Ultrafast N–H Vibrational Dynamics of Cyclic Doubly Hydrogen-Bonded Homo- and Heterodimers

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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., NH···O → N···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 interdimer 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 sites3,5 and has been suggested to be responsible for the photostability 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 homodimers of 7-azaindole (7AI) and 1H-pyrrolo[3,2-h]quinoline (PQ) and their asymmetric heterodimers 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 homodimers 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 causes 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 intermolecular 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 interdimer 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 $\sim$400 cm$^{-1}$ were 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 were performed in the boxcar geometry. The background-free signal produced in feature. Both the TG and PS experiments were performed in that interrogate the sample with finely controlled time delays.

Results

The calculated equilibrium structures of the four dimers are shown in Figure 1. Except for the PQ homodimer, planar structures are obtained. The FTIR spectrum (shown in Figure 2) in the NH region of each homodimer exhibits a single broad feature overlaid with a clear substructure; the substructure is stronger for the 7AI homodimer than that for the PQ homodimer. The heterodimers, 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 at 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 heterodimers. These assignments are based on the comparison with FTIR spectra of similar dimers with only one NH/OH bond (see section S1, Supporting Information).

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, and the 7AI dimer. We thus assign the hydrogen-bonded signal 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 homodimer gives rise to a weaker hydrogen-bonding configuration than that 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 heterodimers broaden and overlap better with the Fermi resonances, giving rise to the broad structured bands of the homodimers.

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 multieponential decay that was then subtracted. Figure 3 depicts the TG response.
measured at the magic angle polarization for the four dimers along with their multiexponential 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, Supporting Information), 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 homodimer, and PQ homodimer, 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.

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 interdimer stretch and twist modes for the planar dimers and also the asymmetric plane-bending modes for the nonplanar PQ homodimer. We thus attribute the observed beating pattern to anharmonic coupling of the high-frequency NH modes to the low-frequency interdimer 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 nonresonant 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, Supporting Information). Except for the missing CCl\(_4\) modes and minor frequency shifts, the beating pattern of all four dimers is reproduced in cyclohexane-\(d\)\(_{12}\).
coherent oscillations due to anharmonic coupling of the high-frequency NH stretch to the low-frequency interdimer 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.

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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.

**References and Notes**


**TABLE 1: Experimental Beat Frequencies Compared to the Calculated Interdimer Low-Frequency Modes**

<table>
<thead>
<tr>
<th></th>
<th>sym twist</th>
<th>asym twist</th>
<th>stretch</th>
<th>plane bend</th>
<th>transient grating</th>
<th>echo peak shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>7Al–7Al</td>
<td>77</td>
<td>96</td>
<td>109</td>
<td>124</td>
<td>167</td>
<td>62, 109</td>
</tr>
<tr>
<td>PQ–PQ</td>
<td>44</td>
<td>70</td>
<td>81</td>
<td>124</td>
<td>167</td>
<td>98, 128, 174</td>
</tr>
<tr>
<td>7Al–Ac</td>
<td>99</td>
<td>155</td>
<td>140</td>
<td>(102)</td>
<td>141, 166</td>
<td>98, 128, 174</td>
</tr>
<tr>
<td>PQ–Ac</td>
<td>100</td>
<td>144</td>
<td>136</td>
<td>(94)</td>
<td>140, 164</td>
<td>101, 137, 164</td>
</tr>
</tbody>
</table>

*All values are in cm⁻¹.

**Discussion**

Theoretical calculations of the acetic acid and 7Al homodimers 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.20,21 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 homodimers of acetic acid and 7Al 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 heterodimers. We observe that the interdimer stretch modulates both the population relaxation and the spectral diffusion dynamics of the four dimers. The measured beat frequencies of the 7Al homodimer 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.23 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 interdimer 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 cannot 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 homodimers of 7-azaindole and 1H-pyrrrolo[3,2-h]quinoline and their two asymmetric heterodimers with acetic acid in solution. All measurements exhibit