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## Extended abstract

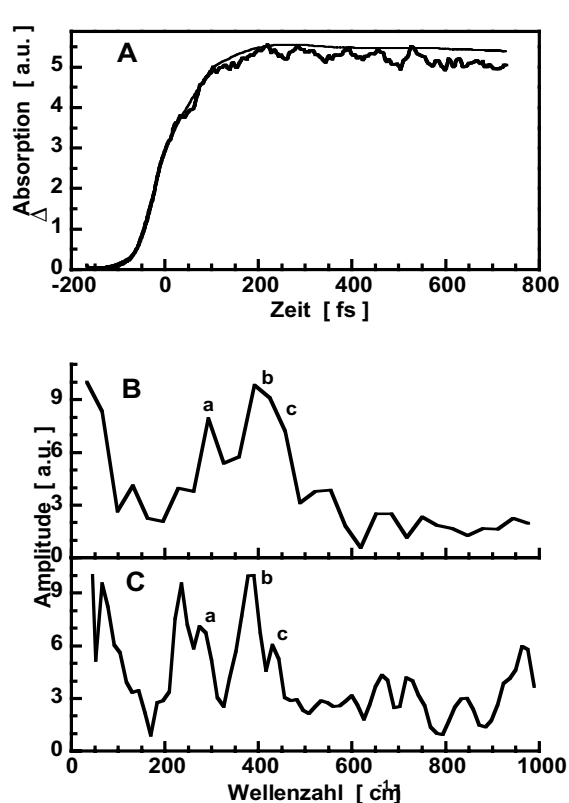
### **Dynamics of Photoinduced Ultrafast Electron Transfer and Recombination: Perylene Chromophore on Titanium Dioxide**

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Electron injection and recombination dynamics in 2,5-ditertiary-butyl-perylene-9-methylphosphonic acid (DTB-Pe-Phos) sensitized colloidal TiO<sub>2</sub> films are investigated under ultrahigh vacuum conditions using femtosecond transient absorption spectroscopy at a pump wavelength of 434 nm [1]. Perylene is used as model chromophore because absorption spectra for the ground, excited, and cationic state are well separated. The perylene chromophore is attached at the semiconductor surface by a -CH<sub>2</sub>- spacer and a -H<sub>2</sub>PO<sub>4</sub> anchor group. The strength of the electronic coupling is controlled by the distance between the chromophore and the TiO<sub>2</sub> surface. Electron injection and recombination are measured by monitoring the rise and decay, respectively, of the two product states, i.e. the oxidized Perylene molecule in the visible (575 nm) and the injected electron in the TiO<sub>2</sub> conduction band in the infrared (1305 nm). Electron transfer from the excited electronic state of the donor chromophore perylene into the wide conduction band of the oxide semiconductor anatase TiO<sub>2</sub> occurs within 75 fs, as fitted in **Figure 1-A** from the optically prepared "hot" vibrational state prior to intramolecular vibrational energy redistribution in the donor molecule. Coherent wavepacket motion in the reactant and also in the product state of the heterogeneous electron transfer reaction leads to oscillatory transient absorption signals (**Figure 1-A**) [2]. Vibrational modes found in the Fourier transform of the oscillatory part of the transient cation absorption signal also show up prominently in the Raman spectrum of this chromophore as well-known totally symmetric vibrational normal modes of the chromophore **perylene** [3] (**Figure 1-B**). As a comparison a Fourier transform of the transient absorption of Perylene in toluene is also shown in **Figure 1-C**.

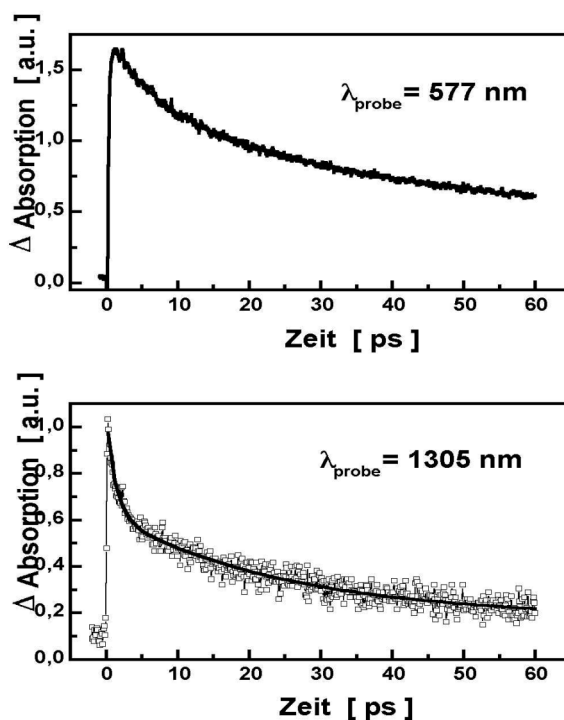
The recombination kinetics measured in UHV are multi-exponential with a fast component of 4,9 ps and a slow one around 30 ps (**Figure 2**, upper part) independent of the number of

absorbed photons indicating geminate recombination . Only the slow decay component is weakly temperature dependent between room temperature and 40 K. The recombination is completely reversible within the repetition rate of our laser system, corresponding to less than 10 s. As a comparison the decay signal of the transient absorption of the injected electrons in the TiO<sub>2</sub> conduction band is shown in the lower part of **Figure 2**.



**Figure 1:**

*A: Wavepacket motion in the transient absorption signal of the ionized Perelene chromophore on the TiO<sub>2</sub> electrode, B: Fourier Transform of the oscillatory part of the upper transient absorption signal, C: Fourier Transform of the oscillatory part of the transient absorption signal of Perylene in Toluene.*



**Figure 2:**

*transient absorption of the recombination signal:*

**upper part:** decay of the ionized Perelene chromophore on the TiO<sub>2</sub> electrode, **lower part:** intraband absorption of TiO<sub>2</sub>.

## References:

- [1] B. Burfeindt, C. Zimmermann, S. Ramakrishna, T. Hannappel, B. Meißner, W. Storck, and F. Willig, Z. physikal. Chemie **212**, 67 (1999)
- [2] C. Zimmermann, F. Willig, S. Ramakrishna, B. Pettinger, B. Burfeindt, N. Biswas, R. Eichberger, Ultrafast Phenomena XII, eds. T. Elsaesser, S. Mukamel, M.M. Murnane, N.F. Scherer, 453 (2000)
- [3] K.K. Ong, J. O. Jensen, and H.F. Hameka, Theo. Chem. 459, 131 (1999)