Change of the Injection Time

\[ V = 0.02 \text{ eV} \quad \text{and} \quad V = 0.2 \text{ eV} \]
Charge injection into the band continuum

\[ \lambda = 0.01 \text{eV} \]

\[ \lambda = 0.025 \text{eV} \]

\[ \lambda = 0.1 \text{eV} \]
Transient Absorption Spectra

\[ \lambda = 0.01 \text{eV} \]
\[ \lambda = 0.025 \text{eV} \]
\[ \lambda = 0.1 \text{eV} \]

\[ \tau = 10 \text{fs} \]
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

$\eta \omega = 0.1 \text{eV}, \lambda = 0.1 - 0.3 \text{eV}$
Laser Pulse Control of Bridge Mediated Heterogeneous ET

\[ V_{e,1} = V_{1,\text{cont}} = 0.05 \text{ eV} \]
\[ V_{e,2} = V_{2,\text{cont}} = 0.07 \text{ eV} \]