

Femtosecond Electron Transfer from the Excited State of Chemically Anchored Chromophores into the Empty Conduction Band of Nanocrystalline Spong-like TiO₂ Films*

By B. Burfeindt², C. Zimmermann¹, S. Ramakrishna², T. Hannappel¹,
B. Meißner¹, W. Storck² and F. Willig¹

¹ Hahn-Meitner-Institut, Dept. CD, Glienickestr. 100, D-14109 Berlin, Germany

² Fritz-Haber-Institut der MPG, Dept. PC, Faradayweg 4–6, D-14195 Berlin, Germany

(Received August 8, 1998; accepted December 10, 1998)

Ultrafast heterogeneous electron transfer / Perylene / Ruthenium-dye / Femtosecond transient absorption / Ultra-high vacuum

Heterogeneous photo-induced electron transfer was measured with femtosecond transient absorption laser spectroscopy in ultra-high-vacuum. The electron acceptor was colloidal anatase TiO₂. The excited donor was a perylene chromophore with covalently attached anchor and spacer groups and also a ruthenium dye. The former showed well-separated absorption spectra in its ground, excited, and cationic state. The rise of the perylene radical cation absorption as product state and the decay of the excited state absorption as reactant state gave an identical electron transfer time. The latter varied between 40 fs and 80 fs for seemingly identical preparations of the TiO₂ film and was found 30 fs and faster for a different anchor group. Radical cation absorption of the ruthenium dye was ambiguous but the rise time of intraband absorption of the injected electrons was measured faster than 25 fs in the case of the ruthenium dye. The ultrafast experimental electron transfer times were in agreement with the prediction of a straightforward adiabatic model.

1. Introduction

Ultrafast heterogeneous electron transfer can be studied as photo-induced electron injection from adsorbed chromophore molecules into the empty conduction band of a wide band gap semiconductor [1, 2]. Photo-induced

* Presented at the "Twelfth International Conference on Photochemical Conversion and Storage of Solar Energy", Berlin, August 9–14, 1998.

E-mail of corresponding author: willig@hmi.de.

electron injection is utilized in the important AgBr-photographic process [3, 4] and in a special type of dye-sensitized solar cell with 10 percent solar power conversion efficiency [5]. Reliable time-resolved measurements of the fundamental electron injection process in such systems require femto-second resolution. Optical spectroscopy with the necessary time-resolution has become available only recently. The second requirement is a sufficiently high amplitude of the signal. Applying optical femtosecond spectroscopy the latter can be obtained in the above experimental systems by exposing a large number of dye molecules adsorbed on a high surface area semiconductor electrode to the laser pulse [6, 7].

A systematic femtosecond time-resolved study is described here of photo-induced electron injection in the above type experimental system. Specifically designed chromophore molecules were used with convenient spectroscopic properties, i.e. distinctly different absorption spectra for ground, excited, and cationic state. A sufficiently high amplitude of the femtosecond transient absorption signals of reactant and product state was obtained by adsorbing a large number of the above chromophore molecules onto nanoporous TiO₂ films with a huge internal surface. An identical time constant of electron transfer was determined firstly from the rise of the product state and secondly from the decay of the reactant state. The measurements were carried out in ultra-high-vacuum (uhv) to ensure a minimum loss of adsorbed dye molecules due to possible spurious side reactions with solvent molecules. The system behaved virtually reversible under laser irradiation. The numerical value for the time constant of electron transfer remained in the range of a few 10 fs irrespective of intentional variations introduced into the preparation procedures for the nanoporous TiO₂ film serving as electron acceptor. The electron transfer time of 40 fs was measured at a typical outer-sphere type reaction distance, i.e. more than 3 Å distance from the edge of the chromophore to the nearest surface atoms of the semiconductor. A straightforward adiabatic model confirmed that the electron transfer time was controlled only by the electronic coupling and was independent of the Franck-Condon factors if the excited donor state was placed sufficiently high above the lower edge of the empty conduction band of the semiconductor.

2. Experimental

Nanoporous anatase TiO₂ films stemming from three different sources were employed for the electron transfer measurements: Firstly, TiO₂ films of about 4 μm thickness were kindly supplied by the EPFL Lausanne [5], secondly, TiO₂ films with thickness between 1 and 4 μm were prepared in our laboratory following the same procedure [5], thirdly films were prepared without autoclaving of the anatase particles [8]. In this case the sol was

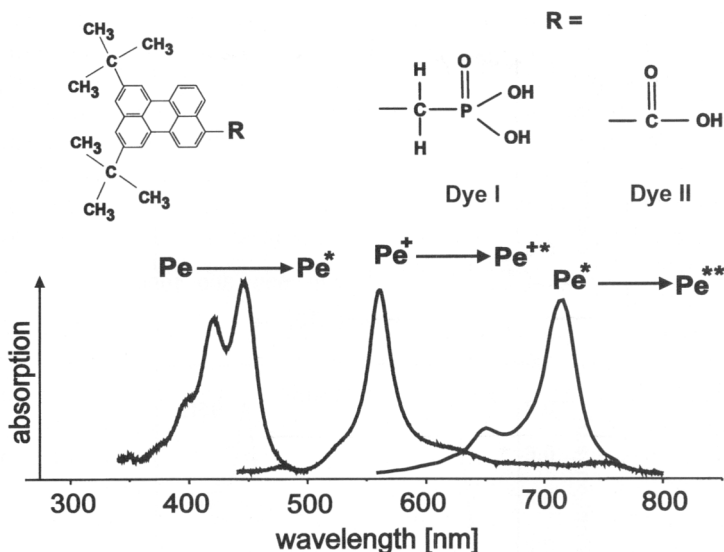


Fig. 1. Chemical formula of Dyes I and II. Absorption spectra of the perylene chromophore in its ground, first excited singlet and cationic state.

dialyzed against deionized water to remove excess HCl and was concentrated by rotary evaporation to reach a concentration of about 5 g/dm^3 TiO_2 . Further film processing followed recipe [5] and provided a mean particle size of about 5 nm in a film with about $1 \mu\text{m}$ thickness.

Dye I was 2,5-di-tertiary-butyl-9-perylenyl-methyl-phosphonic-acid (Dye I). Dye II was identical with Dye I except for the replacement of the methyl-phosphonic-acid group by carboxylic acid (Fig. 1). These dye molecules were adsorbed at room temperature from solution on the huge surface of the sponge-like TiO_2 films. For Dye I the solution was either pure toluene, or a mixture of toluene and methanol (10:1), or a mixture of toluene and acetic acid (200:1). Dye II was always adsorbed from toluene. The dye-covered TiO_2 electrode was rinsed several times with the respective solvent, dried under argon, and afterwards quickly transferred into the ultra-high vacuum (uhv) chamber where a base pressure of 10^{-10} mbar was established.

For transient absorption measurements light pulses were generated with a high repetition femtosecond lasersystem (Coherent Instruments). The Ti:sapphire lasersystem provided pulses of $6 \mu\text{J}$ energy, 100 kHz repetition rate, and a 60 fs pulse width (fwhm) at 800 nm. For the excitation of the perylene dyes I and II at 450 nm the pump pulse was obtained from the frequency doubled idler wave of an OPA pumped with 90 percent of the light intensity. The energy of the pump pulse was about 20 nJ. The remain-

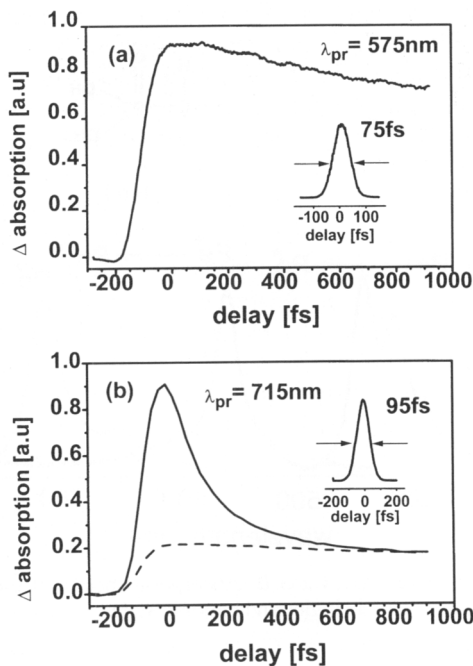


Fig. 2. Transient absorption signals measured in ultra-high vacuum of Dye I adsorbed on colloidal TiO_2 . The respective instrumental functions are shown as insets. Rise and decay of the two signals are controlled by the same electron transfer time of 40 fs. (a) Rise of the product (cationic) state measured at 575 nm (compare Fig. 1). (b) Decay of the reactant (excited singlet) state measured at 715 nm (compare Fig. 1).

ing part of the light intensity was used for the generation of white light that provided the probe pulse. The instrumental response function was obtained as the sum frequency signal of the pump and probe pulse generated in a BBO crystal of 100 μm thickness. Further experimental details were identical with those described in [6].

3. Experimental results

With well separated absorption spectra for the ground, excited, and cationic state (Fig. 1) the perylene chromophore is an excellent model compound for the investigation of electron transfer reactions in the excited state. The rise of the cation absorption (product state) at 575 nm and decay of the excited state absorption (reactant state) at 715 nm are shown for Dye I in Fig. 2a and b. A least mean square deviation fit of a simple model calculation was performed for the rise of the cationic product state (Fig. 2a). The

model function was obtained as convolution of the instrumental function with a single exponential rise and a single exponential decay function. The rise time of 40 ± 7 fs obtained from this fit was identified with the electron transfer time. A least square deviation fit was also performed for the decay signal of the excited state (Fig. 2b). For the latter signal Fig. 1 shows an overlap of the excited state absorption ($\text{Pe}^* \rightarrow \text{Pe}^{**}$) with the cation absorption ($\text{Pe}^+ \rightarrow \text{Pe}^{+*}$). Correspondingly the signal measured at 715 nm must be the superposition of the dominant decay of the excited reactant state and a smaller contribution due to the rise of the cationic product state. This was confirmed by the shape of the experimental signal (Fig. 2b). The corresponding fit parameters were retained in the fit to the rising component in Fig. 2b. The decay behavior of this signal was fitted to a single exponential function yielding a time constant of 40 ± 25 fs. This time constant for the decay in Fig. 2b is identical with that for the rise in Fig. 2a. Thus, the electron transfer time of about 40 fs was established for this system. This same electron transfer time was measured when Dye I was adsorbed on the surface of the three above described different TiO_2 films. The time constant remained the same irrespective of the type of solvent employed for the adsorption of Dye I. Recently, measurements on electron injection by Dye I were repeated on a system prepared 2 years ago and sealed in a quartz tube. In agreement with the results of 2 years ago, these recent measurements yielded also an electron transfer time of about 80 fs and not 40 fs. It is important to note that the respective TiO_2 film was seemingly prepared after the same recipe as those prepared more recently that yielded 40 fs electron transfer time with the same Dye I. Measurements carried out with Dye II gave systematically a shorter electron transfer time of about 30 fs.

Hitherto the cation radical absorption spectrum of the most efficient ruthenium dye (N3 in the Lausanne notation [5]) has remained ambiguous. Therefore, the electron transfer time for the N3 ruthenium dye was measured as rise time of the intraband absorption of the injected electron at 1100 nm [9]. A rise time of the electron absorption signal below 50 fs was recently confirmed by another laboratory who extended the measurements further into the IR [10]. The existing confusion about the absorption spectrum of the cationic state of the N3 ruthenium dye is illustrated in Fig. 3. Curve 1 is the absorption spectrum of the oxidized state of the decarboxylated N3 dye, where the oxidation was performed electrochemically at a potential slightly more oxidative than the oxidation potential of this dye [11]. This ruthenium dye is supposed to be more stable in the oxidized state than the N3 ruthenium dye. Curve 2 was also attributed to the identical oxidation state of the oxidized decarboxylated N3 dye and the corresponding oxidized state was generated by Ce(IV) [12]. The difference between curves 1 and 2 is gross and obvious, in particular the maximum at around 460 nm in curve 1 is completely missing in curve 2. The following three curves were measured as transient absorption spectra for the N3 dye adsorbed on TiO_2

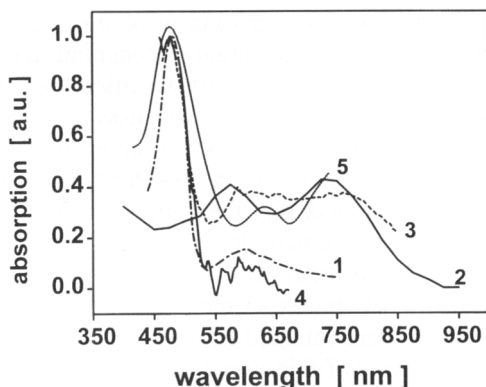


Fig. 3. Currently discussed versions of the absorption spectrum for the oxidized state of the so called N3 ruthenium dye (blue shifted here) and its decarboxylated pendant. Curve 1: Stationary absorption of the oxidized state of $\text{Ru}(\text{bpy})_2(\text{NCS})_2$ in acetonitrile [11]; curve 2: Stationary absorption of the oxidized state of $\text{Ru}(\text{bpy})_2(\text{NCS})_2$ (oxidation by Ce IV) in acetonitrile [12]; curve 3: fs-transient absorption of N3 on TiO_2 in ethylene carbonate/propylene solvent mixture [7]; curve 4: fs-transient absorption in UHV of N3 on TiO_2 corrected for ground state bleaching [13]; curve 5: ns-transient absorption in air of N3 on TiO_2 .

in different environments and each of them was attributed to the oxidized state of the N3 dye. In Fig. 3 these three curves are shifted to the blue such that the main absorption peak coincided with that of curve 1. Curve 3 is the such blue shifted transient absorption spectrum reported for the N3 dye adsorbed on TiO_2 and immersed in a ethylene carbonate/propylene environment [7], curve 4 is the blue shifted transient absorption spectrum for the N3 dye adsorbed on TiO_2 measured in ultra-high-vacuum [13], corrected here for ground state bleaching, curve 5 is a nanosecond measurement of the N3 dye adsorbed on TiO_2 performed in air. Fig. 3 clearly illustrates that there are major discrepancies between the absorption spectra attributed to the oxidized N3 dye and even greater differences between the spectra for the supposedly more stable oxidized state of the decarboxylated N3 ruthenium dye.

4. Discussion

In the case of the perylene chromophore the time constant for electron transfer was derived in each case from two independent measurements on the same sample, i.e. firstly the rise of the product state and secondly the decay of the reactant state. For Dye I and recently prepared TiO_2 films the mea-

surements gave consistently a time constant of about 40 fs for the perylene chromophore separated by the methyl-phosphonic-acid group from the surface of the semiconductor, whereas for Dye II, where the perylene chromophore is attached to the carboxylic group, the time constant was systematically somewhat shorter. The tunneling barrier for electron transfer will depend not only on the distance between the edge of the chromophore and the surface atoms of the semiconductor but in addition, it will depend also on the specific distribution of charges around the chromophore that will be different for different anchor groups. Electron transfer from a high donor level to many lower lying empty electronic acceptor levels in a wide band is temperature independent [2] and represents a different electron transfer mechanism than the well known thermally activated Marcus-Levich-Gerischer-Jortner type [14–16] electron transfer. It was recently confirmed experimentally with Dye I that electron transfer is independent of temperature on a TiO₂ film [17]. A theoretical model based on a modified Fano-Anderson model Hamiltonian and assuming the wide band approximation was found to describe correctly the essential experimental features of the system. This adiabatic theory will be described in detail elsewhere. Since electronic coupling alone is controlling the electron transfer time the model predicted the relationship of electronic interaction energy and electron transfer time in agreement with the energy-time uncertainty relationship [18], where twice the interaction energy corresponds to the halfwidth of the homogeneous lineshape. Accordingly, a small change in the tunneling barrier and thus electronic coupling energy, e.g. 10 meV, will cause a large change in the observed electron transfer time. For comparison an atom directly adsorbed without in-between anchor group onto a jellium-type metal surface is expected to yield electron transfer times < 1 fs [19].

Dye I adsorbed on a seemingly identically prepared sponge-type TiO₂ film [5] gave reproducibly over a period of more than 2 years a time constant of 80 fs instead of 40 fs for the more recent film preparations. This difference cannot stem from a change in the active dye species, since Dye I adsorbed to a surface can neither form dimers nor higher aggregates by virtue of its bulky tertiary-butyl spacer groups. Also, its anchor cum spacer group, methyl-phosphonic-acid, allows only for a small change in the orientation of the perylene chromophore with respect to the surface. Thus, the experimental difference in the electron transfer time for a seemingly identical preparation method of the system must be attributed to the unintentional variation in surface properties of the TiO₂ film. Indirect experimental evidence for this assumption was recently presented by a Japanese group [20]. With high resolution TEM it was demonstrated that a very thin (about 2 nm) amorphous layer can be formed as the surface layer of crystalline TiO₂ particles. The thickness of such an amorphous surface layer could be an insufficiently controlled parameter in the film preparation and thus in the preparation of the tunneling barrier for electron transfer. Electron transfer

times measured in uhv varied over a period of more than 2 years between 40 fs and 80 fs for numerous preparations of Dye I on the surface of sponge-type TiO₂ films. The time scale of a few 10 fs is thus firmly established for such systems.

Electron transfer from a chemisorbed ruthenium dye adsorbed on the surface of a TiO₂ film was measured in ultra-high vacuum in our laboratory with an electron transfer time of less than 25 fs [9]. The measurements corresponded to curve 4 in Fig. 3. This order of magnitude was recently confirmed also by a measurement at the same system in air that was extended also further into the IR range [10]. For the same system immersed in a solvent a slightly longer upper limit, i.e. < 150 fs was reported [7, 12] that was based on the transient absorption signal displayed as blue shifted curve 3 in Fig. 3.

There are earlier reports in the literature of time constants in the ps and ns time scale for electron injection in similar heterogeneous systems as described above [21, 22]. Based on the above described careful studies with femtosecond time-resolution it has to be concluded that the earlier experiments did not address the main electron transfer time in a properly prepared system. For example, luminescence decay measurements employing time-correlated single photon counting or a streak camera [23] cannot time-resolve femtosecond electron transfer. However, due to a superior dynamic range these techniques can address a small fraction of long lived dye molecules at the interface that are not representative for the main population of adsorbed dye species.

In conclusion, electron transfer within a few 10 fs is experimentally firmly established for large organic chromophore species that are adsorbed via an anchor group at a typical "outer-sphere" reaction distance at the surface of a semiconductor, if the excited donor level of the chromophore lies high above the lower edge of a wide conduction band.

Acknowledgement

The authors thank the German Science Foundation, SFB 337, and the Joule III program for financial support. We are grateful to Dr. M. Hilgendorff for the preparation of colloidal TiO₂ films.

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