Thermodynamic changes associated with the formation of the hydrated electron after photoionization of inorganic anions: a time-resolved photoacoustic study †

Claudio D. Borsarelli,*ᵃ Sonia G. Bertolotti ᵇ and Carlos M. Previtali ᵇ

ᵃ *Instituto de Ciencias Químicas, Universidad Nacional de Santiago del Estero, Av. Belgrano (S) 1912, 4200 Santiago del Estero, Argentina. E-mail: cborsa@unse.edu.ar.*
ᵇ *Departamento de Química y Física, Universidad Nacional de Río Cuarto, Ruta 36. Km 601, 5800 Río Cuarto, Argentina*

The enthalpy and volume changes, ΔH and ΔV, associated with the 266 nm laser-induced photoionization reactions of aqueous ferrocyanide and iodide ions, to yield the hydrated electron, e^-_{aq}, and oxidized products were determined by temperature-dependent time-resolved photoacoustics. The photoionization quantum yield as function of temperature (9–30 °C) was determined by laser flash photolysis actinometry. The obtained values were used for the calculation of thermodynamic parameters associated with the formation of e^-_{aq}, such as the apparent partial molar volume, $V^\circ_{e^-} = 26$ cm³ mol⁻¹, and the standard formation enthalpy and entropy changes, $\Delta H^\circ_{f,e^-} = 31$ kJ mol⁻¹ and $T\Delta S^\circ_{f,e^-} = 338$ kJ mol⁻¹. These results indicate that the formation of the aqueous excess electron solution is governed by the increase in entropy in the three-dimensional hydrogen-bonding network of water.
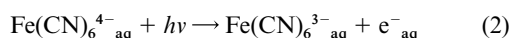
Introduction

The UV irradiation of the charge-transfer-to-solvent (CTTS) band of inorganic anions in water produces hydrated electrons and oxidized species (eqn. 1).[1–7]

$$X^-_{aq} + h\nu \longrightarrow (X^-_{aq})^* \longrightarrow X_{aq} + e^-_{aq} \qquad (1)$$
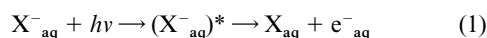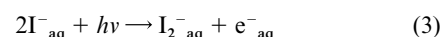
Photoionization reactions are charge-transfer processes that produce changes in the number and/or distribution of electrical charges after photon absorption. Therefore, important changes may be expected in the structure of the solvation sphere of the chemical species.[8] These processes are open to being studied by time-resolved photoacoustics (TRP). This technique has been widely employed to investigate enthalpy and volume changes of photoinduced reactions in solution.[9] In previous reports, we demonstrated the suitability of TRP to obtain volume changes and partial molar volumes of the hydrated proton,[10] of ionic species produced by speciation changes in photoinduced electron-transfer reactions,[11] and of ion radicals generated in photodissociation reactions.[12] The partial molar volumes are relevant parameters in elucidating structural inter-actions (*i.e.* ion–ion, ion–solvent, solvent–solvent) occurring in solution.[13]

In this report, the temperature dependence of the acoustic wave produced on laser flash excitation (266 nm, 20 ns fwhm) of ferrocyanide, $Fe(CN)_6^{4-}$, and iodide, I^-, ions in aqueous solutions was determined using TRP. The experimental data were analyzed in terms of thermal and volume contributions to the acoustic wave, and related to the corresponding enthalpy and volume changes, ΔH and ΔV, of the photoionization reactions. The photoionization reactions of $Fe(CN)_6^{4-}_{aq}$ and I^-_{aq} involve monophotonic fast dissociation, yielding simple ionic species[4,5] (eqn. 2 and 3), which can be easily detected by laser flash photolysis (LFP).[14]

$$Fe(CN)_6^{4-}_{aq} + h\nu \longrightarrow Fe(CN)_6^{3-}_{aq} + e^-_{aq} \qquad (2)$$

$$2I^-_{aq} + h\nu \longrightarrow I_2^-_{aq} + e^-_{aq} \qquad (3)$$

The aim of this paper is to obtain thermodynamic information concerning reactions 2 and 3 which is not easily obtained using conventional calorimetric and volumetric methods. This information can be related to the thermodynamic changes occurring upon formation of the hydrated electron, e^-_{aq}, which is a fundamental species with relevance in solution chemistry and in biological reactions.[15]

Experimental

Materials

Sodium iodide (99%) from Hopkins & Williams Ltd. (Chadwell Heath, Essex, UK) was used as received. Sodium chloride and sodium dichromate ($Na_2Cr_2O_7$) were of analytical grade from Merck Química Argentina (Buenos Aires, Argentina). Potassium ferrocyanide [$K_4Fe(CN)_6$] was of analytical grade from Ciccarelli (Buenos Aires, Argentina). Naphthalene was from Aldrich (Milwaukee, WI, USA) and used as received. Water was triply distilled.

Methods

Absorption spectra were recorded using a Shimadzu UV-2102PC spectrophotometer, operating with ±0.5 nm spectral resolution and a thermostated cuvette holder.

The experiments were performed with 0.1 M NaI and 0.5 mM $K_4Fe(CN)_6$ aqueous solutions. In all cases, the salt solutions were degassed by bubbling with water-saturated Ar for 20 min to reduce the scavenging of the hydrated electrons by dissolved O_2. The temperature range was 9.0–30.0 (±0.1) °C. The pH values of the solutions were monitored before and after each experiment, and, in all cases, they were unchanged (pH 6.5 ± 0.2).

Transient absorption spectra were measured with a home-made laser flash photolysis (LFP) system, described previously,[16,17] using a Spectron SL400 Nd-YAG laser generating 266 nm pulses (fwhm 20 ns) as the excitation source. The photoionization quantum yield (Φ_{e^-}) was determined by laser

---

† Dedicated to Professor Silvia Braslavsky, to mark her great contribution to photochemistry and photobiology particularly in the field of photothermal methods.

actinometry using the triplet–triplet absorption of naphthalene in hexane at 414 nm as the reference.[18]

The details of our time-resolved photoacoustic (TRP) set-up have been reported before.[17] The total laser energy beyond the rectangular slit (0.5 mm w × 5 mm h) was <100 μJ per pulse, measured with a Melles-Griot model 13PEM001 pyroelectric energy meter. The TRP signal handling and the deconvolution procedures were performed using a multi-exponential sequential kinetic model supplied by the Sound Analysis 3000 1.50D software (Quantum Northwest Inc., Spokane, WA, USA).

Typically, the absorbance of the solutions was *ca.* 0.5 at 266 nm and room temperature for both LPF and TRP experiments. Since the ground state absorption spectrum of iodide is dependent on temperature, due to changes in its hydration shell,[19] calibration curves of the NaI absorbance at 266 nm as a function of temperature were plotted, allowing correction of the absorbance values relative to that of the calorimetric reference (*ca.* 0.1 mM $Na_2Cr_2O_7$), which was temperature independent under our experimental conditions. For the TRP experiments with NaI, the reference solution of $Na_2Cr_2O_7$ was prepared in 0.1 M NaCl solution in order to obtain equivalent ionic strength and thermoelastic parameters, as was found previously for aqueous solutions of 0.1 M monovalent salts.[20,21] It was assumed that NaCl does not interfere with the experiments, since the chloride anion is transparent at 266 nm.

The photoionization quantum yield as function of temperature was also corrected for absorption changes in the NaI solutions. All the experiments were performed in duplicate.

Results and discussion

Laser flash photolysis experiments

Fig. 1 shows the transient absorption spectra of 0.5 mM $K_4Fe(CN)_6$ and 0.1 M NaI aqueous solutions observed after 50 ns and 8 μs of 266 nm laser excitation at room temperature. The spectra in Fig. 1 confirm that the e^-_{aq} species was formed immediately after the laser pulse, as indicated by the broad intense band centered at 720 nm.[14] The other transient products of eqn. 2 and 3 were also formed during the laser pulse excitation. This is clearly shown when the literature spectrum of e^-_{aq} (dotted line in Fig. 1) matched at 580 nm (where only the e^-_{aq} species absorbs) is compared with the experimental spectra. For the ferrocyanide solution, a small absorption shoulder is observed at 420 nm due to the weak absorption of the oxidized product $Fe(CN)_6^{3-}_{aq}$ ($\varepsilon_{420} = 1030$ M^{-1} cm^{-1}).[1] In the case of the iodide solutions, in addition to the sharp band at 380 nm

($\varepsilon_{380} = 9400$ M^{-1} cm^{-1}),[14] a small contribution from a broad band due to $I_2^-{}_{aq}$, with a maximum at 750 nm ($\varepsilon_{750} = 3000$ M^{-1} cm^{-1}),[14] is observed. The $I_2^-{}_{aq}$ species is formed by the reaction between the neutral iodine atoms I_{aq}, formed after electron photodetachment, and the excess I^-_{aq} (eqn. 4 and 5).[14]

$$I^-_{aq} + h\nu \longrightarrow I_{aq} + e^-_{aq} \qquad (4)$$

$$I_{aq} + I^-_{aq} \longrightarrow I_2^-{}_{aq} \qquad (5)$$
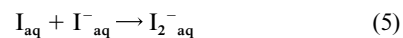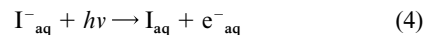
Under the present iodide concentration, and assuming a rate constant value of 5×10^9 M^{-1} s^{-1} as the diffusional limit in aqueous media, it can be expected that reaction 5 occurs in <2 ns. Thus, the global reaction 3 is completely produced during the laser pulse excitation, as shown in Fig. 1. The transient species decayed with an average lifetime of 2.0 ± 0.5 μs, depending on temperature, assuming a first-order law. However, strictly speaking, the decays show a bi-exponential behavior. At 8 μs after the laser pulse, the absorption band due to the hydrated electron has almost disappeared, and the remaining spectra are due to the $Fe(CN)_6^{3-}_{aq}$ and $I_2^-{}_{aq}$ species (Fig. 1). This result indicates that e^-_{aq} decays faster than the other species within the microsecond timescale, probably due to efficient reactions with residual dissolved oxygen and protons,[22] in addition to the recombination reaction with the oxidized species $Fe(CN)_6^{3-}_{aq}$ or $I_2^-{}_{aq}$, respectively. This assumption accounts for the bi-exponential decay behavior observed in all cases (Fig. 1).

Transient actinometry was used to determine the quantum yields of hydrated electrons (Φ_{e^-}). The change in absorption of the hydrated electron was selected at 720 nm ($\varepsilon_{720} = 19\,000$ M^{-1} cm^{-1})[14] for the photolysis of ferrocyanide and at 580 nm ($\varepsilon_{580} = 10\,900$ M^{-1} cm^{-1})[14] for the iodide solutions in order to avoid interference by the $I_2^-{}_{aq}$ species (*vide supra*).[14,18] The triplet–triplet absorption of naphthalene in cyclohexane at 414 nm ($\varepsilon_{414} = 22\,000$ M^{-1} cm^{-1}, $\Phi_T = 0.75$)[18] was used as the reference. The Φ_{e^-} values were determined in the same temperature range as for the TRP experiments (see below). Plots of the extrapolated initial absorbance change, $\Delta Abs(t = 0)$, at the monitored wavelength *vs.* the laser energy are linear with zero intercepts (Fig. 2), confirming the monophotonic nature of the photoionization reactions.[2,5] The Φ_{e^-} values were obtained from the ratio of the slopes in Fig. 2 and using the absorption coefficients given above. They are presented in Table 1 as a function of temperature.

The Φ_{e^-} values at room temperature presented in Table 1 are in agreement with previous reports.[1,6] The small increase in the quantum yields with temperature probably indicates an increment on the escape efficiency of the ionic species from the geminate pair.
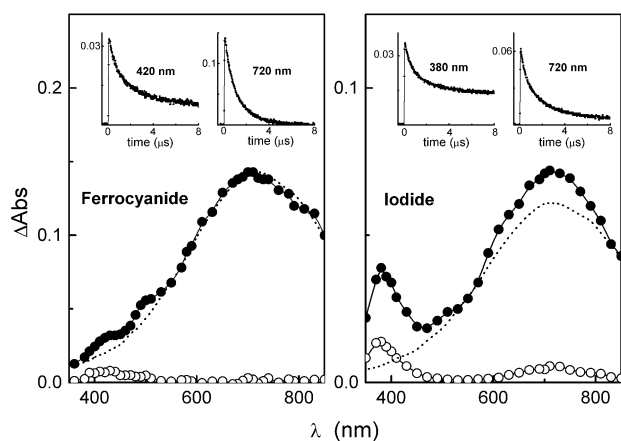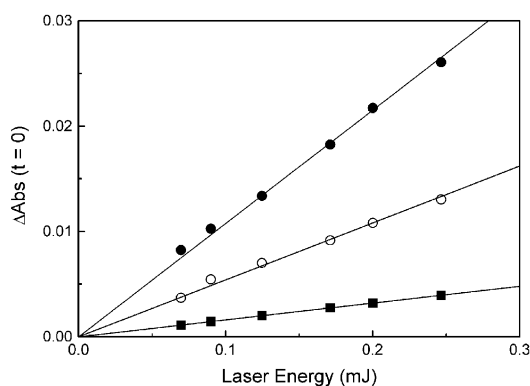

Fig. 1 Transient absorption spectra of 0.5 mM $K_4Fe(CN)_6$ (left) and 0.1 M NaI (right) aqueous solutions upon 266 nm laser excitation observed at (●) 50 ns and (○) 8 μs after the laser pulse. The dotted line represents the spectrum of the hydrated electron from ref. 14, normalized at 580 nm, where the $Fe(CN)_6^{3-}_{aq}$ and $I_2^-{}_{aq}$ species do not absorb (see text for details). The insets show transient decays observed at the maximum wavelengths.

Fig. 2 Initial absorbance change [$\Delta Abs(t = 0)$] *vs.* laser energy at 25 °C: (●) naphthalene in cyclohexane (reference); (○) aqueous 0.5 mM $K_4Fe(CN)_6$; (■) aqueous 0.1 M NaI. Monitored at 414, 720, and 580 nm, respectively (see text for details).

Table 1 Photoionization quantum yield (Φ_{e^-}) thermoelastic parameters ratio ($c_p\rho/\beta$), and prompt amplitude of the photoacoustic signal (φ) as a function of temperature

Temp./°C	0.5 mM Fe(CN)$_6$K$_4$			0.1 M NaI		
	Φ_{e^-}[a]	$(c_p\rho/\beta)$[b]/kJ cm^{-3}	φ[c]	Φ_{e^-}[a]	$(c_p\rho/\beta)$[b]/kJ cm^{-3}	φ[c]
9				0.24	33.9	0.67
9.5	0.43	50.5	4.03			
11				0.26	27.8	0.69
12	0.43	36.5	3.22			
13				0.28	21.9	0.76
15	0.44	28.2	2.30			
19	0.44	21.6	2.08	0.28	17.7	0.79
22				0.28	15.0	0.80
25	0.44	15.9	1.59			
30	0.45	13.2	1.58	0.29	12.9	0.81

Experimental errors: [a] ±10%, [b] ±10%, [c] ±5%.

Time-resolved photoacoustic measurements

In order to estimate the enthalpy and reaction volume changes of reactions 2 and 3, temperature-dependent time-resolved photoacoustic (TRP) measurements were performed under the same experimental conditions as for the LPF experiments. In all cases, the plots of TRP signal amplitude *vs.* laser energy were linear with zero intercepts (data not shown), indicating that bi-photonic processes or signal saturation do not take place.

The analysis of the TRP signals was performed using a deconvolution procedure described elsewhere.[23] In TRP experiments the signal function, $S(t)$, is the convolution of the instrumental function, $R(t)$ (the signal of the calorimetric reference), and the sample function, $H(t)$ (eqn. 6 and 7),[23]

$$S(t) = R(t) \otimes H(t) \tag{6}$$

with

$$H(t) = \sum_i \frac{\varphi_i}{\tau_i}\exp\left(-\frac{t}{\tau_i}\right) \tag{7}$$

where φ_i and τ_i are the reference-normalized amplitude factor and lifetime for the *i*th component of the TRP signal, respectively. In the present case, only the prompt component of the acoustic signal yields information associated with the reactions 2 and 3. As was mentioned earlier, these processes occur much faster than the time resolution limit of our experimental set-up (*ca*. 20 ns).[4,5] However, the acoustic wave also contains contributions from the decay processes of the photoionization products occurring on the microsecond timescale. Therefore, a multi-exponential deconvolution procedure was applied (data not shown), allowing the precise separation of the prompt (<20 ns) amplitude factors (φ) corresponding to the non-radiative processes forming the e$^-_{aq}$ and the oxidized species Fe(CN)$_6^{3-}$$_{aq}$ and I$_2^-$$_{aq}$ from those corresponding to the decay processes of these species on the microsecond timescale. The lifetimes of the slower components of the TRP signals were coincident with those from the LPF experiments (*ca*. 2.0 ± 0.5 μs, see above). This result allows a precise separation of the prompt and slow components of the TRP signals by deconvolution techniques, since both processes are separated in time by more than two orders of magnitude.[23]

Table 1 shows the amplitude factor values for the prompt component of the TRP signal as a function of temperature. The thermal and the volume change contributions to the acoustic wave for the prompt component of the TRP signal were separated using the temperature variation method, which is based on the dependence of φ on the thermoelastic parameters of the solvent, $c_p\rho/\beta$ (eqn. 8),[9] where E_{266} is the excitation molar energy

$$E_{266}\,\varphi = q + \Phi_{e^-}\Delta V\left(\frac{c_p\rho}{\beta}\right) \tag{8}$$

at 266 nm ($\equiv$ 450 kJ mol^{-1}). c_p, ρ, and β are the specific heat capacity, the mass density, and the cubic expansion coefficient of the solvent, respectively.[24] In water, β is strongly dependent on temperature.[24] Thus, the $c_p\rho/\beta$ ratio can be varied almost fourfold by changing the temperature of the solution between 9 and 30 °C. It is well known that the addition of electrolytes at concentrations >10 mM changes the thermoelastic parameters of water.[25] Therefore, the values of $c_p\rho/\beta$ for 0.1 M salt solutions at different temperatures were obtained by comparing the photoacoustic amplitude signal of the calorimetric reference in water and in the solution used, as described previously.[10,11,25] The corrected values of the $c_p\rho/\beta$ ratio for 0.1 M salt solutions are also presented in Table 1.

In eqn. 8, the term q represents the prompt heat released during the photoionization reaction, which is related to the reaction enthalpy change by eqn. 9.

$$q = E_{266} - \Phi_{e^-}\Delta H \tag{9}$$

Combining eqn. 8 and 9, a more convenient expression is obtained:[12]

$$\frac{E_{266}\,(\varphi - 1)}{\Phi_{e^-}} = -\Delta H + \Delta V\left(\frac{c_p\rho}{\beta}\right) \tag{10}$$

Fig. 3 shows the plots of the left-hand term of eqn. 10 *vs.* the $c_p\rho/\beta$ ratio for the studied solutions. The plots were linear, as predicted by eqn. 10, and the intercepts and slopes correspond to the ΔH and ΔV values, respectively, for reactions 2 and 3
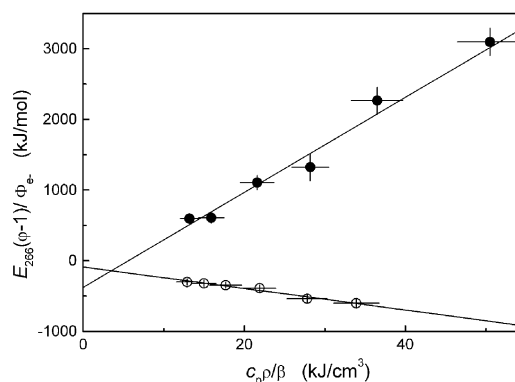

Fig. 3 Plots of eqn. 10 for the prompt component of the photoacoustic signal (τ < 20 ns) produced after 266 nm laser excitation in (○) 0.1 M NaI and (●) 0.5 mM K$_4$Fe(CN)$_6$ aqueous solutions.

Table 2 Enthalpy and volume changes (ΔH and ΔV, respectively) for the UV photoionization reactions of $Fe(CN)_6{}^{4-}{}_{aq}$ and $I^-{}_{aq}$ determined *via* time-resolved photoacoustic measurements

Solution	ΔH/kJ mol^{-1}	ΔV/cm^3 mol^{-1}
0.5 mM K$_4$Fe(CN)$_6$	377 ± 125	67 ± 6
0.1 M NaI	88 ± 30	−15 ± 1

(Table 2). Correction of the ΔV value for ionic strength effects in the 0.1 M NaI solutions resulted in ~0.3 cm^3 mol^{-1}, applying the extended Debye–Hückel equation derived by Pitzer.[26] This value is within the experimental error for ΔV (±1 cm^3 mol^{-1}); thus, in the present case, the ionic strength effect can be neglected.

The partial molar volumes of $e^-{}_{aq}$ and $I_2{}^-{}_{aq}$

At first sight, the volume change data in Table 2 seem contradictory when the ferrocyanide and iodide solutions are compared. However, it must be remembered that the experimental volume change, ΔV, represents the difference between the standard partial molar volume ($V^\circ{}_i$) of the products and reactants of the studied reactions, which are dependent on the individual contributions of the chemical species.[27] $V^\circ{}_i$ represents the actual molar volume of the ion in the aqueous environment. In addition to the intrinsic van der Waals volume, $V^\circ{}_i$ contains also contributions from hydration, electrostatic interactions, and structuring of water molecules around the ions.[28] For example, for reaction 2, it can be written

$$\Delta V = (V^\circ{}_{Fe(CN)_6{}^{3-}} + V^\circ{}_{e^-}) - V^\circ{}_{Fe(CN)_6{}^{4-}} = 67 \text{ cm}^3 \text{ mol}^{-1} \quad (11)$$

The experimental $V^\circ{}_i$ values for the $Fe(CN)_6{}^{4-}$ and $Fe(CN)_6{}^{3-}$ ions are 96 and 137 cm^3 mol^{-1}, respectively.[28] Therefore, eqn. 11 allows us to obtain an estimate of the 'apparent' partial molar volume of the hydrated electron, *i.e.* $V^\circ{}_{e^-} = 26$ cm^3 mol^{-1}.

The conventional picture for the ground state of the equilibrated solvated electron in polar solvents (water, ammonia, alcohols, *etc.*) includes the formation of a cavity (bubble) comparable in size with the solvent intermolecular distance.[29] Quantum molecular dynamics calculations confirm that the ground state charge distribution is s-type and roughly spherical.[30] Thus, if a spherical shape for the electron cavity is assumed, the experimental value of $V^\circ{}_{e^-} = 26$ cm^3 mol^{-1} corresponds to a spherical volume with a radius of 2.18 Å, which is in remarkable agreement with the radius of the hydrated electron cavity obtained from theoretical calculations (1.94–2.33 Å).[29]

In turn, the standard partial molar volume of $I^-{}_{aq}$ is 42 cm^3 mol^{-1},[28] but V° for $I_2{}^-{}_{aq}$ is unknown, due to its transient nature. However, using the experimental ΔV and $V^\circ{}_{I^-}$, values together with the calculated $V^\circ{}_{e^-}$, an estimate of $V^\circ{}_{I_2{}^-}$ can be obtained, in accord with eqn. 12.

$$\Delta V = (V^\circ{}_{I_2{}^-} + V^\circ{}_{e^-}) - 2V^\circ{}_{I^-} = -15 \text{ cm}^3 \text{ mol}^{-1} \quad (12)$$

The calculation yields $V^\circ{}_{I_2{}^-} = 43$ cm^3 mol^{-1}, which is a reasonable value considering that the sum of $V^\circ{}_{I^-}$ and the van der Waals volume of the neutral iodine atom ($V_I \approx 6$ cm^3 mol^{-1}, calculated on the basis of a spherical atom with a radius of 1.33 Å)[24] is 48 cm^3 mol^{-1}. The calculated value is also in line with the experimental value of 63 cm^3 mol^{-1} for the larger $I_3{}^-$ ion.[28]

Enthalpy and entropy of formation of $e^-{}_{aq}$

The experimental ΔH values in Table 2 can be related to the difference between the standard enthalpy of formation ($\Delta H^\circ{}_f$) of the ionic products and reactant. In particular, for the photoionization of iodide, the experimental ΔH value can be expressed as eqn. 13.

$$\Delta H = (\Delta H^\circ{}_{f,I_2{}^-} + \Delta H^\circ{}_{f,e^-}) - 2\Delta H^\circ{}_{f,I^-} = 88 \text{ kJ mol}^{-1} \quad (13)$$

In order to calculate $\Delta H^\circ{}_{f,e^-}$ from eqn. 13, it is necessary to know $\Delta H^\circ{}_f$ for $I_2{}^-{}_{aq}$ and $I^-{}_{aq}$. The reported value of $\Delta H^\circ{}_f$ for $I^-{}_{aq}$ is −55.3 kJ mol^{-1},[24] but, of course, no data is available for $I_2{}^-{}_{aq}$. Nevertheless, an estimate of $\Delta H^\circ{}_{f,e^-}$ can be made if it is assumed that the $\Delta H^\circ{}_f$ for $I_2{}^-{}_{aq}$ is between the reported values for $I^-{}_{aq}$ and $I_3{}^-{}_{aq}$ (−51.5 kJ mol^{-1}).[24] Thus, assuming an average value of $\Delta H^\circ{}_f = -53.6$ kJ mol^{-1} for $I_2{}^-{}_{aq}$, eqn. 12 yields $\Delta H^\circ{}_{f,e^-} = 31$ kJ mol^{-1}. Unfortunately, to our knowledge, no $\Delta H^\circ{}_f$ data for $Fe(CN)_6{}^{4-}{}_{aq}$ and $Fe(CN)_6{}^{3-}{}_{aq}$ are available in order to use the measured ΔH value of reaction 2 for a second set of calculations of $\Delta H^\circ{}_{f,e^-}$.

However, our calculated $\Delta H^\circ{}_{f,e^-}$ and $V^\circ{}_{e^-}$ values can be compared with the free energy of the equilibrated ground state of the hydrated electron of −3.2 eV (≡ 309 kJ mol^{-1}).[30,31] In previous reports, we proposed the empirical relationship $X\Delta V = T\Delta S$, with the empirical constant $X = 13 \pm 1$ kJ cm^{-3}, applied for the solvent hydrogen-bonding rearrangement produced in intra- and intermolecular electron-transfer reactions in aqueous solutions of 0.1 M monovalent salts.[20,21] The units of the empirical constant X are those of the $c_p\rho/\beta$ ratio. Linear correlations between ΔV and ΔS in aqueous media have been reported for several inorganic and organic systems.[32] The formation of the hydrated electron cavity should produce a hydrogen-bonding reorganization in the three-dimensional hydrogen-bonding water network. Thus, using the above empirical relationship with $V^\circ{}_{e^-} = 26$ cm^3 mol^{-1}, we obtain $T\Delta S = 338$ kJ mol^{-1}. Because the thermodynamic identity $\Delta G^\circ{}_{f,e^-} = \Delta H^\circ{}_{f,e^-} - T\Delta S^\circ{}_{f,e^-}$ must be obeyed, our experimental $\Delta H^\circ{}_{f,e^-}$ and $T\Delta S^\circ{}_{f,e^-}$ values yield $\Delta G^\circ{}_{f,e^-} = -307$ kJ mol^{-1}, in complete agreement with the reported free energy for the ground state of the hydrated electron (see above), supporting the calculation procedures for $\Delta H^\circ{}_{f,e^-}$ and $T\Delta S^\circ{}_{f,e^-}$. In addition, these results suggest that the formation of excess electrons is governed by an increase in the entropy in the system, arising from the reorganization of the three-dimensional hydrogen-bonding network of water.

In summary, we have demonstrated the use of the time-resolved photoacoustic technique for the study of photoionization reactions in water. The experimental enthalpy and volume changes obtained allowed, for first time, a direct calculation of thermodynamic parameters associated with the formation of the hydrated electron, *i.e.* $\Delta H^\circ{}_{f,e^-}$, $T\Delta S^\circ{}_{f,e^-}$, and $V^\circ{}_{e^-}$, and the V° value of the transient anion $I_2{}^-{}_{aq}$. These fundamental parameters can be used in the study of further photoionization reactions for thermodynamic calculations involving other transient or stable reaction species.

Acknowledgements

References

1 M. Shirom and G. Stein, Excited state chemistry of the ferrocyanide ion in aqueous solution. I. Formation of the hydrated electron, *J. Chem. Phys.*, 1971, **55**, 3372–3378.
2 U. Lachish, A. Shafferman and G. Stein, Intensity dependence in laser flash photolysis experiments: hydrated electron formation from ferrocyanide, tyrosine, and tryptophan, *J. Chem. Phys.*, 1976, **64**, 4205–4211.
3 A. Horváth, J. Szõke and L. Wojnárovits, Mechanism of photo-induced redox reactions in aqueous solutions of [Fe(bpy)(CN)$_4$]$^{2-}$, *Inorg. Chim. Acta*, 1991, **179**, 97–104.
4 F. H. Long, H. Lu and K. B. Eisenthal, Femtosecond studies of electron photodetachment from simple ions in liquid water: solvation and geminate recombination dynamics, *J. Chem. Phys.*, 1989, **91**, 4413–4414.

5 J. A. Kloepfer, V. H. Vilchiz, V. A. Lenchenkov and S. E. Bradforth, Femtosecond dynamics of photodetachment of the iodide anion in solution: resonant excitation into charge-transfer-to-solvent state, *Chem. Phys. Lett.*, 1998, **298**, 120–128.

6 A. Iwata, N. Nakashima, M. Kusaba, Y. Izawa and C. Yamanaka, Quantum yields of hydrated electrons by UV laser irradiation, *Chem. Phys. Lett.*, 1993, **207**, 137–142.

7 K. L. Stevenson, Prompt and delayed photoejection of electrons in aqueous solution, *J. Am. Chem. Soc.*, 1996, **118**, 6088–6089.

8 E. Whalley, Some comments on electrostatic volumes and entropies of solvation, *J. Chem. Phys.*, 1963, **38**, 1400–1405.

9 S. E. Braslavsky and G. E. Heibel, Time-resolved photothermal and photoacoustic methods applied to photoinduced processes in solution, *Chem. Rev.*, 1992, **92**, 1381–1410.

10 C. D. Borsarelli and S. E. Braslavsky, The partial molar volume of the proton in water determined by laser-induced optoacoustic studies, *J. Photochem. Photobiol., B*, 1998, **43**, 222–228.

11 C. D. Borsarelli, H. Corti, D. Goldfarb and S. E. Braslavsky, Structural volume changes in photoinduced electron transfer reactions. Laser-induced optoacoustic studies of speciation during the quenching reaction of excited $Ru(bpy)_3^{2+}$ by Fe(III) in aqueous solutions, *J. Phys. Chem. A*, 1997, **101**, 7718–7724.

12 M. A. Brusa, M. S. Churio, M. A. Grela, S. G. Bertolotti and C. M. Previtali, Reaction volume and reaction enthalpy upon aqueous peroxodisulfate dissociation: $S_2O_8^{2-} \longrightarrow 2SO_4^{\cdot-}$, *Phys. Chem. Chem. Phys.*, 2000, **2**, 2383–2387.

13 F. Millero, The molal volume of electrolytes, *Chem. Rev.*, 1971, **71**, 147–176.

14 G. L. Hug, *Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solution*, National Standard Reference Data System, U.S. National Bureau of Standards, Washington, DC, 1981 and references therein.

15 E. J. Hart and M. Anbar, *The Hydrated Electron*, Wiley, New York, 1970.

16 C. D. Borsarelli, J. J. Cosa and C. M. Previtali, Interface effect on the properties of exciplexes formed between pyrene derivatives and *N,N*-dimethylaniline in reverse micelles, *Langmuir*, 1993, **9**, 2895–2901.

17 C. D. Borsarelli, S. G. Bertolotti and C. M. Previtali, Thermodynamic changes in the photoinduced proton-transfer reaction of the triplet sate of safranine-T, *Photochem. Photobiol. Sci.*, 2002, **1**, 574–580.

18 I. Carmichael and G. L. Hug, Triplet-Triplet absorption spectra of organic molecules in condensed phases, *J. Phys. Chem. Ref. Data*, 1986, **15**, 1–250.

19 *Fundamentals of UV-Visible Spectroscopy: A Workbook*, Hewlett-Packard Company, Germany, 1998, p. 56.

20 C. D. Borsarelli and S. E. Braslavsky, Volume changes correlate with enthalpy changes during the photoinduced formation of the ³MLCT state of ruthenium(II) bipyridine cyano complexes in the presence of salts. A case of entropy-enthalpy compensation effect, *J. Phys. Chem. B*, 1998, **102**, 6231–6238.

21 C. D. Borsarelli and S. E. Braslavsky, Enthalpy, volume, and entropy changes associated with the electron transfer reaction between the ³MLCT state of $Ru(bpy)_3^{2+}$ and methylviologen cation in aqueous solutions, *J. Phys. Chem. A*, 1999, **103**, 1719–1727.

22 G. V. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($^{\cdot}OH/^{\cdot}O^-$) in aqueous solutions, *J. Phys. Chem. Ref. Data*, 1988, 173–184.

23 J. E. Rudzki, J. L. Goodman and K. S. Peters, Simultaneous determination of photoreaction dynamics and energetics using pulsed, time-resolved photoacoustic calorimetry, *J. Am. Chem. Soc.*, 1985, **107**, 7849–7854.

24 *CRC Handbook of Chemistry and Physics*, ed. R. C. Weast, CRC Press, Boca Raton, FL, 67th edn., 1986–87.

25 M. S. Churio, K. P. Angermund and S. E. Braslavsky, Combination of laser-induced optoacoustic spectroscopy (LIOAS) and semiempirical calculations for the determination of molecular volume changes. The photoisomerization of carbocyanines, *J. Phys. Chem.*, 1994, **98**, 1776–1782.

26 K. S. Pitzer, Thermodynamics of electrolytes. I. Theoretical basis and general equations, *J. Phys. Chem.*, 1973, **77**, 268–277.

27 R. Schmidt, Interpretation of reaction and activation volumes in solution, *J. Phys. Chem. A*, 1998, **102**, 9082–9086.

28 Y. Markus, Thermodynamics of solvation of ions. Part 6. The standard partial molar volumes of aqueous ions at 298.15 K, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 713–718.

29 I. Rips and M. Tachiya, Equilibrium properties of the solvated electron in polar liquids: Finite solvent size effects, *J. Chem. Phys.*, 1997, **107**, 3924–3929 and references therein.

30 D. Borgis and S. Bratos, Theoretical description of the hydrated electron. Shape and spectroscopic properties of the cavity containing the excess electron, *J. Mol. Struct.*, 1997, **436–437**, 537–541.

31 M. Assel, R. Laenen and A. Laubereau, Retrapping and solvation dynamics after femtosecond UV excitation of the solvated electron in water, *J. Chem. Phys.*, 1999, **111**, 6869–6874.

32 J. C. Phillips, Enthalpy/entropy and volume/entropy activation ratios and solute-solvent interactions, *J. Phys. Chem.*, 1985, **89**, 3060–3066 and references therein.