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Photophysics of the S_2 State of Thiocoumarin: A Vibrationally Unequilibrated Luminophore

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A weak fluorescence from the $S_2(\pi,\pi^*)$ state of thiocoumarin in perfluorohydrocarbons and *n*-hexane solutions, of a quantum yield $\sim 6.5 \times 10^{-5}$, and similarly weak phosphorescence from the $T_1(\pi,\pi^*)$ state, at room temperature, were measured. A distinct dependence of the shape and position of the fluorescence band on the energy of vibrational excitation within the $S_2(\pi,\pi^*)$ state was found and interpreted as a result of emission from the unrelaxed vibrational levels. The lifetime of the S_2 state was estimated as ~ 1 ps, which is about 20 times lower than the value expected on the basis of the "energy gap law" for $\Delta E(S_2-S_1)$. To give a satisfactory interpretation of the properties of thiocoumarin in the relaxed vibrational configuration of the S_2 state, a very efficient electronic relaxation should have been considered for which a few possible mechanisms were discussed. A short lifetime of excited vibrational levels was not a consequence of electronic relaxation processes but was rather directly related to the rate of intramolecular vibrational redistribution.

1. Introduction

Thioketones together with azulene, its derivatives, and pseudoazulenes belong to a relatively small group of compounds showing stronger fluorescence from the S_2 than S_1 state.[1–10] The intramolecular lifetime in the S_2 state is relatively long and can reach from 50 ps to 4 ns.[8,11–15] Because of the exceptionally high reactivity of thiones in the S_2 state, the use of any solvents other than perfluoroalkanes, PF, leads to a definite dominance of intermolecular quenching over intramolecular deactivation of S_2 thiones.[8,12,13,16–20] Yet, even in solvents other than PF, fluorescence from the S_2 state is observed but at a significantly lower (2–30 times) quantum yield, $\phi_F \sim (10^{-2}-10^{-4})$.[8,9,11,12,20] Unexpectedly enough, the attempts at observing fluorescence from the S_2 state of thiocoumarin, TC (Figure 1), in benzene solution[21,22] and its 6-methyl derivative, 6MTC, in methanol[23] failed.

The absorption spectrum of TC in the $S_0 \rightarrow S_2(\pi,\pi^*)$ band is similar to and of the same intensity as the spectra of other thiones, so the value of k_F should be of the order of 10^8 s^{-1}. Thus, the absence of a measurable fluorescence of TC was a rather unexpected result, in particular when compared to the experimental data for similar molecules. For example, benzpyranthione, BPT (Figure 1), shows strong fluorescence not only in PF, where its decay is practically intramolecular with $\phi_F = 0.023$[12] and $\tau_{S_2} = 221$ ps,[13] but also in 3-methylpentane, 3MP, in which $\phi_F = 0.002$ and $\tau_{S_2} = 24$ ps.[12] Steer and Rao[24] have proved that 1,1-dimethyl-2-thioxo-1,2-dihydronaphthalene, DTDN (Figure 1), which differs from TC only by the presence of two
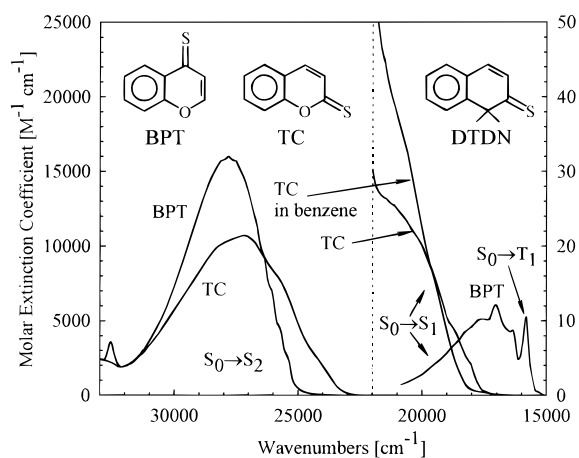

Figure 1. Room-temperature absorption spectra of thiocoumarin, TC, and benzpyranthione, BPT, in PF solvents. The $S_0 \rightarrow S_1$ spectrum of TC in benzene is also shown, as well as structural formulas of BPT, TC, and 1,1-dimethyl-2-thioxo-1,2-dihydronaphthalene, DTDN. The intensity of the part of the spectrum to the right of the dotted line has been magnified 500 times.

methyl groups replacing oxygen atoms in the ring, shows strong fluorescence in PF ($\phi_F = 0.026$, $\tau_{S_2} = 153$ ps) and only a little less intense (1.5 times) fluorescence in a solution of C_6H_{14}. A TC molecule is characterized by a small energy gap $\Delta E(S_2-S_1) \simeq 6000$ cm^{-1} which may foster fast internal conversion. A reference may be made to a thioxanthione molecule whose $\Delta E(S_2-S_1) = 6800$ cm^{-1} and for which in PF $k_{S_2S_1} \sim 2 \times 10^{10}$ s^{-1}, $\phi_F = 2.3 \times 10^{-3}$,[12] and $\tau_{S_2} = 53$ ps[13] while in 3MP the ϕ_F and τ_{S_2} values were twice smaller.[12] If a TC molecule in the S_2 state in a PF solution behaved as a rigid thione, the expected ϕ_F and τ_{S_2} values would only be slightly lower.

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The work reported in this paper was aimed at investigation of spectral and photophysical properties of TC in order to find the origin of the irregular properties (especially radiative ones) of this compound by way of analyzing TC properties against the data for the earlier studied thiones, particularly for BPT and DTDN. To ensure the highest possible accuracy and reliability of results, the measurements were performed in PF solvents and with an exceptionally sensitive spectrofluorimeter permitting emission measurements on the level of quantum yields $\phi \geq 10^{-7}$.

2. Experimental Section

Materials. The thiones were synthesized by reaction of the corresponding ketone with P_4S_{10} or/and Lawesson reagent according to the published methods.[25,26] They were purified by repeated crystallization from benzene and methanol and using column chromatography. Their purities were determined by HPLC (Waters) and by absorption as well as emission spectroscopy. Perfluoroalkane solvents (P.C.R., Aldrich), 3-methylpentane (Aldrich), benzene, methanol, and n-hexane for fluorescence (Merck) were purified by column chromatography and long-term irradiation in a quartz cell with a low-pressure mercury arc, followed by fractional distillation. For examination of the solvents' purity the methods of gas chromatography as well as absorption and emission spectroscopy were applied.

Apparatus and Techniques. Absorption spectra were taken on M-40 (Carl Zeiss Jena) spectrophotometer. Steady-state emission and luminescence excitation spectra were taken on a very sensitive homemade spectrometer with single-photon detection and computer control, based on an upgraded optics of the MPF-3 (Perking-Elmer) instrument.

Quantum yields of emission were measured by the relative method, taking into account appropriate solution refractive index corrections.[27-29] Quinine sulfate in 0.1 N H_2SO_4, $\phi_F = 0.52$, was used as a standard.[27,30] For quantum yield and luminescence excitation spectra measurements, the sample absorbance was normally <0.10, and the same spectral band-passes were used for both absorption and emission experiments.

Dynamics of the short-lived states was studied using a picosecond transient absorption spectrometer equipped with a YAG:Nd^{3+} laser, YG 571 C type, Quantel. The samples were excited with a beam of 355 nm wavelength (the third harmonics of the fundamental frequency) and analyzed with a white beam of picosecond continuum excited in water with the fundamental beam, $\lambda = 1064$ nm, of the YAG:Nd^{3+} laser. The experimental setup was similar to that described earlier,[31] and the only difference was the application of the double-beam geometry realized using the RL1024RAQ-011 (Reticon) double photodiode array, to improve the sensitivity and accuracy of measurements.

All emission experiments, except those involving measurements of fluorescence only, were performed on samples thoroughly deoxygenated by bubbling O_2-free He.

3. Results

The absorption spectrum of TC in PF measured in the range of $S_0 \rightarrow S_1(n,\pi^*)$ and $S_0 \rightarrow S_2(\pi,\pi^*)$ bands enabled determination of the energy gap $\Delta E(S_2-S_1)$. For the sake of comparison, Figure 1 presents absorption spectra of TC and BPT. To analyze the solvent effect on spectral and, consequently, also on photophysical properties, absorption spectra were also measured in 3MP, C_6H_{14}, C_6H_6, and MeOH. Analysis of the absorption spectra of TC in 3MP and C_6H_{14} measured over a wide range of temperatures from +25 to −90 °C and for
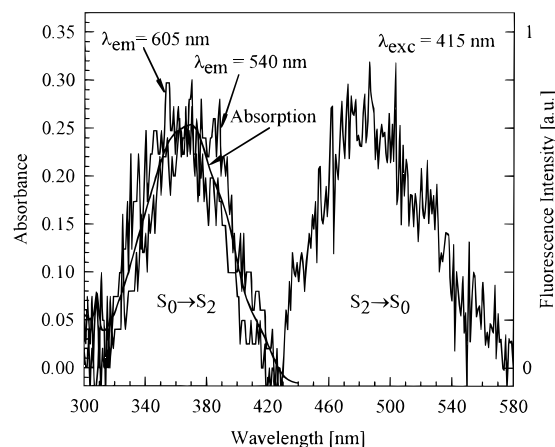
Figure 2. Absorption, fluorescence (corrected), fluorescence excitation (at $\lambda_{em} = 540$ nm) and phosphorescence excitation (at $\lambda_{em} = 605$ nm) spectra for the $S_0 \leftrightarrow S_2$ transition of thiocoumarin, TC, in PF solvent; $c \sim 2 \times 10^{-5}$ M.
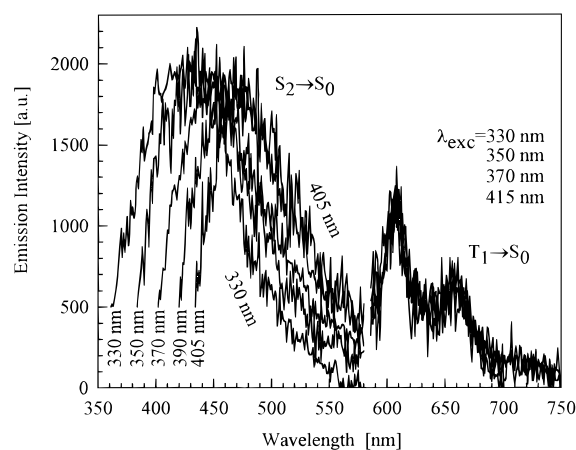
Figure 3. Single scan corrected emission spectra of thiocoumarin, TC ($c \sim 2 \times 10^{-5}$ M), measured at selected excitation wavelengths, in PF solvents, at room temperature. The maximum intensities of all fluorescence and also all phosphorescence spectra have been normalized to the same magnitude.

concentrations from 10^{-6} to 10^{-3} M enabled us to examine the possibility of thermal activation of structural changes in the molecule and to estimate the position of the 0,0 bands.

Figure 2 presents the emission spectrum of TC obtained under excitation in the long wavelength edge of the $S_0 \rightarrow S_2$ band, $\lambda_{ex} = 415-425$ nm. It should be stressed that the emission and luminescence excitation spectra presented in this and the following figures are "as-measured" single scan unsmoothed spectra, taken with relatively narrow excitation slits, to have a well-defined λ_{ex}, with the $\Delta\lambda_{ex}$ band-pass matched to that of the absorption spectrophotometer. To verify whether the studied emission really comes from TC in the S_2 state, we measured the emission excitation spectrum, shown in Figure 2, choosing $\lambda_{em} = 540$ nm from the long wavelength side of the emission band. This spectrum is very similar to the absorption spectrum of TC, which, considered together with the $S_2 \rightarrow S_0$ emission spectrum, provides a direct proof that the emission comes from the S_2 state of TC. Analysis of the spectra of this weak emission measured as a function of λ_{ex} has revealed significant changes in the positions of the short wavelength slope and the emission band maximum (Figure 3). Excitation of the higher and higher vibronic levels of the S_2 state actuates a shift of the emission band toward shorter wavelengths. To ensure that the source of this emission has also been correctly identified, excitation spectra were measured for λ_{em} from a wide range of 450−520 nm.

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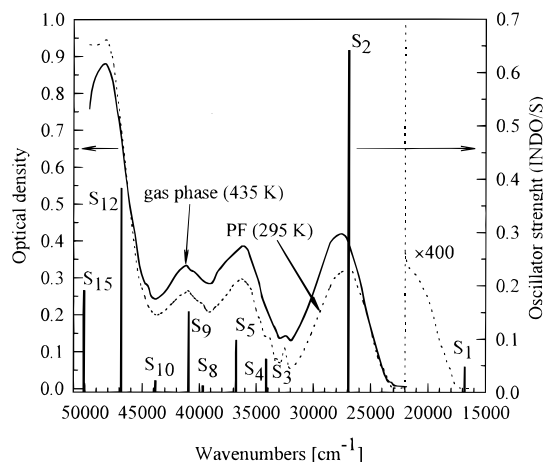*J. Phys. Chem. A, Vol. 102, No. 4, 1998* **679**

Figure 4. Experimental and theoretical (calculated with the INDO/S CI-1 method) electronic spectra of thiocoumarin, TC.

These spectra are similar to that measured for λ_{em} = 540 nm, which proves that the studied emission comes from TC in the S$_2$ state. Analogous results, in particular similar changes of the emission band shape as a function of λ_{ex} chosen from the S$_2$ absorption band, have been obtained using C$_6$H$_{14}$ as a solvent of TC.

Apart from the fluorescence measurements discussed above, we also recorded low-intensity phosphorescence for all λ_{ex} from the S$_0 \rightarrow$ S$_2$ absorption band. In contradiction to fluorescence, neither the shape nor position of the phosphorescence band depended on λ_{ex} (Figure 3). The excitation spectrum of this emission (Figure 2) was identical with the absorption band of TC, which confirms that also phosphorescence comes from TC.

Quantum yields of emission, ϕ_F, were determined by a reference method according to standard procedures. For TC in PF we obtained $\phi_F = 6.5 \times 10^{-5}$, and this value proved almost independent of λ_{ex} in the range 350–415 nm as well as of TC concentration in the range $(1-4) \times 10^{-5}$ M. A similar value, $\phi_F = 5 \times 10^{-5}$, was obtained for TC in C$_6$H$_{14}$ for λ_{ex} = 405 nm. Although the results were reproduced for a few different samples, they can be charged with a significant error, up to 30%, following from the unfavorable experimental conditions.

Unfortunately, the attempts at determination of the lifetime of TC in the S$_2$ state from either transient absorption measurements in the picosecond time scale or emission measurements failed. In both cases the signal did not differ from the instrument response function, which testifies to the fact that the decay time must be very short, not longer than 3 ps.

The INDO/S CI method was used to calculate distribution of electron density in the S$_2$ state as well as other singlet and triplet states. Similarly as for other thiones, the S$_1$ state in TC is of n,π^* type. The very weak S$_0 \rightarrow$ S$_1$ transition corresponds to electron excitation from the lone-pair orbital n of the sulfur atom to the orbital π^*_{C-S} localized on the carbon atom from the thiocarbonyl group. The S$_2$ state is of the π,π^* type, and the transition S$_0 \rightarrow$ S$_2$ corresponds to electron excitation from the orbital π_{C-S} localized primarily on the sulfur atom to the orbital π^* mentioned above. The oscillator strength of this transition is high (>0.5), as for BPT and other thiones. The calculated electronic spectrum is in fair agreement with the experimental data (Figure 4).

In the ground state of TC, there is an excess of electron density on the sulfur ($\sim$0.4e) and oxygen ($\sim$0.18e) atoms, while there is a deficiency of electron density on carbon atom 2. Upon excitation to any of the higher states, the electron density is

shifted from the sulfur atom mainly to the neighboring carbon atom. In particular, in the $\pi \rightarrow \pi^*$ transitions $\sim$0.5e, and in the n $\rightarrow \pi^*$ transitions $\sim$0.75e are shifted. Such a large change of electron density may be responsible for essential difference of the properties of a given thione in the ground and excited states.

As follows from the PM3 CI calculations, a transition to excited states is accompanied by changes in the bond length. In the S$_2$ state, this change is manifested as equalization of the C–C bond lengths. The lengths of these bonds of 1.40–1.42Å are typical of aromatic compounds. Similarly as earlier for BPT and other thiones, also for TC the obtained values of spin–orbit coupling constants between the states S$_1$ and T$_1$ ($\sim$24 cm^{-1}) and S$_2$ and T$_2$ ($\sim$20 cm^{-1}) were very high, while the value determined for the S$_2$ and T$_3$ states (0.018 cm^{-1}) was very low.

4. Discussion

The TC absorption spectrum in the UV range from 33 000 to 23 000 cm^{-1} and partly in the visible range shows close similarity to the BPT absorption spectrum (Figure 1). In the range 32 000–23 000 cm^{-1} the TC absorption spectrum reveals a very intense absorption band, $\epsilon^{max} > 10\,000$ mol^{-1} dm^3 cm^{-1} which, as in the other thiones, corresponds to the S$_0 \rightarrow$ S$_2(\pi,\pi^*)$ transition. A replacement of a solvent from the PF group by another nonpolar solvent (3MP, n-hexane) or even by a stronger interacting one (benzene, methanol) results, like for the other thiones, only in a small bathochromic shift of the absorption band.

In the TC absorption spectrum the S$_0 \rightarrow$ S$_1$ band appears as a characteristic inflection on the long wavelength slope of the S$_0 \rightarrow$ S$_2$ band (Figure 1), which means that the energy gap $\Delta E(S_2-S_1)$ is small relative to that in other thiones. From the TC absorption spectrum measured at a low temperature, we could determine the spectral parameters of the S$_0 \rightarrow$ S$_1$ band ($\bar{\nu}^{0,0} \sim 18\,150$ cm^{-1}, $\epsilon^{max} = 25$ mol^{-1} dm^3 cm^{-1}) and estimate $\bar{\nu}^{max} \sim 20\,300$ cm^{-1} and $\Delta\bar{\nu}^{1/2} \sim 2600$ cm^{-1}, in n-hexane. Devanathan and Ramamurthy[22] obtained for a TC solution in benzene $\bar{\nu}^{max} = 20\,400$ cm^{-1} and $\epsilon^{max} = 60$ mol^{-1} dm^3 cm^{-1}.

A very characteristic feature existing in the visible range of absorption spectra of most aromatic thiones is a low-intensity but well-resolved S$_0 \rightarrow$ T$_1(n,\pi^*)$ band. Contrary to this, in TC the T$_1$ state is of (π,π^*) type, and no trace of the corresponding band in the absorption spectrum can be found. No complex formation with solvent molecules and no aggregation of TC molecules in the ground state have been detected by absorption studies of TC in PF, 3MP, hexane, benzene, and methanol, for the concentration varied from 10^{-6} to 10^{-3} M.

The spectra of TC fluorescence from the S$_2$ state reveal a distinct dependence on λ_{ex} (Figure 3). In a simpler case of fluorescence excitation in the vicinity of the (0,0) band, at λ_{ex} = 415–425 nm, i.e., with a low content of vibrational energy, the mirror-image relationship between the S$_2 \rightarrow$ S$_0$ fluorescence band and S$_0 \rightarrow$ S$_2$ absorption band becomes evident (Figure 2). Contrary to the situation of the same S$_0 \leftrightarrow$ S$_2$ transition in BPT and DTND, the width of the emission band is significantly smaller than that of the absorption band. The Stokes shift $\Delta\bar{\nu}^{0,0}$(abs–em) is for TC much greater than for BPT. Such a significant Stokes shift must be a consequence of distortion of the molecule resulting from the transition to the S$_2$ state.

Analysis of the S$_2 \rightarrow$ S$_0$ fluorescence emission becomes much more complex when TC is excited to higher vibrational levels of the S$_2$ state. A very short lifetime τ_{S_2} estimated for S$_2$ state of TC even in PF, of the value comparable to the lifetime of
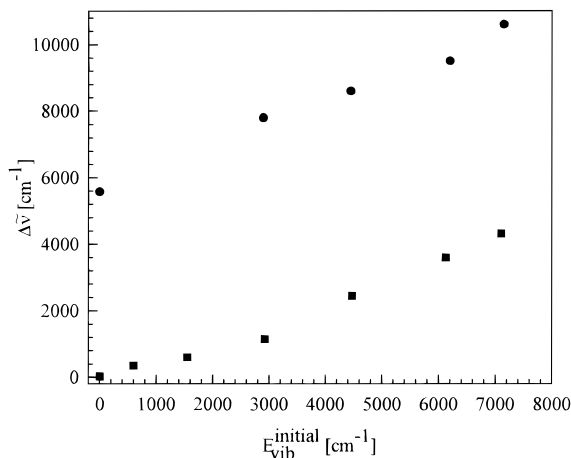
Figure 5. Fluorescence bandwidths (circles) and shift of the short-wavelength edge of thiocoumarin fluorescence band (squares) measured in PF as a function of the initial vibrational energy content, in both cases determined at 0.12 of maximum intensity.

vibrational levels of many polyatomic molecules,[32−40] indicates that for this thioketone molecule a distinct dependence of the emission spectrum on λ_{ex} may be expected. From the fact that τ_{S_2} was too short to be determined directly by means of either emission or picosecond transient absorption measurements, an estimation $\tau_{S_2} \leq 3$ ps could be derived. An approximate value of τ_{S_2} has also been calculated from the

$$\tau_{S_2} = \phi_F/k_F \quad (1)$$

relation, using $k_F = 7 \times 10^7$ s^{-1} calculated on the basis of the $S_0 \leftrightarrow S_2$ absorption and emission spectra from the Strickler−Berg[29,41] equation:

$$k_F = 2.88 \times 10^{-9} \frac{n_F^3}{n_A} \langle \bar{\nu}_F^{-3} \rangle^{-1} \int \frac{\epsilon(\bar{\nu}) \, d\bar{\nu}}{\bar{\nu}} \quad (2)$$

where n_F and n_A are the mean refractive indices of the solvent over the $S_2 \rightarrow S_0$ fluorescence and $S_0 \rightarrow S_2$ absorption spectra, respectively, $\langle \bar{\nu}_F^{-3} \rangle^{-1}$ is the reciprocal of the average value of $\bar{\nu}^{-3}$ over the fluorescence spectrum, $\epsilon(\bar{\nu})$ is the decadic molar extinction coefficient, and the integral is taken over the $S_0 \rightarrow S_2$ absorption spectrum. With $\phi_F = 6.5 \times 10^{-5}$, an adequate lifetime $\tau_{S_2} \approx 1$ ps has been obtained.

As expected for such short-lived species, upon excitation of the TC molecule to the S_2 state of different content of vibrational energy, the fluorescence spectrum was found to change (Figure 3). Changes of λ_{ex} from 320 to 415 nm were accompanied by significant shift of the short wavelength edge of the S_2-fluorescence and the maximum of this emission toward shorter wavelengths. A significant broadening of this band with increasing vibrational excitation (Figure 5) was also observed. It is interesting to note that the position of the short-wavelength edge of the S_2 fluorescence band measured at 12% of the maximum intensity, separated from the excitation wavenumber $\bar{\nu}_{ex}$ by $\Delta\bar{\nu}$, was shifting on the scale of wavenumbers almost in the same magnitude as $\bar{\nu}_{ex}$. The initial $\Delta\bar{\nu}$ interval of about 1500 cm^{-1} measured upon excitation of the (0,0) band increased by 700 cm^{-1} when $\bar{\nu}_{ex}$ was increased by over 6000 cm^{-1}. This fact indicates that the emission comes from the vibrationally unrelaxed S_2 state of TC and that, to a significant degree, it originates from the directly excited vibrational levels. The long-wavelength part of the S_2 fluorescence spectrum upon excitation to higher vibrational levels (especially for $\lambda_{ex} \geq 350$ nm) looks

similar to the emission spectrum obtained upon excitation in the vicinity of the (0,0) band. This means that, during the time the excited TC molecules live in the S_2 state, at least part of them manage to undergo intramolecular vibrational redistribution (IVR) and emit fluorescence until they are at lower vibrational levels.

For the same samples the phosphorescence spectrum, S_2-fluorescence, and T_1-phosphorescence excitation spectra were measured in the whole range of λ_{ex} and λ_{em}. They allowed us to exclude participation of impurities or possible products of photolysis in the studied emission and identify a TC molecule as the sole source of the measured fluorescence. Because of the long lifetime of the T_1 state, phosphorescence emission occurs from a completely equilibrated set of vibrational levels, and due to that, the phosphorescence spectrum shows no trace of the dependence on excitation wavelength (Figure 3).

The lifetime of the S_2 state and, consequently, quantum yield of TC fluorescence are approximately 500 times lower than those measured for BPT[8,12] and DTDP,[24] although the values of k_F for these three compounds are similar. This indicates that deactivation of TC molecule is dominated by a very efficient radiationless process which is not commonly involved in deactivation of other aromatic thiones.

For typical aromatic thiones, the $S_2 \rightsquigarrow S_1$ internal conversion constitutes the most important channel of S_2 state deactivation in unreactive and noninteracting solutions. In the case of rigid thioketone molecules, there is a good correlation between the rate constant of internal conversion $k_{S_2S_1}$ and the energy gap $\Delta E(S_2−S_1)$; see Figure 5 in ref 12. As the TC molecule is an isomer of the BPT molecule for which the $S_2−S_1$ energy gap law is well-satisfied, we can assume that the former is sufficiently rigid. For TC, the energy gap $\Delta E(S_2^{em}−S_1^{abs}) \sim 6000$ cm^{-1}, determined from the emission data for the S_2 state and from the absorption data for the S_1 state, is the smallest from among all values determined so far for thiones. By extrapolation from the above-mentioned graph, we find for TC $k_{S_2S_1} = 5 \times 10^{10}$ s^{-1}. Taking into regard that the quantum yield of photochemical decomposition of TC is $<10^{-2}$ and assuming temporarily that in PF the only active channel of radiationless decay of TC in the S_2 state is the internal conversion $S_2 \rightarrow S_1$, i.e., assuming that $k_{S_2S_1} = k_{nr}$, where k_{nr} denotes the rate constant of nonradiative deactivation, from the well-known formula

$$k_{nr} = (1 − \phi_F)/\tau_{S_2} \quad (3)$$

a hypothetical value of τ_{S_2} can be found, which would describe the S_2 state decay taking place exclusively via internal conversion. This hypothetical value would be 20 ps, so about 20 times longer than the value τ_{S_2} estimated on the basis of experimental data. This means that the $S_2 \rightsquigarrow S_1$ internal conversion cannot be the dominant process of radiationless decay of the S_2 state and that there must be at least one more process involved, of a considerably greater yield.

As follows from the quantum-mechanical calculations performed, the T_3 state of TC lies a few hundred cm^{-1} below the S_2 state. However, the spin−orbit coupling between these states is weak, which excludes the process of $S_2 \rightsquigarrow T_3$ intersystem crossing as responsible for so high a rate constant of radiationless deactivation. Since the solvent used was an unreactive and weakly interacting PF,[42] the S_2 state quenching due to physical or chemical interaction with the solvent could be excluded. Experimental conditions and the evidence gathered allow us also to exclude the effects of molecular aggregation and concentration quenching as potentially responsible for this extremely fast decay.

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It would be difficult to point to a single main reason for the highly effective radiationless deactivation of the S$_2$ state of TC. One of the possible paths would be the effect of conical intersection of the hypersurface of potential energies of the molecule electronic states, which was successfully applied for an explanation of unusually high rate of radiationless deactivation of numerous polyatomic compounds.[43,47] In the case of TC, such a process would be possible between hypersurfaces of both the S$_2$ and S$_1$ states and S$_2$ and S$_0$ states, although in the latter case its probability is much less because of a large energy gap $\Delta E(S_2-S_0)$. This opinion is additionally supported by the ϕ_F/ϕ_P ratio being independent of λ_{ex} (ϕ_P denotes the quantum yield of phosphorescence) which means that the decay to the S$_1$ state proceeds at a constant yield irrespective of the energy of vibrational excitation. This postulated process could orginate from this part of the S$_2$ state hypersurface from which fluorescence is emitted as well as, possibly, from the second, deeper minimum reached as a result of the adiabatic transition.[44,47,48] The occurrence of double minima on the potential energy hypersurfaces of the S$_0$ and S$_2$ states has been proposed for a few thiones.[8,49] Although a TC molecule is too complex to allow the exact determination of the shape and position of the hypersurfaces, the possibility of conical intersection of these surfaces as the reason for very efficient radiationless deactivation should certainly be taken into regard.[50]

Kucsman and Kapovits[51] indicate a possibility of a very efficient process of nonbonded donor−acceptor interactions between the oxygen from the aromatic ring and sulfur from the thio group. Such an interaction can occur when the distance between these atoms varies from 2.0 to 3.25 Å. In the case of a TC molecule this distance is equal to 2.6 Å, so the interaction of this kind is geometrically allowed. Interestingly enough, for all thiones studied so far in whose molecules the oxygen atom from the ring was in direct neighborhood of the thiocarbonyl group, attempts at observing fluorescence from the S$_2$ state failed,[21−23] despite a large k_F.

Still another possible explanation concerns direct, fast transition from the S$_2$ to S$_0$ state occurring by a reversible intramolecular photochemical process such as C−O bond cleavage to form a short-lived ground-state biradical, which then closes quantitatively with little net photochemical consumption of the thione.[52]

In all so far reported studies of thioketones no dependence of the shape of the S$_2$ fluorescence spectrum on the vibrational excitation energy was detected. When considering the relation between the electronic lifetime of a given vibronic level ν,τ^ν, the vibrational lifetime of this level, $\tau_{IVR} = 1/k_{IVR}$ where k_{IVR} is the rate constant of the IVR process, and the actual lifetime of the relaxed configuration of the S$_2$ state, τ_{S_2} a few particular situations can be distinguished. The most common classical situation occurs when a fast IVR process restores thermal equilibrium among vibronic levels of the excited state prior to electronic relaxation from lower vibronic components of this state. No dependence of the shape and the yield of emission can be observed in the above-sketched conditions, characterized by the relations $\tau^\nu > \tau_{IVR}$, $\tau_{S_2} > \tau_{IVR}$. The second case, $\tau^\nu < \tau_{IVR}$, $\tau_{S_2} \approx \tau^\nu$, corresponds to the interpretation proposed for aromatic hydrocarbons in S$_n$ ($n > 2$) states,[53−56] according to which the emission from the upper vibronic levels and the emission spectrum dependence on λ_{ex} are explained by the rate of electronic relaxation faster than that of the IVR one. In this case the emission occurs from the directly excited vibrational levels, and the long-wavelength part of the emission band is not observed.

The most interesting third case refers directly to the discussed TC molecule. The spectral and photophysical properties of TC can be successfully interpreted if, in full agreement with the earlier performed estimations, we assume that $\tau^\nu > \tau_{IVR}$ and $\tau^\nu \geq \tau_{S_2}$. The relation for the lifetimes of the excited vibrational levels is a natural consequence of the system properties and means that in accordance with the physics of the phenomenon the lifetimes of these levels are determined by the rate of IVR while the other kinds of relaxation are much slower. To have a consistent description of the system behavior, it must be assumed that in the above-discussed highly efficient intramolecular process depopulating lower levels the S$_2$ state vibrational manifold runs at a rate faster or at least equal to that of the process of IVR, reducing the effective lifetime of the relaxed configuration of the S$_2$ state to the τ_{IVR} level. In the fluorescence intensity domain the same effect is manifested as a dramatic reduction of intensity of the fluorescence from the lower vibrational levels of the S$_2$ state, which would otherwise (in normal conditions) overwhelm emission from the excited vibronic components of this state. Consequently, each of the excited vibrational levels brings a significant and comparable contribution to the S$_2$ state emission.

Although experimental values of τ_{IVR} for TC have not been available, the estimated τ_{IVR} for TC are close to τ_{IVR} measured for organic dye molecules. As was shown by many authors,[32,35−37,39,40,57] the intramolecular redistribution of vibrational energy of large molecules is extremely rapid in both the ground and excited states. IVR dynamics was usually studied for not particularly high vibrational excitation (<3000 cm^{-1}). This was also the case for the molecule of coumarin 6 whose properties show the closest resemblance to those of TC. For this molecule, containing twice as many atoms as in TC, the vibrational lifetimes determined in a C$_2$Cl$_4$ solution are $\tau_{IVR} \sim 0.3-2.0$ ps.[33] The value $\tau_{IVR} = 2.0$ ps corresponds to the vibrations of the C=O group while $\tau_{IVR} \sim 0.3-0.5$ ps correspond to other vibrations of higher frequency.[33] For the same molecule in CCl$_4$, τ_{IVR} was found equal to 1.3 ps.[34] For the other few polyatomic dye molecules the measured intramolecular lifetime of the excited vibrational levels was reported to be from 0.1 to 1.0 ps.[32−−37] Higher vibrational excitations, such as those used in TC studies, can be expected to result in a certain shortening of τ_{IVR}.

5. Conclusions

In the steady-state studies of the spectral properties of TC in PF and hexane solutions, we succeeded in recording a weak fluorescence from the S$_2(\pi,\pi^*)$ state with $\phi_F = 6 \times 10^{-5}$ and even weaker phosphorescence from the T$_1(\pi,\pi^*)$ state.

The spectrum of fluorescence from the S$_2$ state was found to change its shape and the position of its maximum with changing of λ_{ex}, which induces excitation with an excess of vibrational energy reaching 7000 cm^{-1} above the (0,0) band and thus leads to emission from unrelaxed vibrational levels.

Photophysical properties of TC in the S$_2$ state are essentially different from those of BPT and DTDN, although their spectral properties seem relatively much alike. In aromatic thioketones including BPT and DTDN, in PF, the dominant process of radiationless deactivation of the S$_2$ state is internal conversion to the S$_1$ state, characterized by the rate constant depending on the value of the energy gap $\Delta E(S_2-S_1)$. In the case of TC this process plays an insignificant role, and its contribution to total deactivation is less than 10%.

A much faster and more efficient deactivation process must be considered in order to explain the reported spectral and

photophysical properties of TC. Such processes have been proposed, and their effect on the lifetime of S_2 state as well as on the dependence of the shape of fluorescence band on λ_{ex} has been discussed. Drastic reduction of τ_{S_2} when compared to that of other aromatic thiones is additionally confirmed by the lack of reactivity of TC in the S_2 state in the reaction of photocycloaddition to olefines. Also, no solvent influence on ϕ_F, considered with the exceptional reactivity of thiones in their S_2 state taken into regard, confirms that τ_{S_2} must be very short.

The proposed interpretation, describing TC in its S_2 state as a vibrationally unequilibrated luminophore, provides a successful explanation of certain experimental facts including a low value of ϕ_F at a significant value of k_F, lack of a measurable dependence of ϕ_F on λ_{ex} and the kind of solvent, very short estimated values of τ_{S_2}, a strong dependence of the shape of the emission spectrum on λ_{ex}, and a significant effect of IVR on the shape of the emission spectrum.

The described effect of emission from an unequilibrated manifold of vibrational levels is expected to occur, at a certain level of intensity, in many short-lived fluorescent systems of high enough value of k_F. TC is a molecule particularly suitable for such experiments, because as follows from the results of quantum-mechanical calculations performed with the INDO/S CI method, there are large energy gaps $S_3 - S_2 \geq 7000\ \text{cm}^{-1}$ and $S_2 - S_1 \geq 5000\ \text{cm}^{-1}$ above and below the S_2 state, leaving a wide energy range for purely vibrational excitation of the S_2 state. Also, the unusually efficient radiationless deactivation of the lower vibrational levels of the S_2 state of TC effectively quenches emission from these levels which would otherwise be very strong. Thanks to this, the weak emission from the higher excited vibrational levels is exposed and accessible to investigation.

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