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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

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Laser-induced optoacoustic spectroscopy has been applied to the photoinduced electron-transfer reaction between $Ru(bpy)_3^{2+}$ and various salts of Fe(III) [$Fe(ClO_4)_3$, $Fe_2(SO_4)_3$, and $FeCl_3$]. The reaction volume changes associated with photoinduced ligand exchange derived from these measurements allowed the determination of partial molar volumes at high dilutions of several species such as $FeSO_4$, $FeSO_4^+$, $Fe(SO_4)_2^-$, $Fe(OH)^{2+}$, $FeCl^+$, $FeCl^{2+}$, and $FeCl_2^+$, not attainable from other techniques. The volume change of oxidation of $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$ at high dilution was also calculated.

Introduction

In a recent study by laser-induced optoacoustic spectroscopy (LIOAS[1]), at different temperatures, we observed that the intermolecular photoinduced electron-transfer reaction A between the MLCT state (largely of triplet character) of the ruthenium(II)−tris(bipyridyl) complex, $Ru(bpy)_3^{2+}$, and Fe(III) in sulfuric acid media is accompanied by a volume contraction, ΔV_R, of 11 cm³/mol[2].

$$Ru(bpy)_3^{2+} + Fe^{3+}_{(aq)} \xrightarrow{h\nu} Ru(bpy)_3^{3+} + Fe^{2+}_{(aq)} \quad (A)$$

This relatively large contraction could not be explained only in terms of simple bond changes in the reactants after light absorption, since the electron-transfer reaction reduces the quencher [Fe(III)/Fe(II)] leading to a small expansion and oxidizes $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$, probably leading to a contraction [smaller than the expansion Fe(III)/Fe(II)] of the ligands around the metal. As a result, the volume change observed was largely attributed to a difference in the medium reorganization around the system present after the time window of the LIOAS experiment (ca. 600 ns[1,2]). The enthalpic change (ΔH_R) for reaction A obtained by LIOAS was in good agreement with the literature value of 112 kJ/mol obtained for the spontaneous back electron-transfer reaction between $Ru(bpy)_3^{3+}$ and Fe(II).[3]

As pointed out by Pollmann et al.,[4] the reaction volume change, ΔV_R, may be composed of at least two contributions: (1) an internal variation (ΔV_{int}) due to differences in bond length and/or angles between products and reactants and (2) a variation (ΔV_{ext}) due to reorganization in the solvation shell of the solutes induced by the charge redistribution (ion−solvent interactions) (eq 1)

$$\Delta V_R = \Delta V_{int} + \Delta V_{ext} \quad (1)$$

Following an electron-transfer reaction such as A, water reorganization is expected as a result of changes in the ion sizes, although there is no change in the net charge in the reaction. In principle, the external volume change can be ascribed to electrostriction (organization of the solvent due to a change in charge) and can be calculated using the Drude−Nernst eq 2.[5]

$$V_{(elec)} = \frac{(ze)^2}{2r\epsilon}\frac{\partial(\ln \epsilon)}{\partial p} = -\frac{Bz^2}{r} \quad (2)$$

which describes the contraction of the solvent molecules due to the electric field of an ion of charge z and radius r. The model is relatively simple and assumes that the solvent is a continuum of dielectric constant ϵ interacting with hard sphere ions only through Coulombic forces. The volume change due to electrostriction, $V_{(elec)}$, is thus related to the partial derivative of ln ϵ with respect to the pressure p. In water at 25 °C the theoretical value of constant B is 4.175.[6] However, experimental results have shown that higher B values are needed to explain the partial molar volume of ions in water.[6] The Drude−Nernst model is, however, qualitatively correct to describe the charge and size effects on the ionic volumes in solution. Taking into account that $Fe^{3+/2+}_{(aq)}$ ions are smaller than the $Ru(bpy)_3^{2+/3+}$ complex ions, a qualitative analysis of eq 2 predicts also a *volume expansion* by electrostriction effects after reaction A, and not a volume contraction as observed.[2] It appears that ΔV_R for this reaction is dominated by additional processes, such as changes in the chemical nature of the species, since $Fe^{3+}_{(aq)}$, upon reduction to $Fe^{2+}_{(aq)}$ in sulfuric acid undergoes ligand exchange reactions in its first coordination sphere (speciation). In fact, it has been shown that the rate constant for the back electron-transfer reaction between $Ru(bpy)_3^{3+}$ and Fe(II) cation is several orders of magnitude lower than the diffusional rate and strongly dependent on the composition of the solution, indicating specific effects of the counterions on the rate of the reaction.[7]

To analyze in more detail the origin of the volume changes obtained for reaction A, we present in this report a LIOAS study of the reaction performed with different Fe(III) salts, i.e., perchlorate, chloride, and sulfate, in their respective acid solutions.

LIOAS is the method of choice for studying volume changes of photoinduced processes producing either stable products or transient species in the nanosecond to microsecond time domain.[1,8,9] The experiment consists of measuring the pressure

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wave evolved in a medium after pulse excitation (see for example refs 1,2,8−11). Two processes contribute to the volume change in the solution (leading to the pressure pulse): (i) a thermal term (ΔV_{th}) due to radiationless deactivation and dependent on the thermoelastic parameters of the solution and (ii) a reaction (structural) term (ΔV_R, in turn described by eq 1), independent of these parameters.[11] In aqueous solutions the two terms are separated by measuring the pressure wave at various temperatures, thus taking advantage of the strong temperature dependence of the expansion coefficient, β, of water.

LIOAS has been chosen in the past as an appropriate analytical technique in order to measure speciation at high dilutions, due to its intrinsic higher sensitivity than that of regular absorption techniques.[12,13] Detection of the photothermal effect after absorption of a laser pulse is potentially more sensitive than conventional absorption by ca. 2−3 orders of magnitude.[14] This high sensitivity can be used advantageously to measure other properties such as thermodynamic properties at very high dilutions. In particular, the partial molar volume of metastable species can be obtained from these measurements.

The results of the present study show that ΔV_R for the reaction strongly depends on the nature of the Fe(III) salt and/or on the medium composition, whereas the ΔH_R value is independent of these factors. We describe a chemical model which accounts for the experimental data and allows the assignment of volume changes to the oxidation of $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$ and the partial molar volumes of species for which data are not obtainable by other methods.

Experimental Section

$Ru(bpy)_3Cl_2 \cdot 6H_2O$, $Fe(ClO_4)_3 \cdot 9H_2O$, $FeCl_3 \cdot 6H_2O$, $Fe_2(SO_4)_3 \cdot 5H_2O$, Na_2SO_4, NH_4Cl, NaCl, $HClO_4$, HCl, and H_2SO_4 were obtained from Aldrich and Fluka in the highest purity available and used as received.

The LIOAS setup was the same as described in previous reports.[2,10] Essentially, it consists of a 15 ns, 500 nm laser pulse produced by a FL2000 Lambda Physik-EMG 101 MSC excimer laser (XeCl, repetition rate 1−2 Hz), pumping a Coumarin 307 (Radiant Dyes Chemie) laser dye. The fluence of the pulses was varied by a neutral density filter and measured with a pyroelectric energy meter (RJP735 head connected to a meter RJ7620 Laser Precision Corp.). The pressure pulse was detected with a Pb−Zr−Ti ceramic transducer pressed against the side wall of a quartz cuvette parallel to the laser beam direction. The signal was amplified 100 times (two Comlinear E103 amplifiers) and fed into a transient recorder (Tektronix TDS 684A, operating at 500 megasample/s). Between 200 and 400 signals were averaged and transferred to a VAX station 3100 coupled to a VAX mainframe.

Absorption spectra were registered with a Shimadzu UV-2102PC spectrophotometer. The concentration of $Ru(bpy)_3^{2+}$ was 7.5×10^{-5} M and the absorbances of the samples at 500 nm were matched within 3% to those of the calorimetric reference solution, $Na_2Cr_2O_7$, in the same quencher solution. At 500 nm the absorbance of the quencher solutions was less than 2% of the absorbance of the calorimetric reference. The temperature range for the LIOAS experiments was 30−8 °C, controlled to ±0.1 °C. The samples were deoxygenated by bubbling with water-saturated argon for 10−15 min. The laser beamwidth was shaped with a slit (0.8 × 6) mm, so that the effective acoustic transit time ($\tau_a = w/v_a$; where w = width of beam and v_a = sound velocity), i.e., the heat integration time,[2] was ca. 600 ns. This allowed for a time resolution of 50−60 ns using deconvolution techniques.[15,16]

In all cases, linear dependency with zero intercept for the optoacoustic signal amplitude (H) with the laser fluence was observed, up to 8−10 μJ/pulse. To avoid multiphotonic processes, the LIOAS measurements were performed at laser fluences smaller than 6 μJ/pulse. No photobleaching of the sample or the reference solutions was detected after each experiment.

LIOAS signal analysis was performed using Sound Analysis version 1.13 software (Quantum Northwest).

Luminescence quenching experiments were performed with the previously described Spex Fluorolog equipment.[17]

Results and Discussion

LIOAS Measurements. The LIOAS measurements were carried out using Fe(III) perchlorate, chloride, and sulfate salts as quenchers in $HClO_4$, HCl, and H_2SO_4 (pH ≈ 2.3), respectively, to avoid precipitation of $Fe(OH)_3$. The Fe(III) concentration was ca. 20 mM. Under these conditions, luminescence experiments indicate that between 95% and 90% of quenching is reached at 25 and 6 °C, respectively, in accord with literature data,[7,18] assuring almost complete quenching over the whole temperature range of the LIOAS experiments. The values of the Stern−Volmer quenching constants were 980 and 900 M^{-1} in $HClO_4$, 1100 and 950 M^{-1} in HCl, and 812 and 750 M^{-1} in H_2SO_4, at 25 and 6 °C, respectively.

Furthermore, under the above conditions the back electron-transfer reaction between $Ru(bpy)_3^{3+}$ and $Fe^{2+}_{(aq)}$ takes place in the millisecond time range[7] and exceeds the time window of the experiments (ca. 600 ns, see Experimental Section) by several orders of magnitude. This means that these ions are the final products in our experiments.

Figure 1 shows the LIOAS signals after laser excitation at 500 nm of $Ru(bpy)_3^{2+}$ in the presence of $Fe(ClO_4)_3$ (Figure 1A) and $Fe_2(SO_4)_3$ (Figure 1B) and in acidic solutions at similar temperatures and Fe(III) concentrations, together with the signal of the calorimetric reference $Na_2Cr_2O_7$ under the same conditions.

Note that the sign of the signal for the samples varies with the composition of the solution. However, the waveform of the calorimetric reference is always positive, as is expected for pure thermal processes in aqueous solutions at room temperature, since the expansion coefficient, β, of water is >0 at $T > 4$ °C.[1]

A delay of the arrival time and a broadening of the signals with respect to the reference signal were observed for the sample solutions. This change in shape of the sample wave can occur if processes take place with decay times comparable to the time window. In such cases, it is not possible to analyze the LIOAS signal amplitudes, and a deconvolution procedure must be used in order to obtain the lifetimes and the quantitative contribution of the various processes, as described previously.[10,11b,15,16] In short, the acoustic signal of the sample is regarded as a convolution of the instrumental response (obtained from the calorimetry reference signal which releases all the excitation energy promptly as heat) and a time-dependent multiexponential decay function describing the pressure behavior in the sample after the laser pulse. The reference signal depends only on the heat release multiplied by the thermal expansivity of the solvent, while the sample signal might have an extra contribution from structural volume changes, $\Delta V_r = n\Phi_R \Delta V_R$ (ΔV_r is the total contribution of the volume change to the signal, n is the number of Einsteins absorbed, and Φ_R is the reaction quantum yield), which does not depend on the expansivity. Thus, assuming that the thermal and the structural contributions to the LIOAS wave show the same time behavior, the recovered amplitudes of the

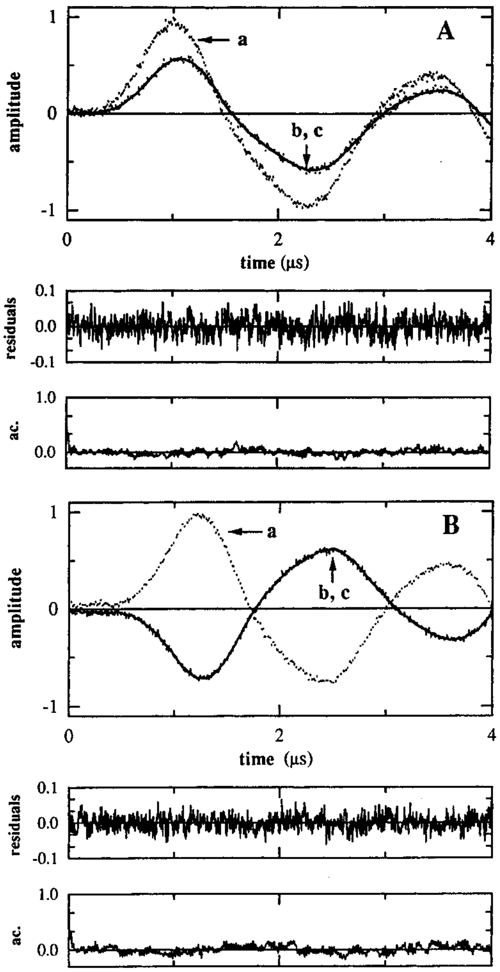

Figure 1. LIOAS signals for reference (a, $Na_2Cr_2O_7$) and sample (b) solutions, after laser excitation of $Ru(bpy)_3^{2+}$ at 500 nm in the presence of (A) 25 mM $Fe(ClO_4)_3$ in 5 mM $HClO_4$ aqueous solution at 20 °C and (B) 10 mM $Fe_2(SO_4)_3$ in 5mM H_2SO_4 aqueous solution at 23 °C. The residuals distribution and autocorrelation function for the fitted curve (c) are included in each case.

multiexponential function, φ_i, normalized with respect to the amplitude of the reference compound ($\varphi = 1$), are given by eq 3,

$$E_\lambda \varphi_i = q_i + \Phi_i \Delta V_{R,i}(c_P\rho/\beta) \qquad (3)$$

where E_λ is the excitation energy per absorbed Einstein (239.32 kJ/mol at 500 nm), $q_i = \Phi_i \Delta H_i$ (with ΔH_i the enthalpy of the ith step) is the fraction of absorbed energy dissipated into the medium as heat, Φ_i is the quantum yield, $\Delta V_{R,i}$ is the structural volume change for the production of 1 mol of the ith species, β is the cubic expansion coefficient, c_P is the heat capacity, and ρ is the mass density. As mentioned in the Introduction, q_i and $\Delta V_{R,i}$ are separable in aqueous solutions by performing temperature-dependent LIOAS measurements, since the $(c_P\rho/\beta)$ ratio is highly temperature dependent, primarily due to the strong temperature dependence of β.

In this framework, $\Delta V_{R,i}$ is considered constant in the temperature range used for the LIOAS experiments (which is a valid assumption over the narrow temperature range of 22 °C in the present case). A plot based on eq 3 should yield a straight line with an intercept q_i and a slope $\Phi_i \Delta V_{R,i}$ for the ith decay.

Since aqueous solutions containing added salts have thermoelastic parameters different from neat water, the determination of $(c_P\rho/\beta)$ at different temperatures was performed by measuring the LIOAS signals for the calorimetric reference in neat water and in the salt solution used. Both signal amplitudes (H) are related by a simple equation already described in the literature.[2,19] Typical LIOAS signal−amplitude dependencies on the absorbed energy for the calorimetric reference in water and in salt solution at 23 °C are presented in Figure 2.

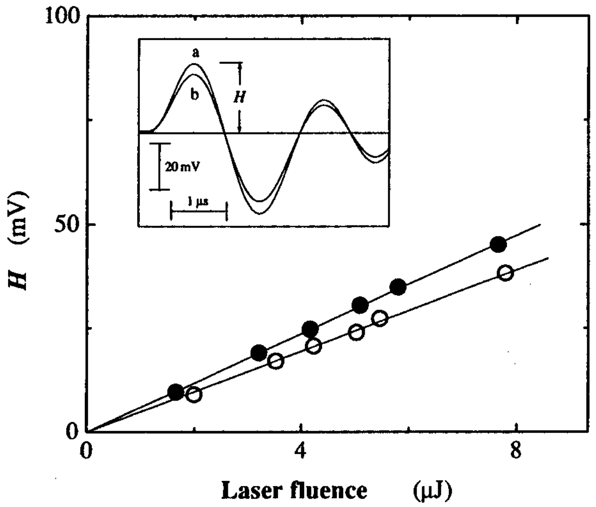

Figure 2. LIOAS signal amplitude H, as a function of the absorbed energy, at 15 °C for (●) $Na_2Cr_2O_7$ plus 25 mM $Fe(ClO_4)_3$, 100 mM $HClO_4$, (○) $Na_2Cr_2O_7$ in neat water. Inset: LIOAS signal for the reference in (a) salt solutions and (b) in neat water both excited with the same laser fluence and under the same conditions.

The value of the sound velocity, v_a, needed for the evaluation of the ratio of thermoelastic parameters[2,19] and estimated from the signal arrival time to the detector, was the same for the reference in salt solutions and in neat water. The densities of the salt solutions were identical within the experimental error (ca. 5%) to that of water. Therefore, the values of $(c_P\rho/\beta)$ were mainly determined by the ratio of the fluence-normalized amplitudes for sample and reference, H_w^n/H_x^n.

As shown in Figure 1, satisfactory fits of the sample signals were obtained using a two-exponential decay model for the pressure evolution. In all cases, the deconvolution program found a fast decay time ($\tau_1 < 5$ ns) and a slow decay τ_2 of about 65 ns, allowing a free fit of four parameters. The value of τ_1 indicates only that this decay is faster than the time resolution of the experiment (<10 ns). Fixing this time component at any value between 1 and 10 ns always resulted in a similar value for the associated amplitude of the process (φ_1). Since the rise time of a spin-allowed excited state (reaction B, vide infra) has been estimated to be 0.3 ps for $Ru(bpy)_3^{2+}$,[20] the fast component should correspond to the formation of the triplet MLCT state of the Ru(II) complex. The value of τ_2 grew longer as temperature decreased, but in all cases its value was in agreement with the quenching efficiencies for the $Ru(bpy)_3^{2+}/Fe^{3+}_{(aq)}$ system measured by stationary luminescence. Thus, the second amplitude factor φ_2 was assigned to the contribution to the LIOAS signal of the intermolecular electron-transfer reaction between $^*Ru(bpy)_3^{2+}$ and $Fe^{3+}_{(aq)}$ (reaction C, vide infra).

Since the difference in lifetimes between the first and second decay was large (by a factor of at least 50), it was possible to assign the observed decays to the inverse of the rate constants of the elementary consecutive reactions B (excitation) and C (quenching). The luminescence pathway decay was ignored, since its contribution ($\Phi_{em}E_{em}$) relative to E_λ is less than 3% in the absence of quenchers ($\Phi_{em} = 0.042$, $E_{em} = 193$ kJ/mol[21]) and should be smaller than 10^{-3} kJ/mol for >90% quenching by the Fe(III) salt (see Experimental Section).

TABLE 1: Prompt (q_1) and Slow (q_2) Heat, Structural Volume Changes, $\Delta V_{R,i}$, and Enthalpy Content, ΔH_i, for the Transient Species Produced in the Photoinduced Electron Transfer between $Ru(bpy)_3^{2+}$ and $Fe^{3+}_{(aq)}$ in Various Salt Solutions

	quencher solution (mM)	salt added (mM)	I_a[a] (M)	q_1[b]	q_2[b]	ΔH_1[c]	ΔH_R[d]	$\Delta V_{R,1}$[e]	$\Delta V_{R,2}$[e]	ΔV_R[f]
1	25 $Fe(ClO_4)_3$ + 100 $HClO_4$	none	0.247	50	80	189	109	−2.7	+1.8	−0.9
2	25 $Fe(ClO_4)_3$ + 5 $HClO_4$	none	0.139	50	84	189	105	−3.4	+2.2	−1.2
		Na_2SO_4								
3		6.5	0.123	59	84	181	96	−3.5	−1.5	−5.0
4		15	0.104	61	84	178	94	−3.1	−5.0	−8.1
5		26	0.092	59	44	180	135	−4.0	−7.0	−11.0
6		32	0.099	54	72	185	113	−3.8	−9.2	−13.0
7	10 $Fe_2(SO_4)_3$ + 5 H_2SO_4	none	0.032	54	92	185	93	−4.0	−17.5	−21.5
8	25 $FeCl_3$ + 5 HCl	none	0.090	61	71	178	107	−3.4	−2.0	−5.4
9		100 NaCl	0.164	61	65	178	113	−3.2	−1.8	−5.0
10		100 NH_4Cl	0.164	59	71	178	109	−3.6	−1.6	−5.2
11[g]	16 $FeCl_3$ + 10 H_2SO_4	none	0.055							−11.0
12	25 $Fe(ClO_4)_3$ + 5 $HClO_4$	27 NaCl	0.145	46	77	193	116	−2.6	+2.0	−0.6
13	10 $Fe_2(SO_4)_3$ + 5 H_2SO_4	50 $(NH_4)_2SO_4$	0.140	58	71	181	110	−3.5	−18.5	−22.0

[a] Corrected ionic strength. [b] kJ/mol ± 20%. [c] Enthalpy content (kJ/mol ± 20%) of the MLCT state of $Ru(bpy)_3^{2+}$, calculated from the prompt heat as $E_\lambda - q_1$. [d] Enthalpy change (kJ/mol ± 20%) of reaction A calculated as $E_\lambda - (q_1 + q_2)$. [e] cm^3/mol ± 10%. [f] Total reaction volume change (mL/mol ± 10%) for reaction A calculated as $\Delta V_R = \Delta V_{R,1} + \Delta V_{R,2}$. [g] From ref 2.

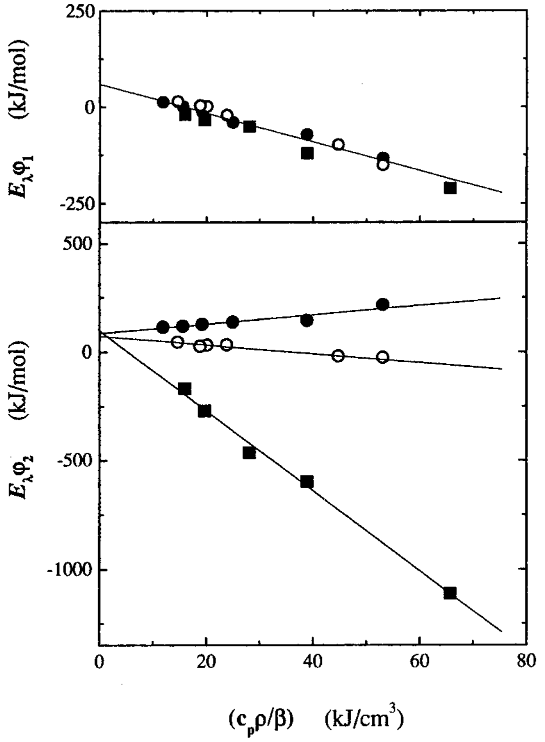

Figure 3. (Top) First and (bottom) second recovered amplitudes of the biexponential fitting function vs the ratio of thermoelastic parameters ($c_P\,\rho/\beta$) (eq 3) for the LIOAS signals after excitation of $Ru(bpy)_3^{2+}$ in various quencher solutions: (●) 25 mM $Fe(ClO_4)_3$ in 5 mM $HClO_4$, (○) 25 mM $FeCl_3$ in 5 mM HCl, and (■) 10 mM $Fe_2(SO_4)_3$ in 5mM H_2SO_4. The temperature range was from 30 °C (extreme left) to 8 °C (extreme right).

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} {}^*Ru(bpy)_3^{2+} \qquad \Delta V_{R,1} \qquad (B)$$

$${}^*Ru(bpy)_3^{2+} + Fe_{(aq)}^{3+} \xrightarrow{k_q} Ru(bpy)_3^{3+} + Fe_{(aq)}^{2+} \qquad \Delta V_{R,2} \qquad (C)$$

The recovered amplitudes for the prompt process were independent of the composition of the solution. The dependence of the amplitudes φ_i on the ratio $(c_p\rho/\beta)$ for both the fast and the slow processes is depicted in Figure 3 for the solutions of the three Fe(III) salts.

The average enthalpy content of the MLCT state, $\Delta H_1 = E_\lambda - q_1 = 183 \pm 6$ kJ/mol (Table 1), was calculated from the intercept of the points for the fastest process. It is similar to the value of 193 kJ/mol obtained from the luminescence maximum of $^*Ru(bpy)_3^{2+}$.[21]

From the slopes of $E_\lambda\varphi_1$ in Figure 3 and using a value of 1 for the quantum yield of formation of the MLCT complex in every solution,[22] an average contraction of $\Delta V_{R,1} = -3.4 \pm 0.5$ cm^3/mol was obtained. This volume change is in agreement with the value reported previously for the formation of the MLCT state of $Ru(bpy)_3^{2+}$[10,23] and attributed to a shortening of the metal−ligand bonds, which corresponds to a small effective radial decrease of about 0.01 Å.[23] The lack of dependence of the volume change for the MLCT formation on the salt composition confirms the assignment of this process to an internal arrangement of the ruthenium complex after light excitation.

Within experimental error, the intercepts q_2 do not depend on the medium, while the slopes affording $\Delta V_{R,2}$ strongly depend on it (Table 1).

For the analysis of the amplitudes associated with the slower step C, i.e., the intermolecular electron-transfer reaction, it is necessary to consider the quantum yield, Φ_2, for the escape of the ions after electron transfer. According to Ferreira and Harriman,[7] the yield of $Ru(bpy)_3^{3+}$ is ca. 70% for the three acid solutions used in our work, albeit at different concentrations. Lin and Sutin reported a value of (80 ± 16)% for the escape reaction in $HClO_4$ solutions.[24] With $\Phi_2 = 1$ the calculated values of $\Delta H_R = E_\lambda - (q_1 + q_2)$ (Table 1) afforded an average 108 ± 11 kJ/mol, which is within the value of 112 kJ/mol reported by Marcus and Sutin.[2] Thus, under our conditions the escape efficiency is near unity and $\Phi_2 = 1$ can be used. In any case, a consideration of escape efficiencies of 0.8−0.9 would result in volume changes differing by ca. 10%, i.e., within experimental error of the experiments.

From the empirical analysis of the volumes and enthalpy changes determined for both components of reaction A, i.e., reactions B and C, after laser excitation of $Ru(bpy)_3^{2+}$ in different salt solutions (Table 1) it is concluded that (i) speciation rather than a bulk effect determines the value of the structural volume change $\Delta V_{R,2}$ for the electron-transfer reaction C. This is particularly evident when comparing solutions 5 with 8 and 2 with 13 (Table 1), each pair having a similar ionic strength. (ii) The nature of the anion and not that of the cations determines the value of ΔV_R (compare, for example, solutions 9 and 10 in Table 1). (iii) The reaction enthalpy change, $\Delta H_R = E_\lambda - (q_1 + q_2) = 108 \pm 11$ kJ/mol, does not depend on the counterion present and is in good agreement with the value reported previously (112 kJ/mol[2,3]).

TABLE 2: Logarithmic Values of the Formation Constants of Chloride and Sulfate Iron Complexes in Aqueous Solutions[24,25]

cation	complex	log K
Fe^{2+}	$FeCl^+$	0.32
	$FeSO_4$	2.20
Fe^{3+}	$FeCl^{2+}$	1.48
	$FeCl_2^+$	2.44
	$FeCl_3$	0.99
	$FeSO_4^+$	4.04
	$Fe(SO_4)_2^-$	5.38
	$Fe(OH)^{2+}$	11.81

Quantitative Interpretation of the Structural Volume Changes after Electron Transfer

The Speciation Model. The presence of anions in solution which tend to form ion pairs with Fe^{3+} and with Fe^{2+}, as is the case of sulfate, has a decisive effect on the reaction volume change (Table 1). This observation led us to describe the results in terms of a chemical model which takes into account the actual speciation in the solution *before* and *after* the electron-transfer reaction A.

Due to the large size of the $Ru(bpy)_3^{2+/3+}$ ions, it was assumed that they do not suffer appreciable changes in the ion pairing (if any) with the anions, at the concentrations in the solutions studied.

The degree of association of $Fe^{3+}_{(aq)}$ and $Fe^{2+}_{(aq)}$ in aqueous solutions is a function of the anion charge/diameter ratio. Thus, the sulfate ion is strongly associated with $Fe^{3+}_{(aq)}$ giving species such as $FeSO_4{+}_{(aq)}$ and $Fe(SO_4)_2{}^-{}_{(aq)}$, while with $Fe^{2+}_{(aq)}$ only the ion pair $FeSO_{4(aq)}$ is formed. The chloride ion is less associated with the $Fe^{3+/2+}_{(aq)}$ ions, and the perchlorate is considered nonassociated with these cations. Values of the association constants for reaction D, K, of the anion−cation complexes as reported in the literature[25,26] (Table 2) were used to evaluate the ionic speciation in solution before and after the laser-induced reaction A. The speciation model also includes the hydrolysis of the $Fe^{3+}_{(aq)}$ ion into $Fe(OH)^{2+}_{(aq)}$, which is important at pH > 1.

$$Fe^{n+} + xA^{m-} \rightleftarrows FeA_x^{(n-xm)+} \qquad (D)$$

In the framework of this chemical model, the total ΔV_R is given by the sum of the intrinsic plus the external volume changes, eq 4.

$$\Delta V_R = \sum_i \Delta m_i V_{\phi,i} \qquad (4)$$

where Δm_i is the concentration change of the species i during the reaction. $V_{\phi,i}$ is the apparent partial molar volume of the ith species expressed as a function of the actual ionic strength, I_a, of the solution (on molality basis) by the extended Debye−Hückel eq 5 derived by Pitzer,[27] valid in the range of concentration (ionic strength) used in this work,

$$V_{\phi,i} = V_i^\circ + \frac{z_i A_v}{2b}\ln(1 + b\sqrt{I_a}) \qquad (5)$$

In this equation V_i° is the partial molar volume at infinite dilution, z_i is the ion charge, $b = 1.2$ (kg/mol)$^{1/2}$, and $A_v = 1.874$ cm^3 kg$^{1/2}$ mol$^{-3/2}$ at 25 °C is the Debye−Hückel limiting slope for the partial molar volume.[28] The values of V_i° for each species in solution include the structural and electrostatic effects. Thus, eqs 4 and 5 can be viewed as a particular case of eq 1, where the contribution of each species is considered individually and the ion−ion interaction is taken into account. It is noted that the value of I_a changed <0.2% for all the solutions during the photoinduced reaction.

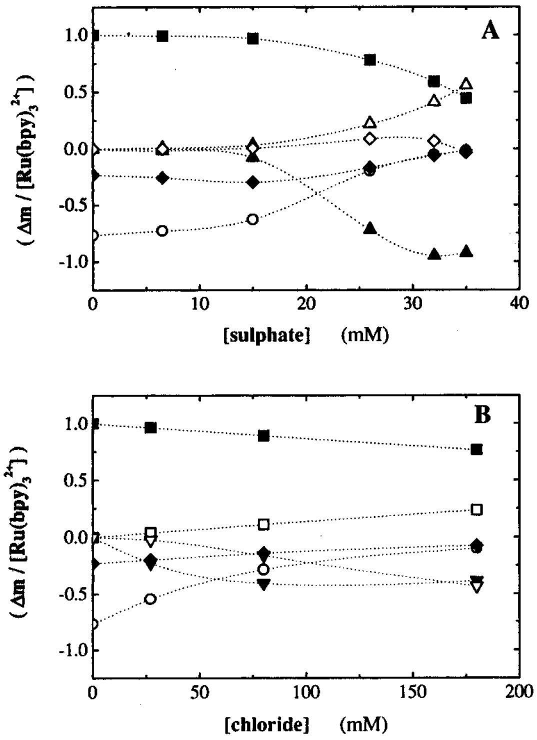

Figure 4. Concentration change for each of the ions as listed, per mole of $Ru(bpy)_3^{2+}$, produced in reaction A for solutions containing: (A) sulfate ions and (B) chloride ions (■) Fe^{2+}, (○) Fe^{3+}, (◆) $Fe(OH)^{2+}$, (△) $FeSO_4$, (▲) $FeSO_4^+$, (◇) $Fe(SO_4)_2$, (□) $FeCl^+$, (▼) $FeCl^{2+}$, (▽) $FeCl_2^+$. The data were calculated with the speciation model using the association constants in Table 2 and used for the evaluation of V° with eq 4. Computer-smoothed lines were drawn through the points.

TABLE 3: Partial Molar Volumes at Infinite Dilution for Various Species in Aqueous Solutions, Obtained from Literature

species	V^o (cm^3/mol)	ref
Fe^{3+}	−36.5	29
Fe^{2+}	−22.1	29
SO_4^{2-}	14.0	28
HSO_4^-	35.7	28
Cl^-	17.8	28
H^+	0.0	28

The values of V° for $Fe^{2+}_{(aq)}$, $Fe^{3+}_{(aq)}$, SO_4^{2-}, HSO_4^-, H^+, and Cl^- determined experimentally are given in Table 3.[29,30] For the iron ions we adopted the molar volume value reported by Swaddle and Mak[30] since these authors measured the volumetric properties for solutions of $Fe(ClO_4)_3$ in 100 mM $HClO_4$. Even in these solutions the value for Fe(III) corresponds to a solution containing 6% of the $Fe(OH)^{2+}_{(aq)}$ species.

There is a lack of information on the volumetric properties of the $Ru(bpy)_3^{2+/3+}$ cations and of the various iron−anions complexes. In the following section the latter properties are calculated using the present LIOAS data.

Application of the Chemical Model

The volume Change Associated with the $Ru(bpy)_3^{2+}$ Oxidation. In every experiment the initial concentration of $Ru(bpy)_3^{2+}$ was 7.5×10^{-5} M. As discussed above, we considered that the oxidation to $Ru(bpy)_3^{3+}$ in the presence of $Fe^{3+}_{(aq)}$ was complete, i.e., $\Phi_2 = 1$ in eq 3.

The concentration changes for each species after excitation, per mole of $Ru(bpy)_3^{2+}$, are given in Figure 4A,B for the solutions containing sulfate and chloride ions, respectively. The actual values of I_a for each of the solutions (Table 1) were calculated on the basis of the actual ion concentrations obtained from the speciation model. The calculated pH for the solutions listed in Table 1 agree with the measured values within experimental error. This confirms that the adopted speciation scheme and the equilibrium constants used are correct.

A first view of the changes in the solution upon reaction indicates that most of the Fe(III) in solutions containing high sulfate anion concentration forms sulfate complexes with charges +1 or −1, while the Fe(II) forms mostly neutral species, thus reducing electrostriction. A similar effect is observed with chloride solutions, although the complexation degree is lower than in sulfate solutions.

This provides a simple explanation for the negative total volume change ΔV_R (last column in Table 1) observed for reaction A. The formation of $Ru(bpy)_3^{3+}$ from $Ru(bpy)_3^{2+}$ increases the electrostriction of water molecules, giving a negative contribution to the volume change. The reduction of the Fe(III) ions does not compensate this effect because both iron ions form complexes with the anions, which leads to a reduction of the charged species in solution.

In the case of perchlorate solutions, in which there is no complex formation and only electrostriction effects are expected, an expansion of $\Delta V_{R,2} = +2.0 \pm 0.2$ cm^3/mol (solutions 1 and 2 in Table 1) is observed after intermolecular electron transfer (reaction C), in good agreement with the qualitative prediction using the Drude−Nernst equation, as commented in the Introduction.

Since the value of ΔV_R is practically the same for solutions 1 and 2, the contribution of the $Ru(bpy)_3^{2+/3+}$ oxidation ($\Delta V°_{Ru}$, eq 6) to ΔV_R and the value of $V°$ for $Fe(OH)^{2+}_{(aq)}$ can be calculated from the data for these two solutions, containing only ClO_4^- anions.

$$\Delta V°_{Ru} = V°_{Ru(bpy)_3{}^{3+}} - V°_{Ru(bpy)_3{}^{2+}} \tag{6}$$

Two equations including both quantities are used. The calculated value, $V° = -35 \pm 8$ cm^3/mol for $Fe(OH)^{2+}_{(aq)}$, indicates that the volume of this ion is similar to that of the nonhydrolized $Fe^{3+}_{(aq)}$ ion (see Table 3). $\Delta V°_{Ru} = -15.4$ cm^3/mol was derived from the data for solutions 1 and 2 and was adopted for the subsequent calculations.

Recently, Sachinidis et al.[31] studied the volume changes for the couple $Fe(bpy)_3^{2+/3+}$ by an electrochemical method (pressure dependence of the redox potential). For the oxidation of the $Fe(bpy)_3^{2+}$ ion these authors report a value $\Delta V_R = -19.9$ cm^3/mol, in good agreement with the value calculated in this work for $Ru(bpy)_3^{2+}$ oxidation using the LIOAS data and the speciation model. We do not expect differences in the electrostriction effect by changing the central metal since the sizes of the ruthenium and the iron ion complexes are large and relatively similar.

Partial Molar Volumes of the Iron Complexes. By solving eqs 4 and 5 with the value $\Delta V°_{Ru} = -15.4$ cm^3/mol, the partial molar volumes at infinite dilution of the three iron−sulfate complexes were calculated, using the ΔV_R values determined for solutions 5, 6, and 7, which contain enough sulfate anions to compete efficiently with the hydrolysis of Fe^{3+}. In any case, for the calculation, the value of $V° = -35$ cm^3/mol for $Fe(OH)^{2+}_{(aq)}$ was used (vide supra). The results summarized in Table 4 seem reasonable when compared with other monovalent ions of similar size.

Thus, the $FeSO_4^+$ ion has a partial molar volume at infinite dilution very close to that reported for HSO_4^-. The uncharged $FeSO_{4(aq)}$ species has a larger $V°$ due to the loss of electrostatic interactions with the solvent molecules. Finally, $Fe(SO_4)_2^-$ has the largest $V°$, as expected because of its bigger size. However, the value of $V°$ for this triple ion has a large uncertainty because of the very small concentration change for this species during the reaction (Figure 4).

TABLE 4: Partial Molar Volumes at Infinite Dilution of the Chloride− and Sulfate−Iron Complexes Calculated in This Work

species	$V°$ (cm^3/mol)
$Fe(OH)^{2+}$	-35 ± 8
$FeSO_4$	47 ± 8
$FeSO_4^+$	28 ± 6
$Fe(SO_4)_2^-$	169 ± 31
$FeCl^+$	8 ± 5
$FeCl^{2+}$	-22 ± 1
$FeCl_2^-$	25 ± 9

When a similar calculation as outlined above for solutions 5, 6, and 7 is applied to the data for solutions 3 and 4, the absolute values obtained for $\Delta V°_{Ru}$ are up to 6 cm^3/mol larger than those obtained with solutions 1 and 2. The complexity of solutions 3 and 4 and the uncertainty of the association constants might be the reason for the discrepancy.

A similar treatment was applied for solutions containing chloride ions. In this case we have considered the values of ΔV_R of solutions 8, 9, 10, and 12. Solution 11[2] was not used since the presence of sulfate makes the system excessively complex. The volume change measured for solution 10 is almost identical with that of solution 9, as expected from the similar speciation if the hydrolysis of the ammonium ion is neglected. Thus, eqs 4 and 5 were solved in order to obtain the values of $V°$ for $FeCl^+_{(aq)}$, $FeCl^{2+}_{(aq)}$, and $FeCl^{2+}_{(aq)}$, also listed in Table 4. The concentration of $FeCl^+_{(aq)}$ and $FeCl^{2+}_{(aq)}$ ions in solution 12 is quite low, and thus, the volume change measured for this solution was used to calculate the volume of the $FeCl^{2+}_{(aq)}$ ion. This species predominates in solutions 8−10, and the calculated values for the other chloride-iron ions bear a large error. The values in Table 4 for these species are consistent with that expected from the electrostriction effect, as follows from the comparison of $V°$ for $Fe^{2+}_{(aq)}$ and $FeCl^{2+}_{(aq)}$. Also, the value of $V°$ for the single charged $FeCl^+_{(aq)}$ is similar to that of the Cl^- anion, while $FeCl^{2+}_{(aq)}$ has the largest volume among the iron−chloride complexes.

Conclusions

Enthalpy changes and volume changes associated with photoinduced ligand exchange reactions are analyzed using LIOAS as a sensitive and relatively simple method suitable for the study and characterization of transient species produced in photoinduced electron-transfer reactions.

As judged from the results obtained with the representative case studied in this work, the reaction volume changes in electron-transfer reactions are very sensitive to the composition of the medium, as a result of specific interactions of the photoreactive ions with the counterions. Using LIOAS to measure these volume changes, it is possible to calculate partial molar volumes of ions and other species at dilutions not attainable by using conventional methods, such as density determinations. This is important since in many measurements performed at higher concentrations the linear extrapolation to infinite dilution is not warranted.

The errors reported in this study for the partial molar volumes of the ion complexes are not a severe limitation of the method. In fact, they are dramatically reduced by performing LIOAS measurements with solutions covering a wider range of compositions.

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