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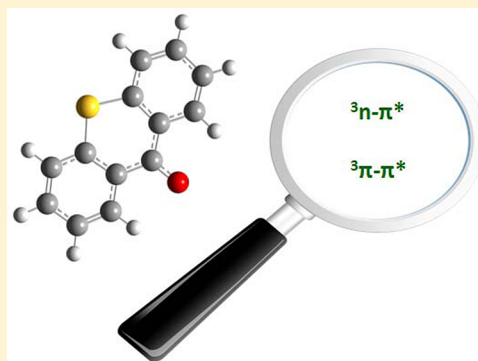
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Simultaneous Detection of Two Triplets: A Time-Resolved Resonance Raman Study

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ABSTRACT: Solvents are known to affect the triplet state structure and reactivity. In this paper, we have employed time-resolved resonance Raman (TR3) spectroscopy to understand solvent-induced subtle structural changes in the lowest excited triplet state of thioxanthone. Density functional theory (DFT) combined with the self-consistent reaction field (SCRF) implicit solvation model has been used to calculate the vibrational frequencies in the solvents. Here, we report a unique observation of the coexistence of two triplets, which has been substantiated by the probe wavelength-dependent Raman experiments. The coexistence of two triplets has been further supported by photoreduction experiments carried out at various temperatures.



INTRODUCTION

Solvents play an important role in determining the structure and reactivity of the transient species formed during a chemical reaction.^{1–3} In the case of aromatic ketones, triplet states are energetically very close, and small perturbations such as substituent and solvent can alter the position of the energy levels.^{1,4–6} This type of change in energy ordering is called electronic state switching and is known to influence the photophysical properties such as radiative and nonradiative decay rate constants. This electronic state switching plays an important role in deciding the triplet state reactivity. For example, the reactivity toward hydrogen abstraction by the triplet state depends primarily on the nature and energy of the lowest triplet excited state. It has generally been known that the triplet excited state with $n-\pi^*$ configuration is more reactive as compared to the $\pi-\pi^*$ state.^{7–9} Solvent polarity is known to reorder the triplet states due to the difference in degree of solvation of the states. Therefore, solvents play a deciding role in determining the lowest triplet excited state configuration and thereby strongly govern the reactivity and stability of the transient species.

Thioxanthone (TX, Figure 1) and its derivatives are known to show solvatochromic behavior and find various pharmaceutical and polymeric applications.^{10–16} The excited state of TX has recently received considerable experimental and theoretical attention.^{17–22} Particularly, the lowest triplet state of TX has been extensively studied as this long-lived state of TX has been attributed to be responsible for most of its photochemical reactions. In most of the studies, the lowest triplet of the TX has been attributed to be $\pi-\pi^*$ in nature.^{12,19,20} Reactivity of the TX excited triplet state toward hydrogen abstracting species contradicts this assignment because the observed fast hydrogen abstraction is a prototype reaction of an $n-\pi^*$ triplet, and the rate constant for the hydrogen abstraction was found to be

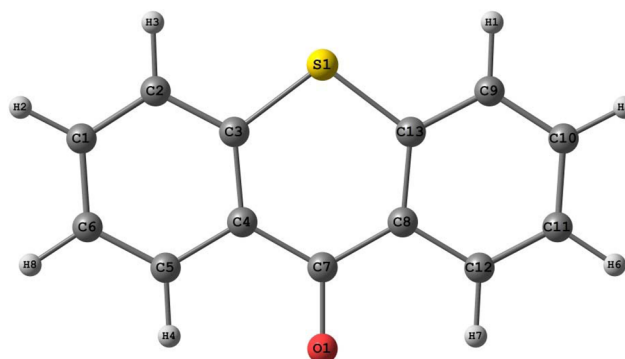


Figure 1. Structure of TX.

comparable with the $n-\pi^*$ triplet state of other similar molecular systems.^{21,23} It has been proposed that if two triplet states are energetically very close and $^3\pi-\pi^*$ lies below the $^3n-\pi^*$, then the aromatic ketone with $^3\pi-\pi^*$ configuration can borrow the photo reduction activity from the thermally accessible $^3n-\pi^*$.^{7,24} Allen et al. have suggested strong mixing between the $^3n-\pi^*$ and $^3\pi-\pi^*$ states in order to explain variations in phosphorescence emission wavelength maxima with solvent polarity.²⁵ The dramatic solvatochromatic behavior shown on the wavelength of T_1-T_n absorption maximum also supports that the lowest triplet state is a mixed state.¹⁴ Ley et al. have employed picosecond pump–probe absorption techniques on xanthone, a structurally similar system, and observed that in nonpolar solvent, two transitions were observed originating from the $^3n-\pi^*$ and $^3\pi-\pi^*$ states, signifying a

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mixed state.²⁶ In a nonpolar solvent, xanthone has predominantly $^3n-\pi^*$ character, whereas $^3\pi-\pi^*$ contributes significantly in the polar solvents. Similarly, TX has also been studied, and the observed absorption band has been deconvoluted into two bands, which have been attributed to the $^3\pi-\pi^*$ and $^3n-\pi^*$ signifying that the lowest triplet state of TX has mixed character.²⁷

Until now, most of the studies on the excited state of the TX have been reported pertaining to its electronic states. In order to probe the structure of transient species and also to assign the nature of the triplet state of aromatic ketones, vibrational spectroscopy remains the technique of choice.^{1,28} The CO stretching frequency of the $^3n-\pi^*$ state has been found to be lower than that of the $^3\pi-\pi^*$.²⁸ Therefore, the carbonyl frequency can be used as a marker band for assignment of the lowest triplet state of aromatic ketones. In the case when both the $^3n-\pi^*$ and $^3\pi-\pi^*$ states coexist, one can expect to observe two different C–O (stretching) bands corresponding to $^3n-\pi^*$ and $^3\pi-\pi^*$. In our attempt to understand structure reactivity correlation, we have recently studied the vibrational structure of the TX in the triplet state in carbon tetrachloride as a solvent and ascribed the lowest triplet state as nearly $n-\pi^*$ in character.²⁹ Our interest in the TX photochemistry stems from the fact that the wavelength of the T–T (triplet–triplet) absorption maximum of the lowest triplet state of TX changes from 580 to 655 nm while changing the solvent from 2,2,2-trifluoroethanol to carbon tetrachloride.¹⁴ Although, the effect of the solvent on the excited state of TX has been studied extensively using various techniques, little is known on the solvent-induced structural changes in the excited state.

In this study, we present experimental and theoretical results on the vibrational structure of the lowest triplet state of TX in two solvents: one polar and one nonpolar solvent. Time-resolved resonance Raman spectroscopy (TR3) has been widely known to be an excellent technique for probing solvent induced subtle changes on the structure of the transient species.^{1,2,30–32} To gain further insight into the structural aspects and to corroborate the experimental findings, density functional (DFT) calculations have also been carried out.

■ EXPERIMENTAL AND THEORETICAL DETAILS

Experimental details. The detailed experimental setup and the procedures used for TR3 spectroscopy have been described elsewhere.³³ Briefly, the third harmonic 355 nm laser pulse (pulse width 8–10 ns, 10 Hz, 3 mJ) from an Nd:YAG laser (DCR 11, Spectra Physics) was used as the photoexcitation (pump) source. The probe pulses (pulse width 6–8 ns, 10 Hz, 1.5–3 mJ) of various wavelengths were generated by the nanosecond OPO (Premiscan, Newport Corp.), which had been pumped by another Nd:YAG laser (GCR 250, Spectra Physics) providing a high-energy laser pulse of wavelength 355 nm. A SPEX 1404 double monochromator was used with two 600 groove gratings to disperse the scattered light. A liquid-N₂ cooled CCD (Jobin Yvon) with 1024 × 256 pixels was used as the multichannel detector. The recorded Raman spectra were calibrated using cyclohexane bands as a reference, and the spectral resolution was estimated as 5 cm^{−1}. The sample solutions (~1 mM) were circulated through a capillary at a rate of ca. 20 mL/min such that each sample volume received only one laser pulse of the 10 Hz laser system. In order to avoid possible accumulation of photoproducts, sample solution was replaced regularly with fresh solution. In addition, the ground-state Raman spectrum was also recorded at various times, and

recorded spectra were compared with the initially recorded (at the start of the experiment) ground-state spectrum, and it was noted that the accumulation of photoproducts was either not present or negligibly small.

The photoreduction experiments were carried out using an Applied Photophysics apparatus (LKS 60). The pump pulse (8–10 ns, 10 Hz, 10 mJ) used in this study was the third harmonic of a Nd:YAG laser (DCR 11, Spectra Physics). The analyzing pulse was obtained from 250 W pulsed xenon lamp, and signals were detected using a Czerny Turner monochromator and an R-928 five-stage photomultiplier tube. The transient signals were acquired and analyzed with a combination of an oscilloscope and a personal computer, and a sample cell of 1 cm path length was used in the present study. For each decay trace, five shots were averaged.

TX, purchased from Aldrich was of high-purity grade (97%) and vacuum sublimed before use. 1,4-cyclohexadiene was obtained from Aldrich and used as received. Solvents used in the study were of spectroscopy grade and used as received. For the photoreduction experiment, the concentration of TX was taken as 0.1 mM. 1,1,2-Trichlorotrifluoroethane (TCTFE) was chosen as solvent for the photoreduction experiment as it does not contain hydrogen atoms. 1,4-Cyclohexadiene was used as a hydrogen donor, and photoreduction experiments were done at various temperatures ranging from 0 to 40 °C. The solutions were degassed for 20 min prior to the experiments using ultrahigh pure (UHP)-grade argon.

Computational Details. The quantum-mechanical calculations of the structure and frequencies of the normal vibrations in the lowest triplet state were performed by the DFT/B3LYP/TZVP method as implemented in Gaussian 09.³⁴ The basis set TZVP was chosen, as it is known to reproduce experimental frequencies accurately on TX and structurally similar systems.^{19,35} The full geometry optimization was carried out with no geometry constraints using Berny's optimization algorithm. To incorporate the solvent effect into the calculation, the polarizable continuum model (PCM) was used as available in the Gaussian 09 suite.³⁶ The vibrational frequencies and the corresponding normal modes were evaluated for the optimized geometries using the analytical differentiation algorithm contained within the program. The optimized structures (in solvents) of TX in the lowest excited triplet state were confirmed to be local minimum, as frequency calculations did not find any imaginary frequency. The time-dependent DFT (TD-DFT) method (B3LYP/TZVP) has been used to calculate the structure and frequencies of TX in the second excited triplet (T_2) state. TD-DFT calculation was done on the S_0 structure optimized with the same level of theory. Computed vibrational frequencies were scaled in order to have better correspondence with experimental results. We have used 0.99 as the scaling factor as used for the above-mentioned basis set.^{35,37} The optimized structure and the calculated normal modes of vibration were visualized using Chemcraft software,³⁸ and the VEDA 4.0 program³⁹ (vibrational energy distribution analysis) was used for the potential energy distribution calculations.

■ RESULTS AND DISCUSSION

The TR3 spectra of TX in acetonitrile and *n*-hexane were recorded under identical conditions, and these two solvents have been chosen as the representatives of polar and nonpolar solvent, respectively. The TR3 spectra of TX in acetonitrile at various delays are presented in Figure 2. It can be seen from the

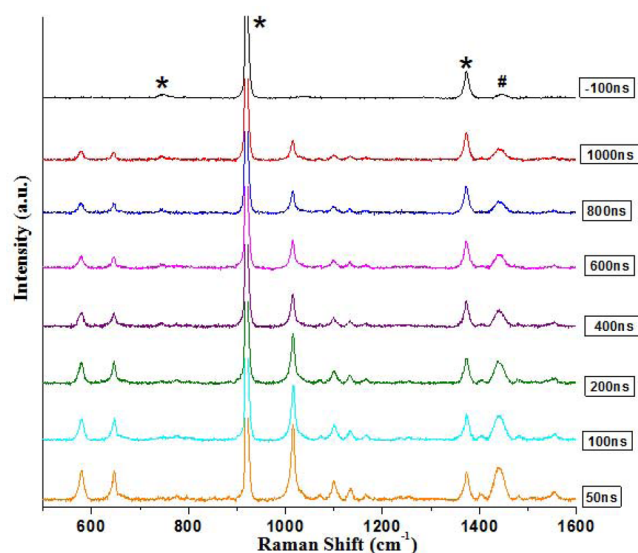


Figure 2. TR3 spectra of TX in acetonitrile at various delays, pump @ 355 nm, probe @ 625 nm; solvent bands have been marked by asterisk. The spectra have been normalized with respect to the 918 cm^{-1} band of acetonitrile.

figure that, except for the solvent bands (marked by an asterisk in the spectra), all other bands decay with time. We attribute the spectra of the transient species to the triplet excited state of TX on the basis of the following observations: (1) the transient Raman spectrum was observable only when the probe wavelength was in resonance with the triplet–triplet absorption of TX, (2) no spectral changes other than decay (no change in peak position/appearance of new peaks) were observed with time in the TR3 spectra, and (3) the observed transient species was found to be significantly quenched by purging oxygen in the solution. Similar TR3 experiments were also carried out in *n*-hexane, and a comparison of the transient Raman spectra (pump only and probe only corrected) of TX in *n*-hexane and acetonitrile as presented in Figure 3 indicates that solvent polarity induces changes in both peak position and relative intensity. The experimental and DFT calculated triplet state frequencies of TX along with tentative band assignments are

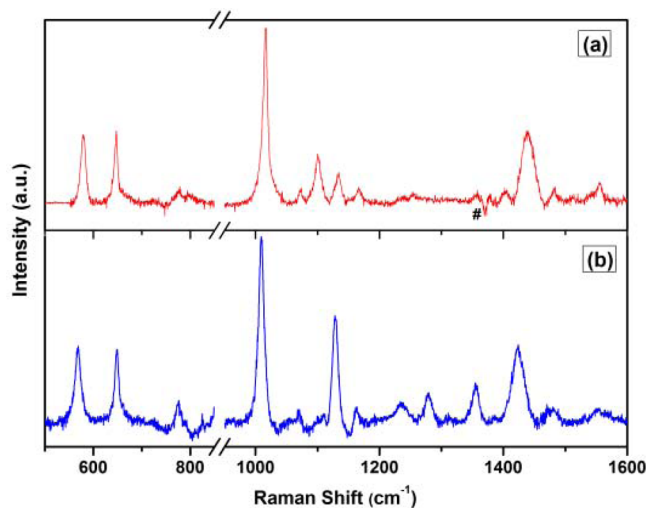


Figure 3. Transient Raman spectra of TX in solvents at 100 ns delay: (a) acetonitrile, (b) *n*-hexane; # = subtraction artifact.

presented in Table 1. From our earlier study on the lowest triplet state structure of TX in CCl_4 , the experimentally observed bands at 1377 cm^{-1} and 1435 cm^{-1} had been tentatively ascribed to CO stretching and CH in-plane bending, respectively.²⁹ The band at 1377 cm^{-1} (observed in CCl_4) has been found to shift to 1355 cm^{-1} and 1403 cm^{-1} in *n*-hexane and acetonitrile, respectively. Similarly, the band at 1435 cm^{-1} is also sensitive to the solvent polarity. This band is observed at 1424 cm^{-1} in the case of *n*-hexane and at 1439 cm^{-1} in the case of acetonitrile. It is interesting to note from Figure 3 that the intensity ratio of the bands (e.g., 1439 and 1403 cm^{-1} , in the case of acetonitrile) is also solvent dependent. There may be two possibilities: the above-mentioned bands either correspond to the two different vibrations (of the same species), which are sensitive to the solvent polarity, or belong to two different transient species. We have found that the decay constants of the above-mentioned bands are different, suggesting that bands are not from the same transient species. These bands are sensitive to the oxygen purging, signifying that both are related to the transient triplet species. Since these two bands are resonance enhanced at the same probe wavelength, it is necessary to understand the transient absorption spectra of the triplet excited state.

Interestingly, the time-resolved absorption study indicates that the absorption band (in the range of 600–650 nm) of the triplet state of TX in acetonitrile could be deconvoluted into two bands.²⁷ This could be due to the presence of two different types of the triplet states, namely, $n-\pi^*$ and $\pi-\pi^*$. On this basis, it seems quite reasonable to postulate that in the present experiment, two triplets are being probed simultaneously. Since solvent polarity is known to stabilize the $^3\pi-\pi^*$ state more as compared to $^3n-\pi^*$, solvent polarity would determine the population ratio of $^3\pi-\pi^*$ and $^3n-\pi^*$ states. As a consequence, with the increase in the solvent polarity, the intensity ratio of the bands corresponding to $^3\pi-\pi^*$ and $^3n-\pi^*$ states would increase.

In order to support the above observation, we carried out DFT calculations on the two possible excited triplet states (i.e., T_1 and T_2) with TZVP basis. The calculated structural parameters (in the gas phase) are presented in Table 2. As shown in the table, the bond distances calculated in this study are in very good agreement with the recent computational results by Rai-Constapel et al.²² The configuration of T_1 and T_2 states have been visualized as $\pi\pi^*$ and $n\pi^*$, respectively. The above results are in agreement with the recent computational studies.^{20,22} The calculated dipole moments of T_1 and T_2 states are 4.22 and 0.65 D, respectively. The calculated C–O bond distances of TX in T_1 and T_2 states are 1.291 to 1.326 Å, respectively. It is therefore expected that CO vibrational frequency would be higher in the T_1 state as compared to the T_2 state. On the basis of computational results and the fact that bands are sensitive to the solvent polarity, 1435 cm^{-1} and 1377 cm^{-1} bands (observed in CCl_4) can be tentatively reassigned as CO stretching vibrations of the T_1 and T_2 states, respectively.

It can be seen from the table 1 that a considerable shift has been observed for CO vibrational bands due to solvation. With the increase in solvent polarity (from *n*-hexane to acetonitrile), the CO stretching band (of T_1 state) shifts from 1424 cm^{-1} to 1439 cm^{-1} , which is consistent with calculated triplet state (T_1) frequencies presented in Table 1. The CO stretching frequency has been known as a marker band for assigning configuration of the triplet state. Triplet state with $^3n-\pi^*$ configuration has been observed to have CO stretching frequency close to the

Table 1. Triplet State Experimental and Calculated Frequencies and Tentative Assignments^a

exptl. frequencies (cm ⁻¹)		calculated frequencies ^b in solvents (T ₁) (cm ⁻¹)		calculated frequencies ^b (T ₁) (cm ⁻¹)	calculated frequencies ^c (T ₂) (cm ⁻¹)	approx. character
acetonitrile	<i>n</i> -hexane	acetonitrile	<i>n</i> -hexane	gas phase	gas phase	
<u>579</u>	<u>568</u>	580	576	574		ring dist.
647	649				620	ring dist.
<u>1016</u>	<u>1010</u>	1034	1032	1031	1046	ring breathing
1072	1070	1077	1075	1075	1079	ring str.+C=O str.
1100	1105	1119	1123	1121	1131	ring str.+C=O str.
1134	1129	1151	1154	1155		CH ip bend.
1167	1162	1226	1229	1230		ring str.
<u>1403</u>	<u>1355</u>				1346	C=O str.
<u>1439</u>	<u>1424</u>	1392	1365	1359		C=O str.
<u>1482</u>	<u>1476</u>				1471	ring str.
1555	1555	1544	1556	1561		ring str.

^aUniform scaling factor 0.99; str. = stretching, bend = bending, ip = in-plane, dist. = distortion. The experimental bands that show solvent-induced shift more than 5 cm⁻¹ have been underlined. ^bCalculated with DFT/B3LYP/TZVP. ^cCalculated with TD-DFT/B3LYP/TZVP.

Table 2. Main Structural Parameters for the First (T₁) and Second (T₂) Excited Triplet States of TX^a

Bond distances	T ₁	T ₂
r _{C1-C2}	1.385(1.386)	1.391(1.391)
r _{C2-C3}	1.398(1.397)	1.391(1.392)
r _{C3-C4}	1.430(1.430)	1.416(1.417)
r _{C4-C5}	1.413(1.415)	1.417(1.417)
r _{C5-C6}	1.381(1.380)	1.381(1.382)
r _{C6-C1}	1.405(1.405)	1.395(1.395)
r _{C-H}	1.083 (1.084) ^a	1.083 (1.084) ^a
r _{C4-C7}	1.444(1.442)	1.429(1.429)
r _{C7-O}	1.291(1.303)	1.326(1.327)
r _{C3-S}	1.754(1.749)	1.775(1.764)

^aMethod: DFT for T₁ and TD-DFT for T₂; functional: B3LYP; basis set: TZVP. For numbering, see Figure 1. All bond lengths are given in Å. Values given in brackets are from ref 22, α -averaged value.

single bond CO frequency as opposed to ³ π - π^* triplet state, which has a CO stretching band close to the CO double bond frequency.²⁸ In the case when a triplet state has both π - π^* and n - π^* characters, the shifting of the CO stretching frequency toward high wavenumber may be correlated with the increased π - π^* character. However, as mentioned earlier, we observe two decay rate constants, indicating the signature of two different triplet states.

In order to rationalize the above observation, probe wavelength dependence (with same pump wavelength and laser pulse energy) TR3 experiments were carried out. These experiments probe the triplet state selectively depending upon the excitation wavelength chosen. However, since both triplet states are very close, changes in the relative intensity ratio of the peaks corresponding to the two different triplet states would be observed. The transient Raman spectra of TX in acetonitrile recorded at 100 ns at different probe wavelengths are presented in Figure 4. As shown in the figure, the intensity ratio of the 1439 cm⁻¹ band to 1439 cm⁻¹ band increases with increase in the wavelength of probe excitation, signifying that the contribution from the π - π^* character increases. For the purpose of visual appreciation, the 1400–1600 cm⁻¹ range has been magnified (Figure 4). In addition, it can also be deduced from Figure 4 (shaded area left side of the graph) that the intensity ratio of two lower wavenumber bands (579 cm⁻¹ to 647 cm⁻¹) changes with change in the probe excitation

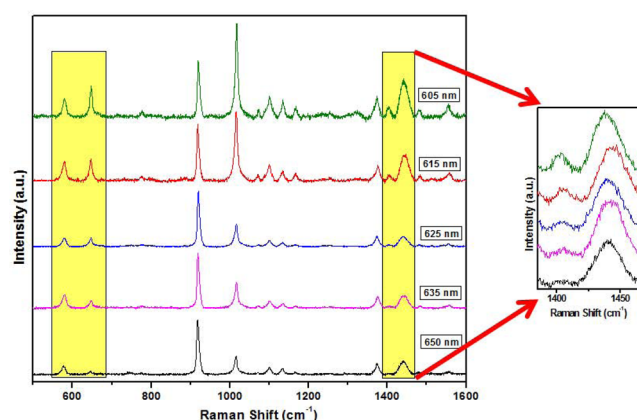


Figure 4. Transient Raman spectra of TX in acetonitrile at different probe wavelengths.

wavelength. These two bands at 579 and 647 cm⁻¹ have been previously assigned to the ring distortion modes.²⁹ The relative intensity ratio of the bands (579 to 647 cm⁻¹) increases with the increase in the probe wavelength. The band at 579 cm⁻¹ and 647 cm⁻¹ can be assigned to ring distortion of the T₁ and T₂ states, respectively, which is consistent with DFT calculations. The band at ~1480 cm⁻¹ has previously been assigned as ring stretching.²⁹ On the basis of decay characteristics and probe dependence behavior, this band (observed at 1482 and 1476 cm⁻¹ in acetonitrile and *n*-hexane, respectively) can be associated with the T₂ state. We observed a new band at ~1555 cm⁻¹ in other solvents, which was not reported earlier, as the band was swamped by the very broad solvent (CCl₄) band. This band behaves in the same way (with the change in the wavelength of probe excitation) as the 1435 cm⁻¹ band and could be related to the T₁ state. With the help of computational results, this band was assigned to ring stretching. We also carried out the probe excitation wavelength dependence study in *n*-hexane, and the transient spectra (at 100 ns) recorded at different probe wavelengths are presented in Figure 5a. As mentioned earlier, in the case of *n*-hexane, the bands at 1355 cm⁻¹ and 1424 cm⁻¹ have been assigned to CO stretching of the T₂ and T₁ states, respectively. The relative intensity ratio (*I_r*) of the 1424 cm⁻¹ to 1355 cm⁻¹ band plotted in Figure 5b indicates that the contribution of the T₁ to the equilibrated triplet increases with the increase in probe wavelength, similar

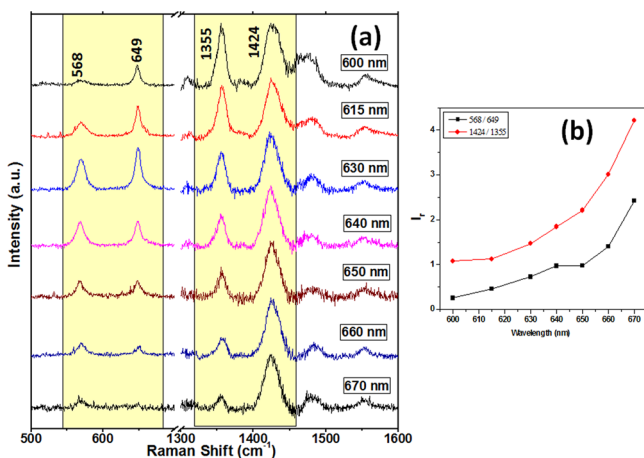


Figure 5. (a) Transient Raman spectra of TX in *n*-hexane at different probe wavelengths. (b) Intensity ratios of the selected bands at different probe wavelengths.

to the observation made in acetonitrile. Similarly, the intensity ratio of the bands observed at 649 cm^{-1} and 568 cm^{-1} , corresponding to the distortion modes of T_1 and T_2 states, also decreases with the increase in the probe wavelength.

The triplet state with pure $\pi-\pi^*$ configuration has been known to be nearly unreactive as opposed to the triplet state with pure $n-\pi^*$ configuration.⁴⁰ When the $n-\pi^*$ triplet state is energetically close (within a few kilocalories per mole) to the lowest triplet $\pi-\pi^*$ state, the unusual reactivity of the $^3\pi-\pi^*$ state may be attributed to the excitation of $^3\pi-\pi^*$ state to the thermally accessible reactive $^3n-\pi^*$ state.^{7,24} In the case when the lowest triplet $\pi-\pi^*$ state borrows the reactivity from the close-lying $^3n-\pi^*$ state, with the increase in the temperature, the photoreduction activity increases due to the increase in the mole fraction of the $^3n-\pi^*$ state, inferring the coexistence of two triplet states. We have carried out the photoreduction experiments on TX in TCTFE, solvent with no hydrogen, using 1,4 cyclohexadiene (hydrogen donor) at various temperatures. The band at $\sim 430\text{ nm}$ has previously been assigned to the ketyl radical of TX. The decay plots of TX in TCTFE at 430 nm in the presence of a fixed concentration of hydrogen donor recorded at different temperatures are presented in Figure 6. As shown in the figure, the absorption at 430 nm increases with the increase in the temperature, indicating that ketyl radical formation is favored at higher temperatures. This may be correlated with the increase in the population ratio of $^3n-\pi^*$ and $^3\pi-\pi^*$ states at high temperature. On the basis of the observed changes in intensity ratios of transient Raman bands with the solvent polarity, the dependence of relative intensities of the bands on the probe wavelength, and the photoreduction experiments carried out at different temperatures, it is apparent that two triplets coexist in the case of TX.

SUMMARY

We have presented the vibrational spectroscopic study on the lowest excited triplet state of TX in both polar and nonpolar solvents. Solvent polarity has been observed to induce the structural changes, and the CO stretching frequency has been found to be sensitive to the solvent polarity. The coexistence of the two lowest triplet states in thermal equilibrium has been proposed, which has been supported by the transient Raman experiments carried out at different probe wavelengths. The above observation has been further supported by temperature-

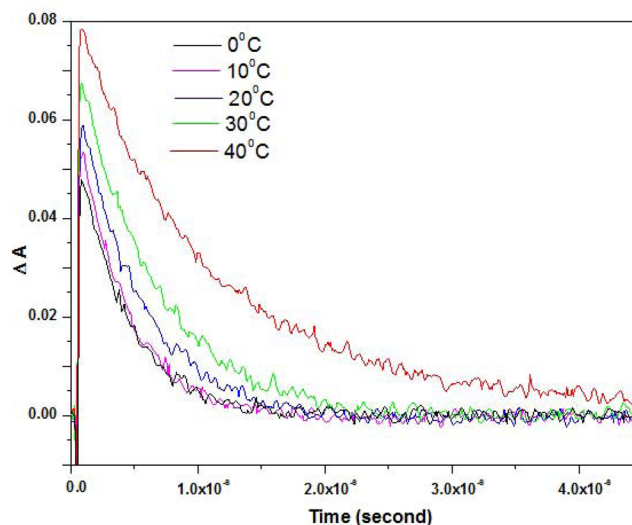


Figure 6. Decay plots of TX ketyl radical at various temperature points recorded at 430 nm .

dependent photoreduction experiments. It has been observed that the contribution from the $^3\pi-\pi^*$ state to the equilibrated triplet increases with the increase in the solvent polarity. To the best of our knowledge, this is the first time that two triplets have been detected simultaneously using TR3 study.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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