# Deactivation of the first excited singlet state of thiophenols

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On the bases of picosecond and nanosecond laser flash photolysis with detection by emission and absorption spectroscopy, a quantitative description is given of all deactivation channels of the first excited singlet state of thiophenols ArSH($S_1$) such as fluorescence, intersystem crossing (ISC), chemical dissociation into radicals, and radiation-less internal conversion (IC). For this purpose, the photolysis of thiophenol and its methyl-, methoxy-, and chloro-substituted derivatives was studied in solvents of increasing polarity: 1-chlorobutane, ethanol, and acetonitrile. The fluorescence lifetime of the thiophenols was found to range from some hundreds of picoseconds up to a few nanoseconds, correlating with fluorescence quantum yields between 0.001–0.040, at room temperature. Depending on the substitution pattern of the aromatic ring, the quantum yield of the S–H bond dissociation was found to be between 0.3–0.5, irrespective of the solvent polarity. In laser photolysis, no triplet formation of the investigated compounds could be observed neither by the direct way nor by subsequent sensitization with β-carotene. As a difference to the total, the radiation-less internal conversion ($\Phi_{IC} \geq 0.5$) was found to be the dominating process.

## Introduction

Because of their antioxidant properties, the photophysics and photochemistry of thiols are of great interest in various fields of science and technology.[1,2] In biological systems, the widespread thiols play a prominent role. Because of their low ionization potential and the relatively weak S–H bond, they are active in radical repair and deactivation as well as in cellular redox processes.[3,4] Thiols are often thought to act as protectors against ionizing radiation *via* their radical scavenging activity. In addition, it was found that thiyl radicals also cause biologically important chemical changes such as the efficient *cis–trans* isomerisation of mono- and polyunsaturated fatty acid residues in model membranes *via* a catalytic action.[5,6] The knowledge about light- and radiation-induced transient reaction behaviour of aliphatic thiols is widely understood, while that of aromatic thiols is limited.

To establish what happens after a thiophenol (ArSH) molecule has been excited by an UV photon with regard to the relaxation of the first excited singlet state ArSH($S_1$), the competing reactions (1)–(6) should be considered.

$$\mathrm{ArSH} + h\nu_1 \rightarrow \mathrm{ArSH(S_1)} \quad (1)$$

$$\mathrm{ArSH(S_1)} \rightarrow \mathrm{ArSH(S_0)} + h\nu_2 \quad \text{fluorescence} \quad (2)$$

$$\rightarrow \mathrm{ArSH(S_0)} + E \quad \text{internal conversion} \quad (3)$$

$$\rightarrow \mathrm{ArSH(T_1)} \quad \text{intersystem crossing} \quad (4)$$

$$\rightarrow \mathrm{ArS^\bullet} + \mathrm{H^\bullet} \quad \text{dissociation} \quad (5)$$

$$+ \mathrm{ArSH} \rightarrow 2\,\mathrm{ArSH(S_0)} \quad \text{self-quenching} \quad (6)$$

$$\mathrm{ArSH} + h\nu/2h\nu \rightarrow [\mathrm{ArSH^{\bullet+}} + e^-_{\mathrm{solv}}] \rightarrow \mathrm{ArS^\bullet} + \mathrm{H^+} + e^-_{\mathrm{solv}} \quad \text{ionization} \quad (7a)$$

$$\mathrm{ArS^-} + h\nu \rightarrow \mathrm{ArS^\bullet} + e^-_{\mathrm{solv}} \quad \text{ionization} \quad (7b)$$

ArSH = thiophenol, $E$ = excess heat.

Our experimental conditions were chosen in such a way that self-quenching (reaction (6)), and a possible photoionization, which occurs at higher laser power (reaction (7a)) or at high pH-values (reaction (7b)) in aqueous solution, could be neglected. Our interest was only focused on the remaining reactions (1)–(5).

Generally, it is known that photoexcitation of aromatic thiols in polar or non-polar solvents at room temperature results in the formation of phenylthiyl radicals ($\mathrm{ArS^\bullet}$).[7–9] Yet, the excited state precursors of the phenylthiyl radical formation of aromatic thiols have not been characterized. Information on the mechanism of the radical formation does not exist, nor has any quantitative data of the deactivation channels of the first excited singlet state of the aromatic thiols been reported.

In a previous paper,[10] we reported a quantitative description of the deactivation channels of the first excited singlet state of 2- and 4-thiosalicylic acids. The main point of that study was the first observation of a directly photogenerated triplet state of those compounds. But, as it will be shown in this paper, triplet states of thiophenols are not generated directly by photoexcitation. The triplet states of these compounds, however, could be generated *via* pulse radiolysis by sensitization experiments with compounds of higher triplet energy.[11]

In this paper, we give a comprehensive picture and a quantitative description of all deactivation channels of the first excited singlet state ($S_1$) of various thiophenols generated by mono-photonic excitation (see reactions (1)–(5)). Because

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of the complexity of the problem and the variety of influencing factors, the treatment is based on the separate investigation of the singlet relaxation processes. Therefore, we *directly* investigated all of the $S_1$ deactivation pathways except for internal conversion (reaction (3)) using the complementary methods of laser photolysis and pulse radiolysis with detection by emission and absorption spectroscopy. The remaining radiationless internal conversion was then determined by a difference calculation using the experimental data.

## Experimental

### Materials

Acetonitrile (AN), ethanol (EtOH), and 1-chlorobutane (1-BuCl) of the highest spectroscopic grade were chosen as solvents (99.9%, VWR). Benzophenone (99.9%), naphthalene (99%) and β-carotene (95%) were obtained from Aldrich. High grade phenol (99.5%) was obtained from Riedel–de Haen. Water treated in a Millipore milli-Q plus system was used for the experiments in aqueous solutions.

The following thiophenols were investigated: thiophenol (ArSH, Acros), 2-, 3-, and 4-thiocresol (2-, 3-, and 4-$CH_3$-ArSH, Aldrich), 2,4-, 2,6-, and 3,5-dimethylthiophenol (2,4-, 2,6-, 3,5-DMTP) (Acros), 2,4,6-trimethylthiophenol (2,4,6-TMTP, Acros), 2-, 3-, and 4-methoxythiophenol (2-, 3-, and 4-MeO-ArSH, Acros), and 4-chlorothiophenol (4-Cl-ArSH, Aldrich). All thiophenols were of the highest analytical grade and partially further purified by recrystallization from an alcohol–water mixture (1 : 2) or preparative chromatography.

### Apparatus and methods

The ground state optical absorption and fluorescence spectra were recorded with an UV/VIS spectrophotometer (UV-2101 PC, Shimadzu) and a FluoroMax-2 (Instruments S. A., Jobin Yvon-Spex), respectively.

**Picosecond laser photolysis.** The fluorescence lifetimes were measured with an amplified (CPA) 10 Hz Ti:Sapphire femtosecond-UV laser system. After excitation with a 250 fs (FWHM) laser pulse at 253 nm, a highly sensitive streak camera C5680/M5676 (Hamamatsu Photonics) recorded the fluorescence kinetics. A time resolution of 1 ps was achieved for the emission studies by applying the deconvolution technique.[12]

**Nanosecond laser flash photolysis.** Real-time nanosecond laser photolysis was applied with detection by absorption spectroscopy. The solutions were photolyzed by the fourth harmonics (266 nm) of a Quanta-Ray GCR-11 Nd:YAG laser (Spectra Physics). Pulses of $<3$ ns duration (FWHM) with energies of 0.5 mJ were used. The optical detection system consisted of a pulsed xenon lamp (XBO 150, Osram), monochromator (SpectraPro-275, Acton Research), R955 photomultiplier tube (Hamamatsu Photonics) or fast Si-photodiode with 1 GHz amplification, and a 500 MHz digitizing oscilloscope (DSA 602 A, Tektronix). The laser power was monitored for every pulse using a bypath with a fast Si photodiode. The laser flash photolysis set-up is reported elsewhere in more detail.[13]

**Electron pulse radiolysis.** The liquid samples were irradiated with high energy electron pulses (1 MeV, 12 ns duration) generated by a pulse transformer type accelerator ELIT (Institute of Nuclear Physics, Novosibirsk, Russia). The dose delivered per pulse was measured with an electron dosimeter and was usually between 50–100 Gy. Detection of the transient species was performed using an optical absorption set-up consisting of a pulsed xenon lamp (XPO 450, Osram), monochromator (SpectraPro-500, Acton Research), R4220 photomultiplier (Hamamatsu Photonics) and 1 GHz digitizing oscilloscope (TDS 640, Tektronix). Further details of this equipment are given elsewhere.[14]

All experiments were performed at room temperature. Freshly prepared solutions were used flowing continuously through a 5 mm or 10 mm quartz sample cell in laser photolysis or pulse radiolysis, respectively. Prior to the laser photolysis and pulse radiolysis experiments, the solutions were deoxygenated by bubbling with purest grade $N_2$ or saturated with the desired gas for 15 min, and were used within 1 h.

**Quantum chemical approach.** Dipole moments and S–H bond dissociation energies for the singlet ground and excited states of the parent thiophenol were calculated using DFT B3LYP method[15] with the 6-311+G(d, p) basis set (Gaussian 03).[16]

## Results and discussion

### Steady state measurements

Fluorescence spectra of thiophenol were studied in polar (acetonitrile and ethanol) and non-polar surroundings (1-chlorobutane) as shown in Fig. 1. In each of these solvents, the spectra consist of a broad and unstructured band. The fluorescence maxima are given in Table 1. The steep decay on the UV side is explained by the background Raman line appearing in all solvents. For substituted thiophenols, an analogous behaviour has been formed. Hence, it was found that the fluorescence maxima of all aromatic thiols are around $\lambda_{F\ (max)} = 295–310$ nm.

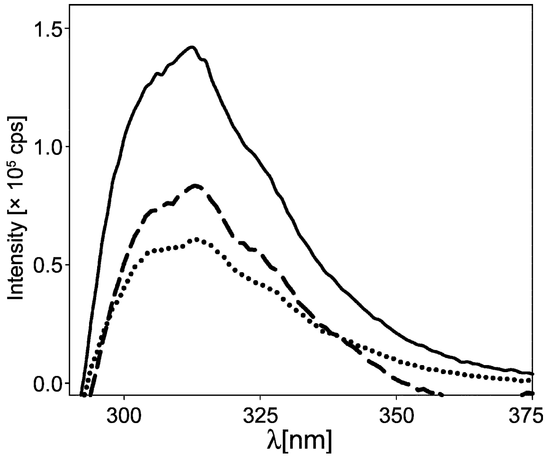


**Fig. 1** Corrected fluorescence spectra ($\lambda_{exc} = 266$ nm) of thiophenol (0.4 mmol $dm^{-3}$) in 1-chlorobutane (· · · ·), ethanol (– – –), and acetonitrile (——) solutions at room temperature.

**Table 1** Spectral parameters of fluorescence and phenylthiyl radicals of thiophenols

| Substances | $\lambda_{F(max)}{}^a$/nm | $ArS^{\bullet b}$ $\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ | $\lambda_{max}$/nm |
|---|---|---|---|
| ArSH | 310 | | 295 |
| | | 2000 | 460 |
| 2-Me-ArSH | 300 | | 300 |
| | | 2200 | 460 |
| 3-Me-ArSH | 300 | | 300 |
| | | 2000 | 470 |
| 4-Me-ArSH | 310 | | 310 |
| | | 2100 | 500 |
| 2-MeO-ArSH | 315 | | 320 |
| | | 2000 | 460 |
| 3-MeO-ArSH | 305 | | 300 |
| | | 2200 | 480 |
| 4-MeO-ArSH | 315 | | 320 |
| | | 6300 | 520 |
| 4-Cl-ArSH | 325 | | 300 |
| | | 3500 | 510 |
| 2,4-DMTP | 310 | | 310 |
| | | 3500 | 480 |
| 3,5-DMTP | 300 | | 300 |
| | | 3000 | 480 |
| 2,6-DMTP | 296 | | 300 |
| | | 3000 | 470 |
| 2,4,6-TMTP | 305 | | 320 |
| | | 3500 | 480 |

[a] The $\lambda_F$ maxima are in polar solvents (EtOH and AN) at room temperature. [b] The $\varepsilon_{(ArS^\bullet)}$ values were calculated in a $N_2O$-saturated alkaline aqueous solution (pH 12) of thiophenols (2 mmol dm$^{-3}$) at $\lambda_{max}$ in the visible region using sodium azide (0.02 mol dm$^{-3}$) by pulse radiolysis. The wavelength accuracy is ±1 nm.

## Fluorescence kinetics

We determined the fluorescence lifetimes, $\tau_F$, by recording the fluorescence decay using a streak camera for the $S_0 \leftarrow S_1$ transition of thiophenols in 1-BuCl, EtOH and AN.

As shown in Fig. 2, the fluorescence kinetics of thiophenol is described by a bi-exponential function. One component decays rapidly in a few tens of ps (a $\tau_{S2}$ = 30–50 ps), and the other decays in longer times ($\tau_{S1}$ = 0.58–2.70 ns (see also Table 2).

For substituted thiophenols, a similar behaviour is observed. The corresponding fluorescence lifetimes are given in Table 2. The only exception is the fluorescence decay of 2-methoxythiophenol, which can be fitted by a single exponential function in all of the solvents used (see Fig. 3). The lifetimes were found to be nearly constant around ~40 ps, irrespective to the solvent polarity.

Due to the use of a cut-off filter ($\lambda$ = 308 nm), the contributions of the 290 nm emission caused by the quartz cell and the scattering light due to the excitation pulse are excluded from consideration. Nevertheless, the fluorescence decay profiles measured within a narrow emission wavelength window did not show the expected single exponential decay. The short component of the decay behaviour might be either be attributed to the spectral shifts which appear when the timescales for relaxation and emission are comparable[17] or to a $S_0 \leftarrow S_2$ transition. Using different cut-off filters (308, 340, and 390 nm), we found that the intensity of the short component ($\tau_{S2}$) was strongly decreased. This suggests a $S_0 \leftarrow S_2$ relaxation.

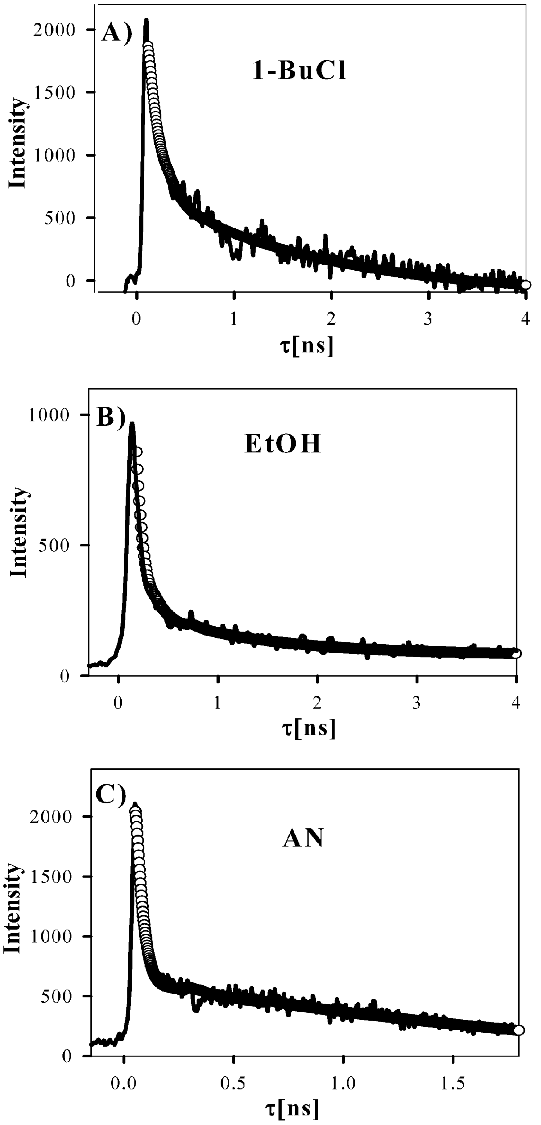


**Fig. 2** Experimental fluorescence decay (—) ($\lambda_{exc}$ = 253 nm) of thiophenol (0.4 mmol dm$^{-3}$) in (A) 1-BuCl, (B) EtOH, and (C) AN solutions. The bi-exponental fit curves (○) describe the fluorescence kinetics.

Obviously, the values of the short component ($\tau_{S2}$) in EtOH, and AN are close to that in 1-BuCl. But for the major component ($\tau_{S1}$) a more pronounced difference is observed. We assume that $S_0 \leftarrow S_2$ transition is too rapid and therefore it occurs without any chemical consequence. Despite of a few exceptions, the following conclusions can be drawn from the data given in Table 2:

(i) For a fixed thiophenol type, the fluorescence lifetime always increases with rising solvent polarity (characterized by the dielectric constant).

(ii) At first inspection, a mono-substitution with an electron-donating group (methyl- or methoxy) enhances the fluorescence lifetime.

(iii) Compared with *m*- or *p*-thiocresol, a methyl group in the *ortho* position enhances the fluorescence lifetime strongly.

(iv) Mono-substitution in the *para* position only slightly affects the fluorescence lifetimes.

**Table 2** Quantum yields ($\Phi$) of all deactivation channels and fluorescence kinetics of the first excited singlet state of thiophenols in 1-BuCl, EtOH, and AN at room temperature. The indices of $\Phi$ refer to fluorescence (F), triplet (T), dissociation (D), and radiation-less internal conversion (IC), $\tau_{S1}$ and $\tau_{S2}$ are the fluorescence lifetimes of $S_1$ and $S_2$, respectively

| | 1-BuCl ($\varepsilon$ = 7 dm$^3$ mol$^{-1}$ cm$^{-1}$)$^a$ | | | | | |
|---|---|---|---|---|---|---|
| | | | | | $\tau_F$/ns $^b$ | |
| | $\Phi_F$ | $\Phi_T$ | $\Phi_D$ | $\Phi_{IC}$ | $\tau_{S1}$ | $\tau_{S2}$ |
| ArSH | 0.003 | 0 | 0.30 | 0.697 | 0.58 | 0.03 |
| 2-CH$_3$-ArSH | 0.006 | 0 | 0.45 | 0.544 | 3.10 | 0.12 |
| 3-CH$_3$-ArSH | 0.006 | 0 | 0.40 | 0.594 | 0.30 | — |
| 4-CH$_3$-ArSH | 0.0006 | 0 | 0.40 | 0.594 | 0.58 | — |
| 2-MeO-ArSH | 0.006 | 0 | 0.40 | 0.594 | 0.03 | — |
| 3-MeO-ArSH | 0.020 | 0 | 0.45 | 0.530 | 1.40 | — |
| 4-MeO-ArSH | 0.001 | 0 | 0.40 | 0.599 | 2.10 | 0.27 |
| 4-Cl-ArSH | 0.0006 | 0 | 0.40 | 0.599 | 1.2 | 0.01 |
| 2,4-DMTP | 0.005 | 0 | 0.40 | 0.595 | 1.50 | 0.04 |
| 2,6-DMTP | 0.004 | 0 | 0.40 | 0.596 | 2.35 | 0.03 |
| 3,5-DMTP | 0.007 | 0 | 0.40 | 0.593 | 3.20 | 0.18 |
| 2,4,6-TMTP | 0.003 | 0 | 0.50 | 0.497 | 1.70 | 0.02 |

| | EtOH ($\varepsilon$ = 24 dm$^3$ mol$^{-1}$ cm$^{-1}$)$^a$ | | | | | |
|---|---|---|---|---|---|---|
| | | | | | $\tau_F$/ns$^b$ | |
| | $\Phi_F$ | $\Phi_T$ | $\Phi_D$ | $\Phi_{IC}$ | $\tau_{S1}$ | $\tau_{S2}$ |
| ArSH | 0.004 | 0 | 0.30 | 0.696 | 1.20 | 0.05 |
| 2-CH$_3$-ArSH | 0.017 | 0 | 0.30 | 0.683 | 3.50 | 0.03 |
| 3-CH$_3$-ArSH | 0.011 | 0 | 0.30 | 0.689 | 0.31 | 0.03 |
| 4-CH$_3$-ArSH | 0.002 | 0 | 0.30 | 0.698 | 1.35 | 0.05 |
| 2-MeO-ArSH | 0.011 | 0 | 0.50 | 0.489 | 0.04 | — |
| 3-MeO-ArSH | 0.03 | 0 | 0.40 | 0.570 | 2.00 | 0.05 |
| 4-MeO-ArSH | 0.002 | 0 | 0.70 | 0.298 | 1.12 | 0.04 |
| 4-Cl-ArSH | 0.002 | 0 | 0.30 | 0.698 | 1.25 | — |
| 2,4-DMTP | 0.01 | 0 | 0.30 | 0.690 | 0.50 | 0.03 |
| 2,6-DMTP | 0.01 | 0 | 0.30 | 0.690 | 2.70 | 0.03 |
| 3,5-DMTP | 0.01 | 0 | 0.45 | 0.540 | 2.90 | 0.03 |
| 2,4,6-TMTP | 0.007 | 0 | 0.55 | 0.443 | 1.70 | 0.01 |

| | AN ($\varepsilon$ = 38 dm$^3$ mol$^{-1}$ cm$^{-1}$)$^a$ | | | | | |
|---|---|---|---|---|---|---|
| | | | | | $\tau_F$/ns$^b$ | |
| | $\Phi_F$ | $\Phi_T$ | $\Phi_D$ | $\Phi_{IC}$ | $\tau_{S1}$ | $\tau_{S2}$ |
| ArSH | 0.004 | 0 | 0.30 | 0.696 | 2.70 | 0.03 |
| 2-CH$_3$-ArSH | 0.013 | 0 | 0.40 | 0.587 | 5.20 | 0.04 |
| 3-CH$_3$-ArSH | 0.013 | 0 | 0.40 | 0.587 | 0.35 | — |
| 4-CH$_3$-ArSH | 0.001 | 0 | 0.50 | 0.499 | 1.20 | 0.03 |
| 2-MeO-ArSH | 0.010 | 0 | 0.80 | 0.190 | 0.04 | — |
| 3-MeO-ArSH | 0.037 | 0 | 0.50 | 0.463 | 2.60 | 0.24 |
| 4-MeO-ArSH | 0.002 | 0 | 0.60 | 0.398 | 3.00 | 0.02 |
| 4-Cl-ArSH | 0.001 | 0 | 0.40 | 0.599 | 1.90 | 0.01 |
| 2,4-DMTP | 0.009 | 0 | 0.50 | 0.491 | 1.00 | 0.03 |
| 2,6-DMTP | 0.009 | 0 | 0.40 | 0.591 | 2.90 | 0.03 |
| 3,5-DMTP | 0.012 | 0 | 0.50 | 0.488 | 3.60 | 0.02 |
| 2,4,6-TMTP | 0.007 | 0 | 0.50 | 0.493 | 1.70 | 0.02 |

[a] The yields are within ±10% accuracy. [b] The error of $\tau_F$ is about ±10%.

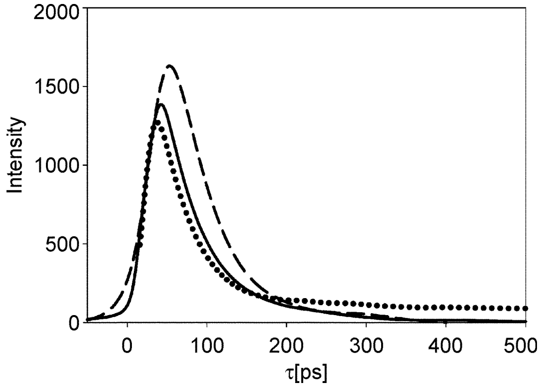


**Fig. 3** Experimental fluorescence decay of 2-methoxythiophenol (0.4 mmol dm$^{-3}$) in 1-BuCl (· · · ·), EtOH (– – –), and AN (——) solutions.

(v) Surprisingly, a methoxy group in the *ortho* (neighbouring) position to the –SH group causes extremely short lifetimes ($\tau_F$ between 30–40 ps).

(vi) A chloro-substituent in the *para* position seems to slightly enhance the fluorescence lifetime.

(vii) The fluorescence lifetimes of di-, and trimethyl-substituted thiophenols are longer than those of the thiophenol. Indeed, the lifetimes ($\tau_{S1}$) increase in the following order: $\tau_{3,5\text{-DMTP}} > \tau_{2,6\text{-DMTP}} > \tau_{2,4,6\text{-DMTP}} > \tau_{2,4\text{-DMTP}}$.

(viii) For 2,4,6-TMTP, the fluorescence lifetimes are quite similar in 1-BuCl, EtOH, and AN ($\tau_{S1}$ = 1.7 ns).

Hence, the fluorescence behaviour of aromatics depends not only on the chemical and physical properties of the surroundings,[18] but also on the nature and position of the substituent. Because of the very complex factors of influence (protic and aprotic media, polarity, viscosity, and dipole moment phenomena), any satisfying interpretation is difficult.

On the basis of our data, general solvent–solute excited state interactions[19] as well as specific interactions were considered. However, we are unable to distinguish between the influences of these effects because of the small polarity of aromatic thiols. On the other hand, it seems that the nature of the chromophore mainly affects the fluorescence lifetimes.

Generally, it seems that electron-donating groups induce stabilization of the first excited singlet state, whereas electron-withdrawing groups do the opposite. Surprisingly, the 2-MeO-ArSH exhibits an extremely short fluorescence lifetime ($\tau_F$ between 30–40 ps). This might be caused by the low stability of the first excited singlet state $S_1$ and points to a more efficient non-radiative relaxation. This peculiar influence might be attributed to the interaction between the –SH group and an oxygen lone electron pair of the methoxy substituent or the formation of something like a hydrogen bond.[20] Such an effect may lead to a destabilization of the first excited singlet state and increases considerably the yield of the non-radiative internal conversion deactivation channel.

## Fluorescence quantum yields ($\Phi_F$)

The fluorescence quantum yields of the investigated compounds were determined by steady state fluorescence measurements using phenol in cyclohexane, ethanol and acetonitrile as standards ($\Phi_F$ = 0.083, 0.16 and 0.19, respectively).[13] The fluorescence quantum yield $\Phi_F$ was determined with the same optical density for the phenol and the investigated aromatic thiols at $\lambda_{exc}$ = 266 nm, *i.e.*, $OD_{266\text{ nm}}$ (ArOH) = $OD_{266\text{ nm}}$ (ArSH). Under these optically matched conditions, $\Phi_F$ was determined for diluted solutions ($\leq$0.5 mmol dm$^{-3}$) by comparing the integrals of the reference and sample substance over the whole emission range.[21,22]

The calculated fluorescence quantum yields in the three solvents 1-chlorobutane, ethanol and acetonitrile with an error limit within ±10% are given in Table 2. It is obvious that aromatic thiols fluoresce with a low quantum yield (in the range between $1 \times 10^{-3}$ and $4 \times 10^{-2}$). For thiophenol, the $\Phi_F$ values are comparable in polar solvents, but slightly higher than those in non-polar surroundings. For substituted thiophenols, the same trend is observed but the increase in the quantum yields from non-polar to polar surroundings is more significant (Table 2). In contrast, $\Phi_F$ values of all *para*-substituted thiophenols ($-CH_3$, $-OCH_3$, and $-Cl$) are in the range between $1 \times 10^{-3}$ and $2 \times 10^{-3}$, irrespective of the solvent polarity.

Hence, the short fluorescence lifetimes as well as the low quantum yields and the large difference between the radiative ($\tau_0 = \tau_F/\Phi_F$) and experimental ($\tau_F$) lifetimes of the investigated compounds indicate that the radiative channel is of minor importance and accounts for less than 4% of the $S_1$ decay. This means that radiation-less and/or photodissociation channels play the main role in the deactivation of the first excited singlet state.

A thorough analysis of the deactivation mechanism should entail a detailed study of all non-radiative processes. According to whether the transition is spin-allowed or spin-forbidden, the radiation-less transitions are known as internal conversion (IC) or intersystem crossing (ISC), both in connection with vibrational relaxation (VR). In the next sections, the radiation-less channels and the dissociation will be characterized quantitatively.

### Flash photolysis, transient absorption

In oxygen-free saturated 1-chlorobutane solution, the time-dependent transient absorption spectra obtained after 266 nm laser flash photolysis of thiophenol (ArSH, 0.4 mmol $dm^{-3}$) are shown in Fig. 4A. The initial spectrum measured 500 ns after the pulse consists of three bands, a sharp and intense one with a maximum at 295 nm, and two moderate and broad bands in the 340–380 and 440–490 nm regions.

Analyzing the time profiles given as insets of Fig. 4A, the long-lived species observed in the UV (295 nm) and visible (450–490 nm) regions is attributed to the phenylthiyl radical ($ArS^\bullet$) which is formed by the homolytic S–H bond fission of the first excited singlet state of thiophenol $ArSH(S_1)$ (*cf.* reaction (5)). The absorption maxima of the phenylthiyl radical agree in laser photolysis[7–9,23–26] and pulse radiolysis measurements.[27–30]

The product obtained 15 µs after the pulse with $\lambda_{max} < 310$ nm (see Fig. 4A) is attributed to molecular disulfide resulting from the recombination of phenylthiyl radicals (reaction (8)). Indeed, thiyl radicals decay with rates close to the diffusion control.[29–31] In addition to the disulfide product, cyclohexadienyl-type radicals (H-adduct), could be the responsible for the band observed in the 340–380 nm region. The H-adduct is formed upon the reaction of the dissociative hydrogen radicals (*cf.* reaction (5)) with the benzene ring of thiophenol as shown by reaction (9). The analysis of the time profiles in this region (340–380 nm) reveals that the species at 360 nm is much longer-lived than the phenylthiyl radicals. Moreover, we assume that the cyclohexadienyl-type radical decays by a second order process (reaction (10)).

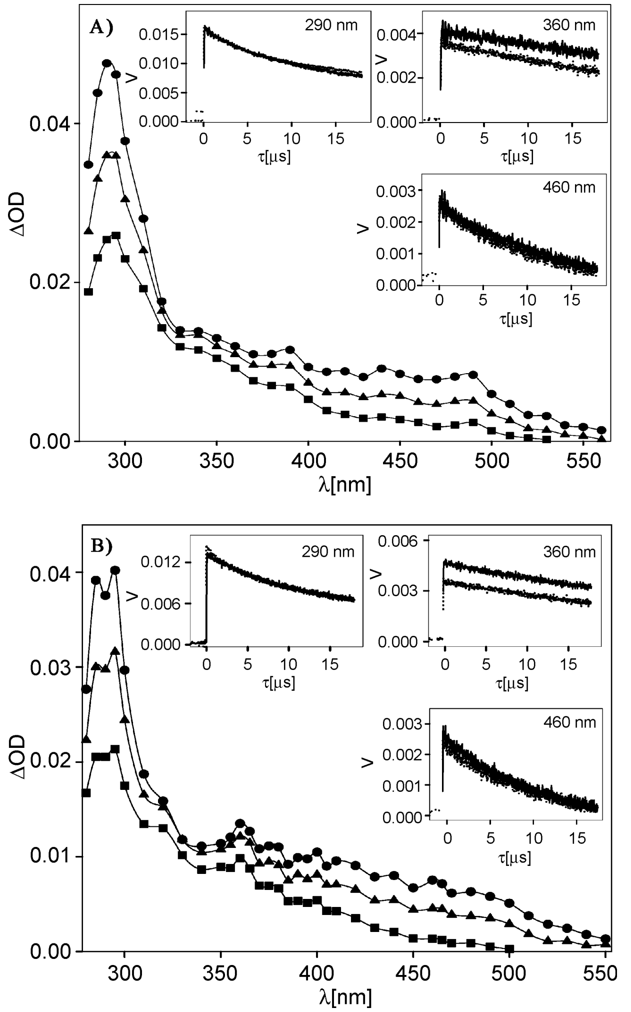
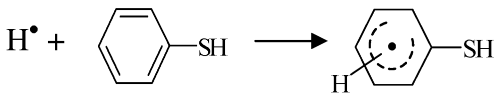
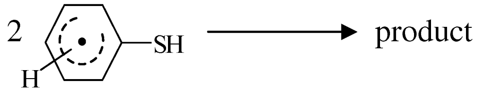


**Fig. 4** Transient absorption spectra obtained after laser photolysis of thiophenol purged with $N_2$ in (A) 1-chlorobutane (0.4 mmol $dm^{-3}$) and (B) acetonitrile (0.6 mmol $dm^{-3}$) solutions taken 0.5 (●), 5 (▲), and 15 (■) µs after the pulse (laser power = 0.7 mJ). The insets show time profiles of $N_2$ (—) and $O_2$ (····) saturated solutions at characteristic wavelengths.

$$2\,ArS^\bullet \rightarrow ArSSAr \quad k_8 \approx 2 \times 10^9\ dm^3\ mol^{-1}\ s^{-1} \qquad (8)$$



(9)



(10)

In oxygen saturated solution, it was found that the transient observed at 360 nm is slightly quenched, whereas those at 290 and 460 nm are not affected (see insets of Fig. 4A). These results support the identification of phenylthiyl radicals which are insensitive toward oxygen.[24,32–34] Therefore, the entire absorption spectra are dominated by the more stable phenylthiyl radical and its disulfide product.

The laser photolysis of thiophenol in EtOH and AN shows a similar trend to that seen for the 1-BuCl solution under similar conditions (see Fig. 4B for an example in AN). Moreover, the solvent change from non-polar (1-BuCl) to polar (EtOH or AN) only causes a very minor bathochromic shift for the absorption maxima of $ArS^\bullet$ ($\leq 5$ nm). Hence, the absorption maxima of the phenylthiyl radicals derived from thiophenols taken independently in various solvents are given in Table 1.

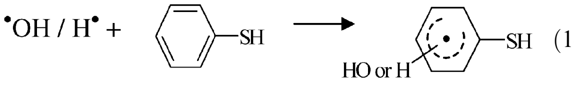
Laser photolysis experiments of the substituted thiophenols were carried out in the same manner and under similar conditions to the experiments carried out for thiophenol. Although, a similar trend to that seen for thiophenol was observed, the spectra showed more pronounced absorption maxima (see Fig. 5). Depending on the substituent nature and its position, it can be seen that the maxima of the phenylthiyl radicals and cyclohexadienyl-type radicals are slightly shifted to longer wavelengths (see also Table 1). The maxima of the phenylthiyl radicals derived from the substituted thiophenols agree well with literature.[7,23–27,29,30]

In order to verify the presence of a cyclohexadienyl-type radical, pulse radiolysis experiments were carried out in acidic aqueous solutions (pH = 1.5) under a nitrogen atmosphere. Under these conditions the solvated electrons are converted to $^\bullet H$ *via* reaction with a proton (reaction (12)). Then, $^\bullet H$ and $^\bullet OH$ abstract an H atom from ArS–H (reaction (13)) as well as add to the aromatic ring (reaction (14)), with the formation of cyclohexadienyl-type radicals, *cf.* Fig. 6.

$$H_2O \rightsquigarrow H^\bullet, OH^\bullet, e_{solv}^-, H_3O^+ \qquad (11)$$

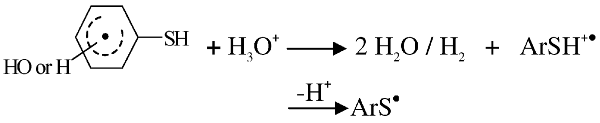
$$e_{solv}^- + H_3O^+ \rightarrow H^\bullet + H_2O \qquad (12)$$

$$^\bullet OH/H^\bullet + ArSH \rightarrow H_2O/H_2 + ArS^\bullet \qquad (13)$$



(14)

It should be taken into account that cyclohexadienyl-type radicals decay under high acidic conditions (pH 1.5) into phenylthiyl type radicals, reaction (15).[35] Therefore, one can rationalize the difference in the kinetics of the cyclohexadienyl-type radicals measured in neutral (see Fig. 4 and 5) and acidic (see Fig. 6) solutions.



(15)

## Intersystem crossing

In the laser photolysis of all of the aromatic thiophenols, no triplet formation could be observed, neither directly nor by subsequent sensitization experiments with β-carotene. This behaviour can be explained by the selection criteria for ISC known as El-Sayed's rules where transitions between identical electronically excited states [such as $^1(n, \pi^*) \leftrightarrow {}^3(n, \pi^*)$ in thiophenol] are forbidden.[36–38] Nevertheless, the thiophenol triplet formation could be identified and characterized indirectly *via* pulse radiolysis by the energy transfer from the triplet state of the solvent benzene.[11]

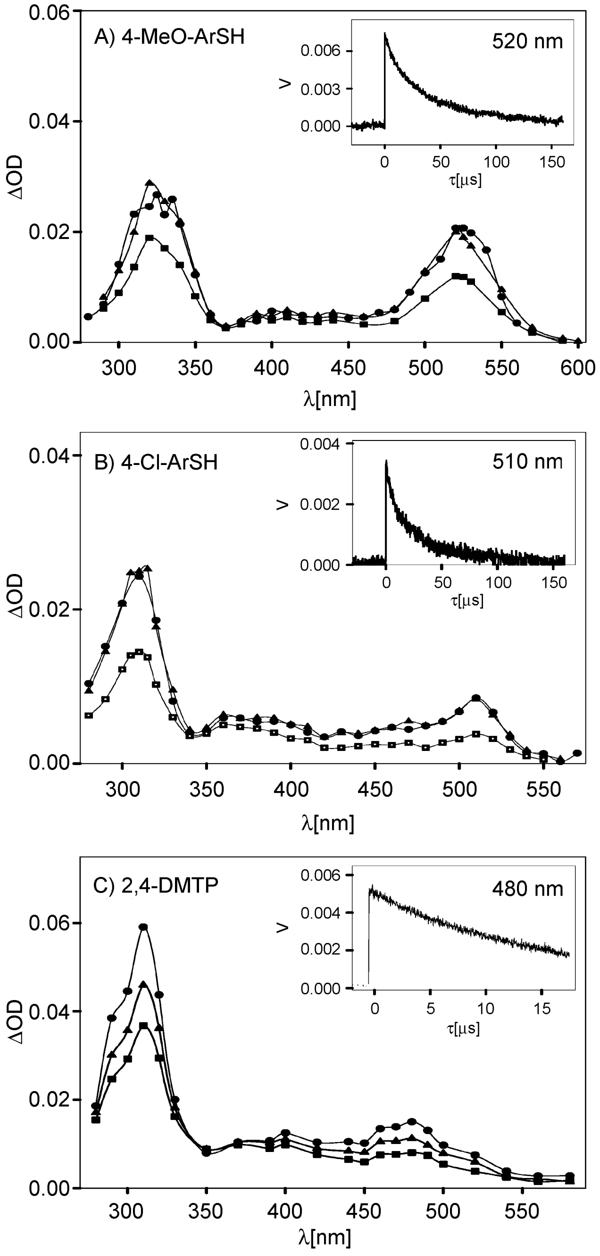


**Fig. 5** Transients absorption spectra obtained after laser photolysis of various substituted thiophenols: (A) 4-MeO-ArSH (0.5 mmol $dm^{-3}$), (B) 4-Cl-ArSH, and (C) 2,4-DMTP (0.3 mmol $dm^{-3}$) in $N_2$-purged acetonitrile solutions taken 0.5 (●), 5 (▲) and 15 (■) μs after the laser pulse (laser energy = 0.7 mJ). The insets show time profiles at characteristic wavelengths.

An exception to this, and in contrast to recent findings on thiophenol and its derivatives, the photo-induced first excited triplet state of the 2- and 4-thiosalicyclic acids is directly observed by its $T_1$–$T_n$ absorption spectra and characterized

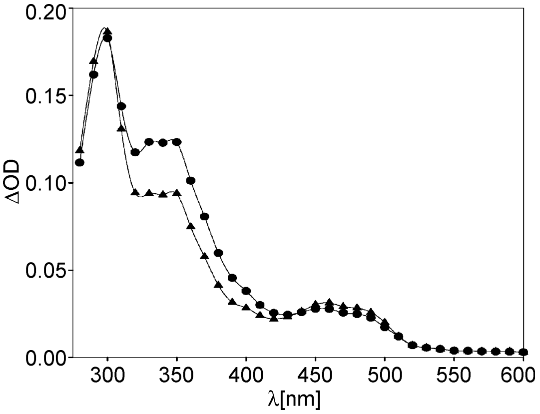


**Fig. 6** Transient absorption spectra obtained after pulse radiolysis of acidic (pH 1.5) aqueous solution of 1 mmol dm$^{-3}$ thiophenol purged with $N_2$ taken 1 (●) and 2 (▲) μs after the pulse.

by sensitization experiments.[10] The reason for this could be the presence of the carboxyl group in these molecules. The first excited singlet state of the thiosalicylic acids is a $^1(\pi, \pi^*)$ state, and as there is a degenerate $^3(n, \pi^*)$ state, this allows the intersystem crossing from the $^1(\pi, \pi^*)$ state to the $^3(\pi, \pi^*)$ state *via* $^3(n, \pi^*)$ state.[39,40]

## Dissociation

**Extinction coefficient of the thiyl radical ($\varepsilon_R$).** In order to verify the spectra of the phenylthiyl radicals as well as to estimate their yields, pulse radiolysis studies of the thiophenols were performed in aqueous alkaline (pH = 12) solution under an $N_2O$ atmosphere in the presence of sodium azide. Under these conditions the solvated electrons are converted to $^{\bullet}OH$, see reaction (16), with subsequent generation of azide radicals, reaction (17). Then the azide radicals react with the thiolate anions leading to the quantitative formation of thiyl radicals and azide anions, reaction (18). For aromatic thiols, the rate constant $k_{18}$ was calculated to be in the range (4–6) × $10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$. From the kinetic data, we found no evidence for the formation of disulfide radical anions, previously observed for aliphatic thiols.[41,42]

$$e^-_{\text{solv}} + N_2O \rightarrow OH^{\bullet} + OH^- + N_2 \qquad (16)$$

$$OH^{\bullet} + N_3^- \rightarrow OH^- + N_3^{\bullet} \qquad (17)$$

$$ArS^- + N_3^{\bullet} \rightarrow ArS^{\bullet} + N_3^- \; k_{18} = 5 \times 10^9\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} (18)$$

Pulse radiolysis of a $N_2O$-saturated alkaline solution containing 0.02 mol dm$^{-3}$ of sodium azide leads to the generation of the azide radical ($N_3^{\bullet}$, $\lambda_{\max}$ = 275 nm) as shown in Fig. 7a. As expected, the transient absorption spectrum monitored by pulse radiolysis of a solution containing 2 mmol dm$^{-3}$ of thiophenol at pH = 12 (Fig. 7a) exhibits a peak at $\lambda_{\max}$ = 460 nm. This band is attributed to the phenylthiyl radical obtained according to reaction (18). The $\varepsilon_{ArS^{\bullet}}$ (see Table 1) was determined by comparing the phenylthiyl and azide absorption maxima (measured separately) using $\varepsilon(N_3^{\bullet})_{275\ \text{nm}}$ = 2300 dm$^3$ mol$^{-1}$ s$^{-1}$.[43] Unfortunately, we could not see the absorption maxima of the phenylthiyl radical in the UV region because of the high thiophenol concentration and the corresponding self absorption which closed the window at the UV border.

The transient absorption spectra of the substituted phenylthiyl radicals were determined in the same manner as those for thiophenol and under the same experimental conditions of dose and concentration. Their corresponding extinction coefficients are given in Table 1. Fig. 7(b–d) shows the absorption spectra of some substituted phenylthiyl radicals (2-, 3-, and 4-thiocresol). The radical spectra in the visible region agree well with the laser photolysis results.

**Quantum yields of the phenylthiyl radicals ($\Phi_D$).** The radical quantum yields of the S–H bond photodissociation of the ArSH($S_1$) were determined by nanosecond laser photolysis using the benzophenone triplet, BP($T_1$), as an external standard. Using the known benzophenone triplet parameters, $\Phi_T$(BP) = 1 and $\varepsilon_T$ = 6250 dm$^3$ mol$^{-1}$ cm$^{-1}$,[44] and the determined $\varepsilon_{ArS^{\bullet}}$, the $\Phi_D$ values were derived for $N_2$-purged diluted solutions (≤0.5 mmol dm$^{-3}$) by comparing the concentration of reference (BP($T_1$)) and sample phenylthiyl radical ($ArS^{\bullet}$) transients. Further details of the method are reported in our previous paper.[10] The radical quantum yields of thiophenol and its substituted compounds were thus determined for solutions in 1-chlorobutane, ethanol and acetonitrile (*cf.* Table 2). The measurements were performed at low laser energy, ~0.6 mJ per pulse, to avoid two-photon ionization. In the case of thiophenol, the radical yields in 1-chlorobutane, ethanol, and acetonitrile are comparable and relatively high ($\Phi_D$ ≈ 0.30). It is obvious that thiyl radical formation shows no influence toward solvent polarity.

For substituted thiophenols, the radical quantum yields in various solvents are given in Table 2. Overall, the following conclusions can be drawn:

(i) Surprisingly, the high radical quantum yields of the substituted thiophenols reflect an pronounced influence of the substituents on the homolytic S–H bond fission of ArSH($S_1$).

(ii) The radical yields of 4-chloro, and mono-, di-, and trimethylthiophenol are comparable, irrespective of the solvent polarity.

(iii) The radical yields of 2- and 4-methoxythiophenol are extremely high, particularly in polar solvents. In contrast, a methoxy group in a *meta* position shows only a small effect.

Because of the inherently weak S–H bond dissociation energy (BDE) of thiophenols, which has less strength than those of the O–H bonds in phenols, the differences in BDE's of thiophenols are small.[45] Therefore, the effect of different substituents and their positions on the homolytic S–H bond is less pronounced. Nevertheless, the strength of S–H bonds depends to some extent on the nature of the substituent. This was supported by quantum chemical estimations of the BDE.[15,16] As expected, it was found that the S–H BDE of the ground and first excited singlet states of unsubstituted thiophenol are 79 and 27 kcal mol$^{-1}$, respectively. This demonstrates the weakness of the S–H bond of ArS–H($S_1$). As a result, a considerable amount of the $S_1$ excitation energy ought to deactivate *via* the photodissociation channel.

The comparable radical quantum yields of mono-, di-, and trimethylated thiophenol can be attributed to the weak

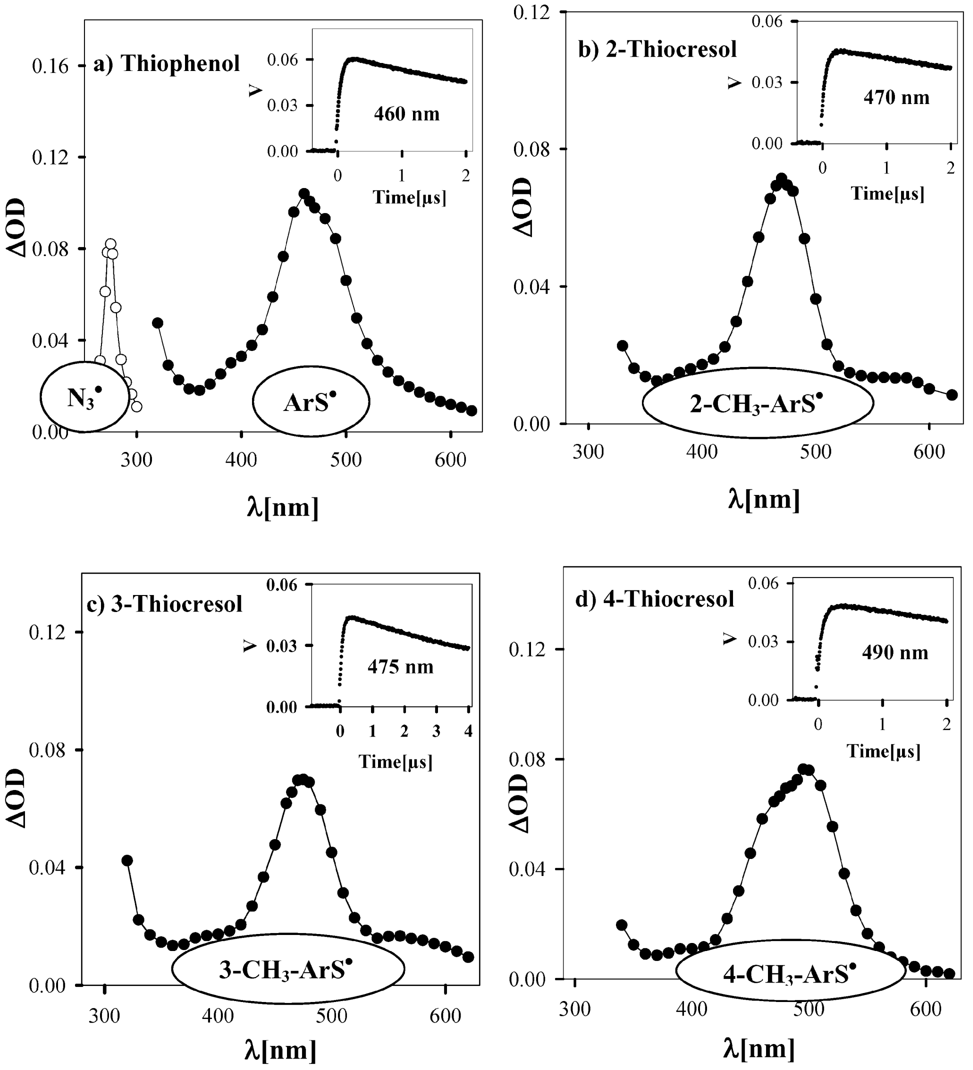


**Fig. 7** Maximum transient optical absorption spectra obtained by pulse radiolysis of $N_2O$-purged aqueous alkaline solutions (pH = 12) of: (a) 0.02 mol dm$^{-3}$ $NaN_3$ only (○), and (a)–(d) thiophenol and its methyl derivatives (2 mmol dm$^{-3}$) in the presence of 0.02 mol dm$^{-3}$ $NaN_3$ (●).

influence of the electron donating methyl group, which has a small effect on the S–H bond homolysis. In other words, neither the number of methyl group nor the position has significant influence on the S–H bond and this may explain why their radical yields are comparable.

A strong electron donating methoxy group at *ortho* and *para* positions causes higher radical quantum yields. This is because a methoxy group in these positions leads to an extra stability of the thiyl radical by decreasing the spin density at the sulfur which leads to a sharp reduction of the BDE (S–H) value. As a result, the S–H homolysis becomes much easier and their corresponding radicals are much more stable than the other substituents. On the other hand, a methoxy group in the *meta* position shows only a minor or no effect on the radical yield. Thiophenols with electron-withdrawing substituents, such as 2- and 4-thiosalicylic acids,[10] exhibit much smaller radical quantum yields than those of thiophenols with electron-donating substituents. Therefore, the dissociation process seems to be influenced mainly by the electronic pattern of the substituent on the aromatic ring. In other words, there is no dependence of the radical yield on the specific or general properties of the solvents.

### Internal conversion

The remaining process is the radiation-less deactivation of the first excited singlet ($S_1$) to the singlet ground state ($S_0$), called internal conversion. In contrast to the other deactivation channels studied, there is no direct and easy way to measure the efficiency of the internal conversion. Using the data directly determined for the competing ArSH($S_1$) deactivation processes, the quantum yield difference to the total gives the fraction of the internal conversion, reaction (19).

$$\Phi_{IC} = 1 - (\Phi_F + \Phi_T + \Phi_D) \qquad (19)$$

The corresponding data are given in Table 2 together with the experimentally determined quantum yields of the previously described deactivation channels calculated for 1-chlorobutane, ethanol and acetonitrile solutions.

It can be seen that the thiophenol singlet state relaxation *via* IC is independent of the solvent nature. This indicates the weak dependence of photophysical and photochemical properties of thiophenols on the general and specific effects of various solvents.

Analyzing the effects of substitution at the aromatic moiety, all these various substances show comparable photophysical characteristics. The $\Phi_{IC}$ values of thiophenol derivatives range from 0.5–0.7. On the basis of the data given in Table 2 (taking singlet lifetime $\tau_{S1}$ as a crude measure for characterizing radiation-less deactivation), the following can be concluded:

(i) The $\Phi_{IC}$ values are comparable and larger than 0.50 (with few exceptions).

(ii) An exception is represented by the methoxy group in *ortho* and *para* positions, particularly in polar solvents, which have efficient photochemical deactivations.

(iii) Mono- and dimethyl substituents, irrespective of their positions on the aromatic moiety, and a chloro substituent in a *para* position have comparable quantum yields. In contrast, 2,4,6-trimethylsubstituted thiophenol shows relatively low $\Phi_{IC}$ values suggesting that photodissociation is more prominent.

Generally, the overall IC process can be understood in terms of the rate controlling resonance interaction (RI) between the $S_1$ and the $S_0$ vibrational levels followed by vibrational relaxation (VR). In liquids, the VR from an excited state, *e.g.*, from $S_1$ to the vibrational ground state $S_0$, is very rapid ($k_{VR} \times 10^{13}$ $s^{-1}$)[46] and the excess energy is converted into heat through collisions with solvent molecules. Because of the observed weak solvent–solute interactions, this suggests that RI is of minor importance. On the other hand, VR determines the internal conversion pathway of the non-radiative relaxation to a high extent.

Usually IC efficiency is directly related to the energy gap ($\Delta E$) between the $S_1$ and $S_0$ states and becomes increasingly unfavorable with increasing energy separation.[47] Here, the energy gap between the $S_1$ and the $S_0$ states is $\sim$120 kcal $mol^{-1}$, but a high IC efficiency is favored together with photodissociation. This reflects a weaker energy gap dependence than that demanded by the "energy gap law". A surface crossing of the $S_1$ and $S_0$ surfaces near the $\nu = 0$ level of $S_1$ could possibly be a reason for this.[47]

## Conclusions

For the first time, this paper gives a comprehensive picture and quantitative information about the deactivation mechanism of the first excited singlet state of aromatic thiols. Because no intersystem crossing is taking place, the mechanism is reduced to the singlet system only. Excitation brings the molecule from the ground state $S_0$ to a vibrationally excited level of $S_1$. According to Kasha's rule,[48] the relaxation to the first electronically excited level $S_1$ takes place extremely rapidly ($10^{13}$ $s^{-1}$). Therefore, the ArSH($S_1$) level is the central point where the deactivation processes (2) to (5) branch out.

With the exception of IC, all other deactivation reaction channels (fluorescence (2) and dissociation (5)) were identified and quantitatively characterized. Consequently, this also enabled the quantitative description of radiation-less IC (3) by a difference calculation. Hence, a complete picture of the decay channels of the first excited singlet state of aromatic thiols is given. A comparison shows that there are significant differences in the deactivation mechanisms of the first excited singlet states of thiophenol and phenol analogs.[13]

Practically no solvent effects were observed on the spectral properties or the kinetics of the first excited singlet state of thiophenols, ArSH($S_1$). Moreover, it seems that the stability of ArSH($S_1$) is mainly determined by the electronic pattern of the substituents. Electron-withdrawing substituents cause shorter fluorescence lifetimes whereas electron-donating groups cause longer fluorescence lifetimes.

In the direct photolysis of all aromatic thiols (with the exception of 2- and 4-thiosalicylic acids[10]), no triplet formation could be observed, either directly or by subsequent sensitization. Independently, the thiophenol triplet formation could be identified and characterized indirectly *via* pulse radiolysis by the direct energy transfer from the triplet state of the solvent benzene.[11]

Finally, the internal conversion, which is unaffected by the solvent nature, plays dominant role in the deactivation mechanism, *i.e.*, $\Phi_{IC} \geq 0.5$ (with some exceptions). The exceptions are 2- and 4-methoxythiophenol and 2,4,6-trimethylthiophenol because of the efficient photochemical deactivation process.

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