Light-Induced Electron Transfer in Colloidal Semiconductor Dispersions: Single vs. Dielectric Reduction of Acceptors by Conduction-Band Electrons

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Abstract: Colloidal particles of TiO2 (anatase, 50-Å radius) were produced via hydrolysis of TiCl4 in aqueous solutions and characterized by electron microscopy, light scattering, and absorption and electrophoresis techniques. Laser photolysis and continuous illumination techniques were applied to investigate the reaction of conduction-band electrons (e−cb) with various acceptor molecules. The rate of reduction of methyl viologen is diffusion controlled in alkaline solution (pH > 10) but becomes limited by interfacial electron transfer at lower pH. No diffusion limit is observed with the functionalized viologen C14MV2+ which is adsorbed at the surface of the TiO2 particles. Preirradiated samples produce hydrated electrons owing to photoionization of C14MV+. A cofacial dimeric viologen (DV4+) is reduced by e−cb via a simultaneous two-electron-transfer step. In contrast, Rh(bpy)32+ undergoes one-electron reduction to Rh(bpy)2+ by e−cb. Subsequent dark reactions produce Rh(bpy)3+. Heterogeneous rate constants and transfer coefficients for these interfacial redox processes are derived and implications for artificial photosynthetic systems discussed.

Introduction

In the field of artificial photosynthesis, attempts are presently made to design functional molecular assemblies that achieve the task of fuel formation by visible light. Colloidal semiconductors exhibit several advantageous features that make them attractive candidates as light-harvesting units in such devices. These particles combine a number of desirable properties, such as high extinction coefficients, fast carrier diffusion to the interface, and suitable positioning of their valence and conduction band, to accomplish high efficiencies in the light-energy-conversion process. Particularly attractive is, furthermore, the possibility of modifying the surface of the semiconducting particle by chemisorption, chemical derivatization, and/or catalyst deposition assisting light-induced charge separation and subsequent fuel-generating dark reaction.

Following our initial water cleavage investigations with colloidal dispersions of TiO2 and CdS, we carried out laser photolysis and luminescence experiments to probe light-induced electron-hole separation and interfacial electron-transfer events involving ultrathin semiconductor particles.1,2 Recently, a number of related investigations have appeared in the literature. Apart from flash photolysis3 and luminescence4 studies, the elegant work of Brus5 and Hester6 using resonance Raman techniques to identify intermediates should be mentioned. The preparation of TiO2 sols in organic solvents and investigation of electron and hole transfer to species in solution have also been recently reported.7

The present report deals with interfacial electron transfer involving colloidal TiO2 dispersions in aqueous medium. An important aspect of the work is related to the achievement of multielectron transfer from the conduction band to suitable acceptors present at the surface of the semiconductor particle.

Experimental Section

Preparation and Characterization of Colloidal TiO2. TiCl4 (Fluka purissimum) was further purified by vacuum distillation (40 °C, ca. 25 torr) until a colorless liquid was obtained. The purified material (5 g) was slowly added to water at 0 °C. The final pH of the solution was about 0.5. The solution was subsequently dialyzed until the pH reached a value of 3. Precise determination of the TiO2 content after dialysis was carried out as described previously.8 At pH 2-3 poly(vinyl alcohol) (PVA, 0.1%) was used to stabilize the colloidal particles. Commercial PVA (Mowiol, Hoechst, W. Germany) was pretreated by UV light (10-98) to remove impurities. This method of preparation has the advantage over the one previously employed,9,10 i.e., hydrolysis of titanium tetraisopropoxide in that it avoids organic compounds that subsequently would have to be removed from the system.

Transmission electron microscopy applied to TiO2 sols obtained in this manner showed that the particles have a roughly spherical shape and are polydisperse. Direct measurement of the size of all the particles and averaging yielded a mean particle radius of 46 Å. These aggregates consist of both amorphous phase and anatase as shown by application of dark field electron microscopy and electron diffraction techniques.

Independent confirmation of the particle dimensions was obtained by applying a quasi-elastic light-scattering technique to aqueous dispersions of the TiO2 sol.11 The temporal decay of the correlation function was evaluated by computer analysis. Optimal fit was obtained for a diffusion coefficient $D = 4.43 \times 10^{-7}$ cm$^2$/s of the particles. Application of the Stokes–Einstein equation yields for the hydrodynamic radius a mean value of 56 Å. Data analysis below will be based on an average radius of 50 Å for the colloidal TiO2 particles.

The point of zero potential (ZZP) of the particles was determined by electrophoretic measurements using a Rank Bros. II instrument equipped with an He–Ne laser.12 Electrophoretic mobilities are plotted as a function of pH in Figure 1. The intersection of the curve with the abscissa corresponds to ZZP = 4.7. This value is higher than that observed for the TiO2 colloid prepared from titanium tetrabutoxide (ZZP = 3.2) but still lower than that reported in the literature13 for very pure anatase (ZZP ≈ 6). Presumably, the presence of C1− on the particle surface produces a decrease in the ZZP with respect to samples that are free of anionic impurities.

The optical absorption spectrum of the TiO2 sol is shown in Figure 2. The absorption rises sharply toward the UV below 380-390 nm. The onset agrees well with the 3.2-eV band gap of anatase and amorphous

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Figure 1. Electrophoretic measurements of the mobility of colloidal TiO₂ particles as a function of pH ([TiO₂] = 20 mg/L, ionic strength = 2 × 10⁻¹¹ M).

Figure 2. UV absorption spectra of TiO₂ sols: 0.5 g of TiO₂/L, 1 of g TiO₂/L, 2 of TiO₂/L, 5 g of TiO₂/L. These curves represent true absorption data. Solutions were transparent, scattering effects being eliminated by use of an integrating sphere. Lambert-Beer's law is observed within this concentration range and the extinction coefficient at λ 347 nm evaluated as ε = 0.785 g⁻¹ L cm⁻¹, optical pathlength 2 mm.

titania. (The optical absorption coefficient near the band edge may be expressed by α = A(hν - Eg)¹/²/hν for an indirect band gap material such as TiO₂.)¹⁷

Apparatus. Laser photolysis experiments employed a frequency-doubled J× K 2000 ruby laser combined with fast kinetic spectroscopy technique to detect transient species.¹⁸ Continuous illumination was carried out with an XBO 450-W Xe lamp (Oriel) equipped with a 15-cm water jacket to remove IR radiation. UV-visible absorption spectra were recorded on a Cary 219 (Varian) spectrophotometer. The absorption spectrum of the TiO₂ sol was measured with a Perkin-Elmer/Hitachi 340 spectrophotometer using an integrating sphere attachment to correct for light scattering. A Philips E.M. 300 instrument was used to perform transmission electron microscopy. The equipment employed for quasielastic light scattering has been previously described.⁵

Materials. N-Tetradecyl-N'-methyl-4,4'-bipyridinium (C₁₄MV²⁺) was synthesized by Dr. A. M. Braun in our laboratory.¹⁹ The o-xylene bridged viologen dimer was a kind gift of Professor Sigfried Hünig, Institute of Organic Chemistry, University of Würzburg, W. Germany. Rh bpp²⁺ trichloride salt was synthesized in our laboratory by Dr. K.

Results and Discussion

i. Dynamics of Light-Induced Reduction of Surfactant and Simple Viologen by e⁻CB(TiO₂). In two previous investigations,¹⁴ we examined the dynamics of methyl viologen (MV²⁺) reduction by conduction-band electrons (e⁻CB) of colloidal TiO₂.

\[
e⁻CB + MV²⁺ \rightarrow MV⁺
\]  (1)

The kinetics of this reaction were found to be controlled by the diffusion of MV²⁺ to the particle surface as well as by the rate of interfacial electron transfer. The pseudo-first-order rate constant kₙ (s⁻¹) was found to increase linearly with MV²⁺ concentration, kₙ = k₂[MV²⁺], where k₂[MV²⁺] is the second-order rate constant for MV²⁺ formation. The value of the latter rate constant, expressed in units of cm³s⁻¹, k₂ = kₙ × 1000/NA (NA = Avogadro’s number), was shown to be given by

\[
\frac{1}{k'₂} = \frac{1}{4πr²} \left( \frac{1}{kₚ} + \frac{r}{D} \right)
\]  (2)

where r is the reaction radius corresponding to the sum of the radii of semiconductor particle and relay and D is the sum of their respective diffusion coefficients. The parameter kₚ (cm/s) is the rate constant for interfacial electron transfer which changes with overvoltage (E - E°) according to the Tafel equation (T = 298 K)

\[
kₚ = kₚ₀ \exp \left( -\frac{\alpha(E - E°)}{0.059} \right)
\]  (3)

where α is the transfer coefficient and kₚ₀ the value of the rate constant for E - E° = 0. The overvoltage can be expressed in terms of the standard redox potential of the MV²⁺/MV⁺ couple and the potential of the TiO₂ conduction band.

\[
E_{CB} = E_{CB}(TiO₂) - E°(MV²⁺/MV⁺)
\]  (4)

where E_{CB}(TiO₂) depends on pH according to

\[
E_{CB} = -0.11 - 0.059(pH)
\]  (5)

From eq 2 to 5 one obtains finally

\[
\frac{1}{k'₂} = \frac{1}{4πr²} \left( \frac{1}{kₚ₀ \exp[\alpha(pH) - \alpha(5.54)]]} + \frac{r}{D} \right)
\]  (6)

In the following section, we shall apply eq 6 to analyze MV²⁺ reduction by e⁻CB(TiO₂). We attempt to obtain information on the effect of TiO₂ particle preparation (i.e., hydrolysis of TiCl₄, viz. titanium isopropoxide) on the kinetic parameters kₚ and α. Furthermore, the behavior of the surfactant viologen C₁₄MV²⁺ is analyzed.

Figure 3 shows data obtained from the laser photolysis of colloidal TiO₂ (500 mg/L) in the presence of 2 × 10⁻³ M viologen. The logarithm of the observed rate constant (kₙ) for the reduction of viologens MV²⁺ and C₁₄MV²⁺ is plotted as a function of solution pH. The kₚ values were determined by monitoring the growth

(20) The rate parameter k₂ is defined as the interfacial electron flux due to MV²⁺ reduction (flux = d[NV⁺]/dτ) at unit bulk concentration of MV²⁺ (mol/cm³): k₂ = flux/[MV²⁺] and is therefore expressed in units of cm/s.

(21) The conductance-band potential (Fermi level) of the TiO₂ particles employed in this study was determined as E_{CB} = -0.11 - 0.059(pH) against NHE by using the same method as described in ref 3. This is slightly more positive than the value E_{CB} = -0.13 - 0.059(pH) derived for TiO₂ particles produced via hydrolysis of titanium isopropoxide.¹⁷ Note that a similar value, i.e., E_{CB} = -0.05 - 0.059(pH), has been estimated recently for the Fermi level of anatase particles from photocatalytic measurements with slurry electrodes [M. D. Ward, J. R. White, and A. J. Bard, J. Am. Chem. Soc., 105, 27 (1983)].
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Figure 3. Reduction of MV²⁺ (O, 2 × 10⁻⁴ M) and CI₄MV²⁺ (Δ, 2 × 10⁻⁴ M) by e⁻CB(TiO₂). The observed rate constant for MV²⁺ and CI₄MV²⁺ formation is plotted as a function of pH. The solid line represents a computer fit for MV²⁺ reduction using α = 0.84 and k₀ = 10⁻² cm/s. A dashed line with a slope of 0.78 was drawn through the CI₄MV²⁺ points. ([TiO₂] = 0.5 g/L protected by 1 g/PVA).

of the 602-nm absorption of the viologen cation radicals after excitation of the TiO₂ colloid by the 20-ns laser pulse. For CI₄MV²⁺ a precisely linear relation is obtained between log k₁ and pH over a domain of at least 7 units,²² the slope of the line being 0.78. A straight line with similar slope is also obtained when MV²⁺ is used as an electron acceptor. However, in this case linearity of the log k₁ (pH) function is restricted to pH < 10. At higher alkalinity the curve bends sharply, k₁ attaining a limit of ~10⁻¹⁰ s⁻¹. Another noteworthy difference between the kinetic behavior of MV²⁺ and CI₄MV²⁺ concerns the effect of concentration on k₁. While k₁ increases with MV²⁺ concentration, it is not affected when [CI₄MV²⁺] is varied from 2 × 10⁻⁴ to 10⁻³ M. The solid line in Figure 3 is a computer plot of eq 6 using the experimentally available parameters: r = 55 Å and D = 10⁻⁵ cm²/s. The results obtained for MV²⁺ are in excellent agreement with the predictions of eq 6, supporting the validity of the kinetic model applied. From this curve α is evaluated as 0.85 ± 0.05 and k₀ = (1 ± 0.5) × 10⁻² cm/s.

In the case of TiO₂ sols prepared via hydrolysis of titanium isopropoxide,³⁴ the kinetic parameters for MV²⁺ reduction by e⁻CB were k₀ = 5 × 10⁻³ cm/s and α = 0.48. Thus, while the heterogeneous rate constants for the two preparations are approximately equal, the α values differ significantly. A transfer coefficient of 0.5 is predicted from a Marcus-type free-energy relation, i.e.

\[ \Delta G^* = \lambda \left(1 + \frac{\Delta G^0}{4\lambda}\right)^2 \]  (7)

where \( \Delta G^* \) and \( \Delta G^0 \) (≈ E - E°), and \( \lambda \) are the free energy of activation, the free energy of reaction, and the reorganization energy. In the region where \( \Delta G^* < 4\lambda \), \( \Delta G^0/d\Delta G^* = 0.5 \), such a relation seems to apply to TiO₂ particles prepared from isopropanol but not for those produced via hydrolysis of TiCl₄. The relatively large α value found for the latter is, however, compatible with other free-energy relations derived empirically.²⁵ For simple one-electron-transfer processes α > 0.5 indicates an unsymmetrical transition state implying that a large fraction of the overvoltage contributes to the decrease of the free energy of activation of the reaction. Alternatively, anomalously large Tafel slopes can result from a multistep reaction mechanism.

Previous investigations of the reduction of a variety of electron acceptors on TiO₂ electrodes have obtained α values exceeding unity²⁶ which have been attributed to the participation of surface states in the electron-transfer events. More recently,²⁷ these surface states have been identified with OH groups coordinated to one lattice Ti⁺⁺ ion.²⁸ By analogy, it is reasonable to assume that the same type of surface hydroxyl function also mediates electron-transfer processes involving the conduction band of TiO₂ particles. Indeed, it has been shown by infrared studies²⁹ that TiO₂ powders prepared from the propoxide and TiCl₄ differ in the nature and density of surface hydroxyl groups. This may explain the difference in the transfer coefficients for the reduction of MV²⁺ by e⁻CB of these two types of TiO₂ particles.

The transfer coefficient for the reduction of TiO₂ conduction band electrons with CI₄MV²⁺ is 0.75 ± 0.05 and hence almost identical with that obtained for MV²⁺. However, the kinetic behavior of the surfactant viologen differs from simple MV²⁺ in two important aspects: (1) k₁ continues to increase and does not attain a diffusion-limited value at pH > 10; (2) within the range 2 × 10⁻⁴ ≤ 10⁻³ M, k₁ is independent of viologen concentration. One infers from this behavior that the reduction of CI₄MV²⁺ by e⁻CB involves mainly surface-bound acceptor molecules. This contrasts with the behavior of MV²⁺ which is predominantly present in the solution bulk. Apparently, the amphiphilic nature of CI₄MV²⁺ enhances adhesion to the TiO₂ particles.

The case of charge transfer from a semiconductor particle to a surface-adsorbed acceptor cannot be treated by eq 6. The correct interpretation of the k₁ values obtained for CI₄MV²⁺ is that of a reciprocal average time for electron transfer from the conduction band of the particle to the adsorbed acceptor molecule. Moreover, since for a 50-Å-radius TiO₂ particle the average transit time of e⁻CB from the particle interior to the surface is only ~2 ps, k₁ reflects properly the rate of the heterogeneous electron-transfer step. A simple consideration shows that k₁ is related to the electrochemical rate constant kₗ via

\[ k₁ = kₗd \]  (8)

where d is the average distance over which the electron jump occurs. Assuming that the CI₄ chain of CI₄MV²⁺ extends radially away from the TiO₂ surface, the viologen moiety facing the aqueous phase, the upper limit for d is calculated as approximately 25 Å. If it is further assumed that the redox potential of the CI₄MV²⁺/²⁻ couple is not affected by adsorption to the TiO₂ particles, the pH value for which \( E - E° = 0 \) is 5.54, as in the case of MV²⁺, and the k₁ value of this pH obtained from Figure 3 is 4 × 10³ s⁻¹. Application of eq 8 yields finally kₗ = 10⁻³ cm/s which is smaller by a factor of ~10 than the corresponding value for methyl viologen. This difference is likely to arise from the closer contact of the latter acceptor to the TiO₂ surface.

ii. Generation of Hydrated Electrons in Preirradiated CI₄MV²⁺/²⁻/TiO₂ Dispersions

Continuous irradiation of colloidal TiO₂ in the presence of CI₄MV²⁺ leads to the formation of a violet color which is due to the buildup of CI₄MV²⁺ and its dimeric form in solution. Exposure of such a preirradiated solution to the 347.1-nm laser flash results in the generation of a short-lived


(28) Two different types of hydroxyl groups exist at the surface of TiO₂:¹⁴ The first bridges two adjacent Ti⁺⁺ sites and is acidic in character (pK ≈ 2.9). The second, basic type OH⁻ is associated with only Ti⁺⁺ site (pK ≈ 12.7). The latter hydroxyls constitute the surface states that play a decisive role in electron-transfer processes involving the conduction band of TiO₂.²¹⁸


(30) At pH > 9.5 the violet color changes to yellow under continued illumination owing to formation of doubly reduced viologen CI₄MV²⁻. Laser photolysis studies have shown that the generation of CI₄MV²⁻ occurs via two sequential and parallel-electron-transfer reactions involving e⁻CB(TiO₂).

(31)
The explanation of this effect is as follows. In preirradiated and concomitant reoxidation of the viologen radical. Since the formation of $e_\text{aq}$ by laser light, confirming that reduced $\text{C}_4\text{MV}^+$ hydrated electron

The yield of $e_\text{aq}$ was found to be linearly dependent on the laser light intensity, indicating that a monophotonic process was operative. The explanation of this effect is as follows. In preirradiated $\text{C}_4\text{MV}^{2+}/\text{TiO}_2$ dispersions the 347.1-nm laser light is not only absorbed by the semiconductor particles but also by $\text{C}_4\text{MV}^+$. Excitation of the latter leads to hydrated electron formation

$$
\text{C}_4\text{MV}^{2+} \xrightarrow{h\nu} \text{C}_4\text{MV}^+ + e_\text{aq}^- \quad (9)
$$

and concomitant reoxidation of the viologen radical. Since the redox potentials for $e_\text{aq}^-$ and the $\text{C}_4\text{MV}^{2+/+}$ couple are $-2.7$ and $-0.44$ V, respectively, the minimum free-energy input required to drive reaction 9 is $2.26$ eV corresponding to a photoionization intensity, indicating that a monophotonic process was operative.

As shown by the oscilloscope trace inserted in the figure, the lifetime of the transient is ca. 300 ns. In the presence of $\text{N}_2\text{O}$, a typical electron scavenger, the lifetime is shortened drastically. A similar mechanism may be operative in the photogeneration of hydrated electrons in colloidal CdS solutions. Several reports on electron injection processes from p-type semiconductor electrodes (GaAs, Si) into liquid ammonia have appeared recently.

iii. Reduction of the Dimeric Viologen $\text{DV}^{4+}$ by Conduction-Band Electrons: Simultaneous Two-Electron Transfer Induced by Light. $\text{DV}^{4+}$ is a potential four-electron acceptor whose redox behavior in aqueous solution has not been investigated so far. Aqueous solutions of $\text{DV}^{4+}$ (0.2 M KCl, phosphate buffer pH 7) were therefore examined by cyclic voltammetry using a basal plane pyrolytic graphite electrode. A first reversible wave corresponding to reduction of $\text{DV}^{4+}$ to $\text{DV}^{2+}$ appears at $E_{1/2} = -0.07$ V (NHE). It is followed by a second one-electron reduction step

$$
E_{1/2}(\text{DV}^{3+/2+}) = -0.30 \text{ V (NHE).} \quad \text{DV}^{2+} \quad \text{can be further reduced at potentials more negative than ca. -800 mV. This reduction wave is irreversible and leads to a product, probably DV, which precipitates from the electrolyte solution. From this study two noteworthy differences in the redox behavior of MV$^{2+}$ and DV$^{4+}$ emerge. (1) The dimer is more readily reduced than the monomer ($E_1/2$ shifted positively by 440 mV). (2) The difference between the first and second reduction potential of DV$^{4+}$ is very small (ca. 70 mV), making it an excellent candidate for participation in simultaneous two-electron-transfer processes.

Figure 5 shows UV-visible absorption spectra resulting from illumination of $10^{-4}$ M $\text{DV}^{4+}$ in deaerated solutions of colloidal $\text{TiO}_2$ (500 mg/L) at pH 1 in a 1 cm pathlength optical cell. Under light exposure the initially colorless solution very rapidly develops an intensively blue color. The spectrum present after 10-s irradiation exhibits a pronounced peak at 632 nm, weaker maxima being located at 700, 398, and 359 nm and shoulders at 585, 536, and 400 nm. Under continuing exposure to light the color changes rapidly from blue to pink. Within 40 s the absorptions at 632 and 398 nm have almost completely disappeared with concomitant growth of the 536- and 359-nm peaks. Distinct isosbestic points located at 714, 547, 447, 380, and 325 nm are associated with this transition, indicating sequential photogeneration of only two light-absorbing species.

These results are interpreted in terms of band-gap excitation of $\text{TiO}_2$ particles producing conduction band electrons and valence band holes. The former reduce $\text{DV}^{4+}$ according to the sequence

$$
\text{CB} + \text{DV}^{4+} \xrightarrow{k_1} \text{DV}^{2+} + \text{CB} \quad (\lambda_{\text{max}} 632 \text{ nm}) \quad (10a)
$$

$$
\text{DV}^{2+} + e_\text{CB} \xrightarrow{k_1} \text{DV}^{+} + \text{CB} \quad (\lambda_{\text{max}} 536 \text{ nm}) \quad (10b)
$$

The absorption maxima at 632 and 398 nm are attributed to $\text{DV}^{2+}$ and those at 536 and 359 nm to $\text{DV}^{+}$, respectively. Extinction coefficients for these species can also be derived from experimental data such as shown in Figure 5. Since the assumption is made that during photolysis, $\text{DV}^{4+}$ is first quantitatively converted to $\text{DV}^{2+}$, which subsequently is transformed completely into $\text{DV}^{+}$ these values represent only lower limits. One obtains for $\text{DV}^{+}$ ($\lambda_{\text{max}} 632 nm$)

$$
\epsilon \geq 14 \, 800 \, M^{-1} \text{ cm}^{-1} \quad \text{and for } \text{DV}^{+} (\lambda_{\text{max}} 536 \text{ nm}) \epsilon \geq 13 \, 000 \, M^{-1} \text{ cm}^{-1} \quad (39)
$$

Note that the spectroscopic features of $\text{DV}^{2+}$ and $\text{DV}^{+}$ distinguish themselves from those of the methyl viologen radical

$$
$$

$$
(32) \text{At pH} > 9.5 \text{ the final product obtained from illuminating } \text{TiO}_2/\text{C}_4\text{MV}^{2+/+} \text{ dispersions is } \text{C}_4\text{MV}^+. \text{ The latter was found to ionize also monophotonically after 347.1-nm laser excitation:}
$$

$$
\text{C}_4\text{MV}^{2+/+} \xrightarrow{h\nu} \text{C}_4\text{MV}^+ + e_\text{aq}^- \quad (33)
$$

$$
$$

$$
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$$
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$$
(37) \text{Cyclic voltammetric measurements have been performed by Dr. T. Geiger in our institute using a Pine Co. instrument.}
$$

$$
(38) \text{A distinct sharpening of the anodic return peak after cyclic voltammetric reduction of } \text{DV}^{2+} \text{ to } \text{DV}^{+} \text{ indicates that the latter adheres at least partially to the surface of the graphite electrode.}
$$

$$
(39) \text{The extinction coefficient of } \text{DV}^{2+} \text{ at 359 nm is 2.3 times larger than at 535 nm. Thus, after 40-s irradiation the absorbance at 359 nm in Figure 7 has increased to ca. 2.8.}
$$

$$
(40) \text{T. Watanabe and K. Honda, J. Phys. Chem., 86, 2617 (1982), and references cited therein.}
$$
or its dimeric form\(^{41}\) (MV\(^+\)). MV\(^+\) has a strong electronic transition at 396 nm (\(4.2 \times 10^6\)) which is almost totally absent in DV\(^{2+}\). Furthermore, the 606-nm band of MV\(^+\) (\(1.3 \times 10^6\)) is significantly red-shifted and enhanced in DV\(^{3+}\). In the case of DV\(^{2+}\), both the visible and UV absorptions are much stronger than the corresponding transitions of (MV\(^+\)). Interestingly, there is close similarity between the spectrum of DV\(^{2+}\) and that of the intramolecular dimer cation–radical \(\text{MVCH}_2\text{CH}_2\text{MV}^+\) which is produced via photoreduction of bisviologen compounds in alcohols.\(^{42}\) In the latter case, formation of a sandwich-type complex is sterically favored by the propylene linkage between the two MV\(^+\) moieties.

The time course of the two consecutive electron-transfer steps leading to DV\(^{2+}\) formation in irradiated TiO\(_2\) dispersions was monitored individually using the laser photolysis technique. Figure 6 shows oscilloscope traces obtained from experiments with 10\(^{-4}\) M DV\(^{4+}\) in colloidal TiO\(_2\) (500 mg/L) dispersions. Excitation of the semiconductor particles by the laser pulse is followed by a pronounced growth of the 635-nm absorption of DV\(^{3+}\) which occurs on a millisecond time scale and reaches a plateau value. Kinetic evaluation of these data yields \(k_1 = 35\) s\(^{-1}\) for the pseudo-first-order rate constant of DV\(^{3+}\) formation. The DV\(^{3+}\) concentration after completion of the e\(^-\)\text{CB} transfer is calculated as 3.7 \times 10^{-5} and corresponds to a quantum yield of 1.2 for DV\(^{2+}\) formation. (This value is based on the same assumptions as made in deriving the extinction coefficient of DV\(^{3+}\).) In order to determine the rate parameter \(k_2\) for the second electron-transfer step from the TiO\(_2\) conduction band to DV\(^{3+}\), DV\(^{4+}\) was converted into DV\(^{2+}\) by preirradiating the solution. The blue DV\(^{3+}\)-containing dispersion of TiO\(_2\) was subsequently exposed to the laser flash. Figure 6b shows the time course of the 535-nm absorption of DV\(^{3+}\) after excitation of the semiconductor particle. A smooth growth of the signal is again observed which attains a plateau in the millisecond time domain. Kinetic evaluation yields the specific rate of the second electron-transfer step \(k_2 = 20\) s\(^{-1}\).

Dividing \(k_1\) and \(k_2\) by the DV\(^{4+}\) concentration gives for the second-order rate constants the values \(k_1' = 3.5 \times 10^5\) M\(^{-1}\) s\(^{-1}\) and \(k_2' = 2 \times 10^6\) M\(^{-1}\) s\(^{-1}\). One concludes that the two consecutive electron-transfer events from the TiO\(_2\) conduction band to the viologen dimer occur at a similar rate which is significantly below the diffusion-imposed limit. Apparently these processes are controlled by the rate of heterogeneous electron transfer at the semiconductor surface, i.e., the parameter \(k_{de}^e\) in eq 6. This is not surprising since at pH 1 the overvoltages available to drive the first and second reduction of DV\(^{4+}\) are only 170 and 100 mV, respectively. Furthermore, since the TiO\(_2\) particles are positively charged at pH 1 they repel the DV\(^{4+}\) and DV\(^{3+}\) ions, decreasing the frequency of diffusional encounter between the reactants.

Included in Figure 6 are oscilloscope traces obtained from the laser photolysis of TiO\(_2\)/DV\(^{4+}\) solutions at pH 7. Care was taken to protect samples from exposure to light prior to performing flash irradiations. Only one laser pulse was applied to each sample. The temporal behavior of the transient absorption is distinguished by an immediate increase of the absorption signals followed by a slower growth at 632 nm which is matched by a decay at 535 nm. A plateau is reached within several milliseconds.

The transitory spectrum present at the end of the fast absorbance rise is essentially the same as that displayed for DV\(^{2+}\) in Figure 5, the maximum in the visible being located at 536 nm. After completion of the slower process when the transient absorption has reached a plateau, the species present has the spectral characteristics of DV\(^{2+}\) with a maximum at 636 nm. From this
behavior one infers that the transient produced first after laser excitation of the TiO₂ particles is the doubly reduced viologen dianion, the monoreduced species being formed in a subsequent process that occurs on a millisecond time scale.

These observations may be rationalized in terms of simultaneous transfer of two electrons from the conduction band of the TiO₂ particle to DV⁴⁺:

\[
2e^-_{\text{CB}} + DV^{4+} \rightarrow DV^{2+} \quad (11)
\]

followed by coproporportionation of DV²⁺ with excess DV⁴⁺ to form the monoreduced radical DV³⁺:

\[
DV^{4+} + DV^{2+} \rightarrow 2DV^{3+} \quad (12)
\]

In the presence of DV⁴⁺ the monoreduced viologen is thermodynamically favored over the doubly reduced form since the equilibrium constant for reaction 12 calculated from the first two reduction potentials of DV⁴⁺ is 16. Its formation reflects therefore relaxation of the redox system into equilibrium following light-driven, two-electron transfer. In principle, it is possible to determine directly the value of the equilibrium constant \(K_{12}\) from transient absorption data such as displayed in Figure 6c,d, which could then be compared with the value derived from the electrochemical measurements. Lack of precise knowledge of the extinction coefficients for DV³⁺ and DV²⁺ prevents us from performing this evaluation at present.

It was mentioned above that the two-electron reduction of DV⁴⁺ by TiO₂ conduction-band electrons is a very rapid process. Experiments with picosecond-time resolution showed that even at DV⁴⁺ concentrations as small as 2 × 10⁻⁵ M, a major fraction of DV²⁺ is already produced within the 20-ns duration of the laser pulse.⁴³ This rapid reaction must involve surface-adsorbed acceptor molecules since there is insufficient time for bulk diffusion. Adsorption of DV⁴⁺ is favored by coulombic interactions with the TiO₂ particles which are negatively charged at pH 7. The remaining part of DV²⁺ grows in within a few microseconds after the laser pulse. We attribute this second component to reaction of \(e^-_{\text{CB}}\) with DV⁴⁺ present in the solution bulk, which is supported by the fact that its rate increases with DV⁴⁺ concentration.

Further studies employing picosecond-time resolution are required to obtain a more quantitative picture of these rapid electron-transfer events. This should clarify whether there is truly concerted transfer of two electrons from the conduction band or whether sequential electron transfer occurs. Experiments with low laser fluence might determine directly the value of the equilibrium term for reaction 12.

iv. Light-Induced Reduction of Rh(bpy)³⁺ by TiO₂ Conduction Band Electrons. In the search for transition metal complexes that could function as multielectron acceptors for conduction-band electrons in colloidal semiconductor dispersions, we selected Rh(bpy)³⁺ as a suitable model compound. The redox behavior of Rh(bpy)³⁺ has been very thoroughly investigated because of its prominence as an electron relay in sacrificial photocatalytic hydrogen-producing systems.⁴⁶⁻⁵¹ From polarographic and coulometric studies of aqueous solutions (pH 10), Kirsch et al.⁴⁸ concluded that Rh(bpy)³⁺ undergoes dielectronic reduction:

\[
\text{Rh(bpy)}^3_+ + 2e^- \rightarrow \text{Rh(bpy)}^2_+ + \text{bpy} \quad E^0 = -0.67 \text{ V} \quad (13)
\]

The product Rh(bpy)²⁺ was found to have an absorption maximum at 520 M⁻¹ cm⁻¹ and the extinction coefficient was determined at 4800 M⁻¹ cm⁻¹. By contrast, Chan et al.⁴⁰ inferred from cyclic voltammetric measurements that the Rh(bpy)³⁺ reduction in aqueous alkaline solution (0.05 M NaOH) similarly to the case where acetoneitrile was used as a solvent,⁴⁴⁻⁵⁵ occurs via two subsequent single-electron-transfer steps

\[
\text{Rh(bpy)}^3_+ + e^- \rightarrow \text{Rh(bpy)}^2_+ \quad E^0 = -0.72 \text{ V} \quad \text{(14)}
\]

From the lack of anodic reoxidation of Rh(bpy)²⁺ even at high scan speeds, they concluded that Rh(bpy)²⁺ undergoes a rapid chemical reaction, suggested to consist of ligand labilization:

\[
\text{Rh(bpy)}^2_+ + e^- \rightarrow \text{Rh(bpy)}^+ \quad E^0 \approx -0.8 \text{ V} \quad \text{(15)}
\]

which is followed by electronic dismutation

\[
\text{Rh(bpy)}^2_+ + \text{Rh(bpy)}^+ \rightarrow \text{Rh(bpy)}^{3+} + \text{Rh(bpy)}^2_+ \quad \text{(18)}
\]

The final reduction product was found to be again the red-colored Rh(bpy)²⁺ complex (λₘₐₓ 520 nm, ε 1.1 × 10⁶ M⁻¹ cm⁻¹). Using pulse radiolysis technique, Mulazanni et al.⁵¹ have determined the UV-visible absorption spectrum of Rh(bpy)³⁺ and that of Rh(bpy)²⁺ (λₘₐₓ 518, ε 9.8 × 10⁵ M⁻¹ cm⁻¹) and derived for the rate parameters \(k_{14}\) and \(k_{17}\) the values 10⁴ and 0.9 s⁻¹, respectively.

Continuous illumination of alkaline (pH >8) aqueous solutions containing Rh(bpy)³⁺ and colloidal TiO₂ with λ > 335-nm light leads within a few minutes to appearance of an intense pink color, Figure 7. The spectrum is readily identified with that of Rh(bpy)³⁺ based on ε₂₅₀ = 10⁴, ca. 25% of the Rh(bpy)³⁺ has been reduced to Rh(bpy)²⁺ after 5 min of photolysis. When the...
Light-Induced Electron Transfer in Colloidal Dispersions

A logarithmic plot of absorbance against pH gives within the pH range of 7-12 a straight line with a slope of 0.64. In acid solution the points show increasingly negative deviation from this line.

To rationalize this behavior we recall that the conduction-band process involves single electron transfer from the colloidal TiO₂ particles to Rh(bpy)³⁺. Inserted in Figure 8 are oscillograms illustrating the kinetics of Rh(bpy)³⁺ formation at two different pH values. In alkaline solution (pH 12) the growth of the 360-nm absorption of Rh(bpy)³⁺ occurs in two distinct phases. A fast rise immediately after the laser pulse accounts for a slope of 0.64. In neutral solution (pH 7.2). Here, the rate of Rh(bpy)³⁺ formation is drastically decreased, the buildup of the 360-nm absorption occurring on a 2000 times (!) longer time scale than at pH 12. The effect of pH on the rate of e⁻CB reaction with Rh(bpy)³⁺

\[ \text{Rh(bpy)}^{3+} + e^{-}_{\text{CB}} \rightarrow \text{Rh(bpy)}^{2+} \]  (19)

is illustrated in Figure 9 in more detail. A logarithmic plot of \( k_{\text{obs}} \) (s⁻¹), the observed rate constant for Rh(bpy)³⁺ formation, against pH gives within the pH range of 7-12 a straight line with a slope of 0.64. In acid solution the points show increasingly negative deviation from this line.

To rationalize this behavior we recall that the conduction-band position of the TiO₂ particles changes with pH according to eq 5, while the redox potential of the Rh(bpy)³⁺/Rh(bpy)²⁺ couple is essentially pH independent. Hence, decreasing the pH by one unit leads to a 59-mV decrease of the driving force (or overvoltage) for reaction 19. This, in turn, decreases the value of the heterogeneous rate constant, \( k_{\text{vol}} \), for electron transfer from the TiO₂ conduction band to Rh(bpy)³⁺ at the particle surface, eq 3. It can be readily shown by applying eq 2 to the data displayed in Figure 9 that it is the interfacial electron transfer and not diffusion

\[ \frac{X \Delta E_{0} \text{vol}}{T} = \frac{X \Delta F \text{vol}}{T} = -0.7 \text{ V} \]

that controls the rate of Rh(bpy)³⁺ formation. (Even at pH 12 where \( k_{\text{obs}} \) is calculated as 7 cm/s, the condition 1/\( k_{\text{obs}} \gg r/D \) is still fulfilled.) A simplified version of eq 2, i.e., \( k_{\text{obs}} = k_{\text{vol}} \times 1000/N_{A} \times \Delta E^{0} \text{vol}/(r/D) \approx 4 \pi \epsilon \sigma_{\text{fil}} \), may therefore be applied to evaluate the data displayed in Figure 9. Hence, the slope of the straight line can be identified with \( \sigma_{\text{fil}} \), the transfer coefficient for reduction of Rh(bpy)³⁺ by TiO₂ conduction-band electrons. The value of 0.64 is distinctively smaller than that obtained for MV³⁻ reduction by \( e^{-}_{\text{CB}} \).

Another electrokinetic parameter which can be derived from Figure 9 is \( k_{\text{vol}} \), the heterogeneous rate constant for electron transfer at zero driving force. Using -0.7 V for the first reduction potential of Rh(bpy)³⁺, the pH 5.2 where \( E_{c} \text{CB}(\text{TiO}_2) = E^{0}(\text{Rh(bpy)}^{3+}/\text{Rh(bpy)}^{2+}) = 10 \text{ at this pH, } k_{\text{vol}} = 1.7 \times 10^{5} \text{ s}^{-1} \) and from eq 2 \( k_{\text{vol}} \) is calculated as 0.4 cm/s. This value is 40 times larger than the heterogeneous rate constant for MV³⁻ reduction by conduction band electrons of TiO₂. It reflects a low intrinsic barrier for electron transfer from TiO₂ particles to Rh(bpy)³⁺ and hence a small reorganization energy associated with the Rh(III) → Rh(II) transition.

Apart from the electron-transfer rate, the pH influences also strongly the yield of Rh(bpy)³⁺ formation. Figure 10 illustrates the effect of pH on the concentration of Rh(bpy)³⁺ determined

\[ (\text{55}) \text{ The concentration of Rh(bpy)³⁺ after completion of } e^{-}_{\text{CB}} \text{ transfer is about } 2.6 \times 10^{10} \text{ M at pH 7 and an initial Rh(bpy)³⁺ concentration of } 2 \times 10^{10} \text{ M. The redox potential of the solution is therefore } 48 \text{ mV more positive than the standard potential } \Delta E^{0}(\text{Rh(bpy)}^{3+}/\text{Rh(bpy)}^{2+}) = -0.7 \text{ V. Strictly speaking, the pH of zero overvoltage is therefore } 9.2 \text{ instead of } 10. \text{ This should be kept in mind when interpreting } k_{\text{vol}} \text{, the rate constant of } e^{-}_{\text{CB}} \text{ transfer under conditions where the Fermi level of the particle equals the standard redox potential } \Delta E^{0}. \text{ The rate constant for Rh(bpy)³⁺ reduction at free zero driving force is } 0.13 \text{ cm/s.} \]
after completion of the Rh(bpy)$_3^{3+}$ reduction by $e_{CB}(\text{TiO}_2)$, i.e., from the plateau region of oscillograms such as shown in Figure 8. In alkaline solution the quantum yield of Rh(bpy)$_3^{2+}$ formation is practically unity. It decreases, however, sharply at pH <7.5. Note that this decrease occurs in the same domain where the points in Figure 9 start to deviate from the Tafel line. Apparently, in this pH range only a fraction of the conduction-band electrons, generated initially by the laser flash, leave the TiO$_2$ particles with equilibrium with the solution redox system being established through simultaneous occurrence of charge ejection (eq 19) and injection via

$$\text{Rh(bpy)}_3^{3+} + e_{CB} \rightarrow \text{Rh(bpy)}_3^{2+}$$

The fact that reoxidation of Rh(bpy)$_3^{3+}$ becomes noticeable only at pH values several units below 10 where $E_C(B_{\text{TiO}_2}) = E^0(\text{Rh(bpy)}_3^{3+/2+})$ can be explained by the occurrence of the competing ligand destabilization process, eq 16. The latter takes place very rapidly (slow = 10$^4$ s$^{-1}$) and produces an electroactive species as shown by the lack of an anodic reoxidation wave in cyclic voltammetry. Therefore, in order to be able to compete with ligand destabilization, charge injection from Rh(bpy)$_3^{3+}$ into the TiO$_2$ particle must occur on a microsecond time scale. At pH <7 the overvoltage for the anodic reaction is at least ~180 mV which appears to be sufficient to reach such high charge injection rates.

In summary, the reduction of Rh(bpy)$_3^{3+}$ by $e_{CB}(\text{TiO}_2)$ in colloidal semiconductor dispersions consists of single electron transfer to form the transient Rh(bpy)$_3^{3+}$. This reaction is characterized by a high electrochemical exchange rate constant $k_{en}$. The reduction is rendered irreversible over a large pH domain by rapid consumption of Rh(bpy)$_3^{3+}$ due to destabilization and loss of a bpy ligand. This is confirmed by the finding that purple-colored Rh(bpy)$_3^{3+}$ is the end product produced by continuous band-gap irradiation of colloidal TiO$_2$ in the presence of Rh(bpy)$_3^{3+}$. Although the mechanistic details of the conversion of Rh(bpy)$_3^{3+}$ into Rh(bpy)$_3^{2+}$ have not been investigated here, it can be assumed that this follows the sequence outlined by eq 16 to 18 which has been established through earlier work with homogeneous Rh(bpy)$_3^{3+}$ solutions.

It should be pointed out in this context that while the reduction of Rh(bpy)$_3^{3+}$ to Rh(bpy)$_3^{2+}$ involves single-electron-transfer steps, reoxidation of the latter could occur via simultaneous transfer of two electrons to a suitable acceptor. Very recently, Winkamp and Stockham have obtained evidence that such a mechanism is operative in the electrocatalytic reduction of NAD$^+$ on a graphite electrode in the presence of Rh(bpy)$_3^{3+}$. From the fact that NADH, and not the NAD dimer, was formed as a product, it was inferred that Rh(bpy)$_3^{2+}$ generated at the cathode acted as a true two-electron donor in this process. Note that this concept could be readily applied to the colloidal TiO$_2$ particles investigated here, which in the presence of Rh(bpy)$_3^{3+}$ as a two-electron relay should achieve photochemical generation of NADH from NAD$^+$. Work in this direction is in progress and will be reported in a subsequent paper.

v. Valence-Band Processes. So far, the discussion has centered on reactions of conduction-band electrons which have been the main interest of the present study. For completeness we wish to deal here briefly with the fate of the valence-band holes (h$^+$) generated concomitantly with $e_{CB}$ by band-gap excitation of the TiO$_2$ particles. It has been known since the earlier work by Honda et al. that holes in illuminated TiO$_2$ crystals react efficiently with water under formation of oxygen. This reaction can, however, be intercepted by a variety of hole scavengers, in particular, organic molecules such as alcohols or reducing inorganic species such as sulfite or halide ions. Holes produced in colloidal TiO$_2$ particles undergo similar redox processes. Using laser photolysis technique, and others have shown hole transfer from the valence band of these particles to adsorbed halide ions (X$^-$) resulting in radical ion (X$^-$) formation. For the latter to compete efficiently with water oxidation, low pH and high halide concentrations were required.

A further process competing with water oxidation by valence-band holes is h$^+$ scavenging by the polymeric agent, i.e., PVA, used to stabilize the TiO$_2$ sol. The latter reaction is believed to occur also in the present system, where PVA polymer was always employed to protect the TiO$_2$ particles from coagulation. Very likely, the product is a α-alcohol-type radical:

$$h^+ + \cdot\text{CHOH--CH}_2^- \rightarrow \cdot\text{COH--CH}_2^- + h^+$$

which due to its reducing properties could inject an electron in the conduction band of the TiO$_2$ particles, producing a "current-doubling" effect. However, recombination and/or dismutation constitute alternative and very efficient pathways for reactions of α-alcohol-type radicals. At present, the contribution of these different processes cannot be quantitatively assessed. Instead of the direct generation of polymer radicals via recombination, one might envisage a sequence involving first hole scavenging by water (or $OH^-$) to product surface-bound $OH^-$ radicals

$$H_2O + h^+ \rightarrow (OH)_n + H^+$$

followed by hydrogen abstraction from the protective agent to produce again an α-alcohol-type radical

$$(OH)_n + \cdot\text{CHOH--CH}_2^- \rightarrow H_2O + \cdot\text{COH--CH}_2^-$$

A similar mechanism has been evoked to explain the chalking of TiO$_2$-based paints in sunlight.

It is also feasible that at least part of the OH radicals produced via reaction 22 yield oxygen as a final product:

$$4(\text{OH})_n \rightarrow 2H_2O + O_2$$

One might argue that such a mechanism is incompatible with the simultaneous generation of air-sensitive species such as Rh(bpy)$_3^{3+}$ via the conduction-band process. As has been shown above, significant quantities of reduced acceptor accumulate in solution which in the presence of oxygen would be rapidly reoxidized. However, numerous studies in the literature including our own observations have shown that TiO$_2$ particles, in particular, highly hydroxylated anatase, can function as oxygen carriers. The role of surface hydroxyl groups in the chemisorption of O$_2$ and subsequent reduction to O$_2^-$ has recently been elucidated. The adsorbed O$_2$ appears to be much less reactive than free oxygen in solution as indicated by the fact that it can coexist with reducing agents such as H$_2$.

Conclusions

This study is part of our continuing effort to explore the behavior of photoinduced charge carriers in ultrafine semiconductor particle dispersion: 50-Å-sized particles of TiO$_2$ were produced via hydrosolysis of TiCl$_4$ in aqueous solution and carefully characterized. The subsequent laser and continuous photolysis investigations centered on conduction-band processes involving various one- and two-electron acceptors in aqueous solution. The important results emerging from this study are summarized as follows. (1) The salient features of the interfacial electron transfer are adequately described by the electrokinetic parameters $k_{en}$ and $\alpha$, which can


be derived from the experimental data by applying a kinetic model
developed earlier.6,3 The transfer coefficient \( \alpha \) for \( MV^{2+} \)
reduction is much larger for particles prepared from \( TiCl_4 \) than those
obtained from the hydrolysis of titanium isopropoxide, indicating
participation of surface states (OH groups) in the electron-transfer
event. (2) Drastic pH effects on the rate of \( MV^{2+} \) reduction by
conduction-band electrons observed earlier are confirmed for other
acceptors and arise from the cathodic shift of the Fermi level of
the particles with increasing pH. (3) A particularly favorable
configuration for rapid electron transfer is achieved with acceptors
which through suitable functionalities adhere to the semiconductor
surface. Thus in the case of the amphiphilic viologen \( C_{14}MV^{2+} \)

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(63) We wish to draw attention to the important work of Albery et al. on
kinetics in colloidal electrode systems which pertains to the present inves-
(1982), and references cited therein.

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Chain-Length Dependence of Electronic and
Electrochemical Properties of Conjugated Systems:
Polyacetylene, Polyphenylene, Polythiophene, and Polypyrrole

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Abstract: The valence effective Hamiltonian (VEH) technique is used to compute ionization potentials, optical transition energies,
electron affinities, and optical properties of oligomers and polymers in four conjugated systems: polyacetylene, poly(p-phenylene), polythiophene,
and polypyrrole. The theoretical results compare very favorably with experimental data on gas-phase ionization potentials,
absorption, and electrochemical redox potentials. The latter case is especially important, and the calculated oxidation
and reduction potentials are in remarkably good agreement with experiment. For polyacetylene the predicted oxidation potential
is 0.4 V vs. SCE, and the predicted reduction potential is -1.1 V, both of which are in good agreement with experimental
observations and reduction onsets. In these systems, the electronic and electrochemical properties predicted by VEH
theory for the oligomers extrapolate to those of the polymer with an inverse chain-length dependence.

Introduction

A number of organic polymers become electrically conducting
on addition of electron donors or acceptors.1-5 Thus far, the
highest conductivities (~1000 \( \Omega^{-1} \) cm\(^{-1} \)) have been obtained for
acceptor doped poly(p-phenylene) and acceptor doped polyacetylene.3
Despite the enormous interest in these conducting polymer systems, many theoretical aspects of the problem remain
poorly understood, especially the electronic properties of the
"doped" (partially ionized) polymers. Progress is being made, however, in understanding the undoped polymer precursors.

In a series of recent papers, we have demonstrated the utility of the
valence effective Hamiltonian (VEH) method in understanding
the ground-state properties of conjugated polymers, in particular,
those which become highly conducting upon doping.6,8 The VEH
method employs atomic potentials derived from double-zeta
basis sets and computes orbital energies and transition
energies for molecular systems in their ground states.7,8

The valence effective Hamiltonian (VEH) technique is used to compute ionization potentials, optical transition energies,
electron affinities, and optical properties of oligomers and polymers in four conjugated systems: polyacetylene, poly(p-phenylene), polythiophene,
and polypyrrole. The theoretical results compare very favorably with experimental data on gas-phase ionization potentials,
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theory for the oligomers extrapolate to those of the polymer with an inverse chain-length dependence.

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