Published in final edited form as:

J Phys Chem B. 2008 October 23; 112(42): 13167–13171. doi:10.1021/jp805338h.

Ultrafast N-H vibrational dynamics of cyclic doubly hydrogen-bonded homo- and heterodimers

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Abstract

Hydrogen-bonded interfaces are essential structural elements in biology. Furthermore they can mediate electron transport by coupling the electron to proton transfer within the interface. The specific hydrogen-bonding configuration and strength have a large impact on the proton transfer, which exchanges the hydrogen bonded donor and acceptor species (i.e. $\text{NH}\cdots\text{O} \rightarrow \text{N}\cdots\text{HO}$). Modulations of the hydrogen-bonding environment, such as the hydrogen-bond stretch and twist modes, affect the proton transfer dynamics. Here we present transient grating and echo peak shift measurements of the NH stretch vibrations of four doubly hydrogen-bonded cyclic dimers in their electronic ground state. The equilibrium vibrational dynamics exhibit strong coherent modulations that we attribute to coupling of the high-frequency NH vibration to the low frequency inter-dimer stretch and twist modes and not to interference between multiple Fermi-resonances that dominate the substructure of the linear spectra.

Introduction

Asymmetric hydrogen-bonded interfaces are critical structural motifs in biology. Ultrafast proton transfer across such interfaces play an important role in mediating electron and energy transfer through its coupling to electronic excitation or electron transfer.^{1–4} The coupling provides a basic mechanism for radical transport and substrate activation at protein active sites^{3,5} and has been suggested to be responsible for the photo-stability of DNA and other organic compounds by quickly dissipating the absorbed energy.^{6–8} All theoretical treatments of electron transfer involving hydrogen bonded interfaces identify the proton configuration and attendant vibrational modes as the crucial determinants of the kinetics, especially when the electron transfer traverses an asymmetric interface.^{9,10} However, few experiments have incisively probed the vibrational structure of these asymmetric interfaces.

We now report a detailed study of four cyclic double hydrogen bonded interfaces in solution. The examined systems are the symmetric homo-dimers of 7-azaindole (7AI) and

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Supporting Information Available: Structures and FTIR spectra of dimers with only one OH/NH vibration, TG anisotropies, and TG beat patterns of the four dimers in cyclohexane-d₁₂. This material is available free of charge via the Internet at <http://pubs.acs.org>.

1Hpyrrolo[3,2-h]quinoline (PQ) and their asymmetric hetero-dimers with acetic acid (Ac) (see Figure 1). 7AI and PQ were chosen for their capability for excited state proton transfer within the chromophore upon UV excitation.^{11–17} 7AI and PQ exhibit different hydrogen-bonded configurations in protic solvents giving rise to very different proton transfer rates. The homodimer of 7AI has been studied extensively with ultrafast visible spectroscopy to determine if the proton transfer mechanism is concerted or stepwise,^{13–17} the mechanism, however, remains controversial.^{16,17} We employ infrared spectroscopy to directly monitor the NH/OH bonds involved in proton transfer. The current study focuses on the equilibrium vibrational dynamics of the NH modes in the electronic ground state. The cyclic double hydrogen-bonded dimers exhibit broad and structured vibrational bands near 3000 cm⁻¹. Changes in the hydrogen-bond environment greatly influence the high frequency vibrations as indicated by the large red-shift and breadth of the band that is related to the hydrogen-bonding strength. Previous infrared studies have mainly focused on the homo-dimers of carboxylic acids and 7AI^{18–25} and intramolecular hydrogen bonds.²⁶ The substructures of the broad bands in the linear spectrum are thought to be mainly due to Fermi resonances, where anharmonic coupling of the high frequency NH/OH vibrations to low frequency modes mainly cause further broadening of the spectrum.^{20,23} Coherent modulation in time-domain spectroscopies could be caused by either excitation of multiple Fermi-resonances within the bandwidth of the excitation pulse or by anharmonic coupling to low-frequency inter-molecular modes of the dimer. This article describes transient grating (TG) and echo peak shift (PS) measurements of the four dimers shown in Figure 1. TG and PS experiments measure population relaxation and spectral diffusion dynamics, respectively, and both are sensitive probes of the underlying transition frequency correlation function.²⁷ Both measurements exhibit strong coherent modulations that we attribute to low-frequency inter-dimer stretch and twist modes rather than Fermi-resonances. Such couplings to the low-frequency interdimer modes are interesting as they will influence the excited state proton transfer rates.

Experimental details

Details about the experimental setup are provided elsewhere.^{28,29} Briefly, 45 fs laser pulses centered near 3000 – 3200 cm⁻¹ and with a bandwidth of ~400 cm⁻¹ are split into three replicas that interrogate the sample with finely controlled time delays. For each dimer, the laser spectrum was centered on the NH feature. Both the TG and PS experiments are performed in the box-car geometry. The background free signal produced in the standard $\mathbf{k}_a - \mathbf{k}_b + \mathbf{k}_c$ phase matched direction is detected on a single-element InSb detector. For the PS measurements, the two 2- pulse echoes in the $\mathbf{k}_a - 2\mathbf{k}_b$ and $\mathbf{k}_b - 2\mathbf{k}_a$ directions were also collected to improve the zero-time correction to better than ± 3 fs. Due to the large non-resonant signal of the solvent and CaF₂ sample cell, only data for τ_2 times longer than 150 fs was used in the analysis. In order to analyze the coherent beat pattern, the TGs were fitted to the square of an offset and either two or three exponentials. Except for the 7AI-Ac hetero-dimer, the PSs were also fitted to an offset and a single exponential. The peak shift for the 7AI-Ac hetero-dimer was fit to an offset and two exponentials, one of the exponentials with negative amplitude. The residuals were windowed, zero-padded and Fourier transformed to extract the beat frequencies. The Fourier transforms were then averaged over three identical

measurements except for the TG measurement of the 7AI homo-dimer where only two measurements were performed.

All samples were dissolved in carbon tetrachloride and the experiments were performed at room temperature. 7-azaindole was obtained from Aldrich and used without further purification. PQ was synthesized and purified by Matthew Kanan using standard techniques.³⁰ The homo-dimer solutions were prepared by dissolving 100 μmol in 0.4 mL CCl_4 giving a formal monomer concentration of 0.25 M. The hetero-dimer solutions were prepared by adding ~ 0.95 equivalent glacial acetic acid to the corresponding homo-dimer solution. Sub-equilibrium amounts of the acids were used to bias against homo-dimer formation of the acid. At these concentrations, few monomers exist in solutions, as indicated by the weak sharp monomer peaks near 3500 cm^{-1} in the FTIR spectra. Since the hetero-dimers are more strongly hydrogen bound than the homo-dimers, negligible amounts of homo-dimers exist in the hetero-dimer solutions. This follows from careful inspection of the FTIR spectra. Roughly 20% of the dimers are excited by each of the three 500 nJ IR excitation pulses, giving rise to around 1% of the dimers contributing to the third order signal. Far-IR FTIR spectra were acquired on a Nicolet Magna 860 FTIR spectrometer with a solid-substrate beamsplitter and a DTGS detector with a polyethylene window.

DFT calculations of the equilibrium structures and IR spectra of all four dimers were performed in Gaussian 98 or 03 using the B3LYP/6-311+G(d,p) functional and basis set and the Onsager model for the CCl_4 solvent.

Results

The calculated equilibrium structures of the four dimers are shown in Figure 1. Except for the PQ homo-dimer, planar structures are obtained. The FTIR spectrum (shown in Figure 2) in the NH region of each homo-dimer exhibits a single broad feature overlayed with a clear sub-structure; the sub-structure is stronger for the 7AI homo-dimer than for the PQ homo-dimer. The hetero-dimers on the other hand exhibit several features. A prominent intense sharp feature, with maximum near 3250 cm^{-1} is assigned to the NH stretch. A broad structured feature around 3000 cm^{-1} is assigned to Fermi-resonances and two broad features at 2500 and 1900 cm^{-1} are assigned to the OH stretch. The latter two features are remarkably similar for the two hetero-dimers. These assignments are based on the comparison with FTIR spectra of similar dimers with only one NH/OH bond (see Section S1).

Comparing all four dimers, we note that the NH spectral feature red-shifts in the order of the 7AI-Ac dimer, the PQ-Ac dimer, the PQ-dimer to the 7AI-dimer. We thus assign the hydrogen-bonded strength of the NH vibration to follow this progression. The differences in the NH stretch can be explained by considering the molecular structures. In the PQ-Ac dimer, the NH bond points directly toward the hydrogen-bonding oxygen whereas in the 7AI-Ac dimer, the hydrogen-bonding configuration is more strained. Similarly, the strained twisted structure of the PQ homo-dimer gives rise to a weaker hydrogen-bonding configuration than in the 7AI homodimer. This is further illustrated by the larger monomer contribution to the PQ spectrum. Upon red-shifting, the fairly narrow NH features in the

hetero-dimers broadens and overlaps better with the Fermi-resonances, giving rise to the broad structured bands of the homo-dimers.

All TG and PS measurements exhibit a smooth decay with strong underdamped coherent beats. In order to analyze the beating patterns, the traces were fit with a multiexponential decay that was then subtracted. Figure 3 depicts the TG response measured at the magic angle polarization for the four dimers along with their multi-exponential fits and residuals. Also shown in Figure 3 are the PSs of each dimer along with their exponential fits. No emphasis is given to the fitted time-scales except for the TG anisotropy measurements (see Section S2), where the traces exhibited single exponential relaxation that were fitted with time-scales of 8.1, 14, 19 and 21 ps for the 7AI-Ac, PQ-Ac, 7AI homo- and PQ homo-dimers, respectively. These time scales follow qualitatively the average moment of inertia of the dimers.

The modulation strengths of the TGs and the magnitude of the PSs are correlated with the hydrogen-bond strength of the different dimers. The stronger hydrogen bonded vibrations exhibit a stronger modulation and a smaller peak shift than the less strongly bound vibrations. In order to reveal the underlying physical phenomena that give rise to the quantum beats, the Fourier transform of the beat pattern was performed. These are shown in Figure 4 and the peak frequencies are listed in Table 1. Figure 4 also includes the far-IR FTIR spectra in the 50–650 cm^{-1} region and the Gaussian frequency calculations for the same frequency range. The excellent agreement between the frequency calculations and the FTIR spectra validate the calculations. In comparison to the measured beating pattern, only the inter-dimer stretch and twist modes that directly modulate the hydrogen-bonding strength are shown for the planar dimers. In the figure, the inter-dimer-stretch is given an amplitude of 1 and the inter-dimer twist modes an amplitude of 0.5 relative to the normalized Fourier transforms. For the non-planar PQ homo-dimer, the monomer out-of-plane bending modes also modulate the hydrogen-bonding strength of the high-frequency NH mode. In this case, the two asymmetric plane-bending modes are also shown and given an amplitude of 0.5. These appear at the high-frequency end of the inter-dimer stretch mode. There is very good agreement between the frequencies observed in the TG and PS measurements and the calculated low-frequency modes that modulate the hydrogen-bonding strength, being the inter-dimer stretch and twist modes for the planar dimers and also the asymmetric plane bending modes for the non-planar PQ homo-dimer. We thus attribute the observed beating pattern to anharmonic coupling of the high-frequency NH modes to the low-frequency inter-dimer modes that modulate the NH hydrogen-bonding strength.

Other higher frequency beats are also observed in the TG measurements. These lines are identical for all four samples and originate from the solvent. CCl_4 exhibits three Raman modes at 218, 315 and 464 cm^{-1} , the first two being anisotropic and the latter isotropic.³¹ In the homodyne detected TG experiment, cross terms appear between the resonant solute and non-resonant solvent responses, causing the observed beat pattern to occur at both the solute and solvent frequencies despite the much weaker solvent TG signal. All three CCl_4 modes appear in the parallel and cross TG measurements as well as the anisotropy (not shown). In the magic angle TG measurements, however, only the isotropic Raman mode contributes. Intensity modulations of the homodyne signal do not appear in the PS beat frequencies. The

TG measurements of all four dimers were also performed using deuterated cyclohexane as a solvent (see Section S3). Except for the missing CCl_4 modes and minor frequency shifts, the beating pattern of all four dimers is reproduced in cyclohexane- d_{12} .

Discussion

Theoretical calculations of the acetic acid and 7AI homo-dimers show that the substructures in the linear FTIR spectra are mainly due to Fermi-resonances but coupling to low frequency modes also needs to be included in order to reproduce the linear FTIR spectra.^{20,23} When multiple Fermi-resonances are excited within the bandwidth of a single excitation pulse, beating patterns can be observed at the difference-frequencies. Such beating patterns should change with the excitation pulse frequency depending on the pulse overlap with the involved Fermi-resonances. Beating patterns due to low-frequency modes, however, should remain constant over the spectral range. Previous time-domain spectroscopies of the symmetric homo-dimers of acetic acid and 7AI and a system with an intramolecular hydrogen-bond have shown that the vibrational dynamics of the high-frequency NH and OH modes are dominated by anharmonic coupling to low-frequency modes.^{19,22,24,26} The TG and echo peak-shift measurements described herein are consistent with this conclusion and extend this finding to the present homo- and hetero-dimers. We observe that the inter-dimer stretch modulates both the population relaxation and the spectral diffusion dynamics of the four dimers. The measured beat frequencies of the 7AI homo-dimer are in good agreement with those observed by Nibbering and co-workers.²² Cheatum and co-workers measured the TG response of asymmetric dimers of formic acid and pyridine as well as formic acid and pyrazine.³² These experiments were performed at different wavelengths in resonance with the broad OH feature and displayed a coherent beating pattern. They concluded that the oscillations are due to the excitation of multiple Fermi resonances in accordance with a model that fit the data. From the beating patterns of these integrated measurements alone, it is difficult to distinguish coupling to low-frequency modes from interference between multiple Fermi-resonances. However, due to the excellent agreement between the observed frequencies and the calculated low-frequency modes of all four dimers, as well as calculations of the two dimers used by Cheatum and co-workers, we conclude that the observed beating pattern is due to coupling of the high-frequency NH modes to the low-frequency inter-dimer modes. These are the same low-frequency modes that directly modulate the hydrogen-bonding strength of the high-frequency modes. Notwithstanding, interference between multiple Fermi-resonances can not be completely excluded as contributing to the observed beating pattern. Frequency resolved pump-probe and 2D-IR measurements of these dimers will aid in resolving this issue.

Conclusions

We have performed TG and PS measurements of the NH-vibrations of the two symmetric homo-dimers of 7-azaindole and 1H-pyrrolo[3,2-h]quinoline and their two asymmetric hetero-dimers with acetic acid in solution. All measurements exhibit coherent oscillations due to anharmonic coupling of the high-frequency NH stretch to the low-frequency inter-dimer stretch and twist modes that directly modulate the hydrogen-bonding strength of the high-frequency mode. Furthermore, the strength of the modulation and the magnitude of PS

correlate with the NH hydrogen-bond strength. The strength of the hydrogen-bond thus controls both the linear spectra and the dynamics of the vibration. Whereas Fermi-resonances might be responsible for the substructures in the linear spectra, the vibrational dynamics appear to be dominated by coupling to low-frequency modes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgement

This work was supported by the U.S. Department of Energy DE-FG02-99ER14988, the ACS Petroleum Research Fund (AT) and the NIH GM47274 (DGN). We also gratefully thank Matthew Kanan for synthesizing the PQ compound. PBP further acknowledges fellowships from the Carlsberg Foundation and the Camille & Henry Dreyfus Foundation.

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Figure 1.

The structures of the four dimers calculated using Gaussian 98 or 03.

Figure 2.

FTIR spectra of the four dimers in CCl_4 . The black, red, green and blue line is the FTIR spectrum of the 7AI homo-dimer, the PQ homo-dimer, the 7AI-Ac hetero-dimer and the PQ-Ac hetero-dimer, respectively.

Figure 3.

TG and PS measurements of the four dimers. The TGs were measured at magic angle (MMZZ) while the PSs were recorded using all parallel (ZZZZ) polarization. The black lines are the measured data and the red lines are the exponential fits as described in the text. The green lines are the residuals of the TG measurements.

Figure 4.

Low-frequency FTIR spectra and beat frequencies. (a) The FIR absorption spectra (black lines) are compared to the low-frequency modes obtained in the Gaussian calculations (red sticks). (b) Fourier components of the residual beat patterns of both TG and PS measurements shown in black and green, respectively. These are compared to the inter-dimer modes shown as red sticks. For the three planar dimers, the inter-dimer stretch mode is given the intensity 1 and the two inter-dimer twist modes are given the intensity 0.5. For the non-planar PQ homo-dimer, the monomer plane-bending modes also modulate the NH

vibrations and the two additional asymmetric plane-bending modes are shown as the higher frequency red sticks of 0.5 intensity. The CCl_4 Raman modes are shown as blue sticks.

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Table 1

Experimental beat frequencies compared to the calculated inter-dimer low frequency modes. All values are in cm^{-1} .

	Gaussian calculations				transient grating	echo peak shift
	sym twist	asym twist	stretch	plane bend	plane bend	
7AI-7AI	77	96	109		62, 109	115
PQ-PQ	44	70	81	124	98,128,174	98,128,174
7AI-Ac	99	155	140		104,161	101,137, (164)
PQ-Ac	100	144	136		(102),141,166	(94),140,164