THE JOURNAL OF
PHYSICAL
CHEMISTRY A

VOLUME 107, NUMBER 4, JANUARY 30, 2003

ARTICLES

Femtosecond Dynamics of the Photoexcited Methyl Viologen Radical Cation

Tilmann Häupl,[†] Reiner Lomoth, and Leif Hammarström*

Department of Physical Chemistry, Uppsala University, P.O. Box 532, SE-751 21 Uppsala, Sweden

Received: July 12, 2002; In Final Form: November 6, 2002

Methyl viologen (*N*,*N*′-dimethyl-4,4′-bipyridine, abbreviated MV^{2+}) is widely used in light-driven molecular devices, where it switches between the redox forms MV^{2+} and $MV^{\bullet+}$. Yet, little is known about the excited-state dynamics of the radical cationic form $MV^{\bullet+}$. Femtosecond pump−probe spectroscopy was used to investigate the excited state dynamics of the electrochemically generated $MV^{\bullet+}$ in acetonitrile solution. Subpicosecond excitation of the D_0−D_1 transition at 730 nm led to rapid relaxation (700 fs), generating two intermediates in the transient absorption spectra. The longer-lived intermediate, with a lifetime of 16 ps, could be assigned to a vibrationally excited ground state of $MV^{\bullet+}$. Its absorption spectrum was very similar to the ground-state spectrum of $MV^{\bullet+}$ in both shape and extinction coefficients, but red-shifted by ca. 810 cm^{-1}. This energy shift equals one quantum of the intraring C−C stretch mode. The shorter lived transient decayed with a time constant of 1.0 ± 0.1 ps and is possibly also a vibrationally excited ground state. Thus, our results show that the excited D_1-state of $MV^{\bullet+}$ in acetonitrile solution relaxes on the subpicosecond time scale via at least one long-lived ($\tau = 16$ ps) vibrationally excited ground state.

Introduction

The electron acceptor methyl viologen (*N*,*N*′-dimethyl-4,4′-bipyridine, abbreviated MV^{2+}) plays a central role in numerous examples of light-induced electron-transfer reactions:[1] in systems mimicking aspects of photosynthetic solar energy conversion[1,2] and in optical and optoelectronic devices based on its electro- and photochromism.[1,3] Viologens are also of interest for molecular devices based on switching the acceptor/donor function of molecular components. As an example, molecular shuttles have been made, in which light-induced molecular motion occurs due to the change in intermolecular interactions when MV^{2+} is reduced to $MV^{\bullet+}$.[4] Also, we have recently shown[5] that, in the excited-state quenching of the important photosensitizer $Ru(bpy)_3{}^{2+}$, methyl viologen changes from being an acceptor when in the common form MV^{2+} to a donor when viologen is reduced to $MV^{\bullet+}$ or MV^0 prior to excitation. Thus, the direction of light-induced electron transfer in a covalently linked Ru−MV dyad could be switched by an applied bias, and we proposed that this could be used as a part of a molecular photosensitive switch. In all these examples excited states of the reduced $MV^{\bullet+}$ may be generated, either via electron- or energy-transfer reactions or by direct excitation of the strongly absorbing $MV^{\bullet+}$ species. The excited $MV^{\bullet+}$ may then undergo new reactions. Molecular switches have been constructed based on diimides playing a multifunctional role, deliberately involving excited states of the reduced diimides.[6] From this point of view the photophysical behavior of the reduced forms, $MV^{\bullet+}$ and possibly also MV^0, themselves are important. So far only a time-resolved resonance Raman study of $MV^{\bullet+}$ in water offers some idea about the subpicosecond kinetics of the excited doublet state.[7]

In this paper we report the electronic absorption spectra and the relaxation kinetics of the photoexcited $MV^{\bullet+}$ radical cation on the fs to ps time scale. The electrogenerated $MV^{\bullet+}$ was excited in the lowest absorption band ($\lambda_{ex} = 730$ nm) with a ca. 150 fs laser pulse. A rapid relaxation ($\tau \approx 700$ fs) generated more long-lived transients with characteristic electronic absorp-

---

* Corresponding author. E-mail: Leifh@fki.uu.se.

[†] Present address: Laser and Medical Technology Berlin, Fabeckstr. 60-62, D-14195 Berlin, Germany.

10.1021/jp0216023 CCC: $25.00

tion spectra that were assigned to a vibrationally excited ground state of $MV^{\bullet+}$. The possible generation of excited products in photoinduced electron transfer reactions is often discussed. Our results show that the excited viologen radical gives readily detectable transients on the time scale of 1−30 ps, which could be used to identify excited viologen products.

Experimental Section

Electrochemistry. Cyclic voltammetry and controlled potential electrolysis were carried out using an Autolab potentiostat with an GPES electrochemical interface (Eco Chemie). The working electrode was a glassy carbon disk (diameter 2 mm, freshly polished) for voltammetry or a platinum grid for bulk electrolysis, respectively. A platinum spiral in a compartment separated from the bulk solution by a fritted disk was used as counter electrode. The reference electrode was a nonaqueous Ag/Ag^+ electrode (CH Instruments, 10 mM $AgNO_3$ in acetonitrile) with a potential of −0.08 V vs the ferrocenium/ferrocene (Fc^+/Fc) couple in acetonitrile as an external standard.

The solution was prepared from dry acetonitrile (Merck, spectroscopy grade, dried with MS 3 Å) with 0.1 M tetrabutylammonium hexafluorophosphate (Fluka, electrochemical grade) as supporting electrolyte that has been dried at 373 K. The glassware used was oven dried, assembled and flushed with argon while hot. Before all measurements oxygen was removed by bubbling the stirred solutions with solvent saturated argon and the samples were kept under argon atmosphere during measurements.

Spectroelectrochemical measurements were made in a OTTLE-type quartz cell with an optical path length of 1 mm. A platinum grid with a size of 10×30 mm^2 and 400 meshes per cm^2 was used as working electrode. The counter and reference electrodes were of the same type as described above. Samples were bubbled for 20 min with solvent saturated argon and transferred to the argon flushed cell with the argon stream. The spectra were recorded on an UV−vis diode array spectrophotometer (Hewlett-Packard 8435) with the background collected on electrolyte solution in the potential free OTTLE cell.

Femtosecond-Pump−Probe Experiments. Femtosecond-pump−probe experiments were carried out using regenerative amplified pulses of a Ti:sapphire laser system (Coherent/Ouantronix, described in detail elsewhere:[8] 120 fs pulse duration, central wavelength 800 nm, 1 kHz repetition rate). The excitation wavelengths of 600 and 730 nm (4 μJ pulse energy) were generated by doubling the frequency of the signal wave of a tunable optical parametric amplifier (TOPAS). The transient absorption changes were probed by delayed white light continuum pulses generated by the fundamental wave (800 nm) in a rotating CaF_2 plate (thickness 5 mm) under magic angle polarization and detected either as a lock-in amplified PMT-signal at a certain probe wavelength or as full spectra (380−740 nm) with a CCD camera connected to a spectrograph (Oriel). Correction for the spectral chirp in the white light continuum was done by recording CCD spectra every 250 fs around zero delay time and reconstructing the true spectrum.

Methyl viologen ($MV[PF_6]_2$) was obtained from the commercially available chloride salt by L. Sun (Stockholm). The samples with 0.22−0.29 mM viologen in argon-purged acetonitrile were reduced to $MV^{\bullet+}$ by exhaustive electrolysis at −1.03 V vs Fc^+/Fc in the OTTLE cell, giving an absorption of 0.3−0.4 at the excitation wavelength (1 mm path length). The cell was moved vertically during measurements to minimize local heating effects. A slit in the working electrode allowed the laser beams to pass the cell without being scattered by the grid. In acetonitrile solution no dimerization of the $MV^{\bullet+}$ was observed. The viologen radical degraded only very slowly during the experiments, over several hours, as judged from the decrease in the absorption. In the dark no degradation was observed over at least 8 h. Thus, degradation was light-induced, but obviously occurred with a very low quantum yield and did not affect the transient experiments.

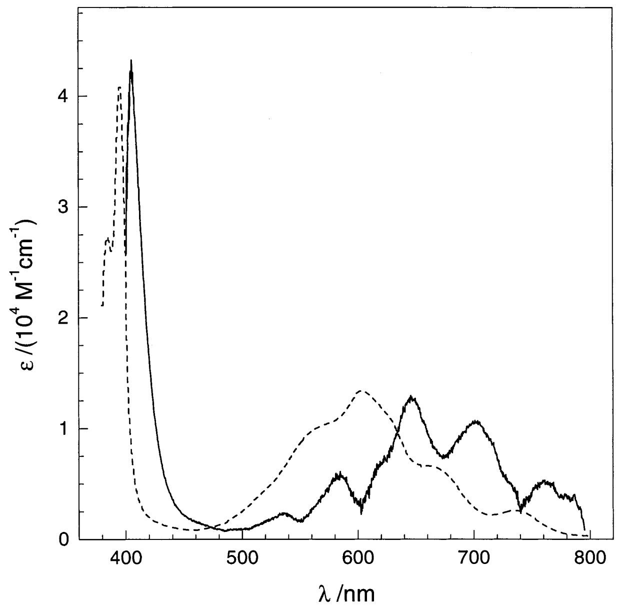

Figure 1. Absorption spectra in acetonitrile of the ground-state $MV^{\bullet+}$ (dashed line) and of the intermediate $\mathbf{I_{(2)}}$, which is assigned to the vibrationally excited ($h\nu = 810$ cm^{-1}) electronic ground state of $MV^{\bullet+}$ (solid line).

Results and Discussion

By exhaustive electrolysis in an OTTLE-type spectroelectrochemical cell at −1.03 V vs Fc^+/Fc, all MV^{2+} was reduced and the characteristic electronic absorption of $MV^{\bullet+}$ in the visible region was observed. The spectrum obtained in acetonitrile with 0.1 M $[N(n\text{-}C_4H_9)_4]PF_6$, shown as a dashed line in Figure 1, is in agreement with that for the chloride salt.[9]

Femtosecond-pump−probe spectroscopy was performed at two different pump wavelengths exciting the D_0−D_1 transition of $MV^{\bullet+}$: at 600 nm in the maximum of the visible absorption band and at 730 nm in the lowest vibronic transition of the same band. Figure 2 shows the transient absorption spectra at 0 and 5 ps after the pump pulse. The initial bleaching feature, corresponding to the bleach of the $MV^{\bullet+}$ ground-state absorption, is overlaid by a broad positive absorption change between 400 and 500 nm and by a characteristic structure between 550 and 800 nm. The latter is on the red edge of the 600 nm band of $MV^{\bullet+}$ ground-state absorption. The former transient (attributed to an intermediate $\mathbf{I_{(1)}}$), giving a shoulder at 460 nm, is short-lived and does not appear in the spectrum after 5 ps while the latter is even more pronounced with absorption maxima at 410, 650, and 700 nm. This relatively long-lived species (attributed to another intermediate $\mathbf{I_{(2)}}$) decays with a time constant of several picoseconds. Traces obtained at some informative probe wavelengths λ_{pr}, after a 730 nm pump pulse, are shown in Figure 3. The traces were fitted according to a consecutive mechanism ($A \rightarrow B \rightarrow C$). At 430 nm, the formation ($\tau_f = 700 \pm 50$ fs) and decay ($\tau_d = 1.0 \pm 0.1$ ps) of the intermediate $\mathbf{I_{(1)}}$ is seen. At 600 nm, the signal is mainly due

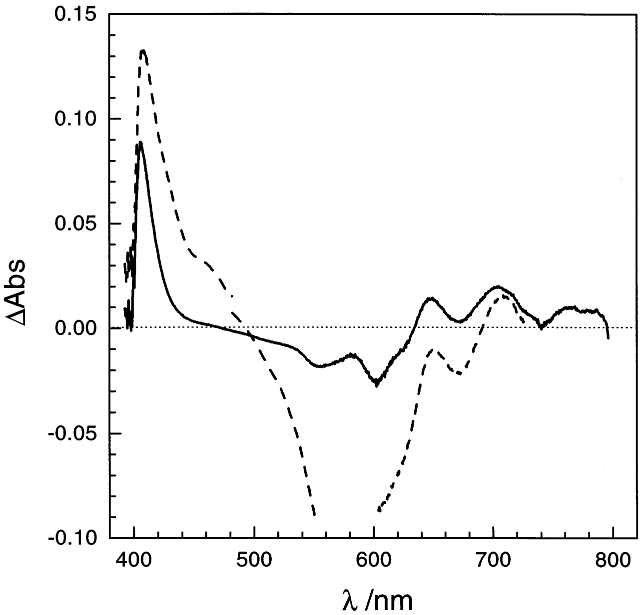

Figure 2. Transient absorption spectra of $MV^{\bullet+}$ in acetonitrile excited at 730 nm at 0 ps (dashed line) and 5 ps (solid line) after excitation.

to the biexponential recovery of the ground-state bleach ($\tau = 700\pm50$ fs and 16 ± 1 ps, respectively), while the 700 nm trace follows the formation ($\tau_f = 700\pm100$ fs) and decay ($\tau_d = 16\pm1$ ps) of the long-lived intermediate $\mathbf{I}_{(2)}$. Thus the signal from both intermediates grow in with a c.a. 700 fs time constant.

Two alternative reaction pathways can be conceived: pathway 1, in which the short-lived intermediate $\mathbf{I}_{(1)}$ is the vibrationally relaxed, electronically excited doublet state $^{D1}MV^{\bullet+}$ and is the precursor of the long-lived intermediate $\mathbf{I}_{(2)}$,

$$^{D0}MV^{\bullet+} \xrightarrow{h\nu} {}^{D1}MV^{\bullet+}\ (\mathbf{I}_{(1)}) \rightarrow \mathbf{I}_{(2)} \rightarrow {}^{D0}MV^{\bullet+} \tag{1}$$

pathway 2, in which both $\mathbf{I}_{(1)}$ and $\mathbf{I}_{(2)}$ are products of the excited doublet state $^{D1}MV^{\bullet+}$,

$$\begin{aligned} {}^{D0}MV^{\bullet+} \xrightarrow{h\nu} {}^{D1}MV^{\bullet+} &\rightarrow \mathbf{I}_{(2)} \rightarrow {}^{D0}MV^{\bullet+} \\ &\rightarrow \mathbf{I}_{(1)} \rightarrow {}^{D0}MV^{\bullet+} \end{aligned} \tag{2}$$

Pathway 2 appears to be more reasonable because, first, both transients were formed with the same time constant of $\tau_f = 700\pm100$ fs, which is slightly different from the decay time of intermediate $\mathbf{I}_{(1)}$, $\tau_d = 1.0\pm0.1$ ps (see trace at $\lambda_{pr} = 430$ nm, Figure 3, left). Second, there was no dependence of the kinetics on the wavelength of excitation ($\lambda_{exc} = 600$ and 730 nm gave the same results), which strongly suggests that the formation time of $\mathbf{I}_{(1)}$ cannot be due to relaxation in the excited doublet state $^{D1}MV^{\bullet+}$. Therefore we conclude that both intermediates with transient absorption in the visible were products of the electronically excited doublet state of the methyl viologen radical cation, $^{D1}MV^{\bullet+}$.

The assignment of the intermediate species $\mathbf{I}_{(1)}$ and $\mathbf{I}_{(2)}$ of reaction 2 is based on the following results. The trace at a probe wavelength of 600 nm (Figure 3, right) follows the recovery of the ground state with a fast contribution (700 ± 50 fs), indicating immediate relaxation from the excited doublet state to the ground state, and a slow component, $\tau_d = 16\pm1$ ps, which corresponds to the lifetime of the long-lived intermediate $\mathbf{I}_{(2)}$. The same time constants were obtained for the 700 nm trace, where $\mathbf{I}_{(2)}$ possesses strong absorption, resulting in a positive absorption change after an initial ground state bleach. At 5 ps after excitation only the long-lived intermediate $\mathbf{I}_{(2)}$ contributes to the transient absorption. Since the absorption spectrum of the $MV^{\bullet+}$ ground state is known, one can obtain the spectrum of $\mathbf{I}_{(2)}$ by subtracting the ground-state bleaching. The amount of ground-state bleach corresponds to c.a. 25 μM (1 mm optical path length) as determined in separate experiments with a standard. The result is shown as the solid line in Figure 1. It is a spectrum that very much resembles the visible absorption spectrum of $MV^{\bullet+}$ but that is red-shifted by approximately 810 cm^{-1} over the whole spectral region. This energy shift equals the quantum of the intraring C−C stretch vibration.[10] The molar extinction coefficients are similar, which together with the similarity in shape indicates that absorption occurs from the same electronic state (the ground state). Therefore we assign the long-lived intermediate $\mathbf{I}_{(2)}$ to a vibrationally excited electronic ground state of $MV^{\bullet+}$, which is formed from the excited D_1-state.

The short-lived intermediate $\mathbf{I}_{(1)}$ cannot be an electronically excited species, since it was formed from the lowest excited D_1 state. Instead it could also be a vibrationally excited ground state, since it is formed with the same time constant as $\mathbf{I}_{(2)}$. However, its unstructured spectrum does not allow an assignment to a certain mode. Because the $\mathbf{I}_{(1)}$ decay did not give rise to further generation of $\mathbf{I}_{(2)}$ we believe that the former is excited in a different vibrational mode that relaxes without energy redistribution to the 810 cm^{-1} mode of the $\mathbf{I}_{(2)}$ species.

Our transient spectra did not give any evidence for viologen decomposition or reactions with the acetonitrile solvent, although

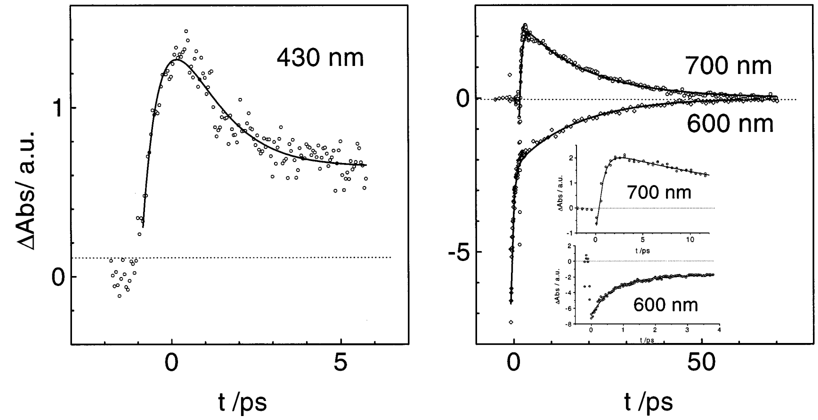

Figure 3. Transient absorption time profiles of $MV^{\bullet+}$ in acetonitrile excited at 730 nm and probed at 430 nm (left) and at 600 and 700 nm (right). The inset shows the early time evolution of the profiles at 600 and 700 nm.

the excited $MV^{\bullet+}$ should be, e.g., a strong reductant. The low photoreactivity can be explained by the very rapid decay of the $^{D1}MV^{\bullet+}$ excited state, and the relatively poor electron accepting and electron solvating properties of acetonitrile. This is favorable for the possible use of viologens and viologen radicals in reversible photoresponsive molecular devices.

A former resonance Raman study,[7] in which $MV^{\bullet+}$ in water was excited at 379,5 nm to a higher excited state, an upper limit of 350 fs was given for the electronically excited-state lifetime of $MV^{\bullet+}$. The population of a vibrationally excited ground state with a lifetime of 2 ps was proposed. These results are in general agreement with ours, and the lifetime differences might be due to the different experimental conditions (solvent, initial excited state). In the present study, we could resolve the formation of the vibrationally excited state and determine its electronic absorption spectrum, and in addition observed the parallel generation of another intermediate with a 1.0 ps lifetime. The $^{D1}MV^{\bullet+}$ state lifetime is short compared to aromatic diimide radicals of similar size. For pyromellitimide radical anions in DMF a D_1 excited-state lifetime of 5−10 ps was reported, without any evidence for vibrationally excited species.[11] The D_1-D_0 energy gap seems similar for the pyromellitimide and methyl viologen radicals, as judged from the absorption spectra. Possibly, the more rapid D_1-D_0 relaxation is induced by the less rigid structure of the latter molecule.

Excited states of $MV^{\bullet+}$ may be generated as an initial product upon electron transfer to MV^{2+}. Peon et al.[12] suggested that a vibrationally excited ground state of $MV^{\bullet+}$ was generated upon reduction of UV-excited methyl viologen MV^{2+} by the solvent methanol. However, the transient reported, with a decay time of 10 ps, had the same spectrum as the $MV^{\bullet+}$ ground state, so it does not seem to reflect the vibrationally excited species reported here.

Conclusion

The methyl viologen radical cation in acetonitrile was excited in the lowest visible absorption band at 730 nm. Two intermediates were detected in the transient absorption spectra. Both were formed in parallel, with $\tau_f = 700 \pm 100$ fs, from the lowest excited doublet state, $^{D1}MV^{\bullet+}$, which itself did not show any detectable absorption in the visible range. The longer lived intermediate with a lifetime of 16 ps could be assigned to a vibrationally excited ground state of $MV^{\bullet+}$. Its absorption spectrum was very similar to the ground-state spectrum of $MV^{\bullet+}$ in shape and extinction coefficients, but red-shifted by ca. 810 cm^{-1}, which equals one quantum of the intraring C−C stretch mode. The shorter lived transient decayed with a time constant of 1.0 ± 0.1 ps, presumably directly to the vibrational ground state, and is also attributed to a vibrationally excited ground state. Thus, our results show that the excited D_1-state of $MV^{\bullet+}$ relaxes on the subpicosecond time scale via at least one relatively long-lived, vibrationally excited ground state that has a lifetime of 16 ps in acetonitrile solution.

No decomposition or reaction with the solvent was detected in the transients, probably due to the short D_1 lifetime. This shows that $MV^{\bullet+}$ is rather stable even under excitation, which is favorable for its use in reversible photoresponsive molecular devices. On the other hand, the short D_1 lifetime ($\leq$700 fs) makes it difficult to use excitation of $MV^{\bullet+}$ for deliberately inducing reactions. Finally, because D_1 excitation produces the vibrationally excited $MV^{\bullet+}$, the characteristic spectrum of this species can be used to detect possible formation of excited products in photoinduced electron-transfer reactions with MV^{2+} as acceptor.

Acknowledgment. The Knut and Alice Wallenberg Foundation and The Swedish Foundation for Strategic Research (SSF) are acknowledged for financial support.

References and Notes

(1) Monk, P. M. S. *The Viologens*; Wiley: Chichester, 1998.

(2) For some recent reviews and examples, see: (a) Scandola, F.; Chiorboli, C.; Indelli, M. T.; Rampi, M. A. In *Electron Transfer in Chemistry*; Balzani V., Ed.; Wiley-VCH: Wienheim, 2001; Vol. 3, p 337. (b) Fukuzumi, S.; Imahori, H. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Wienheim, 2001; Vol. 2, p 927. (c) Sun, L.; Hammarström, L.; Åkermark, B.; Styring, S. *Chem. Soc. Rev.* **2001**, *30*, 36. (d) Sykora, M.; Maxwell, K. A.; DeSimone, J. M.; Meyer, T. J. *Proc. Natl. Acad. Sci. U. S. A.* **2000**, *97*, 7687.

(3) See, e.g., reference 3a,b and references therein: (a) Nanasawa, M. In *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Guglielmetti, R. J., Eds; Plenum: New York, 1999; p 341. (b) Sampanthar, J. T.; Neoh, K. G.; Ng, S. W.; Kang, E. T.; Tan, K. L. *Adv. Mater.* **2000**, *12*, 1536.

(4) (a) Ashton, P. R.; Ballardini, R.; Balzani, V.; Credi, A.; Dress, K. R.; Ishow, E.; Kleverlaan, C. J.; Kocian, O.; Preece, J. A.; Spencer, N.; Stoddart, J. F.; Venturi, M.; Wenger, S. *Chem. Eur. J.* **2000**, *6*, 3558. (b) Pease, A. R.; Jeppesen, J. O.; Stoddart, J. F.; Luo, Y.; Collier, C. P.; Heath, J. R. *Acc. Chem. Res.* **2001**, *34*, 433. (c) Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M. T.; Venturi, M. *Acc. Chem. Res.* **2001**, *34*, 445.

(5) Lomoth, R.; Häupl, T.; Johansson, O.; Hammarström, L. *Chem. Eur. J.* **2002**, *8*, 102.

(6) (a) Hayes, R. T.; Wasielewski, M. R.; Gosztola, D. *J. Am. Chem. Soc.* **2000**, *122*, 5563. (b) Lukas, A. S.; Miller, S. E.; Wasielewski, M. R. *J. Phys. Chem. B.* **2000**, *104*, 931.

(7) Huang, Y.; Hopkins, J. B. *J. Phys. Chem.* **1996**, *100*, 9585.

(8) Andersson, M.; Davidsson, J.; Hammarström, L.; Korppi-Tommola, J.; Peltola, T. *J. Phys. Chem. B* **1999**, *103*, 3258.

(9) Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617.

(10) Hester, R. E.; Susuki, S. *J. Phys. Chem.* **1982**, *86*, 4626.

(11) Gosztola, D.; Niemczyk, M. P.; Svec, W.; Lukas, A. S.; Wasielewski, M. R. *J. Phys. Chem. A.* **2000**, *104*, 6545.

(12) Peon, J.; Tan, X.; Hoerner, J. D.; Xia, C.; Luk, Y. F.; Kohler, B. *J. Phys. Chem. A* **2001**, *105*, 5768.