Real-Time Probing of a Three-Electron Bonded Radical: Ultrafast One-Electron Reduction of a Disulfide Biomolecule

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Abstract: The primary steps of a one-electron reduction of a disulfide molecule (cystamine) by the infrared p-like state of an excited hydrated electron have been investigated by femtosecond laser spectroscopy. The initial electron photodetachment from chloride ion or phenothiazine is triggered by a two-photon ultraviolet excitation. In homogeneous aqueous cystamine solution, a subpicosecond univalent reduction of the disulfide molecule by an infrared prehydrated electron competes with the nonadiabatic relaxation of trapped electrons (electron solvation process). This presolvation one-electron reduction occurs with a characteristic time of 160 ± 20 fs at 294 K. Within the electron solvation regime, this elementary redox process is totally achieved in less than 1×10^{-12} s and exhibits a probability 9 times higher than the radiationless relaxation of an infrared excited electron. In aqueous organized assemblies (cationic micelles) the partitioning of reactants does not influence the frequency rate of a prehydration reaction but modifies the early branching between reactive and nonreactive IR electronic channels. The real-time UV probing of a nascent sulfur-centered radical anion $(RS\therefore SR^-)_{aq}$ is discussed in the framework of a two-center-three-electron bond.

1. Introduction

Electron-transfer processes involving sulfur compounds are of particular interest in chemistry and biochemistry.[1] In this way, disulfide radical anions initiated by an electron attachment or ion−molecule reactions can act either as a reducing agent or a source of oxidant thiyl radicals. Thiols and disulfides such as glutathione and glutathione disulfide participate in the regulation of oxidative metabolism and favor the defense against deleterious effects of reactive oxidative intermediates and ionizing radiation.[2,3] The importance of redox systems with sulfur-centered species is largely dependent on their potential actions toward proteins and the repair of nucleic acids.[4,5] The present contribution is devoted to the microscopic investigation of primary radical processes in the presence of cystamine (Figure 1). The interest in this biological disulfide is 2-fold: the limited number of atoms would favor a synergy between experimental data on transient electronic states and further semiquantum simulations, the radioprotective and clinical properties of cystamine in living systems.[6−9]

In liquid phase, the course of elementary charge-transfer reactions may be assisted or impeded on the time scale of molecular motions.[10−14] Regarding the univalent reduction of sulfur compounds in aqueous environments (eq 1), one of the most important points concerns the mechanisms by which the hydration state of an electron governs the formation of disulfide radical anions ($RS\therefore SR^-$) characterized by a two-center three-electron bond (2c, 3e). The stabilization of this bonding involves the effects of two bonding and one antibonding electrons.[15−22]

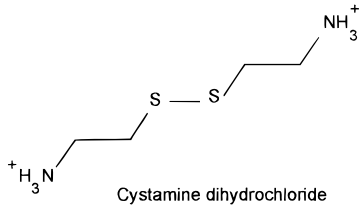

Figure 1. Structure of the disulfide molecule investigated in the present work.

$$(RSSR)_{aq} + \{e^-\} \xrightarrow[\text{reduction}]{\text{one-electron}} (RS\ \therefore\ SR^-)_{aq} \qquad R:\ NH_3{}^+(CH_2)_2 \quad (1)$$

Nanosecond and picosecond pulse radiolysis experiments have investigated the diffusion-controlled univalent reduction of disulfides by hydrated electrons and suggested that ultrafast

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formation of disulfide radical anions would involved hot electron or short-lived precursors of hydrated electrons.[23−28] Due to the existence of primary and secondary ionization phenomena, a stochastic approach of ultrafast electron transfer does not permit the real-time probing of early branchings between short-lived electronic configurations.

Ultrafast photophysical technics and semiquantum molecular dynamics simulations are more appropriate for the investigation of early charge-transfer processes and elementary radical reactions in molecular liquids and solutions.[29−38] Major strides have been performed in the direction of hydration cage reorganization around excess electrons,[39−56] electron-atom pair formation,[57−64] concerted electron−proton transfer,[65,66] and prehydration electron transfer.[67] Concerning the later point, it has been established that an ultrafast univalent reduction of a metallic cation by a p-like state of an IR prehydrated electron competes with the radiationless p → s transition. Indeed, the influence of short-lived electron−solvent configurations on the probability of a nonequilibrium electron transfer may be observable on the time scale corresponding to angstrom or subangstrom displacements.

In the present study, considering the p → s transition of an excess IR electron in aqueous environments, we have focused our attention on the transition-state mechanism involved in the univalent reduction of cystamine and the formation of a three-electron bonded radical anion. Femtosecond UV−IR spectroscopies of ultrafast one-electron reductions have been performed in homogeneous aqueous solution and organized assemblies. Some important aspects of this prehydration IR electron attachment on a S−S bond concern the role of ultrashort-lived solvent configurations on the probability of curve crossing. The transition-state mechanism is analyzed, taking into account the time-dependent overlap between the p-like orbital of the excited electron and those of a disulfide bridge. Femtosecond UV spectroscopy of nascent sulfur-centered radical anion $(RS\therefore SR^-)_{aq}$ is discussed in the framework of an energy-bonding rearrangement due to a nonbonding electron.

2. Experimental Section

The primary steps of a one-electron transfer from aqueous halides ions (Cl^-) or a chromophore (phenothiazine) are initiated by a two-photon excitation process with femtosecond UV laser pulses (2×4 eV). The colliding pulse mode-locked laser followed by five amplifier stages has been previously detailed.[68] The compression of amplified beams through a four-prism arrangment allows output pulses of energy above 1 mJ and is typically of 80−90 fs duration at a 20 Hz repetition rate. The pump beam is generated by frequency doubling of amplified pulses in a 1 mm KDP crystal and focused on the sample. In the sample, pump and probe beams overlap on less than 0.5 mm. The energy of the excitation pulse is adjusted at 7 ± 0.5 μJ and the test beam is selected from a continuum generation with thin optical filters. The time-dependent IR−UV absorption signals are investigated with germanium and silicium photodiodes, respectively. The different procedures that we use to analyze femtosecond spectroscopic data have been published in recent papers.[57,69] Cystamine dihydrochloride (RSSR, $2\ Cl^-$; R = $(CH_2)_2\ NH_3^+$) from Sigma Chemical Co (St. Louis, MO) was of the highest purity available (purity higher than 99.8% by high-pressure liquid chromatography). The unbuffered aqueous solutions of cystamine were used at pH 3.7 ± 0.1. Aqueous sodium chloride solution was

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used as reference. This solution is produced by dissolving sodium chloride (purity 99.999%) from Aldrich Chemical Co in light water at a final concentration of 1 M. For a monovalent cation, this concentration corresponds to a molecular ratio (R) of 55. Water is bidistilled in a quartz distillator with $KMnO_4$, and its resistivity is greater than 19 MΩ at 294 K.

Cationic micelles were prepared by dispersing phenothiazine (PTH: 2×10^{-4} M) in aqueous solution of cetyltrimethylammonium bromide (CTAB: 0.07M). The blend is gently stirred at 55−60 °C during 4 h to obtain complete integration of PTH and a clear solution. Care is taken to exclude light. PTH, from Merck, was of puriss quality and used as received. The concentration of the micellized chromophore was determined by spectrophotometry, assuming that the variation of the solute extinction coefficient on going from a homogeneous to a micellar solution could be neglected. Cationic micellar systems containing cystamine (0.5 M, pH 3.7) have been cautiously prepared by integrating disulfide in the aqueous phase of CTAB micelles (CTAB: 0.07 M, PTH: 2×10^{-4} M). Static UV characterization of micellar samples was run on a dual beam Varian 2300 spectrophotometer. Time-resolved experiments are performed at 294 K on samples with a 1 mm optical path length, continuously moved to avoid local heating. To avoid undesirable oxidative processes of the sample, molecular oxygen was removed by using pure nitrogen gas flow.

2.1 Femtosecond IR−UV spectroscopy. For a given test wavelength (ω_T), the time-dependence of small absorption signals $S^{\omega T}(\tau)$ is expressed by the physical response "R" of the sample and the normalized correlation function between the excitation pulse (I_p) and the probe beam (I_T) separated by a time delay τ (equation 2).

$$S^{\omega T}(\tau) = (R \times \{I_P{}^n I_T\})(\tau) \qquad (2)$$

This correlation function takes into account the propagation of the pump−probe pulses within the sample and the spectral contributions of transient electronic states (equation 3).

$$S^{\omega T}(\tau) = \sum_i \{\alpha_i{}^{\omega T} \int_{-\infty}^{+\infty} n_i(t-\tau) \times \mathrm{Corr}^{\omega P,\omega T}(\tau)\, dt\} \qquad (3)$$

The calculated maximum of a photoinduced absorption signal ($S^{\omega T}{}_{max}$) takes into account the contribution of multiple transient electronic states:

$$S^{\omega T}_{max} = \sum_i \alpha_i^{\omega T} n_i^{\tau Smax} \qquad (4)$$

In this expression, $\alpha_i^{\omega T}$ is the absorption contribution of the electronic state "i" at a given test wavelength (ω_T), and $n_i^{\tau Smax}$ represents the computed level of transient electronic states at τ_{Smax}. At this time delay, the signal amplitude is maximum. When the analyses are performed with signals normalized between 0 and 1 ($S^{\omega T}{}_{nor}(\tau)$), the expression 4 becomes:

$$S^{\omega T}{}_{nor}(\tau) = \sum_i \alpha_i^{\omega T} n_i(\tau) / \sum_i \alpha_i^{\omega T} n_i(\tau_{Smax}) \qquad (5)$$

In this expression, $n_i(\tau)$ represents the computed level of a transient electronic state i for a time delay τ. For a given test wavelength (ω_T), the relative spectral contributions (RSC) of different electronic states to the transient absorption signal is defined by the following expression:

$$\mathrm{RSC}_{ni}^{\omega T} = \frac{\alpha_i^{\omega T}}{\sum \alpha_i^{\omega T}} = \sigma_i^{\omega T} P_i n_i^* \qquad (6)$$

In eq 6, $\sigma_i^{\omega T}$ represents the cross section of a given electronic state i, P_i is the probability of a channel i and n_i^* corresponds to the initial level of virtual electronic states (high excited CTTS states). This parameter equals 1 when the analysis are performed on curves normalized between 0 and 1. From computed fits obtained at different test wavelengths, the expression 6 allows to investigate ultrafast electronic pathways whose the prevailing spectral signatures peak in the visible or in the infrared. The detailed procedures developed for the computed treatment of optical broadening factors due to the group velocity dispersion in liquids and ionic solutions have been detailed in recent papers.[57,68,69]

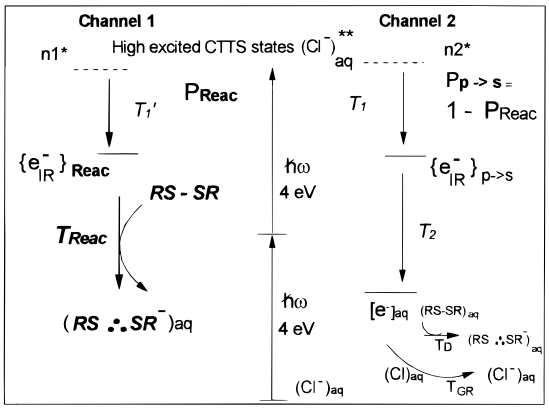

Figure 2. Kinetic models developed for the analysis of ultrafast one-electron reduction of cystamine following the femtosecond UV excitation of chloride ion in homogeneous solution. The model describes an early partition between a prehydration univalent reduction of cystamine by IR p-like excited electron (channel 1) and an electron solvation process (channel 2). The minor channel involving high excited CTTS and electron-atom pairs (eqs 12, 13) are not reported on the figure.

2.2 Computed Kinetic Models. Femtosecond UV−IR spectroscopic data are analyzed with kinetic models developped on a Sparc-station Sun C1+. They take into account primary photophysical and photochemical events triggered by a two-photon excitation of chloride ion or phenothiazine. These computed models will be detailed in the Results section.

3. Results

3.1 One-Electron Reduction of Cystamine in Homogeneous Solution. Charge transfer processes involving nonequilibrium electrons and fully hydrated electrons (s state) have been studied by femtosecond infrared and visible spectroscopy. For different temporal windows (4 and 100 ps), the dynamics and amplitude of induced absorption signals are investigated. The main results are reported in Figures 2−5 and Table 1.

The careful analysis of experimental data are performed with a kinetic model detailed in Figure 2. We focused our attention on the discrimination of early branchings between a prehydration reduction of disulfide (channel 1) and an electron hydration process (channel 2). The early steps triggered by a femtosecond two-photon UV excitation of aqueous halide anions involve very short-lived precursors of prehydrated electron. Up to now, as we cannot directly investigate an early branching of these high excited precursors in reactive and nonreactive pathways, our model defines two primary populations (n_1*, n_2*). In this model we consider that the presence of cystamine does not change the ultrafast photophysical steps which lead to precursors of IR prehydrated electron. Physically speaking these two primary populations are similar but cannot be directly investigated during the vertical transition from Cl^- ground state to excited states. For different test wavelengths, these initial parameters equal 1 and permit the computed investigation of experimental curves normalized between 0 and 1. The most important point is that the model examines the probability of an ultrafast reduction of cystamine by IR prehydrated electron (channel 1). This reactive pathway is described by the time dependent behavior of

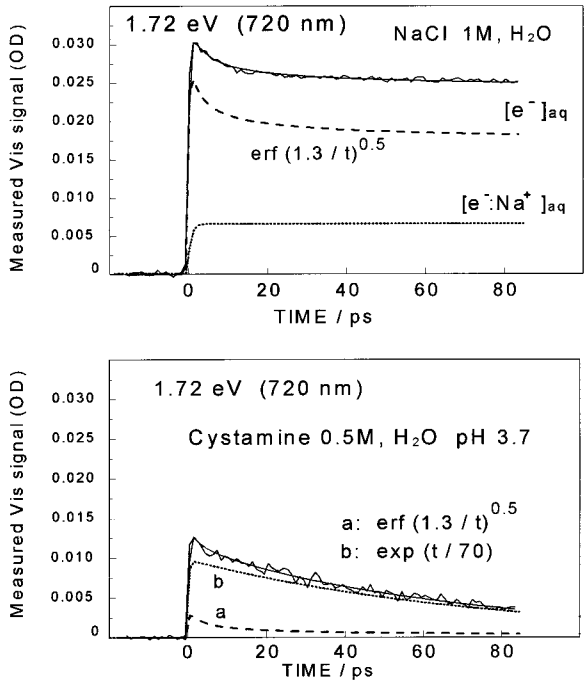

Figure 3. Time dependence of induced absorption signal at 1.72 eV (720 nm), following the femtosecond UV excitation of chloride ions in aqueous solutions of NaCl (1 M) and cystamine (0.5 M). The smooth and dotted lines represent the computed best fits of experimental traces and the contribution of photoinduced electronic states, respectively. The early signal decay is assigned to a 1D geminate recombination between a fraction of $[e^-]_{aq}$ and chlorine atom. In presence of cystamine, a diffusion-controlled reaction with $[e^-]_{aq}$ follows a monoexponential law.

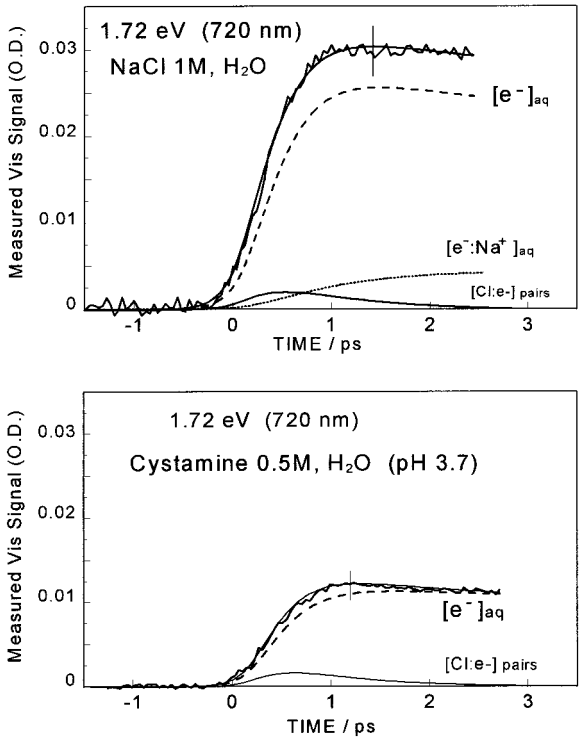

Figure 4. Influence of cystamine on the rise time and amplitude of induced absorption signal at 1.72 eV following the femtosecond UV excitation of aqueous halide ions in aqueous solutions of NaCl (1 M) and cystamine (0.5 M). The contributions of prevailing electronic states are reported.

$\{e^-_{IR}\}_{Reac}$ population and characterized by a probability P_{Reac} (eqs 7, 8).

$$\frac{dn_1^*}{dt} = P_{Reac}\beta_P \frac{I_P^2}{2h\omega_P} - \frac{n_1^*}{T_1'} \tag{7}$$

$$\frac{dn_{(e\text{-}IR)Reac}}{dt} = \frac{n_1^*}{T_1'} - \frac{n_{(e\text{-}IR)Reac}}{T_{Reac}} \tag{8}$$

In these equations, n_1^* represents the initial level of high excited charge-transfer-to-solvent states of chloride ion (excited precursor of prehydrated electron), β_P is the absorption coefficient for a two-photon excitation of Cl^-, T_1' and T_{Reac} are the formation and reaction time of IR prehydrated electron $\{e^-_{IR}\}_{Reac}$. In this model, the prehydration formation of a disulfide radical anion $(RS\therefore SR^-)_{aq}$ is expressed by the following equation:

$$\frac{dn_{(RS\therefore SR^-)_{aq}}}{dt} = \frac{n_{(e\text{-}IR)Reac}}{T_{Reac}} \tag{9}$$

The second electronic channel yields fully hydrated electrons (channel 2). This electron hydration pathway is characterized by the probability $P_{p\to s}$ and involves an activated two-state process for which transient IR prehydrated electrons ($\{e^-_{IR}\}_{p\to s}$) relax toward a hydrated electron ground state $[e^-]_{aq}$. The time-dependent electronic populations of this electron hydration channel are expressed as follows:

$$\frac{dn_2^*}{dt} = P_{p\to s}\beta_P \frac{I_P^2}{2h\omega_P} - \frac{n_2^*}{T_1} \tag{10}$$

$$\frac{dn_{(e\text{-}IR)p\to s}}{dt} = \frac{n_2^*}{T_1} - \frac{n_{(e\text{-}IR)p\to s}}{T_2} \tag{11}$$

In these equations, T_1, T_2 are the trapping and solvation times, respectively, of a photodetached electron. The model considers that a fraction of $[e^-]_{aq}$ either recombines with polarizable chlorine atom (T_{GR}) or exhibits a reaction with cystamine (T_D). The electron−chlorine recombination is expressed by a random walk law controlled by a 1D diffusion process.[57] Considering previous femtosecond investigations of aqueous electrolyte solutions,[57,58,69] two minor channels involving IR CTTS** and electron−Cl atom pairs are not neglected (eqs 12, 13). For a clarification of the presentation, they are not reported in Figure 2. To avoid numerous adjustable parameters, these two nonreactive channels are kept similar in reference and cystamine solutions.

$$(Cl^-)_{aq} + 2h\nu \xrightarrow{t\ll 50\text{ fs}} \text{CTTS**} \xrightarrow{t\approx 50\text{ fs}} \text{CTIS*} \tag{12}$$

$$(Cl^-, X^+)_{aq} + 2h\nu \xrightarrow{t=270\text{ fs}} (Cl{:}e^-{:}X^+)_{Pairs} \xrightarrow{t\approx 750\text{ fs}} (X^+{:}e^-)_{aq}, (Cl)_{aq} \tag{13}$$

In aqueous sodium chloride solution, the best computed fits of spectroscopic curves at 1.72 eV include the contribution of

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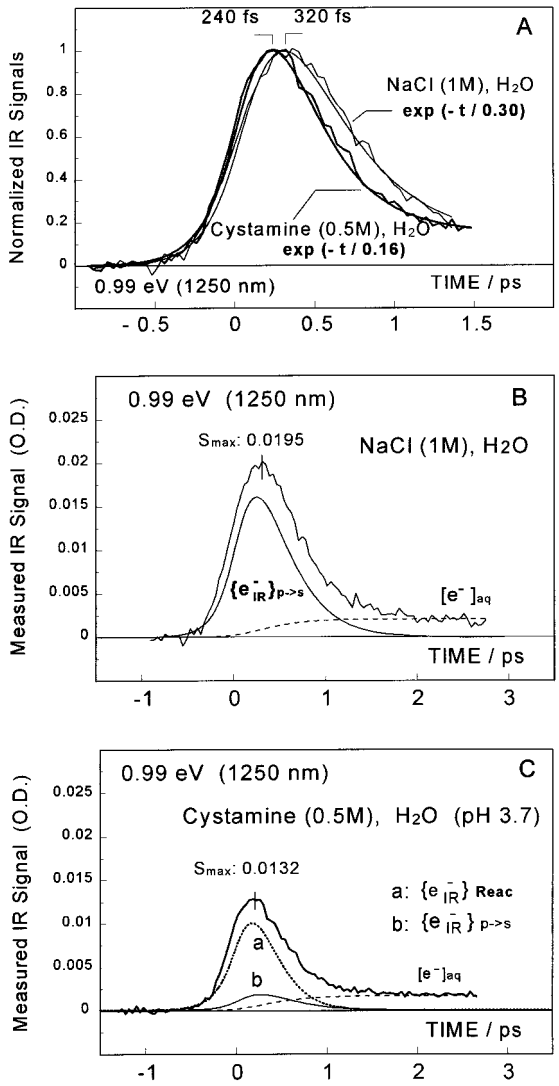

Figure 5. Infrared spectroscopy of an ultrafast one-electron reduction of a sulfur−sulfur bond of cystamine by IR p-state prehydrated electron. (A) Comparison of normalized IR signals between the reference solution (NaCl: 1 M) and cystamine (0.5 M). Smooth lines represent the best computed fits of nonexponential IR signal decays. (B) Short-time contributions of $\{e^-_{IR}\}_{p\rightarrow s}$ and $[e^-]_{aq}$ triggered by the femtosecond UV excitation of aqueous Cl^- in a reference NaCl solution. (C) Computed analysis of the ultrafast univalent reduction of cystamine (0.5 M) by IR p-like excited electron $\{e^-_{IR}\}_{Reac}$ (channel 1). This prehydration redox reaction contributes to the ultrafast IR decay. The incomplete recovery of the 0.99 eV signal is due to a low-energy tail contribution of fully hydrated electron (channel 2). The minor contributions of high excited CTTS (CTTS**) and $(Cl{:}e^-)_{pairs}$ are not reported.

two populations of fully relaxed electrons (Figures 2, 3A, 4A). A prevailing contribution is assigned to $[e^-]_{aq}$ whose a fraction (∼30%) exhibits an early geminate recombination with chlorine atom. The characteristic time ($T_{GR} = 1.3$ ps) of this nonexponential dynamics is expressed by an erf function[57] which satisfies the time-dependence ($1/\sqrt[2]{t}$) of the signal decay observed at short and long times (4, 100 ps). It can be noticed that a fraction of the 1.72 eV signal is due to the contribution of a long-lived polaron-like state $[Na^+{:}e^-]_{aq}$ that is, to an electron trapped in the hydration shells of sodium ion.

Some significant changes of visible spectroscopic signals are observed in the presence of cystamine: a lowering of the signal amplitude and a significant picosecond signal decay (Figures 3B, 4B). The major fraction of $[e^-]_{aq}$ follows an exponential

Table 1. Computed Spectral Contributions of Electronic States to Experimental Visible Absorption Signals at 1.72 eV Following the Femtosecond UV Excitation of Chloride Ions in Aqueous Sodium Chloride (1 M) and Cystamine (0.5 M) Solutions

			τS_{max}	
time	$\tau = 520$ fs		1.44 ps	1.20 ps
signal analysis	NaCl	cystamine	NaCl	cystamine
CTTS**	0	0	0	0
$\{e^-_{IR}\}_{p\rightarrow s}$	0.0240	0.00015	0.00168	0.00002
$\{e^-_{IR}\}_{Reac}$	0	0.00085	0	0.00003
$(Cl{:}e^-)_{pairs}$	0.0522	0.0411	0.0189	0.0237
$[e^-]_{aq}$	0.4517	0.177	0.655	0.254
$[e^-{:}Na^+]_{aq}$	0.0267	0	0.0686	0
calculated signal^{1,72eV} (au)	0.554	0.219	0.744	0.278
experimental signal^{1,72eV}(OD)	0.020	0.0075	0.031	0.012
	$S^{1.72eV}_{NaCl}/S^{1.72eV}_{Cystamine}$			
model	0.395		0.374	
experiment	0.375		0.387	
C_{37}	$\tau = 520$ fs		$\tau = 1.2$ ps	
measured	0.510 M		0.511 M	
calculated	0.503 M		0.533 M	

decay with a rate constant T_D of 70 ± 5 ps. In experimental conditions where $[e^-]_{aq} \ll$ [cystamine], a pseudo-first-order dynamics prevails and it is reasonable to assign this signal decay to a diffusion-controlled reaction between hydrated electron and disulfide molecules. The estimate of a bimolecular rate constant can be obtained by the expression: $k_{[e^-]aq+Cystamine} = 1/T_{D[Cystamine]}$. For a cystamine concentration of 0.5 M, $k_{[e^-]aq+Cystamine}$ equals $2.8 \pm 0.25 \times 10^{10}$ M^{-1} s^{-1}. This value agrees with experimental subnanosecond data obtained for a concentration of cystamine in the range 0.1−1 M.[25] From kinetics analysis it can be observed that a small fraction of $[e^-]_{aq}$ recombines with chlorine atom (Figures 3B, 4B).

To understand more completely the influence of cystamine on the early level of fully hydrated electrons we have performed a comparison between measured and calculated data (Table 1). In NaCl solution, the maximum of the photoinduced absorption signal at 1.44 ps ($S^{1.72eV}_{max}$) involves a prevailing contribution of $[e^-]_{aq}$ and a small absorption of long-lived polaron-like state $[Na^+{:}e^-]_{aq}$. In cystamine solution, the polaron-like state population is not discriminated and 91% of the calculated $S^{1.72eV}_{max}$ at 1.20 ps is due to $[e^-]_{aq}$ (Table 1). It can be observed that the calculated $S^{1.72eV}_{max}$ in NaCl and cystamine solutions capture well the dramatic $Na^+/NH_3^+(CH_2)_2SS(CH_2)_2NH_3^+$ substitution effect on measured $S^{1.72eV}_{max}$ Considering an early partition between a prehydration reduction of cystamine (channel 1) and an electron solvation process (channel 2), we have estimated the short-time dependent C_{37} value of disulfide molecules. This interesting parameter represents the concentration of cystamine required to reduce the early level of hydrated electron ground state $[e^-]_{aq}$ to $1/e = 37\%$ of the reference value in NaCl solution. In this way, C_{37} value characterizes the ability of cystamine to react with IR precursors of fully hydrated electron. From femtosecond spectroscopic data, the short-time-dependent C_{37} of cystamine

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Table 2. IR Electron Dynamics, Early Partition between a Presolvation Reduction of a SS Bond (eq 1a) and an Electron Hydration Channel (eq 1b) in Aqueous Cystamine Dihydrochloride Solution (RSSR, 2 HCl^-; R = $(CH_2)_2NH_3^+$) Solution[a]

	reference solutions		cystamine solution
parameters	$[H_2O]/[NaCl] = 55$	$[H_2O]/[MgCl_2] = 110$	$[H_2O]/[RSSR] = 110$
T_1	130 ± 10 fs	130 ± 10 fs	130 ± 10 fs
T_1'	-	-	130 ± 10 fs
T_2	300 ± 20 fs	300 ± 20 fs	300 ± 20 fs
T_{Reac}	-		160 ± 20 fs
$P_{p\rightarrow s}$	1	1	0.1
P_{Reac}	0	0	0.9
$P_{Reac}/P_{p\rightarrow s}$			9

[a] The parameters are calculated from the kinetic model of Figure 1.

Table 3. Computed Spectral Contributions of Electronic States to Experimental IR Absorption Signals at 0.99 eV and for Different Time Delays Following the Femtosecond UV Excitation of Chloride Ions in Aqueous Sodium Chloride Solution ($[H_2O]/[NaCl] = 55$) and Aqueous Cystamine Dihydrochloride Solution ($[H_2O]/[Cystamine] = 110$)

	τ S_{max}			
time	320 fs	240 fs	$\tau = 2$ ps	
signal analysis	NaCl	cystamine	NaCl	cystamine
CTTS**	0.0013	0.0042	0	0
$\{e^-_{IR}\}_{\rightarrow s}$	0.141	0.016	0.0002	0
$\{e^-_{IR}\}_{eac}$	0	0.096	0	0
$(Cl{:}e^-)_{pairs}$	0.0294	0.0097	0.0018	0.0030
$[e^-]_{aq}$	0.0056	0.0052	0.0151	0.0142
$[e^-{:}Na^+]_{aq}$	0.00011	0	0.0006	0
calculated signal$^{0.99eV}$(au)	0.178	0.132	0.0177	0.0172
experimental signal$^{0.99eV}$(OD)	0.0195	0.0133	0.0025	0.0023
	$S^{0.99eV}_{NaCl}/S^{0.99eV}_{Cystamine}$			
model	1.35		1.03	
experiment	1.46		1.08	

is determined as follows:[67]

$$\frac{S^{1.72eV}[e^-S]_{RSSR}(\tau)}{S^{1.72eV}[e^-S]_{NaCl}(\tau)} = \exp^{-[RSSR]/C_{37}(\tau)} \Rightarrow C_{37}(\tau) = \frac{ln\left(\frac{S^{1.72eV}[e^-S]_{NaCl}(\tau)}{S^{1.72eV}[e^-S]_{RSSR}(\tau)}\right)}{0.5} \quad (14)$$

In this equation, $S^{1.72eV}[e^-S]_{NaCl}(\tau)$, $S^{1.72eV}[e^-S]_{RSSR}(\tau)$ represent the short-time contributions of $[e^-]_{aq} + [Na^+{:}e^-]_{aq}$ in NaCl and $[e^-]_{aq}$ in cystamine solutions.

For different time-delays (τ = 520 fs and 1.2 ps), the calculated C_{37} values are reported in Table 1. There is a good agreement between calculated estimates and values obtained from measured absorption signals. These data emphasize that a prehydration electron transfer takes place in the presence of cystamine (channel 1) and contributes to decrease the early yield of fully hydrated electron (channel 2).

Femtosecond IR spectroscopic investigations of nonequilibrium electronic states permit to verify this important point and validate the concistency of our kinetic model. The most significant results are reported in Figure 5 and Tables 2, 3. Following the femtosecond UV excitation of aqueous NaCl solution, a prevailing electron photodetachment process involves p-like excited electrons $\{e^-_{IR}\}_{p\rightarrow s}$ whose the nonradiative internal conversion yields $[e^-]_{aq}$. The best computed fits of IR curves indicate that the build-up time (T_1) of the $\{e^-_{IR}\}_{p\rightarrow s}$ population equals 130 ± 10 fs. The relaxation of this nonequilibrium state toward $[e^-]_{aq}$ follows an exponential law with a time constant (T_2) of 300 ± 20 fs (Table 2).

The effect of a NaCl/cystamine substitution on the experimental IR signals are reported in Figure 5 and Table 2. The results show that in aqueous cystamine solution, the prevailing IR channel involves an ultrafast attachment of $\{e^-_{IR}\}_{Reac}$ on disulfide molecule with a characterictic time T_{Reac} of 160 ± 20 fs. This prehydration electron transfer on cystamine is 1.87 times faster than the nonadiabatic p → s transition of IR p-like electrons. It contributes to lower IR signal amplitude $S^{0.99eV}_{max}$ by 30%. Computed spectral contributions of electronic states well capture experimental measurements obtained at 240−320 fs and at 2 ps (Figure 5, Table 3). These IR spectroscopic results substantiate the existence of an early branching between a prehydration disulfide molecule reduction by $\{e^-_{IR}\}_{Reac}$ (channel 1) and an electron hydration process (channel 2). From experimental IR signals, we have calculated the early partition between reactive ($\{e^-_{IR}\}_{Reac}$) and nonreactive ($\{e^-_{IR}\}_{p\rightarrow s}$) electronic pathways. Equation 15 reports the short-time early branching ratio we establish from the adjusted spectral contributions of transient IR electron populations ($\alpha^{\omega T}_{\{e\text{-}IR\}Reac}$, $\alpha^{\omega T}_{\{e\text{-}IR\}p\rightarrow s}$).

$$\frac{\alpha^{\omega T}_{\{e\text{-}IR\}Reac}}{\alpha^{\omega T}_{\{e\text{-}IR\}p\rightarrow s}} = \frac{\sigma^{\omega T}_{\{e\text{-}IR\}Reac}\cdot P_{Reac}}{\sigma^{\omega T}_{\{e\text{-}IR\}p\rightarrow s}\cdot P_{p\rightarrow s}} \quad (15)$$

In this expression, P_{Reac},$P_{p\rightarrow s}$ represent the probability to get a prehydration reduction of cystamine (channel 1) or an electron hydration (channel 2), respectively. For aqueous cystamine solution, P_{Reac} is defined as follows:

$$\frac{P_{Reac}}{P_{p\rightarrow s}} = \frac{\alpha^{\omega T}_{\{e\text{-}IR\}Reac}}{\alpha^{\omega T}_{\{e\text{-}IR\}p\rightarrow s}} \quad (16)$$

$$P_{Reac} = 1 - P_{p\rightarrow s} = 1 - \frac{\alpha^{\omega T}_{\{e\text{-}IR\}p\rightarrow s}}{(\alpha^{\omega T}_{\{e\text{-}IR\}Reac} + \alpha^{\omega T}_{\{e\text{-}IR\}p\rightarrow s})} \quad (17)$$

In eq 17, $\alpha^{\omega T}_i$ represents the adjusted spectral contribution of an electronic state i at 0.99 eV. Indeed, the probability P_{Reac} of an ultrafast univalent reduction of disulfide by $\{e^-_{IR}\}_{Reac}$ equals 0.9 (Table 2). In agreemeent with the calculated C_{37} value of cystamine, the high IR branching ratio ($P_{Reac}/P_{p\rightarrow s}$ = 9) contributes to lower the early yield of hydrated electrons. The effect of cystamine on short-time IR and visible signals being well captured by our kinetic model, we conclude to the prehydration formation of a disulfur radical anion $(RS\therefore SR^-)_{aq}$. From the available data in the literature, the presence of an antibonding electron ($2\sigma/1\sigma^*$) is generally characterized by a UV spectral signature.[15−19,70,75] In our experimental conditions, the contribution of short-lived excited CTTS states linked to chloride ions represents a real hindrance for the real-time UV probing of this nascent disulfide radical.[57,58] To perform the real-time probing of $(RS\therefore SR^-)_{aq}$, we have considered a second experimental system.

3.2 Prehydration One-Electron Attachment in Organized Micellar System. In cationic PTH/CTAB/H_2O micellar solutions, the presence of a charged surfactant interface favors the organization of reactants (electron donor and acceptor) at a molecular level. The electron donor (phenothiazine) is embedded inside the hydrophobic core of CTAB micelles,[71,72] and cysta-

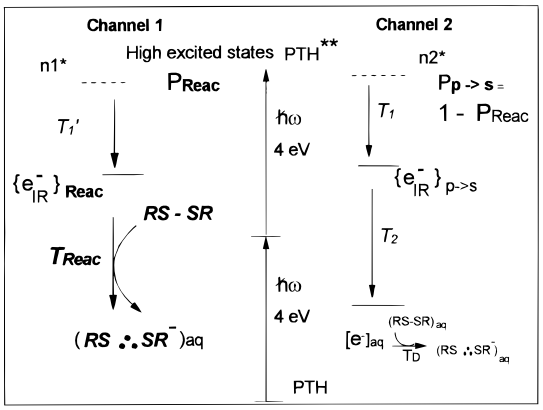

Figure 6. Kinetic model developed for the analysis of ultrafast one-electron reduction of cystamine following the femtosecond UV excitation of phenothiazine (PTH) in aqueous organized assemblies (CTAB micelles). The model consider an early partition between a prehydration univalent reduction of cystamine by IR p-like excited electron (channel 1) and an electron solvation process (channel 2).

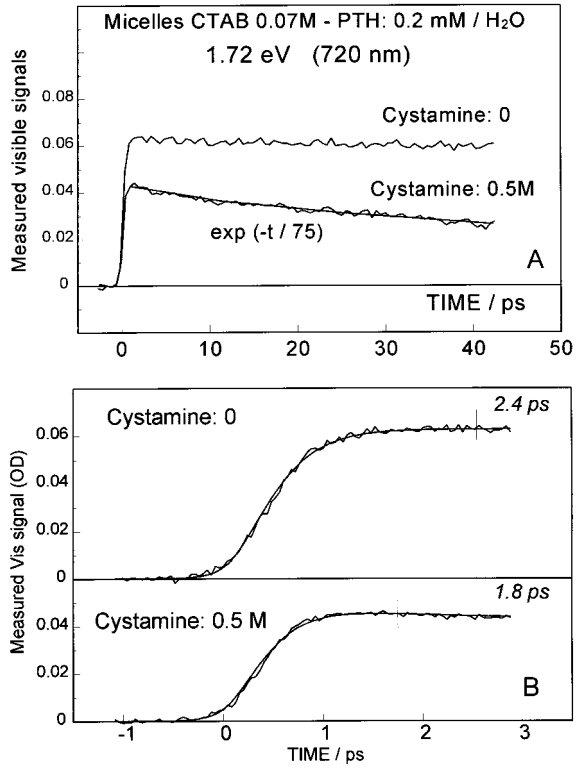

Figure 7. Effect of cystamine (0.5 M) on the time-resolved visible spectroscopy of an electron hydration process in aqueous micellar system (CTAB: 0.07 M, PTH: 2×10^{-4} M). (A) Signal decay is assigned to a diffusion-controlled reaction between cystamine and the ground state of hydrated electron (s state). (B) Short-time effect of cystamine on the amplitude of induced absorption signals at 1.72 eV. The vertical lines indicate the position of τS_{max}.

mine dihydrochloride is localized in the aqueous phase. The kinetic model used for the investigation of ultrafast electron transfers in aqueous CTAB micelles is detailed in Figure 6. As for aqueous electrolyte solutions, we haved focused our attention on early branchings between IR reactive and nonreactive transfers. The two-photon excitation of PTH within its band centered at 312.5 nm leads to an ultrafast charge separation inside the micelle and a subsequent electron transfer across the hydrocarbon chain of surfactant molecules. The time-dependent electronic channels are investigated with differential equations

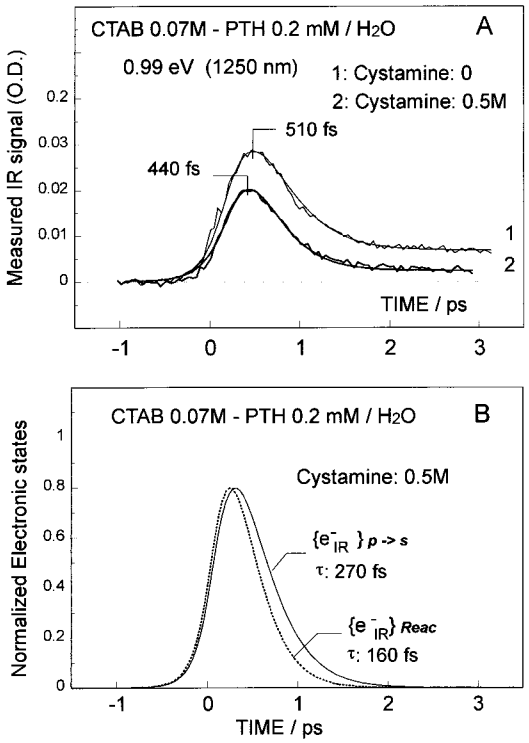

Figure 8. A: Influence of cystamine (0.5 M) on measured IR signals at 0.99 eV following an electron photodetachment triggered by femtosecond UV excitation of PTH in aqueous cationic micelles system (CTAB: 0.07 M, PTH: 2×10^{-4} M). (B) Computed dynamics of IR presolvation reduction of cystamine and nonadiabatic p→s transition of IR excited electrons in aqueous CTAB/PTH micelles.

similar to those used for homogeneous solutions (eqs 7−11). Time-resolved visible and IR spectroscopic results are reported in Figures 7, 8. In reference CTAB micelles, the signal rise time at 1.72 eV is dominated by the electron hydration process. The complete electron photodetachment from excited PTH involves a short-lived IR prehydrated electron whose the nonradiative deactivation toward an hydrated electron follows an exponential law with a time constant T_2 of 270 ± 20 fs (Figure 8). By comparison with IR data in aqueous NaCl solution, the absence of an instaneous signal rise time at 0.99 eV substantiates that high excited CTTS states of bromide ions do not participate to an electron photodetachment process. This point is also confirmed by the absence of a significant picosecond $[e^-]_{aq}$−Br recombination at 1.72 eV. Concerning the $[e^-]_{aq}$ population originating from PTH, the presence of a negative interfacial potential in the Stern layer prevents its early recombination with PTH^+ embedded in the hydrophobic core of micelles.

In PTH/CTAB/Cystamine−H_2O micelles, the dynamics of photoinduced visible and IR absorption signals are significantly modified. At 1.72 eV, the absorption signal decay follows a pseudo-first-order dynamics with a time constant T_D of 75 ± 5 ps (Figure 7A). This relaxation dynamics is assigned to a reduction of cystamine by $[e^-]_{aq}$. For a cystamine concentration of 0.5 M, the estimate of a bimolecular reaction constant $k_{(e^-+cystamine)}$ equals 2.65 ± 0.2 × 10^{10} M^{-1} s^{-1}. The most important point concerns the consequence of an early partition between IR reactive and nonreactive electronic channels on the amplitude and short-time dynamics of signals (Figures 7B, 8). The IR prehydration reaction dynamics between cystamine and $\{e^-_{IR}\}_{Reac}$ follows a monoexponential law whose the time constant (T_{Reac}) equals 160 ± 20 fs. This ultrafast electron attachment on a SS bond is faster than the radiationless p → s

Table 4. Computed Spectral Contributions of Electronic States to Experimental Visible and UV Absorption Signals (1.72 eV and 3.03 eV) at τ S_{max} Following the Femtosecond UV Excitation of PTH in Cationic Micellar System (CTAB 0.07M, PTH 2 10^{-4} M)

time	λ_{test} = 720 nm		λ_{test} = 410 nm	
signal analysis	cystamine: 0 τS_{max}: 2.4 ps	cystamine: 0.5 M τS_{max}: 1.8 ps	cystamine: 0 τS_{max}: 1.5 ps	cystamine: 0.5 M τS_{max}: 1.5 ps
PTH^+	0	0	0.250	0.230
$\{e^-_{IR}\}_{p\rightarrow s}$	0.00006	0.000001	0	0
$\{e^-_{IR}\}_{Reac}$	0	0.00004	0	0
$[e^-]_{aq}$	0.951	0.607	0.246	0.095
$[RSSR^-]_{aq}$	0	0	0	0.077
calculated signal$^{\lambda test}$ (au)	0.951	0.607	0.496	0.402
experimental signal$^{\lambda test}$ (OD)	0.0655	0.0437	0.0357	0.0294
		$S^{\lambda test}_{Cysta.0.5M}/S^{\lambda test}_{Cysta.:0}$		
model	0.64		0.81	
experiment	0.66		0.82	

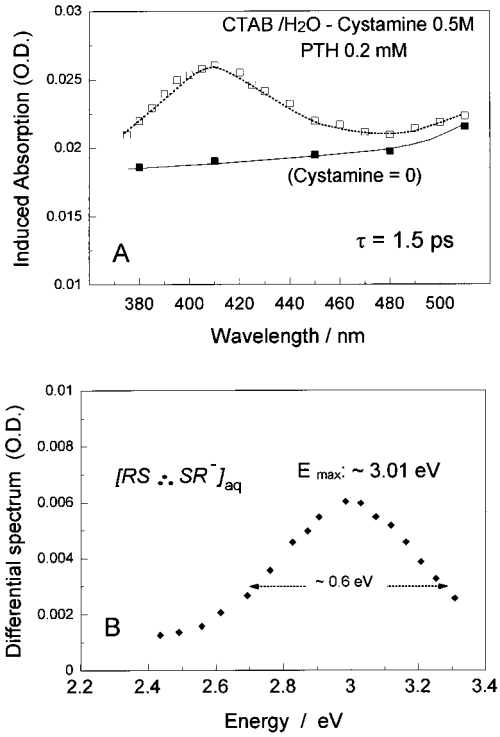

Figure 9. A: Measured transient absorption spectrum of a three-electron-bonded radical anion of cystamine ($RS\therefore SR^-$, R = $(CH_2)_2$-NH_3^+) in biomicellar system (CTAB: 0.07 M, PTH: 2 × 10^{-4} M, cystamine: 0.5 M, pH: 3.7). Normalized spectrum of high energy tails of PTH^+ and hydrated electron ground state (normalization in the spectral range 480−510 nm) are also reported. (B) Short-time differential spectrum of $(RS\therefore SR^-)_{aq}$ following an ultrafast univalent reduction of cystamine by IR p-like excited electron $\{e^-_{IR}\}_{Reac}$.

transition of IR excited electrons and lowers the signal amplitude at 0.99 eV ($S^{0.99eV}_{max}$). The direct consequence of this reactive IR channel on the initial yield of electron hydration is determined by visible absorption spectroscopy (Figure 7B, Table 4). The calculated C_{37} value of disulfide molecules at 1.72 eV (C_{37} = 1.11 M at 1.8 ps) strongly supports the ultrafast attachment of IR prehydrated electron on cystamine. Consequently, the influence of a prehydration reaction on the electron hydration efficiency can be defined as $\varphi_{(e-aq)} = S_{max}{}^{1/72eV}{}_{RSSR=0}/S_{max}{}^{1.72eV}{}_{RSSR=0.5}$. For an experimental $\varphi_{(e^-aq)}$ value of 0.66 at 1.72 eV (Table 4), the estimate of a prehydration cystamine reduction probability (P_{Reac}) equals 0.38 ± 0.02.

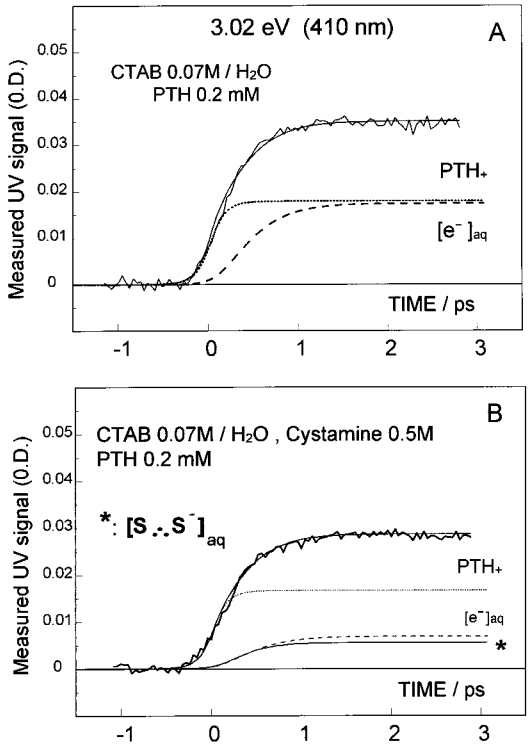

Figure 10. Influence of cystamine (0.5 M) on the time dependence of measured UV absorption signal following an electron photodetachment from PTH in aqueous CTAB micellar systems system (CTAB: 0.07 M, PTH: 2 × 10^{-4} M).

Infrared and visible spectroscopic investigations have been completed by the femtosecond UV spectroscopy of nascent disulfur radical $(RS\therefore SR^-)_{aq}$. Short-time spectral data obtained in CTAB micellar systems between 375 and 510 nm (3.30−2.43 eV) are reported in Figure 9. In absence of cystamine, the structureless absorption band contains the signature of $[e^-]_{aq}$ and PTH cation (PTH^+).[29,71−73] By scanning the PTH/CTAB/H_2O−cystamine micellar solution with different test wavelengths, the absorption spectrum was determined at 1.5 ps. The short-time differential UV spectrum exhibits a band centered around 3.01 eV (412 nm) and a half width of 0.6 eV at 294 K. This UV band is assigned to a neoformed "product" of the cystamine univalent reduction by IR p-state electron that is, to a three-electron bonded radical anion $(RS\therefore SR^-)_{aq}$. The time-dependent UV contributions of different species are analyzed at 3.02 eV (Figure 10 and Table 4). In reference CTAB micelles, the signal rise time is well fitted to a combination of an instantaneous PTH^+ contribution and a slower one assigned to $[e^-]_{aq}$. In CTAB-cystamine micelles, the best fit of the short-time UV absorption signal ($\Delta S^{3.02eV}_{[RSSR=0.5]}(\tau)$) is defined by the following expression:

$$\Delta S^{3.02eV}_{[Cyst=0.5M]}(\tau) = \alpha^{3.02eV}_{(RS\therefore -SR)} n^{\tau}_{(RS\therefore -SR)}(\tau) + \alpha^{3.02eV}_{(e^-aq)} \cdot n^{\tau}_{e^-aq}(\tau) + \alpha^{3.02eV}_{(PTH^+)} \cdot n^{\tau}_{(PTH^+)}(\tau) \quad (18)$$

in which $\alpha^{3.02eV}_{(RS\therefore SR^-)} n^{\tau}_{(RS\therefore SR^-)}(\tau)$ represents the spectral contribution of nascent cystamine radical anion $(RS\therefore SR^-)_{aq}$.

From data of Figure 10, it can be underlined that cystamine affects the UV contribution of $[e^-]_{aq}$ but does not change the early level of photoinduced PTH^+ in micelles. The subpicosecond contribution of a neoformed radical anion $(RS\therefore SR^-)_{aq}$ to the total UV signal ($S^{3.02eV}_{max}$) is well-captured by the computed model (Table 4). The estimate of the early $(RS\therefore SR^-)_{aq}$

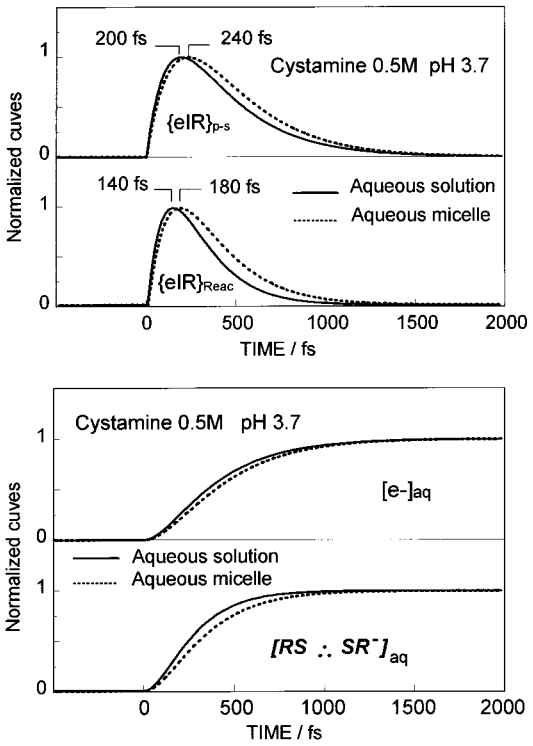

Figure 11. Comparative analysis of time-dependent IR−UV electronic channels with cystamine (0.5 M) in aqueous homogeneous solution and organized assemblies (CTAB: 0.07 M, PTH: 2×10^{-4} M).

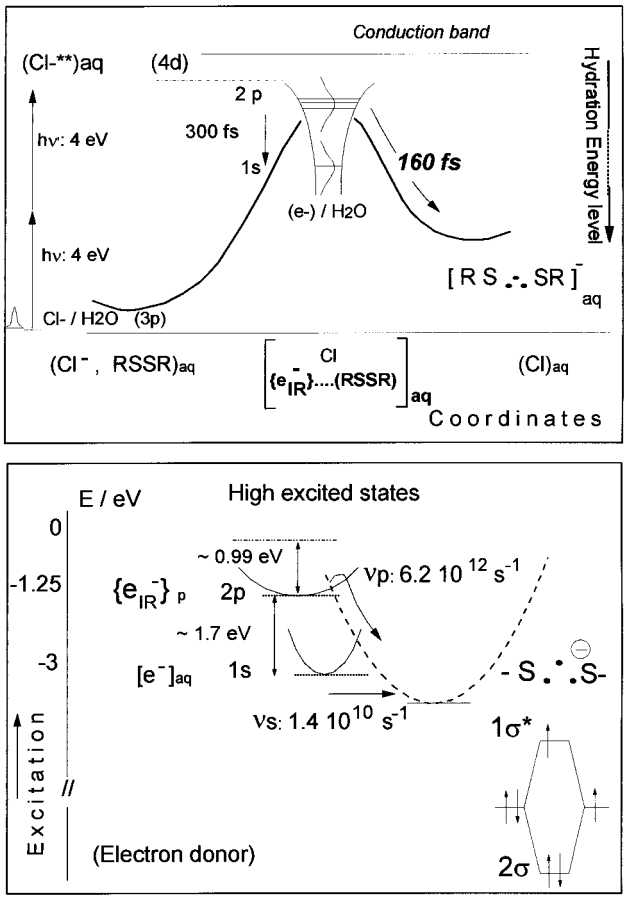

Figure 12. Energy level diagram of a one-electron reduction of cystamine in homogeneous aqueous solution. (A) In the prethermal regimen, the activated barrrier involves a crossing zone between a radiationless p → s transition and an efficient collapse of IR p-like state of excited electron on the disulfide bridge ($\nu_p = 1/T_{Reac}$). (B) The univalent reduction of cystamine by a s-state of hydrated electron follows a diffusion-controlled process ($\nu_s = 1/T_D$). This diffusive electron transfer is 4.4×10^2 times slower than that of the prehydration univalent reduction of cystamine by IR p-like excited electron $\{e^-_{IR}\}_{Reac}$.

population has been determined from the measured 3.02 eV signal amplitude assigned to the anionic radical and taking an exctinction coefficient of 8.2×10^3 M^{-1} cm^{-1}.[25] At 1.5 ps, the initial concentration of $(RS\therefore SR^-)_{aq}$ equal $7.4 \pm 0.2 \times 10^{-6}$ M. Simulatenously, taking an exctinction coefficient of 5.9×10^3 M^{-1} cm^{-1} [29] for PTH^+, we obtained an early concentration of $27 \pm 0.4 \times 10^{-6}$ M. These results suggest that if all electrons photodetached from PTH become prehydrated in the aqueous phase (Gouy−Chapman layer), then 25−30% of this IR electron population would participate to an ultrafast reduction of cystamine. This indirect UV estimate remains in good agreement with the calculated P_{Reac} value we have determined from femtosecond IR spectroscopy of p-like prehydrated electron.

4. Discussion

The present work deals with elementary steps of a prehydration univalent reduction of cystamine in homogeneous solution and organized assemblies. *The femtosecond UV−IR spectroscopies of primary electronic channels provide direct evidence for an ultrafast univalent reduction of disulfide biomolecule by IR p-like prehydrated electron.* Considering two different electron donors (Cl^-, PTH), these elementary steps involve a two-photon electron photodetachment process. A comparative analysis of elementary electron-transfer dynamics underlines some differences between homogeneous solution and cationic micelles (Figure 11). In aqueous CTAB/PTH micelles, the presence of an interfacial electric potential slowers the electron trapping process leading to IR p-like state of excited electron (T_1 Mic/T_1 Sol ≈ 2.1) but the nonadiabatic relaxation of $\{e^-_{IR}\}_{p\rightarrow s}$ remains similar to the internal conversion dynamics measured in homogeneous solution (T_2 Mic/T_2 Sol ≈ 0.9). Consequently, the level of $[e^-]_{aq}$ is completely filled in less than 2 ps. This result substantiates that the localization and solvation of the photodetached electron likely occurs in the Gouy−Chapman layer, far from the micellar surface. The similarity of T_2 in aqueous solution and aqueous CTAB micelles agrees with the fact that electron solvation takes place preferentially in the outer region of water boundary, that is, a region in which the local dielectric constant and ionic strength are similar to that of bulk water.

In presence of cystamine, the key point we have investigated concerns the early partition that occurs between IR reactive and nonreactive pathways. The kinetic models can account for all the major spectroscopic features seen in short-time. At pH 3.7, the influence of free hydrated proton on early IR electronic partition can be totally neglected because, even in concentrated acid solution, IR p-like excited electron does not react with hydronium ion.[74] In aqueous solutions, the femtosecond competition between the IR electron attachment on a sulfur−sulfur bond and the energy gap relaxation from the first excited state to the ground state of trapped electron is characterized by a high branching ratio ($P_{Reac} \approx 0.9$). The partitioning of donor and acceptor by surfactant molecules (CTAB micelles) reduces the probability of a prehydration reduction of cystamine by p-state IR electron (P_{Reac} Mic/P_{Reac} Sol ≈ 0.41) but does not significantly change the dynamics of this ultrafast electron transfer (T_{Reac}Sol/T_{Reac}Mic ≈ 1). This result emphasizes that a prehydration electron transfer on cystamine would be dependent on the local order of reactional area. The ultrafast electron-transfer argues for an efficient overlap between the p-like orbital

of an IR electron and those of SS bridge. The lifetime of $\{e^-_{IR}\}_{Reac}$ represents a temporal limit for that early rearrangements of SS bond energy facilitate an electron tunneling through a potential barrier separating the IR excited electron and that of an unpaired electron in a sulfur−sulfur radical anion $(RS\therefore SR^-)_{aq}$. At the microscopic level, this ultrafast one-electron transfer in the vicinity of a sulfur−sulfur bond would involve some distortions of p-like orbitals of excited electron.

Some complementary analyses have been performed between the ultrafast one-electron reduction of cystamine by IR excited electron (p-like state) and visible spectroscopy of fully hydrated electron (s state). As estimated by the short-time expression of C_{37}, the efficiency of disulfide molecules to interfer with IR nonequilibrium electron is 2 times higher in aqueous solutions than in micellar system (C_{37} Solution$_{(\tau = 1.2\ ps)}$/C_{37} Micelle$_{(\tau = 1.8\ ps)}$ = 0.46). In these two experimental systems, the prehydration formation of a three-electron bonded radical $(RS\therefore SR^-)_{aq}$ is achieved before the complete electron hydration. It can be also noticed that the prehydration reduction of cystamine by p-like state IR electron is 4.4×10^2 times faster than a diffusion-controlled reduction by $[e^-]_{aq}$ (Figure 12).

An important point investigated in this study concerns the prehydration formation of a disulfide radical anion characterized by a σ^* antibonding electron. This ultrafast radical reaction competes with a nonadiabatic electron hydration process. Previous experimental and theoretical works have established that sulfur-centered radicals with two-center three-electron bond (2c, 3e bond) exhibit an optical absorption in the UV or green region.[16−19,70,75] The absorption band is generally understood as a transition between the uppermost doubly occupied lone pair representing the σ energy level disturbed by a nonbonding-sulfur electron and the singly occupied sulfur−sulfur σ^* orbital ($2\sigma/1\sigma^*$).[17−19] Consequently, the energy of a S∴S bond is lower than a normal two-electron bond and an energy difference $a_g\{\sigma - n^-\}/b_u(\sigma^*)$ of about 2.5−3 eV corresponds to an UV transition. The real-time probing of a UV band buildup characterized by a maximum around 3.0 eV and a halfwidth of 0.6 eV substantiate that the subpicosecond formation of $(RS\therefore SR^-)_{aq}$ parallels the ultrafast prehydration reduction of cystamine. The position of the short-time UV band agrees with the nanosecond absorption spectrum of a cystamine radical anion, centered around 3.02 eV.[25] The ultrafast SS^- bond formation whose the strength is in the range 40−120 kJ mol^{-1} [18,21] raises a fundamental question about the efficient overlap between a nondegenerated p-like state of IR prehydrated electron ($2p_x$, $2p_y$, $2p_z$) and sulfur atom orbitals. The ultrafast attachment of a short-lived IR electron $\{e^-_{IR}\}_{Reac}$ on a disulfide molecule would be assisted by a solvent cage effect near the S∴S bond. With regard to the early spectral signature of a disulfide radical anion, works are in progress to extend our understanding of the real-time effects of a σ^* antibonded third electron and water molecules on the weakening of a disulfide bridge within a nascent 2c, 3e radical complex.

In conclusions, our femtosecond spectroscopic investigation provide new insight on the ultrafast univalent reduction of a disulfide biomolecule in a nondiffusive regim. The agreements we obtain betweeen short-time IR and UV spectroscopies substantiate that the prehydration one-electron reduction of cystamine by IR excited p-like electron leads to the subpicosecond formation of a three-electron bonded radical anion $(RS\therefore SR^-)_{aq}$. These results would open a new area of sulfur biochemistry and provide also guidance for further theoretical investigations on an early S−S bond weakening by reducing agents.

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