Ultrafast fluorescence studies of excited-state hydrogen transfer reactions in solution
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Chapter 7

Femtosecond Studies of Orientational Anisotropy Decay of Benzopyranthione in the Excited $S_2$ State in Hydrocarbons

Abstract

Reorientational dynamics of 4H-1-benzopyrane-4-thione (BPT) in the $S_2$ state, in hydrocarbon solution, is studied from the anisotropy decay of fluorescence upconversion and pump-probe absorption transients with femtosecond time resolution. The anisotropy decay is found to be monoexponential in $n$-hexane, $n$-heptane, $n$-octane, $n$-decane, $n$-dodecane and cyclohexane. The dependence of the rotational time constant, $\tau_{rot}$, on the solvent viscosity is approximated by a linear function with a slope of $2.6 \pm 1$ ps/cP indicating slip conditions. The decay of orientational anisotropy is observed for the first time for a molecule in the $S_2$ state.
7.1 Introduction

The characteristic spectroscopic properties of aromatic thioketones have been well documented [1]. Aromatic thioketones are known to exhibit direct $S_0 \rightarrow T_1$ absorption, well-resolved $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ absorption bands, thermally activated $S_1$-fluorescence, efficient fluorescence from the $S_2$ state and phosphorescence from the $T_1$ state in solution at room temperature [1]. The large energy gap between thioketone $S_2$ and $S_1$ states ($\Delta E(S_2-S_1) \approx 7000 - 11000 \text{ cm}^{-1}$) is the cause for the long $S_2$-state lifetime and the fluorescence from the $S_2$ state. Emission from the $S_1$ state is insignificant due to fast intersystem crossing to the $T_1$ state ($\tau_{S_1}=0.5\times10^{-12} \text{ s}$) [2]. Thioketones in the $S_2$ state are very reactive because of efficient intermolecular quenching by most solvents. This has been verified for thioketones dissolved in hydrocarbons, acetonitrile and water. By contrast, in perfluorohydrocarbons, thioketones are inert and the $S_2$-state decay is exclusively intramolecular [1, 3 - 8].

Aromatic thioketone molecules, such as 4H-1-benzopyrane-4-thione (BPT) or the $n$-butyl derivative of BPT, 2-butyl-4H-1-benzopyrane-4-thione (BPTC$_4$), are characterized by a relatively small molecular volume and a long-lived $S_2$ state. Reorientational motions of these molecules in liquid solution might even be fast compared to the lifetime of the excited $S_2$ state and this opens up the possibility that the dynamics of the reorientational motions of the solute molecules in the $S_2$ state might be studied when the $S_2$-state fluorescence or pump-probe transients manifest temporal anisotropy behaviour. For most other molecules it is not possible to experimentally probe orientational anisotropy in the excited $S_2$ state because (i) the lifetime of a $S_2$ state is usually too short for fluorescence upconversion or pump-probe transients to be observed and (ii) the typical solute rotational correlation times are much longer than the $S_2$-state lifetime so that during this time rotational motions remain negligible [9 - 11]. In this paper, we study by means of femtosecond fluorescence upconversion and transient absorption techniques, the decay of the orientational anisotropy in the photoexcited $S_2$ state of BPT and BPTC$_4$ in a series of hydrocarbons of similar polarity but different bulk viscosity. To the authors' knowledge, the decay of orientational anisotropy of a solute excited into the $S_2$ state has previously not been observed in real time.
Chapter 7

7.2 Experimental

Details of the fluorescence upconversion and transient absorption experimental set-ups have been described previously [7, 8]. The molecular rotational diffusion effects were investigated at the 0° and 90° polarization configurations of the pump excitation and gate (fluorescence) or probe (absorption) pulses. Measurements at the magic angle (54.7°) were also performed to get a reference signal free from any rotational diffusion effect. The excitation wavelength was set at 380 nm or 403 nm. The Levenberg-Marquardt algorithm was chosen to perform non-linear least squares fits without deconvolution procedure, since the anisotropy decay constants are much longer than the instrument response function of transient absorption (120 fs fwhm) and fluorescence upconversion (300 fs fwhm) experiments. The transient absorption spectra probed below 1 ps were left out of consideration since they might be obscured by different photophysical side-effects (solvent two photon absorption, stimulated Raman scattering, cross-phase modulation). BPT and BPTC₄ were synthesized and purified by methods described elsewhere [12, 13]. Hydrocarbon solvents (n-hexane, n-heptane, n-octane, n-decane, n-dodecane and cyclohexane) were purchased from Aldrich and used as received. The aromatic thioketone concentration in all solutions was approximately 5×10⁻⁴ M. All measurements were performed at room temperature (20°C).

7.3 Results

7.3.1 Femtosecond fluorescence upconversion measurements

Results of steady-state absorption and emission measurements on BPT have been presented previously [6, 7]. From these results, it appears that the choice of a pump wavelength at 380 nm ensures selective excitation of the S₂ state (λ_max(S₀ → S₂) = 365 nm; the energy difference between the vibrationally relaxed S₃ and S₂ states is about 7000 cm⁻¹). In order to determine the influence of the solvent bulk viscosity on the orientational anisotropy dynamics of BPT in the S₂ state, the S₂ → S₀ fluorescence kinetics were probed by fluorescence upconversion in different linear hydrocarbons (n-hexane, n-heptane, n-octane, n-decane and n-dodecane) and in cyclohexane (see examples in Figure 7.1). In all solvents, the induced anisotropy r(t) was extracted from the two experimental fluorescence kinetic traces obtained on setting the pump excitation polarization parallel (∥) and perpendicular (⊥), respectively, to the gate pulse, where

\[ r(t) = \frac{I_∥(t) - I_⊥(t)}{I_∥(t) + 2I_⊥(t)} \]

I_∥(t) and I_⊥(t) being the detected light responses polarized parallel (∥) and perpendicular (⊥) to the polarization of the gating field [14]. The corresponding anisotropy decay curves are well-fitted by monoexponential kinetics,

\[ r(t) = r(\infty) \exp(-t/\tau_{\text{rot}}) + C, \]
where $\tau_{or}$ is the orientational time constant and $C$ is the offset (insets in Figure 7.1). The fits lead to initial anisotropy values $r(t_{0})$ comprised in the 0.29 to 0.34 range and $C$ values lower than 0.05. The orientational times obtained from the fits are plotted in Figure 7.2 as a function of the solvent viscosity.

Figure 7.1: Polarized femtosecond upconverted fluorescence kinetics at 465 nm after photoexcitation at 380 nm of $3 \times 10^{-4}$ M solutions of BPT in n-hexane (a) and in n-dodecane (b), and of BPTC$_4$ in n-hexane (c). The corresponding anisotropy decay curves are presented in the insets.
For BPT, the dependence of the rotational time-constant $\tau_{rot}$ on the solvent viscosity $\eta$ can be approximated by a linear function with a slope of $2.6 \pm 1$ ps/cP and an intercept of 2.6 ps (Figure 7.2). An intercept in plots of $\tau_{rot}$ against $\eta$ in the limit of zero viscosity has been found before for several other systems [15, 16]. However, its physical meaning is still not well understood [17-19] and we prefer not to speculate on its origin in the case of the BPT-hydrocarbon solutions investigated in this paper. The replacement of BPT in $n$-hexane by the $n$-butyl derivative BPTC$_4$ leads to an increase of the value of $\tau_{rot}$ from $3.2 \pm 1.0$ ps to $4.2 \pm 1.0$ ps (Figure 7.1c).

![Figure 7.2: Dependence of the rotational time constant of BPT (•) and BPTC$_4$ (*) in the $S_2$ state upon the viscosity of the hydrocarbon solvent: (1) n-hexane, (2) n-heptane, (3) n-octane, (4) n-decane, (5) cyclohexane and (6) n-dodecane. The inset presents the optimized structure of BPT (6-31G* level) and the representation of the inertial axes x, y, and z](image_url)

At the magic angle configuration, the kinetic trace measured in $n$-hexane at 465 nm (fluorescence peak position) is monoexponential with an $S_2$-state lifetime of $20.2 \pm 0.5$ ps for BPT. At other fluorescence wavelengths, on the red or blue side of the $S_2 \rightarrow S_0$ emission band, a bi-exponential decay is observed. The slower component corresponds to the $S_2$ state depopulation ($20.2 \pm 0.5$ ps), while the faster one ($2.8 \pm 0.5$ ps) is attributed to arise from vibrational cooling. (Note that excitation of the $S_3$ state near 380 nm leads to a significant amount of vibrational excess energy (1500 cm$^{-1}$)). Both components were previously also obtained from a femtosecond...
transient absorption analysis (20.0 ± 1.0 ps and 2.2 ± 0.5 ps [7]) using the same pump wavelength (380 nm).

7.3.2 Femtosecond transient absorption measurements

Fluorescence upconversion experiments were complemented by femtosecond transient absorption measurements performed with excitation in the low-energy tail of the $S_0 \rightarrow S_2$ absorption band, at 403 nm. Under these conditions, the $S_2$ state was excited without any excess vibrational energy. Previous experiments, performed under magic angle conditions [7], had shown that two species contribute to the transient absorption spectra of BPT in $n$-hexane: (i) transitions originating in the $S_2$ state ($S_2 \rightarrow S_n$ absorption at 650 nm and $S_2 \rightarrow S_0$ stimulated emission at 465 nm) and (ii) transitions originating in the $T_1$ state ($T_1 \rightarrow T_n$ absorption at 465 nm). Both the $S_2$ state decay and the $T_1$ state rise show the same kinetics [7]. As in the fluorescence upconversion experiment, the anisotropy of the transients originating from the $S_2$ state was determined. Now the anisotropy is given as, $r(t) = (\Delta OD_\parallel(t) - \Delta OD_\perp(t))/(\Delta OD_\parallel(t) + 2\Delta OD_\perp(t))$ [20], where the kinetic traces $\Delta OD_\parallel(t)$ and $\Delta OD_\perp(t)$ represent the net changes in the optical density, measured at the wavelength where the stimulated emission (negative) signal has its maximum value (465 nm), for parallel and perpendicular pump/probe polarizations, respectively (Figure 7.3 a). The anisotropy decay can be well described by a single exponential function (Figure 7.3 b) with an orientational time constant, $\tau_{\text{ors}}$, of 3.7 ps in $n$-hexane, consistent with the value of 3.2 ps measured by means of the fluorescence upconversion method. Although the $T_1 \rightarrow T_n$ absorption band is superimposed on the $S_2 \rightarrow S_0$ stimulated emission at 465 nm, the measured time constant of 3.7 ps must indeed be considered as essentially characterizing the orientational relaxation of BPT in the $S_2$ state and cannot be attributed to some additional population relaxation process. In fact, the characteristic time for the decay of the $S_2$ state and the rise of the $T_1$ state is much slower (20 ps), and furthermore, the $T_1 \rightarrow T_n$ absorption is 7 times less intense than the $S_2 \rightarrow S_0$ stimulated emission [7], so the contribution of the $T_1$ state absorption to the 465 nm signal during the anisotropy decay is negligible. The anisotropy was also determined at probe wavelengths other than 465 nm. Initial $r(t_0)$ values close to 0.4 and 0.05 were found in the 440 - 550 nm ($S_2 \rightarrow S_0$ transition) and 615 - 700 nm ($S_2 \rightarrow S_n$ transition) spectral ranges respectively (Figure 7.3 c). According to the expression $r(t) = 0.6cos^2\beta - 0.2$ [14], relating the anisotropy decay $r(t)$ in the $S_2$ state to the angle $\beta$ between the dipole moments of the $S_0 \rightarrow S_2$ absorption and the probed transition, $S_2 \rightarrow S_0$ or $S_2 \rightarrow S_n$, respectively, we estimate that the $S_2 \rightarrow S_n$ absorption dipole moment lies at about 50° from the direction of the $S_2 \rightarrow S_0$ transition dipole moment.
Figure 7.3: (a) Stimulated emission kinetics recorded at 465 nm for BPT in n-hexane (1 x 10^{-3} M) after photoexcitation at 403 nm, (b) corresponding anisotropy decay r(t), and (c) calculated spectral distribution of the initial anisotropy r_{ti}.
7.4 Discussion

We have shown above that the measured $S_2$-state anisotropy decay curves (Figures 7.1 and 7.3) could be well fitted to single-exponential functions, for all investigated thiketone-hydrocarbon solutions. BPT being a rigid molecule with a fixed transition dipole moment, intramolecular configurational dynamics is of no relevance and only reorientational motions of the thioketone solute molecules in the $S_2$ state can give rise to the observed anisotropy decay.

In order to achieve a more quantitative analysis of the reorientational dynamics, the molecular geometry of BPT in the ground state was optimized by ab initio treatment at the HF level using the 6-31G* basis set (HyperChem 7 software package). A molecular volume of about 140 Å$^3$ (van der Waals model) with radius dimensions of 4.5 Å, 4.0 Å, and 1.9 Å along the $x$, $y$, and $z$ axis, respectively, and moments of inertia of 318, 539, 857 amu Å$^2$ around the $x$, $y$ and $z$ rotation axis, respectively, were found (see inset in Figure 7.2). The results can be transferred to the $S_2$ state as no significant change in volume between the $S_0$ and $S_2$ states is expected.

Molecular reorientation can have frictional (rotational diffusion) and frictionless (inertial free rotation) contributions. In frictionless conditions the orientational time $\tau_{\text{free}}$ can be estimated by the following expression [21]:

$$\tau_{\text{free}} = \frac{2\pi}{9} \left( \frac{l}{kT} \right)^{1/2},$$

(7.1)

where $l$ is the moment of inertia, $k$ is the Boltzmann constant, and $T$ is the temperature in Kelvin. According to the above components of the moment of inertia around the $x$, $y$ and $z$ axis, Eq. (7.1) leads to orientational times $\tau_{\text{free}}$ of 0.8, 1.0 and 1.3 ps respectively. Though these values are within the same order of magnitude as the 3.2 ps rotational time determined experimentally in $\alpha$-hexane, we observe that the rotational time constant increases with solvent viscosity (Figure 7.2), which indicates that the molecular reorientation of BPT in the $S_2$ state becomes more diffusional than inertial as the viscosity is increased.

It is known that rotational diffusion depends on the solvent viscosity, on the size and shape of the diffusing species, as well as on the specific solute-solvent interactions [19]. The latter are expected to be relatively weak due to the non-polar character of the hydrocarbon solvents used and the absence of hydrogen bonds. It is worth comparing the experimental slope of the dependence of the rotational time constant $\tau_\eta$ on the solvent viscosity ($\eta$), $\tau_\eta/\eta = 2.6 \pm 1$ ps/cP (Figure 7.2), with the value derived from theoretical estimation, even if such a comparison can only be qualitative [19]. For a simple estimation of the rotational correlation time ($\tau_\omega$), a modified Debye-Stokes-Einstein model can be used [19, 22],

$$\tau_\omega = \frac{\eta}{\rho},$$

where $\rho$ is the density of the solvent. For $\eta = 2.6 \pm 1$ ps/cP and $\rho = 0.85$ g/cm$^3$, we obtain $\tau_\omega = 3.2$ ps, which is in good agreement with the experimental value.

It is important to note that the above calculations are based on the assumption of a rigid molecule and neglect any possible configurational changes. However, even in the ground state, BPT is expected to have a somewhat dynamic character, which can be probed by ultrafast spectroscopy. Theoretical calculations at the HF level are a good starting point, but further refinement using more advanced methods, such as coupled-cluster singles and doubles (CCSD), will be necessary to fully describe the molecular dynamics of BPT in the excited state.
\[ \tau_{or} = \frac{\eta VF}{kTS}, \]  

(7.2)

where \( k \) is the Boltzmann constant, \( T \) is the temperature in Kelvin, \( V \) is the hydrodynamic volume of the solute, \( S \) is a shape factor accounting for the nonspherical nature of the solute molecule and calculated from Perrin's equations [23], and \( F \) is a solvent-solute rotational friction coefficient. This coefficient is equal to 1 if the solvent exerts a tangential force on the rotating solute ("stick-boundary condition"), in which case a solvent layer adjacent to the solute rotates with it and retards its motion. The \( F \) coefficient is \(< 1\) if the solvent can exert no tangential force on the rotating solute ("slip-boundary condition"). In this case \( F \) depends strongly on the molecular shape of the solute. In fact, whereas the rotation of a nonspherical solute is still experiencing some mechanical resistance from the solvent molecules that must be pushed, there is no friction for a spheroid solute rotating about its symmetry axis \((F = 0)\).

According to the molecular dimensions calculated for BPT, the molecule looks rather like an oblate rotor (disk-shaped) than a prolate ellipsoid (rod-shaped). For a rotation around the \( z \) axis (perpendicular to the plane of the molecule), a slip friction coefficient \( F \) of 0.06 and a shape factor \( S \) of 0.66 (symmetric oblate ellipsoid approximation) are determined from the reported numerical calculation methods [23 - 27]. Including these values in Eq. (7.2) leads to theoretical values for the \( \tau_{or}/\eta \) term of 3.1 ps/cP and 52 ps/cP at \( T = 293 \) K under slip \((F = 0.06)\) and stick \((F = 1)\) boundary conditions, respectively. Despite the approximations made in this calculation, the predicted stick value is manifestly in complete disagreement with the experimental value \((2.6 \pm 1 \) ps/cP\) while the slip value is in reasonable agreement. We conclude that BPT in the \( S_2 \) state is rotating under slip conditions in all investigated hydrocarbons.

It can be expected from Eq. (7.2) that increasing the solute volume \( V \) must result in an increase in the orientational time \( \tau_{or} \). This prediction is confirmed experimentally by the longer \( \tau_{or} \) \((4.2 \pm 1.0 \) ps\) measured in \( n \)-hexane for the \( n \)-butyl derivative BPTC\textsubscript{4} \((V = 210 \) Å\textsuperscript{3}\)) compared to that found for BPT \((3.2 \pm 1.0 \) ps\). As can be seen from Table 7.1, it is interesting to note that these values are consistent with those reported for comparable aromatic molecules in hydrocarbon solvents of similar viscosity [19, 21, 22, 28 - 30]. According to the disk-like molecular shape of BPT, rotations around the \( x \) and \( y \) axis result necessarily in much larger solvent displacements and are thus obviously much slower than rotation around the \( z \) axis. Consequently, the above fast \( \tau_{or} \) values, characteristic of BPT and BPTC\textsubscript{4} in the \( S_2 \) state, show the dominant influence of rotations of the molecules around the \( z \) axis. This assignment is consistent with the fact that the \( S_0 \leftrightarrow S_2 \) transition dipole moments lie in the molecular plane of BPT, as previously observed also for xanthione [31].
Table 7.1: Orientational time constant values for different singlet excited aromatic solutes in hydrocarbons determined by femto-picosecond transient absorption (TA) or fluorescence upconversion (FUP) experiments

<table>
<thead>
<tr>
<th>Solute</th>
<th>Solute volume [Å³]</th>
<th>Solvent</th>
<th>Solvent viscosity [cP]</th>
<th>Rotational time ( \tau_{\text{rot}} ) [ps]</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPT</td>
<td>140</td>
<td>( n )-hexane</td>
<td>0.3</td>
<td>3.2± 1.0</td>
<td>FUP</td>
<td>22</td>
</tr>
<tr>
<td>BPTC₄</td>
<td>210</td>
<td>( n )-hexane</td>
<td>0.3</td>
<td>4.2± 1.0</td>
<td>FUP</td>
<td>28</td>
</tr>
<tr>
<td>Perylene</td>
<td>225</td>
<td>( n )-hexane</td>
<td>0.3</td>
<td>11± 2.0</td>
<td>TA</td>
<td>29</td>
</tr>
<tr>
<td>7-azaindole dimer</td>
<td>~225</td>
<td>( n )-hexane</td>
<td>0.3</td>
<td>12</td>
<td>FUP</td>
<td>22</td>
</tr>
<tr>
<td>Tetracene</td>
<td>224</td>
<td>( n )-heptane</td>
<td>0.34</td>
<td>13</td>
<td>FUP</td>
<td>29</td>
</tr>
<tr>
<td>Coumarin 153</td>
<td>246</td>
<td>( n )-hexane</td>
<td>0.3</td>
<td>13</td>
<td>FUP</td>
<td>19</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>150</td>
<td>( n )-hexane</td>
<td>0.3</td>
<td>6.5</td>
<td>TA</td>
<td>30</td>
</tr>
<tr>
<td>Aniline</td>
<td>100</td>
<td>isopentane</td>
<td>0.22</td>
<td>0.94± 0.05</td>
<td>FUP</td>
<td>21</td>
</tr>
</tbody>
</table>

The initial anisotropy \( r(t_0) = 0.4 \) measured in \( n \)-hexane for the stimulated emission signal, following 403 nm excitation, corresponds to the theoretical value derived from the usual expression for the correlation of transition moment directions, in the case of parallel pumped and probed transition moments [25]. This occurs at time zero, i.e., before any reorientation of the excited solute could have occurred. Remarkably, the \( r(t_0) \) value measured from the time-resolved fluorescence upconversion signal, following 380 nm excitation, is slightly lower \( (r(t_0) = 0.29 - 0.34) \). The discrepancy is likely due to the difference in the excitation wavelengths used in the two measurements, 380 nm excitation in the upconversion experiment and 403 nm in the pump-probe experiment. Upon 380 nm excitation, the BPT molecule is produced in the \( S^2 \) state with an excess vibrational energy of about 1500 cm⁻¹, whereas no excess vibrational energy is deposited upon excitation at 403 nm. We infer that, as noticed by several authors for other aromatic solutes [30, 32, 33], a slightly out of the \( xy \) plane vibrationally induced component in the transition dipole moment affects the initial anisotropy value \( r(t_0) \).

7.5 Conclusions

In conclusion, in order to determine the influence of the bulk solvent viscosity on the orientational anisotropy dynamics of BPT in the \( S^2 \) state, time-resolved fluorescence
upconversion and transient absorption measurements with femtosecond time resolution were performed in different linear hydrocarbon solvents (n-hexane, n-heptane, n-octane, n-decane and n-dodecane) and in cyclohexane. BPT is a rigid molecule with fixed transition dipoles ($S_0 \leftrightarrow S_2$) lying in the plane of the molecule. In all solvents, the anisotropy decay was found to be monoexponential. The initial value $r(t_0)$ obtained for the anisotropy is in the 0.29 to 0.40 range, depending on the amount of excess vibrational energy deposited in the $S_2$ state. The dependence of the rotational time constant ($\tau_{ro}$) on the solvent viscosity can be approximated by a linear function with a slope of $2.6 \pm 1$ ps/cP. The rotation dynamics can be explained in terms of the Stokes-Einstein-Debye hydrodynamics theory applied for slip conditions.

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7.6 References

Femtosecond Studies of Anisotropy Decay of BPT in the Excited S₂ State in Hydrocarbons