

Solvent-induced changes on the polarity of the triplet excited state of 2-chlorothioxanthone: From time-resolved absorption and resonance Raman spectroscopies



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ARTICLE INFO

Article history:

Received 20 April 2013

In final form 9 October 2013

Available online 22 November 2013

Keywords:

Raman spectroscopy

Solvent effect

Triplet state

2-Chlorothioxanthone

ABSTRACT

Solvent polarity has been known to influence the triplet state structure and reactivity. Here, we present our experimental and theoretical study on the effect of solvent on the lowest triplet excited state structure of 2-chlorothioxanthone (CTX). Time-resolved absorption (TA) spectroscopy has been employed to understand the triplet state electronic structure; whereas solvent-induced structural changes have been studied using time-resolved resonance Raman (TR3) spectroscopy. Both the DFT and TD-DFT calculations have been performed in the solution phase employing self-consistent reaction field implicit solvation model to support the experimental data. It has been observed that CO stretching frequencies of the excited triplet state are sensitive to the solvent polarity and increase with the increase in the solvent polarity. Both TA and TR3 studies reveal that specific solvent effect (H-bonding) is more pronounced in comparison to the nonspecific solvent effect.

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1. Introduction

Solvents play a key role in many photochemical, photophysical and biochemical processes [1–4]. Solvent effect is an indication of the solute–solvent interactions present in the immediate vicinity of the solute molecules. The specific and nonspecific interactions between the solvent and the solute molecules have been reported to influence the electronic configuration as well as structure of the excited triplet state [1,5–8]. The influence of the solvent polarity can be understood in terms of the Coulombic and dispersive interactions between the charge distribution in the solute and the polarizability of the solvent. In the case of aromatic ketones, the two lowest triplet states are energetically very close and therefore small perturbations induced by either a substituent or solvent can modify the energy level ordering [6,9]. This type of change in energy level ordering is known to influence the triplet state reactivity. For example, in a non-polar solvent, the lowest triplet of 2,2,2-trifluoroacetophenone is more like $n-\pi^*$, whereas in a polar solvent it acquires $\pi-\pi^*$ configuration [1]. The triplet state with $n-\pi^*$ configuration has been known to be very reactive towards photoreduction as opposed to the state with pure $\pi-\pi^*$ configuration [10]. If the $n-\pi^*$ triplet state is energetically close (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 [11,12]. The reactivity of $^3\pi-\pi^*$ triplet state has also been explained in terms of the vibronic mixing of the $n\pi^*$ and $\pi\pi^*$ [13]. There have been number of reports in the literature concerning the coexistence of two lowest triplet states [5,6,14].

Thioxanthone (TX) and its derivatives are known to exhibit solvatochromic behavior and find various pharmaceutical and polymeric applications. Among TX derivatives, 2-chlorothioxanthone (CTX, Fig. 1) is one of the most widely used TX-based type-II commercial photoinitiators and the lowest triplet state is primarily responsible for most of its photochemical and photophysical properties. It is, therefore, imperative to understand the solvent induced structural changes [15]. We have previously demonstrated the coexistence of two lowest triplet states in the case of CTX and the lowest triplet excited state (T_1) has been ascribed as $\pi-\pi^*$ while $n-\pi^*$ configuration has been assigned to the T_2 state [16]. In the case of coexistence of the two triplets, the extent of stabilization by the solvent depends upon the nature of triplet state configuration. Therefore, the solvent polarity is likely to determine the population ratio of $^3\pi-\pi^*$ and $^3n-\pi^*$ states. Furthermore, it has previously been reported in the case of the parent compound (TX) that solvent polarity plays a vital role in determining the triplet state electronic structure [17–21].

Classically, several macroscopic solvent parameters have been defined in terms of static dielectric constant, permanent dipole moment and refractive index to account for solvent polarity. The above-mentioned solvent parameters are derived using idealized

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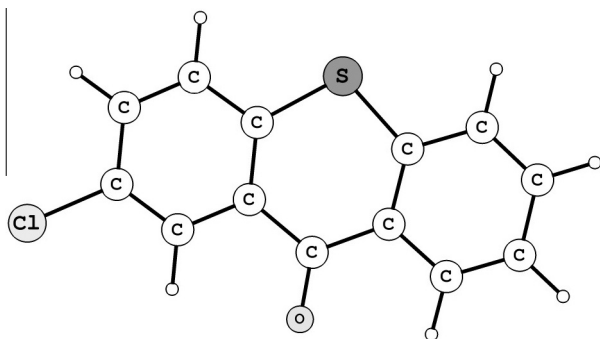


Fig. 1. Structure of 2-chlorothioxanthone.

electrostatic model and based on the assumption that solvents are non-structured continuum, however solute–solvent interactions take place at the molecular level within the structured discontinuum. The macroscopic solvent parameters only account for nonspecific Coulombic interactions. Because of the negligence of specific solute–solvent interactions, the electrostatic approach to account the solvent effect has failed to correlate well with the observed solvent effects [22]. Attempts have been made to define the solvent polarity empirically based on the microscopic property to account for various specific and nonspecific solvent interactions and various polarity scales, such as, $E_T(30)$, π^* , α , β , etc. In particular, the scale based on the $E_T(30)$ values has been identified as comprehensive scale to measure the solvent polarity [23–26].

Time-resolved resonance Raman (TR3) spectroscopy is proven as an excellent technique to study the molecular structure of the transient species in microsecond–picosecond time scale [1,27–29]. We have carried out TR3 experiments to investigate solvent-induced subtle changes in the vibrational structure of the lowest excited triplet state. In this paper, we present combined time-resolved absorption (TRA) and TR3 studies on the lowest triplet excited state of CTX carried out in a wide variety of solvents. In order to corroborate the experimental results, DFT and TD-DFT calculations have also been carried out. Further, TD-DFT computations have been carried out in solvents of varying polarity to understand the solvent effect on energy of the excited states.

2. Materials and experimental methods

CTX (99%) was purchased from Alfa Aesar and recrystallized twice with ethanol before use. All the solvents were of spectroscopy/HPLC grade and used as received.

The time-resolved absorption measurements in various solvents were carried out using applied photophysics LKS.60 set-up. The photoexcitation laser pulse (355 nm, 8–10 ns, 10 mJ, 10 Hz) was derived from the third harmonic of an Nd-YAG laser (DCR 11, Spectra Physics) and the pulsed xenon lamp (150 W) was used as probe light source. The transient signals were detected using the combination of Czerny–Turner monochromator and R-928 five stage photomultiplier tube. The transient signals were acquired by oscilloscope and analyzed using personal computer. The instrument response time of the time-resolved absorption set-up was ~ 11 ns. For each decay trace, 5 shots were averaged and time-resolved absorption spectra were recorded at the interval of 5 nm. The concentration of the CTX solution was ~ 0.1 mM and the sample cell of 1 cm path length was used in this study. The solutions were deoxygenated for 20 min prior to the experiments using ultra high pure (UHP) grade argon.

The detailed experimental set-up and the procedures used for TR3 measurements have been described previously [30]. Briefly, the pump excitation pulse (355 nm, 8–10 ns, 10 Hz, 1.5 mJ) used

in the present study was the third harmonic of the Nd-YAG laser (DCR 11, Spectra Physics). The probe pulses (6–8 ns, 10 Hz, 2–4 mJ) in the wavelength range of 610–655 nm were derived from the nanosecond OPO (Premiscan, Newport Corp.) which was pumped by a high power Nd-YAG laser (GCR 250, Spectra Physics) operating at 355 nm. The scattered light was dispersed by a SPEX 1404 double monochromator (equipped with 600 grooves/mm gratings) and detected by a liquid-N₂ cooled CCD. The calibration of the recorded Raman spectra was done using known cyclohexane solvent bands as reference and the spectral resolution was estimated as ~ 5 cm⁻¹. Sample solutions (~ 2.5 mM) were continuously circulated through a quartz capillary at a rate of *ca.* 20 ml/min during the entire span of spectral recording to avoid the local heating and formation of undesirable photoproducts. Sample solution was replaced regularly with the fresh solution to avoid possible accumulation of photoproducts. Further, ground-state Raman spectra were recorded at various time intervals and the spectra were compared with the initially recorded (at the start of the experiment) ground-state spectrum. It was noted that the accumulation of photoproducts was not present or negligibly small.

3. Computational details

Structural optimization and frequency calculation of CTX in the lowest triplet state (T_1) was performed using DFT/B3LYP/TZVP method as implemented in Gaussian 09 [31]. TZVP was chosen as basis set as this has previously been recognized to reproduce experimental frequencies quite accurately on TX and structurally similar systems [19,32–34]. The full geometry optimization was carried out without any geometry constraints using Berny's optimization algorithm. To include the solvent effect into the computation, the default version of polarizable continuum model (PCM), as implemented in Gaussian 09 program suite, has been used for geometry optimization and frequency calculation [35,36]. The vibrational frequencies and the corresponding normal modes were evaluated on the optimized geometries using analytical differentiation algorithm contained within Gaussian 09. For structural optimization and frequency calculation of the second excited triplet state (T_2), TD-DFT/B3LYP/TZVP has been used as the computational method. TD-DFT calculation was performed on S_0 geometry optimized with the same level of theory. No imaginary frequency was obtained in the frequency calculations on optimized structures of CTX in both T_1 and T_2 states confirming the stationary points. Computed vibrational frequencies were scaled by 0.99 in order to have better correspondence with experimental results [19,32,34]. Chemcraft software was used for the visualization of optimized structure and calculated normal modes of vibration [37].

4. Results and discussion

Laser flash photolysis experiments have been performed in the solvents of varying polarities in the identical conditions. The representative time-resolved spectra of CTX in 2-propanol are presented in Fig. 2. The transient absorption spectrum has been found to be very sensitive to the deoxygenation. The band observed in the 600–650 nm range (depending upon the solvent chosen) has previously been ascribed due to the triplet state [38]. On this basis, the spectra in Fig. 2 have been attributed to the transient spectra of the triplet state of CTX. The band observed in the ~ 600 –650 nm range has been observed to be broad and unsymmetrical. In the case of the TX and xanthone (a structurally similar system), this transient absorption band observed at ~ 600 –650 nm has previously been attributed as the convolution of two absorption bands arising due to ${}^3\pi$ – π^* and 3n – π^* states [39,40]. The transient absorption spectra of CTX in *n*-hexane and acetonitrile are presented in

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