

**Reply to Comment on “Measurement of Ultrafast Photoinduced Electron Transfer from Chemically Anchored Ru–Dye Molecules into Empty Electronic States in a Colloidal Anatase TiO<sub>2</sub> Film”**

Thomas Hannappel,<sup>†</sup> Carsten Zimmermann,<sup>†</sup>  
Britta Meissner,<sup>†</sup> Bernd Burfeindt,<sup>‡</sup>  
Winfried Storck,<sup>‡</sup> and Frank Willig\*,<sup>†</sup>

Hahn-Meitner-Institut, CD, Glienickerstrasse 100,  
14109 Berlin, Germany, and Fritz-Haber-Institut, PC,  
Faradayweg 4-6, 14195 Berlin, Germany

Received: January 28, 1998

The Comment by Moser et al. is ignoring the essential point of our Letter; i.e., the femtosecond time-resolved signals in the Letter<sup>1</sup> were measured in ultrahigh-vacuum (uhv) and not in any of the solvent environments addressed in the Comment by Moser et al. The uhv data in our Letter give the transient absorption/transmission signals of the electrons injected into TiO<sub>2</sub> and the difference spectrum due to bleaching of the N3 dye and formation of its oxidized state on the surface of TiO<sub>2</sub> electrode.

In preparing the sample for the uhv measurements, the N3 dye was adsorbed from ethanolic solution onto the TiO<sub>2</sub> electrode under argon. The preparation procedure for the sample followed meticulously the Lausanne recipe<sup>2</sup> and utilized only the N3 dye and TiO<sub>2</sub> electrode kindly supplied to the FHI by the Lausanne group or by Solaronix, Lausanne. After adsorption of the dye, the sample was transferred within 5 min into uhv, and the whole preparation and transfer procedure was completed within 35 min. Our already published<sup>3</sup> and ongoing studies of the photoinjection behavior of the perylene/TiO<sub>2</sub> system have clearly shown that data collected in uhv are far more trustworthy, with respect to retaining the originally prepared system, than data collected in any solvent environment, where impurities are unavoidable. Both the perylene/TiO<sub>2</sub> system and the N3 dye/TiO<sub>2</sub> system show a completely reversible and reproducible photoinjection and recombination behavior in uhv, after preparation following the Lausanne recipe.<sup>2</sup> In the case of perylene a dispute over the relevant transient absorption spectrum of the oxidized state cannot arise, since it was already well established via several different routes in other laboratories and is reproduced in our lab.<sup>3</sup>

The Comment by Moser et al. addresses the absorption spectrum shown as Figure 1a in our Letter.<sup>1</sup> It was obtained by carefully dosing the amount of oxidant added to the N3 dye in a solvent environment. Whatever opinion one might form concerning this secondary issue, it remains a totally independent item from the transient absorption data obtained in uhv (Figures 1b, 2, and 3 in our Letter). Instead of listing our pros and cons regarding the chemistry described in the Comment by Moser et al., we like to focus here on the point of genuine and common concern in our Letter<sup>1</sup> and in the Comment by Moser et al.

The transient absorption spectrum due to electron injection into TiO<sub>2</sub> from the electronic excited state of the adsorbed N3 dye is clearly different when the measurement is carried out under different experimental conditions, i.e., when the sample is in a solvent environment (T-spectrum, curve 2 of Figure 3b in the Comment<sup>4</sup>) and when it resides in uhv (H-spectrum, Figure 1b of our Letter<sup>1</sup>). Moser et al. relate the T-spectrum to the absorption spectrum (curve 3 of Figure 1 in the Comment) of an oxidized dye species that is generated by adding the very strong oxidant Ce(IV) to a dye related to the N3 dye. At present the situation is further complicated by the fact that the sample was exposed to essentially single-shot high-power laser pulses in the solvent environment,<sup>4</sup> whereas it was exposed to low power laser pulses with a high repetition rate in uhv.<sup>1</sup> For clarifying the origin of the T- and H-spectrum it appears necessary to realize in an actual experiment the in-situ transition between these two different spectra. Work in this direction is in progress at the HMI, and our current state of knowledge is as follows.

The T-spectrum<sup>4</sup> was reproduced in the HMI, when the N3 dye/TiO<sub>2</sub> sample was immersed in ethanol and excited with a Nd:YAG laser. The number of photons per laser pulse is about 100 times larger than during the measurement of the H-spectrum in uhv.<sup>1</sup> The shape of the T-spectrum and its lifetime suggest that it is most likely representing an oxidized state of the sample and does not stem from an excited electronic state of the N3 dye. The shape of the T-spectrum<sup>4</sup> differs from the H-spectrum<sup>1</sup> (uhv) not only at the red side but also at the blue side of the visible spectrum. At the HMI the T-spectrum was measured also in 10<sup>−2</sup> Torr ambient (glovebox preparation) and in addition in laboratory air, where it could be detected also over several hours.

Since the Lausanne recipe<sup>2</sup> was strictly obeyed prior to transferring the sample into uhv,<sup>1</sup> the reasoning put forward in the Comment by Moser et al. would lead to the prediction that the transient absorption spectrum in uhv should be the T-spectrum.<sup>4</sup> In the actual experiment, however, the H-spectrum is measured as transient absorption spectrum in uhv.<sup>1</sup> The latter's time behavior shows excellent agreement with the behavior of the transient absorption spectrum for the electrons injected into TiO<sub>2</sub>.<sup>1</sup> To explain a change from the T- to the H-spectrum in uhv, one would have to propose that the N3 dye performs an unknown reaction on the surface of TiO<sub>2</sub>, but only in uhv and not in any solvent environment or at an ambient pressure of 10<sup>−2</sup> Torr. Though not excluded by the presently known experimental results, this scenario appears to be rather unlikely. On the other hand, the T-spectrum has been obtained until now only under experimental conditions, where the presence of impurities such as water cannot be excluded, and thus chemical side reactions of the N3 dye have to be taken into account. This view finds strong support in the experimental results obtained with perylene<sup>3</sup> in the place of the N3 dye on the TiO<sub>2</sub> electrode. The perylene/TiO<sub>2</sub> sample behaves ideally only in uhv, and thus we consider it reasonable to assume that this holds true also for the N3 dye/TiO<sub>2</sub> sample.

A more general point arises from the Comment by Moser et al. which concerns the N3 dye's stability in the solar cell.<sup>2</sup> It was shown by Papageorgiou et al.<sup>5</sup> that reduction of the oxidized dye molecules through iodide, i.e., return to the initial state, is becoming a diffusion-controlled reaction at higher solar power. This means automatically exposure of the oxidized N3 dye state

\* To whom correspondence should be addressed.

<sup>†</sup> Hahn-Meitner-Institut.

<sup>‡</sup> Fritz-Haber-Institut.

to its wet chemistry environment during a longer waiting time. Accepting the N3 dye's instability in a solvent environment would mean here accepting the occurrence of side reactions.

### References and Notes

- (1) Hannappel, T.; Burfeindt, B.; Storck, W.; Willig, F. *J. Phys. Chem. B* **1997**, *101*, 6799–6802.
- (2) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphrey-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382–6390.
- (3) Burfeindt, B.; Hannappel, T.; Storck, W.; Willig, F. *J. Phys. Chem.* **1996**, *100*, 16463–16465. Burfeindt, B. Ph.D. Thesis, Technical University of Berlin, 1997.
- (4) Tachibana, Y.; Moser, J. E.; Grätzel, M.; Klug, D. R.; Durrant, J. R. *J. Phys. Chem.* **1996**, *100*, 20056–20062.
- (5) Papageorgiou, N.; Grätzel, M.; Infelta, P. P. *Sol. Energy Mater. Sol. Cells* **1996**, *44*, 405–438.