Direct Observation of Charge-Transfer Reactions across Semiconductor:Aqueous Solution Interfaces Using Transient Raman Spectroscopy

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Abstract: Surface redox reactions in aqueous colloidal semiconductor solutions have been probed by using time-resolved Raman spectroscopy. One optical pulse above the semiconductor band gap creates a transient population of electrons and holes inside the crystallite. After a fixed delay, a second pulse below the band gap generates Raman spectra of surface reaction products. Four simple electron-transfer reactions involving ionic species on TiO_2 and CdS colloidal crystallites are investigated. One is hole transfer to SCN^- on TiO_2. The other three are electron transfer to MV^{2+} on TiO_2, to MV^{2+} on CdS, and to $C_{14}MV^{2+}$ on TiO_2. In the case of MV^{2+} on CdS, the MV^+ signal shows Langmuir isotherm saturation with respect to MV^{2+}, indicating that the MV^+ observed occupies adsorption sites on the CdS crystallites. In all four cases, the initial Raman spectra (at $\simeq 5$ ns) are indistinguishable from that of the same species fully solvated in water, under our experimental conditions. There is no evidence for the large cross-section enhancements and spectral shifts characteristic of SERS (surface enhanced Raman scattering) spectra for molecules adsorbed on colloidal metal particles. The electron transfer is discussed in terms of a "direct" model in which the electron tunnels from the conduction band to the molecular precursor which retains its first water solvation layer.

The elementary processes in electrochemistry involve the transfer of electrical charge from bulk materials to surface-adsorbed molecular species. The equilibrium behavior of electrochemical processes is well described by the Nernst equation and classical thermodynamics. However, the molecular level surface kinetics remain less well understood, despite the valuable inferences that have been drawn from analysis of current and voltage characteristics. An experimental technique sensitive to molecular structure and applicable in the time frame of the elementary steps would be an asset in the study of these surface kinetic processes.

Transient electronic absorption spectroscopy offers excellent detection sensitivity and is widely used in fast solution kinetics. However, electronic spectra are often so broad that the spectra carry no vibronic information about the actual structure of transient species present in the reaction sequence. It is principally for this reason that the technology of transient resonance Raman spectroscopy has been developing in recent years. The resonance Raman spectra of chemical intermediates provides direct, albeit partial, structural information and in some cases provides evidence for structural modification due to solvation. The Raman spectrum is a specific molecular "fingerprint" that often enables spectroscopic identification among similar species.

Fleischmann and Hendra[1] and Van Duyne[2] first used CW Raman spectroscopy to study molecules on and near metal electrodes. The SERS (surface enhanced Raman scattering) spectra of molecules adsorbed on rough metal (mostly silver) electrodes have been intensively investigated.[3] Enhancement is also observed on colloidal particles of the same metals. In SERS, the Raman cross section of an adsorbed molecule is enhanced by many orders of magnitude, principally, but not entirely, by electromagnetic effects. This enhancement makes it possible to actually detect the Raman spectra of the surface species. Fast time-resolved Raman studies of surface charge-transfer reactions on metals have not been reported.

The physics of charge transfer across a semiconductor surface is far different than across a metal surface.[4] On a semiconductor one is dealing with the reactions of individual electrons and holes at fixed redox energies instead of a degenerate Fermi gas at high kinetic energy. The static potential gradients, Debye–Huckel screening lengths, and electromagnetic properties are far different in the two cases. At wavelengths to the red of the band gap, the semiconductor is a transparent dielectric, and there is no SERS effect on molecular Raman cross sections.

We apply time-resolved resonance Raman spectroscopy to charge-transfer reactions across semiconductor surfaces. On a semiconductor surface one can use an optical pulse to generate charge (electrons and holes) as well as to generate Raman spectra. In our experiment, a first optical pulse (above the band gap) is absorbed by the semiconductor creating a transient population of electrons and holes. After a fixed delay, a second optical pulse (normally below the band gap) generates Raman spectra. The second pulse is in molecular electronic resonance with a reaction product. Raman cross-section enhancement due to molecular electronic resonance is generally necessary in order to detect the reaction product in the presence of Raman scattering from the solvent and other species. This pump–probe Raman technique has been previously employed in the study of solution-phase photochemistry.[5,6]

We work with the semiconductor finely divided in a true colloidal solution instead of with a macroscopic semiconductor electrode. In colloids a very large surface area is available in an optically homogeneous solution. In addition, the kinetics of the electrons and holes in the small crystallites is dominated by surface processes.

M. Grätzel,[7–9] A. Henglein,[10] J. K. Thomas,[11] and M. A. Fox[12] have all characterized surface photochemical reactions in colloidal TiO_2 or CdS using transient absorption spectroscopy. We examine via transient Raman spectroscopy four elementary hole h^+ and

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(1) Fleischmann, M.; Hendra, P. J.;f McQuillan, A. J. *J. Chem. Soc., Chem. Commun.* **1973**, 82; *Chem. Phys. Lett.* **1974**, *26*, 163.

(2) Jeanmaire, D. L.; Van Duyne, R. P. *J. Electroanal. Chem.* **1975**, *66*, 235. Jeanmaire, D. L.; Suchanski, M. R.; Van Duyne, R. P. *J. Am. chem. Soc.* **1975**, *97*, 1699.

(3) "Surface Enhanced Raman Scattering", Chang, R. K, Furtak, T., Eds.; Plenum: New York, 1982.

(4) For reviews of semiconductor photoelectrochemistry, see: Heller, A. *Acc. Chem. Res.* **1981**, *14*, 154. Bard, A. J. *J. Phys. Chem.* **1982**, *86*, 172.

(5) Beck, S. M.; Brus, L. E. *J. Am. Chem. Soc.* **1982**, *104*, 1805.

(6) Beck, S. M.; Brus, L. E. *J. Am. Chem. Soc.* **1982**, *104*, 4789.

(7) Duonghong, D.; Ramsden, J.; Grätzel, M. *J. Am. Chem. Soc.* **1982**, *104*, 2977.

(8) Humphry-Baker, R.; Lilie, J.; Grätzel, M. *J. Am. Chem. Soc.* **1982**, *104*, 422.

(9) Moser, J.; Grätzel, M. *J. Am. Chem. Soc.* **1983**, *105*, 6547.

(10) Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1982**, *86*, 241; *J. Phys. Chem.* **1982**, *86*, 2291.

(11) Kuczynski, J.; Thomas, J. K. *Chem. Phys. Lett.* **1982**, *88*, 445.

(12) Fox, M. A.; Lindig, B.; Chen, C.-C. *J. Am. Chem. Soc.* **1982**, *104*, 5828.

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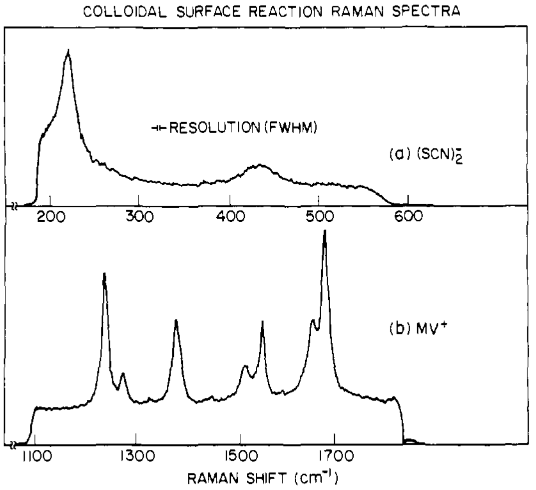

Figure 1. Raman spectra observed with an average delay of 10 ns after excitation of colloidal TiO_2 particles: (a) 355-nm excitation with a 532-nm probe pulse. The product $(SCN)_2^-$ in reaction 1 is observed. (b) 320-nm excitation with a 395-nm probe pulse. The product MV^+ in reaction 2 is observed. In both cases the molecular Raman lines are on top of continuous scattering representing H_2O Raman scattering and weak e^-–h^+ recombination luminescence.

electron e^- reactions that have previously been observed via absorption spectroscopy:

$$h^+(TiO_2) + SCN^- \rightarrow SCN\cdot \xrightarrow{SCN^-} (SCN)_2^- \qquad (1)$$

$$e^-(TiO_2) + MV^{2+} \rightarrow MV^+ \qquad (2)$$

$$e^-(TIO_2) + C_{14}MV^{2+} \rightarrow C_{14}MV^+ \qquad (3)$$

$$e^-(CdS) + MV^{2+} \rightarrow MV^+ \qquad (4)$$

The Raman data provide a firm identification of the nanosecond time scale intermediates, confirming the earlier absorption studies. They additionally provide information about the degree of vibrational distortion due to the nearby semiconductor surface and the extent of molecular precursor adsorption on the surface before optical excitation of the crystallite. Preliminary results for reactions 1 and 2 have been previously published.[13]

Experimental Section

The pulsed-laser Raman apparatus has been previously described.[14,15] There are two independent, Q-switched Nd:YAG lasers. Various wavelengths are generated by stimulated Raman scattering of the YAG harmonics in high-pressure H_2 and CH_4. The Raman spectra are extensively averaged by using a multichannel Reticon detector and a triple spectrograph. The sample is flowing such that the colloidal solution in the interaction region is exchanged between pulse pairs.

The CdS colloid was prepared by slowly injecting 20 cm^3 of 9×10^{-3} M $CdSO_4$ solution into 100 cm^3 of a stirred $\simeq 5 \times 10^{-3}$ M $(NH_4)_2S$ solution at pH 10 (NaOH).[16] The $(NH_4)_2S$ solution also contained 0.1% styrene/maleic anhydride copolymer (Aldrich 20060-3) in order to stabilize the final CdS colloid, whose concentration is 0.22 g/L. The solution is used within an hour of preparation, before aging processes occur significantly. Transmission electron microscopy and in situ Raman studies show that the initial CdS particles are crystalline with a fairly narrow diameter distribution in the range 40–50 Å.[17]

The TiO_2 colloids were prepared from titanium isopropoxide or from $TiCl_4$ in a fashion similar to that described by Grätzel and co-workers.[7,9] In the case of the $TiCl_4$ preparation, the initial colloid (2 g of TiO_2 per L) at pH $\simeq 0.5$ was dialyzed to pH $\simeq 2.5$ and then stabilized with $\simeq 0.5$% PVA (M_w ~10 000, Aldrich 18463-2) before further adjustment of pH (NaOH). In the case of the isopropoxide preparation, the initial colloid containing isopropyl alcohol was evaporated under vacuum to near dryness and then redissolved in a PVA solution as above. Moser and Grätzel report that the TiO_2 particles have a moderately wide range of diameters with a mean diameter of $\simeq 90$ Å.[9]

Table I. Comparison of the $C_{14}MV^+$ Resonance Raman Frequencies (cm^{-1}) in the 1400-cm^{-1} Region to Those of MV^+ [18]

MV^+	$C_{14}MV^+$
1662	1660
1534	1530
1356	1358
1212	1206

Observations

(A) TiO_2 Colloids. Reaction 1 was studied at pH 1 in a colloid prepared by the isopropoxide procedure and without PVA stabilizer. In a system containing 0.04 M KSCN, the TiO_2 particles were excited at 355 nm, and Raman spectra were generated with 532-nm pulses. The TiO_2 particles have a net positive surface charge at this pH, and the SCN^- ions are attracted to the surface. Hole oxidation of SCN^- competes with hole oxidation of H_2O.[7]

A reference Raman spectrum of $(SCN)_2^-$ solvated in water, in the absence of colloidal TiO_2, was generated by oxidation of SCN^- by electronically excited triplet *p*-benzoquinone. At 532 nm, the $(SCN)_2^-$ Raman spectrum is dominated by the S=S fundamental at 221 cm^{-1}. In the colloidal experiments, the $(SCN)_2^-$ Raman signal in Figure 1 grows approximately as the convolution of the two laser pulses, showing no kinetic rise time in agreement with the earlier transient absorption results.[7] The $(SCN)_2^-$ Raman spectrum is independent of time and is experimentally indistinguishable from the reference $(SCN)_2^-$ spectrum in water.[13] There is no detectable change in the spectrum due to the presence of the TiO_2 surface under our present conditions.

The electron reaction (eq 2) was studied in TiO_2 colloids made by both the isopropoxide and $TiCl_4$ preparations, with essentially identical results. In the $TiCl_4$ case, a 2g/L TiO_2 colloid stabilized with $\simeq 0.5$% PVA at pH 10 was excited with a 341-nm pulse. The probe pulse at 395 nm is to the red of the TiO_2 band gap and the far ultraviolet absorption of methylviologen MV^{2+}. It is in resonance with an intense absorption of the reduced species MV^+, and there is a large resonance enhancement in the Raman cross section.[18] Raman spectroscopy at 395-nm is thus a sensitive probe for the presence of MV^+. In aqueous solution the MV^+ detection limit is below 10^{-6} M in our present apparatus.

Figure 1 shows the 1200–1700-cm^{-1} region where there are intense Raman lines due to C–C, C=C, and C=N motions of the aromatic ring system.[18] A reference spectrum of aqueous MV^+, in the absence of TiO_2 colloid, was generated by reduction with dithionite at pH 10. In the colloidal systems, the MV^+ signal shows a kinetic rise time dependent upon pH in qualitative agreement with the earlier transient absorption results.[7] Figure 1 shows the colloidal spectrum from the isopropoxide preparation. The shape of the spectrum is independent of time and is indistinguishable from the aqueous MV^+ reference.[13] Our shortest delay time corresponds to overlapping 341- and 395-nm pulses, and is effectively $\simeq 5$ ns.

Moser and Grätzel showed that, at pH 10–11, the kinetic rise time for MV^+ is short and dependent upon MV^{2+} diffusion from bulk solution to the surface.[9] The rise time is dependent upon MV^{2+} concentration. The viologen $C_{14}MV^{2+}$ has a long hydrocarbon chain on one end and has a greater hydrophobic character than MV^{2+}. This species showed no measurable $C_{14}MV^+$ rise time after excitation of the TiO_2 particle, and the $C_{14}MV^+$ signal was *independent* of $C_{14}MV^{2+}$ concentration.[9] It was concluded that the $C_{14}MV^{2+}$ had saturated the TiO_2 surface. We therefore studied reaction 3 via time-resolved Raman spectroscopy to see if there was any indication in the initial Raman spectra of $C_{14}MV^{2+}$ prior adsorption.

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(13) Rossetti, R.; Beck, S. M.; Brus, L. E. *J. Am. Chem. Soc.* **1982**, *104*, 7322.

(14) Beck, S. M.; Brus, L. E. *J. Chem. Phys.* **1981**, *75*, 4934.

(15) Rossetti, R.; Beck, S. M.; Brus, L. E. *J. Phys. Chem.* **1983**, *87*, 3058.

(16) This is an adaptation of the procedure of: Kalyanasundaram, K.; Borgarello, E.; Duonghong, D.; Grätzel, M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 987.

(17) Rossetti, R.; Brus, L. E. *J. Chem. Phys.* **1983**, *79*, 1086.

(18) Forster, M.; Girling, R. B.; Hester, R. E. *J. Raman Spec.* **1982**, *12*, 36.

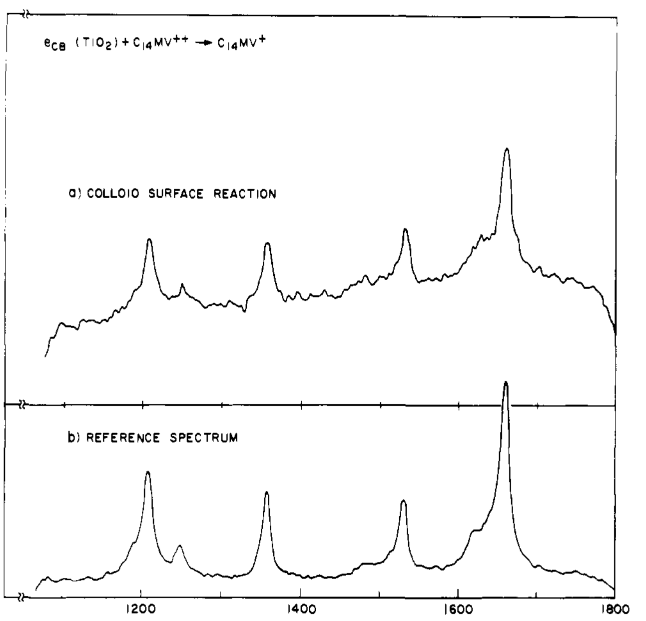

Figure 2. $C_{14}MV^+$ Raman spectra at 395 nm: (a) 1-μs delay after excitation of colloidal TiO_2 as in reaction 3. (b) Reference spectrum made by reduction of micelle-solubilized $C_{14}MV^{2+}$.

$C_{14}MV^{2+}$ has a low solubility in water, and in order to generate a reference Raman spectrum, we dissolved 10^{-3} M in a 1% Triton aqueous micellar solution at pH 10.[9] The 395-nm Raman spectrum after reduction with dithionite appears in Figure 2. The $C_{14}MV^+$ spectrum in this range is close to, yet reproducibly distinguishable from, that of MV^+ in Figure 1. In Table I there are 2–6-cm^{-1} shifts of the major bands of $C_{14}MV^+$ with respect to those of MV^+; in addition, the relative intensity of some minor bands has changed. This comparison provides a measure of the extent of Raman spectral shift that is clearly detectable.

The colloidal transient Raman experiments were carried out in a similar fashion to those described previously for MV^{2+} via the $TiCl_4$ preparation. Essentially the same result was obtained. The $C_{14}MV^+$ Raman spectrum observed following excitation of the TiO_2 particle was independent of time and was indistinguishable from that of the reference spectrum. Figure 2 shows the observed spectrum at a delay of 10^{-6} s; in this system our shortest delay time is about 10 ns. There is no detectable effect on the $C_{14}MV^+$ spectrum in this region due to adsorption of the precursor.

(B) CdS Colloids. The photophysical and photochemical properties of CdS colloids have been intensively investigated. Reaction 4 has been observed by a number of workers via absorption spectroscopy.[7,10,11] Metcalfe and Hester recently used a CW laser to both excite CdS crystallites above the band gap and generate Raman spectra of the reaction product MV^+.[19] The MV^+ spectra, which were indistinguishable from aqueous solution MV^+ spectra, are an average over the reported 10^{-6}-s lifetime of MV^+.[11]

In a pulsed Raman experiment, the shortest effective time resolution occurs if one pulse is used to both excite the crystallite and probe the surface reaction product. With our Q-switched Nd:YAG lasers, this resolution is $\simeq$5 ns. This time resolution allows us to observe the initial MV^+ spectra and to compare them with the average spectra over the entire MV^+ lifetime.

Spectra were initially obtained in the 1400-cm^{-1} region, where we observe the same transitions as in Figure 1. These spectra were again identical with the aqueous solution spectrum. Further quantitative experiments, as a function of MV^{2+} concentration and 395-nm flux, were carried out in the 600-cm^{-1} region. In this region MV^+ has two strong lines at 604 and 818 cm^{-1}. As previously reported, the in situ CdS crystallites exhibit a LO phonon Raman line ($\simeq$305 cm^{-1}).[17] We now use this line as an internal standard, in the sense that the intensity of this line provides an independent measure of the 395-nm flux in the sample.

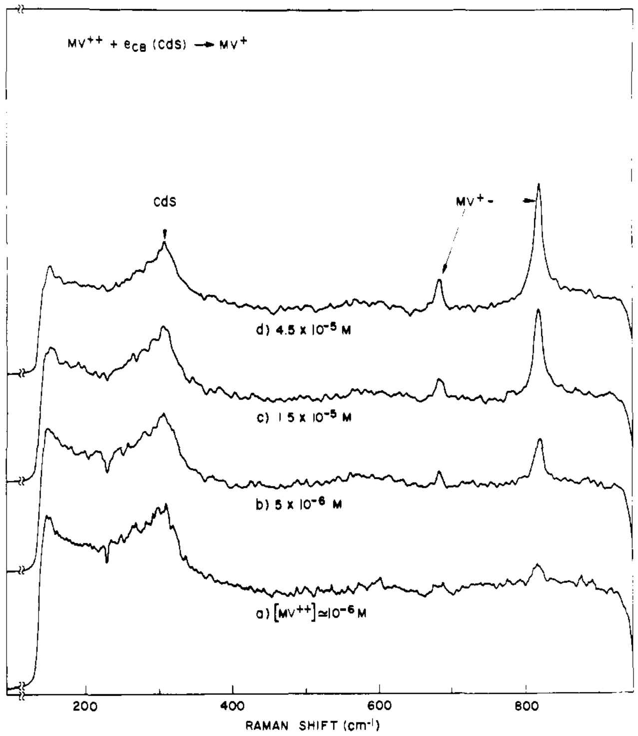

Figure 3. Low-frequency-shift Raman spectra of CdS, and MV^+ in reaction 4, as a function of initial MV^{2+} concentration. One 395-nm pulse excites e^-–h^+ and generates Raman spectra. CdS phonon line at $\simeq$306 cm^{-1}. MV^+ lines are marked.

TEM micrographs of these CdS crystallites show an average dimension of 40–45 Å. The CdS crystallites appear to be slightly smaller than the ones prepared earlier at a more neutral pH.[17] The 305-cm^{-1} Raman line is broader, indicating that at 40–45-Å size the LO phonon mode observed is becoming sensitive to crystallite size.

The interaction of small particles with electromagnetic fields is described formally by Mie scattering theory.[20] The interaction can be written as an expansion in electric and magnetic multipole moments. At $\simeq$40-Å size, only the electric dipole term is important. In this limit absorption dominates over Raleigh scattering, and the crystallite interaction with the electromagnetic field is the same as for individual molecules. In particular, light is absorbed throughout the bulk of the particle; there is no "shading" of one side of the particle by the other. At 395 nm the absorption cross section of a CdS crystallite is 16 Å^2, as calculated from the absorption spectrum. For comparison, the absorption cross section of MV^+ at 395 nm is 1 Å^2 (ϵ = 60 000 M^{-1} cm^{-1}).

This relatively large cross section causes each CdS particle to absorb many photons during a 395-nm pulse. Under the conditions of the experiment, an average of $\sim$100 photons are absorbed at a fluence of $\sim 10^{17}$ photons/cm^2 pulse. Experimentally we find that, for $[MV^{2+}]$ in the range 10^{-5}–10^{-4} M, the strength of the reduced $[MV^+]$ signal increases with intensity I as I^n such that $n = 1.3 \pm 0.2$. If both Raman scattering and MV^+ production were proportional to I, then we would expect $n = 2$. We know experimentally that the aqueous MV^+ Raman signal is proportional to I in this intensity range. We conclude that the MV^+ yield has saturated.

During the laser pulse, the crystallite is sequentially excited many times. The holes appear to have a very short lifetime due to surface reaction with excess S^{2-}, as we shall see under Discussion. Excess conduction-band electrons will transiently build up, and thus the saturation in MV^+ yield suggests that the surface

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[19] Metcalfe, K.; Hester, R. E. *J. Chem. Soc., Chem. Commun.* **1983**, 133.

[20] Born, M.; Wolf, E. "Principles of Optics", 3rd ed.; Pergamon Press: Oxford, 1965; Chapter 13.5.

available MV^{2+}, on the time scale of the pulse, has been exhausted. As negative charge builds up, the hole lifetime will further shorten due to recombination with excess electrons. A few holes may survive to reoxidize surface MV^+.

Saturation is also apparent in the MV^+ signal vs. $[MV^{2+}]$ at constant I, as shown in Figure 3. The strong MV^+ line at 818 cm^{-1} becomes detectable at $[MV^{2+}] \simeq 2 \times 10^{-6}$ M. Above 10^{-5} M, the MV^+ signal saturates. In view of the fact that each CdS crystallite is multiply excited, this effect appears to represent exhaustion of surface adsorbed MV^{2+} available for reduction. The MV^+ data in Figure 3 are well represented by a Langmuir adsorption isotherm.[21]

$$\theta = \frac{K[MV^{2+}]}{1 + K[MV^{2+}]} \tag{5}$$

Here θ is the fractional surface coverage normalized to one monolayer, and K is the adsorption equilibrium constant. If we take θ to be proportional to $[MV^+]$, we find $K = 9.5 \times 10^4$ M^{-1}. At $[MV^{2+}] = 10^{-5}$ M, $\theta = 0.5$ showing that there is a strong attraction of MV^{2+} for the available surface sites at pH 10.

θ can be converted from fractional to absolute units if we calibrate the MV^+ signal in the colloid experiments to MV^+ at known concentration and the same I. We have done this using MV^{2+}, reduced with sodium dithionite, in Ar-bubbled solution. We find that the MV^+ signal from a $[MV^{2+}] = 3 \times 10^{-5}$ M colloid, where $\theta = 0.75$, corresponds to $[MV^+] \simeq 2 \times 10^{-6}$ M. In this calibration we have corrected for absorption of the laser beam and Raman scattered light by the colloidal particles. As the calculated concentration of colloidal particles is $\simeq 2 \times 10^{-6}$ M, we see that the $[MV^+]$ signal saturates at about one MV^+ per CdS particle. This may represent the adsorption capacity for MV^{2+} at this small crystalline size. It may also be that the adsorption capacity is somewhat higher, and that the MV^+ signal is limited by a photostationary state at our peak 395 flux. Experiments at lower fluxes could decide this point—however, we presently do not have sufficient signal to noise to work at significantly lower fluxes.

Discussion

(A) Crystallite Excited-State Photophysics. The e^- and h^+ recombination luminescence in these crystallites provides an independent means of monitoring kinetics. We showed earlier that the luminescence of larger CdS colloidal crystallites (≥100-Å diameter) can be detected and is quenched by good electron acceptors such as *p*-benzoquinone.[22] A direct attempt to measure the e^-–h^+ luminescence lifetime of the 40–45-Å aqueous crystallites used in this study yields $\tau \leq 10^{-11}$ s.[23] Our 395-nm pulse in the Raman experiments has a time width of 10^{-8} s. Therefore the fact that each crystallite absorbs $\simeq$100 photons per 395-nm pulse is best interpreted as a sequence of 1-photon excitations followed in each case by fast excited-state e^-–h^+ relaxation.

The e^-–h^+ lifetime is short probably because the holes react at the surface in a net process that has been previously observed on CdS electrodes:[24]

$$2h^+(CdS) + CdS \rightarrow Cd^{2+}\ (aq) + S \tag{6}$$

In our colloidal CdS preparations there are excess sulfide ions on the surface that can also be oxidized. Henglein has presented indirect evidence that nanosecond pulsed excitation can build up excess negative charge on larger CdS particles during the pulse width.[25]

The redox potential of one e^- in a small CdS crystallite of this size should be shifted cathodically by several tenths of a volt with respect to the conduction band edge of the bulk crystal.[22,26] This occurs principally due to the kinetic energy of localization of the electron in the crystallite. In addition, if net negative conduction band charge builds up in the crystallite, there will be a further negative shift due to electron–electron repulsion. This latter point was originally made by Henglein.[25]

(B) Adsorption, Raman Spectra, and SERS. In reactions 1–4, the Raman spectra of the primary products at the semiconductor surface $\sim 5 \times 10^{-9}$ s after crystallite excitation are indistinguishable, under our present conditions, from the Raman spectra of the same species in aqueous solution. The Raman spectra provide strong confirmation that the elementary charge-transfer processes (1)–(4) occur following photoexcitation of the colloidal crystallites.

If these species were adsorbed on the semiconductor surface in the Helmholtz layer, would the spectra be distinguishable from aqueous spectra? Molecules adsorbed on metal electrodes show SERS spectra with shifts up to 30 cm^{-1} from solution Raman spectra.[3] However, molecules on metal surfaces experience stronger forces than those on dielectric surfaces; the expected perturbations would not be equivalent. In other physical environments, Raman spectra are sensitive to solvation phenomena. In hemoglobin, the Raman transitions of the heme chromophore shift by $\sim$2–3 cm^{-1} as a function of the conformation of surrounding protein.[27] The Raman spectra of an organic cation asymmetrically solvated at the hydrocarbon/water boundary in aqueous micellar solution is distorted somewhat from the homogeneously solvated cation.[28] I_2 and benzene adsorbed on silica from the vapor, and benzene adsorbed on silica from an aqueous phase, all show slight distortions ($\sim$2–3 cm^{-1}) in their Raman spectra.[29,30]

Reactions 1–4 all involve ionic reactants and products. Aqueous ionic solvation energies are very high, with most of the stabilization due to the first solvation shell or sheath. The shape and exact positions of the Raman bands we observed are likely to be controlled by the first solvation shell around each ion. We believe that the undistorted nature of the Raman spectra in our experiments indicates that these products have aqueous first solvation shells at the time we observe them.

The physics of adsorption and charge transfer across semiconductor/aqueous interfaces is extensively reviewed in the Morrison's monograph.[31] Two types of ion adsorption are distinguished: "specific adsorption", in which the ion is bonded to the surface with at least partial loss of water solvation, and "electrostatic adsorption", in which ions approach an oppositely charged surface while retaining their water solvation sheath. The somewhat limited available evidence indicates that, on oxide semiconductor surfaces, only the second type of adsorption occurs[31,32] (the H^+ and OH^- ions are exceptions). This behavior holds even as the entire surface is covered with electrostatically adsorbed ions, i.e., in the saturation limit of a Langmuir adsorption isotherm.

An extensive series of electrochemical measurements involving e^- transfer from a ZnO electrode to aqueous oxidizing agents has been interpreted in terms of a "simple" or "ideal" charge transfer via direct tunnelling theory.[33-35] Agreement with this theory implies that (a) there is no specific adsorption, and (b) the acceptor ion is solvated by water with the Marcus solvent reorganization

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(21) Other Langmuir saturation examples in semiconductor dispersions are known. See: Herrmann, J.; Pichat, P. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1138.

(22) Rossetti, R.; Brus, L. *J. Phys. Chem.* **1982**, *86*, 4470.

(23) Huppert, D. Rentzepis, P.; Rossetti, R.; Brus, L. E., unpublished results. The streak camera apparatus is described in: Barabara, P. F.; Brus, L. E.; Rentzepis, P. M. *Chem. Phys. Lett.* **1980**, *69*, 447.

(24) Miller, B.; Heller, A. *Nature (London)* **1976**, *262*, 680.

(25) Alfassi, Z.; Bahnemann, O.; Henglein, A. *J. Phys. Chem.* **1982**, *86*, 4656.

(26) Brus, L. E. *J. Chem. Phys.* **1983**, *79*, 5566.

(27) Lyons, K. B.; Friedman, J. M.; Fleury, P. A. *Nature (London)* **1978**, *275*, 565.

(28) Beck, S. M.; Brus, L. E. *J. Am. Chem. Soc.* **1983**, *105*, 1106.

(29) Nagasao, T.; Yamada, H. *J. Raman Spec.* **1975**, *3*, 153.

(30) Sayed, M. B.; Cooney, R. P. *J. Colloid Interface Sci.* **1983**, *91*, 552.

(31) Morrison, S. R. "Electrochemistry at Semiconductor and Oxidized Metal Electrodes"; Plenum: New York, 1980.

(32) James, R. O.; Healy, T. W. *J. Colloid Interface Sci.* **1972**, *40*, 65.

(33) Pettinger, B.; Schöppel, H. R.; Gerischer, H. *Ber. Bunsenges. Phys. Chem.* **1974**, *78*, 450.

(34) Memming, R.; Möllers, F. *Ber. Bunsenges. Phys. Chem.* **1972**, *76*, 475.

(35) Reference 31, Section 6.2.1.

energy playing a major role in the transfer kinetics. This ZnO experiment basically demonstrates that, with a correct alignment of energy levels, electron transfer can take place by direct tunneling to solvated ions within about 15 Å of the surface. The reduced reaction product is born fully solvated. We suggest that an initial Raman spectrum under these conditions would be essentially that of the aqueous species.

In our experiments we observe reaction products with a shortest delay time of $\sim 5 \times 10^{-9}$ s. In aqueous solution a small, free inorganic ion could diffuse $\sim$40 Å in this time. However, in our pH 10 CdS and TiO_2 experiments, the crystallite surfaces have a net negative charge due to OH^- specific adsorption. Both reactant MV^{2+} and product MV^+ are electrostatically attracted to the surface. In the CdS experiment, the observation that the product MV^+ shows Langmuir isotherm saturation implies (a) that the MV^{2+} surface sites available for reduction are filled before the light pulse excites the crystallite and (b) possible MV^+ desorption and subsequent adsorption of another MV^{2+} from further out in the double layer is slow with respect to $\sim 5 \times 10^{-9}$ s. In this sense the MV^+ remains "adsorbed" as its Raman spectrum is generated. Some angstrom-scale movement and resolvation of the MV^+ after formation is certainly possible.

In a similar fashion, the $C_{14}MV^+$ signal in the TiO_2 experiments is reported to be independent of initial $C_{14}MV^{2+}$ concentration and to show no kinetic rise time.[9] The surface must be saturated with $C_{14}MV^{2+}$. The hydrophobic C_{14} chain presumably anchors MV^{2+} and reduced MV^+ with respect to the TiO_2 surface and its supporting copolymer. The MV^{2+} moiety appears to retain its solvation sheath.

The SERS effect on metal surfaces is characterized by (a) a $\sim 10^6$ enhancement in cross section and (b) a substantial shift in Raman frequencies for chemisorbed molecules in the first layer. In reactions 1–4, we see no frequency shift. There is also no evidence for a large cross-section enhancement for any species on the surface, although we cannot make a quantitative statement here. This absence of SERS is consistent with (a) the apparent absence of strong chemisorption coupling the molecule to the crystallite delocalized electrons and (b) the expected absence of enhanced electromagnetic fields near these crystallites. The intensity of the local field[36] near a small material sphere (in vacuum) is proportional to

$$I_{\text{loc}} \propto \left[\frac{\epsilon - 1}{\epsilon + 2}\right]^2 \qquad (7)$$

where ϵ is the complex dielectric coefficient. For Ag near 380 nm, $\mathrm{Re}\,\epsilon \simeq -2$ and $\mathrm{Im}\,\epsilon < 1$, yielding a large I_{loc}. However, these conditions are not satisfied by bulk CdS at 395 nm[37] and any semiconductor at wavelengths below the band gap.

Conclusions

The initial Raman spectra provide strong confirmation that the elementary surface electron-transfer processes 1–4 occur when colloidal crystallites are irradiated above their band gaps.

The Langmuir isotherm behavior coupled with the absence of perceptible distortion in the Raman spectra suggests but does not rigorously prove, that charge transfer occurs to electrostatically adsorbed reactants that retain their first water solvation layers. The strong distortion characteristic of SERS spectra is not observed.

We stress that we have studied simple e^- transfer involving ionic species. Solvation energies are highest for ionic species in water. It is possible that with neutral precursors and/or in less polar solvents, a stronger interaction with the surface will be found. There are also numerous more complex electrode surface reactions that are exothermic, yet kinetically very slow. In these cases it may be that "specific adsorption" at special sites is necessary for reaction.

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Registry No. TiO_2, 13463-67-7; CdS, 1306-23-6; MV^{2+}, 4685-14-7; SCN^-, 302-04-5; $C_{14}MV^{2+}$, 79039-57-9; $(SCN)_2^-$, 34504-17-1; MV^+, 25239-55-8; $C_{14}MV^+$, 88376-68-5.

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(36) Gersten, J.; Nitzan, A. *J. Chem. Phys.* **1980**, *73*, 3023, eq 5.9.

(37) Cook, R. K.; Christy, R. W. *J. Appl. Phys.* **1980**, *51*, 668.

Kinetics of the Chemical and Electrochemical, Reversible Oxidation of Bis(dithiooxalato-*S*,*S′*)cuprate(II), $[Cu(Dto)_2]^{2-}$. A Facile, Light-Activated, Intramolecular Electron Transfer and Cleavage of the C–C Bond in the Coordinated Dto Ligands in the $[Cu(Dto)_2]^-$ Anion

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Abstract: The rates of reaction of bis(dithiooxalato-*S*,*S′*)cuprate(II), $[Cu(Dto)_2]^{2-}$, with Cu(II) and Fe(III) have been measured and the corresponding rate constants and activation parameters are reported. In addition, the electrochemistry of this complex and of the oxidation product $[Cu(Dto)_2]^-$ was studied in detail. The $[Cu(Dto)_2]^-$ anion undergoes a light-activated, intramolecular, Dto → Cu two-electron transfer with cleavage of the C–C bond in the Dto ligand and generation of gaseous SCO. Addition of triphenylphosphine to $[Cu(Dto)_2]^-$ in the presence or absence of light also results in intramolecular redox and cleavage of the C–C bond.

In a previous communication[2] we reported on the unusual, reversible, oxidative C–C bond cleavage of the coordinated dithiooxalate (Dto) ligand in the $[Cu(Dto)_2]^{2-}$ complex (I). This oxidation was effected chemically in dimethylformamide (DMF)

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