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Ultrafast Solvation Dynamics and Vibrational Coherences of Halogenated BODIPY Derivatives Revealed Through Two-Dimensional Electronic Spectroscopy

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Abstract

Boron-dipyrromethene (BODIPY) chromophores have a wide range of applications; spanning areas from biological imaging to solar energy conversion. Understanding the ultrafast dynamics of electronically excited BODIPY chromophores could lead to further advances in these areas. In this work, we characterize and compare the ultrafast dynamics of halogenated BODIPY chromophores through applying two-dimensional electronic spectroscopy (2DES). Through our studies, we demonstrate a new data analysis procedure for extracting the dynamic Stokes shift from 2DES spectra revealing an ultrafast solvent relaxation. In addition, we extract the frequency of the vibrational modes that are strongly coupled to the electronic excitation, and compare the results of structurally different BODIPY chromophores. We interpret our results with the aid of DFT calculations, finding that structural modifications lead to changes in the frequency, identity, and magnitude of Franck-Condon active vibrational modes. We attribute these changes to differences in the electron density of the electronic states of the structurally different BODIPY chromophores.

Graphical Abstract

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

The details of the synthetic procedure, experimental setup, pulse characterization, DFT calculations, extraction of frequencies from 2DES spectra, and procedure for assigning normal modes are given in the supporting information. (PDF)

The authors declare no competing financial interests.

Keywords

BODIPY; 2DES; Raman active modes; dynamic Stokes shift; wavepackets; Franck-Condon active modes

1. Introduction

Boron-dipyrromethene (BODIPY) based chromophores are well-known for their biological applications in intracellular imaging and photodynamic therapy, as well as applications for solar energy conversion and molecular electronics.^{1–8} This diversity in applications stems from the structural modifiability of the BODIPY core, leading to tunability in the relative energies of the electronic states and the corresponding photophysics and photochemistry.^{1, 5, 7, 9} Understanding how structural changes to the BODIPY core manifest as changes in photophysical properties has motivated much research.⁵ Recently, pump-probe based spectroscopies have been applied to isolated BODIPY chromophores to characterize their photophysical properties and explore their applications for solar energy conversion.^{10–23} However, many of the previous studies performed on single isolated BODIPY chromophores focused on energy transfer among different electronic states occurring on timescales ranging from 100's of femtoseconds to nanoseconds and milliseconds. A better understanding of the ultrafast dynamics of BODIPY chromophores could lead to further insight into the design and modification of BODIPY based probes and materials for solar energy conversion.¹ In this work, we expand on previous studies resolving the ultrafast dynamics within the S_0 and S_1 electronic states of BODIPY chromophores through applying ultrafast two-dimensional electronic spectroscopy (2DES) to structurally different BODIPY chromophores shown in Fig.1.

2DES has proven to be a powerful technique for resolving ultrafast photoinitiated dynamics.^{24–30} Applying this technique to the BODIPY chromophores in Fig. 1 we (1) extract the ultrafast timescales of relaxation of the S_1 excited electronic state and (2) resolve low frequency vibrational modes strongly coupled to electronic excitation (the Franck-Condon active modes).

In a 2DES experiment femtosecond visible pulses excite a molecule creating wavepackets composed of Franck-Condon active vibrational modes in the ground and excited electronic

states.^{31–33} After the vertical transition, the system evolves. The molecule begins to relax – adjusting to the altered charge distribution, and wavepackets are launched.

As time evolves the electronic excited state relaxes through intra-and intermolecular vibrational energy redistribution and/or solvent reorganization reaching a new equilibrium position in the excited electronic state.^{34–36} The extent of this relaxation is characterized by the Stokes shift, the difference in energy between the absorption and emission. Time-resolving this relaxation of the S_1 excited state is described by the dynamic Stokes shift, where the Stokes shift function, $S(t)$, is given by the following expression (Eq. 1), where n represents the time-dependent frequency changes associated with the energy gap between the excited and ground electronic states.^{35–36}

$$S(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \quad (1)$$

There has been much previous work focusing on measuring the dynamic Stokes shift as it can be used to understand how chromophores interact with the local solvent environment (system-bath interactions) and reactivity.^{35, 37–40} The Stokes shift function is sensitive to system-bath interactions as it is related to the frequency-frequency correlation function (FFCF), $C(t)$ (Eq. 2), through $M(t)$ (Eq. 3), which is the FFCF (Eq. 2) normalized by the variance.^{35–36, 40} According to linear response the Stokes shift function is equivalent to $M(t)$ (Eq. 3).^{35–36, 40}

$$C(t) = \langle \delta\omega_{eg}(t)\delta\omega_{eg}(0) \rangle \quad (2)$$

$$M(t) = \frac{\langle \delta\omega_{eg}(t)\delta\omega_{eg}(0) \rangle}{\langle (\delta\omega_{eg})^2 \rangle} \quad (3)$$

Previous studies have shown that time-resolved fluorescence measurements and third-order spectroscopies including photon-echo based experiments and pump-probe spectroscopy can be used to monitor the dynamic Stokes shift.^{25, 35–37, 40–48, 49, 50–57} Though these experiments probe different spectroscopic observables – they are related in their ability to monitor the FFCF through $M(t)$ or $C(t)$.^{35, 37, 40} Two-dimensional spectroscopy has also been shown to be a powerful technique for extracting FFCFs and various methods have been devised to extract $C(t)$ from 2D electronic and vibrational spectra.^{25, 45, 47, 58–59, 60, 61, 62, 63–65}

In this work, we demonstrate a procedure to extract the dynamic Stokes shift (and $M(t)$) from 2D electronic spectra focusing on monitoring the frequency changes associated with the stimulated emission. This procedure is complementary to previous techniques but may provide an additional means to extract this information from congested 2DES spectra with multiple overlapping transitions. The procedure is general and can be applied to 2DES

spectra where the incoming pulses overlap with some portion of the absorption and emission spectra. The results are interpreted through the correlation function, $M(t)$, to gain insight into the ultrafast relaxation of the S_1 excited state of BODIPY chromophores.

As the electronic state relaxes through the dynamic Stokes shift the vibrational modes orthogonal to the relaxation coordinate are also evolving under the system's Hamiltonian. In addition to extracting the dynamic Stokes shift, we resolve these low-frequency Franck-Condon active vibrational modes and compare the results of the two BODIPY chromophores. The vibrational modes are assigned through quantum chemical calculations. Through comparative studies, a deeper understanding of how derivatization of BODIPY chromophores effects vibrational motion strongly coupled to the electronic excitation is gained.

2. Experimental Section

Sample Preparation

BODIPY-2I and BODIPY-2H (Fig.1) were synthesized according to the previous protocol set out by Lim and coworkers⁶⁶, and characterized with UV/VIS and fluorescence measurements. Further details on the synthesis and characterization are given in the supporting information. 2DES spectra were performed on BODIPY-2I and BODIPY-2H samples dissolved in methanol having an OD of ~ 0.3 in a quartz cuvette having a pathlength of 1 mm (STARNA, 21-Q-1).

2DES

2DES is a third-order nonlinear spectroscopy where three field matter interactions (E_1 , E_2 , and E_3) generate a polarization that leads to the emission of the signal (E_s).^{65, 67–68} The pulse sequence used for 2DES is given in the supporting information (Fig. S5(a)) The first field (E_1) interacts with the sample creating a coherence and initiating the t_1 time. Interaction of the second field (E_2) leads to the creation of a population or coherence, marking the end of the t_1 time and beginning of the t_2 time, the waiting time. The system is free to evolve during the waiting time. Interaction of the third field (E_3) creates another coherence marking the beginning of the t_3 time and leading to the emission of the signal (E_s). The signal is emitted in the same direction as the probe pulse and detected through spectral interferometry. Fourier-transformation along the t_1 and t_3 time axis yields the ω_1 and ω_3 axis. The resulting 2D spectrum can be thought of as a correlation map where each excitation frequency is correlated to each detection frequency.²⁵ Our experimental setup used to obtain 2D electronic spectra is based on previous designs^{69–70} and a detailed explanation of the setup is given in the supporting information. Briefly, 2DES was performed in the pump-probe geometry yielding absorptive 2D spectra.^{69–72} An acousto-optic programmable dispersive filter pulse shaper (DAZZLER, FASTLITE) scans the t_1 time delay from -100 fs to 0 fs in 0.39 fs step sizes for BODIPY-2H and -50 fs to 0 fs in 0.20 fs step sizes for BODIPY-2I. For each t_1 delay, we applied phase-cycling to remove the background and scattering. The measurements were performed using the partially rotating frame with a frame rotation frequency of 350 THz.⁷³ The t_2 waiting time was scanned from -43 fs to 2.5 ps in 7 fs steps with a computer controlled delay stage (NEWPORT ILS250cc, XPS Q8).

The incoming pulses were characterized with SFG-FROG yielding a temporal duration of 22~26 fs for the cross-correlation between the pump and probe pulses.⁷⁴ The SFG-FROG along with representative pump and probe pulse spectra are shown in the supporting information. All 2DES data reported were obtained with the pulses set to the magic angle polarization: 54.7° for the pump pulse (with respect to the probe), and the probe and analyzer polarizer were set to horizontal (parallel to the optical table).

Calculations

DFT calculations were performed with the Gaussian09 software package.⁷⁵ Geometry optimizations were performed at the B3LYP level of theory with 6-311++g(d,p) basis set for all the atoms except for the iodine atoms of BODIPY-2I where the 3-21G basis was used, consistent with previous studies.¹⁰ Frequency calculations were performed to confirm an optimized ground state geometry and to determine the Raman active vibrational modes. Further details along with the optimized coordinates are given in the supporting information.

3. Results

2DES Spectra

Absorptive 2DES spectra of BODIPY-2H and BODIPY-2I in methanol are shown in Fig. 2 for three representative waiting times. Excitation of the BODIPY derivatives in the visible region results in a π -to- π^* transition that gives rise to the main peak in the 2D spectra. Both sets of spectra show one main peak with a rich structural profile that evolves as a function of waiting time. To assign the structural features and time evolution we first consider the tuning of the incoming laser pulses. The spectra of the incoming probe pulse (tan) along with the linear absorption (blue) and fluorescence (green) spectra are plotted in Fig. 2 (right panel). The plots show that the incoming laser pulses are tuned to spectrally overlap with both the absorption and emission spectra, giving a spectral window where the dynamics associated with the ground state bleach and stimulated emission can be observed. To put these transitions in context of the 2D spectra the maximum of the linear absorption ($\lambda_{\text{max,abs}}$) and fluorescence spectra ($\lambda_{\text{max,FL}}$) are indicated with dashed lines in the 2D spectra at $\lambda_3 = \lambda_{\text{max,abs}}$, $\lambda_3 = \lambda_{\text{max,FL}}$ and $\lambda_1 = \lambda_{\text{max,abs}}$.

For both BODIPY derivatives the main peak in the 2D spectra has contributions from both the ground state bleach and stimulated emission, where the 2D spectral profile is filtered by the incoming laser pulses. The shoulders that are present are attributed to the excitation of strongly coupled (Franck-Condon active) vibrational modes that lie within the bandwidth of the incoming laser pulses. As the waiting time increases the peak becomes elongated along the λ_3 axis and the maximum intensity shifts along the λ_3 axis towards $\lambda_{\text{max,FL}}$. This is more readily observed by taking projections along the λ_1 axis onto the λ_3 axis. The panel in Fig. 2 plots projections onto λ_3 for the representative 2DES spectra. As the waiting time increases the peak broadens along the λ_3 axis with the maximum amplitude of the projection shifting to lower frequencies.

4. Discussion

In the next two sections, we first discuss (1) the ultrafast relaxation along the λ_3 axis and then move on to discuss (2) the vibrational modes strongly coupled to the electronic excitation.

4.1 Ultrafast Relaxation of the S_1 Excited State

After electronic excitation, the BODIPY derivatives begin to relax in response to the change in charge distribution through solvent reorganization and/or intra- and intermolecular vibrational energy redistribution. As the S_1 state relaxes, the energy gap decreases leading to a red shift in the stimulated emission.

Previous 2DES studies have attributed red-shifted spectral features to the dynamic Stokes shift.^{25, 45, 76–79} Here we expand on these previous studies presenting a method for extracting $\nu(t)$ (Eq. 1) from 2DES spectra through monitoring the evolution of the ground state bleach and stimulated emission. In the 2DES spectra one would expect to see the relaxation of the S_1 state as a peak shifting to lower frequencies along the λ_3 axis centered at $\lambda_1 = \lambda_{\text{max,abs}}$.^{25, 45, 76, 78–79} After relaxation is complete, an off-diagonal peak associated with stimulated emission centered at the $\lambda_1 = \lambda_{\text{max,abs}}$, $\lambda_3 = \lambda_{\text{max,FL}}$ should be observed. For the BODIPY derivatives the relevant coordinates are indicated with dashed lines on the 2DES spectra. Due to the limited bandwidth of the incoming laser pulses two distinct transitions associated with absorption (ground state bleach) and emission (stimulated emission) are not observed; however, in comparing the 2DES spectra at $t_2 = 13$ fs and $t_2 = 2.5$ ps, the relaxation of the S_1 state (the dynamic Stokes shift) manifests as an asymmetric broadening of the peak along the λ_3 axis, where amplitude is gained below the diagonal.

To extract $\nu(t)$ from the 2DES spectra we first establish a procedure based on projecting the 2DES spectra onto the λ_3 axis. We then demonstrate this procedure for slices taken along the λ_1 axis (for a given λ_1 as a function of λ_3) and λ_3 projections over smaller areas.

Representative projections onto the λ_3 axis are shown as dashed red, orange, and blue lines in Fig. 2. The projection of the 2DES spectrum onto the λ_3 axis is equivalent to the pump-probe spectrum taken under the same experimental conditions.^{76, 80} Previous pump-probe measurements have shown that information regarding solvent dynamics can be extracted through analyzing the time evolution of the spectral line shapes.^{48, 49, 50–57} More recently, pump-probe spectroscopy has been used to obtain $\nu(t)$, and extract timescales associated with the relaxation of electronic excited states through monitoring the time-dependent frequency change in the node resulting from excited state wavepackets in the stimulated emission.^{81–82} Though the projection of the 2DES spectra onto the λ_3 axis is equivalent to the pump-probe spectra, due to the limited spectral bandwidth of the incoming pulses this analysis cannot be applied to the current data as distinct transitions arising from the ground state bleach and stimulated emission are not resolved. However, information regarding the relaxation of the BODIPY S_1 state can still be extracted from the 2DES spectra through analyzing spectral lineshape changes of the λ_3 projection.

To extract $\nu(t)$ the projections onto the λ_3 axis are first normalized as shown in Fig. 3. Fig. 3b displays normalized projections as a function of ν_3 (c/λ_3) for $t_2 = 500$ fs for BODIPY-2H (top) and BODIPY-2I (bottom). From the normalized projections, the frequencies at half of the maximum ($I=0.5$) are extracted with the higher frequency labeled as ν_o and the lower frequency labeled as ν_+ (labels are also defined in Fig. 3b). Along with the projection, the linear absorption (shaded orange) and emission (shaded green) spectra are plotted in Fig. 3b. Through overlaying the projection with the linear spectra it can be seen that ν_o will have a larger contribution from the ground state bleach, and ν_+ will have a larger contribution from the stimulated emission, and the time dependent behavior of $\nu(t)$ is interpreted in this context.

The extracted $\nu_{+/o}$ for BODIPY-2H (blue) and BODIPY-2I (green) are plotted in Fig. 3a as a function of waiting time (t_2). The energy gap associated with the ground state bleach should not vary as a function of waiting time; therefore, we expect ν_o to remain constant. We use this information to set the time for which the data is reporting on the molecular response of the system, and not dominated by artifacts due to pulse overlap. Using the ν_o plots as a guide, we only analyze data after the first 40 fs for BODIPY-2H and the first 60 fs for BODIPY-2I. The excluded data points are indicated by grey shaded areas in Fig. 3a and grey dots in Fig. 4. Fig. 3a shows that ν_+ continues to relax after ν_o has leveled off as the energy gap between the S_1 excited state and the ground state decreases.

From the extracted ν_+ and ν_o points, the Stokes shift function $S(t)$ can be obtained from Eq. 1, where ν_+ is taken as $\nu(t)$. There are different experimental methods to determine the values of $\nu(0)$ and $\nu(\infty)$ which depend on the experiment performed to extract the Stokes shift response function.⁴³ To obtain the $S(t)$ from the 2DES spectra we were required to devise a new method for setting $\nu(\infty)$ as our incoming pulse width was not able to cover the entire absorption and emission bands. We take the final ν_+ value, at 2.5 ps as the relaxed frequency, $\nu(\infty)$, on the timescales that we are able to probe. For the denominator ($\nu(0) - \nu(\infty)$), we use the Stokes shift obtained from the linear spectra shown in Fig. 1 (22 THz for BODIPY-2H and 24 THz for BODIPY-2I). The resulting Stokes shift functions for BODIPY-2H and BODIPY-2I are shown in Fig. 4(a, b) zooming in on the first 500 fs with the insets displaying $S(t)$ extending to 2.5 ps.

To extract the ultrafast timescales of solvation for both BODIPY-2H and BODIPY-2I in methanol the Stokes shift functions are fit with a Gaussian and single exponential function to account for the inertial and diffusive solvent response in accord with previous studies.^{35, 39–40, 42–43, 83–85} The results of the fit are given in Table 1. Our results are consistent with previous measurements where an ultrafast component of ~ 100 fs or less was observed and attributed to the inertial component of the solvent response of methanol, and a longer timescale component of a few picoseconds was observed and attributed to the diffusive component of the solvent response.^{42, 43, 46, 82, 86–94} In our studies performed on BODIPY chromophores in methanol, we observe an ultrafast relaxation of 57 fs for BODIPY-2I and 59 fs for BODIPY-2H and attribute this ultrafast component to an inertial solvent response – consistent with previous studies.^{42, 43, 46, 82, 86–94} The longer timescale component of ~ 2 ps for BODIPY-2H and ~ 1 ps for BODIPY-2I is attributed to the diffusive solvent response. Note that the values for these components are only considered estimates as the longest

waiting time probed experimentally is 2.5 ps. For this reason, we do not analyze the longer timescale components, but note that previous studies have observed diffusive components on the ps timescale for methanol.⁴² The agreement between the observed inertial solvent response, along with the presence of a longer ~ps timescale diffusive component with previous results validates our described analysis procedure for extracting the dynamic Stokes shift from 2DES spectra.

As a next step, we apply our analysis procedure to slices taken along the λ_1 axis of the 2DES spectra (indicated as dashed lines in the 2DES insets in Fig. 4(c, d)) and projections onto the λ_3 taken over a smaller area in the 2DES spectrum (indicated with a shaded box in the inset in Fig. 4(c, d)). For both BODIPY-2H and BODIPY-2I ν_+ and ν_0 points were extracted from the normalized slices and smaller-area projections according to the procedure described above. The extracted ν_+ and ν_0 points resemble those presented in Fig. 3 and are plotted in the supporting information (Fig. S10). Taking ν_+ as $\nu(t)$, the Stokes shift function $S(t)$ is obtained using the same procedure described above for determining $\nu(\infty)$ and $(\nu(0) - \nu(\infty))$. $S(t)$ for the slices and smaller-area projections are shown in Fig. 4(c, d). The extracted $S(t)$ were fit with the same Gaussian and exponential functions described above to extract timescales for the ultrafast inertial solvent response. The results are reported in Table 1.

In general, we find similar results when comparing the ultrafast solvation dynamics extracted from the projection of the 2DES spectra onto the λ_3 axis, slices along the λ_1 axis, and smaller-area λ_3 projections. Comparing the timescales for the inertial solvent response (a graphical representation is given in the supporting information (Fig. S12)) we find the timescales to be similar within error and consistent with previous reports on the ultrafast inertial response of methanol,^{42, 43, 46, 82, 86–94} validating the described technique for extracting $\nu(t)$ and the Stokes shift response function from slices taken along the λ_1 axis of the 2DES spectra and smaller-area λ_3 projections. Though not an issue with the BODIPY chromophores investigated here, extracting the Stokes shift response from slices along the λ_1 axis could serve as a means for extracting the dynamic Stokes shift from congested spectra, such as the spectra of light harvesting complexes, where the projection of the 2DES spectra onto the λ_3 axis results in multiple overlapping spectral features. In addition, this technique offers an opportunity to readily investigate the excitation frequency dependence of the dynamic Stokes shift for congested spectra.

4.2 Franck-Condon Active Vibrational Modes

When the incoming laser pulse excites the $\pi-\pi^*$ transition of the BODIPY derivatives vibrational coherences having a nonzero Franck-Condon overlap and that lie within the bandwidth of the incoming laser pulse are also excited. The excitation of the vibrational coherences gives rise to the shoulders present in the lineshape of the peak in the 2DES spectra (Fig. 2). Though not all the vibrational modes excited lead to clear structural components in the lineshape, as the structural components of lower frequency vibrational modes are masked by the lineshape of the electronic transition. However, information on the frequency of these vibrational modes can be extracted by analyzing the time-dependence of the 2DES spectra where the vibrational coherences oscillate as a function of the waiting time

at a frequency that corresponds to the difference in energy between the vibrational states. Previous studies have applied 2DES to systems in order to characterize vibrational coherences.^{25, 59–60, 77, 79, 95–100} Here we use this aspect of 2DES to determine which vibrational modes are strongly coupled to the electronic excitation of the BODIPY derivatives and determine how these modes vary as a function of structural derivatization.

To extract this information from the 2DES data we first isolate the vibrational contributions to the waiting time dependent dynamics. This is accomplished by fitting the amplitude for a given λ_1, λ_3 trace in the 2D spectra with a bi-exponential that captures the population dynamics. A representative trace with corresponding fit is included in the supporting information. The resulting population dynamics are then subtracted from the traces yielding residuals that contain the isolated oscillatory components. Fig. 5 plots 2DES spectra along with representative residuals where the t_2 time has been truncated at 2.5 ps for BODIPY-2H (top) and BODIPY-2I (bottom). Fourier transformation of the residual along the t_2 axis yields the power spectrum. This procedure was applied to every λ_1, λ_3 coordinate where amplitude is observed in the 2DES spectra. The averaged power spectrum obtained from applying the above described procedure for each λ_1, λ_3 coordinate is displayed in the final panel of Fig. 5. The frequencies of the Franck-Condon active modes are obtained by fitting the frequency domain data of three different individual slices with Gaussian functions and averaging the extracted parameters. The results are reported in Table 2. Note that we have only focused on frequencies that are greater than 100 cm^{-1} . Within this window, three vibrational modes are observed for BODIPY-2H: 165 cm^{-1} ($\Delta\tilde{\nu}_{1/2\text{max}} = 10.5 \text{ cm}^{-1}$), 179 cm^{-1} ($\Delta\tilde{\nu}_{1/2\text{max}} = 12.9 \text{ cm}^{-1}$), and 479 cm^{-1} ($\Delta\tilde{\nu}_{1/2\text{max}} = 16.2 \text{ cm}^{-1}$), and four vibrational modes are observed for BODIPY-2I: 144 cm^{-1} ($\Delta\tilde{\nu}_{1/2\text{max}} = 15.8 \text{ cm}^{-1}$), 435 cm^{-1} ($\Delta\tilde{\nu}_{1/2\text{max}} = 13.3 \text{ cm}^{-1}$), 523 cm^{-1} ($\Delta\tilde{\nu}_{1/2\text{max}} = 14.9 \text{ cm}^{-1}$), 570 cm^{-1} ($\Delta\tilde{\nu}_{1/2\text{max}} = 15.6 \text{ cm}^{-1}$). We find that the vibrational modes for both BODIPY-2H and BODIPY-2I have similar $\Delta\tilde{\nu}_{1/2\text{max}}$; however, the frequencies and nuclear motion associated with the vibrational modes differ as do the relative intensities with the Franck-Condon active modes of BODIPY-2H having amplitudes of $\sim 2.5 \times 10^4$ and for BODIPY-2I the amplitudes are $\sim 11 \times 10^4$ in the power spectra.

Vibrational Mode Assignment—To assign the vibrational modes we compare the experimentally extracted vibrational frequencies in Table 2 to the DFT calculated vibrational modes of BODIPY-2H and BODIPY-2I. As the vibrational wavepackets generated in the 2DES spectra are similar to those generated through Raman spectroscopic techniques we constrain our assignment to vibrational modes having a large Raman activity. The DFT calculated non-resonant Raman spectra are shown in the supporting information. We note that there are amplitude discrepancies between the calculated and experimental power spectra arising from the fact that 2DES is more akin to resonant Raman than non-resonant Raman techniques. Due to the amplitude discrepancies, we limit the assignment of the Franck-Condon active vibrational modes to the symmetric vibrational modes^{101–104} to

further aid in the assignment of the power spectra. Fig. S14 in the supporting information plots the Raman active vibrational modes indicating the subset of symmetric modes. The experimentally determined frequencies are assigned through comparison with this subset of calculated frequencies and the results are reported in Table 2. A detailed description of the assignment procedure is given in the supporting information.

Comparing the experimental and calculated results of BODIPY-2H and BODIPY-2I, we find that derivatization of the BODIPY core structure with halogen atoms leads to changes in the overall intensity (Franck-Condon factors) and the nuclear motion coupled to the electronic excitation. The overall amplitudes of the peaks in the power spectrum of BODIPY-2I are an order of magnitude larger than those of BODIPY-2H, which is consistent with the larger calculated Raman activity for BODIPY-2I. We attribute this to the larger polarizability of BODIPY-2I due to the incorporation of the two iodine atoms. The nuclear motion coupled to the electronic excitation is also different for the two BODIPYs. Fig. 6 displays DFT optimized structures of BODIPY-2H and BODIPY-2I where nuclear displacements are indicated with arrows for a given normal mode. Visualizing the normal modes shows that the main structural motion is associated with ring distortions. The normal modes of BODIPY-2I are mainly ring stretching modes that involve the motion of the iodine atoms. The normal modes of BODIPY-2H have large contributions from ring bending motions and include a larger motion of the methyl substituents when compared to the normal modes of BODIPY-2I.

To further understand the difference in nuclear motion of the associated Franck-Condon active modes we compare the HOMO and LUMO orbitals of BODIPY-2I and BODIPY-2H. The HOMO and LUMO orbitals are displayed in Fig. 7 and confirm the π - π^* character of the transitions. Comparing the HOMO and LUMO of BODIPY-2I and BODIPY-2H a similar change in the p-nodal character on the core structure is observed; however, the electron density at the halogenated position differs for the two complexes with the p-character of the BODIPY-2I HOMO extending onto the iodine atoms.

We consider the electron density of the HOMO and LUMO orbitals to be representative of the changes in electron density that occur upon excitation of the π - π^* transition, and where large changes in electron density are observed, we would expect the local bonds to change. For BODIPY-2I the lack of electron density on the iodine atoms in the LUMO compared to the HOMO, and the change in nodal structure on the BODIPY core indicates that the iodine carbon bond length and the bonds of the core ring structure will change in response to the electronic excitation. For BODIPY-2H the change in nodal structure indicates that the bond lengths associated with the ring structure and the methyl substituents will change in response to electronic excitation. These predictions are consistent with the motion of the nuclei of the Franck-Condon active vibrational modes (Fig. 6). We attribute the differences in Franck-Condon active modes of BODIPY-2H and BODIPY-2I to the differences in the change in electron density upon electronic excitation for BODIPY-2H and BODIPY-2I complexes as indicated by the HOMO and LUMO orbitals (Fig. 7).

4. Conclusions

In conclusion, we have characterized the ultrafast dynamics of structurally different BODIPY chromophores through applying 2DES. Through applying different data analysis procedures to the 2D electronic spectra, our studies reveal (1) ultrafast solvation dynamics of BODIPY chromophores in methanol on sub-100 fs timescales and (2) the frequency and identity of vibrational modes strongly coupled to the electronic excitation.

We demonstrate a data analysis procedure for extracting the dynamic Stokes shift from 2DES spectra performed with limited bandwidth pulses. This procedure is general and only requires that the incoming pulses spectrally overlap with portions of both the absorption and emission spectra. Applying our data analysis procedure to BODIPY-2I and BODIPY-2H in methanol we observe two time components for relaxation a ~60 fs inertial component and a longer ps timescale diffusive component. These observations are consistent with previous studies focusing on the solvation dynamics of methanol^{42, 43, 82, 86–94}, confirming our data analysis procedure. Future work will extend on these studies applying 2DES to BODIPY chromophores in different local environments with different derivatizations. Understanding the ultrafast solvation dynamics of BODIPY chromophores in various environments may lead to a better understanding of system-bath interactions that could dictate photophysical and photochemical properties relevant for imaging or applications for solar energy conversion.^{35, 38, 105}

On longer timescales, we observe oscillatory components in the 2D electronic spectra of BODIPY-2H and BODIPY-2I arising from the creation of vibrational coherences in the ground and electronic excited states. The frequency and dephasing time of the oscillatory components were extracted from the 2D electronic spectra and assigned through DFT calculations. Our results show that derivatization of BODIPY chromophores alters the vibrational modes (including nuclear motion, frequency, and activity) that are strongly coupled to the electronic excitation. Recent studies have shown that vibrational motion plays an important role in charge separation for natural and artificial photosynthetic complexes and in organic photovoltaic materials.^{99, 106–109} A better understanding of the vibrational modes strongly coupled to electronic excitation of BODIPY chromophores, and how derivatization of BODIPYs influences this vibrational motion, can provide further insight into the design of BODIPY based systems for solar energy conversion.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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BODIPY-2H (1) **BODIPY-2I (2)** **Figure 1.**

The chemical structures of BODIPY-2H (1) and BODIPY-2I (2) are displayed along with the normalized linear absorption (solid line) and fluorescence (dashed line) spectra of BODIPY-2H (blue) and BODIPY-2I (green).

Figure 2.

Absorptive 2DES spectra at magic angle polarization of BODIPY-2H (a, top) and BODIPY-2I (b, bottom) at three different waiting times: $t_2 = 13$ fs, 100 fs and 2.5 ps. The panels on the right display the linear absorption (blue) and emission (green) spectra as solid lines, the spectrum of the incoming probe pulse (shaded area), and the normalized projection of the 2DES spectra onto the λ_3 axis for three different waiting times: $t_2 = 13$ fs (dashed red), $t_2 = 100$ fs (dashed orange), and $t_2 = 2.5$ ps (dashed blue).

Figure 3.

(a) Plots of $\nu_{+/-o}$ for BODIPY-2H (blue) and BODIPY-2I (green) as a function of waiting time are shown. Values of $\nu_{+/-o}$ are obtained from the normalized projection of the 2DES spectra onto the λ_3 axis. (b) Representative projections (blue dots) are shown with ν_+ indicated with (–) and ν_o with circles (o) for BODIPY-2H (top) and BODIPY 2I (bottom). The orange shaded area is the linear absorption spectrum and the light green shaded area is the emission spectrum.

Figure 4.

(top) Dynamic Stokes shift response functions ($S(t)$) generated by Eq. 1 from projections of the 2DES spectra onto the λ_3 axis and corresponding fit resulting from the sum of Gaussian and exponential decay functions (blue line) for (a) BODIPY-2H and (b) BODIPY-2I. Inset plots for (a) and (b) show the Stokes shift response functions for up to 2.5 ps and the main plots zoom in on the first 500 fs. (bottom) The dynamic Stokes shift response functions ($S(t)$) along with corresponding fit for three representative slices along the λ_1 axis for $\lambda_1 = 505$ (purple), 502 (blue), and 500 (cyan) nm for BODIPY-2H (c), and $\lambda_1 = 529$ (purple), 526 (blue), and 523 (cyan) nm for BODIPY-2I (d) are shown. $S(t)$ generated from projecting the green boxed area of the 2DES spectrum onto λ_3 axis along with resulting fit are shown green (c,d).

Figure 5. Representative residuals are shown in green for traces taken at the λ_1, λ_3 coordinate indicated with a green dot in the 2D spectra. The mean of the power spectra for each λ_1, λ_3 coordinate is plotted in blue for (a) BODIPY-2H (top) and (b) BODIPY-2I (bottom).

Figure 6.
Nuclear motion associated with the assigned vibrational modes is indicated with arrows for (a) BODIPY-2H and for (b) BODIPY-2I

(a) BODIPY-2H

HOMO(E: -5.80 eV)

(b)

LUMO(E: -2.80 eV)

(c) BODIPY-2I

HOMO(E: -5.95 eV)

(d)

LUMO(E: -3.04 eV)

Figure 7.
The HOMO and LUMO molecular orbitals for BODIPY-2H (top) and BODIPY-2I (bottom).

Table 1.

Fit results for solvation relaxation times of BODIPY dyes in Methanol^a

	A ₁	t ₁ (fs)	A ₂	t ₁ (ps)
Projection of 2DES				
BODIPY-2H	0.3041 (±0.1010)	59 (±15)	0.0210 (±0.0175)	~ 2
BODIPY-2I	0.2695 (±0.0724)	57 (±8)	0.0225 (±0.0073)	~ 1
BODIPY-2H Slices along λ_1 ^c				
$\lambda_1 = 505$ nm	0.2008 (±0.0355)	60 (±7)	0.0346 (±0.0064)	~ 2
$\lambda_1 = 502$ nm	0.2579 (±0.0341)	55 (±5)	0.0200 (±0.0053)	~ 2
$\lambda_1 = 500$ nm	0.3587 (±0.0525)	50 (±5)	0.0083 (±0.0066)	~ 2
BODIPY-2I Slices along λ_1 ^c				
$\lambda_1 = 529$ nm	1.0066 (±0.1954)	41 (±3)	0.0139 (±0.0063)	~ 1
$\lambda_1 = 526$ nm	0.3414 (±0.1633)	44 (±8)	0.0284 (±0.0070)	~ 1
$\lambda_1 = 523$ nm	0.4558 (±0.2800)	39 (±8)	0.0381 (±0.0076)	~ 1
Projection over boxed area ^{b,c}				
BODIPY-2H	0.2612 (±0.0322)	56 (±5)	0.0172 (±0.0051)	~ 2
BODIPY-2I	0.3371 (±0.2034)	42 (±9)	0.0275 (±0.0074)	~ 1

^a the parameters for relaxation times and their weights are estimated by the fitting function $M(t) = A_1 \exp(-(1/2)(t/t_1^2)) + A_2 \exp(-t/t_2)$;^b box range of λ_1 axis for BODIPY-2H starts from 500 nm to 505nm, and for BODIPY-2I starts from 523 nm to 529 nm;^c The t_2 time component was constrained based on values obtained from the projection of the 2DES spectra onto the λ_3 axis.

Table 2.

Experimental and calculated Franck-Condon active vibrational modes of BODIPY-2H and BODIPY-2I

	Exp. Freq (cm ⁻¹)	Cal. Freq (cm ⁻¹) ^a	Raman Activity
BODIPY-2H	165	ν_{12} (157)	0.7
	179	ν_{15} (187)	1.6
	479	ν_{31} (480)	9.5
BODIPY-2I	144	ν_{13} (144)	12.7
	435	ν_{35} (475)	12.0
	523	ν_{37} (522)	7.7
	570	ν_{39} (566)	26.9

^aDFT calculated Raman active modes assignments where a scaling factor of 0.97 for BODIPY-2H and 1 for BODIPY-2I are used.