Ultrafast fluorescence studies of excited-state hydrogen transfer reactions in solution
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Chapter 8

Femtosecond Fluorescence Upconversion Study of a Boron Dipyrrromethene Dye in Solution

Abstract

A femtosecond fluorescence upconversion study is reported for the borondipyrrromethene (BDP) dye 2,6-diethyl-1,3,5,7-tetramethyl-8-phenyl-4-difluorobora-3a,4a-diaza-(s)-indacene (BDP-1) dissolved in cyclohexane, chloroform and acetonitrile. After pulsed photoexcitation into the higher excited $S_2$ or $S_1$ excited states (at energies of ~ 26,300 cm$^{-1}$ and ~ 30,000 cm$^{-1}$ above the $S_0$ state, respectively), the fluorescence upconversion transients show an ultrafast solvent-dependent rise (between ~ 100 fs and 230 fs) that is discussed to be representative of internal conversion and vibrational relaxation dynamics. From the detection wavelength dependence of the fluorescence transients the temporal dependence of the emission spectrum could be reconstructed. The reconstructed emission spectrum shows picosecond intensity changes typical of vibrational cooling effects in the excited $S_1$ state.
8.1 Introduction

Boron-dipyrromethene (BDP) dyes (scheme 8.1) have attracted much interest [1-5]. The compounds have been applied as fluorescent labels in studies of DNA sequencing [6, 7] and as tags in mutant forms of proteins [1, 8, 9]. In addition, they possess potential for optical and optoelectric applications such as electrogenerated luminescence or electroluminescent devices [2, 10], chiroptical and molecular switching [11, 12], fluorescent chemosensors [2, 13, 15] or when incorporated in polymer-dispersed liquid crystal thin films [16]. For the fluorophore, 2,6-diethyl-1,3,5,7-tetramethyl-8-phenyl-4-difluorobora-3a,4a-diaza-(s)-indacene (BDP-1) the absorption spectrum shows in acetonitrile a strong transition ($\varepsilon \sim 70,000 \text{ M}^{-1}\text{cm}^{-1}$) at about 520 nm, which has been attributed to the $S_0 \rightarrow S_1$ transition and a much weaker transition at about 375 nm that has been attributed to the $S_0 \rightarrow S_2$ transition. Using semi-empirical AM1 and ab-initio configuration interaction (CI) calculations, we have recently assigned these optical absorption bands in the visible and near UV as $\pi \rightarrow \pi^*$ excitations [17].

In this paper, we report a study of the excited-state dynamics of the BDP dye, 2,6-diethyl-1,3,5,7-tetramethyl-8-phenyl-4-difluorobora-3a,4a-diaza-(s)-indacene (BDP-1), in liquid solution, utilizing the femtosecond fluorescence upconversion technique. To our knowledge, for BDP dyes ultrafast spectroscopic experiments have not yet been performed. The fluorescence upconversion data for BDP-1 show that the dynamics for relaxation from higher electronic states, $S_n$ ($n \geq 2$), to the fluorescent $S_1$ state can be resolved. The relaxation time is found to be $\sim 100$ fs for 1 dissolved in acetonitrile, $\sim 150$ fs for the solute in chloroform and $\sim 250$ fs when the solvent is cyclohexane. It is proposed that internal conversion and inertial free streaming motions of the solvent molecules are significant for the relaxation processes. In addition, it is found that BDP-1 fluorescence upconversion transients contain decay components with a typical time of tens of
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picoseconds. It is discussed that these picosecond decay components are characteristic of cooling of vibrationally ‘hot’ BDP molecules in the solution.

8.2 Experimental

2,6-Diethyl-1,3,5,7-tetramethyl-8-phenyl-4-difluorobora-3a,4a-diaza-(s)-indacene (BDP-1) was synthesized from 3-ethyl-2,4-dimethyl-1H-pyrrole and benzaldehyde, according to the following procedure. All reactions were carried out under nitrogen atmosphere. A mixture of 3-ethyl-2,4-dimethyl-1H-pyrrole (616 mg, 5 mmol), benzaldehyde (265 mg, 2.5 mmol) and three drops of trifluoro acetic acid (TFA) in CH₂Cl₂ (200 mL) were stirred for 1.5 h at room temperature. Thereafter 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (568 mg in 50 mL CH₂Cl₂, 2.5 mmol) was added. Then stirring for 15 min. continued and the solution was subjected to reaction with ethyl diisopropyl amine and BF₃·OEt₂ (each 4 mL). After another 30 min. the solution was washed with water, dried over Na₂SO₄ and concentrated by evaporating the solvent. The crude product was purified by chromatography on silica using CH₂Cl₂ as eluent. Recrystallization from CHCl₃/hexane gave BDP-1 as red, green shining solid. (416 mg, 44% yield), mp: 181-185°C; MS (EI, 70eV) m/z (%): 380 (100) [M⁺]; ¹H-NMR (CDCl₃, 400 MHz): δ 7.46-7.50 (m, 3H), 7.26-7.30 (m, 2H), 2.53 (s, 6H), 2.30 (q, 4H, J = 7.5 Hz), 1.27 (s, 6H), 0.98 (t, 6H, J = 7.5 Hz); ¹B-NMR (CDCl₃, 128 MHz): δ 0.6 (t, J = 34 Hz); CHN (in %) calcld.: C: 72.64, H: 7.16, N: 7.37, observed: C: 72.00, H: 7.17, N: 7.32.

The solvents, anhydrous cyclohexane (Merck), chloroform (Merck) and acetonitrile (Merck), were of spectrograde quality. In the spectroscopic experiments solutions of the BDP-1 dye in a concentration of about 10⁻³ mol/L were used.

Steady-state absorption spectra were measured by means of a Shimadzu UV-240 spectrophotometer. The steady-state fluorescence spectra were measured using the emission spectrometer described previously [18]. The emission spectra were corrected for the wavelength-dependent sensitivity of the monochromator-photomultiplier detection system.

Femtosecond fluorescence upconversion transients were measured by means of the set-up described previously [19]. A wavelength-tunable laser (TOPAS Light Conversion Ltd.) provided excitation pulses (1kHz repetition rate) that could be varied between 320 nm and 380 nm. The laser pulse width was measured from the cross-correlation signal of the excitation and gating pulses at 360 nm and 800 nm; the width (FWHM) is about 150 fs. Laser power was about 5μJ/pulse and fluorescence was kept low enough to ensure that the fluorescence intensity was linear dependent on the laser intensity. The upconversion signal was generated by means of wave mixing of the gating beam with the laser-induced fluorescence in a 1 mm BBO crystal (type I
phase matching conditions). The upconverted fluorescence light was led through an UG 11 band pass filter and focused onto the entrance slit of a Zeiss M4 prism monochromator outfitted with an EMI 9863 QB/350 photomultiplier. Detection of the output signal from the photomultiplier was by means of lock-in detection. The upconversion signals were accumulated for 1 s for each time-delay step of the translational stage, and were recorded and stored on a personal computer. To remove contributions from rotational reorientation motions of the solute molecules, measurements were performed under magic angle conditions (with the laser-excitation polarization at an angle of 54.7° relative to the vertically polarized gating beam). In addition, the fluorescence polarization was monitored parallel and perpendicular relative to the polarization axis of the gating beam; from this the fluorescence depolarization with time was determined.

For the measurement of fluorescence transients in a time span from 15 ps to 5 ns, a second laser system, outfitted with a time-correlated single-photon-counting (TCSPC) detection system, was used [18]. In these experiments the instrument response was about 16 ps (FWHM). Here too the fluorescence transients were measured under magic angle conditions. All experiments were performed at room temperature.

8.3 Results and discussion

![Steady-state absorption and emission spectra of BDP-1 in the solvents cyclohexane (a), chloroform (b) and acetonitrile (c). Emission spectra were measured with the excitation wavelength at 323 nm. The intensities are normalized to the same value for the band maxima. Inset shows UV part of the absorption spectrum on enlarged scale.](image)
Figure 8.1 shows the cw absorption and steady-state emission spectra of BDP-1 dissolved in cyclohexane, chloroform and acetonitrile. The positions of the main absorption and emission bands are summarized in Table 8.1. The absorption and emission spectra display perfect mirror symmetry, showing that the main bands correspond to the $S_0 \leftrightarrow S_1$ transition. The Stokes shift, obtained from the difference of the positions of the main absorption and emission bands, is approximately 850 cm$^{-1}$ for BDP-1 dissolved in cyclohexane and about 550 cm$^{-1}$ for the solute in acetonitrile. The larger Stokes shift (to the red) for 1 in the apolar solvent cyclohexane as compared to the shift for the solute in the polar solvents acetonitrile and chloroform does not comply with the Lippert-Mataga relation [20, 21]; possibly in cyclohexane dispersive interactions contribute to the Stokes shift [22].

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Absorption</th>
<th>Emission</th>
<th>Stokes shift</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(cm$^{-1}$)</td>
<td>(nm)</td>
<td>(cm$^{-1}$)</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>~ 19,050</td>
<td>525</td>
<td>~ 18,200</td>
</tr>
<tr>
<td>chloroform</td>
<td>~ 19,050</td>
<td>525</td>
<td>~ 18,500</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>~ 19,250</td>
<td>520</td>
<td>~ 18,700</td>
</tr>
</tbody>
</table>

Fluorescence upconversion transients were measured for a series of detection wavelengths ranging from 520 nm to 620 nm. To circumvent that the emission signal and the excitation pulse exhibit spectral overlap, the wavelength of the excitation pulse was kept below 380 nm. Figure 8.2 displays a few fluorescence upconversion transients for 1, dissolved in cyclohexane, chloroform and acetonitrile, observed for short and long time windows (Figure 8.2 a and b, respectively). The transients were measured using magic angle conditions, with excitation at 350 nm and detection at the wavelengths indicated. The kinetics of the transients was not affected when changing the excitation wavelength between 320 nm and 380 nm.
Figure 8.2: Femtosecond fluorescence upconversion transients of BDP-1. Solvents and detection wavelengths are indicated. Excitation is at 350 nm. The time windows are 3 ps (a) and 60 ps (b). Figure (a) includes the system response function. The drawn curves represent the multiexponential best-fit functions. The inserts show the residuals with (drawn curves) and without (dotted curves) rise terms in the fit functions.

Using the fitting procedure described elsewhere [19], best-fit curves for the measured transients were obtained. The drawn curves in the figure depict the fittings to multiexponential...
functions convoluted with the instrument response function. The latter is included in Figure 8.2 *a*. The insets in Figure 8.2 *a* show the residual intensities when in the fittings a rise component is taken into account (straight line) and when the rise is excluded (dashed curve). We infer that subpicosecond rise components can clearly be resolved. For BDP-1 in cyclohexane, the fluorescence transients show an initial rise for which a time constant of ~ 230 fs is found. This rise is significantly slower than the rise time of ~ 150 fs observed for BDP-1 dissolved in chloroform and ~ 100 fs rise in acetonitrile.

By means of the well-known spectral reconstruction procedure [19, 23], the temporal behavior of the fluorescence spectrum of BDP-1 could be examined. Figure 8.3 displays the time dependence of the reconstructed emission spectrum for BDP-1 in cyclohexane, chloroform and acetonitrile. The points in the figure reflect the results as calculated from the experimental data, the curves show the best-fits connecting the points. As illustrated in Figure 8.3, within ~ 500 fs after excitation the emission spectra are already almost identical to the steady-state fluorescence spectrum; within our time resolution dynamic Stokes shifts are not observed.

In considering the ultrafast formation of the fluorescence spectra, we first note that the energy of the exciting photons (~ 26,300 cm\(^{-1}\)) is well in excess of the energy corresponding to the origin of the emissive electronic transition near 18,500 cm\(^{-1}\). Ultrafast dissipation of the excess excitation energy (4000 cm\(^{-1}\) or more within 100 fs – 250 fs) involves distinct degrees of freedom. Firstly, electronic relaxation of the initially excited \(S_2\) state (at ~ 26,300 cm\(^{-1}\)) to the \(S_1\) state implies \(S_2 \rightarrow S_1\) internal conversion (IC). Generally, IC is an ultrafast process with an upper limit of ~ 100 fs [24, 25]. Likewise we consider the \(S_2 \rightarrow S_1\) internal conversion for BDP-1 in solution to be ultrafast and this may well give rise to the observed rise times in the range between 150 fs and 250 fs. On the other hand, ultrafast solvation dynamics is also well known to occur on a time scale extending from 50 fs up to several hundred of femtoseconds, in particular for organic molecules in excited charge transfer states in polar solvents. E.g., solvation dynamics in chloroform with a typical time of ~ 150 fs (in acetonitrile ~ 65 fs) was recently reported [26]. The subps rise times of BDP-1 in chloroform and in acetonitrile could thus well also result from solvation of the solute. However, the temporal dependence of the reconstructed emission spectra as apparent from Figure 8.3, does not reveal the dynamic Stokes shift normally observed in the case of solvation dynamics. We infer that the observed subps dynamics in the BDP-1 fluorescence is predominantly due to IC. The slower IC kinetics in cyclohexane compared to that in the more polar solvents acetonitrile and chloroform is indicative of the influence of the solvent polarity on the energy gap between the \(S_2\) and \(S_1\) levels; a smaller gap in the more polar solvents enhances the IC process [27].
In addition to IC, vibrational relaxation of the Franck-Condon vibrational wave packet due to intramolecular vibrational energy redistribution (within tens of femtoseconds [28, 29]) and vibrational cooling (up to tens of picoseconds [29-31]) naturally also contribute to the subps rise behavior since excitation is at an energy of 26,300 cm$^{-1}$ or higher and the steady-state emission (at an energy of 18,500 cm$^{-1}$ or lower) is produced on the subpicosecond time scale.

As can be seen from Figure 8.2 b, for BDP-1 dissolved in cyclohexane and acetonitrile, following the subpicosecond rise, the intensity of the fluorescence transients in the picosecond
regime is detection wavelength dependent. In both solvents, a fluorescence rise is observed when
detection is at the blue side of the emission band and a decay for detection more to the red. The
rise and decay parts of the BDP-1 fluorescence could be fitted to multiexponential functions. The
characteristic times and relative amplitudes of the components at various detection wavelengths
are summarized in Table 8.2.

Table 8.2: Best-fit parameters for fluorescence transients of BDP-1 in upconversion and time-correlated
single-photon counting experiments after fitting to convoluted function \( I \propto \sum A_i \exp(-t/\tau_i) \)

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Wavelength (nm)</th>
<th>Timeconstants</th>
<th>( \tau_1 ) (ps)</th>
<th>( \tau_2 ) (ps)</th>
<th>( \tau_3 ) (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexane</td>
<td>520</td>
<td>0.16 (-0.88)</td>
<td>13.5 (-0.12)</td>
<td>4000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>540</td>
<td>0.25 (-0.95)</td>
<td>18.3 (-0.05)</td>
<td>4000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>560</td>
<td>0.25 (-1)</td>
<td>26.5 (0.23)</td>
<td>4000 (0.77)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>0.26 (-1)</td>
<td>11.1 (0.37)</td>
<td>4000 (0.63)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>640</td>
<td>0.23 (-1)</td>
<td>8.0 (0.45)</td>
<td>4000 (0.55)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>520</td>
<td>0.15 (-1)</td>
<td>26.8 (0.20)</td>
<td>5300 (0.80)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>540</td>
<td>0.21 (-1)</td>
<td>18.3 (0.15)</td>
<td>5300 (0.85)</td>
<td></td>
</tr>
<tr>
<td>chloroform</td>
<td>560</td>
<td>0.12 (-1)</td>
<td>26.7 (0.18)</td>
<td>5300 (0.82)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>580</td>
<td>0.15 (-1)</td>
<td>15.6 (0.20)</td>
<td>5300 (0.80)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>0.18 (-1)</td>
<td>34.4 (0.17)</td>
<td>5300 (0.83)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>510</td>
<td>0.11 (-0.66)</td>
<td>11.0 (-0.34)</td>
<td>5400</td>
<td></td>
</tr>
<tr>
<td></td>
<td>530</td>
<td>0.10 (-0.90)</td>
<td>10.0 (-0.10)</td>
<td>5400</td>
<td></td>
</tr>
<tr>
<td>acetonitrile</td>
<td>545</td>
<td>0.14 (-1)</td>
<td>17.2 (0.19)</td>
<td>5400 (0.81)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>580</td>
<td>0.15 (-1)</td>
<td>13.2 (0.25)</td>
<td>5400 (0.75)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>640</td>
<td>0.11 (-1)</td>
<td>10.4 (0.39)</td>
<td>5400 (0.61)</td>
<td></td>
</tr>
</tbody>
</table>

Relative weights \( A_i \) are given in brackets.

The multiexponential and wavelength-dependent decay behavior of the fluorescence of BDP-1 is
characteristic of an inhomogeneous distribution of excited-state lifetimes. In principle, a possible
cause for this spread in lifetimes (on the order of ps) could be solvation [32]. However, solvation
would give rise to a decay when detection is near the blue side of the emission band and a rise
when detection is more to the red. The opposite behavior is observed. Moreover, solvation is not
expected to be important when an apolar solvent such as cyclohexane is used. Alternatively, a
spread in excited-state lifetimes might arise when the emission in part is due to vibrationally 'hot' molecules. Indeed, vibrational cooling, i.e., vibrational energy dissipation to the bath, generally occurs on a time scale of several to tens of picoseconds [29-31, 33]. Thus, when cyclohexane is the solvent, the picosecond decay observed at 620 nm (top panel, Figure 8.2 b) is attributed to the cooling of vibrationally excited levels in the \( S_1 \) state, whereas the picosecond rise at 520 nm is due to feeding from higher (less emissive) vibrationally excited levels in the \( S_1 \) state. Feeding of the \( S_1 \) state is also manifested in the initial intensity increase of the emission near the emission band maximum for BDP-1 in cyclohexane (Figure 8.3) until about 5 ps after the pulsed excitation.

As illustrated in Figure 8.2 b, middle panel, for BDP-1 dissolved in chloroform, picosecond fluorescence dynamics are virtually absent. It seems that for this solution the vibrational effects are compensated by opposite intensity changes with similar dynamics. It is likely that now solvation comes into play, since solvation will lead to a decay in the blue part of the emission and a rise in the red part and it is expected to be on the picosecond time scale [32]. This is further supported by the results for BDP-1 dissolved in acetonitrile (cf Figure 8.2 b, lower panel). For the latter solution, a typical solvation time of \(~100\) fs is expected [26, 34] (in chloroform the solvation time is \(~2\) ps [34]). Thus, the solvation is so fast that it will not show up in the transients on a picosecond time scale, and the transients will be similar as for the cyclohexane solution, i.e., a decay for detection at 620 nm and a rise when detection is at 510 nm. In conclusion, vibrationally 'hot' molecules are formed after subpicosecond internal conversion and vibrational relaxation. In the apolar solvent, cyclohexane, vibrational cooling takes place with a characteristic time of 20 ps. In the more polar solvent chloroform, solvation and vibrational cooling effects on the fluorescence are balanced, whereas in acetonitrile solvation is so fast that it does not manifest itself in the transients in the picosecond range. After approximately 60 ps, the fluorescence decays slowly, with a time of 5.3 ns, i.e., the lifetime of the relaxed excited \( S_1 \) state.

For excitation energies above \(~30,000\) cm\(^{-1}\) (< 330 nm), the \( S_3 \) state and higher lying electronic states become excited. This is concluded from time-resolved fluorescence depolarization experiments. In the latter, the fluorescence transients polarized parallel and perpendicular relative to the polarization of the exciting laser pulses, were measured. The polarized transients were fitted to multiexponential functions, \( I_\parallel (t) \) and \( I_\perp (t) \), respectively, convoluted with the instrument response function. The time dependence of the fluorescence anisotropy, \( r(t) \), was obtained from \( r(t) = [I_\parallel (t) - I_\perp (t)]/[I_\parallel (t) + 2 I_\perp (t)] \) [35]. Fluorescence depolarization measurements were carried out as a function of the detection wavelength and as a function of the excitation wavelength. Interestingly, whereas the depolarization dynamics (vide
infra) did not vary with the detection wavelength, a significant change in the initial polarization, \( r(0) \), was observed when varying the excitation wavelength in the range 323 nm – 370 nm. In Figure 8.4 we present, for a few excitation wavelengths, polarized transients as observed for BDP-I in cyclohexane and chloroform.

![Figure 8.4: Polarized fluorescence upconversion transients for BDP-I in cyclohexane (left) and chloroform (right). Best-fit exponential curves are given by drawn lines. Inserts show time dependence of fluorescence anisotropy as calculated from best-fit curves.](image)

The drawn curves show the convoluted curves of \( I_\parallel(t) \) and \( I_\perp(t) \). In Table 8.3 we have collected the characteristic times and the relative weights of the components of the functions \( I_\parallel(t) \) and \( I_\perp(t) \). The inserts in Figure 8.4 display the time dependences of the fluorescence anisotropy, as extracted from the fit functions, \( I_\parallel(t) \) and \( I_\perp(t) \), at the various excitation wavelengths. The decay
of the fluorescence anisotropy, at every excitation wavelength, was fitted to a single exponential function; the corresponding time constants are included in Table 8.3. The results were the same when the solute is dissolved in acetonitrile.

As seen from Table 8.3, the initial fluorescence anisotropy, \(r(0)\), varies from \(\sim 0.25\) to about \(-0.05\) as the excitation wavelength is changed from 380 nm to 320 nm. It is well-known that the fluorescence anisotropy attains the maximum value of 0.4 when the directions of the electronic transition dipole moments corresponding to optical absorption and emission coincide, provided of course that during the feeding time of the emissive level, directional relaxation of either of these moments does not take place [35]. The somewhat smaller value than 0.4 for \(r(0)\), of about 0.25, when excitation of BDP-1 is near 380 nm, shows that either the electronic transition dipole moments for absorption and emission are at a small angle of about 30° or that during the rapid (~100 fs up to ~230 fs) feeding of the fluorescent state some incomplete decay in the cross-correlation function for the directions of the two electronic transition dipole moments has occurred. Regardless which of these possibilities prevails, the observed decrease in the value of \(r(0)\) when excitation is at shorter wavelengths implies that the electronic wave function part(s) in the initially excited Franck-Condon wavepacket or in the vibronic decay channel must have changed. The change of the initial anisotropy from \(\sim +0.25\) to \(\sim -0.05\) when the excitation is changed from 380 nm to 320 nm, shows that the direction of the absorptive transition dipole moment has been altered from almost parallel to almost perpendicular to that of the emissive dipole. It follows that absorption near 320 nm is to an electronic state that must be different from that involved in the 380 nm absorption. As already mentioned above, excitation of BDP-1 at 380 nm corresponds to the \(S_2 \leftarrow S_0\) transition. From our anisotropy experiments we propose that the weak absorption band near 320 nm (Figure 8.1) is due to the \(S_3 \leftarrow S_0\) transition. Results of CI calculations are in agreement with this assignment [17]. In these calculations it is found that the directions for the moments of the \(S_0 \rightarrow S_1\) or \(S_0 \rightarrow S_3\) transitions are more or less parallel, whereas these moments are predicted to be practically perpendicular to that for the \(S_0 \rightarrow S_3\) transition. When excitation is near 320 nm (\(S_3 \leftarrow S_0\) transition), the relative weight of the \(\sim 20\) ps decay component in the fluorescence transients is found to be higher than for 380 nm excitation and thus the yield of hot molecules has been enhanced. As seen from Table 8.3, for the characteristic decay time of \(r(t)\) we find \(\sim 25\) ps for BDP-1 in chloroform and \(\sim 40\) ps in cyclohexane. Thus the depolarization time in chloroform is very close to the typical vibrational cooling time of \(\sim 20\) ps as deduced from the initial decay of the BDP-1 emission band (Figure 8.3).
Table 8.3: Characteristic times of the multi-exponential fit functions of the fluorescence transients of BDP-1 in cyclohexane. The pre-exponential factors are given in parentheses

<table>
<thead>
<tr>
<th>Excitation (nm)</th>
<th>Detection (nm)</th>
<th>Polarization</th>
<th>Time constants (ps)</th>
<th>Anisotropy: r(t) = (0.25\exp(-t/85))</th>
</tr>
</thead>
<tbody>
<tr>
<td>380</td>
<td>540</td>
<td>(\parallel)</td>
<td>0.2 (-0.80)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\perp)</td>
<td>0.2 (-0.65)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\parallel)</td>
<td>26 (0.25)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\perp)</td>
<td>100 (-0.35)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\parallel)</td>
<td>4000 (0.75)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\perp)</td>
<td>4000 (1)</td>
<td></td>
</tr>
</tbody>
</table>

Anisotropy: r(t) = \(0.08\exp(-t/82)\)

<table>
<thead>
<tr>
<th>Excitation (nm)</th>
<th>Detection (nm)</th>
<th>Polarization</th>
<th>Time constants (ps)</th>
<th>Anisotropy: r(t) = (-0.05\exp(-t/44))</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>540</td>
<td>(\parallel)</td>
<td>0.2 (-0.80)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\perp)</td>
<td>0.2 (-1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\parallel)</td>
<td>45 (-0.20)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\perp)</td>
<td>4000 (1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\parallel)</td>
<td>4000 (1)</td>
<td></td>
</tr>
</tbody>
</table>

The pre-exponential factors are given in parentheses.

The ~ 40 ps depolarization component for BDP-1 in cyclohexane is still orders of magnitude shorter than the intrinsic lifetime of the relaxed excited \(S_1\) state. Hence, when excitation is at higher energies, the rate of the fluorescence anisotropy decay follows that of vibrational cooling in the excited \(S_1\) state. On the other hand, the fluorescence anisotropy decay is determined by the temporal dependence of the electronic part of the transition dipole moment responsible for the emission intensity. Therefore, cooling of the hot molecules in the \(S_1\) state is not just a “pure” vibrational relaxation process but also implies some electronic relaxation. This is evidence that the “hot” states should be considered as vibronic rather than as vibrational. Finally, when excitation is near 340 nm or at longer wavelengths, the decay of the fluorescence anisotropy is exponential with a typical time of about 60 ps (Table 8.3). Now the yield of hot molecules is less...
and the vanishing of the fluorescence polarization is due to the rotational diffusion motions of the photoselectively excited BDP-1 molecules.

In conclusion, by means of femtosecond fluorescence upconversion experiments it has been demonstrated that the deactivation of the $S_n$ ($n \geq 2$) higher excited states and the simultaneous population of the $S_1$ state of BDP-1 in solution occur on a time scale of a few hundred femtoseconds. Measurement of the initial fluorescence anisotropy as a function of the wavelength of the exciting laser pulses revealed that the energy of the $S_1$ state is about 31,250 cm$^{-1}$ above the $S_0$ state. Vibrational cooling of ‘hot’ BDP-1 molecules in the $S_1$ state occurs with a characteristic time of about 20 ps.

8.4 References

Femtosecond Fluorescence Upconversion Study of a Boron Dipyrrromethene Dye in Solution