Influence of intramolecular vibrations in third-order, time-domain resonant spectroscopies. I. Experiments

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Influence of intramolecular vibrations in third-order, time-domain resonant spectroscopies. I. Experiments

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This is the first in a two-paper series that investigates the influence of intramolecular vibrational modes on nonlinear, time-domain, electronically resonant signals. Both Transient Grating (TG) and Three Pulse Photon Echo Peak Shift (3PEPS) signals were collected from several probe molecules: Nile Blue, N,N-bis-dimethylphenyl-2,4,6,8-perylenetetracarbonyl diamide, and Rhodamine 6G dissolved in different solvents: benzene, dimethylsulfoxide, and acetonitrile. The effects of excitation of different vibronic transitions on the electronically resonant signals were identified by comparing signals collected with laser pulses at different excitation wavelengths. In the 3PEPS profiles, we find that excitation on the blue edge of the absorption spectrum causes a decreased initial peak shift values and more rapid initial decays, whilst in the TG signals, the magnitude of the “coherent spike” is strongly wavelength dependent. Additional thermally activated vibronic effects were studied via temperature dependent 3PEPS profiles. Our results reveal the sensitivity of the nonlinear signals to the excitation wavelengths and to the distinct vibronic structure of the different chromophores studied. Pronounced modulations in both the 3PEPS and TG signals originating from coherently excited vibrational modes were directly observed. Additional oscillations were observed that are attributed to difference frequencies and higher harmonics of the fundamental modes. In paper II we demonstrate that detailed account of the vibronic nature of the chromophore is required to describe the wavelength dependent signals.

I. INTRODUCTION

Rapid improvements in the generation of ultrafast laser pulses have made it possible to create optical pulses with durations shorter than 10 fs.1–3 Such ultrashort pulses allow for the direct investigation of underdamped coherent vibrational dynamics, observed as weak modulations in time-domain, nonlinear optical signals.4 These oscillations have been observed in a wide variety of systems: from small molecules5,6 to complex biological systems.7–10 These modulations can provide useful information on the intramolecular dynamics of the system, such as vibrational coherence7–10 and vibrational population relaxation11–13 that play an important role in chemical reactions.14 However, the presence of these modulations in the nonlinear signals may also obscure the characterization of other significant dynamical processes (e.g., solvation and energy transfer dynamics).15

Third order nonlinear optical techniques such as Three Pulse Photon Echo Peak Shift (3PEPS), Transient Grating (TG), and Transient Absorption (TA) measurements have been used to obtain detailed information on the coupling strengths and the time scales of solvation dynamics. Information about solvation dynamics can be obtained via the correlation function of the energy gap (transition frequency) fluctuations of the chromophore dissolved in condensed phase. It was shown previously that 3PEPS profiles directly reflect the transition frequency correlation function for times longer than the bath correlation time.25 Based on the transition frequency correlation function, we can calculate the linear absorption, fluorescence spectrum, and third-order nonlinear optical signals such as TA, TG, and 3PEPS via the response function formalism developed by Mukamel and co-workers.26 The high time resolution inherent in 3PEPS techniques allows for the separation of vibrational and solvation contributions to the dephasing dynamics. One of the unique advantages of the 3PEPS techniques is the ability to measure the static inhomogeneity of the system. We previously demonstrated this aspect for dye molecules in polymer glasses27,28 and the B820 subunit of LH1.29 We also applied 3PEPS measurements to investigate the energy transfer dynamics in static disordered systems.30 Peak shift measurements have also been shown to be useful in extracting valuable information in molecular aggregates where the interplay among the intermolecular electronic couplings and electron–phonon interactions is important31,32

An idealized and often used approach to introduce vibrational effects in optical signals is to treat the chromophore–bath system as a two-level electronic system dressed with several key vibrational modes.19,33 Typical chromophores used in experimental studies have many vibrational modes that can influence the nonlinear signals. Information on which intramolecular vibrations are Franck–Condon active can be obtained from the underdamped modulations in the time domain signals or from resonance Raman and fluorescence line-narrowing spectra in the frequency domain. It is

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assumed that only those vibrational modes lying within the laser spectrum are observed. Therefore, at different excitation wavelengths, different sets of excitations in the vibrational manifold can be prepared. Furthermore, the distinction between the low frequency intramolecular vibrational modes with short damping times and the exponential decays of the solvation components is sometimes difficult to make because short damping times can hinder the observation of clear oscillations in the signals.

Previous TA and TG studies have revealed wavelength dependent effects in both experimentally collected and simulated signals. Simon and co-workers\textsuperscript{35} used femtosecond one-color TA measurements to study the electronic dephasing dynamics of the dye molecule, HITCI, in ethylene glycol. They presented a detailed analysis of laser pulse duration and wavelength dependence effects in the TA signals using the Multimode Brownian Oscillator (MBO) model.\textsuperscript{35} They observed that the amplitude of the coherent spike in the experimental TA signals increases as the excitation wavelength is tuned to the red edge of the absorption band. Huppert and co-workers\textsuperscript{36} measured heterodyne-detected resonant optical Kerr signals of Rhodamine 800 in water at two different excitation wavelengths. In contrast to the wavelength dependent trend observed by Simon and co-workers, they observed that the amplitude of the coherent spike increases when the laser wavelength is tuned to the blue edge of the absorption spectrum.

Recently, Vauthey and co-workers\textsuperscript{22} studied the solvation dynamics of a dye molecule, IR140, in polar solvents with TG measurements. They observed a pronounced wavelength dependent trend in the TG traces, where the coherent spike amplitude decreases appreciably as the laser spectrum was tuned to the blue side of the absorption spectrum. They attributed this dependence to the destructive interference from accumulated thermal gratings originating from the high repetition rate of the laser. They also observed a weaker wavelength dependent trend in the TG signals collected with a ‘‘crossed grating geometry’’ that was ascribed to the selective probing of different sets of solvated chromophores (each exhibiting different solvation dynamics) within the absorption spectrum.\textsuperscript{22}

It is clear that a detailed understanding of the wavelength dependent properties of such nonlinear optical experiments is important to analyze the results described above and answer questions such as: Is the solvation dynamics measured in different regions of the absorption spectrum inherently different? Which wavelength is the best to study the solvation dynamics? Is the mechanism(s) responsible for the wavelength dependent effects properly accounted for in the simulations of the signals? Do previous analyses of third-order nonlinear signals need to be modified to include an improved description of the vibrational contribution?

We have carried out a detailed investigation of the role of vibrational modes in the nonlinear optical signals. In this paper (hereafter paper I), we present experimental results from wavelength dependent 3PEPS (WD-3PEPS), wavelength dependent Transient Grating (WD-TG), and temperature dependent 3PEPS (TD-3PEPS) measurements. We used three different probe molecules: Nile Blue, N,N-bis-dimethylphenyl-2,4,6,8-perylenetetracarbonyl diamide (PERY), and Rhodamine 6G (R6G).

![Molecular structures of the model probe chromophores used to study the wavelength dependent properties of the nonlinear signals.](image)

**FIG. 1.** Molecular structures of the model probe chromophores used to study the wavelength dependent properties of the nonlinear signals: (A) Nile blue, (B) N,N-bis-dimethylphenyl-2,4,6,8-perylenetetracarbonyl diamide (PERY), (C) Rhodamine 6G (R6G).

II. TRANSIENT GRATING AND THREE PULSE PHOTON ECHO PEAK SHIFT TECHNIQUES

Both the TG and 3PEPS techniques are third order time domain spectroscopies that have been extensively used to study solvation dynamics.\textsuperscript{19,20,36} Both techniques require three laser pulses to interact with the system resulting in an induced nonlinear polarization. This induced polarization is the source for a radiated field. Since all three interacting laser pulses impinge on the sample with different wave vectors, appropriate phase-matching\textsuperscript{37} requires the generated electric field to be created in a unique direction \(\mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_1\) that allows for the background-free (heterodyne detected) measurement of the nonlinear signals.

For TG measurements, the first and second pulses are overlapped in time and the signal is measured by scanning the time delay between the second and third pulses. In the limit of delta-function pulses, the TG signals are insensitive to solvation dynamics,\textsuperscript{20} but are sensitive to the population dynamics\textsuperscript{20,38} (i.e., excited state lifetimes), and solute rotational motion.\textsuperscript{38,39} In addition, TG signals are also sensitive to the quantum mechanical interference between the differing ground and excited state contributions to the response as discussed in paper II. TG signals measured with finite pulses...
are also sensitive to solvation dynamics, since the system can evolve in a coherent superposition of the ground and excited states during the time between the first and second pulse interactions. An analogous situation also applies to TA signals collected with finite duration laser pulses. A detailed description of the sensitivity of the TG and TA signals to solvation dynamics has been given elsewhere.

While the TG measurement is a one-dimensional technique since only one time duration is scanned, the 3PEPS experiment is two-dimensional and requires two time periods to be varied during data collection. The first pulse creates a coherence between the ground and excited state, the second pulse creates a population, either in the excited or ground state, and the third pulse again creates a coherence state. The time delay between the first and second pulse is the coherence period ($\tau$) and the time delay between the second and third pulse is the population period ($T$). If the phase during the second coherence period is the complex conjugate of the first, the sample generates an echo signal at some time $t$ after the last pulse. In a 3PEPS experiment, we measure the position of the maximum of the photon echo intensity, as a function of $\tau$, for fixed population times (Fig. 2). We refer to the shift of the maximum from $\tau=0$ as the peak shift, $\tau^*(T)$. The peak shift profiles have been shown to directly measure the loss of the memory of transition frequency of the system as it evolves.

Since the 3PEPS profiles are calculated from the peak positions of the photon echo signals and not from the amplitudes, the 3PEPS technique is not directly sensitive to population dynamics (except when excited stated lifetimes are comparable with the duration of the echo signals). Cho et al. showed that for the systems with small inhomogeneous widths (e.g., room temperature solvent systems) and for times longer than the bath correlation time, the 3PEPS profile mirrors the transition frequency correlation function. Thus, the 3PEPS experiment allows the direct observation of the amplitudes and time scales of the motions that modulate the electronic transition frequency.

III. EXPERIMENT

The signals were collected using either a commercial or a homebuilt laser system. The details of the laser systems have been given elsewhere, but are briefly reviewed here. The signals measured for the PERY and R6G systems were collected on the commercial system, while the Nile Blue data were measured on the home built system. The home built system consists of a mode-locked Ti:sapphire laser pumped with ~4 W of 532 nm laser power from a solid state Nd:YVO$_4$ laser (Coherent Verdi: V-5). The resulting 87.8 MHz train of ~22 fs pulses then seed an intracavity stretched regenerative amplifier creating a 1.46 kHz train of ~45–65 fs pulses centered near 800 nm. These amplified pulses are then compressed and converted to ~40 fs pulses in the visible region in an optical parametric amplifier (Coherent OPA 9450). The commercial system consists of a Ti:sapphire laser (Coherent Mira Seed) pumped with a large frame Ar$^+$ ion laser (Coherent INNOVA 400). The resulting 76 MHz train of ~40 fs pulses, centered at 790 nm are then stretched by a grating expander before seeding a regenerative amplifier (Coherent RegA 9050). The amplified pulses are then compressed with an optical parametric amplifier (Coherent OPA 9450) used to create the final pulses at the desired center wavelengths. The pulse durations of both systems range from 38 to 46 fs intensity FWHM (Tables I and II) following precompensation of the pulses with a prism pair compressor (SF-10 glass). Autocorrelation functions were measured with 0.3 mm thick BBO crystal located at the sample position and the laser spectra were measured either with a homebuilt spectral analyzer or a commercial spectral analyzer (Ocean Optics S2000).

The experimental setup for the 3PEPS and TG studies is shown in Fig. 2 and has been described previously in detail. In short, the three laser beams, with wave vectors: $k_1$, $k_2$, and $k_3$, are arranged in an equilateral triangle geometry and are focused into the sample with a 20 cm singlet lens. The integrated echo profiles are then simultaneously measured in two different phase-matched directions, $k_0 = k_1 \pm (k_1 - k_2)$, as a function of the coherence time, $\tau$, for fixed values of the population time, $T$ (Fig. 2(b)). The two integrated echo signals are mirror images of each other since they differ only in the sign of the pulse timing.
TABLE I. Experimental detuning factors for R6G and PERY systems. The experimental detuning factors are calculated from the difference in energy between the peak of the laser spectrum and the peak of the absorption spectrum. The absorption maximum for each system is shown in parentheses.

<table>
<thead>
<tr>
<th>Center wavelength</th>
<th>R6G in MeOH</th>
<th>PERY in DMSO</th>
<th>PERY in benzene</th>
<th>Laser pulse intensity autocorrelation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(527 nm)</td>
<td>(530 nm)</td>
<td>(526 nm)</td>
<td>width (FWHM), fs ΔνΔτ^c</td>
</tr>
<tr>
<td>493 nm</td>
<td>...</td>
<td>0^c +1540 cm^{-1}</td>
<td>...</td>
<td>46 0.45</td>
</tr>
<tr>
<td>520 nm</td>
<td>+255 cm^{-1}</td>
<td>+363 cm^{-1}</td>
<td>+219 cm^{-1}</td>
<td>43 0.49</td>
</tr>
<tr>
<td>525 nm</td>
<td>...</td>
<td>+179 cm^{-1}</td>
<td>0 cm^{-1}</td>
<td>38 0.50</td>
</tr>
<tr>
<td>530 nm</td>
<td>−107 cm^{-1}</td>
<td>...</td>
<td>−143 cm^{-1}</td>
<td>42 0.54</td>
</tr>
<tr>
<td>535 nm</td>
<td>−283 cm^{-1}</td>
<td>−176 cm^{-1}</td>
<td>−319 cm^{-1}</td>
<td>38 0.46</td>
</tr>
</tbody>
</table>

^aThe difference between the peak frequency and ω_2, estimated by the average frequency, is 400 cm^{-1}, 890 cm^{-1}, and 901 cm^{-1} for R6G in MeOH, PERY in DMSO, and PERY in benzene respectively.

^bZero with respect to the peak of the second vibronic peak and 1540 cm^{-1} with respect to the first peak for PERY.

^cThe time-bandwidth values were calculated by fitting Gaussian profiles to both the pulse spectra and pulse autocorrelation functions. The transform limited time-bandwidth value is 0.441.

sequently, we determine the peak shift values by measuring half of the span between the peak maxima of the signals in the two phase matched directions [Fig. 2(c)]. Determining the peak shift values in this manner improves the accuracy of the peak shift value by removing the uncertainty of determining the absolute value of τ. In the TG measurements, the signals were recorded as a function of T while τ is set to zero.

As the integrated photon echo profiles generally peak at positive τ values, only signals collected at positive coherence times are needed to determine the peak shift value from a specific phase-matched signal. We use a seemingly complex method of measuring the signals to concentrate on collecting useful data effectively and quickly so that experimental variations (e.g., laser fluctuations and timing drift) will have a reduced effect on the measured 3PEPS profiles, though such effects contribute to the total intensity of the signals. We scan τ at fixed values of T until τ is 0, then both τ and T are stepped such that the difference is constant. In this collection scheme, negative τ values correspond to the positive coherence time for the signal [left signal in Fig. 2(c)] and positive τ values correspond to the positive coherence time for the other signals (hence the symmetry of the signals).

The uncertainties of the peak shift values are estimated at around ±300–500 attoseconds at 95% confidence. The peak shift values were determined by fitting the integrated echo signals to Gaussian functions at long population times (T > 50 fs) and fitting only the positive edges of the echo signals to Gaussian functions at earlier times as shown in Fig. 3. As observed previously, the integrated echo signals exhibit a pronounced asymmetry at short population times that obscures the determination of the peak shifts values from full Gaussian fitting. This asymmetry originates from the different time ordering in the experiment between negative and positive coherence times. Other fitting schemes, such as cubic and higher order polynomials and asymmetric Gaussian functions were used previously, but we find that partial Gaussian fitting at short times best describes the echo profiles.

The solutes: Nile Blue (Exciton), PERY (Aldrich), and Rhodamine 6G (LambdaChrome) and the solvents (spectroscopic grade from Aldrich) were used without further purification. The samples were flowed through a 200 μm quartz cell with a peristaltic pump at 30 ml/min to decrease local heating of the solvent. All measurements were made at room temperature (20.5 °C ± 0.5 °C) and the sample concentrations were kept low (0.1–0.15 o.d. in a 200 μm cell) to reduce the possibility of aggregation and solute–solute interactions. In the temperature dependent 3PEPS experiment, the temperatures were controlled via a Neslab RTE-111 recirculator and measured with a home built thermocouple detector. A large sample reservoir (6 l) and increased pumping rate (50 ml/min) were used to ensure that the sample temperatures remained within ±0.5 °C of the desired value. The temperature dependent experiments were performed at a fixed laser wavelength of 530 nm.

IV. RESULTS AND DISCUSSION

The static absorption spectra of Nile Blue in acetonitrile, and PERY in DMSO and in benzene are shown in Fig. 4.
The 3PEPS and TG signals were measured with excitation wavelengths both to the red side and to the blue side of the main peaks of the absorption spectra at the wavelengths indicated in Fig. 4. The laser pulse characteristics and their relative central wavelengths for each experiment are summarized in Tables I and II.

A. Wavelength dependent 3PEPS

The WD-3PEPS data for Nile Blue in acetonitrile are shown in Fig. 5 and the results of fits of these data to a sum of exponentials are summarized in Table III. We find significant wavelength dependence of 3PEPS profiles taken at different excitation wavelengths. The 3PEPS profiles collected with pulses centered at the blue edge of the absorption spectrum (582 nm and 606 nm) exhibit a fast (<50 fs) decay component with no observable slow decay time components, while excitation on the red edge leads to profiles with slower initial decays (e.g., the initial decay time constants vary from 72 fs with 660 nm pulses to 21 fs with 582 nm pulses). For the red-edge excitation, the slowly decaying components in the 3PEPS profile exhibit the largest relative amplitude.

The WD-3PEPS profiles for PERY/DMSO and PERY/benzene are displayed in Figs. 6(a) and 6(b), respectively. The initial decay time scales and peak shift values for PERY in DMSO, obtained from fitting the 3PEPS profiles to a sum of exponentials and damped cosines, are given in Table IV. The observed wavelength dependent trend is similar to that observed for the Nile Blue data (Fig. 5): the initial decays of the 3PEPS profiles for the PERY systems become faster as the laser pulses are tuned to the blue (from 98 fs with 535 nm pulses to 19 fs with 520 nm pulses). The signals also display a pronounced 139 cm\(^{-1}\) oscillation that has been observed previously. Upon closer inspection, with both Fourier analysis and nonlinear fitting, an additional 278 cm\(^{-1}\) oscillation is also observed and is ascribed to the second harmonic of the 139 cm\(^{-1}\) oscillation. The amplitudes of these oscillations decrease when the excitation wavelength is tuned to the blue and these oscillations are not clearly observed in the 3PEPS traces measured furthest to the blue (493 nm).

The initial peak shift values also display pronounced wavelength dependence for all three probe molecules. As Table III and Fig. 5 illustrate, the initial peak shift value for Nile Blue/acetoniitrile peaks near the absorption maximum (~14.7 fs at 640 nm) and decreases to near half the maximum value on the red and blue edges (7.7 fs and 8.5 fs for 582 nm and 660 nm excitation, respectively). The initial peak shift value for the PERY/benzene system (Fig. 6) also peaks near the absorption maximum (526 nm). In contrast, for the PERY/DMSO system, the initial peak shift value is largest for the red-most excitation (17.4 fs at 535 nm) and decreases upon detuning to the blue (5.7 fs at 493 nm).
A trend similar to Nile Blue is also observed for the R6G/methanol system (Table IV).

To summarize, the WD-3PEPS data in Figs. 5 and 6 and tabulated in Tables III and IV show the following trends: as the excitation wavelength is tuned towards the blue, a more rapid initial decay (<100 fs) is observed, and the oscillations in the signals decrease in amplitude. As the excitation wavelength is shifted away from the absorption spectrum maximum, the initial peak shift value decreases. The wavelength dependence observed in our 3PEPS data therefore poses a serious challenge to the accurate characterization of solvation (intermolecular) dynamics of the systems studied.

By shifting the center wavelength of the laser pulses, different vibronic transitions within the chromophore are excited, since the laser spectrum is narrower than the absorption spectrum. The wavelength dependent data, displayed in Figs. 5 and 6, emphasize the pronounced effect that vibronic transitions have on the signals. Small shifts (~5 nm) in the laser spectrum can lead to different decay times and amplitudes of the oscillations. As the laser pulses are tuned toward the blue, more vibrational modes from the chromophore’s vibronic manifold can be excited. This leads to additional dynamical processes that affect the resulting signals. For example, intramolecular vibrational energy redistribution and vibrational energy relaxation processes may also affect the signals when excess energy is introduced into the system.

In paper II we simulate the experimentally observed wavelength dependence of the signals without explicitly introducing such effects. This is accomplished by introducing a more realistic model of the vibronic structure for the chromophore molecules, including nonimpulsively excited high frequency vibrational modes, into the numerical simulations.

**FIG. 5.** Experimental WD-3PEPS profiles for Nile Blue in acetonitrile. The data were collected with pulses centered at 582 nm (solid line), 606 nm (dotted line), 630 nm (dashed–dotted line), 640 nm (dashed line), 650 nm (solid line with triangles), and 660 nm (solid line with circles). The inset shows the same data extended to 10 ps on a log population time scale.

**FIG. 6.** Experimental WD-3PEPS profiles for PERY in DMSO and benzene. (a) The PERY in DMSO data were measured with laser pulses centered at 493 nm (solid line), 520 nm (dashed line), 525 nm (solid line with filled upright triangles), and 535 nm (solid line with filled circles). (b) The PERY in benzene data were collected at 535 nm (solid line with filled circle), 530 (solid line with filled downward angled triangles), 525 nm (dashed line) and 520 nm (solid line). The insets show the same data extended to 10 ps on a log scale.

**TABLE III.** WD-3PEPS initial times scales for Nile Blue in acetonitrile. The 3PEPS were fit to a sum of exponentials, $T^{*}(T=0)=a_1 \exp(-\tau_1)+a_2 \exp(-\tau_2)+a_3 \exp(-\tau_3)$. Slowly decaying components were not observed in the blue-most data.

<table>
<thead>
<tr>
<th>Central wavelength</th>
<th>$T^{*}(T=0)$</th>
<th>$a_1$ (fs)</th>
<th>$a_1$ (%)</th>
<th>$\tau_1$ (fs)</th>
<th>$a_2$ (fs)</th>
<th>$\tau_2$ (fs)</th>
<th>$a_3$ (fs)</th>
<th>$\tau_3$ (fs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>582 nm</td>
<td>7.7 fs</td>
<td>7.7</td>
<td>100</td>
<td>21 fs</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>606 nm</td>
<td>10.6 fs</td>
<td>10.6</td>
<td>100</td>
<td>23 fs</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>630 nm</td>
<td>12.2 fs</td>
<td>11.3</td>
<td>92</td>
<td>26 fs</td>
<td>0.9</td>
<td>382 fs</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>640 nm</td>
<td>15.1 fs</td>
<td>9.7</td>
<td>64</td>
<td>51 fs</td>
<td>1.4</td>
<td>841 fs</td>
<td>4.0</td>
<td>2.4 ps</td>
</tr>
<tr>
<td>650 nm</td>
<td>11.9 fs</td>
<td>8.1</td>
<td>68</td>
<td>62 fs</td>
<td>1.6</td>
<td>740 fs</td>
<td>2.2</td>
<td>2.8 ps</td>
</tr>
<tr>
<td>660 nm</td>
<td>8.5 fs</td>
<td>6.0</td>
<td>70</td>
<td>72 fs</td>
<td>1.7</td>
<td>846 fs</td>
<td>0.8</td>
<td>2.3 ps</td>
</tr>
</tbody>
</table>

*Relative amplitude values are expressed as a percentage of the initial peak shift value.
The 3PEPS technique combines a large dynamic range with the ability to characterize the time scales and coupling strengths of both solvation dynamics and intramolecular (solute) vibrational dynamics. This has been observed in experiments performed with the laser spectrum centered on the red edge of the absorption spectrum. However, when the wavelength of the laser pulses is shifted toward the blue side of the absorption band, additional vibronic effects contribute to the 3PEPS signals, resulting in rapid decays (<50 fs) with a weak sensitivity to the solvation dynamics (Table IV). To observe slower dynamics in the 3PEPS profiles, excitation on the red edge of the absorption spectrum (where fewer vibronic modes are excited) is required. Even if nonzero peak shift values are observed over a wide temporal range, the corresponding time scales and amplitudes exhibit a discernable wavelength dependence with small shifts of the laser spectrum centered on the red edge of the absorption band (Figs. 5 and 6 and Table III). This suggests a single wavelength analysis of the nonlinear signals may not provide unique knowledge of the coupling strengths and time scales of the underlying dynamics.

### B. Wavelength dependent TG

The WD-TG signals for Nile Blue in acetonitrile are displayed in Fig. 7 and the results of fitting the TG signals to a sum of exponential functions are summarized in Table V. As the excitation wavelength is tuned to the blue, the amplitude of the coherent spike decreases, resulting in larger terminal values observed on a 5 ps time scale. The coherent spike amplitude is weakest at shorter wavelengths (0.12 at 582 nm) and increases to the maximum value as the wavelength is tuned towards red (0.72 at 660 nm). The slower decay components in the traces are approximately wavelength independent, where with the exception of the 582 nm trace, the ~800 fs and ~3 ps decay components are clearly observed.

Weak oscillations are also observed in the signals. Most of these oscillations can be attributed to vibrational modes observed in resonance Raman scattering experiments, and other time domain studies. The oscillations are more clearly observed in the signals collected with excitation wavelengths on the red edge of the absorption spectrum. This is verified by comparing the magnitude of the peaks in the power spectra at different wavelengths (not shown). The power spectra obtained from the TG signals, after subtracting the slowly decaying components (Table V), collected at 660 nm, 630 nm, and 606 nm, are displayed in Fig. 8. The power spectra are normalized to the maximum peak (590 cm\(^{-1}\) for the red most traces) for comparison of the relative magnitudes. The first 20 vibrational modes of Nile Blue, characterized in Ref. 18, are tabulated in Table VI for comparison with the power spectra. Peaks associated with the oscillations of fundamental frequencies (Table VI) up to 1100 cm\(^{-1}\) can be observed in the TG signals collected

![Fig. 7](image-url)
TABLE V. WD-TG fittings parameters for Nile Blue in acetonitrile. Transient grating curves were fit to a sum of three exponential decays plus an offset, $S(t) = \Sigma a_i \exp(-t/\tau_i) + \text{constant}$. The time axis was truncated at the peak maximum and the amplitude was normalized to the peak value.

<table>
<thead>
<tr>
<th>Central wavelength</th>
<th>$a_1$</th>
<th>$\tau_1$</th>
<th>$a_2$</th>
<th>$\tau_2$</th>
<th>$a_3$</th>
<th>$\tau_3$</th>
<th>Offset</th>
</tr>
</thead>
<tbody>
<tr>
<td>582 nm</td>
<td>0.12</td>
<td>45 fs</td>
<td>0.09</td>
<td>140 fs</td>
<td>0.13</td>
<td>4 ps</td>
<td>0.72</td>
</tr>
<tr>
<td>606 nm</td>
<td>0.40</td>
<td>73 fs</td>
<td>0.09</td>
<td>850 fs</td>
<td>0.15</td>
<td>6 ps</td>
<td>0.40</td>
</tr>
<tr>
<td>630 nm</td>
<td>0.45</td>
<td>100 fs</td>
<td>0.12</td>
<td>979 fs</td>
<td>0.05</td>
<td>2.8 ps</td>
<td>0.39</td>
</tr>
<tr>
<td>640 nm</td>
<td>0.68</td>
<td>69 fs</td>
<td>0.12</td>
<td>649 fs</td>
<td>0.06</td>
<td>1.6 ps</td>
<td>0.37</td>
</tr>
<tr>
<td>650 nm</td>
<td>0.72</td>
<td>81 fs</td>
<td>0.05</td>
<td>793 fs</td>
<td>0.09</td>
<td>4 ps</td>
<td>0.25</td>
</tr>
<tr>
<td>660 nm</td>
<td>0.72</td>
<td>63 fs</td>
<td>0.12</td>
<td>690 fs</td>
<td>0.10</td>
<td>6 ps</td>
<td>0.26</td>
</tr>
</tbody>
</table>

These parameter values are used to represent the wavelength dependent "coherent spike" amplitudes in the TG measurements.

The uncertainties are higher for these parameter values due to their small amplitude and the limited fitting range (10 ps).

at the red edge (660 nm–630 nm) of the absorption spectrum, whilst the signals measured on the blue side (606 nm and 582 nm) do not show oscillations that can be clearly identified as fundamental frequencies. In addition to peaks associated with fundamental vibrational frequencies, low frequency peaks can be identified, arising from the difference frequencies of the fundamental oscillations (e.g., $\nu_6 - \nu_3$ peak at 95 cm$^{-1}$ and $\nu_6 - \nu_2$ at 239 cm$^{-1}$).

Figure 9 displays the WD-TG signals of PERY in DMSO with excitation wavelength varying from the red edge of the first vibronic peak to the top of the second vibronic peak. As with the WD-TG traces for Nile Blue, the WD-TG signals for PERY exhibit slowly decaying (∼700 fs and ∼2 ps) components (fitting results not shown) that are wavelength independent. In comparison to the WD-TG signals for Nile Blue in acetonitrile, the magnitude of the coherent spike of PERY in DMSO demonstrates an opposite wavelength dependent trend. The coherent spike amplitude decreases as the excitation wavelength is tuned from the blue side to the red side of the absorption maximum.

The strong modulations associated with the 139 cm$^{-1}$ oscillation mode and the 278 cm$^{-1}$ second harmonic are clearly observed in the TG traces and persist for several picoseconds. The well resolved, large amplitudes of these oscillations display a similar wavelength dependence in both the 3PEPS signals for the PERY systems and the TG signal for Nile Blue/acetonitrile; the magnitude of the oscillations is largest for excitation on the red edge of the absorption spectrum, decreases upon shifting to the blue, and is barely observed in the traces collected with the bluest (493 nm) pulses. A similar wavelength dependent trend is also observed with the PERY/benzene and R6G/methanol systems (results not shown).

In contrast to the WD-3PEPS data presented in Figs. 5 and 6, the WD-TG traces are also probe dependent. The most striking contrast between the Nile Blue/acetonitrile and the PERY/DMSO data is in the wavelength dependent coherent spike amplitude. Previously, the presence of the coherent spike was attributed to the sub-100 fs, ultrafast solvation time scale, so that the increased coupling of this process leads to an increased magnitude of the coherent spike.

FIG. 8. Wavelength dependent power spectra for TG signals from Nile Blue in acetonitrile measured at (a) 660 nm, (b) 630 nm, and (c) 606 nm. Spectral intensity was normalized to the most intense mode: the 590 cm$^{-1}$ mode for 660 nm and 630 nm and the 100 cm$^{-1}$ mode for the 606 nm power spectrum, hence direct comparison of absolute frequency intensity from different spectra should be avoided. Only those frequencies readily attributed to fundamental and combination modes are labeled. TG traces were cut at 4 ps and slow relaxation time scales (Table III) were removed prior to the Fourier transform to increase contrast of underdamped oscillations in the signals. The spectral resolution is ∼8 cm$^{-1}$. Inset in panel (a) shows the high frequency portion of the power spectrum at 660 nm with greater resolution (∼4 cm$^{-1}$) obtained from the Fourier transform of the full 10 ps TG trace. The laser pulse spectra (dashed line) for 40 fs intensity FWHM pulses are superimposed over the spectra.
The WD-TG results show that the vibronic bands contribute significantly to the coherent spike amplitude. A detailed explanation for these effects will be provided in paper II.

C. Temperature dependent 3PEPS results

The temperature dependent 3PEPS (TD-3PEPS) profiles displayed in Fig. 10 were measured for PERY in benzene at four different temperatures ranging from 10 °C to 70 °C (excitation wavelength=530 nm). The results are qualitatively similar to the wavelength dependent PERY data presented in Fig. 6. As the temperature is increased, the 3PEPS profiles exhibit a slower initial decay (increasing from 105 fs at 10 °C to 176 fs at 70 °C). This result is surprising as we would expect the time scales of the solvation dynamics to become faster at increased temperatures. The results from analyzing the raw 3PEPS data with a Linear Prediction-Singular Value Decomposition (LP-SVD) algorithm are

![Graphs and tables]

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The WD-TG results show that the vibronic bands contribute significantly to the coherent spike amplitude. A detailed explanation for these effects will be provided in paper II.
A discernable temperature dependence. Although the damp-
damped fundamental and the second harmonic oscillations do not exhibit

for comparison, we also analyzed the wavelength dependent

to be temperature independent (\( \tau \approx 700 \) fs), the damping
time of the second harmonic oscillation is strongly tempera-
ture dependent (decreasing from \(~660\) fs at 10 °C to \(~300\) fs
at 70 °C). The phases of both oscillations are relatively tem-
perature independent with values of \(~0.9\) rad for the funda-
mental and 1.5 rad for the second harmonic.

The most pronounced temperature dependent trends in
the TD-3PEPS data are the amplitudes of the oscillations and
the time constants of the exponential decays. As Fig. 10
shows, at elevated temperatures the amplitude of the second
harmonic frequency is considerably more pronounced. The
amplitudes of the fundamental and the second harmonic os-
cillations display contrasting temperature dependent trends.

While the amplitude of the fundamental oscillation decreases
with increasing temperature (3.1 fs at 10 °C to 2.1 fs at
70 °C), the second harmonic amplitude increases (1.1 fs
at 10 °C to 1.6 fs at 70 °C). These effects lead to a clearly
resolved, temperature dependent peak within the first 100 fs.

Two decaying components are clearly resolved: a fast (\(~150\)
fs) component and a slower picosecond component. The am-
plitudes of these two components display contrasting tem-
perature dependent properties. As would be expected at
higher temperatures, the picosecond component proceeds
faster (3.5 ps at 10 °C to 1.9 ps at 70 °C) and in striking
contrast, the fast component slows down at elevated tem-
peratures (105 fs at 10 °C to 176 fs at 70 °C).

The temperature dependent 3PEPS behavior of PERY in
benzene can be partially explained by the wavelength depen-
dent effects observed in Figs. 8 and 9. The absorption spec-
trum of PERY in benzene exhibits a particularly strong tem-
perature dependent spectral shift (\(~2.5\) cm\(^{-1}\)/°C); conse-
quently, the absorption maximum shifts by \(~150\) cm\(^{-1}\)
to higher energy as the temperature is increased from 10 to
70 °C (Fig. 11). The shifting of the absorption spectrum to
the blue leads to detuning of the laser pulse from the absorp-
tion maximum at elevated temperatures. Hence the TD-
3PEPS data contain a portion of WD-3PEPS character, and
careful analysis is required to extract the pure temperature
dependent properties from the wavelength dependent prop-
ties. For example, higher energy levels of the low frequency
mode (139 cm\(^{-1}\)) observed in the PERY data are signifi-
cantly occupied at room temperature in contrast to most of
the vibrational modes observed in Nile Blue (Table VI).

Though the populations of the excited levels do not change
appreciably within the temperature range (the population of
\( n = 1 \) changes from 0.49 at 10 °C to 0.56 at 70 °C), the mag-
nitude of the second harmonic in the TD-3PEPS data in-
creases by 50% over the same temperature range (Table VII).

Preliminary analysis based on a thermal population of a har-
monic vibrational mode fails to describe the data (not
shown).

Tabulated in Table VII. The LP-SVD analysis effectively
models the 3PEPS data as a sum of exponential decays and
damped cosinusoids with phases,

\[
\tau_i(T) = \sum_j A_j \exp\left(-\frac{t}{\tau_i}\right) 
+ \sum_j A_{vib,j} \exp\left(-\frac{t}{\tau_{vib,j}}\right) \cos(\omega_{vib,j}t + \phi_{vib,j}).
\]

For comparison, we also analyzed the wavelength dependent
3PEPS profiles of PERY in benzene and the results are tabu-
lated in Table VIII.

As Table VII illustrates, the frequencies of both the funda-
mental and the second harmonic oscillations do not exhibit
a discernable temperature dependence. Although the damp-
ing constant of the fundamental 139 cm\(^{-1}\) oscillation appears
to be temperature independent (\( \tau_{vib} \approx 700 \) fs), the damping
time of the second harmonic oscillation is strongly tempera-
ture dependent (decreasing from \(~660\) fs at 10 °C to \(~300\) fs
at 70 °C). The phases of both oscillations are relatively tem-
perature independent with values of \(~0.9\) rad for the funda-
mental and 1.5 rad for the second harmonic.

TABLE VII. Temperature dependent 3PEPS LP-SVD parameters for PERY in benzene.

<table>
<thead>
<tr>
<th>Temperature and detuning factor</th>
<th>Amplitude</th>
<th>Frequency</th>
<th>Time constant</th>
<th>Phase</th>
</tr>
</thead>
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<tr>
<td></td>
<td>( A_i )</td>
<td>( \omega_i )</td>
<td>( \tau_i )</td>
<td>( \phi_i )</td>
</tr>
<tr>
<td>10 °C 118 cm(^{-1}) Oscillation 1</td>
<td>3.14</td>
<td>136</td>
<td>670 fs</td>
<td>0.92</td>
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<tr>
<td></td>
<td>Oscillation 2</td>
<td>1.08</td>
<td>275</td>
<td>667 fs</td>
</tr>
<tr>
<td></td>
<td>Exponential 1</td>
<td>1.17</td>
<td>105 fs</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Exponential 2</td>
<td>3.3</td>
<td>3.5 ps</td>
<td>1</td>
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<tr>
<td>20 °C 143 cm(^{-1}) Oscillation 1</td>
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<td>136</td>
<td>710 fs</td>
<td>0.92</td>
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<tr>
<td></td>
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<td>271</td>
<td>454 fs</td>
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<td>Exponential 2</td>
<td>3.31</td>
<td>3.4 ps</td>
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</tr>
<tr>
<td>50 °C 218 cm(^{-1}) Oscillation 1</td>
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<td>652 fs</td>
<td>0.96</td>
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<td></td>
<td>Oscillation 2</td>
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<td>371 fs</td>
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<tr>
<td></td>
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<td>125 fs</td>
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</tr>
<tr>
<td></td>
<td>Exponential 2</td>
<td>3.9</td>
<td>2.3 ps</td>
<td>1</td>
</tr>
<tr>
<td>70 °C 268 cm(^{-1}) Oscillation 1</td>
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<td>134</td>
<td>720 fs</td>
<td>1.15</td>
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<td></td>
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<td>271</td>
<td>295 fs</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>Exponential 2</td>
<td>5.4</td>
<td>1.87 ps</td>
<td>1</td>
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</tbody>
</table>

The detuning factors are calculated from the difference between the peak of the laser spectrum (set at 530 nm) and the peak of the temperature dependent absorption spectrum.

The amplitude parameters are unscaled values.

The oscillations were modeled as \( A_i \exp(-t/\tau_i)\cos(\omega_i t + \phi_i) \) with finite phases \( \phi_i \).

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V. CONCLUDING REMARKS

The striking changes in both photon echo peak shift and transient grating signals as a function of excitation wavelength strongly imply that a detailed model for the influence of intramolecular vibrations on these nonlinear signals is an essential prerequisite to the extraction of meaningful dynamical information from such data. A key observation is that in addition to fundamental frequencies, frequencies assignable as differences between two vibrational mode frequencies are clearly visible in the data. Mechanisms accounting for the origin of these differences frequencies will be described in paper II, in the context of numerical simulations of wavepacket dynamics in TG and 3PEPS profiles.

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