

# Thermodynamic changes in the photoinduced proton-transfer reaction of the triplet state of safranine-T †

Claudio D. Borsarelli,<sup>\*a</sup> Sonia G. Bertolotti<sup>b</sup> and Carlos M. Previtali<sup>b</sup>

<sup>a</sup> 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; Fax: 54-385-4509585

<sup>b</sup> Departamento de Química y Física, Universidad Nacional de Río Cuarto, Río Cuarto, Argentina

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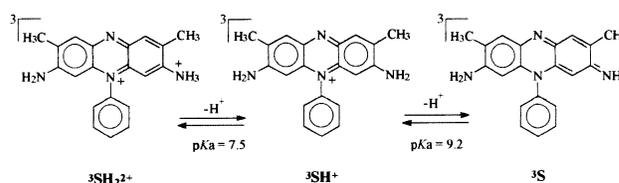
The enthalpy and volume changes occurring in the triplet excited state proton-transfer reactions of safranine-T ( $^3\text{SH}^+$ ) in aqueous solutions at pH 4.8, 8.3, and 10.4 were investigated using time-resolved photoacoustics (TRP). The transient triplet state species were also studied using laser-flash photolysis (LFP). The LFP experiments showed the prompt formation of  $^3\text{SH}^+$  with a triplet quantum yield  $\Phi_T = 0.28$  between pH 4.8 and 10.4. At pH 8.3  $^3\text{SH}^+$  decays directly to the ground state. However, at pH 4.8 and 10.4,  $^3\text{SH}^+$  reacts with protons or hydroxy ions to form the dication  $^3\text{SH}_2^{2+}$  or the neutral  $^3\text{S}$  species, with diffusion-controlled rate constants of  $k_{\text{H}^+} = 1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , and  $k_{\text{HO}^-} = 2.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , respectively. Under the same experimental conditions, the TRP measurements allowed the accurate determination of the energy content of the rapidly formed triplet state  $^3\text{SH}^+$ , *i.e.*  $E_T = 175 \text{ kJ mol}^{-1}$ . The slow component (0.1–3  $\mu\text{s}$ ) of the TRP signal at pH 4.8 and 10.4 was attributed to the formation of the species  $^3\text{SH}_2^{2+}$  and  $^3\text{S}$ , respectively. The enthalpy changes associated with the proton-transfer reactions of  $^3\text{SH}^+$ , calculated from the values of the heat released as obtained by TRP, were in remarkable agreement with the values estimated from the thermodynamic data of the acid–base equilibria of the triplet states of the dye. The formation of  $^3\text{SH}^+$  was accompanied by a volume expansion of  $1.8 \text{ cm}^3 \text{ mol}^{-1}$ , which was explained by changes in the hydrogen-bonding interaction of the dye with its solvation sphere. Instead, the volume changes observed upon the formation of  $^3\text{SH}_2^{2+}$  and  $^3\text{S}$  accounted for the electrostrictive effect produced by the change in the charge distribution on the dye after the proton-transfer reaction.

## Introduction

The time-resolved photoacoustic (TRP) technique has been widely employed to investigate enthalpy and volume changes of excited species in solution.<sup>1</sup> However, the use of this method for accurate determination of heats of reaction involving excited states, particularly intermolecular proton-transfer reactions, has not received much attention. One of the objectives of this paper is to explore the suitability of TRP measurements for determining enthalpy changes in excited state proton-transfer reactions. To this end we chose the well-known triplet state properties of the synthetic dye safranine-T as a model compound.

In recent years, the photochemistry of the cationic dye safranine-T ( $\text{SH}^+$ ) has received considerable attention because of its photoredox properties,<sup>2,3</sup> and its potential application as a sensitizer for photo-initiating polymerization.<sup>4–6</sup> In pioneering work, Baumgartner *et al.*<sup>7</sup> have studied the triplet state reactivity of  $\text{SH}^+$  as a function of pH in aqueous media using conventional flash photolysis. They have reported the existence of two triplet state acid–base equilibria, with  $\text{p}K_a$ 's of 7.5 and 9.2, and triplet species denoted  $^3\text{SH}_2^{2+}$ ,  $^3\text{SH}^+$ , and  $^3\text{S}$  (Scheme 1). More recently, Pastre and Neumann have used the protonation reaction rate of  $^3\text{SH}^+$  in order to determine the local proton concentration in the microdomains created by surfactants and polyelectrolytes when dissolved in water.<sup>8</sup>

In this report, the temperature dependence of the acoustic wave produced on laser-flash excitation of safranine-T was measured at pH 4.8, 8.3 and 10.4. At the extreme pH's the



**Scheme 1** Acid–base equilibria between the diprotonated, mono-protonated and neutral forms of the triplet states of safranine-T.

initially formed neutral triplet state ( $^3\text{SH}^+$ ) undergoes proton transfer in a few microseconds after the laser pulse. Thus, the experimental data can be analyzed in terms of a thermal and volume contribution to the acoustic wave, which can be related to the corresponding enthalpy and volume changes in the proton-transfer reactions. To this end, the photophysics of safranine-T was re-investigated by laser-flash photolysis (LFP). The previous work<sup>7</sup> on the photophysics of  $\text{SH}^+$  in aqueous solution was performed by means of the conventional flash photolysis technique, and therefore the time resolution (larger than 50  $\mu\text{s}$ ) precluded the determination of the proton-transfer kinetics in the triplet excited state. The quantum yields for triplet state formation at the different pH's were also determined by LFP.

## Experimental

### Materials

Safranine-T chloride ( $\text{SH}^+\text{Cl}^-$ ) from Aldrich (Milwaukee, USA) was recrystallized from ethanol before used. Evans Blue

† Dedicated to Professor Silvia E. Braslavsky on the occasion of her 60th birthday.

(EB) and Cresyl Violet (CV) were from Sigma Chemical Co. (St. Louis, USA) and used as received. HCl, NaOH, NaH<sub>2</sub>PO<sub>4</sub>, and Na<sub>2</sub>HPO<sub>4</sub> were analytical grade from Merck Química Argentina (Buenos Aires, Argentina). Acetonitrile (HPLC grade) was from Sintorgan (Buenos Aires, Argentina). The water used in the preparation of solutions had been triply distilled.

## Methods

UV-vis and fluorescence spectra were determined with a Hewlett-Packard 8453 diode array spectrophotometer and a Spex Fluoromax spectrofluorimeter, respectively. Under the experimental conditions ( $4.8 \leq \text{pH} \leq 10.4$ ) both the UV-vis and the fluorescence emission spectra of SH<sup>+</sup> in 1 mM phosphate buffer solution (PBS) were independent of the pH. The ground state absorption coefficient at the wavelength maximum (520 nm) as  $\epsilon_S^{520} = 31200 (\pm 500) \text{ M}^{-1} \text{ cm}^{-1}$  and the fluorescence quantum yield  $\Phi_f = 0.058 (\pm 0.005)$  were determined. The fluorescence quantum yield was measured using a CV solution in methanol as actinometer ( $\Phi_f = 0.54$ ),<sup>9</sup> and with correction for the difference in refractive index.<sup>10</sup>

Triplet-triplet transient absorption spectra were measured with a homemade laser-flash photolysis (LFP) system described previously,<sup>2,11</sup> using a Spectron SL400 Nd-YAG laser generating 532 nm pulses (fwhm 20 ns) as excitation source.

The details of our time-resolved photoacoustic (TRP) set-up have been reported before.<sup>12</sup> The same laser source for LFP was used. In this case, the laser beam width was shaped with a rectangular slit (0.5 mm w × 5 mm h), allowing a time resolution of the TRP experiments from *ca.* 20 ns up to 3  $\mu\text{s}$  using deconvolution techniques.<sup>13</sup> The total laser energy after the slit was <150  $\mu\text{J}$  per pulse, measured with a pyroelectric energy meter, Melles-Griot model 13PEM001. The dye EB was used as calorimetric reference.<sup>1,12,14</sup>

In all cases the plots of the amplitude of the photoacoustic signal *vs.* the laser energy were linear with zero intercepts, indicating that bi-photonic processes or signal saturation did not take place. 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).

Typically, *ca.* 30  $\mu\text{M}$  SH<sup>+</sup> solutions were prepared in 1 mM phosphate buffer solutions (PBS), at pH 4.8, 8.3, and 10.4 ( $\pm 0.1$  units). In non-buffered solutions at pH 4.8 and 10.4, the pH was adjusted by adding small aliquots of concentrated HCl or NaOH solutions, respectively, after removing the residual CO<sub>2</sub> by bubbling with N<sub>2</sub>.

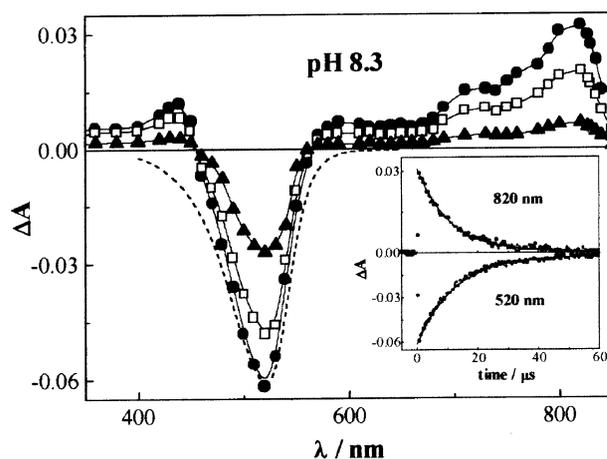
In all cases, the SH<sup>+</sup> solutions were degassed during 15 min by bubbling with solvent-saturated Ar. The temperature range for the TRP experiments was 8.0–39.0 ( $\pm 0.1$ ) °C. The pH values of the solutions were monitored before and after each experiment, and in all cases they were unchanged. All the experiments were performed in duplicate.

## Results and discussion

### Laser-flash photolysis (LFP) experiments

The lack of changes in the absorption and emission spectra over the range  $4.8 \leq \text{pH} \leq 10.4$  indicates that the dye remains in the monocationic form SH<sup>+</sup> in both the ground state and the singlet excited state. In contrast, a strong pH dependence of the triplet-triplet transient absorption spectra of SH<sup>+</sup> at times longer than 50  $\mu\text{s}$  has been reported.<sup>7</sup> This result was interpreted in terms of a protonation-deprotonation equilibrium of <sup>3</sup>SH<sup>+</sup> with pK<sub>a</sub> values of 7.5 and 9.2, Scheme 1.

In order to interpret the TRP experiments a good knowledge of the kinetics and yields of the triplet state in its three forms is necessary. Therefore, we carried out a detailed study of the



**Fig. 1** Transient absorption spectra of SH<sup>+</sup> (30  $\mu\text{M}$ ) in deaerated 1 mM phosphate buffer solutions (pH 8.3) observed at: (●) 0  $\mu\text{s}$  (extrapolated from exponential fit of the decays); (□) 3  $\mu\text{s}$ ; and (▲) 10  $\mu\text{s}$  after laser excitation at 532 nm. (---) Normalized ground state absorption spectrum of SH<sup>+</sup>. Inset: absorption decay profiles of the triplet decay (820 nm) and for the bleaching recovery (520 nm).

spectral properties and kinetics of the triplet state of the dye at shorter times by LFP.

Fig. 1 shows the transient absorption spectra observed after 532 nm laser excitation of SH<sup>+</sup> at pH 8.3. The spectra showed a relatively intense maximum band at 820 nm with a shoulder at *ca.* 730 nm, and a less intense maximum at 440 nm. Negative absorbance was observed in the 460–550 nm region, which was assigned to the depletion of the SH<sup>+</sup> ground state absorption ( $\lambda_{\text{max}} = 520 \text{ nm}$ ). The absorption decay curves over the whole spectral range (including the negative absorption region) followed a first-order decay law with a lifetime of 11  $\mu\text{s}$ . This result indicates the presence of a unique transient species formed during the laser pulse ( $\tau < 20 \text{ ns}$ ). All these observations agree with the general features of the triplet-triplet absorption spectrum of the dye, <sup>3</sup>SH<sup>+</sup>, as previously reported by Baumgartner *et al.*<sup>7</sup> in aqueous solution, and with those observed in organic polar solvents, such as methanol and acetonitrile.<sup>2,3,15</sup>

On the other hand, the time evolution of the spectra of SH<sup>+</sup> at pH 4.8 and 10.4 indicated the prompt formation (during the laser pulse) of the <sup>3</sup>SH<sup>+</sup> species, with the characteristic absorptions at 440 and 820 nm. Subsequently, these bands decay with the simultaneous formation of new absorption bands, with maxima positions depending on the pH conditions (Figs. 2 and 3).

At pH 4.8 the new bands were centered at 390 and 660 nm (Fig. 2) and at pH 10.4 the absorption maxima were at 420 and 650 nm (Fig. 3). In both cases, the decay of the <sup>3</sup>SH<sup>+</sup> species (monitored at 820 nm) was kinetically correlated with the build-up of the new absorption bands, as shown in the insets of Figs. 2 and 3. The rise and decay times are collected in Table 1. The observed spectral features are consistent with the mechanism shown in Scheme 2.

At pH 8.3 the signal observed at 820 nm can be ascribed to the decay of <sup>3</sup>SH<sup>+</sup> to the ground state with a first-order rate constant  $k_o = 0.091 \mu\text{s}^{-1}$ . At pH 4.8 and 10.4 the observed first-order decays at 820 nm correspond to the proton-transfer processes of <sup>3</sup>SH<sup>+</sup>, with pseudo-first-order rate constants  $k_{\text{obs}}$  and  $k'_{\text{obs}}$ , to yield the acidic triplet <sup>3</sup>SH<sub>2</sub><sup>2+</sup>, or the basic triplet <sup>3</sup>S [eqns. (1) and (2)], respectively.

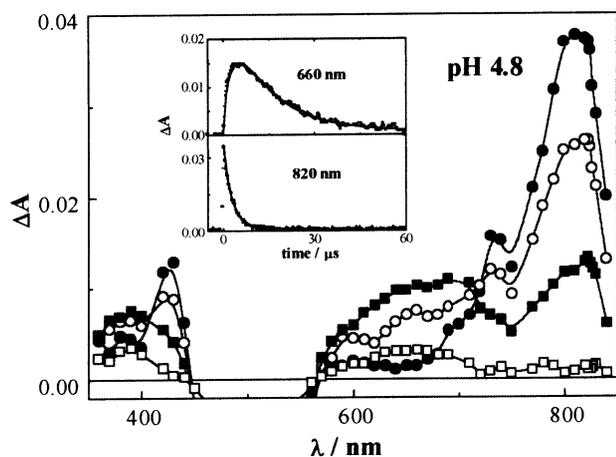
$$k_{\text{obs}} = k_o + k_{\text{H}^+}[\text{H}^+] \quad (1)$$

$$k'_{\text{obs}} = k_o + k_{\text{HO}^-}[\text{HO}^-] \quad (2)$$

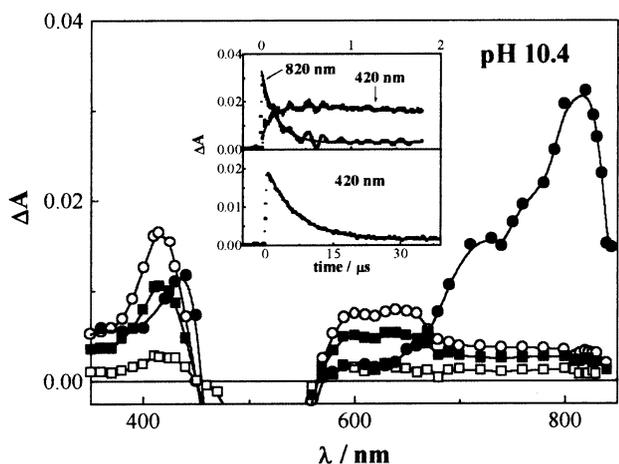
**Table 1** Photophysical properties of the triplet state species of Safranine-T in aqueous solutions

Species	$\lambda_{\max}/\text{nm}$	$\epsilon_T/\text{M}^{-1}\text{cm}^{-1}$	$\tau_{\text{rise}}/\mu\text{s}$	$\tau_{\text{decay}}/\mu\text{s}$	$\Phi_T$	$E_T/\text{kJ mol}^{-1}$
${}^3\text{SH}_2^{2+}$	390	$12500 \pm 300$				
${}^3\text{SH}^+$	660	$20000 \pm 600$ (21500 at 660 nm) <sup>a</sup>	$2.9 \pm 0.1^b$	$10.0 \pm 0.2^b$	$0.22 \pm 0.05^b$	$>129 \pm 29^f$
	820	$16200 \pm 400$ (15500 at 800 nm) <sup>a</sup>	$>20\text{ ns}^c$	$2.8 \pm 0.1^b$		
				$11.0 \pm 0.2^c$	$0.28 \pm 0.2^c$	$175 \pm 15$
${}^3\text{S}$	650	$8000 \pm 200$ (10000 at 420 nm) <sup>a</sup>	$0.12 \pm 0.01^d$	$0.17 \pm 0.01^d$	$0.28 \pm 0.05^d$	$>146 \pm 15^f$
				$7.0 \pm 0.2^d$		

<sup>a</sup> From ref. 7. <sup>b</sup> pH 4.8. <sup>c</sup> pH 8.3. <sup>d</sup> pH 10.4. <sup>e</sup>  $4.8 \leq \text{pH} \leq 10.4$ . <sup>f</sup> Lower limit.



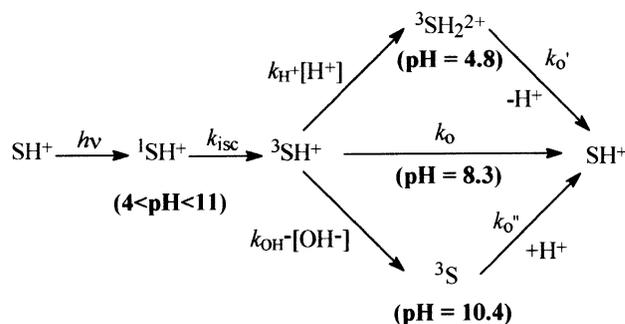
**Fig. 2** Transient absorption spectra of  $\text{SH}^+$  ( $30\ \mu\text{M}$ ) in deaerated 1 mM phosphate buffer solutions (pH 4.8) observed at: (●) 0  $\mu\text{s}$  (extrapolated from exponential fit of the decays); (○) 1  $\mu\text{s}$ ; (■) 3  $\mu\text{s}$ ; and (□) 10  $\mu\text{s}$  after laser excitation at 532 nm. Insets: absorption decay profiles at different wavelengths together with their respective exponential fits (solid line).



**Fig. 3** Transient absorption spectra of  $\text{SH}^+$  ( $30\ \mu\text{M}$ ) in deaerated 1 mM phosphate buffer solutions (pH 10.4) observed at: (●) 0  $\mu\text{s}$  (extrapolated from exponential fit of the decays); (○) 1  $\mu\text{s}$ ; (■) 3  $\mu\text{s}$ ; and (□) 10  $\mu\text{s}$  after laser excitation at 532 nm. Insets: absorption decay profiles at different wavelengths together with their respective exponential fitting (solid line).

Under the present experimental conditions at pH 4.8 and 10.4, the bimolecular rate constants  $k_{\text{H}^+}$  and  $k_{\text{HO}^-}$  were  $1.6 (\pm 0.2) \times 10^{10}\ \text{M}^{-1}\ \text{s}^{-1}$  and  $2.6 (\pm 0.2) \times 10^{10}\ \text{M}^{-1}\ \text{s}^{-1}$ , respectively. The  $k_{\text{H}^+}$  obtained here is similar to that reported by Pastre and Neumann<sup>8</sup> of  $1.3 \times 10^{10}\ \text{M}^{-1}\ \text{s}^{-1}$ . The values of  $k_{\text{H}^+}$  and  $k_{\text{HO}^-}$  are in agreement with the expected values for a diffusion-controlled reaction of  $\text{H}^+$  or  $\text{HO}^-$  in water at room temperature.<sup>16</sup>

The transient spectral changes observed under acidic conditions were similar to those reported previously.<sup>8</sup> However, in

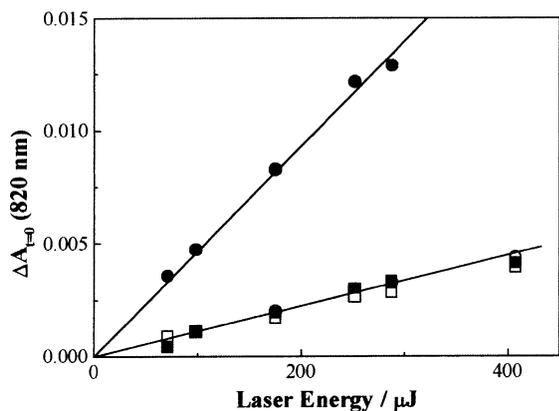


**Scheme 2** Kinetic mechanism for the proton-transfer reactions of the  ${}^3\text{SH}^+$  state at  $4 < \text{pH} < 11$ .

basic media a new band at 650 nm was observed, which was not noticed previously.<sup>7</sup> The absorption at this wavelength increases with a time constant similar to that at 420 nm, and it can also be ascribed to the deprotonated form of the triplet state. In order to ensure that the bands in acidic and basic PBS media were not perturbed by specific effects produced by the buffer salts, LFP experiments in HCl and NaOH aqueous solutions at pH 1 and 13 (data not shown) were performed. The same spectral features were observed as in the buffered solutions, indicating the lack of any specific salt effects. In this case, the absorption bands corresponding to the  ${}^3\text{SH}_2^{2+}$  and  ${}^3\text{S}$  species were formed during the laser pulse, in accord with the fast proton-transfer reactions of  ${}^3\text{SH}^+$  [eqns. (1) and (2)]. Once formed these species decay after several microseconds to the ground state, where the form  $\text{SH}^+$  is re-established (Scheme 2).

In order to determine the triplet quantum yield  $\Phi_T$  at the different pH's, the absorption coefficients of the triplet species are necessary. They were determined by the singlet depletion method<sup>17</sup> (Table 1), using the transient absorbance at 520 nm, since the bleaching in the narrow region of the maximum is similar to the ground state absorption. In spite of the lack of a complete matching between the bleaching and ground state absorption bands, the estimated absorption coefficient values were in agreement with those previously reported<sup>7</sup> (Table 1). Nevertheless, the reported values should be considered as upper-limit values, since there could be a possible small positive absorption at 520 nm.

The triplet quantum yields,  $\Phi_T$ , were also determined between pH 4.8 and 10.4 using LFP actinometry.<sup>17</sup> The  ${}^3\text{SH}^+$  in acetonitrile was used as reference using  $\epsilon_T^{820} = 39000\ \text{M}^{-1}\ \text{cm}^{-1}$ ,<sup>3</sup> and  $\Phi_T = 0.5$ .<sup>18</sup> The extrapolated initial absorbance change at 820 nm vs. the laser energy was compared in the organic solvent and in the buffered aqueous solutions (Fig. 4). It can be seen that the top absorbance after the laser pulse due to the  ${}^3\text{SH}^+$  species is the same at the pH values investigated. By comparing the slopes of the actinometry plots, a value of  $\Phi_T = 0.28 (\pm 0.05)$  was obtained for the aqueous solutions, using  $\epsilon_T^{820} = 16200\ \text{M}^{-1}\ \text{cm}^{-1}$  (Table 1). At pH 4.8 and 10.4 the efficiencies of the acid–base processes for the formation of  ${}^3\text{SH}_2^{2+}$  and  ${}^3\text{S}$  from the  ${}^3\text{SH}^+$  state were estimated as 0.75 and 1, respectively, considering their respective rise times under these conditions. In this way  $\Phi_T = 0.22 (\pm 0.05)$  and  $0.28 (\pm 0.05)$  were estimated for



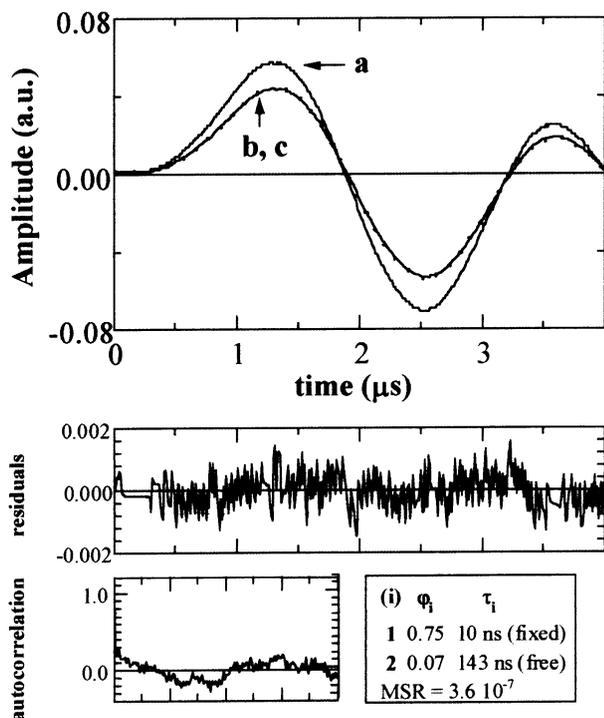
**Fig. 4** Actinometry plots of the initial absorbance change ( $\Delta A_{t=0}$ ) at 820 nm of  ${}^3\text{SH}^+$  as function of the laser energy in (●) acetonitrile solutions, and in 1 mM phosphate buffer solutions at (■) pH 4.8; (○) pH 8.3; and (□) pH 10.4.

${}^3\text{SH}_2^{2+}$  and  ${}^3\text{S}$ , respectively. It was noted that the above  $\Phi_T$  values are much lower than 0.5, as was previously reported in aqueous media.<sup>7</sup>

### Time-resolved photoacoustic (TRP) measurements

In order to estimate the enthalpy and reaction volume changes produced upon formation of the triplet states of the dye, time-resolved photoacoustic (TRP) measurements were performed, under the same experimental conditions as for the LPF experiments.

Fig. 5 shows a typical set of photoacoustic signals for the dye



**Fig. 5** TRP signals obtained after laser excitation at 532 nm of deaerated 1 mM phosphate buffer solutions at pH 10.4 and 27 °C, for the calorimetric reference Evans blue (curve a) and for  $\text{SH}^+$  (curve b), together with the fit (curve c), residuals and autocorrelation waveforms obtained after the bi-exponential deconvolution procedure.

and the calorimetric reference EB. Analysis of the TRP signals was performed using a deconvolution procedure that has been described elsewhere.<sup>1,12-14</sup> 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  $H(t)$  [eqns. (3) and (4)],<sup>1,13</sup>

$$S(t) = R(t) \otimes H(t) \quad (3)$$

with

$$H(t) = \sum_i \frac{\varphi_i}{\tau_i} \exp\left(-\frac{t}{\tau_i}\right) \quad (4)$$

where  $\varphi_i$  and  $\tau_i$  are the amplitude factor and lifetime for the  $i$ -th component of the TRP signal, respectively.

At pH 8.3 satisfactory fits were obtained with a mono-exponential decay with a lifetime  $\tau_1 < 30$  ns. This value means only that the process involved was faster than the lower time resolution limit of our experimental set-up (*ca.* 20 ns). In fact, fixing this parameter at any value between 1 and 50 ns always resulted in the same value for the pre-exponential factor  $\varphi_1$  [eqn. (4)]. At this pH, the only triplet state species formed is  ${}^3\text{SH}^+$  (see previous section). Therefore,  $\varphi_1$  is a reliable measure of the “prompt” processes related to the formation of the  ${}^3\text{SH}^+$  state during the laser pulse. Furthermore, the LPF experiments showed that  ${}^3\text{SH}^+$  decays with a lifetime of 11  $\mu\text{s}$ , which is longer than the upper detection limit of our experimental set-up for the TRP experiment (*ca.* 3  $\mu\text{s}$ ). Therefore,  ${}^3\text{SH}^+$  can be considered as a “stable product” during the time window of the TRP experiment.

On the other hand, at pH 4.8 and 10.4 good fits of the TRP signals were obtained using a bi-exponential function in the deconvolution procedure, as shown in Fig. 5 for pH 10.4. The lifetime of the fast component was also  $\tau_1 < 30$  ns. This component was again assigned to the prompt formation of the  ${}^3\text{SH}^+$ . In turn, the lifetime ( $\tau_2$ ) of the slow component of the TRP signal was in the range 0.1–3  $\mu\text{s}$ , depending on the pH and the temperature conditions. At room temperature, the  $\tau_2$  values at pH 4.8 and 10.4 were in agreement with the lifetimes of the decay signals observed by LPF at 820 nm at these pH's (Tables 1 and 2). Therefore, the second component of the TRP signals accounts for the formation of the triplet species  ${}^3\text{SH}_2^{2+}$  and  ${}^3\text{S}$  due to the proton-transfer reactions of the precursor triplet state  ${}^3\text{SH}^+$  (Scheme 2).

In order to separate the thermal and the volume change contributions to the acoustic wave the temperature variation method was used, which is based on the dependence of the amplitude factor  $\varphi_i$  on the thermoelastic parameters of the solvent [eqn. (5)],<sup>1,12-14</sup>

$$E_i \varphi_i = q_i + \Delta V_i \left( \frac{c_p \rho}{\beta} \right) \quad (5)$$

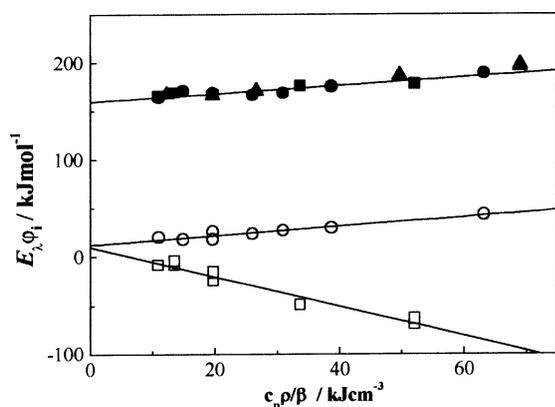
where  $q_i$  is the heat released and  $\Delta V_i$  is the reaction volume change associated with the  $i$ -th process, and  $E_i$  is the excitation molar energy (= 225 kJ mol<sup>-1</sup> at 532 nm).  $c_p$ ,  $\rho$ , and  $\beta$  are the specific heat capacity, the mass density, and the cubic expansion coefficient of the solvent.<sup>19</sup> It is well known that the addition of electrolytes at concentrations >10 mM changes the thermoelastic parameters of water.<sup>12,20</sup> However, the photoacoustic signals for the calorimetric reference EB in pure water and in the buffer solutions were coincident ( $\pm 3\%$ ) over the whole temperature range, indicating that the buffer salts do not modify the thermoelastic parameters of the solution.

In all cases, the amplitude factors  $\varphi_i$  obtained from the fitting of the TRP signals followed a linear dependence with the  $(c_p \rho / \beta)$  ratio, as predicted by eqn. (5) (Fig. 6). The intercept of this plot represents the heat  $q_i$  released in the radiationless processes leading to the different triplet states. The slope of the plots is a measure of the reaction volume changes  $\Delta V_i$  associated with these reactions. The experimental values of  $q_i$  and  $\Delta V_i$  are summarized in Table 2. In order to ensure that the results

**Table 2** Heat released ( $q_i$ ), volume changes ( $\Delta V_i$ ) and lifetime of the slow component of the TRP signals ( $\tau_2$ ) observed upon laser excitation at 532 nm of  ${}^3\text{SH}^+$  in buffered and non-buffered aqueous solutions as a function of pH

pH	$q_1/\text{kJ mol}^{-1}$	$\Delta V_1/\text{cm}^3 \text{mol}^{-1}$	$q_2/\text{kJ mol}^{-1}$	$\Delta V_2/\text{cm}^3 \text{mol}^{-1}$	$\tau_2/\mu\text{s}$
4.8 <sup>a</sup>	163 ± 3	0.3 ± 0.1	10 ± 4	-1.5 ± 0.1	2.6 ± 0.5
4.8 <sup>b</sup>	169 ± 5	0.7 ± 0.1	9 ± 4	-1.2 ± 0.2	2.7 ± 0.5
8.3 <sup>a</sup>	158 ± 7	0.6 ± 0.1	n.d. <sup>d</sup>	n.d.	n.d.
10.4 <sup>a</sup>	160 ± 5	0.4 ± 0.1	8 ± 5	0.5 ± 0.2	0.16 ± 0.03
10.4 <sup>c</sup>	164 ± 5	0.6 ± 0.1	7 ± 3	0.5 ± 0.1	0.15 ± 0.04

<sup>a</sup> 1 mM phosphate buffer solutions. <sup>b</sup> pH adjusted with HCl. <sup>c</sup> pH adjusted with NaOH. <sup>d</sup> n.d. = not detected.



**Fig. 6** Plots of eqn. (5) for the rapidly formed component,  $E_i\phi_1$  ( $\tau < 20$  ns) at ( $\blacktriangle$ ) pH 8.3; ( $\blacksquare$ ) pH 4.8; ( $\bullet$ ) pH 10.4; and for the slow component,  $E_i\phi_2$ , at ( $\square$ ) pH 4.8 ( $\tau \approx 3$   $\mu\text{s}$ ), and ( $\circ$ ) pH 10.4 ( $\tau \approx 150$  ns) of the TRP signals.

were not affected by the presence of the buffer, we performed similar experiments in non-buffered solutions at pH 4.8 and 10.4 in the presence of HCl or NaOH. As shown in Table 2, the results were identical (within experimental error) to those observed in buffer solutions.

#### Thermochemical analysis of the calorimetric results

As was mentioned before, the prompt contribution to the TRP signal was attributed to the intramolecular formation of the  ${}^3\text{SH}^+$  state in a few nanoseconds after the laser pulse. Under the present experimental conditions, this process is expected to be independent of the pH, as confirmed by the similar  $q_1$  values (Table 2). Therefore, an average value of  $q_1 = 163 (\pm 4) \text{ kJ mol}^{-1}$  was determined for this process, and it includes contributions from vibrational relaxation  $S_n \rightarrow S_0$ , nonradiative deactivation  $S_1 \rightarrow S_0$ , and  $S_1 \rightarrow T_1$  transition. In this case, the energy balance including the formation of  ${}^3\text{SH}^+$  is given by eqn. (6),

$$E_i = q_1 + \Phi_f E_s + \Phi_T E_T \quad (6)$$

where  $\Phi_f E_s = 13 (\pm 1) \text{ kJ mol}^{-1}$  is the energy lost as fluorescence from the  ${}^1\text{SH}^+$  state, calculated with the energy of the singlet state  $E_s = 230 (\pm 5) \text{ kJ mol}^{-1}$ ,<sup>18</sup> and  $\Phi_f = 0.058$  (see Experimental section). The quantity  $\Phi_T E_T$  is the energy stored by  ${}^3\text{SH}^+$ . Thus, a molar triplet energy content  $E_T = 175 (\pm 15) \text{ kJ mol}^{-1}$  was calculated with eqn. (6) and using  $\Phi_T = 0.28$  as determined by our LFP experiments. The calculated  $E_T$  value for  ${}^3\text{SH}^+$  in aqueous media agrees with the energy values reported in methanol ( $178 \text{ kJ mol}^{-1}$ ),<sup>4</sup> and in acetonitrile ( $176 \text{ kJ mol}^{-1}$ ).<sup>3,4</sup> Alternatively, if  $\Phi_T = 0.5$  is used (as reported by Baumgartner *et al.*<sup>7</sup> in aqueous solutions), the photoacoustic data yield  $E_T = 98 (\pm 10) \text{ kJ mol}^{-1}$ , which is too low compared with the values reported in polar solvents.<sup>3,4</sup> Therefore, our estimate of  $\Phi_T = 0.28 (\pm 0.05)$  in water seems to be a more reliable one for the dye.

In accordance with Scheme 2, the slow  $q_2$  values observed at pH 4.8 and 10.4 are related by the molar enthalpy change

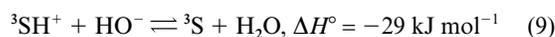
(exothermic)  $\Delta H_r$ , associated in the proton-transfer reactions for the formation of  ${}^3\text{SH}_2^{2+}$  or  ${}^3\text{S}$  from the  ${}^3\text{SH}^+$  species,

$$\Delta H_r = \frac{-q_2}{\Phi_T} \quad (7)$$

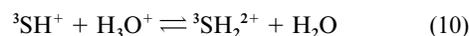
Thus, eqn. (7) yields  $\Delta H_r = -46 (\pm 20)$  and  $-29 (\pm 15) \text{ kJ mol}^{-1}$  for the formation of the  ${}^3\text{SH}_2^{2+}$  and  ${}^3\text{S}$  species, using  $\Phi_T$  as 0.22 and 0.28, respectively. The feasibility of these values obtained by the TRP technique can be confirmed by the following simple thermodynamic analysis of the protonation equilibria of the triplet states. According to the  $\text{p}K_a$  value reported by Baumgartner *et al.*,<sup>7</sup> a standard Gibbs energy change of  $\Delta G^\circ = 53 \text{ kJ mol}^{-1}$  can be estimated for eqn. (8).



Assuming that the entropy of hydration of  ${}^3\text{SH}^+$  is negligible due to its size and charge delocalization, we can use  $\Delta S^\circ = -84 \text{ J mol}^{-1} \text{ K}^{-1}$  for eqn. (8), which is a mean value for the dissociation of neutral organic acids in aqueous solutions.<sup>21</sup> In this way a standard enthalpy change of  $\Delta H^\circ = 28 \text{ kJ mol}^{-1}$  can be approximated for eqn. (8), which together with the  $-57 \text{ kJ mol}^{-1}$  for the heat of neutralization in diluted aqueous solution,<sup>22</sup> affords an estimation of  $\Delta H^\circ$  for the relevant equilibrium at basic pH [eqn. (9)].



In turn, for acidic solutions, *e.g.* pH = 4.8, the relevant equilibrium is,



where eqn. 10 is the inverse of the acid dissociation of  ${}^3\text{SH}_2^{2+}$  with a  $\text{p}K_a$  of 7.5.<sup>7</sup> By using this equilibrium constant and assuming now a similar entropy change contribution for the dication  ${}^3\text{SH}_2^{2+}$  as for  $\text{H}_3\text{O}^+$ , a value of  $\Delta H^\circ = -43 \text{ kJ mol}^{-1}$  was estimated for eqn. (10).

The calculated  $\Delta H^\circ$  values are in remarkable agreement with the values of  $\Delta H_r$  obtained from the TRP measurement of  $q_2$  [eqn. (7)], *i.e.*  $-46 (\pm 20)$  and  $-29 (\pm 15) \text{ kJ mol}^{-1}$  for  ${}^3\text{SH}_2^{2+}$  and  ${}^3\text{S}$ , respectively. This shows the versatility of the TRP technique in determining the thermodynamic quantities associated with excited state acid–base equilibria in solution, such as eqns. (9) and (10). The above results also indicate that when intermolecular processes lead to the formation of long-lived excited species or radicals, the heat release observed by TRP may not be a direct measurement of the energy level difference between the excited states of the transient species. Instead, if it is assumed that the experimental  $\Delta H_r$  value is only a measure of the energy difference between the triplet species, it would place the energy levels (relative to the  $\text{SH}^+$  ground state) of the triplet states  ${}^3\text{SH}_2^{2+}$  and  ${}^3\text{S}$  at  $129 (\pm 20)$  and  $146 (\pm 15) \text{ kJ mol}^{-1}$ , respectively. In fact, the agreement between the TRP data and the thermodynamic calculations supports the assumption that  $\Delta H_r$  contains an important contribution from the

proton-transfer reaction of  ${}^3\text{SH}^+$  with the medium, and therefore the actual intrinsic energy content of the  ${}^3\text{SH}_2^{2+}$  and  ${}^3\text{S}$  species must lie higher than the above values.

### Molecular volume changes

As shown in Table 2, the formation of  ${}^3\text{SH}^+$  was accompanied by a small volume change  $\Delta V_1 = +0.5 (\pm 0.2) \text{ cm}^3 \text{ mol}^{-1}$  (average value from Table 2). This value must be corrected by the quantum yield of the process in order to obtain the reaction volume change per photoconverted mole of triplet state,  $\Delta V_T = \Delta V_1/\Phi_T$ . Thus,  $\Delta V({}^3\text{SH}^+) = +1.8 (\pm 0.7) \text{ cm}^3 \text{ mol}^{-1}$  was obtained, and represents the partial molar volume difference between the triplet and ground state of  $\text{SH}^+$ .

In order to explain molecular volume changes in solution, three contributions to the partial molar volume of a solute may be considered: (i) the van der Waals molecular volume  $V_{\text{vdw}}$ , (ii) the contraction of the solvent due to electrostrictive effects  $V_{\text{el}}$  (if electrical charges or permanent dipole moments are created), and (iii) a positive contribution resulting from the discontinuous structure of the solvent and the additional void volume in the direct solvent shell surrounding the solute,  $V_{\text{ss}}$ .<sup>23–25</sup> This last term results from the perturbation of the packing of the solvent molecules in the liquid due to the addition of a solute molecule.<sup>25</sup> In aqueous media or proton donor solvents, a fourth contribution due to hydrogen bonding interactions between the solute and the solvent molecules,  $V_{\text{hb}}$ , should also be considered.<sup>26</sup> In any case, the reaction volume change is given by the difference between the partial molar volume(s) of the product(s) and reactant(s) [eqn. (11)].

$$\Delta V_R = \Delta V_{\text{vdw}} + \Delta V_{\text{el}} + \Delta V_{\text{ss}} + \Delta V_{\text{hb}} \quad (11)$$

In the formation of the  ${}^3\text{SH}^+$  state it is expected that  $\Delta V_{\text{vdw}} \approx 0$  and  $\Delta V_{\text{ss}} \approx 0$ , because the process only involves a prompt intersystem crossing without bond breaking, isomerization, or chemical reaction, *etc.* The electrostrictive effect  $\Delta V_{\text{el}}$  of the change in molecular dipolar moment upon the formation of the  ${}^3\text{SH}^+$  state can be estimated by using a modification of the Drude–Nernst equation,<sup>27</sup> which is essentially applicable when there is no total charge separation [eqn. (12)].

$$\Delta V_{\text{el}} = -3N_A \frac{\Delta\mu^2}{r^3} \left( \frac{\partial\epsilon}{\partial P} \right)_T \frac{1}{(2\epsilon + 1)^2} \quad (12)$$

Here  $N_A$  is the Avogadro constant,  $\Delta\mu$  is the dipole moment change of the species,  $r$  is the effective cavity radius, and  $(\partial\epsilon/\partial P)_T$  is the pressure dependence of the relative permittivity at constant temperature ( $3.68 \times 10^{-3} \text{ bar}^{-1}$  at  $25^\circ\text{C}$ , in water).<sup>28</sup> Eqn. (12) yields a value of  $\Delta V_{\text{el}} \leq \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$  using  $r = 5.5 \text{ \AA}$ ,<sup>8</sup> and assuming  $\Delta\mu \leq \pm 10 \text{ D}$ , which is a large enough change in dipole moment for triplet formation. Thus, the electrostrictive contribution  $\Delta V_{\text{el}}$  was ruled out because of its low magnitude. Therefore, the expansion observed for  ${}^3\text{SH}^+$  can be associated with a reduction of the hydrogen bonding interactions with the solvent sphere molecules upon formation of the triplet state, due to a decrease of charge density at the interaction site. Similar behavior with hydrogen bonding interaction between excited states and their solvation spheres has been shown to be an important factor in structural volume changes in both inorganic and organic compounds.<sup>26,29–31</sup>

On the other hand, the formation of the  ${}^3\text{SH}_2^{2+}$  and  ${}^3\text{S}$  states involves a new charge distribution [eqn. (10) and (11)]. Thus, a more significant reaction volume change per photoconverted mole of triplet state can be anticipated. The respective values resulting from  $\Delta V_T = \Delta V_2/\Phi_T$ , are  $\Delta V({}^3\text{SH}_2^{2+}) = -6.1 (\pm 0.9) \text{ cm}^3 \text{ mol}^{-1}$ , and  $\Delta V({}^3\text{S}) = +1.8 (\pm 0.7) \text{ cm}^3 \text{ mol}^{-1}$ . These volume changes represent the partial molar volume difference between  ${}^3\text{SH}_2^{2+}$  or  ${}^3\text{S}$  with  ${}^3\text{SH}^+$ . In both cases, it can also be

assumed that  $\Delta V_{\text{vdw}} \approx 0$ , since the van der Waals radius of  ${}^3\text{SH}_2^{2+}$  and  ${}^3\text{S}$  should be almost the same as for  ${}^3\text{SH}^+$ . Since a change in the electrical charge distribution is produced, electrostrictive effects are expected. An approximate estimation of the electrostrictive effect in processes where electrical charges are destroyed and/or created can be obtained with the Drude–Nernst [eqn. (13)],<sup>32</sup> which describes the contraction of the solvent molecules with a homogeneous relative permittivity  $\epsilon$ , due to the electrical field of an ion of charge  $z$  and radius  $r$ .

$$V_{\text{el}}/\text{cm}^3 \text{ mol}^{-1} = -N_A \frac{z^2 e^2}{2r\epsilon^2} \left( \frac{\partial\epsilon}{\partial P} \right)_T = -B \frac{z^2}{r} \quad (13)$$

In water, the semiempirical reduced constant  $B$  ( $B \approx 10$ , if the ionic radius is expressed in  $\text{\AA}$  and the ion charge  $z$  as an integer number) contains corrections due to the structured organization of water.<sup>32</sup> Therefore, an estimation of the  $\Delta V_{\text{el}}$  contribution in the formation of  ${}^3\text{SH}_2^{2+}$  or  ${}^3\text{S}$  from  ${}^3\text{SH}^+$  is obtained from eqn. (13) with the same molecular radius ( $5.5 \text{ \AA}$ )<sup>8</sup> for all triplet states, as shown in eqns. (14) and (15).<sup>29</sup>

$$\Delta V_{\text{el}}[{}^3\text{SH}_2^{2+}/{}^3\text{SH}^+] = -\frac{B}{r} \Delta z^2 = -B \frac{3}{r} = -5.5 \text{ cm}^3 \text{ mol}^{-1} \quad (14)$$

$$\Delta V_{\text{el}}[{}^3\text{S}/{}^3\text{SH}^+] = -\frac{B}{r} \Delta z^2 = +\frac{B}{r} = +1.8 \text{ cm}^3 \text{ mol}^{-1} \quad (15)$$

The calculated  $\Delta V_{\text{el}}$  values are in very good agreement with the experimental  $\Delta V_T$  ones, considering the simplicity of the Drude–Nernst equation. This agreement supports the assumption that the main volume change contribution in the proton-transfer reactions of  ${}^3\text{SH}^+$  arises from electrostrictive effects involving the change in charge distribution on the dye molecules rather than from hydrogen bonding or solvent packing effects.

### Conclusions

In summary, laser-flash photolysis experiments over the pH range of 4–11 showed the prompt formation of  ${}^3\text{SH}^+$  with  $\Phi_T = 0.28$ . At pH 8.3 this species decays to the ground state, but at pH 4.8 and 10.4, it reacts with protons or hydroxy ions with diffusion-controlled rate constants to form the dicationic  ${}^3\text{SH}_2^{2+}$  and the neutral  ${}^3\text{S}$  triplet states, respectively.

The time-resolved photoacoustic (TRP) technique allows the accurate determination of the energy content (relative to the  $\text{SH}^+$  ground state) of the rapidly formed triplet state  ${}^3\text{SH}^+$ , *i.e.*  $E_T = 175 \text{ kJ mol}^{-1}$ . However, at pH 4.8 and 10.4 the observed slow heat release values  $q_2$  should be related more to the thermochemical balance associated with the intermolecular proton-transfer reactions for formation of  ${}^3\text{SH}_2^{2+}$  or  ${}^3\text{S}$  from the  ${}^3\text{SH}^+$  species, rather to the energy gap between the different triplet state species. This conclusion is drawn from the remarkable agreement with the enthalpy changes obtained from the thermodynamic data of the acid–base equilibria of the triplet states of the dye.

This is an important point when considering the use of the heat release measured by TRP for the calculation of the energy levels of transient or permanent species when intermolecular or solvent reactions are occurring.

Finally, the volume expansion of  $1.8 \text{ cm}^3 \text{ mol}^{-1}$  observed upon formation of the  ${}^3\text{SH}^+$  state accounts for the partial molar volume difference between the triplet and the ground state of the dye, mainly as a result of the changes in the hydrogen bonding interaction of the dye with its solvation sphere. The volume changes observed upon formation of  ${}^3\text{SH}_2^{2+}$  and  ${}^3\text{S}$  account for the electrostrictive effect produced by the change in the distribution of charges after the proton-transfer reactions in the excited triplet states.

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