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Vibrational self-trapping in beta-sheet structures observed with femtosecond nonlinear infrared spectroscopy

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Self-trapping of NH-stretch vibrational excitations in synthetic β-sheet helices is observed using femtosecond infrared pump-probe spectroscopy. In a dialanine-based β-sheet helix, the transient-absorption change upon exciting the NH-stretch mode exhibits a negative absorption change at the fundamental frequency and two positive peaks at lower frequencies. These two induced-absorption peaks are characteristic for a state in which the vibrational excitation is self-trapped on essentially a single NH-group in the hydrogen-bonded NH···OC chain, forming a small (Holstein) vibrational polaron. By engineering the structure of the polymer we can disrupt the hydrogen-bonded NH···OC chain, allowing us to eliminate the self-trapping, as is confirmed from the NH-stretch pump-probe response. We also investigate a trialanine-based β-sheet helix, where each side chain participates in two NH···OC chains with different hydrogen-bond lengths. The chain with short hydrogen bonds shows the same self-trapping behavior as the dialanine-based β-sheet helix, whereas in the chain with long hydrogen bonds the self-trapping is too weak to be observable. © 2009 American Institute of Physics. [doi:10.1063/1.3229891]

I. INTRODUCTION

In α-helices, the most common secondary structure in proteins, the peptide (–CO–NH–) groups in the backbone form chains held together by NH···OC hydrogen bonds. The high-frequency internal vibrational modes of neighboring peptide groups in such a chain interact through resonant dipole-dipole coupling. Combined with the translational symmetry of the chain, this tends to delocalize vibrational excitations over the chain to form vibrational excitons. However, for the CO- and NH-stretch vibrations of the peptide group, the situation is different because these modes are strongly coupled to the NH···OC hydrogen bonds. This nonlinear coupling can cause self-trapping of the vibrational excitation, leading to the formation of vibrational polarons.1) Such self-trapping, in which distortion of the hydrogen-bond chain localizes the energy of a vibrational excitation, counteracts the dispersion-induced spreading of vibrational wavepackets along the chain of peptide units. This is one of the requirements for the formation of traveling vibrational solitons,1 which have been suggested as a mechanism for directional energy transport in proteins.2,3)

Whereas vibrational self-trapping has been studied extensively in crystalline model systems,4–11 the existence of vibrational self-trapping in actual α-helices has been demonstrated only recently. It was found that NH-stretch vibrational excitations in α-helices form self-trapped states which are localized on essentially a single N–H bond.12–16 Using femtosecond infrared pump-probe spectroscopy, the self-trapping could be demonstrated in an unambiguous way by directly observing the infrared response upon excitation of the NH-stretching mode.12 It is as yet unknown whether vibrational self-trapping occurs only in α-helices or whether it can also occur in other parts of proteins. Here, we show that self-trapped NH-stretch excitations can also occur in the other common secondary protein structure, the β-sheet. To this purpose we use the same experimental approach as was used previously to demonstrate self-trapping in α-helices,12,13) femtosecond infrared pump-probe spectroscopy.

It is not possible to investigate the NH-stretch response of β-sheets in aqueous solution because of the strong OH-stretch absorption band of water, which overlaps with the NH-stretch band. For this reason, we study synthetic β-sheet structures that can be dissolved in infrared-transparent liquids. We polymerize isocyanopeptides to synthesize long (105–106 dalton) polymers that fold in a proteinlike fashion to give helical strands in which the peptide chains are arranged in β-sheets (see Fig. 1).17,18 The central helical core of the polymers acts as a director for the β-sheet arrangement of the peptide side arms. We study polyisocyanides with L,D-dialanine and with L,D,L-trialanine side chains, which will be referred to as L,D-PIAA and L,D,L-PIAAA, respectively. By engineering the structure of the polymer we can disrupt the hydrogen-bonded –CO–NH··· chain without changing the backbone structure. This gives us the unique possibility to switch the vibrational self-trapping on
FIG. 1. Left: Chemical structures of the polymers studied. Right: Spatial structure of the L,D-L-PIAAA β-sheet helix.17 The backbone is shown in green. For clarity, the octyl esters at the end of the side chains have been omitted.

and off without changing the overall structure of the molecule.

II. EXPERIMENT

Using a setup described previously,19 we generate mid-infrared pump and probe pulses with energies of 10 μJ and ~100 nJ, respectively, that are independently tunable from 2800 to 4000 cm⁻¹. The pulses have a duration of 150 fs, and bandwidths of ~80 cm⁻¹ (pump) and ~200 cm⁻¹ (probe). The cross correlation function is measured using two-photon absorption in Ge placed in a sample cell identical to the one used in the experiments on the solution samples. The pump and probe pulses are focused and spatially overlapped in the sample by means of f=100 mm and f=50 mm CaF₂ lenses (focal diameters of ~400 and ~250 μm for pump and probe, respectively), and transient-absorption changes ∆α are measured by frequency-dispersed detection of the probe and reference pulses using a 2×32 HgCdTe array detector. To cover the entire frequency region of interest, the center frequency of the probe pulse is subsequently tuned to three or four values, chosen such that the observed transient-absorption spectra have sufficient overlap, and the spectra are merged afterward. The probe polarization is at 45° with respect to that of the pump, and using a polarizer after the sample, either the parallel or the perpendicular polarization component of the probe pulse is measured. For the L,D-IAA monomers, rotation-free transient spectra, in which the effect of orientational diffusion of the molecules is eliminated,20 are constructed from the data measured with parallel and perpendicular polarizations (∆αRF=∆α∥+2∆α⊥). The rotational diffusion of the polymers takes place on a time scale much slower than the pump-probe delay ranges investigated here, and therefore can be neglected.

The synthesis and characterization of L,D-IAA, L,D-PIAA, and L,D,L-PIAAA have been reported elsewhere.17,18 The same holds for the synthesis and characterization of random polyisocyanide copolymers in which most (94%) of the –NH– groups are replaced by –O– groups.21 All experiments are carried out at room temperature on ~10 mM solutions (concentration of repeating unit) in CDCl₃, kept between two CaF₂ windows separated by a 1 mm Teflon spacer.

III. RESULTS AND DISCUSSION

To investigate vibrational self-trapping in β-sheet polymers, we measure the change in the NH-stretch absorption spectrum upon excitation of the NH-stretch mode. We study polymers containing either di- or trialanine-based side chains (containing one and two amide groups, respectively, see Fig. 1). As a check, we first measure the pump-probe response of the isocyanide L,D-dialanine (L,D-IAA) monomer, in which no self-trapping can occur.

A. Regular vibrational response in IAA monomers

The gray curve in Fig. 2 shows the steady-state absorption spectrum of L,D-IAA in CDCl₃ (solvent background subtracted). The NH-stretch absorption band at ~3425 cm⁻¹ shows a small splitting, which can be ascribed to the presence of a conformer with a weak intramolecular hydrogen bond.22 The bands in the 2900–3000 cm⁻¹ region are due to CH-stretching modes. The points show the rotation-free (magic-angle) absorption change observed upon resonantly exciting the NH-stretch mode at 3425 cm⁻¹. This Δα spectrum is the regular pump-probe response of an anharmonic oscillator,23 v=0→1 excitation of the NH-stretch mode leads to a Δα<0 peak at the fundamental frequency due to the bleaching of the vibrational ground state and ν=1→0 stimulated emission, and a Δα>0 peak at a lower frequency (3275 cm⁻¹) due to ν=1→2 excited-state absorption. The ~150 cm⁻¹ anharmonic shift of the ν=1→2 frequency with respect to the ν=0→1 frequency is due to the anharmonicity of the NH-stretch potential. The inset shows the absorption change at the ν=0→1 (fundamental) and ν=1→2 fre-
frequency as a function of the delay time with respect to the pump pulse. The absorption changes are found to decay with the same time constant. This confirms that the decays reflect the $v=1$ population relaxation, and from the observed decay constants we find a vibrational population lifetime $T_1$ of 4.3 ± 0.3 ps.

### B. Vibrational self-trapping in PIAA $\beta$-sheet helices

In L.D-PIAA the NH-groups participate in the hydrogen bonds that make up the $\beta$-sheet structure, leading to a red-shift of the NH-stretch frequency with respect to that of the L.D-IAA monomer. The NH-stretch frequency in PIAA [see gray curve in Fig. 3(a)] is 3260 cm$^{-1}$, which is close to the value of 3280 cm$^{-1}$ observed in poly(l-alanine) $\beta$-sheets, indicating that the hydrogen-bond lengths in the synthetic $\beta$-sheet helix are very similar to those in normal $\beta$-sheets.

The response to the NH-stretch excitation of the $\beta$-sheet helices is very different from that of the monomer. Figure 3 shows the transient-absorption change upon exciting the NH-stretch mode in the dialanine-based polymer L.D-PIAA. As in the case of the monomer, the transient-absorption spectrum exhibits a $\Delta \alpha < 0$ peak at the fundamental frequency due to ground-state bleaching and $v=1 \rightarrow 0$ stimulated emission. However, there are two $\Delta \alpha > 0$ bands, whereas in the monomer only one $\Delta \alpha > 0$ band is observed (see Fig. 2).

A similar double induced-absorption feature was observed previously for the NH-stretch mode of $\alpha$-helices, and could be assigned convincingly to self-trapping of the vibrational excitation. To confirm that the double-peak structure observed here is also due to NH-stretch self-trapping, we have performed several experimental checks. First, we have determined the polarization dependence of the observed nonlinear response [see the inset of Fig. 3(a)]. The three bands in the transient-absorption spectrum are found to exhibit identical dependence on the polarizations of pump and probe, which confirms that all three peaks are related to the same vibrating covalent bond. Second, we find that the three bands decay with increasing pump-probe delay with the same time constant [see Fig. 3(b)], which implies that they all arise from the $v=1$ state of the NH-stretching mode. From a least-squares fit to the decay [curves in Fig. 3(b)], we find an NH-stretch $v=1$ population lifetime of 0.77 ps. Finally, we have verified that the second $\Delta \alpha > 0$ peak occurs only when the NH group is in a chain of NH···OC hydrogen bonds. To do this, we have synthesized a polysucyanide, in which >94% of the amide (−NH−CO−) groups is replaced by ester (−O−CO−) groups. In this way, the remaining NH-groups are still hydrogen bonded to carbonyl groups in the same way as in the $\beta$-sheet helix, but these no longer form a hydrogen-bonded chain, see Fig. 4. The nonlinear response of this
polymer shows the regular nonlinear response with a single \( \Delta \alpha > 0 \) peak [see Fig. 4(c)], comparable to the response of the monomer. Hence, the double-peak induced-absorption feature arises only when the NH group is part of a hydrogen-bonded chain. The vanishing of the double-peak structure in the copolymer also rules out Fermi resonance between the NH-stretch and amide II modes as a potential explanation for the double-peak structure in PIAA. This Fermi resonance would involve the first overtone of the NH-stretch mode \( (2v_{\text{NH}}) \) and the combination mode involving one NH-stretch and two amide II quanta \( (v_{\text{NH}}+2v_{\text{amide II}}) \). Because of the comparable intensities of the two observed peaks, the Fermi resonance would have to be almost symmetric, and the splitting of \( \sim 150 \) cm\(^{-1} \) between the peaks would be determined mainly by the anharmonic coupling (in the case of a completely symmetric Fermi resonance, it would be twice the coupling strength). Upon changing from PIAA to the copolymer, the NH-stretch frequency changes by \( 40 \) cm\(^{-1} \) and the amide II frequency by \( 15 \) cm\(^{-1} \). The change in energy mismatch between the \( 2v_{\text{NH}} \) and \( v_{\text{NH}}+2v_{\text{amide II}} \) states is thus much smaller than the presumed Fermi splitting of \( 150 \) cm\(^{-1} \). Consequently, if the double-peak structure would arise from Fermi resonance, changing from PIAA to the copolymer could never result in a complete vanishing of the double-peak structure. Hence, as in the case of the \( \alpha \)-helical system studied previously, this alternative explanation for the double-peak structure can be ruled out. All these checks confirm that both induced-absorption peaks arise from the NH-stretch mode, and that the double-peak structure requires the interaction of neighboring amide units. Based on the above evidence and on the similarity of the transient spectra with those of the NH-stretch self-trapped states in \( \alpha \)-helices, we assign the double-peak induced-absorption structure to self-trapping of the NH-stretch excitations in the \( \beta \)-sheet helices.

In contrast to CO-stretch self-trapping, NH-stretch self-trapping occurs essentially on a single amide unit, forming a small (Holstein) polaron. This is because the NH/NH exciton coupling \( \sim 5 \) cm\(^{-1} \) (Ref. 12) in the hydrogen-bonded chain is so much smaller than the polaron binding energy \( 120 \) cm\(^{-1} \), see below) that it can essentially be neglected. In this limit of strong localization, the vibrational self-trapping is well described by the semiclassical displaced-oscillator model, which describes the self-trapping as follows. The NH-stretch mode of each amide unit is coupled to both of the hydrogen bonds connected to it, and the couplings to these two hydrogen bonds are of similar strength. This can be seen from the fact that removing one of the hydrogen bonds results in a NH-stretch frequency of \( 3330 \) cm\(^{-1} \) (see Fig. 4), which is between the value for two hydrogen bonds \( 3260 \) cm\(^{-1} \), see Fig. 3) and the value for no hydrogen bonds \( \sim 3425 \) cm\(^{-1} \) in solution, see Fig. 2; the value in vacuum is not known, but for the comparable compound N-methylacetamide it is \( 3510 \) cm\(^{-1} \). As a consequence of the NH-stretch/hydrogen-bond couplings, a \( v_{\text{NH}}=0 \rightarrow 1 \) excitation of an amide group results in a contraction of the hydrogen bonds. This decrease in hydrogen-bond length causes a lowering of the NH-stretch frequencies of the excited, and of the two neighboring NH-groups (an effect that can be regarded as the vibrational analog of a Stokes shift).

The NH-stretch frequency of the excited amide group lowers more than that of the two neighboring amide groups since it is coupled to two contracting hydrogen bonds, whereas the neighboring NH-stretch modes are coupled to only one contracting hydrogen bond. This explains the appearance of two \( \Delta \alpha > 0 \) peaks upon exciting the NH-stretch mode: The most redshifted one is due to the amide unit with \( v_{\text{NH}}=1 \), the other due to the two neighboring NH-groups. It may be noted that although an XH-stretch/hydrogen-bond \( (X=O,N) \) coupling is present in all hydrogen-bonded systems, the double \( \Delta \alpha > 0 \) peak structure will occur only if the XH group forms part of an ordered hydrogen-bonded chain, and if hydrogen-bond contraction upon XH-stretch excitation influences not only the XH-stretch frequency of the excited XH group but also that of proximate XH groups. This can be seen from the transient spectrum of the NH:O copolymer [Fig. 4(c)], in which a NH-stretch/hydrogen-bond coupling is present (as can be concluded from the redshift of the NH-stretch frequency compared to the monomeric value), but which exhibits a regular pump-probe response.

In the completely quantum-mechanical description of NH-stretch self-trapping, the delocalization of the NH-stretch and hydrogen-bond excitations (which is neglected in the above semiclassical picture) has to be taken into account. Dipole-dipole coupling between the NH-groups delocalizes the NH-stretch excitation, leading to the formation of vibrons. In the same way, the delocalized hydrogen-bond stretch excitations in the NH\( \cdots \cdot \cdot \cdot \)OC chain form phonons. These phonons interact with the vibrons due to the NH-stretch/hydrogen-bond interaction, leading to the formation of mixed vibron-phonon states. In our system, the NH/NH coupling (vibron bandwidth) is much smaller than the phonon cutoff frequency (which is proportional to the stretching frequency of an individual hydrogen bond), and it can be shown that in this case the mixed vibron-phonon states consist of a vibron accompanied by a lattice (hydrogen-bond) distortion located on a single site (a small polaron). In our experiment, two photons are absorbed per molecule, leading to the formation of two-vibron states. Both the anharmonicity of the NH-stretching mode and the vibron-polaron interaction can lead to the formation of such two-vibron states at energies lower than twice the one-vibron energy (two-vibron bound states). It can be shown that as a consequence of these two effects, a hydrogen-bonded \( \cdots \cdot \cdot \cdot \)CO\( \cdots \cdot \cdot \cdot \)NH\( \cdots \cdot \cdot \cdot \) chain supports two types of two-vibron bound states: one in which the vibron part involves a single \( v=2 \) NH-stretch excitation, and one in which the vibron part involves two \( v=1 \) excitations on neighboring NH-groups.

The two \( \Delta \alpha > 0 \) peaks in the transient-absorption spectrum correspond to transitions from the one-vibron state to either of these two-vibron bound states. A quantitative description of vibrational self-trapping requires advanced mathematical methods. However, in the limit of strong localization, an approximate estimate for an important parameter characterizing the self-trapping, the polaron binding energy (the amount by which self-trapping lowers the energy with respect to the situation of a delocalized NH-stretch mode) can be obtained directly from...
the transient vibrational spectrum. This limiting case applies in the β-sheet since the NH/NH-dipolar coupling (~5 cm⁻¹) (Ref. 12) is much smaller than the binding energy (which turns out to be on the order of 100 cm⁻¹, see below and Ref. 12). Neglecting the NH/NH excitonic coupling, the Hamiltonian of the coupled system of NH-stretch and hydrogen-bond modes in the hydrogen-bonded chain can be written as

\[ H = \sum_{i} (\hbar \Omega \hat{b}_{i}^{\dagger} \hat{b}_{i} + \Delta b_{i}^{2}) + \sum_{j} \frac{1}{2} w(u_{j+1} - u_{j})^{2} \]

\[ + \sum_{m} \chi(u_{m+1} - u_{m-1}) \hat{b}_{m}^{\dagger} \hat{b}_{m} \]

\[ - \sum_{m} \chi'(u_{m+1} - u_{m-1}) \hat{b}_{m}^{2} \hat{b}_{m}^{\dagger}, \]

where the notation of Ref. 12 has been used, in which \( \hat{b}_{i}^{\dagger} \) and \( \hat{b}_{i} \) denote the raising and lowering operators of the NH-stretch mode of amide group \( i \), \( \Omega \) the NH-stretch frequency, and \( u_{j} \) is the displacement of amide group \( j \) from its equilibrium position in the NH-stretch ground state. Since the hydrogen-bond mode is damped and its frequency much lower than that of the NH-stretch mode, we can use an adiabatic approximation and omit the kinetic-energy term of the hydrogen-bond vibrations when predicting the NH-stretch spectra. The intrinsic NH-stretch anharmonicity is characterized by the parameter \( A \), and \( w \) denotes the hydrogen-bond force constant. The second line in the Hamiltonian contains the coupling between the NH-stretch and hydrogen-bond modes, and the last term was added by Edler et al. (Ref. 15) to allow for state-dependent coupling. In this Hamiltonian, which corresponds to the original Davydov model, it is assumed that the two hydrogen bonds connected to a peptide unit couple with the same strength to the NH-stretch mode. Scott proposed an alternative Hamiltonian, in which the NH-stretch mode is coupled only to the hydrogen bond in which it participates as a donor, but such a Hamiltonian gives rise to only one two-vibron bound state, whereas two are observed experimentally. Moreover, the NH-stretch redshift in going from the NH:O copolymer to the 100% NH polymer (Fig. 4) shows that in PIAA, the NH-stretch mode is also coupled to the hydrogen bond in which the peptide group acts as an acceptor. A more realistic description of NH-stretch self-trapping would require a Hamiltonian in which two different coupling strengths are used for each of the two hydrogen bonds connected to a peptide unit.

The vibrational frequencies observed in the transient spectra can be derived from the above Hamiltonian using a semiclassical approximation. It can be shown that in this approximation the polaron binding energy is \( \chi^{2}/w \), and that this is equal to the difference between the frequencies of the NH-stretch fundamental transition and the \( v_{NH}=0 \rightarrow 1 \) transition of the two NH-groups next to a vibrationally excited NH-group, i.e., to the difference between the fundamental frequency and the frequency of the \( \Delta \alpha > 0 \) peak with the highest frequency in the transient spectrum. This frequency difference can be read off from Fig. 3(a) (the value is the same as that observed in an α-helix), and we obtain an estimate of 120 ± 15 cm⁻¹ for the polaron binding energy. The similarity of the transient infrared spectra and of the polaron binding energies in the α-helical and β-sheet systems suggests that the self-trapping behavior is determined mainly by the strength of the hydrogen bonds in the ⋯CO–NH⋯chain (which are similar, as may be concluded from the similar NH-stretch frequencies in the two systems) rather than the overall (three-dimensional) secondary structure. This is in contrast with the situation for the CO-stretch mode, where the three-dimensional structure is essential for the infrared response. The difference stems from the fact that in the latter case the intra- and interchain excitonic (CO/ CO) couplings and the hydrogen-bond/CO-stretch coupling are all of comparable magnitude.

C. Vibrational self-trapping in PIAAA β-sheet helices

We also measured the response of the trialanine-based polymer L,D,L-PIAAA in which each side chain participates in two different hydrogen-bonded ⋯CO–NH⋯chains, see Fig. 1. The polyisocyanide backbone of the β-sheet helix has approximately a 39₁₀ helical conformation so that the amide units in the β-sheet side-chain structure are not exactly in a plane. The resulting displacement effect becomes larger with increasing distance from the polyisocyanide backbone. As a consequence, whereas the inner hydrogen-bonded chain has a hydrogen-bond length comparable to that in a regular β-sheet, the outer chain can be regarded as a stretched out β-sheet. This difference in hydrogen-bond length is also reflected in the NH-stretch frequencies of the amide groups in the inner and outer chains, which are 3260 cm⁻¹ (the same value as in L,D-PIAAA, and as in regular β-sheets) and 3400 cm⁻¹, respectively. The coupling between these two types of NH-stretch modes (on the order of 10 cm⁻¹, assuming transition-dipole coupling) is much smaller than their frequency difference so that mixing of the inner and outer chain NH-stretch modes can be neglected, and the two chains can be regarded as isolated from each other.

The response upon exciting either of the NH-stretch modes is shown in Fig. 5. Whereas the inner chain exhibits
the NH-stretch self-trapping in the same manner as L-D-PIAA, the outer, weakly hydrogen-bonded chain shows an apparently regular pump-probe response (see Sec. III A). This suggests that in the outer chain, the polaron binding energy, and hence the redshift of the high-frequency $\Delta \alpha > 0$ peak with respect to the fundamental frequency, is smaller than the linewidth of the transitions. As a result, the high-frequency $\Delta \alpha > 0$ peak essentially coincides with the $\Delta \alpha < 0$ peak at the fundamental frequency, leading to a partial cancellation of the latter, and leaving only the low-frequency $\Delta \alpha > 0$ peak (redshifted due to the intrinsic NH-stretch anharmonicity).

The much smaller polaron binding energy in the outer chain is not surprising since this energy depends quadratically on the coupling $\chi$ between the NH-stretch and hydrogen-bond mode. This coupling is much weaker in the outer than in the inner chain, as is evidenced by the redshifts of the NH-stretch fundamental frequencies with respect to the (non-hydrogen-bonded) monomer value. These hydrogen-bond induced redshifts (with respect to the monomer is solution) are 165 and 25 cm$^{-1}$ for the inner and outer chains, respectively. Since the redshift is approximately proportional to the coupling $\chi$, this implies that $\chi$ is seven times smaller in the outer than in the inner chain. The polaron binding energy is proportional to $\chi^2$ so the polaron binding energy (and hence the redshift of the high-frequency $\Delta \alpha > 0$ peak) in the outer chain may well be less than the linewidth of the NH-stretch band ($\sim 30$ cm$^{-1}$), resulting in a vanishing of the double-peak $\Delta \alpha > 0$ structure in the spectrum.

IV. CONCLUSIONS

We have observed self-trapping of NH-stretch vibrational excitations in synthetic $\beta$-sheet structures by measuring the response of the NH-stretch mode upon $n_{NH}=0\rightarrow 1$ excitation in a time- and frequency-resolved manner. Although the $\beta$-sheet structure was a synthetic one, the same self-trapping behavior should occur in $\beta$-sheets in proteins. Interestingly, the results on PIAAA show that stretching the $\beta$-sheet structure can decrease the NH-stretch/hydrogen-bond coupling sufficiently to make the polaron binding energy less than the linewidth, making the self-trapping effect so weak as to be unobservable.

One important advantage of studying vibrational self-trapping in synthetic $\beta$-sheet structures is that the structure of the isocyanopeptide polymers can be controlled by tailoring of the side branches and the hydrogen-bonding network in the $\beta$-sheets. In particular, it is possible to disrupt the NH–OH hydrogen-bond chain by replacing $>94\%$ of the –NH– groups with –O– groups, upon which the self-trapping is observed to disappear. Such precise control of the NH-stretch self-trapping in synthetic $\beta$-sheet structures makes it possible to investigate the role of the molecular (and notably hydrogen-bond) conformation in vibrational self-trapping in unprecedented detail.

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