7. Summary

This work reports investigations of the photocatalytic activity of titanium dioxide nanoparticles (2.4 nm diameter) in aqueous suspensions by applying laserpulse-induced optoacoustic calorimetry (LIOAC). The investigations cover photoreaction systems containing water as the only oxidizable substrate as well as suspensions wherein halide oxidation occurs concurrently with water oxidation.

For the systems $2.4\,\mathrm{nm\,TiO_2}|\mathrm{H_2O,\,O_2,\,0.01\,mol\,dm^{-3}}\ldots\mathrm{0.1\,mol\,dm^{-3}\,X^-}$, pH = 1, containing the halides $\mathrm{X^-} = \mathrm{Br^-}$ or $\mathrm{Cl^-}$, the enthalpy changes of photoinduced reactions were compared with the photon energy deposited in the systems by applying LIOAC for the first time. In all of these systems, the amount of released heat was greater than the amount of absorbed optical energy, indicating exothermic photoprocesses in TiO_2-suspensions with added halides. The maximum ratio between the released heat and the absorbed energy was found to be $\alpha = 1.3$ in the system $2.4\,\mathrm{nm\,TiO_2}|\mathrm{H_2O,\,O_2,\,0.03\,mol\,dm^{-3}\,Cl^-}$, pH = 1. In a photodeaggregation model, derived in this work, the adsorption of halides onto TiO_2-single-particles photoformed from particle aggregates was identified as the principle exothermic process. This model considers all reaction processes occurring within 6 µs after photon absorption. It covers the following endothermic photoreactions whose enthalpy changes have been calculated or determined here: oxidation of X^- to $X_2^{\bullet-}$ ($\Delta H^\circ(\mathrm{Br}^{\bullet-}_{2(aq)}) \approx 171\,\mathrm{kJ\,mol^{-1}}$ or $\Delta H^\circ(\mathrm{Cl}^{\bullet-}_{2(aq)}) \approx 232\,\mathrm{kJ\,mol^{-1}}$, respectively), oxidation of H_2O to $HO^\bullet$ ($\Delta H^\circ(\mathrm{HO}^\bullet_{(aq)}) = 281\,\mathrm{kJ\,mol^{-1}}$) as well as the respective reduction of O_2 to $HO_2^\bullet$. The core of the photodeaggregation model is a process discovered by LIOAC: the photodissoziation of TiO_2-aggregates ($\Delta H^\circ_{\mathrm{Dis}} \approx 28\,\mathrm{kJ\,mol^{-1}}$) which uncovers additional photocatalyst surface. During the subsequent establishment of the thermodynamic equilibrium in the additional TiO_2-surface area the following three processes proceed: protonation ($\Delta H^\circ_{\mathrm{Prot}} \approx -17\,\mathrm{kJ\,mol^{-1}}$), halide-adsorption ($-70\,\mathrm{kJ\,mol^{-1}}\cdots-90\,\mathrm{kJ\,mol^{-1}}$) and formation of the double layer ($W_{\mathrm{DS,m}} = -11.4\,\mathrm{kJ\,mol^{-1}}$). Several details of the photodeaggregation model could be confirmed by further investigations applying cryo-TEM and methodically improved LIOAC. Comprehensive investigations of the kinetics of photoinduced processes complement the photodeaggregation model. Results of additional studies are discussed and explained without constraints by using the photodeaggregation model. These include $2.4\,\mathrm{nm\,TiO_2}$-suspensions containing the organic prototype substances methanol or isopropyl alcohol.

In the system $2.4\,\mathrm{nm\,TiO_2}|\mathrm{H_2O,\,O_2}$, pH = 1, the enthalpy changes of photoinduced reactions are compared with the photon energy deposited in the system by applying LIOAC. It is shown that 90% ($\alpha = 0.9$) of the absorbed optical energy are converted to heat within 30 ns. The remaining 10% are stored in the system for at least a few µs and are assigned to the formation of free hydroxyl radicals. On the basis of energy conservation considerations as well as standard one-electron reduction potentials for the radicals and enthalpies of hydration taken from the literature, the quantum yield of the hydroxyl radical formation was determined as $\Phi(\mathrm{HO}^\bullet) = 12\%$. This result was confirmed in the context of the photodeaggregation model by using a theore-

tically and methodically improved LIOAC. Therefore, the existence of free hydroxyl radicals in illuminated aqueous suspensions of TiO_2-nanoparticles is corroborated in terms of energy considerations.

Additional results show the applicability of potassium dichromate as a calorimetric reference substance in neutral and acidified solutions (pH = 1). Thermoelastic coefficients of acid solutions were determined in the range $12^\circ C \ldots 27^\circ C$.

Laserpulse-Induced Deaggregation of TiO_2-Nanoparticles in Aqueous Suspension. Investigations of Water Oxidation and Adsorption of Halide Ions by Optoacoustic Calorimetry