Structure and dynamics of complex hydrogen-bonded systems
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Two-dimensional vibrational spectroscopy of a molecular shuttle

5.1 Introduction

Investigation of the dynamical behavior of molecular machines requires time-resolved methods with high structural sensitivity. Ideally, one would like to know the relative positions and orientations of the components of a molecular machine at various stages of the motion. Such information would provide a valuable insight into the operation mechanism of molecular machines. As already shown, this kind of structural sensitivity can be achieved using two-dimensional and two-color infrared spectroscopy (see Chapter 3 and 4). 2D-IR Spectroscopy allows to determine molecular conformations by measuring couplings between molecular vibrations. These couplings depend on the relative orientation and distance between the vibrating chemical bonds. The 2D-IR spectrum can therefore give direct access to the conformation of a molecule or its parts. 35, 51, 68, 86–88

Here, we present a first step towards experiments with both structural sensitivity at the molecular level and sufficient time resolution to observe molecular motion of rotaxane-based devices. Investigation of the relative positions and orientations of the mechanically interlocked components can be determined from their 2D-IR spectra. We demonstrate how we can use 2D-IR spectra of separate components and model compounds to disentangle the spectrally congested 2D-IR spectrum of the succinamide-naphthalimide rotaxane shown in Fig. 5.2A. This rotaxane-based shuttling device, previously investigated by Brouwer et al., 3 consists of a benzylicamide-based macrocycle and a succinamide-naphthalimide-based thread. In the electronic ground state, the macrocycle binds predominantly to
the succinamide station (equilibrium constant for succinamide binding $>100$). In the presence of an electron donor, UV excitation of the naphthalimide station leads to its reduction. The CO groups of the naphthalimide radical anion thus created are much stronger hydrogen-bond acceptors than those of the succinamide station (equilibrium constant for binding of the naphthalimide radical anion $>1500$). As a consequence, the macrocycle shuttles from the succinamide to the naphthalimide station, a process that in solution can occur in less than a microsecond (for further details, see the next chapter).

5.2 Materials and methods

We have used 2D-IR and 2-color pump-probe spectroscopy to probe the structure of the naphthalimide rotaxane. These techniques are described in Sections 2.3.4 and 2.3.5. The synthesis and purification of the rotaxanes and the naphthalimide station have been described in detail elsewhere. The experiments were carried out at room temperature on a 3 mM solution of the rotaxane and a 5 mM solution of the naphthalimide station in water-free CDCl$_3$. The sample was kept in a sealed, 1 mm thick, IR sample cell.

5.3 Results and discussion

5.3.1 Decomposing the 2D-IR spectrum of a molecular shuttle

Figure 5.1 shows the steady-state absorption spectra of the naphthalimide and succinamide rotaxane in CDCl$_3$, with the absorption peaks numbered according to the notation in Fig. 5.2A. The spectrum of the succinamide rotaxane studied in Section 4.3.4 is significantly less congested compared to the spectrum of this molecular shuttle. Peak 1 in the steady-state absorption spectrum of the molecular shuttle (at 1641 cm$^{-1}$) is assigned to the CO-stretch mode of the thread. The peak at 1658 cm$^{-1}$ consists of two contributions coming from the CO-stretch mode of the macrocycle (2) and the antisymmetric CO-stretch mode of the naphthalimide station (4as). The other two peaks (3 and 4s) at 1631 cm$^{-1}$ and 1698 cm$^{-1}$ belong to the antisymmetric CO-stretch and aromatic ring-stretch mode of the naphthalimide station, respectively (see Section 7.2). Peak 1* found at 1610 cm$^{-1}$ in the spectrum of the succinamide rotaxane arises from the CO-stretch mode of the thread. The succinamide CO-stretch mode has a higher frequency in the molecular shuttle than in the rotaxane of Fig. 3.1, because the CO groups are part of a secondary instead of a tertiary amide group. The congested steady-state absorption spectrum of the molecular shuttle suggests that the 2D-IR experiments on the molecular shut-
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**Figure 5.1:** Steady-state absorption spectrum of the succinamide rotaxane (dashed) and of the succinamide-naphthalimide rotaxane (solid).

te will be challenging compared to the relatively simple 2D spectrum of the short rotaxane discussed in Chapter 3. This is because the molecular shuttle has more CO-stretch modes than the succinamide rotaxane, and additional IR-active naphthalimide aromatic ring-stretching modes (3 and 5) in the same frequency region.

Our experimental results confirm that the CO/CO 2D-IR spectrum of the molecular shuttle, shown in Fig. 5.2D, is too congested to allow for a straightforward interpretation of the cross peaks. This problem can be solved to some extent by measuring 2D spectra of the separate components of the molecular shuttle. The device consists of two parts, the succinamide station with a macrocycle and the naphthalimide station, indicated by gray boxes in Fig. 5.2A. Since these parts do not interact, the 2D spectrum of the shuttle should be the sum of their 2D spectra. This assumption is confirmed by the data shown in Fig. 5.2B–D. Due to solubility problems we have used a succinamide rotaxane with a fullerene stopper instead of a 2,2-diphenylethyl stopper. We can safely do this, since the main object of our study, the succinamide station, is present in both these molecules. The steady-state absorption spectrum of the fullerene-stoppered rotaxane, shown in Fig. 5.2B, consists of the absorption peaks 1 and 2 of the succinamide and macrocycle CO-stretch modes, respectively. As a consequence, the absorption bands of the CO-stretch modes of thread and macrocycle overlap, so that the ring and thread diagonal peaks essentially merge into one feature, and ring/thread cross peaks cannot be distinguished. The steady-state absorption spectrum of the naphthalimide

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Figure 5.2: (A) Rotaxane-based molecular shuttle. The numbering of the CO and NH groups matches that of the absorption peaks in B–D and in Fig. 5.3. (B) 2D-IR spectrum of the left moiety of the shuttle. (C) 2D-IR spectrum of the naphthalimide moiety of the shuttle. s=symmetric, as=antisymmetric CO-stretch mode. (D) 2D-IR spectrum of the complete shuttle.
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station, shown in Fig. 5.2C, contains three well-separated peaks, which, as in case of the complete molecular shuttle, arise from the symmetric ($4s$) and antisymmetric ($4as$) CO-stretch modes, and from aromatic ring-stretch modes ($3$). Each pair of modes gives rise to intense and well-separated cross peaks, leading to a total of 6 cross peaks. These cross peaks and their anisotropies are related to the intramolecular geometry of the naphthalimide stopper. By merging the 2D spectra of Fig. 5.2B and C we obtain the 2D spectrum of the complete molecular shuttle. Using the assignments of B and C, the spectrum of D can now be interpreted qualitatively. The overlap of some of the peaks (notably peaks 1 and 3) hinders the observation of the individual cross-peaks, however. This makes it difficult to obtain quantitative information from the CO-stretch 2D spectrum of the molecular shuttle. In particular, the cross peak between modes 1 and 2, which arises from the ring/thread coupling, overlaps completely with the strong cross peak between modes 3 and 4.

5.3.2 Two-color 2D-IR spectrum of a molecular shuttle

Because of the spectral congestion in the CO-stretch region, we investigate NH/NH and NH/CO couplings as alternative probes of the co-conformation of the molecular shuttle. Figure 5.3 shows the 2D-IR spectrum of the naphthalimide rotaxane with an extended frequency range covering both the NH- and CO-stretch modes. This extended 2D-IR spectrum comprises the (CO)$_{\text{pump}}$/(CO)$_{\text{probe}}$ (shown in Fig. 5.2D and discussed in the previous section), (NH)$_{\text{pump}}$/(NH)$_{\text{probe}}$, and two color (NH)$_{\text{pump}}$/(CO)$_{\text{probe}}$ spectral regions.

The steady-state absorption spectrum of the naphthalimide rotaxane exhibits two NH-stretch peaks in the 3 $\mu$m spectral region, see Fig 5.3B (the peaks are numbered according to the notation in Fig. 5.2A). These peaks correspond to the NH groups in the macrocycle (5) and in the succinamide station (6). Each of the two NH-stretch peaks gives rise to a diagonal peak in the NH/NH 2D-IR spectrum (Fig. 5.3D). However, these diagonal peaks have very different shapes. The peaks of the succinamide NH-stretch mode at ($\nu_{\text{probe}}, \nu_{\text{pump}}$) = (3450, 3450 cm$^{-1}$) are vertical, whereas the features of the macrocycle NH stretch mode at (3300, 3300 cm$^{-1}$) are tilted along the diagonal. As explained in the Chapter 1.7 this tilt reflects the width of the distribution of hydrogen-bond strengths of the rotaxane system.$^{41}$ The succinamide NH groups are not or very weakly hydrogen-bonded. As a result, their NH-stretch absorption band does not exhibit significant spectral inhomogeneity. Because of the proximity of the succinamide and macrocycle NH groups, one might expect cross peaks between the NH-stretch modes at (3300, 3450 cm$^{-1}$) and (3450, 3300 cm$^{-1}$), but these are so weak as to be obscured by the diagonal peaks. We have estimated (see Eq. (3.3)) the coupling between the
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![Figure 5.3](image)

**Figure 5.3:** Two-color 2D-IR spectrum of the molecular shuttle. Absorption peaks are numbered according to the notation introduced in Fig. 5.2A. (A) and (B): absorption spectra in the NH and CO-stretch regions. (C) NH/CO 2D spectrum. (D) NH/NH 2D spectrum. (E) CO/CO 2D spectrum. (F) Horizontal cross section through (C), as indicated by dashed black line.

succinamide and macrocycle NH modes to be $-1.3 \text{ cm}^{-1}$. Calculated NH/NH 2D-IR spectra show that cross peaks will only be visible when the coupling is on the order of $5 \text{ cm}^{-1}$ or larger, and thus the NH/NH 2D-IR spectrum is not well suited to obtain structural information on the macrocycle/thread co-conformation.

On the other hand, the hetero-vibrational NH/CO 2D-IR spectrum (shown in Fig. 5.3C) combines the relative lack of congestion of the NH/NH spectra with the structural information of the CO/CO 2D-IR spectra. Although the NH/CO 2D-IR spectrum of the molecular shuttle contains only one positive and two negative peaks, there are actually two signals present. This is due to overlap—and consequent partial canceling—of the two cross peaks. A horizontal cross section through the 2D spectrum (shown in Fig. 5.3F) shows how the observed response arises from combining both cross peaks. The left cross peak can be assigned to the coupling between the macrocycle NH-stretch mode ($\text{NH}_{\text{m,cycle}}$-stretch) and the CO-stretch mode of the thread ($\text{CO}_{\text{thread}}$-stretch), and the right cross peak to the coupling be-
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tween the macrocycle NH-stretch and macrocycle CO-stretch modes (CO\textsubscript{m,cycle}-stretch). To understand the hetero-vibrational NH/CO 2D-IR spectrum one has to realize that the only peaks that can be observed are a direct result of the coupling of the CO-stretch modes with the excited NH\textsubscript{m,cycle}-stretch mode. For example, when the macrocycle is bound to the succinamide station, exciting the NH\textsubscript{m,cycle}-stretch mode will stimulate a response only from CO\textsubscript{thread}-stretch and CO\textsubscript{m,cycle}-stretch, and no response from the CO-stretch modes in the naphthalimide station.

Since the magnitude of this coupling, and therefore the cross-peak intensity, is determined by the macrocycle-NH/thread-CO distance and orientation, this cross peak is ideally suited to probe the instantaneous position of the macrocycle on the thread. The cross-anisotropy can be used in the same manner as is done for the short rotaxane (see Chapter 4) to determine the ring-thread orientation. The time resolution of the structural probe provided in this way is the duration of the convolution of the pump and probe pulses, which is about 100 fs.

5.3.3 Mechanism of vibrational relaxation of the NH/CO cross peaks

To further investigate the possibilities of hetero-vibrational IR spectroscopy, we have studied the dynamics of the CO\textsubscript{m,cycle}-stretch and CO\textsubscript{thread}-stretch modes upon NH\textsubscript{m,cycle}-stretch excitation in the molecular shuttle (Fig. 5.2A). As explained in previous sections, the response of the CO-stretch and aromatic ring-stretch modes of the naphthalimide station upon NH\textsubscript{m,cycle}-stretch excitation can be neglected due to the lack of coupling between the macrocycle and this station when the macrocycle resides on the succinamide station. Figure 5.4 shows a decay of the transient absorption signal at various probe frequencies as a function of the delay between the pump and probe pulse. The bleaching of the CO\textsubscript{m,cycle}-stretch mode at 1669 cm\textsuperscript{-1} and the induced absorption of the CO\textsubscript{thread} mode at 1621 cm\textsuperscript{-1} are shown in black and blue, respectively. The up-and-down shape of the transient absorption decay at 1639 cm\textsuperscript{-1} (shown in red) is a consequence of the overlapping CO\textsubscript{thread}-stretch bleaching and CO\textsubscript{m,cycle}-stretch induced absorption.

The decay of the hetero-vibrational transient absorption signal can be described with a bi-exponential decay function. Using a global least-square fit to the whole data set, we determine the decay constants to be 2.4±0.1 ps and 10±1.6 ps. These decay constants are comparable to the ones found in our previous study on the short succinamide rotaxane (see Chapter 4). The lack of the up-and-down feature in the dynamics of the short rotaxane (shown in Fig. 4.7) is a consequence of the well separated absorption bands of the CO\textsubscript{thread} and CO\textsubscript{m,cycle}-stretch modes. From the structural similarities and comparable relaxation dynamics we can conclude that the relaxation mechanism in the naphthalimide and succinamide rotaxanes is similar. Upon excitation of the NH\textsubscript{m,cycle}-stretch mode the vibrational energy is
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Figure 5.4: The 2-color pump-probe spectra of the naphthalimide rotaxane as a function of delay. The symbols represent the data and the lines fitted bi-exponential model. The inset shows the respective steady-state absorption spectrum at 3 µm (right) and 6 µm (left) with arrows indicating the pump and probe frequencies. The color coding of the arrows matches the colors in the delay scans.

transferred to an unknown intermediate mode X, that is strongly coupled to the CO_{m,cycle}-stretch mode. Since the CO_{m,cycle}-stretch mode is coupled to both the NH_{m,cycle}-stretch and mode X, its relaxation dynamics are governed by the relaxation lifetimes of both these modes. The first 2.4 ps decay component represents the lifetime of the NH_{m,cycle}-stretch mode itself and is observed in the CO_{thread}-stretch relaxation dynamics due to the coupling between them. The second 10 ps component is assigned to the vibrational lifetime of the intermediate mode.

5.4 Conclusions

To summarize, our results demonstrate that 2D-IR spectroscopy can be used to obtain quantitative information about the co-conformation of a rotaxane shuttle with picosecond time resolution. In particular, we have shown that the angles and distances between specific chemical bonds in the macrocycle and thread of a rotaxane can be determined directly from its 2D-IR spectrum. This can be done for two CO-stretch modes, or for a NH-stretch and CO-stretch mode. In both cases, the cross-peak intensity and anisotropy provide a sensitive and time-resolved probe of the co-conformation of the rotaxane. The application of 2D-IR spectroscopy
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to rotaxane-based molecular machines can be complicated because of the larger number of vibrational modes. Hetero-nuclear 2D-IR provides an efficient way to circumvent this spectral congestion, and probe the co-conformation in these larger rotaxanes as well.