Research Article

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Ultrafast dephasing in hydrogen-bonded pyridine–water mixtures

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Abstract: Hydrogen-bonded mixtures with varying concentration are a complicated networked system that demands a detection technique with both time and frequency resolutions. Hydrogen-bonded pyridine–water mixtures are studied by a time-frequency resolved coherent Raman spectroscopic technique. Femtosecond broadband dual-pulse excitation and delayed picosecond probing provide sub-picosecond time resolution in the mixtures temporal evolution. For different pyridine concentrations in water, asymmetric blue versus red shifts (relative to pure pyridine spectral peaks) were observed by simultaneously recording both the coherent anti-Stokes and Stokes Raman spectra. Macroscopic coherence dephasing times for the perturbed pyridine ring modes were observed in ranges of 0.9–2.6 ps for both 18 and 10 cm^{-1} broad probe pulses. For high pyridine concentrations in water, an additional spectral broadening (or escalated dephasing) for a triangular ring vibrational mode was observed. This can be understood as a result of ultrafast collective emissions from coherently excited ensemble of pairs of pyridine molecules bound to water molecules.

Keywords: coherent anti-Stokes Raman scattering, cooperative phenomenon, non-linear optics, spectroscopy

1 Introduction

Hydrogen bonding is one of the most important yet common chemical interactions. It is one of the main factors in giving proteins their secondary structures as well as giving rise to the double helix shape of DNA [1]. Hydrogen bonding also serves to help enzymes bond to substrate molecules, antibodies to antigens and transcription factors to both DNA and each other. As such, the details of hydrogen are so crucial to biological processes and more in-depth understanding is still immensely in demand [2–5]. That is partly because hydrogen bonding and hydrogen bond interactions are difficult to model, and although several different possible models have been offered, they require experimentation to refine [6,7].

In this work, we choose pyridine–water mixtures. Pyridine is remarkably close to pyrimidine in terms of molecular interaction [8] and pyrimidine is one of the two base pair types that bond across the helix structure of both DNA and RNA [9–11]. When pyridine and water are combined in a mixture, several different mixtures can occur. They all form through the process of hydrogen bonding with one or more water molecules. Pyridine–water (Py–W) mixtures can be represented by the general form Py_nW_m in which “Py” represents pyridine, “W” represents water, and “ n ” and “ m ” represent the number of each molecule, respectively. Common mixtures include Py_2W_1 , Py_1W_1 , Py_1W_2 , and Py_1W_3 . One of the best ways to study hydrogen bonding in Py–W mixtures is by using vibrational spectroscopic techniques because the reorientation of pyridine is so slow that it contributes nothing to the overall spectral shifts. This means that any detected shift is necessarily a result of a change in the vibrational mode due to hydrogen bonding [12].

On one hand, ordinary (incoherent) Raman spectroscopic study provides data in frequency domain revealing spectral red shifts due to the hydrogen bonding, which can be compared with the analyses obtained from density functional theory [13]. Vibrational dephasing times can be extracted from spectral profiles [12]. On the other

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hand, in coherent anti-Stokes Raman scattering (CARS) [14] spectroscopy these dephasing times can also be extracted by fitting the observed spectra. In multiplex (femtosecond) time-resolved CARS [15], the beatings due to unresolved ring modes observed and separations of Raman peaks for the mixtures can be extracted, whereas in the interferometric CARS [16] the ultra-precise measurement of Raman shifts can also be obtained in addition to dephasing times. Hydrogen-bonded mixtures are a complicated networked system [17] that needs both time and frequency-resolved detection technique that is able to remove the unwanted non-resonant background. Simultaneous time and frequency resolved detection in ultrafast CARS has been extensively reported [18–29]. In particular, the combination of femtosecond excitation together with picosecond probing technique (referred to as hybrid fs/ps CARS) was developed [20,27,28]. The 10^5 -fold enhancement due to coherent excitation of the pyridine ring modes over standard incoherent Raman signal [25] and detection of pyridine molecules in a gas at 30 ppm [26] were demonstrated by this technique.

The theoretical and experimental work for simultaneous CARS and coherent Raman Stokes scattering (CSRS) have been reported [21,22,30–32], and the fs/ps hybrid CARS technique has been improved further by controlling asymmetry in the simultaneously recorded CARS and CSRS spectra [23,24] as offering higher spectral resolution.

In this work, we adopt the CARS/CSRS spectroscopic technique developed in refs. [23,24] to study Py–W mixtures with varied concentrations. The present technique involves three ultrashort pulses: the first two (pump and Stokes pulses) selectively excite only the pyridine ring modes into their macroscopic coherence with a negligible contribution from the background water solvent molecules, and the third pulse (probe) is scattered off to produce both blue and red-shifted spectral peaks. In ref. [24], the authors studied the Py–W mixture at fixed probe delays and introduced a new second-order correlation function in frequency domain to interpret the data. In this work, the ring modes' dephasing times and broadening were measured and analyzed for varied concentrated pyridine in water. Particular interest is dedicated to the higher pyridine concentration in water in context with collective emission phenomena.

2 Materials and methods

We adopt the CARS/CSRS spectroscopy developed in refs. [23,24], which involves three ultrashort pulses: the fs

pump and fs Stokes pulses selectively excite the pyridine ring breathing mode at ν_1 (992 cm^{-1}) and triangular mode at ν_{12} ($1,031\text{ cm}^{-1}$) with a separation of 39 cm^{-1} (see refs. [23,24]) into their macroscopic coherence with a negligible contribution from the background water solvent molecules and the ps probe pulse is scattered off to produce signal to be recorded in the forward direction. The experiment was performed using a ytterbium-doped fiber amplified high-average-power femtosecond laser (Clark-MXR) (Figure 1). This laser creates $\sim 250\text{ fs}$ pulses at a 1 MHz repetition rate with a center wavelength of 1030 nm . These pulses (the laser beam) are then passed through a non-collinear optical parametric amplifier (NOPA – Clark-MXR). First, the output $1,030\text{ nm}$ laser beam is split into two beams inside the NOPA box. One beam is used to produce a broad continuum seed (white light) and the second one is used to produce the second harmonics of the laser beam. These two beams are overlapped in the Beta Barium Borate crystal in non-collinear geometry to generate tunable amplified pump beam either 900 or 914 nm . Next, the residual $1,030\text{ nm}$ beam is split again: one beam is used to produce 520 nm probe beam and the other one is the Stokes beam. The probe beam is passed through a pulse shaper to be either 18 or 10 cm^{-1} narrowband, then through a computer-controlled delay stage before all three beams are recombined at the sample. The generated signal is measured in the forward direction (details of the experimental setup have been reported [23,24]). Powers of the input beams before sample were measured to be about 100 mW (Stokes), 40 mW (pump), and $0.5\text{ }\mu\text{W}$ (probe). For this experiment, the probe delay stage varied between -2 ps and 8 ps with an increment of 13 fs . At the -2 ps delay, the probe pulse strikes the sample 2 ps before

Figure 1: Experimental setup. A femtosecond laser with a modified non-collinear parametric amplifier produces pump (orange), Stokes (brown), and probe (green) beams. The probe beam passes through a home-made pulse shaper and delay stage to be combined with other two on pyridine–water complex in a collinear configuration. A spectrograph with an EMCCD records both anti-Stokes and Stokes Raman signal simultaneously in the forward direction at each probe delay up to 8 ps .

the arrival of the pump and Stokes pulses. While at 8 ps delay, the probe pulse strikes the sample 8 ps after the pump and Stokes pulses. At each delay increment 30 (or 10) samples were taken by an electron multiplied charge-coupled device (EMCCD – Andor) with a spectrograph (Andor) and averaged with each sample having an integration time of 0.2 s. This procedure was repeated for every volume concentration of pyridine in water, ranging from pure pyridine to 10% pyridine in water in 10% increments including empty cuvette and pure water sample. The samples were prepared with pyridine (grade 99.8% – Sigma Aldrich) and distilled water.

3 Results and discussion

The data for all Py–W mixtures were treated by several methods. First, the background count of ~ 300 was subtracted from each datum. Then, linear scale of data as a function of probe delay was converted into a logarithmic scale. In a logarithmic scale, exponential function with a particular dephasing time converts into a linear function where its slope is a measure of the dephasing time. To compare the results for different mixtures, the processed data were next normalized to the highest peak in each mixture, respectively. Finally, the data were truncated at 1.5 ps for 18 cm^{-1} probe pulse (or 3.4 ps for 10 cm^{-1} probe pulse), leaving out all data from -2 ps to this delay time. This truncation was done because four-wave mixing plays a large role in this region and is irrelevant to the investigation at hand. Delay times 1.5 and 3.4 ps are selected because they are node positions of these probe pulses [20]. In the region of interest to this study, this background contamination had a negligible effect. In Figure 2 spectral data (subject to the methods above) are shown. The set on the top (or bottom) is for 18 cm^{-1} (or 10 cm^{-1}) probe pulse. From left to right are decreasing concentrations of pyridine in water, starting from pure pyridine and stepping down to 10% pyridine in water in 10% increments. The CARS and CSRS plots are displayed in a mirrored fashion (CARS on top and CSRS on the bottom) to help clarify both the symmetric and asymmetric aspects of two measurements. Peaks are initially at ν_1 ($\sim 992\text{ cm}^{-1}$) and ν_{12} ($\sim 1,031\text{ cm}^{-1}$) for pure pyridine, although they shift in response to concentration changes.

The probe pulse has a full width at a half maximum (FWHM) of 18 cm^{-1} , while the pyridine peaks are separated by 39 cm^{-1} ; so we expected the two peaks to be spectrally resolved, and this can clearly be seen above. The connecting blurs, however, are result of broader

Figure 2: A mirror images of coherent anti-Stokes (top row in each set) and Stokes Raman (bottom row in each set) signals as functions of probe pulse delay for pyridine concentrations from 10 to 90% in water with pure pyridine (far left) for comparison. A top (bottom) set is for probe pulse with 18 cm^{-1} (10 cm^{-1}) width. Upper (lower) labels correspond to anti-Stokes (Stokes) Raman shifts.

bandwidth of the low intensity portions of the probe. These portions are not sufficiently narrowband to resolve the two peaks distinctly and, thus, create a beating. As the peaks shift, as a result of the formation of Py–W mixtures, frequency of the beating also changes. The change is subtle and will be elucidated later. For the probe pulse with a FWHM of 10 cm^{-1} is narrow enough to resolve the pyridine two peaks, thus no beating is observed. CARS and CSRS spectra are mostly symmetric. Dephasing times and beating frequency were extracted by fitting the unnormalized data. The dephasing times for pure pyridine at ν_1 and ν_{12} were found to be $T_d = 2.6\text{ ps}$ and 2.0 ps , respectively, as reported earlier [26].

Figure 3: Macroscopic coherence dephasing (in logarithmic scale) as a function of probe delay for ν_1 (fitted by magenta lines) and ν_{12} (fitted by green lines) peaks for 100% pyridine, 90 and 10% pyridine in water. The CARS and CSRS data are shown in blue and red colors, respectively. The values of dephasing times (T_d) are noted in each figure. Left (right) column for probe pulse with 18 cm^{-1} (10 cm^{-1}) width.

Dephasing times are alternately determined as $T_d/2 = 1.3$ and 1 ps [12].

In Figure 3, the fitted data are shown for pure pyridine, 90 and 10% pyridine in water arranged from top to bottom. For both probe pulses with different widths, dephasing rates are observed to be the same. Dephasing times are also found to be the same for both CARS and CSRS signals for all mixtures, except for 60 and 30% mixtures (about 0.2 ps slight discrepancy between CARS and CSRS). The data for 10 cm^{-1} broad probe are a slightly noisier since it is averaged by ten samples only; thus, some of the ν_{12} peaks for 40–60% mixtures were weak.

The beating in pure pyridine exhibits a period of 0.85 ps for both CARS and CSRS. This corresponds to a separation of 39 cm^{-1} between the peaks of the ring modes [21]. At 90% pyridine in water, CARS and CSRS both have a beating period of 0.97 ps, which corresponds to a separation of 34 cm^{-1} between the peaks. This indicates that the peaks are shifting to be closer together (i.e., they are both shifting in the same direction, but the peak ν'_1 is shifting faster). In 10% pyridine the beating period was 1.05 ps for CARS and 0.99 ps for CSRS, which corresponds to a separation of 32 and 34 cm^{-1} , respectively.

The general trend is that the two peaks are shifting in such a way to be closer to one another. The peak at ν_1 shifts more dramatically than the ν_{12} peak, closing the separation by $\sim 7 \text{ cm}^{-1}$. At low concentrations of pyridine, the difference between CARS and CSRS starts to manifest itself. Overall fitting parameters were estimated with errorbars less than ± 0.1 ps for dephasing times and ± 0.02 ps for periods.

4 Additional broadening and ultrafast collective emissions

Dephasing time for ν'_1 mode in the ordinary Raman spectral data for different pyridine concentrations in water was numerically extracted by the Fourier transforms [12]. However, in the present work, we obtained dephasing times for both ν'_1 and ν'_{12} directly from the time-resolved CARS/CSRS spectrogram data. As seen from Figure 4, data for ν'_1 are consistent with the extracted numerical data [12] up to a factor of 2. This represents decay of the intensity

Figure 4: Dephasing times in picoseconds for the ν_1 and ν_{12} modes for CARS at various volume concentrations of pyridine in water (blue curves) and FWHM in wavenumber for these modes at 1.5 and 3.4 ps delay times for probe pulses with 18 and 10 cm^{-1} widths, respectively.

rather than the amplitude of the signal. In Figure 4, data for ν_{12} mode were particularly intriguing. Pure pyridine has a dephasing time of 2 ps and at 90% pyridine in water the dephasing time drops sharply down to 1.4 ps. However, as the concentration of pyridine decreases further, it increases gradually back to 2 ps at 10% pyridine in water. This escalated dephasing rate effect will be explained later in the context of collective emission. This effect has not been observed in the case of spontaneous Raman scattering experiment as in ref. [12]. At higher concentrations (80 and 90%), mixtures form mostly (Py_2W_1) pairs of pyridine molecules bonded to single water molecules. As the ratio of pyridine to water decreases, the water-rich $\text{Py}-\text{W}$ mixtures (Py_1W_1 , Py_1W_2 , and Py_1W_3) become more common. FWHM for both ν_1 and ν_{12} CARS peaks is obtained and shown in Figure 4 (see, red curves). At 90% pyridine in water the peaks have additionally broadened compared to the cases for pure pyridine and the 10% mixture. However, due to the weak signals detected at some cases of 60, 50, and 40% mixtures excited with 10 cm^{-1} probe pulse, their FWHMs are large. But for the strong signals, the additional broadening is clearly demonstrated. It is also worth noting that ν_1 peak also demonstrates this effect (see red curves for this peak in Figure 4) and the additional broadening in the CSRS data was observed to be not as consistent as for

the CARS data as in Figure 4. The main result of this work is thus an observation of this dip in dephasing time dependence on pyridine volume concentration in water. Escalated rate of decay process from atoms or molecules is one of the key characteristic measures of the so-called collective effect [33]. The pyridine-rich mixtures (80 or 90% pyridine and 20 or 10% water) tend to form mostly Py_2W_1 mixtures in addition to pure pyridine molecules [15]. However, it is important to note that only pyridine ring modes are selectively excited but not the ones of water. As a result, we believe that this system consists of mostly pairs of pyridine molecules excited in phase. From these pairs, therefore, collective emissions are expected. Although, the present system is not two-level atomic system, an analogy between the standard collective emission from coherently prepared two-state system and coherent Raman scattering from multi-state system has been pointed out [34].

In a standard theory, collective emissions from ensemble of two-state atoms are governed by their dipole–dipole interactions [33]. They collectively emit a pulse of light when excited by a laser to its phased coherent superposition of two states, as long as radiative transition is allowed between them. The decay (i.e., emission) occurs on a time scale much shorter than spontaneous decay from the independent individual atoms (or molecules). The picosecond collective emissions from alkali atomic ensemble excited by femtosecond laser pulses have been extensively studied in a series of experiments [35–38]. The present system of pairs of molecules is simplified into three-level system considering only the triangular ring mode. As mentioned above, for CARS/CSRS only pyridine mode (though perturbed by hydrogen bonding) is excited effectively preparing an ensemble of the pair pyridine molecules. The two molecules are excited by the pump and Stokes fields. The broadening of optical and Raman transitions depends on randomly perturbed pump and Stokes fields by the interactions with phonons (ring vibrations) and also with water molecules. The strength of the interaction depends on the dipole moment of these systems and the effective dipole moment of the system of two molecules is given by $\wp_{\text{eff}} = (\wp_1 e^{i\phi_1} + \wp_2 e^{i\phi_2}) / \sqrt{2}$, where $\wp_1$ and $\wp_2$ are the dipole moments of two molecules and ϕ_1 and ϕ_2 are the phases of molecular dipoles.

On one hand, if the dipoles are far away (individual molecules), then the relative phases between the molecular dipoles are random and after averaging over these phases, the effective dipole is given by $\langle |\wp_{\text{eff}}|^2 \rangle_{\phi_1, \phi_2} = (|\wp_1|^2 + |\wp_2|^2) / 2 = |\wp_1|^2$. This means that the coupling with the pump and Stokes fields as well as with the broadening is the result of individual molecules.

On the other hand, if the molecules are close to each other (in this case, bound together with an “invisible” water molecule) within the field wavelength range or much smaller, then the phases are approximately the same ($\phi_1 \approx \phi_2$). For example, a similar physical process occurs when two excited dye molecules are close to a nanoparticle where collective states involve two groups of transitions: super-radiant and sub-radiant states that give rise to bi-exponential decays [39,40]. Due to an in-phase ($\phi_1 \approx \phi_2$) linear combination of these states, the dipole moments become larger. For instance, the effective molecular dipole is doubled: $\langle |\mu_{\text{eff}}|^2 \rangle_{\phi_1, \phi_2} = 2|\mu_1|^2$, suggesting the emission occurs two times faster. The molecular coherence is the main factor to enhance CARS/CSRS signal [25,34]. Therefore, fast dephasing of this coherence means fast (collective) emission to occur. Rigorous theoretical simulations are underway and will be presented in a separate work.

5 Conclusion

Hydrogen-bonded pyridine–water mixtures were revealed to be a complicated networked system by using a specially designed time-frequency resolved coherent Raman spectroscopic technique. For different pyridine concentrations in water both coherent anti-Stokes and Stokes Raman spectra were recorded as functions of probe delay. Spectral asymmetry in blue versus red shifts of pyridine ring modes due to hydrogen bonding was observed. Picosecond dephasing times for the perturbed pyridine ring modes were observed in ranges of 0.9–2.6 ps. For high pyridine concentrations in water, an additional spectral broadening (i.e., escalated dephasing) was observed. In particular, for a triangular ring vibrational mode, this can be understood as the effect of ultrafast collective emissions from coherently excited pairs of pyridine molecules bound to water molecules.

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